Quantum Mechanics in Nanoscience and Engineering

Exercises Solution Manual

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Contents

1 Motivation

Exercise 1.1.1 *The distance between adjacent atomic layers in a nickel crystal is* $d = 2.03 \times 10^{-10}$ *meter. An electron beam is scattered from the face of the crystal at an angle,* $\alpha_{in} = 45^o$. *Given the electron mass,* $m = 9 \cdot 10^{-31}$ *Kg, calculate the kinetic energy for the three most resolved maxima in the reflected flux at* $\alpha_{out} = 45^o$ *(see Figs. 1.1.1 and 1.1.2).*

Solution 1.1.1

The best resolved maxima are the ones for which $(\lambda_n - \lambda_{n+1}) / \lambda_{n+1}$ *obtains maximal values, namely,* $n = 1,2,3$. *Using Eqs. (1.1.2 ,1.1.3) and the momentum-energy relation,* $E_n = \frac{p_n^2}{2m}$, *we obtain* $E_n = \frac{h^2}{2m\lambda_n^2} = \frac{h^2}{2m(2d\sin(\alpha_{in})/n)^2} = \frac{h^2 n^2}{8md^2\sin^2(\alpha_{in})}$. *For* $\alpha_{out} = 45^o$, $d = 2.03 \times 10^{-10}$ *meter, and* $m = 9 \cdot 10^{-31}$ *Kg, using* $h = 6.626 \cdot 10^{-34}$ $Joul \cdot \sec$, *we obtain* $E_1 = 18.5$, $E_2 = 74$, $E_3 = 166.5$ *eV.*

Exercise 1.1.2 *In the "classical world", the de-Broglie wavelength is typically much smaller than the characteristic length-scale of the system under consideration. Consider for example a tennis ball at a mass* $m = 0.058$ *Kg, flying at a typical serving-velocity, i.e., 50 meter/sec. What is the associated de-Broglie wavelength? How does it compare with the length of a tennis court (24 meter), or with the diameter of the ball itself (6.7 cm)?*

Solution 1.1.2

The particle's de-Broglie wavelength reads $\lambda = h/(mv)$. *Using* $m = 0.058$ *Kg, v=50 meter/sec,* $h = 6.626 \cdot 10^{-34}$ $Joul \cdot \sec$, *we obtain* $\lambda = 6.626 \cdot 10^{-34} / (0.058 \cdot 50) = 2.28 \cdot 10^{-34}$ *meter, which is by far smaller than the length of a tennis court (24 meter) or the diameter of the ball itself (0.067 meter).*

2 The State of a System

Exercise 2.3.1 *The probability density of finding a point particle along the x-axis at a certain time is given by* $\rho(x) = \alpha e^{-\frac{(x-x_0)^2}{2\sigma^2}}$ *. (a) What is the most probable position for this particle (Does it depend on the value of* α *?). (b) Determine the value of* α *for which the probability density is normalized, recalling that* $\int_{-\infty}^{-\infty} e^{-\beta y^2} dy = \sqrt{\frac{\pi}{\beta}}$ *. (c) The average position associated with a probability density,* $\rho(x)$*, is defined as* $\langle x \rangle \equiv \int_{-\infty}^{-\infty} x\rho(x)dx$*. Calculate the average position of the given point particle. (d) The corresponding standard deviation in the position probability distribution is defined as* $\Delta x \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ *. Calculate the standard deviation in the position of the given point particle.*

Solution 2.3.1

(a) The most probable place for the particle is where the probability density distribution obtains its maximal value. A necessary condition for a maximum read $\frac{d}{dx}\rho(x) = 0$*, from which follows in the present case,* $-(x-x_0)\frac{2\alpha}{2\sigma^2} e^{\frac{-(x-x_0)^2}{2\sigma^2}} = 0$*. This is satisfied for,* $x \to \pm\infty$*, where the probability density is minimal (vanishes), as well as for* $x = x_0$*, which is the most probable place for the particle. As we can see, the result does not depend on* α *, as "most probable" is a relative term, independent of the wave function normalization.*

(b) Using the given integral, we obtain $\int_{-\infty}^{-\infty} e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx = \int_{-\infty}^{-\infty} e^{-\frac{y^2}{2\sigma^2}} dy = \sqrt{\pi 2\sigma^2}$ *. Setting,* $\alpha = 1/\sqrt{\pi 2\sigma^2}$ *a normalized distribution is obtained, namely* $\int_{-\infty}^{-\infty} \rho(x)dx = 1$*.*

(c) Using the normalized distribution, we obtain

$$\langle x \rangle = \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} x e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx = \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} (x-x_0) e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx + x_0 \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx$$

$$= \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} y e^{\frac{-y^2}{2\sigma^2}} dy + x_0 \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx = x_0 \ .$$

(d) The average value of x^2 *reads*

$$\left\langle x^2 \right\rangle = \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} x^2 e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx = \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} (x-x_0)^2 e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx$$
$$-x_0{}^2 \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx + 2x_0 \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} x e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx$$

$$= \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} (x-x_0)^2 e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx + x_0{}^2 \quad .$$

Since $\left\langle x \right\rangle = x_0$, *we have* $\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2 = \int_{-\infty}^{-\infty} \frac{1}{\sqrt{\pi 2\sigma^2}} (x-x_0)^2 e^{-\frac{(x-x_0)^2}{2\sigma^2}} dx$. *Changing integration variable,* $z = 1/(2\sigma^2)$, *we finally obtain*

$$\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2 = \frac{1}{\sqrt{\pi 2\sigma^2}} \frac{-d}{dz} \int_{-\infty}^{-\infty} e^{-z(x-x_0)^2} dx$$

$$= \frac{1}{\sqrt{\pi 2\sigma^2}} \frac{-d}{dz} \sqrt{\frac{\pi}{z}} = \frac{1}{\sqrt{\pi 2\sigma^2}} \frac{1}{2} \sqrt{\frac{\pi}{z^3}} = \frac{1}{\sqrt{\pi 2\sigma^2}} \frac{1}{2} \sqrt{\pi 8\sigma^6} = \sigma^2 ,$$

where $\Delta x = \sqrt{\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2} = \sigma$.

Exercise 2.3.2 *The state of a particle is described as a "superposition of wave functions", namely* $\psi(x) = \sum_{n=1}^{\infty} c_n \phi_n(x)$, *where {* c_n *} are given scalar expansion coefficients, and {* $\phi_n(x)$ *} is a given set of "orthonormal wave functions," namely,* $\int_{-\infty}^{\infty} \phi_m{}^*(x) \phi_n(x) dx = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$ *. Normalize* $\psi(x)$. *(Express the normalized wave function in terms of the given expansion coefficients.)*

Solution 2.3.2

Given, $\psi(x)=\sum_{n=1}^{\infty}c_n\phi_n(x)$, *we also have* $\psi^*(x)=\sum_{m=1}^{\infty}c_m^*\phi_m^*(x)$. *The normalization integral,* $\int_{-\infty}^{\infty}\psi^*(x)\psi(x)dx$, *therefore reads*

$$\int_{-\infty}^{\infty}\sum_{m=1}^{\infty}c_m^*\phi_m^*(x)\sum_{n=1}^{\infty}c_n\phi_n(x)dx=\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}c_m^*c_n\int_{-\infty}^{\infty}\phi_m^*(x)\phi_n(x)dx=\sum_{m=1}^{\infty}|c_m|^2,$$

where in the last step we used the orthonormality of the set of functions. The normalized wave function is therefore:

$$\psi(x)=\sum_{n=1}^{\infty}\frac{c_n}{\sqrt{\sum_{m=1}^{\infty}|c_m|^2}}\phi_n(x)$$

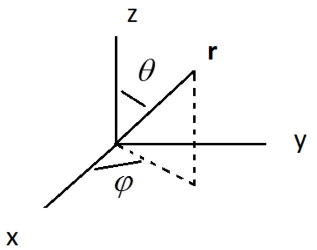
.

Exercise 2.3.3 *An isolated hydrogen-like atom is composed of a nucleus with Z protons and a single electron. At the minimal energy state of the atom, the probability density for finding the electron at a given position reads* $\rho(\mathbf{r})=\alpha e^{-2Zr/a_0}$; $r=|\mathbf{r}|$, *where* $\mathbf{r}$ *is the three-dimensional vector of the relative position between the nucleus to the electron, and* $a_0=0.0529$ *nm is the Bohr radius. Show that the most probable distance between the electron and the nucleus in this state is* a_0/Z. *What is the probability density of finding the electron at the most probable distance,* r, *in this state?*

Solution 2.3.3

Since the probability density depends only on $r=|\mathbf{r}|$, *it is convenient to use spherical coordinates:*

$$x=r\sin(\theta)\cos(\varphi)$$
$$y=r\sin(\theta)\sin(\varphi)$$
$$z=r\sin(\theta)\sin(\varphi)$$
$$\mathrm{dxdydz}=r^2\sin(\theta)\,\mathrm{drd}\,\theta d\varphi$$



Notice that $\rho(\mathbf{r})\equiv\rho(r)$ *does not depend on* (θ,φ), *while the normalization integral over the three-dimensional space reads* $\int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\int_0^{\infty}drr^2\sin\theta\rho(r)=\int_0^{\infty}4\pi r^2\rho(r)dr$. *To calculate the most* *probable distance we must account also for the volume element,* $4\pi r^2$, *and search for* $"r"$ *which maximizes* $4\pi r^2 \rho(r)$, *namely*

$$\frac{d}{dr} 4\pi\alpha r^2 e^{-2Zr/a_0} = 4\pi\alpha 2re^{-2Zr/a_0} - 4\pi\alpha r^2 2Z / a_0 e^{-2Zr/a_0} = 0,$$

which yields $r = r^2 Z / a_0$, *and therefore* $r = 0$ *or* $r = a_0 / Z$. *Clearly,* $r = 0$ *is a point of minimum, whereas* $r = a_0 / Z$ *is a maximum.*

To calculate the probability density of finding the electron at the most probable distance (within an interval dr*), we must first normalize the probability density. Using the integral,*

$$4\pi \int_0^\infty r^2 \rho(r) \,\mathrm{d}r = 4\pi \int_0^\infty r^2 \alpha e^{-2Zr/a_0} \,\mathrm{d}r = \pi a_0^{\,2} \alpha \frac{d^2}{dZ^2} \int_0^\infty e^{-2Zr/a_0} \,\mathrm{d}r$$
$$= \pi a_0^{\,2} \alpha \frac{d^2}{dZ^2} \frac{a_0}{Z} = \pi a_0^{\,3} \alpha \frac{-d}{dZ} \frac{1}{Z^2} = 2\pi a_0^{\,3} \alpha \frac{1}{Z^3} ,$$

we find that the value of α *for which the probability distribution is normalized, namely* $\alpha = \dfrac{Z^3}{2\pi a_0^{\,3}}$.

Consequently, the probability density of finding the electron at the most probable distance from the nucleus reads $\dfrac{Z^3}{2\pi a_0^{\,3}} r^2 e^{-2Zr/a_0} \,|_{r=a_0/Z} = \dfrac{Z}{2\pi a_0} e^{-2}$.

3 Observables and Operators

Exercise 3.1.1 *Write explicit expressions for the following commutators:* $[\sin x, \frac{d}{dx}]$, $[\frac{1}{x}, \frac{d}{dx}], [\frac{d}{dx}, \frac{d^2}{dx^2}]$.

Solution 3.1.1

Operating on a generic function $f(x)$, we obtain

$$[\sin x, \frac{d}{dx}] f(x) = \sin x \cdot \frac{df(x)}{dx} - \frac{d}{dx} \sin x \cdot f(x) = \sin x \cdot \frac{df(x)}{dx} - \cos(x) \cdot f(x) - \sin x \cdot \frac{df(x)}{dx}$$
$$= -\cos(x) \cdot f(x)$$
$$\Rightarrow [\sin x, \frac{d}{dx}] = -\cos(x)$$

$$[\frac{1}{x}, \frac{d}{dx}] f(x) = \frac{1}{x} \cdot \frac{df(x)}{dx} - \frac{d}{dx}\left[\frac{1}{x} \cdot f(x)\right] = \frac{1}{x} \cdot \frac{df(x)}{dx} + \frac{f(x)}{x^2} - \frac{1}{x} \cdot \frac{df(x)}{dx}$$
$$= \frac{f(x)}{x^2}$$
$$\Rightarrow [\frac{1}{x}, \frac{d}{dx}] = \frac{1}{x^2}$$

$$[\frac{d}{dx}, \frac{d^2}{dx^2}] = \frac{d}{dx} \frac{d^2 f(x)}{dx^2} - \frac{d^2}{dx^2} \frac{df(x)}{dx} = \frac{d^3 f(x)}{dx^3} - \frac{d^3 f(x)}{dx^3} = 0$$

$$\Rightarrow [\frac{d}{dx}, \frac{d^2}{dx^2}] = 0.$$

Exercise 3.1.2 *Verify the following identities for any linear operators (*$\hat{A}$, $\hat{B}$, $\hat{C}$*):*

$$\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right] \;;\; \left[\hat{A}, \hat{B}+\hat{C}\right] = \left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{C}\right] \;;\; \left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right].$$

Solution 3.1.2

(i)

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} = -\left(\hat{B}\hat{A} - \hat{A}\hat{B}\right) = -\left[\hat{B}, \hat{A}\right]$$

(ii)

$$\left[\hat{\mathrm{A}},\hat{\mathrm{B}}+\hat{\mathrm{C}}\right]=\hat{\mathrm{A}}\left(\hat{\mathrm{B}}+\hat{\mathrm{C}}\right)-\left(\hat{\mathrm{B}}+\hat{\mathrm{C}}\right)\hat{\mathrm{A}}=\hat{\mathrm{A}}\hat{\mathrm{B}}+\hat{\mathrm{A}}\,\hat{\mathrm{C}}-\hat{\mathrm{B}}\hat{\mathrm{A}}-\hat{\mathrm{C}}\hat{\mathrm{A}}=\hat{\mathrm{A}}\,\hat{\mathrm{B}}-\hat{\mathrm{B}}\hat{\mathrm{A}}+\hat{\mathrm{A}}\,\hat{\mathrm{C}}-\hat{\mathrm{C}}\hat{\mathrm{A}}$$
$$=[\hat{\mathrm{A}},\hat{\mathrm{B}}]+[\hat{\mathrm{A}},\hat{\mathrm{C}}]$$

(iii)

$$\left[\hat{\mathrm{A}},\hat{\mathrm{B}}\hat{\mathrm{C}}\right]=\hat{\mathrm{A}}\,\hat{\mathrm{B}}\hat{\mathrm{C}}-\hat{\mathrm{B}}\hat{\mathrm{C}}\hat{\mathrm{A}}=\hat{\mathrm{A}}\,\hat{\mathrm{B}}\hat{\mathrm{C}}-\hat{\mathrm{B}}\hat{\mathrm{C}}\hat{\mathrm{A}}-\hat{\mathrm{B}}\hat{\mathrm{A}}\hat{\mathrm{C}}+\hat{\mathrm{B}}\hat{\mathrm{A}}\hat{\mathrm{C}}$$
$$=\hat{\mathrm{A}}\,\hat{\mathrm{B}}\hat{\mathrm{C}}-\hat{\mathrm{B}}\hat{\mathrm{A}}\hat{\mathrm{C}}+\hat{\mathrm{B}}\hat{\mathrm{A}}\hat{\mathrm{C}}-\hat{\mathrm{B}}\hat{\mathrm{C}}\hat{\mathrm{A}}=\left(\hat{\mathrm{A}}\,\hat{\mathrm{B}}-\hat{\mathrm{B}}\hat{\mathrm{A}}\right)\hat{\mathrm{C}}+\hat{\mathrm{B}}\left(\hat{\mathrm{A}}\hat{\mathrm{C}}-\hat{\mathrm{C}}\hat{\mathrm{A}}\right)$$
$$=\left[\hat{\mathrm{A}},\hat{\mathrm{B}}\right]\hat{\mathrm{C}}+\hat{\mathrm{B}}\left[\hat{\mathrm{A}},\hat{\mathrm{C}}\right]$$

Exercise 3.1.3 *The operators:* $\hat{\mathrm{A}}$ *;* $\hat{\mathrm{B}}$ *;* $\hat{\mathrm{C}}$ *;* $\hat{\mathrm{D}}$ *are defined by the results of their operation on any function* $f(x)$*:* $\hat{\mathrm{A}}f(x)=x^n f(x)$ *;* $\hat{\mathrm{B}}f(x)=\frac{d}{dx}f(x)$*;* $\hat{\mathrm{C}}f(x)=\sin\left(f(x)\right)$*;* $\hat{\mathrm{D}}f(x)=\sqrt{f(x)}$*. Which ones are linear?*

Solution 3.1.3

By definition, an operator $\hat{O}$ *is linear if* $\hat{O}[a_1 f_1(x)+a_2 f_2(x)]=a_1\hat{O}f_1(x)+a_2\hat{O}f_2(x)$ *for any scalars* a_1,a_2 *and functions* $f_1(x), f_2(x)$*. This trivially holds for the given* $\hat{A}$ *and* $\hat{B}$ *but does not hold for* $\hat{C}$ *and* $\hat{D}$*, which are non-linear operators,*

$$\sin[a_1 f_1(x)+a_2 f_2(x)]=\sin[a_1 f_1(x)]\cos[a_2 f_2(x)]+\cos[a_1 f_1(x)]\sin[a_2 f_2(x)]$$
$$\neq a_1\sin[f_1(x)]+a_2\sin[f_2(x)]$$

$$\sqrt{a_1 f_1(x)+a_2 f_2(x)}\neq a_1\sqrt{f_1(x)}+a_2\sqrt{f_2(x)}\,.$$

Exercise 3.1.4 *Given that* $\hat{A}$ *and* $\hat{B}$ *are linear operators, show that* $\hat{C}=\hat{A}\hat{B}$ *and* $\hat{D}=\hat{A}+\hat{B}$ *are also linear operators.*

Solution 3.1.4

(i) *Using first the linearity of* $\hat{B}$*, and then the linearity of* $\hat{A}$*, we obtain*

$$\hat{A}\hat{B}\,[a_1 f_1(x)+a_2 f_2(x)]=\hat{A}[a_1\hat{B}\;f_1(x)+a_2\hat{B}\;f_2(x)]$$

$$= a_1 \hat{A}\hat{B}\ f_1(x) + a_2 \hat{A}\hat{B}\ f_2(x) \quad .$$

(ii) *Using the linearity of $\hat{B}$ and $\hat{A}$ independently, we obtain*

$$\begin{aligned}
&[\hat{A}+\hat{B}]\,[a_1 f_1(x) + a_2 f_2(x)] \\
&= a_1 \hat{A}\, f_1(x) + a_2 \hat{A}\, f_2(x) + a_1 \hat{B}\, f_1(x) + a_2 \hat{B}\, f_2(x) \\
&= a_1 \hat{A}\, f_1(x) + a_1 \hat{B}\, f_1(x) + a_2 \hat{A}\, f_2(x) + a_2 \hat{B}\, f_2(x) \\
&= a_1 [\hat{A}+\hat{B}]\, f_1(x) + a_2 [\hat{A}+\hat{B}]\, f_2(x)) \ .
\end{aligned}$$

Exercise 3.1.5 *$\hat{D}$ is a linear differential operator, and ϕ and φ are two solutions of the homogeneous linear equation defined by $\hat{D}$,*

$$\hat{D}\phi = 0 \quad ; \quad \hat{D}\varphi = 0 .$$

Show that any linear combination of ϕ and φ (i.e., $a\phi + b\varphi$ with constant scalars a and b) is also a solution of the homogeneous equation (the "superposition principle").

Solution 3.1.5

For a linear operator, $\hat{D}$, we have by definition $\hat{D}[a_1\phi(x) + a_2\varphi(x)] = a_1\hat{D}\phi(x) + a_2\hat{D}\varphi(x)$, for any scalars a_1, a_2 and functions $\phi(x), \varphi(x)$. Given that $\hat{D}\phi = 0$, and $\hat{D}\varphi = 0$, we also have $\hat{D}[a_1\phi(x) + a_2\varphi(x)] = a_1\hat{D}\phi(x) + a_2\hat{D}\varphi(x) = 0$, for any scalars a_1, a_2, which means that any linear combination, $\psi(x) \equiv a_1\phi(x) + a_2\varphi(x)$, is a solution to the homogeneous equation, $\hat{D}\psi(x) = 0$.

Exercise 3.2.1 *Show that, $[\hat{\mathbf{r}}, \hat{\mathbf{p}}] = 3i\hbar$.*

Solution 3.2.1

$$\begin{aligned}
&[\hat{\mathbf{r}}, \hat{\mathbf{p}}] = \hat{\mathbf{r}} \cdot \hat{\mathbf{p}} - \hat{\mathbf{p}} \cdot \hat{\mathbf{r}} = \hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z - \hat{p}_x\hat{x} - \hat{p}_y\hat{y} - \hat{p}_z\hat{z} \\
&= \hat{x}\hat{p}_x - \hat{p}_x\hat{x} + \hat{y}\hat{p}_y - \hat{p}_y\hat{y} + \hat{z}\hat{p}_z - \hat{p}_z\hat{z} \\
&= [\hat{x}, \hat{p}_x] + [\hat{y}, \hat{p}_y] + [\hat{z}, \hat{p}_z] \\
&= 3i\hbar
\end{aligned}$$

Exercise 3.3.1 *Prove the relations in Eqs. (3.3.3, 3.3.5).*

Solution 3.3.1

Given the definitions, $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$, $\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$, $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$, *we obtain*

$$
\begin{aligned}
&[\hat{L}_x, \hat{L}_y] = [(y\hat{p}_z - \mathrm{z}\,\hat{p}_y), (z\hat{p}_x - x\hat{p}_z)] = [(y\hat{p}_z - \mathrm{z}\,\hat{p}_y), z\hat{p}_x] - [(y\hat{p}_z - \mathrm{z}\,\hat{p}_y), x\hat{p}_z] \\
&= [y\hat{p}_z, z\hat{p}_x] + [\mathrm{z}\,\hat{p}_y, x\hat{p}_z] \\
&= y\hat{p}_z z\hat{p}_x - z\hat{p}_x y\hat{p}_z + \mathrm{z}\,\hat{p}_y x\hat{p}_z - x\hat{p}_z\,\mathrm{z}\,\hat{p}_y \\
&= \hat{p}_z z y\hat{p}_x - z\hat{p}_z y\hat{p}_x + x\hat{p}_y\,\mathrm{z}\,\hat{p}_z - x\hat{p}_y\hat{p}_z\,\mathrm{z} \\
&= x\hat{p}_y[\mathrm{z}, \hat{p}_z] - [z, \hat{p}_z] y\hat{p}_x \\
&= i\hbar x\hat{p}_y - i\hbar y\hat{p}_x \\
&= i\hbar\hat{L}_z \quad .
\end{aligned}
$$

Using the cyclic permutation $(x, y, z) \to (y, z, x)$, *we readily obtain*

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x .$$

Using the cyclic permutations $(y, z, x) \to (z, x, y)$, *we readily obtain*

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y .$$

Using the commutation relations: $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$, $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$, $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$, *we obtain*

$$
\begin{aligned}
&[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] \\
&= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\
&= \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_z[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z \\
&= i\hbar[\hat{L}_y(-\hat{L}_z) + (-\hat{L}_z)\hat{L}_y + \hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z] \\
&= 0 \qquad .
\end{aligned}
$$

Noticing that $\hat{L}^2$ *is invariant to the cyclic permutations,* $(x, y, z) \to (y, z, x)$ *and* $(y, z, x) \to (z, x, y)$ *, we obtain* $[\hat{L}^2, \hat{L}_y] = 0$ *and* $[\hat{L}^2, \hat{L}_z] = 0$.

Exercise 3.4.1 *Show that the following function of the linear momentum operator,* $\hat{M}_\alpha = e^{\frac{i\alpha}{\hbar}\hat{p}_x}$ *, is a displacement operator, namely,* $\hat{M}_\alpha \psi(x) = \psi(x+\alpha)$ *, where* α *is a constant.*

Solution 3.4.1

The exponential operator can be expressed in terms of its Taylor expansion:

$$\hat{M}_\alpha = e^{\frac{i\alpha}{\hbar}\hat{p}_x} = e^{\frac{i\alpha}{\hbar}(-i\hbar\frac{d}{dx})} = e^{\alpha\frac{d}{dx}} = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!}\frac{d^n}{dx^n}.$$

Operation on a generic (analytic) function yields

$$\hat{M}_\alpha f(x) = e^{\alpha\frac{d}{dx}} f(x) = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!}\frac{d^n}{dx^n} f(x) = f(x+\alpha),$$

where in the last step we identified the Taylor expansion of $f(x+\alpha)$.

4 The Schrödinger Equation

Exercise 4.3.1 *Show that if* $f_1(x)$ *is an eigenfunction of a linear operator* $\hat{A}$ *with an eigenvalue* α*, so is* $f_2(x) = cf_1(x)$*, where* c *is a constant scalar.*

Solution 4.3.1

If $f_1(x)$ *is an eigenfunction of an operator* $\hat{A}$*, then* $\hat{A}f_1(x) = \alpha f_1(x)$*. Consequently,* $c\hat{A}f_1(x) = c\alpha f_1(x)$*. For a linear operator* $\hat{A}$ *we therefore have,* $\hat{A}cf_1(x) = \alpha cf_1(x)$*, and hence,*

$\hat{A}f_2(x) = \alpha f_2(x)$.

Exercise 4.3.2 *(a) Determine whether the following functions* $f_1(x) = x^2$*,* $f_2(x) = e^{iax}$*, and* $f_3(x) = \sin(ax)$ *are (independently) eigenfunctions of the operator* $\frac{d}{dx}$*. In cases where the answer is positive, determine the respective eigenvalue. (b) Repeat the exercise for the operator* $\frac{d^2}{dx^2}$.

Solution 4.3.2

$f\left(x\right)$ *is an eigenfunction of an operator* $\hat{O}$*, only if* $\hat{O}f\left(x\right) = \lambda f\left(x\right)$ *for any* x*, where* λ *is a scalar. Testing explicitly, we obtain*

$$\frac{d}{dx}x^2 = 2x \neq \lambda x^2 \quad ; \quad \frac{d^2}{dx^2}x^2 = 2 \neq \lambda x^2$$
$$\frac{d}{dx}e^{iax} = i\alpha e^{iax} = \lambda e^{iax} \Rightarrow \lambda = i\alpha \quad ; \quad \frac{d^2}{dx^2}e^{iax} = -\alpha^2 e^{iax} = \lambda e^{iax} \Rightarrow \lambda = -\alpha^2$$
$$\frac{d}{dx}\sin(ax) = a\cos(ax) \neq \lambda\sin(ax) \quad ; \quad \frac{d^2}{dx^2}\sin(ax) = -a^2\sin(ax) = \lambda\sin(ax) \Rightarrow \lambda = -a^2 .$$

We can see that $f_2(x)$ *is an eigenfunction of both* $\frac{d}{dx}$ *and* $\frac{d^2}{dx^2}$*, and* $f_3(x)$ *is an eigenfunction of* $\frac{d^2}{dx^2}$ *(only).*

Exercise 4.3.3 *In section 4.2 we encountered two different solutions to the Schrödinger equation with a harmonic potential energy well,* $V(x)=\frac{1}{2}m\omega^2x^2$. *The respective probability density was time-dependent only in one of these cases (presented in Fig. 4.2.3), whereas the other solution (presented in Fig. 4.2.4) was stationary. These two solutions correspond to different choices of the parameters* (x_0, p_0) *in the initial wave function (see Eq. (4.2.1)). Check whether* $\psi(x,0)$ *is an eigenfunction of the system Hamiltonian for these two choices and explain the observed difference between the two solutions.*

Solution 4.3.3

The Hamiltonian for a harmonic oscillator reads $\hat{H}=\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2$ *and the initial wave function (Eq. (4.2.1)) is* $\psi(x,0)=\left(\frac{1}{2\pi\sigma^2}\right)^{1/4}e^{\frac{-(x-x_0)^2}{4\sigma^2}}e^{ip_0x/\hbar}$. *To find the conditions in which* $\psi(x,0)$ *is an eigenfunction of* $\hat{H}$, *let us calculate* $\hat{H}\psi(x,0)$. *Using,*

$$\frac{d^2}{dx^2}e^{\frac{-(x-x_0)^2}{4\sigma^2}}e^{ip_0x/\hbar}=e^{ip_0x/\hbar}\left(\frac{d^2}{dx^2}e^{\frac{-(x-x_0)^2}{4\sigma^2}}\right)+e^{\frac{-(x-x_0)^2}{4\sigma^2}}\left(\frac{d^2}{dx^2}e^{ip_0x/\hbar}\right)+2\left(\frac{d}{dx}e^{\frac{-(x-x_0)^2}{4\sigma^2}}\right)\frac{d}{dx}\left(e^{ip_0x/\hbar}\right)$$

$$=e^{ip_0x/\hbar}\left(\frac{-1}{2\sigma^2}e^{\frac{-(x-x_0)^2}{4\sigma^2}}+\frac{(x-x_0)^2}{4\sigma^4}e^{\frac{-(x-x_0)^2}{4\sigma^2}}\right)+e^{\frac{-(x-x_0)^2}{4\sigma^2}}\left(\frac{-p_0^2}{\hbar^2}e^{ip_0x/\hbar}\right)$$

$$+2\left(\frac{-(x-x_0)}{2\sigma^2}e^{\frac{-(x-x_0)^2}{4\sigma^2}}\right)\left(\frac{ip_0}{\hbar}e^{ip_0x/\hbar}\right)$$

$$=\left[\frac{-1}{2\sigma^2}+\frac{x^2-2x_0x+x_0^2}{4\sigma^4}+\frac{-p_0^2}{\hbar^2}+\frac{-(x-x_0)}{\sigma^2}\frac{ip_0}{\hbar}\right]e^{\frac{-(x-x_0)^2}{4\sigma^2}}e^{ip_0x/\hbar},$$

we obtain

$$\hat{H}\psi(x,0)=\left\{\frac{-\hbar^2}{2m}\left[\frac{-1}{2\sigma^2}+\frac{x^2-2x_0x+x_0^2}{4\sigma^4}+\frac{-p_0^2}{\hbar^2}+\frac{-(x-x_0)}{\sigma^2}\frac{ip_0}{\hbar}\right]+\frac{m\omega^2}{2}x^2\right\}\psi(x,0).$$

Rearranging, we see that $\hat{H}\psi(x,0)=\left[\alpha+\beta x+\gamma x^2\right]\psi(x,0)$, *namely*

$$\hat{H}\psi(x,0)$$
$$=\left[\left(\frac{\hbar^2}{4m\sigma^2}+\frac{p_0^2}{2m}-i\frac{\hbar p_0x_0}{2m\sigma^2}-\frac{\hbar^2x_0^2}{8m\sigma^4}\right)+x\left(i\frac{\hbar p_0}{2m\sigma^2}+\frac{\hbar^2x_0}{4m\sigma^4}\right)-x^2\left(\frac{\hbar^2}{8m\sigma^4}-\frac{m\omega^2}{2}\right)\right]\psi(x,0).$$

For $\psi(x,0)$ *to be an eigenfunction of* $\hat{H}$ *(namely, to have* $\hat{H}\psi(x,0)=\alpha\psi(x,0)$ *), the coefficients* β *and* γ *must vanish. In partiucular,* $\beta=0 \Rightarrow \frac{\hbar^2 x_0}{4m\sigma^4}+i\frac{\hbar p_0}{2m\sigma^2}=0$, *from which we conclude that both the real and imaginary parts must vanish, namely,* $x_0=0$ *and* $p_0=0$. *Additionally,* $\gamma=0 \Rightarrow \frac{\hbar^2}{8m\sigma^4}=\frac{m\omega^2}{2}$, *from which we conclude that,* $\sigma=\sqrt{\frac{\hbar}{2m\omega}}$. *(Notice that for this choice the eigenvalue can be readily identified as* $\alpha=\frac{\hbar^2}{4m\sigma^2}+\frac{p_0^2}{2m}-i\frac{\hbar p_0 x_0}{2m\sigma^2}-\frac{\hbar^2 x_0^2}{8m\sigma^4}=\frac{\hbar\omega}{2}$ *.)*

Testing the parameters of Figures. 4.2.3, 4.2.4, we find that only the latter corresponds to an eigenfunction of the system Hamiltonian. Indeed, the solution to the Schrodinger equation is stationary in that case, where the probability density does not change in time.

Exercise 4.3.4 *An* N *-dimensional system is associated with the spatial coordinates,* $x_1,x_2,....,x_N$. *Let us consider the case where the system Hamiltonian is separable, namely, it can be written as a sum,* $\hat{H}=\sum_{j=1}^{N}\hat{H}_{x_j}$ *, where* $\hat{H}_{x_j}$ *is a Hamiltonian of a system associated only with the coordinate* x_j. *The eigenfunctions and eigenvalues of the* j *th Hamiltonians are defined by the set of eigenvalue equations,* $\hat{H}_{x_j}\varphi_{n_j}(x_j)=E_{n_j}\varphi_{n_j}(x_j)$. *Show that any product function,* $\psi_{n_1,n_2,...,n_N}(x_1,x_2,...,x_N)=\varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots\varphi_{n_N}(x_N)$, *is an eigenfunction of the full Hamiltonian,* $\hat{H}$ *, with the corresponding eigenvalue,* $E_{n_1,n_2,...,n_N}=E_{n_1}+E_{n_2}+\cdots+E_{n_N}$ *.*

Solution 4.3.4

Introducing the product function, $\hat{H}\psi_{n_1,n_2,...,n_N}(x_1,x_2,...,x_N)=\left[\sum_{j=1}^{N}\hat{H}_{x_j}\right]\varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots\varphi_{n_N}(x_N)$

,

we can use the linearity of each $\hat{H}_{x_j}$ *to obtain*

$$\left[\sum_{j=1}^{N}\hat{H}_{x_j}\right]\varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots\varphi_{n_N}(x_N)=\sum_{j=1}^{N}\varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots\hat{H}_{x_j}\varphi_{n_N}(x_N)\cdots\cdots\varphi_{n_N}(x_N)\,.$$

Using $\hat{H}_{x_j}\varphi_{n_j}(x_j)=E_{n_j}\varphi_{n_j}(x_j)$, *we obtain*

$$\sum_{j=1}^{N} \varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots \hat{H}_{x_j}\varphi_{n_j}(x_j)\cdots\cdots\varphi_{n_N}(x_N) = \sum_{j=1}^{N} \varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots E_{n_j}\varphi_{n_j}(x_j)\cdots\cdots\varphi_{n_N}(x_N)$$
$$= \sum_{j=1}^{N} E_{n_j}\varphi_{n_1}(x_1)\varphi_{n_2}(x_2)\cdots\varphi_{n_j}(x_j)\cdots\cdots\varphi_{n_N}(x_N) = \sum_{j=1}^{N} E_{n_j}\psi_{n_1,n_2,...,n_N}(x_1,x_2,...,x_N)$$
$$= \left[\sum_{j=1}^{N} E_{n_j}\right]\psi_{n_1,n_2,...,n_N}(x_1,x_2,...,x_N)$$
$$= E_{n_1,n_2,...,n_N}\psi_{n_1,n_2,...,n_N}(x_1,x_2,...,x_N) .$$

Exercise 4.5.1 *Given a Hermitian operator, $\hat{A}$, prove that (a) $(\hat{A})^n$ is also Hermitian (for any natural n). (b) $\alpha\hat{A}$ is also Hermitian (for any real valued α); (c) $i\hat{A}$ is anti-Hermitian (namely $(i\hat{A})^\dagger = -(i\hat{A})$).*

Solution 4.5.1

By Eq. (4.5.1), if $\hat{A}$ is Hermitian, then for any $f(x)$ and $g(x)$ we have,

$$\int_{-\infty}^{\infty} f(x)\hat{A}g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}f^*(x)dx\right]^* .$$

(a) Rewriting $\hat{A}^n = \hat{A}\hat{A}^{n-1}$ and using the Hermiticity of $\hat{A}$, we obtain

$$\int_{-\infty}^{\infty} f(x)\hat{A}^n g(x)dx = \int_{-\infty}^{\infty} f(x)\hat{A}\left[\hat{A}^{n-1}g(x)\right]dx = \left[\int_{-\infty}^{\infty}\left[\hat{A}^{n-1}g(x)\right]^*\hat{A}f^*(x)dx\right]^*$$
$$= \left[\int_{-\infty}^{\infty}\left[\hat{A}f^*(x)\right]\left[\hat{A}^{n-1}g(x)\right]^* dx\right]^* = \int_{-\infty}^{\infty}\left[\hat{A}f^*(x)\right]^*\hat{A}^{n-1}g(x)dx .$$

Repeating this process, we obtain

$$\int_{-\infty}^{\infty}\left[\hat{A}f^*(x)\right]^*\hat{A}^{n-1}g(x)dx = \int_{-\infty}^{\infty}\left[\hat{A}^2 f^*(x)\right]^*\hat{A}^{n-2}g(x)dx = ... = \int_{-\infty}^{\infty}\left[\hat{A}^n f^*(x)\right]^* g(x)dx ,$$

and therefore,

$$\int_{-\infty}^{\infty} f(x)\hat{A}^n g(x)dx = \int_{-\infty}^{\infty}\left[\hat{A}^n f^*(x)\right]^* g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}^n f^*(x)dx\right]^* ,$$

which means that $\hat{A}^n$ *is also Hermitian.*

(b) For $\hat{B} = \alpha \hat{A}$ *with real-valued* α *, we have*

$$\int_{-\infty}^{\infty} f(x)\hat{B}g(x)dx = \alpha \int_{-\infty}^{\infty} f(x)\hat{A}g(x)dx = \alpha \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}f^*(x)dx \right]^*$$

$$= \left[\int_{-\infty}^{\infty} g^*(x)\alpha\hat{A}f^*(x)dx \right]^* = \left[\int_{-\infty}^{\infty} g^*(x)\hat{B}f^*(x)dx \right]^* .$$

Hence, $\hat{B}$ *is Hermitian.*

(c) For $\hat{B} = i\hat{A}$ *we have*

$$\int_{-\infty}^{\infty} f(x)\hat{B}g(x)dx = i \int_{-\infty}^{\infty} f(x)\hat{A}g(x)dx = i \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}f^*(x)dx \right]^*$$

$$= \left[\int_{-\infty}^{\infty} g^*(x)(-i)\hat{A}f^*(x)dx \right]^* = -\left[\int_{-\infty}^{\infty} g^*(x)\hat{B}f^*(x)dx \right]^* .$$

Hence, $\hat{B}$ *is anti-Hermitian.*

Exercise 4.5.2 *Given two Hermitian operators,* $\hat{A}$ *and* $\hat{B}$*, prove that (a)* $\hat{A} + \hat{B}$ *is also Hermitian; (b) if* $\hat{A}$ *and* $\hat{B}$ *commute,* $\hat{A}\hat{B}$ *is also Hermitian.*

Solution 4.5.2

If $\hat{A}$ *and* $\hat{B}$ *are Hermitian, then for any* $f(x)$ *and* $g(x)$ *we have*

$$\int_{-\infty}^{\infty} f(x)\hat{A}g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}f^*(x)dx \right]^*$$

$$\int_{-\infty}^{\infty} f(x)\hat{B}g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{B}f^*(x)dx \right]^*$$

(a) For $\hat{A}+\hat{B}$ *:* $\int_{-\infty}^{\infty} f(x)\left[\hat{A}+\hat{B}\right]g(x)dx = \int_{-\infty}^{\infty} f(x)\left[\hat{A}\right]g(x)dx + \int_{-\infty}^{\infty} f(x)\left[\hat{B}\right]g(x)dx$

$$= \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}f^*(x)dx\right]^* + \left[\int_{-\infty}^{\infty} g^*(x)\hat{B}f^*(x)dx\right]^* = \left[\int_{-\infty}^{\infty} g^*(x)\left[\hat{A}+\hat{B}\right]f^*(x)dx\right]^*.$$

Hence, $\hat{A}+\hat{B}$ *is Hermitian.*

(b) For $\hat{A}\hat{B}=\hat{B}\hat{A}$*:*

$$\int_{-\infty}^{\infty} f(x)\hat{A}\hat{B}g(x)dx = \left[\int_{-\infty}^{\infty}\left[\hat{B}g(x)\right]^*\hat{A}f^*(x)dx\right]^* = \left[\int_{-\infty}^{\infty}\left[\hat{A}f^*(x)\right]\left[\hat{B}g(x)\right]^*dx\right]^*$$

$$= \int_{-\infty}^{\infty}\left[\hat{A}f^*(x)\right]^*\left[\hat{B}g(x)\right]dx = \int_{-\infty}^{\infty}\left[\hat{A}f^*(x)\right]^*\hat{B}g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{B}\left[\hat{A}f^*(x)\right]dx\right]^*$$

$$= \left[\int_{-\infty}^{\infty} g^*(x)\hat{B}\hat{A}f^*(x)dx\right]^* = \left[\int_{-\infty}^{\infty} g^*(x)\hat{A}\hat{B}f^*(x)dx\right]^* .$$

Hence, given $\hat{A}\hat{B}=\hat{B}\hat{A}$, $\hat{A}\hat{B}$ *is Hermitian.*

Exercise 4.5.3 *Using the results of Exs. 4.5.1, 4.5.2, prove, independently, that the potential energy operator* ($V(\hat{x})$)*, the kinetic energy operator (*$\hat{p}_x^2/(2m)$*), the Hamiltonian, (*$\hat{H}=\hat{p}_x^2/(2m)+V(\hat{x})$*), and the angular momentum operators (*$\hat{L}_x, \hat{L}_y$*, and* $\hat{L}_z$*, as defined in Eq. (3.3.2)) are all Hermitian.*

Solution 4.5.3

According to Ex. 4.5.1 (a) and (b), if $\hat{A}$ *is Hermitian, so is* $\alpha(\hat{A})^n$ *for real-valued* α*, and according to Ex. 4.5.2 (a), the sum of Hermitian operators is Hermitian. Therefore, any analytic real-valued function of a Hermitian operator is Hermitian. In particular, the potential energy is a real-valued analytic function of the position operator,* $\hat{V}=V(\hat{x})=\sum_{n=0}^{\infty} v_n(\hat{x})^n$*, and since* $\hat{x}$ *is Hermitian (see Eq. (4.5.4)), so is* $\hat{V}$.

Similarly, the kinetic energy is a real-valued analytic function of the linear momentum operator, $\hat{T}=\hat{p}_x^2/(2m)$*, and since* $\hat{p}_x$ *is Hermitian (see Eq. (4.5.5)), so is* $\hat{T}$.

The Hamiltonian is a sum of the two Hermitian operators, $\hat{H} = \hat{T} + \hat{V}$ *, and therefore* $\hat{H}$ *is Hermitian.*

According to Ex. 4.5.2. (b), the product of two commuting Hermitian operators is Hermitian. The components of the angular momentum operator, as defined in Eq. (3.3.2), are sums of products of commuting Hermitian operators: $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$ *;* $\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$ *;* $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$ *, and are therefore Hermitian.*

Exercise 4.5.4 *An operator* $\hat{U}$ *is termed unitary if its Hermitian conjugate equals its inverse, namely,* $\hat{U} = (\hat{U}^{-1})^\dagger$*, where,* $\hat{U}^{-1}\hat{U} = \hat{I}$ *. Use the Hermiticity of the Hamiltonian, to prove that the time evolution operator for a time-independent Hamiltonian,* $e^{-i(t-t_0)\hat{H}/\hbar}$ *(Eq. (4.1.2)), is unitary.*

Solution 4.5.4

We need to show that for the operator $\hat{U} = e^{-i(t-t_0)\hat{H}/\hbar}$ *the Hermitian conjugate (*$\hat{U}^\dagger$*) identifies with the inverse operator (*$\hat{U}^{-1}$*). By Eq. (4.5.2), the Hermitian conjugate of* $\hat{U}$ *is defined such that for any* $f(x)$ *and* $g(x)$ *we have,* $\int_{-\infty}^{\infty} f(x)\hat{U}^\dagger g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{U}f^*(x)dx\right]^*$ *. Starting from the right-hand side, we obtain*

$$\left[\int_{-\infty}^{\infty} g^*(x)\hat{U}f^*(x)dx\right]^* = \left[\int_{-\infty}^{\infty} g^*(x)e^{-i(t-t_0)\hat{H}/\hbar} f^*(x)dx\right]^* = \left[\int_{-\infty}^{\infty} g^*(x)\sum_{n=0}^{\infty}\frac{\left[-i(t-t_0)\hat{H}/\hbar\right]^n}{n!} f^*(x)dx\right]^*$$

$$= \sum_{n=0}^{\infty}\left[\frac{\left[-i(t-t_0)/\hbar\right]^n}{n!}\right]^*\left[\int_{-\infty}^{\infty} g^*(x)\hat{H}^n f^*(x)dx\right]^* .$$

Using the hermiticity of $\hat{H}^n$ *(see Ex. 4.5.1 (a)), we have*

$$\left[\int_{-\infty}^{\infty} g^*(x)\hat{H}^n f^*(x)dx\right]^* = \int_{-\infty}^{\infty} f(x)\hat{H}^n g(x)dx .$$

Therefore,

$$\left[\int_{-\infty}^{\infty} g^*(x)\hat{U}f^*(x)dx\right]^* = \sum_{n=0}^{\infty}\frac{\left[i(t-t_0)/\hbar\right]^n}{n!}\int_{-\infty}^{\infty} f(x)\hat{H}^n g(x)dx = \int_{-\infty}^{\infty} f(x)\sum_{n=0}^{\infty}\frac{\left[i(t-t_0)/\hbar\right]^n}{n!}\hat{H}^n g(x)dx$$

$$= \int_{-\infty}^{\infty} f(x)e^{i(t-t_0)\hat{H}/\hbar}g(x)dx \ .$$

Returning to the definition, $\left[\int_{-\infty}^{\infty} g^*(x)\hat{U}f^*(x)dx\right]^* = \int_{-\infty}^{\infty} f(x)\hat{U}^\dagger g(x)dx$*, we identify:* $\hat{U}^\dagger = e^{i(t-t_0)\hat{H}/\hbar}$.

Noticing that the inverse of $\hat{U}$ *equals,* $\hat{U}^{-1} = [e^{-i(t-t_0)\hat{H}/\hbar}]^{-1} = e^{i(t-t_0)\hat{H}/\hbar}$*, we obtain,* $\hat{U}^{-1} = \hat{U}^\dagger$*, which means that* $\hat{U}$ *is unitary.*

Exercise 4.6.1 *Let* $f_e(x)$ *and* $f_o(x)$ *be any even and odd functions respectively, namely,* $f_e(-x) = f_e(x)$ *and* $f_o(-x) = -f_o(x)$*. Prove that* $f_e(x)$ *and* $f_o(x)$ *are orthogonal according to the definition in Eq. (4.6.2).*

Solution 4.6.1

Changing integration variable, we have $\int_{-\infty}^{\infty} f_e^*(x)f_o(x)dx = \int_{-\infty}^{\infty} f_e^*(-x)f_o(-x)dx$*. Using* $f_e(-x) = f_e(x)$ *and* $f_o(-x) = -f_o(x)$*, we have* $\int_{-\infty}^{\infty} f_e^*(-x)f_o(-x)dx = -\int_{-\infty}^{\infty} f_e^*(x)f_o(x)dx$*, and consequently,*

$$\int_{-\infty}^{\infty} f_e^*(x)f_o(x)dx = -\int_{-\infty}^{\infty} f_e^*(x)f_o(x)dx \Rightarrow \int_{-\infty}^{\infty} f_e^*(x)f_o(x)dx = 0 \ .$$

Exercise 4.6.2 *The parity operator is defined by its operation:* $\hat{P}f(x) = f(-x)$*. (a) Prove that* $\hat{P}$ *is Hermitian. (b) Show that even or odd functions of* x *are eigenfunctions of* $\hat{P}$*. What are the corresponding eigenvalues? (c) Explain the result of Ex. 4.6.1, using (a) and (b).*

Solution 4.6.2

(a) For any f and g, $\int_{-\infty}^{\infty} f(x)\hat{P}g(x)dx = \int_{-\infty}^{\infty} f(x)g(-x)dx$.

Similarly, $\left[\int_{-\infty}^{\infty} g^*(x)\hat{P}f^*(x)dx\right]^* = \left[\int_{-\infty}^{\infty} g^*(x)f^*(-x)dx\right]^* = \int_{-\infty}^{\infty} g(x)f(-x)dx = \int_{-\infty}^{\infty} g(-x)f(x)dy$,

where in the last step we changed the integration variable. Consequently,

$\int_{-\infty}^{\infty} f(x)\hat{P}g(x)dx = \left[\int_{-\infty}^{\infty} g^*(x)\hat{P}f^*(x)dx\right]^*$ *, namely,* $\hat{P}$ *is Hermitian.*

(b) By definition,

$$\hat{P}f_e(x) = f_e(-x) = 1f_e(x)$$

$$\hat{P}f_o(x) = f_o(-x) = -1f_o(x) \ .$$

Hence even and odd functions are eigenfunctions of the parity operator with the eigenvalues "1" and "-1", respectively.

(c) Since $f_e(x)$ *and* $f_o(x)$ *are two eigenfunctions of a Hermitian operator (*$\hat{P}$*), associated with different eigenvalues (1,-1), they must be orthogonal to each other.*

Exercise 4.6.3 *Prove that if* $\hat{A}$ *is a linear operator, and if* $\varphi_1(x),\varphi_2(x),...,\varphi_N(x)$ *are degenerate eigenfunctions of* $\hat{A}$*, namely,* $\hat{A}\varphi_n(x) = \alpha\varphi_n(x)$*, for* $n \in 1,2,...,N$*, then any linear combination of these functions is an eigenfunction of* $\hat{A}$*, with the eigenvalue* α *.*

Solution 4.6.3

Let us consider any linear combination, $\psi(x) = \sum_{n=1}^{N} c_n\varphi_n(x)$*. Since* $\hat{A}$ *is linear we have,*

$\hat{A}\psi(x) = \sum_{n=1}^{N} c_n\hat{A}\varphi_n(x)$*. Using* $\hat{A}\varphi_n(x) = \alpha\varphi_n(x)$*, we have,*

$$\hat{A}\psi(x) = \sum_{n=1}^{N} c_n\alpha\varphi_n(x) = \alpha\sum_{n=1}^{N} c_n\varphi_n(x) = \alpha\psi(x) .$$

Hence, $\psi(x)$ *is an eigenfunction of* $\hat{A}$ *with the eigenvalue* α *.*

Exercise 4.6.4 *Given two degenerate normalized eigenfunctions of a linear operator* $\hat{A}$, $\hat{A}\varphi_1(x) = \alpha\varphi_1(x)$ *and* $\hat{A}\varphi_2(x) = \alpha\varphi_2(x)$, *show that the following functions,*

$$\psi_1(x) = \varphi_1(x) \quad ; \quad \psi_2(x) = \varphi_2(x) - \varphi_1(x)\int_{-\infty}^{\infty} dx'\varphi_1^*(x')\varphi_2(x'),$$

are two orthogonal eigenfunctions of $\hat{A}$ *corresponding to the same eigenvalue* α.

Solution 4.6.4

Noticing that $\psi_1(x)$ *and* $\psi_2(x)$ *are linear combinations of the degenerate eigenfunctions of* $\hat{A}$ ($\varphi_1(x)$ *and* $\varphi_2(x)$*), these functions are also eigenfunctions of* $\hat{A}$, *corresponding to the same eigenvalue,* α *(see Ex. 4.6.3). To prove that* $\psi_1(x)$ *and* $\psi_2(x)$ *are orthogonal to each other, we use their definitions,*

$$\int_{-\infty}^{\infty} dx\psi_2^*(x)\psi_1(x) = \int_{-\infty}^{\infty} dx\left[\varphi^*{}_2(x) - \varphi^*{}_1(x)\int_{-\infty}^{\infty} dx'\varphi_1(x')\varphi_2^*(x')\right]\varphi_1(x)$$

$$= \int_{-\infty}^{\infty} dx\varphi^*{}_2(x)\varphi_1(x) - \int_{-\infty}^{\infty} dx\varphi^*{}_1(x)\varphi_1(x)\int_{-\infty}^{\infty} dx'\varphi_2^*(x')\varphi_1(x')) = 0,$$

where in the last step we used the fact that $\varphi_1(x)$ *is normalized, namely,* $\int_{-\infty}^{\infty} dx\varphi^*{}_1(x)\varphi_1(x) = 1$.

Exercise 4.6.5 $\varphi_1(x)$, $\varphi_2(x)$ *and* $\varphi_3(x)$ *are eigenfunctions of a Hamiltonian* $\hat{H}_x$, *that is,* $\hat{H}_x\varphi_n(x) = E_n\varphi_n(x)$, *where* $E_1 \neq E_2 = E_3$. *Each* $\varphi_n(x)$ *corresponds to a stationary solution of the time-dependent Schrödinger equation,* $\psi_n(x,t) = \varphi_n(x)\mathrm{e}^{\frac{-iE_nt}{\hbar}}$. *Show that the following linear combinations of stationary solutions (*a_1, a_2, *and* a_3 *are non-zero scalars) are solutions to the time-dependent Schrödinger equation. Which of these solutions is stationary (namely, associated with a time-independent probability density function)? What is the conclusion?*

a. $\Psi(x,t) = a_1\psi_1(x,t) + a_2\psi_2(x,t)$

b. $\Psi(x,t) = a_3\psi_3(x,t) + a_2\psi_2(x,t)$

c. $\Psi(x,t) = a_3\psi_3(x,t) + a_1\psi_1(x,t)$

Solution 4.6.5

First, we can see that any linear combination of stationary solutions, $\Psi(x,t) = a_n\psi_n(x,t) + a_m\psi_m(x,t)$, *is a solution to the time-dependent Schrödinger equation:*

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\left[a_n\psi_n(x,t) + a_m\psi_m(x,t)\right] = i\hbar\frac{\partial}{\partial t}\left[a_n\varphi_n(x)\,\mathrm{e}^{\frac{-iE_nt}{\hbar}} + a_m\varphi_m(x)\,\mathrm{e}^{\frac{-iE_mt}{\hbar}}\right]$$
$$= \left[a_nE_n\varphi_n(x)\,\mathrm{e}^{\frac{-iE_nt}{\hbar}} + a_mE_m\varphi_m(x)\,\mathrm{e}^{\frac{-iE_mt}{\hbar}}\right] = \left[a_n\hat{H}_x\varphi_n(x)\,\mathrm{e}^{\frac{-iE_nt}{\hbar}} + a_m\hat{H}_x\varphi_m(x)\,\mathrm{e}^{\frac{-iE_mt}{\hbar}}\right]$$
$$= \hat{H}_x\left[a_n\varphi_n(x)\,\mathrm{e}^{\frac{-iE_nt}{\hbar}} + a_m\varphi_m(x)\,\mathrm{e}^{\frac{-iE_mt}{\hbar}}\right] = \hat{H}_x\Psi(x,t)\ .$$

Then, let us calculate the probability density:

$$|\Psi(x,t)|^2 = |a_n\psi_n(x,t) + a_m\psi_m(x,t)|^2$$
$$= |a_n\varphi_n(x)\,\mathrm{e}^{\frac{-iE_nt}{\hbar}} + a_m\varphi_m(x)\,\mathrm{e}^{\frac{-iE_mt}{\hbar}}|^2$$
$$= |a_n\varphi_n(x)\,\mathrm{e}^{\frac{-i(E_n-E_m)t}{\hbar}} + a_m\varphi_m(x)|^2\,|\mathrm{e}^{\frac{-iE_mt}{\hbar}}|^2$$
$$= |a_n\varphi_n(x)\,\mathrm{e}^{\frac{-i(E_n-E_m)t}{\hbar}} + a_m\varphi_m(x)|^2 .$$

The probability density is shown to depends on time unless $E_m = E_n$. *This means that a superposition of two* <u>*degenerate*</u> *stationary solutions with the same energy is also a stationary solution. Therefore, only case (b.) corresponds to a stationary solution.*

Exercise 4.6.6 *Show that the two Hamiltonians* $\hat{H}_x$, *and* $\hat{H}_x + \alpha$, *where* α *is a scalar constant, have the same eigenfunctions. What is the relation between the corresponding eigenvalues?*

Solution 4.6.6

Let $\varphi(x)$ *be an eigenfunction of* $\hat{H}_x$, *associated with an eigenvalue* λ, *namely,*

$\hat{H}_x\varphi(x) = \lambda\varphi(x)$. *Therefore,* $\left[\hat{H}_x + \alpha\right]\varphi(x) = \lambda\varphi(x) + \alpha\varphi(x) = [\lambda + \alpha]\varphi(x)$.

Consequently, $\varphi(x)$ *is an eigenfunction also of* $\hat{H}_x + \alpha$, *with a "displaced" eigenvalue,* $\lambda + \alpha$.

5 Energy Quantization

Exercise 5.3.1 *Prove that the solutions of the time-independent Schrödinger equation for the particle-in-a-box model (denoted as, $\psi_n(x)$), associated with different energy levels, are orthogonal to each other, as required by the Hermiticity of the Hamiltonian (Eq. (4.6.3)).*

Solution 5.3.1

Let us consider the overlap integral, $S=\int_{-\infty}^{\infty}\psi_n^*(x)\psi_m(x)dx$. *Using Eq. (5.3.9) for the explicit expressions of the normalized particle-in-a-box eigenfunctions,* $\psi_n(x)=\sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$, *we obtain*

$$S=\frac{2}{L}\int_0^L \sin(\frac{n\pi}{L}x)\sin(\frac{m\pi}{L}x)dx.$$

Using the trigonometric identity: $\sin(\alpha)\sin(\beta)=\frac{1}{2}[\cos(\alpha-\beta)-\cos(\alpha+\beta)]$, *we obtain*

$$S=\frac{1}{L}\int_0^L [\cos(\frac{(n-m)\pi x}{L})-\cos(\frac{(n+m)\pi x}{L})]dx,$$ *where for any two integers,* $n\neq m$, *we obtain*

$$S=\left.\frac{\sin(\frac{(n-m)\pi x}{L})}{(n-m)\pi}-\frac{\sin(\frac{(n+m)\pi x}{L})}{(n+m)\pi}\right|_0^L=0.$$

Hence, $\psi_n(x)$ *and* $\psi_m(x)$ *with* $n\neq m$ *are orthogonal functions.*

Exercise 5.4.1 *(a) Use Eq. (5.4.2) and the chain rule to derive Eq. (5.4.3) from Eq. (5.4.1). (b) Show that the z-component of the angular momentum reads* $\hat{L}_z=-i\hbar\frac{\partial}{\partial\varphi}$. *(c) Show that the kinetic energy operator for the particle on the ring reads* $\hat{H}=\frac{\hat{L}_z^2}{2\mu r^2}$.

Solution 5.4.1

(a) The derivatives of the polar coordinates with respect to the Cartesian ones read

$$\frac{\partial r}{\partial x} = \frac{\partial}{\partial x}\sqrt{x^2+y^2} = \frac{2x}{2\sqrt{x^2+y^2}} = \frac{x}{r}$$

$$\frac{\partial r}{\partial y} = \frac{\partial}{\partial y}\sqrt{x^2+y^2} = \frac{2y}{2\sqrt{x^2+y^2}} = \frac{y}{r}$$

$$\frac{\partial \varphi}{\partial x} = \frac{\partial}{\partial x} arc\cos(\frac{x}{r}) = \frac{-1}{\sqrt{1-\frac{x^2}{r^2}}}\frac{r-\frac{x^2}{r}}{r^2} = \frac{-1}{y}\frac{y^2}{r^2} = \frac{-y}{r^2}$$

$$\frac{\partial \varphi}{\partial y} = \frac{\partial}{\partial y} arc\cos(\frac{x}{r}) = \frac{-1}{\sqrt{1-\frac{x^2}{r^2}}}\frac{-x\frac{y}{r}}{r^2} = \frac{1}{y}\frac{xy}{r^2} = \frac{x}{r^2} \quad .$$

The chain rule therefore leads to

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \varphi}{\partial x}\right)\frac{\partial}{\partial \varphi} = \frac{x}{r}\frac{\partial}{\partial r} - \frac{y}{r^2}\frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial y} = \left(\frac{\partial r}{\partial y}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \varphi}{\partial y}\right)\frac{\partial}{\partial \varphi} = \frac{y}{r}\frac{\partial}{\partial r} + \frac{x}{r^2}\frac{\partial}{\partial \varphi} \quad .$$

For the second derivatives we then obtain

$$\begin{aligned}\frac{\partial^2}{\partial x^2} &= \frac{\partial}{\partial x}\frac{x}{r}\frac{\partial}{\partial r} - \frac{\partial}{\partial x}\frac{y}{r^2}\frac{\partial}{\partial \varphi}\\ &= \left(\frac{\partial}{\partial x}\frac{x}{r}\right)\frac{\partial}{\partial r} + \frac{x}{r}\frac{\partial}{\partial x}\frac{\partial}{\partial r} - \left(\frac{\partial}{\partial x}\frac{y}{r^2}\right)\frac{\partial}{\partial \varphi} - \frac{y}{r^2}\frac{\partial}{\partial x}\frac{\partial}{\partial \varphi}\\ &= \frac{y^2}{r^3}\frac{\partial}{\partial r} + \frac{x^2}{r^2}\frac{\partial^2}{\partial r^2} - \frac{xy}{r^3}\frac{\partial^2}{\partial \varphi \partial r} + \frac{2yx}{r^4}\frac{\partial}{\partial \varphi} - \frac{xy}{r^3}\frac{\partial^2}{\partial \varphi \partial r} + \frac{y^2}{r^4}\frac{\partial^2}{\partial \varphi^2}\end{aligned}$$

$$\begin{aligned}\frac{\partial^2}{\partial y^2} &= \frac{\partial}{\partial y}\frac{y}{r}\frac{\partial}{\partial r} + \frac{\partial}{\partial y}\frac{x}{r^2}\frac{\partial}{\partial \varphi}\\ &= \left(\frac{\partial}{\partial y}\frac{y}{r}\right)\frac{\partial}{\partial r} + \frac{y}{r}\frac{\partial}{\partial y}\frac{\partial}{\partial r} + \left(\frac{\partial}{\partial y}\frac{x}{r^2}\right)\frac{\partial}{\partial \varphi} + \frac{x}{r^2}\frac{\partial}{\partial y}\frac{\partial}{\partial \varphi}\\ &= \frac{x^2}{r^3}\frac{\partial}{\partial r} + \frac{y^2}{r^2}\frac{\partial^2}{\partial r^2} + \frac{xy}{r^3}\frac{\partial^2}{\partial \varphi \partial r} - \frac{2yx}{r^4}\frac{\partial}{\partial \varphi} + \frac{xy}{r^3}\frac{\partial^2}{\partial \varphi \partial r} + \frac{x^2}{r^4}\frac{\partial^2}{\partial \varphi^2} ,\end{aligned}$$

where, using $x^2 + y^2 = r^2$ *, we readily obtain,*

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}$$
$$=\frac{y^2}{r^3}\frac{\partial}{\partial r}+\frac{x^2}{r^2}\frac{\partial^2}{\partial r^2}-\frac{xy}{r^3}\frac{\partial^2}{\partial\varphi\partial r}+\frac{2yx}{r^4}\frac{\partial}{\partial\varphi}-\frac{xy}{r^3}\frac{\partial^2}{\partial\varphi\partial r}+\frac{y^2}{r^4}\frac{\partial^2}{\partial\varphi^2}$$
$$+\frac{x^2}{r^3}\frac{\partial}{\partial r}+\frac{y^2}{r^2}\frac{\partial^2}{\partial r^2}+\frac{xy}{r^3}\frac{\partial^2}{\partial\varphi\partial r}-\frac{2yx}{r^4}\frac{\partial}{\partial\varphi}+\frac{xy}{r^3}\frac{\partial^2}{\partial\varphi\partial r}+\frac{x^2}{r^4}\frac{\partial^2}{\partial\varphi^2}$$
$$=\frac{y^2}{r^3}\frac{\partial}{\partial r}+\frac{x^2}{r^2}\frac{\partial^2}{\partial r^2}+\frac{y^2}{r^4}\frac{\partial^2}{\partial\varphi^2}+\frac{x^2}{r^3}\frac{\partial}{\partial r}+\frac{y^2}{r^2}\frac{\partial^2}{\partial r^2}+\frac{x^2}{r^4}\frac{\partial^2}{\partial\varphi^2}$$
$$=\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2} \quad .$$

Therefore, the Hamiltonian transforms to:

$$\hat{H}=\frac{-\hbar^2}{2\mu}[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}]+V(x,y)=\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right)+V(r,\varphi).$$

For a constant potential energy, $V(r,\varphi)=0$*, and a constant distance,* $r=const$ *(the "particle on a ring" model), the derivatives with respect to* r *are null, hence, the Hamiltonian reads* $\hat{H}=\frac{-\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial\varphi^2}$

.

(b) By its definition, the z component of the angular momentum operator reads
$\hat{L}_z=\hat{x}\hat{p}_y-\hat{y}\hat{p}_x=-i\hbar\left[x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right].$

Using, $\frac{\partial}{\partial x}=\frac{x}{r}\frac{\partial}{\partial r}-\frac{y}{r^2}\frac{\partial}{\partial\varphi}$ *and* $\frac{\partial}{\partial y}=\frac{y}{r}\frac{\partial}{\partial r}+\frac{x}{r^2}\frac{\partial}{\partial\varphi}$ *(see (a)), we obtain*

$$\hat{L}_z=-i\hbar\left[\frac{xy}{r}\frac{\partial}{\partial r}+\frac{x^2}{r^2}\frac{\partial}{\partial\varphi}-\frac{xy}{r}\frac{\partial}{\partial r}+\frac{y^2}{r^2}\frac{\partial}{\partial\varphi}\right]=-i\hbar\left[\frac{x^2}{r^2}\frac{\partial}{\partial\varphi}+\frac{y^2}{r^2}\frac{\partial}{\partial\varphi}\right]=-i\hbar\frac{\partial}{\partial\varphi}.$$

(c) Using $\hat{L}_z=-i\hbar\frac{\partial}{\partial\varphi}$ *we obtain* $\frac{1}{2\mu r^2}\hat{L}_z^{\,2}=\frac{-\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial\varphi^2}$*, which identifies with the Hamiltonian for "a particle on a ring" (see (a)).*

Exercise 5.4.2 *Prove that the solutions to the time-independent Schrödinger equation for the particle-on a ring model, defined in Eq. (5.4.7), are orthogonal to each other. Recall that the relevant coordinate space is,* $0\le\varphi<2\pi$.

Solution 5.4.2

Let us consider the overlap integral, $S = \int_0^{2\pi} \Phi_m^*(\varphi)\Phi_{m'}(\varphi)d\varphi$.

Using Eq. (5.4.7) for the explicit expression of the normalized particle-on-a-ring eigenfunctions, we obtain

$S = \frac{1}{2\pi}\int_0^{2\pi} \left(e^{im\varphi}\right)^* e^{im'\varphi}d\varphi = \frac{1}{2\pi}\int_0^{2\pi} e^{i(m'-m)\varphi}d\varphi$, *where for any two integers,* $m' \neq m$, *we obtain,*

$S = \frac{1}{2\pi}\frac{e^{i(m'-m)2\pi}-1}{i(m'-m)} = 0$.

Hence, $\Phi_m(\varphi)$ *and* $\Phi_{m'}(\varphi)$ *with* $m' \neq m$ *are orthogonal functions.*

6 Wave Function Penetration, Tunneling and Quantum Wells

Exercise 6.2.1 *Derive Eq. (6.2.8).*

Solution 6.2.1

Using $\psi_1(x) = b_1 e^{-ik_1 x}$ *;* $\psi_2(x) = a_2 e^{ik_2 x} + b_2 e^{-ik_2 x}$ *;* $\psi_3(x) = a_3 e^{ik_3 x}$*, there are four continuity conditions (Eq. (6.2.7)) which impose the following limitations on the scalar coefficients:*

$\psi_1(0) = \psi_2(0) \Rightarrow b_1 = a_2 + b_2 \Rightarrow a_2 + b_2 - b_1 = 0$.

$$\frac{d}{dx}\psi_1(\mathrm{x})\bigg|_{x=0} = \frac{d}{dx}\psi_2(\mathrm{x})\bigg|_{x=0} \Rightarrow -ik_1 b_1 = ik_2(a_2 - b_2) \Rightarrow ik_2 a_2 - ik_2 b_2 + ik_1 b_1 = 0\,.$$

$$\psi_2(L) = \psi_3(L) \Rightarrow \psi_2(x) = a_2 e^{ik_2 L} + b_2 e^{-ik_2 L} = a_3 e^{ik_3 L} \Rightarrow e^{ik_2 L} a_2 + b_2 e^{-ik_2 L} - e^{ik_3 L} a_3 = 0\,.$$

$$\frac{d}{dx}\psi_2(\mathrm{x})\bigg|_{x=L} = \frac{d}{dx}\psi_3(\mathrm{x})\bigg|_{x=L} \Rightarrow ik_2\left(a_2 e^{ik_2 L} - b_2 e^{-ik_2 L}\right) = ik_3 a_3 e^{ik_3 L} \Rightarrow ik_2 e^{ik_2 L} a_2 - ik_2 e^{-ik_2 L} b_2 - ik_3 e^{ik_3 L} a_3 = 0$$

.

These four equations can be readily rearranged as a homogeneous matrix equation, Eq. (6.2.8).

Exercise 6.2.2 *Show that, when* $V_0 \to \infty$*, the energy levels and the stationary solutions of the Schrödinger equation for a finite square well potential converge to the results for an infinite box, obtained in chapter 5.*

Solution 6.2.2

The solutions to the Schrodinger equation for the symmetric finite square-well potential read

$$\psi(x) = \begin{cases} b_1 e^{-ik_1 x} & ; \quad x < 0 \\ a_2 e^{ik_2 x} + b_2 e^{-ik_2 x} & ; \quad 0 \le x \le L \\ a_3 e^{ik_3 x} & ; \quad x > L \end{cases},$$

where, $k_1 = k_3 = \sqrt{\dfrac{2m(E - V_0)}{\hbar^2}}$ *and* $k_2 = \sqrt{\dfrac{2mE}{\hbar^2}}$.

The continuity conditions (see Ex. 6.2.1) at $x = 0$ *are* $-ik_1 b_1 = ik_2(a_2 - b_2)$ *and* $b_1 = a_2 + b_2$, *which yields* $\frac{a_2}{b_2} = \frac{ik_2 - ik_1}{ik_2 + ik_1}$.

The continuity conditions at $x = L$ *are* $ik_2\left(a_2 e^{ik_2 L} - b_2 e^{-ik_2 L}\right) = ik_3 a_3 e^{ik_3 L}$ *and* $a_2 e^{ik_2 L} + b_2 e^{-ik_2 L} = a_3 e^{ik_3 L}$, *which yields* $\frac{a_2}{b_2} = e^{-2ik_2 L}\frac{ik_2 + ik_3}{ik_2 - ik_3}$. *Merging these results, recalling that* $k_1 = k_3$, *we obtain* $\left(\frac{ik_2 - ik_1}{ik_2 + ik_1}\right)^2 = e^{-2ik_2 L}$, *namely* $\frac{ik_2 - ik_1}{ik_2 + ik_1} = \pm e^{-ik_2 L}$.

For $V_0 \to \infty$ *we obtain* $ik_1 = ik_3 = i\sqrt{\frac{2m(E - V_0)}{\hbar^2}} = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \to \infty$ *, whereas* k_2 *remains finite for any finite energy* E. *Therefore, we obtain in this limit* $\frac{ik_2 - ik_1}{ik_2 + ik_1} \xrightarrow[ik_1 \to \infty]{} -1$. *Consequently,* $e^{-ik_2 L} \to \pm 1$, *from which follows* $k_2 L = n\pi$ *for* $n = 0, \pm 1, \pm 2, \ldots$. *This reproduces the quantization condition obtained directly for the infinite box in chapter 5 (Eq. (5.3.8)), where the corresponding energy levels are* $E = \frac{\hbar^2 k_2^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$ *(recalling that* $n = 0$ *is a trivial, improper solution, and that solutions associated with* $\pm n$ *are linearly dependent).*

Exercise 6.4.1 *Show that if the two linear operators, denoted* $\hat{H}$ *and* $\hat{P}$, *commute (* $[\hat{H}, \hat{P}] = 0$ *), and if* ψ *is an eigen function of* $\hat{H}$ *that corresponds to a non-degenerate eigenvalue, than* ψ *is also an eigenfunctions of* $\hat{P}$.

Solution 6.4.1

Let ψ *be an eigen function of* $\hat{H}$ *that corresponds to a non-degenerate eigenvalue* λ, $\hat{H}\psi = \lambda\psi$, *and let* $[\hat{H}, \hat{P}] = 0$. *Then,* $\hat{P}\hat{H}\psi = \hat{P}\lambda\psi \Rightarrow \hat{H}\hat{P}\psi = \lambda\hat{P}\psi$. *Consequently,* $\hat{P}\psi$ *is an eigenfunction of* $\hat{H}$ *with the same eigenvalue* λ. *Since the eigenvalue is nondegenerate,* ψ *and* $\hat{P}\psi$ *must be proportional to each other, namely,* $\hat{P}\psi = \alpha\psi$, *which means that* ψ *must be an eigenfunction also of* $\hat{P}$.

7 The Continuous Spectrum and Scattering States

Exercise 7.1.1 *A system of N particles is associated with the Hamiltonian* $\hat{H} = \sum_{n=1}^{N} \frac{-\hbar^2}{2m_n} \left[\frac{\partial^2}{\partial x_{1,n}^2} + \frac{\partial^2}{\partial x_{2,n}^2} + \frac{\partial^2}{\partial x_{3,n}^2} \right] + V(x_{1,1}, x_{2,1}, x_{3,1}, x_{1,2}..., x_{3,N})$, *where the nth particle is associated with the Cartesian coordinates,* $(x_{1,n}, x_{2,n}, x_{3,n})$. *The state of the system is represented by a solution to the time-dependent Schrödinger equation,* $\psi(x_{1,1}, x_{2,1}, x_{3,1}, x_{1,2}..., x_{3,N}, t) \equiv \psi(\mathbf{x}, t)$. *Prove the following identity:* $\frac{\partial}{\partial t} |\psi(\mathbf{x},t)|^2 = -\sum_{n=1}^{N} \sum_{j=1}^{3} \frac{\partial}{\partial x_{j,n}} J_{j,n}(\mathbf{x},t)$, *where* $J_{j,n}(\mathbf{x},t) \equiv \frac{\hbar}{m_n} \mathrm{Im}[\psi^*(\mathbf{x},t) \frac{\partial}{\partial x_{j,n}} \psi(\mathbf{x},t)]$.

Solution 7.1.1

The time-derivative of the probability density can be rewritten as

$$\frac{\partial}{\partial t} |\psi(\mathbf{x},t)|^2 = \frac{\partial}{\partial t} \psi^*(\mathbf{x},t)\psi(\mathbf{x},t) = \psi^*(\mathbf{x},t) \frac{\partial}{\partial t} \psi(\mathbf{x},t) + \psi(\mathbf{x},t) \frac{\partial}{\partial t} \psi^*(\mathbf{x},t) = 2\,\mathrm{Re}\left[\psi^*(\mathbf{x},t) \frac{\partial}{\partial t} \psi(\mathbf{x},t) \right]$$

, and the Schrodinger equation with the given Hamiltonians, $\hat{H} = \sum_{n=1}^{N} \sum_{j=1}^{3} \frac{-\hbar^2}{2m_n} \frac{\partial^2}{\partial x_{j,n}^2} + V(\mathbf{x})$, *reads* $\frac{\partial}{\partial t} \psi(\mathbf{x},t) = \left(\frac{1}{i\hbar} \sum_{n=1}^{N} \sum_{j=1}^{3} \frac{-\hbar^2}{2m_n} \frac{\partial^2}{\partial x_{j,n}^2} \psi(\mathbf{x},t) \right) + \frac{1}{i\hbar} V(\mathbf{x})\psi(\mathbf{x},t)$. *Consequently, we obtain*

$$\frac{\partial}{\partial t} |\psi(\mathbf{x},t)|^2 = 2\,\mathrm{Re}\left[\left(\frac{1}{i\hbar} \sum_{n=1}^{N} \sum_{j=1}^{3} \frac{-\hbar^2}{2m_n} \psi^*(\mathbf{x},t) \frac{\partial^2}{\partial x_{j,n}^2} \psi(\mathbf{x},t) \right) + \frac{1}{i\hbar} \psi^*(\mathbf{x},t) V(\mathbf{x}) \psi(\mathbf{x},t) \right].$$

Since the second term in the square brackets is purely imaginary, its real part vanishes, where the first term yields

$$\frac{\partial}{\partial t} |\psi(\mathbf{x},t)|^2 = -\sum_{n=1}^{N} \sum_{j=1}^{3} \frac{\hbar}{m_n} \mathrm{Im}\left[\psi^*(\mathbf{x},t) \frac{\partial^2}{\partial x_{j,n}^2} \psi(\mathbf{x},t) \right].$$

Using the identity,

$$\mathrm{Im}[\psi^*(\mathbf{x},t)\frac{\partial^2}{\partial x_{j,n}^2}\psi(\mathbf{x},t)] = \mathrm{Im}[\frac{\partial}{\partial x_{j,n}}\psi^*(\mathbf{x},t)\frac{\partial}{\partial x_{j,n}}\psi(\mathbf{x},t) - (\frac{\partial}{\partial x_{j,n}}\psi^*(\mathbf{x},t))(\frac{\partial}{\partial x_{j,n}}\psi(\mathbf{x},t))]$$

$$= \mathrm{Im}[\frac{\partial}{\partial x_{j,n}}\psi^*(\mathbf{x},t)\frac{\partial}{\partial x_{j,n}}\psi(\mathbf{x},t)],$$

where in the last step we used the fact that the last term in the square brackets is purely real, we obtain

$$\frac{\partial}{\partial t}|\psi(\mathbf{x},t)|^2 = -\sum_{n=1}^{N}\sum_{j=1}^{3}\frac{\hbar}{m_n}\mathrm{Im}[\frac{\partial}{\partial x_{j,n}}\psi^*(\mathbf{x},t)\frac{\partial}{\partial x_{j,n}}\psi(\mathbf{x},t)].$$

Identifying, $\frac{\hbar}{m_n}\mathrm{Im}[\psi^*(\mathbf{x},t)\frac{\partial}{\partial x_{j,n}}\psi(\mathbf{x},t)] \equiv J_{j,n}(\mathbf{x},t)$, *we finally obtain*

$$\frac{\partial}{\partial t}|\psi(\mathbf{x},t)|^2 = -\sum_{n=1}^{N}\sum_{j=1}^{3}\frac{\partial}{\partial x_{j,n}}J_{j,n}(\mathbf{x},t).$$

Exercise 7.2.1 *A single particle in a one-dimensional coordinate space (x) is associated with a proper stationary wave function. Show that the probability flux vanishes anywhere in space in this case.*

Solution 7.2.1

For a proper state the probability density vanishes at some boundaries, e.g., in one dimension, $|\psi(x,t)|^2 \xrightarrow[x\to\pm\infty]{} 0$. *Consequently, the wave function itself must vanish (Eq. (2.2.1)),* $\psi(x,t)\xrightarrow[x\to\pm\infty]{} 0$, *which means that the probability flux,* $J_E(x,t) = \frac{\hbar}{m}\mathrm{Im}[\psi_E^*(x,t)\frac{\partial}{\partial x}\psi_E(x,t)]$ *must also vanish,* $J_E(x,t)\xrightarrow[x\to\pm\infty]{} 0$. *For a stationary state the probability flux is constant in the entire space (Eq. (7.2.4)). Since for a proper state it vanishes at the boundaries, the probability flux must vanish everywhere for any proper stationary state.*

Exercise 7.3.1 *Given the scattering states* $\psi_{L\to R}(x)$ *and* $\psi_{R\to L}(x)$ *in Eqs. (7.3.1, 7.3.2), show that* $\psi_{R\to L}(x)$ *can be expressed as a linear combination of* $\psi_{L\to R}(x)$ *and* $\psi_{L\to R}^*(x)$, *and prove the result in Eq. (7.3.3).*

Solution 7.3.1

Using Eq. (7.3.1),

$$\psi_{L\to R}(x)=\begin{cases} e^{ik_1x}+b_1e^{-ik_1x} & ; \quad x<x_1 \\ \vdots & \\ a_Ne^{ik_Nx} & ; \quad x>x_{N-1} \end{cases},$$

and taking its complex conjugate, we obtain

$$\psi^*_{L\to R}(x)=\begin{cases} e^{-ik_1x}+b_1^*e^{ik_1x} & ; \quad x<x_1 \\ \vdots & \\ a_N^*e^{-ik_Nx} & ; \quad x>x_{N-1} \end{cases}.$$

The following superposition of the two degenerate states, $\tilde{\psi}(x)=\frac{1}{a_N{}^*}\psi^*_{L\to R}(x)-\frac{b_1^*}{a_N{}^*}\psi_{L\to R}(x)$, *reads*

$$\tilde{\psi}(x)=\begin{cases} \frac{1-|b_1|^2}{a_N{}^*}e^{-ik_1x} & ; \quad x<x_1 \\ \vdots & \\ e^{-ik_Nx}-\frac{b_1{}^*a_N}{a_N{}^*}e^{ik_Nx} & ; \quad x>x_{N-1} \end{cases}.$$

Comparing the result to $\psi_{R\to L}(x)$ *in Eq. (7.3.2),*

$$\psi_{R\to L}(x)=\begin{cases} \bar{a}_1e^{-ik_1x} & ; \quad x<x_1 \\ \vdots & \\ e^{-ik_Nx}+\bar{b}_Ne^{ik_Nx} & ; \quad x>x_{N-1} \end{cases},$$

we can see that $\psi_{R\to L}(x)$ *can indeed be expressed as superposition of* $\psi_{L\to R}(x)$ *and* $\psi^*_{L\to R}(x)$, *where we identify relations between the parameters* $\bar{a}_1$ *and* $\bar{b}_N$ *(defining the transmission and reflection associated with* $\psi_{R\to L}(x)$*) to* a_N *and* b_1 *(defining the transmission and reflection associated with* $\psi_{L\to R}(x)$*), namely,* $\bar{b}_N=-\frac{b_1{}^*a_N}{a_N{}^*}$ *and* $\bar{a}_1=\frac{1-|b_1|^2}{a_N{}^*}$.

Using the definitions of the reflection (Eq. (7.2.18)): $R(E)_{L\to R}=|b_1|^2$ *and* $R(E)_{R\to L}=|\bar{b}_N|^2$, *we obtain* $\bar{b}_N=-\frac{b_1{}^*a_N}{a_N{}^*}\Rightarrow|b_1|^2=|\bar{b}_N|^2$, *and therefore,*

$$R(E)_{L\to R}=R(E)_{R\to L}.$$

Using the definitions of the transmission (Eqs. (7.2.18, 7.2.19)): $T(E)_{L\to R} = |a_N|^2 \frac{k_N}{k_1} = 1 - |b_1|^2$ *and* $T(E)_{R\to L} = |\bar{a}_1|^2 \frac{k_1}{k_N}$*, we obtain*

$$\bar{a}_1 = \frac{1-|b_1|^2}{a_N^{\ *}} = \frac{T(E)_{L\to R}}{a_N^{\ *}} = \frac{|a_N|^2 \frac{k_N}{k_1}}{a_N^{\ *}} = a_N \frac{k_N}{k_1} \Rightarrow |\bar{a}_1|^2 = |a_N|^2 \frac{k_N^{\ 2}}{k_1^2} \Rightarrow |\bar{a}_1|^2 \frac{k_1}{k_N} = |a_N|^2 \frac{k_N}{k_1}, \quad and$$

therefore,

$T(E)_{R\to L} = T(E)_{L\to R}$.

Exercise 7.3.2 *Given a single potential energy step,* $V(x) = \begin{cases} x \le 0 & ; & V_1 \\ x > 0 & ; & V_2 \end{cases}$*, where* $V_2 > V_1$*, use Eq. (7.2.20) to show that the reflection probability equals unity in the scattering energy range,* $V_1 < E < V_2$.

Solution 7.3.2

For $V(x) = \begin{cases} x \le 0 & ; & V_1 \\ x > 0 & ; & V_2 \end{cases}$*, with* $V_2 > V_1$*, the wave function corresponding to a stationary flux from a left source at any energy,* $E > V_1$*, reads* $\psi_E(x) = \begin{cases} a_1 e^{ik_1 x} + b_1 e^{-ik_1 x} & ; & x \le 0 \\ a_2 e^{ik_2 x} & ; & x > 0 \end{cases}$*, where,* $k_1 = \sqrt{\frac{2m(E-V_1)}{\hbar^2}}$ *and* $k_2 = \sqrt{\frac{2m(E-V_2)}{\hbar^2}}$*. Using the recursion relation, Eq. (7.2.20), for this case, we have* $x_1 = 0$ *and* $r_2 = 0$*. Consequently, we obtain* $r_1 = \frac{k_2 - k_1}{-k_2 - k_1}$*. For* $E < V_2$*,* $k_2 = \sqrt{\frac{2m(E-V_2)}{\hbar^2}}$ *is purely imaginary, hence,* $R(E) \equiv |r_1|^2 = 1$.

Alternatively, we can use the fact that $\psi_{L\to R}(x) \xrightarrow[x\to\infty]{} 0$ *and therefore the asymptotic flux (see Eq. (7.2.3)) vanishes,* $J_E(x) = \frac{\hbar}{m} \mathrm{Im}[\psi_E^*(x) \frac{\partial}{\partial x} \psi_E(x)] \xrightarrow[x\to\infty]{} 0$*. Since for a stationary solution the probability flux obtains a constant value in the entire space (Eq. (7.2.4)), the flux vanishes also in the* *region* $x \leq 0$*, where we have (Eq. (7.2.3))* $J_E = \frac{k_1 \hbar}{m}(|a_1|^2 - |b_1|^2) = 0$*, which means that* $|b_1|^2 = |a_1|^2$*. Therefore, the reflection probability (see Eq. (7.2.18)) is unity,* $R(E) = \frac{|b_1|^2}{|a_1|^2} = 1$.

Exercise (7.4.1) *Derive the result Eq. (7.4.3) for the transmission and reflection probabilities for particles scattering from a square potential energy barrier (or well).*

Solution (7.4.1)

For $V(x) = \begin{cases} V_0 & ; \quad x < 0 \\ V_1 & ; \quad 0 \leq x < L \\ V_0 & ; \quad L \leq x \end{cases}$*, the wave function corresponding to a stationary flux from a left source at any energy,* $E > V_0$*, reads* $\psi(x) = \begin{cases} a_1 e^{ik_1 x} + b_1 e^{-ik_1 x} & ; \quad x < 0 \\ a_2 e^{ik_2 x} + b_2 e^{-ik_2 x} & ; \quad 0 \leq x < L \\ a_3 e^{ik_1 x} & ; \quad L \leq x \end{cases}$*, where* $k_1 = k_3 \equiv \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$ *and* $k_2 \equiv \sqrt{\frac{2m(E - V_1)}{\hbar^2}}$*. Implementing the recursion relation (Eq. (7.2.20)) for this case, we have* $r_3 = 0$, $r_2 = e^{2ik_2 L}\frac{k_2 - k_1}{k_2 + k_1}$*, and* $r_1 = \frac{k_1^2 - k_2^2}{k_2^2 + k_1^2 + 2ik_1 k_2 \cot(k_2 L)}$*. The reflection probability is given as,* $R(E) = |r_1|^2$*, where, using Eq. (7.2.19),* $T(E) = 1 - R(E)$.

For $E > V_1$, $k_2 \equiv \sqrt{\frac{2m(E - V_1)}{\hbar^2}}$ *is real-valued, hence,*

$$R(E) = |r_1|^2 = \left|\frac{k_1^2 - k_2^2}{k_2^2 + k_1^2 + 2ik_1 k_2 \cot(k_2 L)}\right|^2 = \frac{(k_1^2 - k_2^2)^2}{(k_2^2 + k_1^2)^2 + 4k_1^2 k_2^2 \cot^2(k_2 L)}.$$

For $E < V_1$, $k_2 \equiv \sqrt{\frac{2m(E - V_1)}{\hbar^2}} = i\alpha$*, is purely imaginary, hence,*

$$R(E) = |r_1|^2 = \left|\frac{k_1^2 - k_2^2}{k_2^2 + k_1^2 + 2ik_1 k_2 \cot(k_2 L)}\right|^2 = \left|\frac{k_1^2 + \alpha^2}{-\alpha^2 + k_1^2 - 2\alpha k_1 \cot(i\alpha L)}\right|^2$$

$$= \left|\frac{k_1^2 + \alpha^2}{-\alpha^2 + k_1^2 + i2\alpha k_1 \coth(\alpha L)}\right|^2 = \frac{\left(k_1^2 + \alpha^2\right)^2}{\left(-\alpha^2 + k_1^2\right)^2 + 4\alpha^2 k_1^2 \coth^2(\alpha L)} \quad .$$

Using $\alpha = -ik_2$*, and the formal relations,*

$$\coth^2(\alpha L) = \left(\frac{e^{\alpha L}+e^{-\alpha L}}{e^{\alpha L}-e^{-\alpha L}}\right)^2 = \left(\frac{e^{-ik_2 L}+e^{ik_2 L}}{e^{-ik_2 L}-e^{ik_2 L}}\right)^2 = \left(\frac{2\cos(k_2 L)}{-2i\sin(k_2 L)}\right)^2 = -\cot^2(k_2 L),$$

we obtain also in this case,

$$R(E) = \frac{\left(k_1^2+\alpha^2\right)^2}{\left(-\alpha^2+k_1^2\right)^2+4\alpha^2 k_1^2\coth^2(\alpha L)} = \frac{\left(k_1^2-k_2^2\right)^2}{\left(k_2^2+k_1^2\right)^2+4k_2^2 k_1^2\cot^2(k_2 L)}.$$

Exercise 7.5.1 *Given a symmetric double barrier potential,*

$$V(x) = \begin{cases} V_0 & ; \quad x < -(L+d/2) \\ V_1 & ; \quad -(L+d/2) \le x < -d/2 \\ V_0 & ; \quad -d/2 \le x < d/2 \\ V_1 & ; \quad d/2 \le x < d/2+L \\ V_0 & ; \quad d/2+L \le x \end{cases},$$

obtain an equation for the scattering energies in which the transmission probability is 100%.

Solution 7.5.1

Given the five segments potential energy function and considering a left flux source, the reflection in the fifth (right most) segment vanishes by the boundary conditions (Eq. (7.2.14)), $r_5 = 0$*. The condition of 100% transmission means that also in the left most segment reflection should vanish, namely,* $r_1 = 0$ *. A simple condition on the energies fulfilling these conditions is based on the recursion relation, Eq. (7.2.20). Propagating backward from* $r_5 = 0$ *and forward from* $r_1 = 0$ *we can obtain different expressions for* r_3*, which must match each other at the set of energies associated with full transmission.*

Using the definitions that comply with the given potential energy function,

$$V(x) = \begin{cases} V_0 & ; \quad x < -(L+d/2) \\ V_1 & ; \quad -(L+d/2) \le x < -d/2 \\ V_0 & ; \quad -d/2 \le x < d/2 \\ V_1 & ; \quad d/2 \le x < d/2+L \\ V_0 & ; \quad d/2+L \le x \end{cases}$$ *, namely*

$$\begin{aligned} x_1 &= -(L+d/2) \\ x_2 &= -d/2 \\ x_3 &= d/2 \\ x_4 &= L+d/2 \end{aligned} \quad ; \quad k_1 = k_3 = k_5 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \quad ; \quad k_2 = k_4 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \,,$$

and the recursion relation (Eq. (7.2.20)), $r_n = e^{2ik_n x_n} \dfrac{(k_{n+1}-k_n)e^{ik_{n+1}x_n} - (k_{n+1}+k_n)e^{-ik_{n+1}x_n} r_{n+1}}{-(k_{n+1}+k_n)e^{ik_{n+1}x_n} + (k_{n+1}-k_n)e^{-ik_{n+1}x_n} r_{n+1}}$ *, we obtain*

$$r_5 = 0 \Rightarrow r_4 = e^{2ik_4 x_4} \frac{k_4-k_3}{k_4+k_3} \Rightarrow r_3 = e^{2ik_3 x_3} \frac{e^{-2ik_4 L} - 1}{\frac{k_4+k_3}{k_3-k_4} e^{-2ik_4 L} + \frac{k_4-k_3}{k_4+k_3}} \,,$$

and

$$r_1 = 0 \Rightarrow r_2 = e^{-2ik_4 x_4} \frac{k_4-k_3}{k_4+k_3} \Rightarrow r_3 = e^{2ik_3 x_2} \frac{e^{2ik_4 L} - 1}{\frac{k_4+k_3}{k_3-k_4} e^{2ik_4 L} + \frac{k_4-k_3}{k_4+k_3}} \,.$$

Denoting, $\alpha = \dfrac{k_4+k_3}{k_3-k_4}$ *, and comparing the two equations we obtain the condition for perfect transmission for this model,* $\alpha^2 = \dfrac{\cos(k_3 d) + i\sin(k_3 d - 2k_4 L)}{\cos(k_3 d) - i\sin(k_3 d + 2k_4 L)}$.

8 Mechanical Vibrations and the Harmonic Oscillator Model

Exercise 8.3.1 *Show that the function* $\chi(y) = e^{\pm y^2/2} y^n$ *, satisfies the asymptotic equation for the harmonic oscillator; namely,* $\frac{\partial^2}{\partial y^2}\varphi(y) \xrightarrow[y\to\pm\infty]{} y^2\varphi(y)$ *, for any finite* n *.*

Solution 8.3.1

$$\frac{\partial^2}{\partial y^2}\left(y^n e^{\pm y^2/2}\right) = \frac{\partial}{\partial y}(ny^{n-1} \pm y^{n+1})e^{\pm y^2/2}$$

$$\xrightarrow[y\to\pm\infty]{} \frac{\partial}{\partial y}(\pm y^{n+1})e^{\pm y^2/2} = (\pm(n+1)y^n + y^{n+2})e^{\pm y^2/2}$$

$$\xrightarrow[y\to\pm\infty]{} y^{n+2}e^{\pm y^2/2} = y^2\left(y^n e^{\pm y^2/2}\right) \quad .$$

Exercise 8.3.2 *Verify that* $\varphi_0(y)$ *and* λ_0 *, as defined in Eq. (8.3.5), are indeed an eigenfunction and its corresponding eigenvalue of Eq. (8.3.3).*

Solution 8.3.2

Using Eq. (8.3.5), $\varphi_0(y) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} e^{-y^2/2}$ *and* $\lambda_0 = \frac{1}{2}$ *. Consequently,*

$$\frac{1}{2}[y^2 - \frac{\partial^2}{\partial y^2}]\varphi_0(y) = \frac{1}{2}[y^2 - \frac{\partial^2}{\partial y^2}]\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} e^{-y^2/2}$$
$$= \frac{1}{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} y^2 e^{-y^2/2} + \frac{1}{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \frac{\partial}{\partial y} \mathrm{y}\, e^{-y^2/2}$$
$$= \frac{1}{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} y^2 e^{-y^2/2} - \frac{1}{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} y^2 e^{-y^2/2} + \frac{1}{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} e^{-y^2/2}$$

$$= \frac{1}{2}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} e^{-y^2/2} = \frac{1}{2}\varphi_0(y) \ ,$$

which implies that $\varphi_0(y) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} e^{-y^2/2}$ *is an eigenfunction of* $\frac{1}{2}[y^2 - \frac{\partial^2}{\partial y^2}]$, *associated with the eigenvalue,* $\lambda_0 = \frac{1}{2}$.

Exercise 8.3.3 *Show that if* $\varphi_n(y)$ *is a solution to the eigenvalue equation for a harmonic oscillator, that is,* $\frac{1}{2}[y^2 - \frac{\partial^2}{\partial y^2}]\varphi_n(y) = \lambda_n \varphi_n(y)$ *, then:*

(a) $[y - \frac{\partial}{\partial y}]\varphi_n(y)$ *is also an eigenstate solution, with the respective eigenvalue,* $(\lambda_n + 1)$ *,*

(b) $[y + \frac{\partial}{\partial y}]\varphi_n(y)$ *is also an eigenstate solution, with the respective eigenvalue,* $(\lambda_n - 1)$.

You can use the commutators, $[(y^2 - \frac{\partial^2}{\partial y^2}), (y \mp \frac{\partial}{\partial y})] = \pm 2(y \mp \frac{\partial}{\partial y})$.

Solution 8.3.3

First let us verify the given commutator,

$$[(y^2 - \frac{\partial^2}{\partial y^2}), (y \mp \frac{\partial}{\partial y})] = (y^2 - \frac{\partial^2}{\partial y^2})(y \mp \frac{\partial}{\partial y}) - (y \mp \frac{\partial}{\partial y})(y^2 - \frac{\partial^2}{\partial y^2})$$
$$= \mp y^2 \frac{\partial}{\partial y} - \frac{\partial^2}{\partial y^2} y + y \frac{\partial^2}{\partial y^2} \pm \frac{\partial}{\partial y} y^2$$
$$= \mp y^2 \frac{\partial}{\partial y} - y \frac{\partial^2}{\partial y^2} - 2\frac{\partial}{\partial y} + y \frac{\partial^2}{\partial y^2} \pm 2y \pm y^2 \frac{\partial}{\partial y}$$
$$= 2(\pm y - \frac{\partial}{\partial y}) = \pm 2(y \mp \frac{\partial}{\partial y}).$$

Given $\varphi_n(y)$ *that satisfies the equation,* $\frac{1}{2}[y^2 - \frac{\partial^2}{\partial y^2}]\varphi_n(y) = \lambda_n \varphi_n(y)$ *, we obtain*

(a)

$$\frac{1}{2}(y^2 - \frac{\partial^2}{\partial y^2})(y - \frac{\partial}{\partial y})\varphi_n(y)$$
$$= \frac{1}{2}(y - \frac{\partial}{\partial y})(y^2 - \frac{\partial^2}{\partial y^2})\varphi_n(y) + \frac{1}{2}[(y^2 - \frac{\partial^2}{\partial y^2}), (y - \frac{\partial}{\partial y})]\varphi_n(y) = (\lambda_n + 1)(y - \frac{\partial}{\partial y})\varphi_n(y) \quad .$$
$$= (y - \frac{\partial}{\partial y})\lambda_n \varphi_n(y) + (y - \frac{\partial}{\partial y})\varphi_n(y)$$

(b)

$$\frac{1}{2}(y^2-\frac{\partial^2}{\partial y^2})(y+\frac{\partial}{\partial y})\varphi_n(y)$$
$$=\frac{1}{2}(y+\frac{\partial}{\partial y})(y^2-\frac{\partial^2}{\partial y^2})\varphi_n(y)+\frac{1}{2}[(y^2-\frac{\partial^2}{\partial y^2}),(y+\frac{\partial}{\partial y})]\varphi_n(y)$$
$$=(y+\frac{\partial}{\partial y})\lambda_n\varphi_n(y)-(y+\frac{\partial}{\partial y})\varphi_n(y)$$
$$=(\lambda_n-1)(y+\frac{\partial}{\partial y})\varphi_n(y) \quad .$$

Exercise 8.3.4 *Let* $\varphi_n(y)$ *be a normalized solution to the Schrödinger equation for the harmonic oscillator:* $\frac{1}{2}[y^2-\frac{\partial^2}{\partial y^2}]\varphi_n(y)=(n+\frac{1}{2})\varphi_n(y)$. *Show that:*

(a) $\varphi_{n+1}(y)=\frac{1}{\sqrt{2(n+1)}}[y-\frac{\partial}{\partial y}]\varphi_n(y)$ *is also normalized.*

(b) $\varphi_{n-1}(y)=\frac{1}{\sqrt{2n}}[y+\frac{\partial}{\partial y}]\varphi_n(y)$ *is also normalized.*

Solution 8.3.4

First, using integration by parts we can readily see that the following identity holds for any proper functions, $f(y)\xrightarrow[y\to\pm\infty]{}0$ *and* $g(y)\xrightarrow[y\to\pm\infty]{}0$,

$$\int_{-\infty}^{\infty} f(y)\left(y+\frac{\partial}{\partial y}\right)g(y)dy=\int_{-\infty}^{\infty} g(y)\left(y-\frac{\partial}{\partial y}\right)f(y)dy\,.$$

Using the given normalization condition, $\int_{-\infty}^{\infty} dy\varphi_n^*(y)\varphi_n(y)=1$, *we therefore obtain*

(a)

$$\int_{-\infty}^{\infty} dy\varphi_{n+1}^*(y)\varphi_{n+1}(y) = \frac{1}{2(n+1)}\int_{-\infty}^{\infty} dy[y-\frac{\partial}{\partial y}]\varphi_n^*[y-\frac{\partial}{\partial y}]\varphi_n(y)$$

$$= \left[\frac{1}{2(n+1)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[y+\frac{\partial}{\partial y}][y-\frac{\partial}{\partial y}]\varphi_n(y)\right]^*$$

$$= \left[\frac{1}{2(n+1)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[y^2-\frac{\partial^2}{\partial y^2}+[\frac{\partial}{\partial y},y]]\varphi_n(y)\right]^*$$

$$= \left[\frac{1}{2(n+1)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[2\frac{1}{2}[y^2-\frac{\partial^2}{\partial y^2}]+1]\varphi_n(y)\right]^*$$

$$= \left[\frac{1}{2(n+1)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[2[n+\frac{1}{2}]+1]\varphi_n(y)\right]^* = \left[\int_{-\infty}^{\infty} dy\varphi_n^*(y)\varphi_n(y)\right]^* = 1 .$$

(b)

$$\int_{-\infty}^{\infty} dy\varphi_{n-1}^*(y)\varphi_{n-1}(y) = \frac{1}{2(n)}\int_{-\infty}^{\infty} dy[y+\frac{\partial}{\partial y}]\varphi_n^*[y+\frac{\partial}{\partial y}]\varphi_n(y)$$

$$= \left[\frac{1}{2(n)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[y-\frac{\partial}{\partial y}][y+\frac{\partial}{\partial y}]\varphi_n(y)\right]^*$$

$$= \left[\frac{1}{2(n)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[y^2-\frac{\partial^2}{\partial y^2}-[\frac{\partial}{\partial y},y]]\varphi_n(y)\right]^*$$

$$= \left[\frac{1}{2(n)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[2\frac{1}{2}[y^2-\frac{\partial^2}{\partial y^2}]-1]\varphi_n(y)\right]^*$$

$$= \left[\frac{1}{2(n)}\int_{-\infty}^{\infty} dy\varphi_n^*(y)[2[n+\frac{1}{2}]-1]\varphi_n(y)\right]^* = \left[\int_{-\infty}^{\infty} dy\varphi_n^*(y)\varphi_n(y)\right]^* = 1 .$$

Exercise 8.3.5 *Let us denote the classical amplitude of motion for a harmonic oscillator at energy E_n as Δ_n. Show that the level spacing near E_n ,namely, $E_{n+1}-E_n$, is inversely proportional to Δ_n, namely, a larger amplitude of motion corresponds to a more dense energy spectrum (the quantum size effect).*

Solution 8.3.5

Denoting by Δ_n the classical amplitude of motion at an energy E_n, we obtain $E_n = \frac{1}{2}m\omega^2\Delta_n{}^2$. The level spacing for the harmonic oscillator reads $E_{n+1}-E_n = \hbar\omega$. Consequently,

$$E_{n+1} - E_n \propto \sqrt{\frac{2E_n}{m\Delta_n^{\ 2}}} = \sqrt{\frac{2E_n}{m}}\frac{1}{\Delta_n}.$$

Exercise 8.5.1 *Use the definition of a Hermitian conjugate, Eq. (4.5.2), and show that $\hat{b}^\dagger$ is the Hermitian conjugate of $\hat{b}$, using their definitions in Eqs. (8.5.5, 8.5.6).*

Solution 8.5.1

In Ex. 8.3.4 we used the fact that for any two proper functions, $f(y) \xrightarrow[y\to\pm\infty]{} 0$ *and* $g(y) \xrightarrow[y\to\pm\infty]{} 0$, *we have* $\int_{-\infty}^{\infty} f(y)\left(y + \frac{\partial}{\partial y}\right)g(y)dy = \int_{-\infty}^{\infty} g(y)\left(y - \frac{\partial}{\partial y}\right)f(y)dy$. *Using this result, we readily obtain* $\int_{-\infty}^{\infty} f(y)\frac{1}{\sqrt{2}}\left(y + \frac{\partial}{\partial y}\right)g(y)dy = \left(\int_{-\infty}^{\infty} g^*(y)\frac{1}{\sqrt{2}}\left(y - \frac{\partial}{\partial y}\right)f^*(y)dy\right)^*$. *Recalling the definition of Hermitian conjugates,* $\int_{-\infty}^{\infty} f(x)\hat{A}^\dagger g(x)dx = \left(\int_{-\infty}^{\infty} g^*(x)\hat{A}f^*(x)dx\right)^*$ *we can conclude that* $\frac{1}{\sqrt{2}}\left(y + \frac{\partial}{\partial y}\right)$ *and* $\frac{1}{\sqrt{2}}\left(y - \frac{\partial}{\partial y}\right)$ *are Hermitian conjugates in the space of proper functions.*

Alternatively, we can use the identity, $\left(y \pm \frac{\partial}{\partial y}\right) = \hat{y} \pm i\hat{p}_y$, *and the Hermiticity of the operators* $\hat{y}$ *and* $\hat{p}_y$, *to show that* $\frac{1}{\sqrt{2}}\left(y + \frac{\partial}{\partial y}\right)$ *and* $\frac{1}{\sqrt{2}}\left(y - \frac{\partial}{\partial y}\right)$ *are Hermitian conjugates, namely*

$$\int_{-\infty}^{\infty} f(y)\hat{b}g(y)dy = \int_{-\infty}^{\infty} f(y)\frac{1}{\sqrt{2}}(y+\frac{\partial}{\partial y})g(y)dy$$

$$= \int_{-\infty}^{\infty} f(y)\frac{1}{\sqrt{2}}(\hat{y}+i\hat{p}_y)g(y)dy$$

$$= \frac{1}{\sqrt{2}}\int_{-\infty}^{\infty} f(y)\hat{y}g(y)dy + i\frac{1}{\sqrt{2}}\int_{-\infty}^{\infty} f(y)\hat{p}_y g(y)dy$$

$$= \frac{1}{\sqrt{2}}\left(\int_{-\infty}^{\infty} g^*(y)\hat{y}f^*(y)dy\right)^* + i\frac{1}{\sqrt{2}}\left(\int_{-\infty}^{\infty} g^*(y)\hat{p}_y f^*(y)dy\right)^*$$

$$= \frac{1}{\sqrt{2}}\left(\int_{-\infty}^{\infty} g^*(y)\hat{y}f^*(y)dy - i\int_{-\infty}^{\infty} g^*(y)\hat{p}_y f^*(y)dy\right)^*$$

$$= \frac{1}{\sqrt{2}}\left(\int_{-\infty}^{\infty} g^*(y)\left(\hat{y}-i\hat{p}_y\right)f^*(y)dy\right)^*$$

$$= \frac{1}{\sqrt{2}}\left(\int_{-\infty}^{\infty} g^*(y)\left(y-\frac{\partial}{\partial y}\right)f^*(y)dy\right)^*$$

$$= \frac{1}{\sqrt{2}}\left(\int_{-\infty}^{\infty} g^*(y)\hat{b}^\dagger f^*(y)dy\right)^* \quad .$$

Exercise 8.5.2 *Use the definition the creation and annihilation operators (Eqs. (8.5.5, 8.5.6)), and show that* $[\hat{b},\hat{b}^\dagger]=1$.

Solution 8.5.2

$$[\hat{b},\hat{b}^\dagger]f(y) = \frac{1}{2}[(y+\frac{\partial}{\partial y})(y-\frac{\partial}{\partial y}) - (y-\frac{\partial}{\partial y})(y+\frac{\partial}{\partial y})]f(y)$$

$$= \frac{1}{2}[(y^2-\frac{\partial^2}{\partial y^2}+\frac{\partial}{\partial y}y - y\frac{\partial}{\partial y}) - (y^2-\frac{\partial^2}{\partial y^2}+y\frac{\partial}{\partial y}-\frac{\partial}{\partial y}y)]f(y)$$

$$= \frac{1}{2}[(2\frac{\partial}{\partial y}\mathrm{y} - 2y\frac{\partial}{\partial y})]f(y)$$

$$= [\frac{\partial}{\partial y}\mathrm{y} - y\frac{\partial}{\partial y}]f(y)$$

$$= f(y) \ .$$

Exercise 8.5.3 *The rate of transitions between stationary states of a system via a "weak" external perturbation is proportional to the "perturbation matrix element" squared (see chapters 17-20). In the case of a molecular vibration interacting with an electromagnetic field, the perturbation operator is the molecular dipole, which is proportional to the interatomic distance,* y*, and the stationary states are approximated as the harmonic oscillator eigenfunctions. The transition rate between two stationary states,* $\varphi_n(y)$ *and* $\varphi_{n'}(y)$*, is therefore given by* $k_{n\to n'} \propto \left|\int_{-\infty}^{\infty} \varphi_{n'}^*(y) y \varphi_n(y) dy\right|^2$ *. (a) Use Eqs. (8.5.3, 8.5.4, 8.5.8) and the orthonormality of the stationary states to show that the transition is subject to a "selection rule":* $k_{n\to n'} \propto \left[n\delta_{n',n-1} + (n+1)\delta_{n',n+1} \right]$*. (b) Use this result to show that the transition from the ground state is restricted to the first excited state.*

Solution 8.5.3

(a) Using $y = \frac{1}{\sqrt{2}}(\hat{b} + \hat{b}^\dagger)$*, the transition rate can be expressed in terms of Dirac's ladder operators,*

$$k_{n\to n'} \propto \left|\int_{-\infty}^{\infty} \varphi_{n'}^*(y) y \varphi_n(y) dy\right|^2 \propto \left|\int_{-\infty}^{\infty} \varphi_{n'}^*(y)(\hat{b} + \hat{b}^\dagger)\varphi_n(y) dy\right|^2$$

$$= \left|\int_{-\infty}^{\infty} \varphi_{n'}^*(y)\hat{b}\varphi_n(y) dy + \int_{-\infty}^{\infty} \varphi_{n'}^*(y)\hat{b}^\dagger\varphi_n(y) dy\right|^2 .$$

Using $\hat{b}\varphi_n(y) = \sqrt{n}\varphi_{n-1}(y)$ *and* $\hat{b}^\dagger\varphi_n(y) = \sqrt{n+1}\varphi_{n+1}(y)$*, we obtain*

$$k_{n\to n'} \propto \left|\int_{-\infty}^{\infty} \varphi_{n'}^*(y)\sqrt{n}\varphi_{n-1}(y) dy + \int_{-\infty}^{\infty} \varphi_{n'}^*(y)\sqrt{n+1}\varphi_{n+1}(y) dy\right|^2$$

$$= \left|\sqrt{n}\int_{-\infty}^{\infty} \varphi_{n'}^*(y)\varphi_{n-1}(y) dy + \sqrt{n+1}\int_{-\infty}^{\infty} \varphi_{n'}^*(y)\varphi_{n+1}(y) dy\right|^2 .$$

Using the orthonormality of the harmonic oscillator eigenstates, we finally obtain

$$k_{n\to n'} \propto \left|\sqrt{n}\delta_{n',n-1} + \sqrt{n+1}\delta_{n',n+1}\right|^2 = n\delta_{n',n-1} + (n+1)\delta_{n',n+1}.$$

(b) Associating "n*" with the ground stat (*$n = 0$*), and recalling that the proper eigenfunctions of the harmonic oscillator Hamiltonian are associates with* $n' = 0,1,2,...$*, we obtain,* $k_{0\to n'} \propto \left|0 + \sqrt{1}\delta_{n',1}\right|^2 = \delta_{n',1}$*. Hence, the transition rate vanishes unless* $n' = 1$*, which corresponds to the first excited state.*

Exercise 8.5.4 *Prove Eq. (8.5.12) using Eqs. (8.5.7, 8.5.10, 8.5.11).*

Solution 8.5.4

Using the relations between ($\hat{q}$, $\hat{p}$) and ($\hat{b}$, $\hat{b}^\dagger$), we obtain

$$\hat{H} = \frac{m\omega^2}{2}\hat{q}^2 + \frac{1}{2m}\hat{p}^2 = \frac{m\omega^2}{2}\frac{\hbar}{2m\omega}(\hat{b}+\hat{b}^\dagger)^2 - \frac{1}{2m}\frac{m\omega\hbar}{2}(\hat{b}-\hat{b}^\dagger)^2$$
$$= \frac{\hbar\omega}{4}[(\hat{b}+\hat{b}^\dagger)^2 - (\hat{b}-\hat{b}^\dagger)^2]$$

$$= \frac{\hbar\omega}{2}[\hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b}] \quad .$$

Using the commutation relation, $[\hat{b},\hat{b}^\dagger] = \hat{b}\hat{b}^\dagger - \hat{b}^\dagger\hat{b} = 1$ *, we obtain,*

$$\hat{H} = \frac{m\omega^2}{2}\hat{q}^2 + \frac{1}{2m}\hat{p}^2 = \frac{\hbar\omega}{2}[\hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b}] = \frac{\hbar\omega}{2}[2\hat{b}^\dagger\hat{b}+1] = \hbar\omega[\hat{b}^\dagger\hat{b}+\frac{1}{2}].$$

9 Two-Body Rotation and Angular Momentum

Exercise 9.1.1 *Use the transformation from Cartesian to spherical coordinates,* $x = r\sin(\theta)\cos(\varphi)$*;* $y = r\sin(\theta)\sin(\varphi)$*;* $z = r\cos(\theta)$*, to derive Eq.(9.1.5) from the kinetic energy in Cartesian coordinates,* $\frac{-\hbar^2}{2\mu}\hat{\Delta}_{\mathbf{r}} = \frac{-\hbar^2}{2\mu}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})$.

Solution 9.1.1

The solution of this exercise is left for self-practice.

Exercise 9.1.2 *Using the transformation from Cartesian to spherical coordinates,* $x = r\sin(\theta)\cos(\varphi)$*;* $y = r\sin(\theta)\sin(\varphi)$*;* $z = r\cos(\theta)$*, derive (a) the explicit expressions for* $\hat{L}_x$ *,* $\hat{L}_y$*,* $\hat{L}_z$ *in Eq.(9.1.7); (b) Eq. (9.1.6) by summing over the component of the angular momentum vector,* $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$.

Solution 9.1.2

The solution of this exercise is left for self-practice.

Exercise 9.1.3 *Show that any product function* $\psi(r,\theta,\varphi) \equiv Y(\theta,\varphi)R(r)$*, where* $Y(\theta,\varphi)$ *and* $R(r)$ *are defined as solutions to Eq. (9.1.10) and Eq. (9.1.11), respectively, is a solution to Eq. (9.1.9).*

Solution 9.1.3

Let $\psi(r,\theta,\varphi) \equiv Y(\theta,\varphi)R(r)$, *where,* $\hat{L}^2 Y(\theta,\varphi) = \lambda Y(\theta,\varphi)$, *and*

$$\frac{-\hbar^2}{2\mu}[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}]R(r) + [V(r)+\frac{\lambda}{2\mu r^2}]R(r) = ER(r) .$$

Substituting in the left-hand side of Eq. (9.1.9), using $\hat{L}^2 Y(\theta,\varphi) = \lambda Y(\theta,\varphi)$*, we obtain*

$$\left[\frac{-\hbar^2}{2\mu}[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}] + \frac{\hat{L}^2}{2\mu r^2} + V(r)\right]Y(\theta,\varphi)R(r)$$

$$=\left[\frac{-\hbar^2}{2\mu}[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}]+\frac{\lambda}{2\mu r^2}+V(r)\right]Y(\theta,\varphi)R(r)\ .$$

Since $\frac{-\hbar^2}{2\mu}[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}]R(r)+[V(r)+\frac{\lambda}{2\mu r^2}]R(r)=ER(r)$, *we obtain*

$$\left[\frac{-\hbar^2}{2\mu}[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}]+\frac{\hat{L}^2}{2\mu r^2}+V(r)\right]Y(\theta,\varphi)R(r)=EY(\theta,\varphi)R(r)\,.$$

Hence, the given product, $Y(\theta,\varphi)R(r)$, *is a solution of Eq. (9.1.9).*

Exercise 9.2.1 *Recalling the definition of the parity operator:* $\hat{P}f(\xi)=f(-\xi)$, *do the following. (a) Prove that* $\hat{P}$ *commutes with the differential operator on the left-hand side of Eq. (9.2.8). (b) Use the result of Ex. 6.4.1 and Eq. (9.2.12) to show that the eigenfunctions of Eq. (9.2.8) must be either even or odd functions of* ξ.

Solution 9.2.1

(a)

$$[\left((\xi^2-1)\frac{d^2}{d\xi^2}+2\xi\frac{d}{d\xi}+\frac{m^2}{1-\xi^2}\right),\hat{P}]f(\xi)$$
$$=\left((\xi^2-1)\frac{d^2}{d\xi^2}+2\xi\frac{d}{d\xi}+\frac{m^2}{1-\xi^2}\right)f(-\xi)-\hat{P}\left((\xi^2-1)\frac{d^2}{d\xi^2}+2\xi\frac{d}{d\xi}+\frac{m^2}{1-\xi^2}\right)f(\xi)$$
$$=\left((\xi^2-1)\frac{d^2}{d\xi^2}f(-\xi)+2\xi\frac{d}{d\xi}f(-\xi)+\frac{m^2}{1-\xi^2}f(-\xi)\right)$$
$$-\left((\xi^2-1)\frac{d^2}{d\xi^2}f(-\xi)+2\xi\frac{d}{d\xi}f(-\xi)+\frac{m^2}{1-\xi^2}f(-\xi)\right)$$

$$=0\ .$$

(b)

According to Eqs. (9.2.8, 9.2.12) $f_{\lambda,m}(\xi)$ *are eigenfunctions of the operator* $[(\xi^2-1)\frac{d^2}{d\xi^2}+2\xi\frac{d}{d\xi}+\frac{m^2}{1-\xi^2}]$, *whose spectrum is non-degenerate. In this case, as shown in Ex. 6.4.1,* $f_{\lambda,m}(\xi)$ *are also eigenfunctions of any operator that commutes with*

$[(\xi^2-1)\frac{d^2}{d\xi^2}+2\xi\frac{d}{d\xi}+\frac{m^2}{1-\xi^2}]$. *Specifically, using (a), they are eigenfunctions of the parity operator, which implies that,* $\hat{P}f_{\lambda,m}(\xi)=f_{\lambda,m}(-\xi)=\gamma f_{\lambda,m}(\xi)$. *Since* $\hat{P}^2=\hat{I}$, *we must have,* $\gamma^2=1$, *and hence, the only eigenvalues of* $\hat{P}$ *are* $\gamma=\pm1$. *The solutions associated with* $\gamma=1$ *and* $\gamma=-1$ *correspond, respectively, to* $f_{\lambda,m}(-\xi)=f_{\lambda,m}(\xi)$ *and* $f_{\lambda,m}(-\xi)=-f_{\lambda,m}(\xi)$, *namely, they are either even or odd functions of* ξ.

Exercise 9.2.2 *The angular momentum ladder operators,* $\hat{L}_+$ *and* $\hat{L}_-$, *are defined in Eq. (9.2.15). Show the following:*

(a) $\hat{L}_+$ *and* $\hat{L}_-$ *are Hermitian conjugates of each other.*

(b) $[\hat{L}_+,\hat{L}_-]=2\hbar\hat{L}_z$, $[\hat{L}_z,\hat{L}_\pm]=\pm\hbar\hat{L}_\pm$, *and* $[\hat{L}^2,\hat{L}_\pm]=0$.

(c) $\hat{L}^2-\hat{L}_z^2=\frac{1}{2}(\hat{L}_+\hat{L}_-+\hat{L}_-\hat{L}_+)$.

Solution 9.2.2

(a)

Using the definition of $\hat{L}_+$, *for any two proper functions,* $\chi(x,y,z)$ *and* $\psi(x,y,z)$, *we obtain*

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_+)\psi(x,y,z)dxdydz$$
$$=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_x+i\hat{L}_y)\psi(x,y,z)dxdydz$$
$$=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_x)\psi(x,y,z)dxdydz+i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_y)\psi(x,y,z)dxdydz\,.$$

Using the Hermiticity of $\hat{L}_x$ *and* $\hat{L}_y$ *we obtain*

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_+)\psi(x,y,z)dxdydz$$
$$=\left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_x)\chi^*(x,y,z)dxdydz\right)^*+i\left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_y)\chi^*(x,y,z)dxdydz\right)^*$$
$$=\left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_x)\chi^*(x,y,z)dxdydz-i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_y)\chi^*(x,y,z)dxdydz\right)^*$$

$$=\left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_x - i\hat{L}_y)\chi^*(x,y,z)dxdydz\right)^* .$$

Recalling the definition of $\hat{L}_-$,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_+)\psi(x,y,z)dxdydz = \left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_-)\chi^*(x,y,z)dxdydz\right)^*,$$

and the definition of a Hermitian conjugate,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi(x,y,z)(\hat{L}_+)\psi(x,y,z)dxdydz = \left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(x,y,z)(\hat{L}_+)^\dagger\chi^*(x,y,z)dxdydz\right)^*,$$

we readily identify, $(\hat{L}_+)^\dagger = \hat{L}_-$.

(b)

Using the commutation relations between the angular momentum components (Eq. (3.3.3)),

$$[\hat{L}_+,\hat{L}_-] = [\hat{L}_x + i\hat{L}_y, \hat{L}_x - i\hat{L}_y] = [\hat{L}_x, -i\hat{L}_y] + [i\hat{L}_y, \hat{L}_x] = -i(i\hbar\hat{L}_z + i\hbar\hat{L}_z) = 2\hbar\hat{L}_z$$

$$[\hat{L}_z,\hat{L}_\pm] = [\hat{L}_z,\hat{L}_x] \pm i[\hat{L}_z,\hat{L}_y] = i\hbar\hat{L}_y \pm (i)(-i\hbar)\hat{L}_x = \pm\hbar\hat{L}_x + i\hbar\hat{L}_y$$

$$= \pm\hbar(\hat{L}_x \pm i\hat{L}_y) = \pm\hbar\hat{L}_\pm .$$

Using Eq. (3.3.5),

$$[\hat{L}^2,\hat{L}_\pm] = [\hat{L}^2,\hat{L}_x] \pm i[\hat{L}^2,\hat{L}_y] = 0 .$$

(c)

Noticing that, $\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-)$ *and* $\hat{L}_y = \frac{-i}{2}(\hat{L}_+ - \hat{L}_-)$, *we obtain*

$$\hat{L}^2 - \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2 = \frac{1}{4}(\hat{L}_+ + \hat{L}_-)^2 - \frac{1}{4}(\hat{L}_+ - \hat{L}_-)^2$$

$$= \frac{1}{4}[\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+ + \hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+] = \frac{1}{2}[\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+] .$$

Exercise 9.2.3 *(a) Derive Eq. (9.2.23) using Eqs. (9.1.7,9.2.15). (b) Changing variable,* $\xi = \cos(\theta)$, *show that* $\hat{L}_\pm = \hbar e^{\pm i\varphi}[\mp\sqrt{1-\xi^2}\frac{d}{d\xi} + i\frac{\xi}{\sqrt{1-\xi^2}}\frac{\partial}{\partial\varphi}]$.

Solution 9.2.3

(a)

Using $\hat{L}_x = i\hbar[\sin(\varphi)\frac{\partial}{\partial\theta} + \cot(\theta)\cos(\varphi)\frac{\partial}{\partial\varphi}]$; $\hat{L}_y = -i\hbar[\cos(\varphi)\frac{\partial}{\partial\theta} - \cot(\theta)\sin(\varphi)\frac{\partial}{\partial\varphi}]$

and $\hat{L}_+ \equiv \hat{L}_x + i\hat{L}_y$, *we obtain*

$$\hat{L}_+ = \hbar[i\sin(\varphi)\frac{\partial}{\partial\theta} + i\cot(\theta)\cos(\varphi)\frac{\partial}{\partial\varphi}] + \hbar[\cos(\varphi)\frac{\partial}{\partial\theta} - \cot(\theta)\sin(\varphi)\frac{\partial}{\partial\varphi}]$$
$$= \hbar[(\cos(\varphi) + i\sin(\varphi))\frac{\partial}{\partial\theta} - \cot(\theta)[\sin(\varphi) - i\cos(\varphi)]\frac{\partial}{\partial\varphi}]$$
$$= \hbar[(\cos(\varphi) + i\sin(\varphi))\frac{\partial}{\partial\theta} + i\cot(\theta)[i\sin(\varphi) + \cos(\varphi)]\frac{\partial}{\partial\varphi}]$$

$$= \hbar e^{i\varphi}[\frac{\partial}{\partial\theta} + i\cot(\theta)\frac{\partial}{\partial\varphi}] .$$

Similarly (or by identifying the Hermitian conjugate of $\hat{L}_+$*), we obtain*

$$\hat{L}_- = \hbar e^{-i\varphi}[-\frac{\partial}{\partial\theta} + i\cot(\theta)\frac{\partial}{\partial\varphi}].$$

(b)

Let us define, $\xi = \cos(\theta)$ *and* $\Theta(\theta) = f(\xi)$. *Using,* $\frac{d\xi}{d\theta} = -\sin(\theta) = -\sqrt{1-\xi^2}$ *, and the chain rule,* $\frac{d\Theta}{d\theta} = \frac{d\xi}{d\theta}\frac{df}{d\xi} = -\sqrt{1-\xi^2}\frac{df}{d\xi}$, *we obtain*

$$\hat{L}_\pm = \hbar e^{\pm i\varphi}[\pm\frac{\partial}{\partial\theta} + i\cot(\theta)\frac{\partial}{\partial\varphi}] = \hbar e^{\pm i\varphi}[\mp\sqrt{1-\xi^2}\frac{d}{d\xi} + i\frac{\xi}{\sqrt{1-\xi^2}}\frac{\partial}{\partial\varphi}].$$

Exercise 9.2.4 *The associated Legendre polynomials are defined in Eq. (9.2.25). (a) Show that (for nonnegative* m*) we have* $P_l^{m+1}(\xi) = (-1)[\sqrt{1-\xi^2}\frac{d}{d\xi} + \frac{m\xi}{\sqrt{1-\xi^2}}]P_l^m(\xi)$. *(b) Derive the relations in Eq. (9.2.26).*

Solution 9.2.4

(a)

For $m \geq 0$ *we have,* $P_l^m(\xi) = (-1)^m (\sqrt{1-\xi^2})^m \frac{d^m}{d\xi^m} P_l^0(\xi)$. *Consequently,*

$$P_l^{m+1}(\xi) = (-1)^{m+1}\sqrt{1-\xi^2}(\sqrt{1-\xi^2})^m \frac{d}{d\xi}\frac{d^m}{d\xi^m} P_l^0(\xi)$$

$$= (-1)^{m+1}\left[\sqrt{1-\xi^2}\frac{d}{d\xi}(\sqrt{1-\xi^2})^m \frac{d^m}{d\xi^m}P_l^0(\xi) - \sqrt{1-\xi^2}[\frac{d}{d\xi}(\sqrt{1-\xi^2})^m]\frac{d^m}{d\xi^m}P_l^0(\xi)\right]$$

$$= (-1)\sqrt{1-\xi^2}\frac{d}{d\xi}P_l^m(\xi) - (-1)^{m+1}\sqrt{1-\xi^2}m(\sqrt{1-\xi^2})^{m-1}\frac{-2\xi}{2\sqrt{1-\xi^2}}\frac{d^m}{d\xi^m}P_l^0(\xi)$$

$$= (-1)[\sqrt{1-\xi^2}\frac{d}{d\xi} + \frac{m\xi}{\sqrt{1-\xi^2}}]P_l^m(\xi) \ .$$

(b)

Using the relation between $P_l^m(\xi)$ *and* $P_l^{m+1}(\xi)$ *derived in (a), and the result of Ex. 9.2.3 (b) for* $\hat{L}_+$ *, we obtain*

$$\hat{L}_+ P_l^m(\xi)e^{im\varphi}$$
$$= \hbar e^{i\varphi}[-\sqrt{1-\xi^2}\frac{d}{d\xi} + i\frac{\xi}{\sqrt{1-\xi^2}}\frac{\partial}{\partial\varphi}]P_l^m(\xi)e^{im\varphi}$$
$$= \hbar e^{i\varphi}[-\sqrt{1-\xi^2}\frac{d}{d\xi}P_l^m(\xi) - \frac{m\xi}{\sqrt{1-\xi^2}}P_l^m(\xi)]e^{im\varphi}$$
$$= \hbar(-1)[\sqrt{1-\xi^2}\frac{d}{d\xi}P_l^m(\xi) + \frac{m\xi}{\sqrt{1-\xi^2}}P_l^m(\xi)]e^{i(m+1)\varphi}$$

$$= \hbar P_l^{m+1}e^{i(m+1)\varphi} \ .$$

Similarly,

$$\hat{L}_- P_l^{|m|}(\xi)e^{im\varphi}$$
$$= \hbar e^{-i\varphi}[\sqrt{1-\xi^2}\frac{d}{d\xi} + i\frac{\xi}{\sqrt{1-\xi^2}}\frac{\partial}{\partial\varphi}]P_l^{|m|}(\xi)e^{im\varphi}$$
$$= \hbar[\sqrt{1-\xi^2}\frac{d}{d\xi} + \frac{|m|\xi}{\sqrt{1-\xi^2}}]P_l^{|m|}(\xi)e^{i(m-1)\varphi}$$

$$= -\hbar P_l^{|m|+1}(\xi)e^{i(m-1)\varphi} \ .$$

Exercise 9.2.5 *Let* $Y_{l,m}(\theta,\varphi)$ *and* $Y_{l,m\pm1}(\theta,\varphi)$ *be normalized functions:* $\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m}{}^*(\theta,\varphi) Y_{l,m}(\theta,\varphi) = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m\pm1}{}^*(\theta,\varphi) Y_{l,m\pm1}(\theta,\varphi) = 1$, *and let* $Y_{l,m\pm1}(\theta,\varphi) = c_\pm \hat{L}_\pm Y_{l,m}(\theta,\varphi)$. *Use the results of Ex. 9.2.2, to show that (for* $|m| < l$ *),* $c_\pm = \dfrac{1}{\hbar\sqrt{(l \pm m+1)(l \mp m)]}}$.

Solution 9.2.5

Given,

$$Y_{l,m\pm1}(\theta,\varphi) = c_\pm \hat{L}_\pm Y_{l,m}(\theta,\varphi)$$

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m}{}^*(\theta,\varphi) Y_{l,m}(\theta,\varphi) = 1$$

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m\pm1}{}^*(\theta,\varphi) Y_{l,m\pm1}(\theta,\varphi) = 1,$$

we obtain

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta [\hat{L}_\pm Y_{l,m}(\theta,\varphi)]^* \hat{L}_\pm Y_{l,m}(\theta,\varphi) = \frac{1}{|c_\pm|^2}.$$

Using $\left(\hat{L}_\pm\right)^\dagger = \hat{L}_\mp$ *we have,*

$$\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi g^*(\theta,\varphi) \hat{L}_\pm f^*(\theta,\varphi) \sin(\theta) d\theta d\varphi = \left[\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi f(\theta,\varphi) \hat{L}_\mp g(\theta,\varphi) \sin(\theta) d\theta d\varphi \right]^*,$$

and therefore,

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m}(\theta,\varphi)^* \hat{L}_\mp \hat{L}_\pm Y_{l,m}(\theta,\varphi) = \frac{1}{|c_\pm|^2}.$$

Using, $[\hat{L}_\pm, \hat{L}_\mp] = \pm 2\hbar \hat{L}_z \Rightarrow \hat{L}_\mp \hat{L}_\pm = \hat{L}_\pm \hat{L}_\mp \mp 2\hbar \hat{L}_z$ *, we obtain the two identities:*

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m}(\theta,\varphi)^* [\mp 2\hbar L_z + \hat{L}_\pm \hat{L}_\mp] Y_{l,m}(\theta,\varphi) = \frac{1}{|c_\pm|^2}$$

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m}(\theta,\varphi)^* [\mp 2\hbar L_z + \hat{L}_\pm \hat{L}_\mp + \hat{L}_\mp \hat{L}_\pm] Y_{l,m}(\theta,\varphi) = \frac{2}{|c_\pm|^2}.$$

Using $\frac{1}{2}(\hat{L}_+ \hat{L}_- + \hat{L}_- \hat{L}_+) = \hat{L}^2 - \hat{L}_z^2$ *, we obtain*

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y_{l,m}(\theta,\varphi)^* [\mp\hbar L_z + \hat{L}^2 - \hat{L}_z^2] Y_{l,m}(\theta,\varphi) = \frac{1}{|c_\pm|^2}.$$

Considering that $Y_{l,m}(\theta,\varphi)$ *is a normalized eigenfunction of* $\hat{L}_z$, $\hat{L}^2$ *and* $\hat{L}_z^2$, *we finally obtain*

$$\hbar^2[\mp m + l(l+1) - m^2] = \frac{1}{|c_\pm|^2} \Rightarrow \hbar^2[l \mp m + (l+m)(l-m)] = \frac{1}{|c_\pm|^2},$$

and therefore (for $|m| < l$*),*

$$c_+ = \frac{1}{\hbar\sqrt{(l+m+1)(l-m)]}} \qquad ; \qquad c_- = \frac{1}{\hbar\sqrt{(l+m)(l-m+1)}}.$$

Exercise 9.2.6 *Use Eqs. (9.2.26, 9.2.28) and* $Y_{l,0}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l^0(\cos(\theta))$ *to derive Eq. (9.2.29).*

Solution 9.2.6

To express $Y_{l,m}(\theta,\varphi)$ *for any positive* m, *we can use* $\hat{L}_+$ *recursively. Applying Eq. (9.2.28),* $Y_{l,m+1}(\theta,\varphi) = \frac{1}{\hbar\sqrt{(l-m)(l+m+1)}} \hat{L}_+ Y_{l,m}(\theta,\varphi)$, *we obtain in this case,*

$$Y_{l,m}(\theta,\varphi) = \left(\frac{1}{\hbar}\right)^m \left(\frac{1}{\sqrt{(l)(l+1)}\sqrt{(l-1)(l+2)}\sqrt{(l-2)(l+3)}\cdots\sqrt{(l-m+1)(l+m)}}\right) \left(\hat{L}_+\right)^m Y_{l,0}(\theta,\varphi)$$

$$= \left(\frac{1}{\hbar}\right)^m \left(\sqrt{\frac{(l-m)!\,l!}{l!\,(l+m)!}}\right) \left(\hat{L}_+\right)^m Y_{l,0}(\theta,\varphi) \quad .$$

Using, $Y_{l,0}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l^0(\cos(\theta))$, *we obtain*

$$Y_{l,m}(\theta,\varphi) = \left(\frac{1}{\hbar}\right)^m \sqrt{\frac{2l+1}{4\pi}} \left(\sqrt{\frac{(l-m)!}{(l+m)!}}\right) \left(\hat{L}_+\right)^m P_l^0(\cos(\theta)),$$

and using Eq. (9.2.26) for $m \geq 0$, *we obtain*

$$\hat{L}_+ P_l^m(\xi) e^{im\varphi} = \hbar P_l^{m+1}(\xi) e^{i(m+1)\varphi} \Rightarrow \left(\hat{L}_+\right)^m P_l^0(\xi) = \left(\hbar\right)^m P_l^m(\xi) e^{im\varphi}.$$

Therefore,

$$Y_{l,m}(\theta,\varphi)=\sqrt{\frac{2l+1}{4\pi}}\left(\sqrt{\frac{(l-m)!}{(l+m)!}}\right)P_l^m(\xi)e^{im\varphi} \quad ; \quad m\geq 0 .$$

To express $Y_{l,m}(\theta,\varphi)$ *for any negative* m, *we can use* $\hat{L}_-$ *recursively. Using Eq. (9.2.28),* $Y_{l,m-1}(\theta,\varphi)=\frac{1}{\hbar\sqrt{(l+m)(l-m+1)}}\hat{L}_-Y_{l,m}(\theta,\varphi)$, *we obtain in this case,*

$$Y_{l,m}(\theta,\varphi)=\left(\frac{1}{\hbar}\right)^{|m|}\frac{1}{\sqrt{(l)(l+1)}\sqrt{(l-1)(l+2)}\sqrt{(l-2)(l+3)}\cdots\sqrt{(l-|m|+1)(l+|m|)}}\left(\hat{L}_-\right)^{|m|}Y_{l,0}(\theta,\varphi)$$

$$=\left(\frac{1}{\hbar}\right)^{|m|}\sqrt{\frac{(l-|m|)!l!}{l!(l+|m|)!}}\left(\hat{L}_-\right)^{|m|}Y_{l,0}(\theta,\varphi) .$$

Using, $Y_{l,0}(\theta,\varphi)=\sqrt{\frac{2l+1}{4\pi}}P_l^0(\cos(\theta))$, *we obtain,*

$$Y_{l,m}(\theta,\varphi)=\sqrt{\frac{2l+1}{4\pi}}\left(\frac{1}{\hbar}\right)^{|m|}\sqrt{\frac{(l-|m|)!}{(l+|m|)!}}\left(\hat{L}_-\right)^{|m|}P_l^0(\cos(\theta)),$$

and using Eq. (9.2.26) for $m\leq 0$, *we obtain,*

$$\hat{L}_-P_l^{|m|}(\xi)e^{im\varphi}=-\hbar P_l^{|m|+1}(\xi)e^{i(m-1)\varphi}\Rightarrow\left(\hat{L}_-\right)^{|m|}P_l^0(\xi)=\left(-\hbar\right)^{|m|}P_l^{|m|}(\xi)e^{-i|m|\varphi} .$$

Therefore,

$$Y_{l,m}(\theta,\varphi)=\left(-1\right)^m\sqrt{\frac{2l+1}{4\pi}}\sqrt{\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\xi)e^{im\varphi} \quad ; \quad m\leq 0 .$$

We therefore reproduce Eq. (9.2.29) for any m,

$$Y_{l,m}(\theta,\varphi)=(-1)^m\sqrt{\frac{2l+1}{4\pi}}\sqrt{\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos(\theta))e^{im\varphi},$$

where we notice that the pre-factor $\left(-1\right)^m$ *is conventionally kept for any* m, *although it does not affect the wave function normalization.*

Exercise 9.3.1 *The rate of transitions between stationary states of a system via a "weak" external perturbation is proportional to the "perturbation matrix element" squared (see chapters 17-20). In the case of rotation of a diatomic molecule, interacting with an electromagnetic field, the perturbation operator is the projection of the molecular dipole on the electric field vector ($-\boldsymbol{\mu}\cdot\mathbf{E}$). When the direction of the electric field vector is fixed in the lab reference frame, it is convenient to identify it with the z axis direction of the molecular reference frame. The perturbation operator is then proportional to $\cos(\theta)$, where θ is the polar angle of the spherical coordinate system. The rate of field-induced transitions between two rotational eigenfunctions, $Y_{l,m}(\theta,\varphi)$ and $Y_{l',m'}(\theta,\varphi)$, reads $k_{l,m\to l',m'} \propto \left| \int_0^{2\pi} d\varphi \int_0^{\pi} \sin(\theta) d\theta Y^*_{l',m'}(\theta,\varphi)\cos(\theta) Y_{l,m}(\theta,\varphi) \right|^2$. Use the relation of the spherical harmonics to the associated Legendre polynomials (Eq. (9.2.29)), a known recursive relation for associated Legendre polynomials, $(2l+1)\cos(\theta)P_l^m(\cos(\theta)) = (l-m+1)P_{l+1}^m(\cos(\theta)) + (l+m)P_{l-1}^m(\cos(\theta))$ [9.4], and the orthonormality of the spherical harmonics, Eq. (9.2.32)) to derive the "selection rule" for rotational transitions induced by a (weak) electromagnetic field, $k_{l,m\to l',m'} \propto \delta_{m',m}\delta_{l',l\pm 1}$.*

Solution 9.3.1

Using the expression for the spherical harmonics in terms of the associated Legendre polynomials (Eq. (9.2.29)), we obtain

$$\cos(\theta)Y_{l,m}(\theta,\varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-|m|)!}{(l+|m|)!}} \cos(\theta) P_l^{|m|}(\cos(\theta)) e^{im\varphi} .$$

Using the property of the associated Legendre polynomial,

$$\cos(\theta)P_l^{|m|}(\cos(\theta)) = \frac{1}{(2l+1)}(l-|m|+1)P_{l+1}^{|m|}(\cos(\theta)) + \frac{1}{(2l+1)}(l+|m|)P_{l-1}^{|m|}(\cos(\theta)) ,$$

we have

$$\cos(\theta)Y_{l,m}(\theta,\varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-|m|)!}{(l+|m|)!}}$$

$$\cdot\left[\frac{1}{(2l+1)}(l-|m|+1)P_{l+1}^{|m|}(\cos(\theta))e^{im\varphi} + \frac{1}{(2l+1)}(l+|m|)P_{l-1}^{|m|}(\cos(\theta))e^{im\varphi} \right] .$$

Using again Eq. (9.2.29), we obtain

$$P_{l+1}^{|m|}(\cos(\theta))e^{im\varphi} = (-1)^{-m} \sqrt{\frac{4\pi}{2l+3}} \sqrt{\frac{(l+1+|m|)!}{(l+1-|m|)!}} Y_{l+1,m}(\theta,\varphi)$$

$$P_{l-1}^{|m|}(\cos(\theta))e^{im\varphi} = (-1)^{-m}\sqrt{\frac{4\pi}{2l-1}}\sqrt{\frac{(l-1+|m|)!}{(l-1-|m|)!}}Y_{l-1,m}(\theta,\varphi) \ .$$

Therefore,

$$\cos(\theta)Y_{l,m}(\theta,\varphi) =$$
$$\sqrt{\frac{1}{(2l+1)(2l+3)}}\sqrt{\frac{(l-|m|)!(l+1+|m|)!}{(l+|m|)!(l+1-|m|)!}}(l-|m|+1)Y_{l+1,m}(\theta,\varphi)$$
$$+\sqrt{\frac{1}{(2l-1)(2l+1)}}\sqrt{\frac{(l-|m|)!(l-1+|m|)!}{(l+|m|)!(l-1-|m|)!}}(l+|m|)Y_{l-1,m}(\theta,\varphi)$$

$$=\sqrt{\frac{(l+1+|m|)(l+1-|m|)}{(2l+1)(2l+3)}}Y_{l+1,m}(\theta,\varphi)+\sqrt{\frac{(l-|m|)(l+|m|)}{(2l-1)(2l+1)}}Y_{l-1,m}(\theta,\varphi) \ .$$

Substitution of the last result in the expression for the transition rate,

$$k_{l,m\to l',m'} \propto \left|\int_0^{2\pi} d\varphi\int_0^{\pi}\sin(\theta)d\theta Y_{l',m'}^{*}(\theta,\varphi)\cos(\theta)Y_{l,m}(\theta,\varphi)\right|^2$$
$$=|\sqrt{\frac{(l+1+|m|)(l+1-|m|)}{(2l+1)(2l+3)}}\int_0^{2\pi} d\varphi\int_0^{\pi}\sin(\theta)d\theta Y_{l',m'}^{*}(\theta,\varphi)Y_{l+1,m}(\theta,\varphi)$$

$$+\sqrt{\frac{(l-|m|)(l+|m|)}{(2l-1)(2l+1)}}\int_0^{2\pi} d\varphi\int_0^{\pi}\sin(\theta)d\theta Y_{l',m'}^{*}(\theta,\varphi)Y_{l-1,m}(\theta,\varphi)|^2,$$

using the orthonormality of the spherical harmonics (Eq. (9.2.32)), we obtain

$$k_{l,m\to l',m'} \propto |\sqrt{\frac{(l+1+|m|)(l+1-|m|)}{(2l+1)(2l+3)}}\delta_{l+1,l'}\delta_{m,m'}+\sqrt{\frac{(l-|m|)(l+|m|)}{(2l-1)(2l+1)}}\delta_{l-1,l'}\delta_{m,m'}|^2$$
$$=\frac{(l+1+|m|)(l+1-|m|)}{(2l+1)(2l+3)}\delta_{l+1,l'}\delta_{m,m'}+\frac{(l-|m|)(l+|m|)}{(2l-1)(2l+1)}\delta_{l-1,l'}\delta_{m,m'} \ .$$

Hence, the transition rate vanishes unless $m'=m$ *, and* $l'=l\pm 1$.

Exercise 9.3.2 *Use the definition of the rotational constant to show that the rotational constant of* $H^{35}Cl$ *is larger by* 0.15% *than that of* $H^{37}Cl$ *, and by* 95% *than that of* $D^{35}Cl$ *.*

Solution 9.3.2

Given the definitions of the rotational constant, $B \equiv \frac{\hbar}{4\pi c \mu r_0^2}$ *, and of the reduced mass of two particle of masses* m_1 *and* m_2 *,namely* $\mu = \frac{m_1 m_2}{m_1 + m_2}$ *, we obtain*

$$\frac{B_{H^{35}Cl}}{B_{H^{37}Cl}} = \frac{\mu_{H^{37}Cl}}{\mu_{H^{35}Cl}} = \frac{\frac{37\cdot 1}{37+1}}{\frac{35\cdot 1}{35+1}} = \frac{37\cdot 36}{35\cdot 38} = 1.0015.$$

$$\frac{B_{H^{35}Cl}}{B_{D^{35}Cl}} = \frac{\mu_{D^{35}Cl}}{\mu_{H^{35}Cl}} = \frac{\frac{35\cdot 2}{35+2}}{\frac{35\cdot 1}{35+1}} = \frac{70\cdot 36}{37\cdot 35} = 1.946.$$

Exercise 9.4.1 *Use the definition* $\chi(r) \equiv rR(r)$*, and derive Eq. (9.4.4) from Eq. (9.4.3).*

Solution 9.4.1

First let us notice that

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\frac{\chi(r)}{r} = \frac{\partial}{\partial r}\frac{\chi'(r)r - \chi(r)}{r^2} + \frac{2}{r}\frac{\chi'(r)r - \chi(r)}{r^2}$$

$$= \frac{r^3\frac{\partial^2}{\partial r^2}\chi(r) + r^2\frac{\partial}{\partial r}\chi(r) - r^2\frac{\partial}{\partial r}\chi(r) - 2r^2\frac{\partial}{\partial r}\chi(r) + 2r\chi(r)}{r^4} + \frac{2}{r}\frac{r\frac{\partial}{\partial r}\chi(r) - \chi(r)}{r^2}$$

$$= \frac{r^3\frac{\partial^2}{\partial r^2}\chi(r) - 2r^2\frac{\partial}{\partial r}\chi(r) + 2r\chi(r)}{r^4} + \frac{2r^2\frac{\partial}{\partial r}\chi(r) - 2r\chi(r)}{r^4}$$

$$= \frac{r^3\frac{\partial^2}{\partial r^2}\chi(r) - 2r^2\frac{\partial}{\partial r}\chi(r) + 2r\chi(r) + 2r^2\frac{\partial}{\partial r}\chi(r) - 2r\chi(r)}{r^4}$$

$$= \frac{\frac{\partial^2}{\partial r^2}\chi(r)}{r} .$$

The substitution $R(r) = \frac{\chi(r)}{r}$ *in Eq. (9.4.3) yields,*

$$\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\frac{\chi(r)}{r} + \left[\frac{\mu\omega^2}{2}(r - r_0)^2 + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]\frac{\chi(r)}{r} = E\frac{\chi(r)}{r} .$$

Using the identity, $(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r})\frac{\chi(r)}{r}=\frac{1}{r}\frac{\partial^2}{\partial r^2}\chi(r)$, *we obtain the differential equation for* $\chi(r)$ *(Eq. (9.4.4)),*

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}\chi(r)+[\frac{\mu\omega^2}{2}\left(r-r_0\right)^2+\frac{\hbar^2 l(l+1)}{2\mu r^2}]\chi(r)=E\chi(r).$$

Exercise 9.4.2 *Use Eqs. (9.4.12-9.4.13) to derive Eq. (9.4.11) from Eq. (9.4.10).*

Solution 9.4.2

Starting from Eq. (9.4.10), $-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2}\phi(q)+[\frac{\mu\omega^2}{2}q^2-\mu\omega_l^2 r_0\, q+\frac{\mu\omega_l^2 r_0^{\ 2}}{2}]\phi(q)=E\phi(q)$,

we use $q_l=q-r_0\frac{\omega_l^2}{\omega^2}$ *(Eq. (9.4.12)), which yields*

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2}\phi(q)+[\frac{\mu\omega^2}{2}q_l^2+\frac{\mu\omega^2}{2}2q_l r_0\frac{\omega_l^2}{\omega^2}+\frac{\mu\omega^2}{2}r_0^2\frac{\omega_l^4}{\omega^4}-\mu\omega_l^2 r_0\, q_l-\mu r_0^2\frac{\omega_l^4}{\omega^2}+\frac{\mu\omega_l^2 r_0^{\ 2}}{2}]\phi(q)=E\phi(q)$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2}\phi(q)+\frac{\mu\omega^2}{2}q_l^2\phi(q)=[E-\frac{\mu\omega^2}{2}r_0^2\frac{\omega_l^4}{\omega^4}+\mu r_0^2\frac{\omega_l^4}{\omega^2}-\frac{\mu\omega_l^2 r_0^{\ 2}}{2}]\phi(q)$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2}\phi(q)+\frac{\mu\omega^2}{2}q_l^2\phi(q)=[E+\frac{\mu r_0^2\omega_l^2}{2}(\frac{\omega_l^2}{\omega^2}-1)]\phi(q)\ .$$

Using the relation (Eq. (9.4.13)), $\varepsilon_l=\frac{\mu\omega_l^2 r_0^2}{2}(1-\frac{\omega_l^2}{\omega^2})$, *we obtain*

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2}\phi(q)+\frac{\mu\omega^2}{2}q_l^2\phi(q)=[E-\varepsilon_l]\phi(q),$$

and changing variables, $\tilde{\phi}(q_l)=\phi(q)$, *we obtain Eq. (9.4.11),*

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q_l^2}\tilde{\phi}(q_l)+\frac{\mu\omega^2}{2}q_l^2\tilde{\phi}(q_l)=(E-\varepsilon_l)\tilde{\phi}(q_l).$$

Exercise 9.4.3 *Use the solutions of the Schrödinger equation for the harmonic oscillator (Eqs. (8.3.1,8.3.7,8.3.8)), and change variables, to obtain Eqs. (9.4.14, 9.4.15).*

Solution 9.4.3

Eq. (9.4.11) is perfectly analogous to Eq. (8.3.1) for the harmonic oscillator,

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q_l^2}\tilde{\phi}(q_l)+\frac{\mu\omega^2}{2}q_l^2\tilde{\phi}(q_l)=(E-\varepsilon_l)\tilde{\phi}(q_l).$$

The energy levels (Eq. (8.3.7) therefore read, $E_n-\varepsilon_l=\hbar\omega(n+\frac{1}{2})\quad;\quad n=0,1,2,\ldots$ *Eq. (9.4.14) is readily obtained by using Eqs. (9.4.6, 9.4.13) for* ε_l *,*

$$E_{n,l}=\hbar\omega(n+\frac{1}{2})+\frac{\mu\omega_l^2r_0^2}{2}(1-\frac{\omega_l^2}{\omega^2})=\hbar\omega(n+\frac{1}{2})+\frac{\hbar^2l(l+1)}{2\mu r_0^2}(1-\frac{\omega_l^2}{\omega^2}).$$

The corresponding eigenfunctions are given by Eq. (8.3.8), hence,

$$\tilde{\phi}_n(q_l)=\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4}\sqrt{\frac{1}{n!2^n}}H_n[\sqrt{\frac{\mu\omega}{\hbar}}q_l]e^{\frac{-m\omega}{2\hbar}q_l^2}.$$

Changing variable, $q_l=q-r_0\frac{\omega_l^2}{\omega^2}$*, we obtain,*

$$\phi_{n,l}(q)\equiv\tilde{\phi}_n(q-r_0\frac{\omega_l^2}{\omega^2})=\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4}\sqrt{\frac{1}{n!2^n}}H_n[\sqrt{\frac{\mu\omega}{\hbar}}(q-r_0\frac{\omega_l^2}{\omega^2})]e^{\frac{-m\omega}{2\hbar}(q-r_0\frac{\omega_l^2}{\omega^2})^2}.$$

Changing again, $q=r-r_0$ *(under the assumption that for small deviations from* r_0*, the radial variable* r *can be related to the cartesian variable* q *(see the text)) we obtain,*

$$\chi_{n,l}(r)\equiv\phi_{n,l}(r-r_0)=\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4}\sqrt{\frac{1}{n!2^n}}H_n[\sqrt{\frac{\mu\omega}{\hbar}}(r-r_0(1+\frac{\omega_l^2}{\omega^2}))]e^{\frac{-m\omega}{2\hbar}(r-r_0(1+\frac{\omega_l^2}{\omega^2}))^2}.$$

Finally, defining the radial functions, $R_{n,l}(r)\equiv\frac{\chi_n(r)}{r}$*, Eq. (9.4.15) is obtained,*

$$R_{n,l}(r)=\frac{1}{r}\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4}\sqrt{\frac{1}{n!2^n}}H_n[\sqrt{\frac{\mu\omega}{\hbar}}(r-r_0(1+\frac{\omega_l^2}{\omega^2}))]e^{\frac{-m\omega}{2\hbar}(r-r_0(1+\frac{\omega_l^2}{\omega^2}))^2}.$$

Exercise 9.4.4 *A non-rigid diatomic molecule is associated with a (normalized) stationary state,* $\psi_{n,l,m}(r,\theta,\varphi)=Y_{l,m}(\theta,\varphi)R_{n,l}(r)$*, where* $R_{n,l}(r)$ *is given by Eq. (9.4.15). Show that the average* *interatomic distance becomes larger with increasing angular momentum quantum number,* $<r_{n,l}>=\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \int_0^{\infty} dr \cdot r \cdot r^2 \sin(\theta) |\psi_{n,l,m}(r,\theta,\varphi)|^2 = r_0(1+\frac{\omega_l^2}{\omega^2})$. *(Notice that when the probability density is confined to a range where* $|r| << r_0(1+\frac{\omega_l^2}{\omega^2})$, *the boundaries of the radial integral can be changed:* $\int_0^{\infty} dr \to \int_{-\infty}^{\infty} dr$ *.)*

Solution 9.4.4

Using the factorization of the wave function, $\psi_{n,l,m}(r,\theta,\varphi) = Y_{l,m}(\theta,\varphi) R_{n,l}(r)$, *and the fact that* $Y_{l,m}(\theta,\varphi)$ *are normalized, we obtain*

$$<r_{n,l}>=\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \int_0^{\infty} drr^3 \sin(\theta) |\psi_{n,l,m}(r,\theta,\varphi)|^2 = \int_0^{\infty} drr^3 |R_{n,l}(r)|^2 .$$

Defining: $\chi_{n,l}(r) \equiv rR_{n,l}(r)$, *we obtain* $<r_{n,l}>=\int_0^{\infty} drr |\chi_{n,l}(r)|^2$. *Changing variables,* $x \equiv r - r_0(1+\frac{\omega_l^2}{\omega^2})$ *and* $\psi_{n,l}(x) \equiv \chi_{n,l}(r)$, *we obtain* $<r_{n,l}>=\int_0^{\infty} dx(x+r_0(1+\frac{\omega_l^2}{\omega^2})) |\psi_n(x)|^2$, *where using Eq. (9.4.15),* $\psi_n(x) = \left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4} \sqrt{\frac{1}{n!2^n}} H_n(\sqrt{\frac{\mu\omega}{\hbar}}x) e^{\frac{-m\omega}{2\hbar}x^2}$ *.When the probability density,* $|\psi_{n,l}(x)|^2$, *is significantly larger than zero only in a small region around* $x \approx 0$, *the integration limits can be extended with a negligible effect on the result, namely*

$$<r_{n,l}>\cong \int_{-\infty}^{\infty} dx(x+r_0(1+\frac{\omega_l^2}{\omega^2})) |\psi_n(x)|^2 = \int_{-\infty}^{\infty} dxx |\psi_n(x)|^2 + r_0(1+\frac{\omega_l^2}{\omega^2}) \int_{-\infty}^{\infty} dx |\psi_n(x)|^2 .$$

Since $|\psi_n(x)|^2$ *is normalized, and since it is an even function of* x, *we obtain* $<r_{n,l}>\cong r_0(1+\frac{\omega_l^2}{\omega^2})$. *Using the definition of* ω_l^2 *(Eq. (9.4.6)) we can see that the average interatomic distance increases with the rotation quantum number,* l *.*

Exercise 9.4.5 *Use the definition of the rotational frequency (Eq. (9.4.6)) and Eq. (9.4.16) to derive Eq. (9.4.17).*

Solution 9.4.5

Using Eq. (9.4.16) for the absorption wavelengths, $\frac{1}{\lambda_l} = 2B(1 - \frac{\omega_l^2}{\omega^2})(l+1)$ *and* $\frac{1}{\lambda_{l+1}} = 2B(1 - \frac{\omega_{l+1}^2}{\omega^2})(l+2)$, *we obtain* $\frac{1}{\lambda_{l+1}} - \frac{1}{\lambda_l} = 2B + \frac{2B}{\omega^2}\left(\omega_l^2(l+1) - \omega_{l+1}^2(l+2)\right)$.

Using the definition (Eq. (9.4.6)), $\omega_l^2 \equiv \frac{\hbar^2 l(l+1)}{\mu^2 r_0^4}$, *we have,* $\omega_{l+1}^2 \equiv \frac{\hbar^2(l+2)(l+1)}{\mu^2 r_0^4}$, *and hence,*

$$\frac{1}{\lambda_{l+1}} - \frac{1}{\lambda_l} = 2B + \frac{2B}{\omega^2}\left(\frac{\hbar^2 l(l+1)(l+1)}{\mu^2 r_0^4} - \frac{\hbar^2(l+2)(l+1)(l+2)}{\mu^2 r_0^4}\right)$$

$$= 2B + \frac{2B}{\omega^2}\frac{\hbar^2}{\mu^2 r_0^4}(l+1)\left(l(l+1) - (l+2)^2\right)$$

$$= 2B + \frac{2B}{\omega^2}\frac{\hbar^2}{\mu^2 r_0^4}(l+1)\left(-3l-4\right)$$

$$= 2B - \frac{2B}{\omega^2}\frac{\hbar^2}{\mu^2 r_0^4}(l+1)(l+2(l+2))$$

$$= 2B - \frac{2B}{\omega^2}\left(\omega_l^2 + 2\omega_{l+1}^2\right) .$$

10 The Hydrogen-Like Atom

Exercise 10.2.1 *Use the definitions of the dimensionless variables (Eqs. (10.2.11, 10.2.13)) to derive Eq. (10.2.12) from Eq. (10.2.10).*

Solution 10.2.1

Starting from Eq. (10.2.10), $\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}\chi(r)+[\frac{-KZe^2}{r}+\frac{\hbar^2 l(l+1)}{2\mu r^2}]\chi(\mathrm{r})=E\chi(\mathrm{r})$, *we multiply by a constant,* $\frac{-2\hbar^2}{\mu e^4 K^2}$, *to obtain*

$$\frac{\hbar^4}{\mu^2 e^4 K^2}\frac{\partial^2}{\partial r^2}\chi(r)+[\frac{2Z^2}{r}\frac{\hbar^2}{\mu e^2 K}-\frac{\hbar^4}{\mu^2 e^4 K^2}\frac{l(l+1)}{r^2}]\chi(\mathrm{r})=-\frac{2\hbar^2}{\mu e^4 K^2}E\chi(\mathrm{r}).$$

Changing variables in this equation, $\rho\equiv r\frac{\mu e^2 K}{\hbar^2}$ *and* $\Phi(\rho)\equiv\chi(r)$, *we obtain Eq. (10.2.10),*

$$\frac{\partial^2}{\partial\rho^2}\Phi(\rho)+[\frac{2Z^2}{\rho}-\frac{l(l+1)}{\rho^2}]\Phi(\rho)=\lambda^2\Phi(\rho).$$

Exercise 10.2.2 *Show that the functions* $\chi(y)=e^{\pm\lambda\rho}\rho^p$ *satisfy the asymptotic radial equation for the hydrogen-like atom, namely,* $\frac{\partial^2}{\partial\rho^2}\Phi(\rho)\xrightarrow[\rho\to\infty]{}\lambda^2\Phi(\rho)$, *for any nonnegative finite power,* p, *and use it to show that* $\Phi(\rho)$, *defined in Eq. (10.2.18), is a solution to this equation.*

Solution 10.2.2

For any nonnegative and finite p *we have,*

$$\frac{\partial^2}{\partial\rho^2}\rho^p e^{\pm\lambda\rho}=\frac{\partial}{\partial\rho}((p\rho^{p-1}\pm\lambda\rho^p)e^{\pm\lambda\rho})\xrightarrow[\rho\to\pm\infty]{}\frac{\partial}{\partial\rho}(\pm\lambda\rho^p e^{\pm\lambda\rho})$$

$$=(\pm\lambda p\rho^{p-1}+\lambda^2\rho^p)e^{\pm\lambda\rho}\xrightarrow[\rho\to\pm\infty]{}\lambda^2\rho^p e^{\pm\lambda\rho}\ .$$

Therefore, for any finite order polynomial, $P_p(\rho)=\sum_{k=0}^{p}a_k\rho^k$*, we have* $\frac{\partial^2}{\partial\rho^2}P_p(\rho)e^{\pm\lambda\rho}\xrightarrow[\rho\to\pm\infty]{}\lambda^2P_p(\rho)e^{\pm\lambda\rho}$*. Identifying the degree of the polynomial with,* $p=s+q$*, this relation is shown to hold for* $\Phi(\rho)$ *defined in Eq. (10.2.18).*

Exercise 10.2.3 *Derive Eq. (10.2.19), using Eqs. (10.2.12, 10.2.18).*

Solution 10.2.3

Using the definition (Eq. (10.2.18)): $\Phi(\rho)=P_{q,s}(\rho)e^{-\lambda\rho}$ *with* $P_{q,s}(\rho)=\sum_{k=0}^{q}a_k^{(q)}\rho^{k+s}$*, in Eq. (10.2.12), we obtain*

$$e^{-\lambda\rho}\frac{\partial^2}{\partial\rho^2}P_{q,s}(\rho)-e^{-\lambda\rho}2\lambda\frac{\partial}{\partial\rho}P_{q,s}(\rho)+e^{-\lambda\rho}\frac{2Z}{\rho}P_{q,s}(\rho)-e^{-\lambda\rho}\frac{l(l+1)}{\rho^2}P_{q,s}(\rho)=0.$$

Multiplying from the right by $e^{\lambda\rho}$*, we obtain the differential equation for the polynomials,*

$$\frac{\partial^2}{\partial\rho^2}P_{q,s}(\rho)-2\lambda\frac{\partial}{\partial\rho}P_{q,s}(\rho)+\frac{2Z}{\rho}P_{q,s}(\rho)-\frac{l(l+1)}{\rho^2}P_{q,s}(\rho)=0.$$

Using $P_{q,s}(\rho)=\sum_{k=0}^{q}a_k^{(q)}\rho^{k+s}$, $\frac{\partial}{\partial\rho}P_{q,s}(\rho)=\sum_{k=0}^{q}(k+s)a_k^{(q)}\rho^{k+s-1}$ *and* $\frac{\partial^2}{\partial\rho^2}P_{q,s}(\rho)=\sum_{k=0}^{q}(k+s)(k+s-1)a_k^{(q)}\rho^{k+s-2}$*, this equation yields*

$$\sum_{k=0}^{n}[(s+k)(s+k-1)-l(l+1)]a_k^{(q)}\rho^{s+k-2}+\sum_{k=0}^{n}2[Z-\lambda(s+k)]a_k^{(q)}\rho^{s+k-1}=0\cdot$$

Shifting the summation index in the second term, we obtain Eq. (10.2.19)

$$\sum_{k=0}^{n}[(s+k)(s+k-1)-l(l+1)]a_k\rho^{s+k-2}+\sum_{k=1}^{n+1}2[Z-\lambda(s+k-1)]a_{k-1}\rho^{s+k-2}=0\cdot$$

Exercise 10.2.4 *The radial wave functions for a hydrogen-like atom are of the form* $\Phi_{n,l}(\rho)=e^{-Z\rho/n}\rho^{l+1}\sum_{k=0}^{n-l-1}a_k^{(n,l)}\rho^k$*. The polynomial coefficients, {* $a_k^{(n,l)}$ *}, are defined by the recursion* *relation, Eq. (10.2.20). Use Eqs. (10.2.21-10.2.23) and derive the explicit expression for these coefficients, Eq. (10.2.28).*

Solution 10.2.4

Noticing that q *is uniquely defined by* n *and* l*:* $q = n - l - 1$, *hence* $a_k^{(q)} \equiv a_k^{(n,l)}$, *and using the relations,* $s = l + 1$, *and* $\lambda = Z / n$, *the recursion relation for the polynomial coefficients (as given in Eq. (10.2.20)) can be rewritten as,*

$$a_k^{(n,l)} = \frac{2[\lambda(s+k-1) - Z]}{(s+k)(s+k-1) - l(l+1)} a_{k-1}^{(n,l)}$$
$$= \frac{2[\lambda(l+k) - Z]}{(l+1+k)(l+k) - l(l+1)} a_{k-1}^{(n,l)}$$

$$= \frac{-2Z}{n} \frac{(n-l-k)}{k(2l+1+k)} a_{k-1}^{(n,l)} \ .$$

To obtain an explicit expression for the coefficients, it is convenient to define, $b_k^{(n,l)} \equiv (-2\frac{Z}{n})^{-k} a_k^{(n,l)}$,

where, $\frac{b_k^{(n,l)}}{b_{k-1}^{(n,l)}} = (-2\frac{Z}{n})^{-1} \frac{a_k^{(n,l)}}{a_{k-1}^{(n,l)}} = \frac{(n-l-k)}{k(2l+1+k)} \equiv \frac{q-k+1}{k(p+k)}$. *(In the last step we used the notations,* $q = n - l - 1$, *and* $p = 2l + 1$.*) Using* $b_k^{(n,l)} = \frac{q-k+1}{k(p+k)} b_{k-1}^{(n,l)}$ *recursively, we obtain*

$$b_1^{(n,l)} = \frac{q}{(p+1)} b_0^{(n,l)}$$
$$b_2^{(n,l)} = \frac{q-1}{2(p+2)} b_1^{(n,l)}$$
$$b_3^{(n,l)} = \frac{q-2}{3(p+3)} b_2^{(n,l)}$$
$$\vdots$$

$$b_k^{(n,l)} = \frac{q(q-1)(q-2)\cdots(q-k+1)}{k!(p+1)(p+2)\cdots(p+k)} b_0^{(n,l)} = \frac{q!\,p!}{k!(q-k)!(p+k)!} b_0^{(n,l)} \ .$$

Expressing q *and* p *in terms of* n *and* l, *and using* $a_k^{(n,l)} \equiv (-2\frac{Z}{n})^k b_k^{(n,l)}$, *we obtain Eq. (10.2.18),*

$$a_k^{(n,l)} = (-2\frac{Z}{n})^k \frac{(n-l-1)!(2l+1)!}{(n-l-1-k)!(2l+1+k)!k!} a_0^{(n,l)} .$$

Exercise 10.2.5 *Use Eqs. (10.2.27, 10.2.28) for the radial wave functions of the hydrogen-like atom, and Eq. (10.2.29) for the associated Laguerre polynomials, to derive Eq. (10.2.30).*

Solution 10.2.5

Identifying: $q \equiv n-l-1$ *and* $p \equiv 2l+1$, *and using Eq. (10.2.28) in Eq. (10.2.27) we obtain*

$$\Phi_{n,l}(\rho) = a_0^{(n,l)} e^{-Z\rho/n} \rho^{l+1} \sum_{k=0}^{q} (-1)^k \frac{q!\,p!}{(q-k)!(p+k)!k!} \left(\frac{2Z}{n}\rho\right)^k .$$

Identifying the associated Laguerre polynomials, $L_q^p(\xi) \equiv \sum_{k=0}^{q} (-1)^k \frac{(p+q)!}{(q-k)!(p+k)!k!} \xi^k$ *, the result can be rewritten as,*

$$\Phi_{n,l}(\rho) = a_0^{(n,l)} e^{-Z\rho/n} \rho^{l+1} \frac{q!\,p!}{(p+q)!} L_q^p(\frac{2Z}{n}\rho)$$

$$= a_0^{(n,l)} e^{-Z\rho/n} \rho^{l+1} \frac{(n-l-1)!(2l+1)!}{(n+l)!} L_{n-l-1}^{2l+1}(\frac{2Z}{n}\rho) ,$$

which reproduced Eq. (10.2.30).

Exercise 10.2.6 *Use the normalization condition (Eqs. (10.2.15)) to normalize the radial function given by Eq. (10.2.30), and change variables to obtain* $R_{n,l}(r)$ *in Eq. (10.2.31).*

Solution 10.2.6

Considering the expression for the radial function (Eq. (10.2.30)), $\Phi_{n,l}(\rho) = c_{n,l} e^{-Z\rho/n} \rho^{l+1} L_{n-l-1}^{2l+1}(\frac{2Z}{n}\rho)$, *the normalization integral reads,* $\int_0^\infty |\Phi(\rho)|^2 d\rho = c_{n,l}^2 \int_0^\infty e^{-2Z\rho/n} \rho^{2l+2} [L_{n-l-1}^{2l+1}(2Z\rho/n)]^2 d\rho$. *Changing variable,* $x = \frac{2Z\rho}{n}$, *we obtain:*

$$\int_0^\infty |\Phi(\rho)|^2 d\rho = c_{n,l}^2 \left(\frac{n}{2Z}\right)^{2l+3} \int_0^\infty e^{-x} x^{2l+2} [L_{n-l-1}^{2l+1}(x)]^2 dx .$$

Using the property of the associated Legendre Polynomials, $\int_0^\infty e^{-x} x^{p+1} [L_q^p(x)]^2 dx$ $= (2q+p+1)(q+p)!/q!$, *we obtain* $\int_0^\infty |\Phi(\rho)|^2 d\rho = c_{n,l}^2 \left(\frac{n}{2Z}\right)^{2l+3} \frac{2n(n+l)!}{(n-l-1)!}$.

The normalization condition (Eq. (10.2.15)) reads, $\int_0^\infty d\rho |\Phi(\rho)|^2 = \frac{1}{a_0}$, *which sets the pre-factors to:*

$c_{n,l} = \left(\frac{2Z}{n}\right)^{l+1} \sqrt{\frac{Z(n-l-1)!}{a_0 n^2 (n+l)!}}$. *Changing variables* $r = \rho a_0$, *where* $\chi_{n,l}(r) = \Phi_{n,l}(\rho)$, *we obtain*

$$\Phi_{n,l}(\rho) = \left(\frac{2Z}{n}\right)^{l+1} \sqrt{\frac{Z(n-l-1)!}{a_0 n^2 (n+l)!}} e^{-Z\rho/n} \rho^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2Z}{n}\rho\right)$$

$$\chi_{n,l}(r) = \sqrt{\frac{Z(n-l-1)!}{a_0 n^2 (n+l)!}} e^{\frac{-Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2Z}{na_0} r\right) .$$

Finally, dividing by r, *the explicit radial wave function, Eq. (10.2.31), is obtained*

$$R_{n,l}(r) = \frac{\chi_{n,l}(r)}{r} = \sqrt{\frac{4Z^3(n-l-1)!}{a_0^3 n^4 (n+l)!}} \left(\frac{2Zr}{na_0}\right)^l e^{\frac{-Zr}{na_0}} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right).$$

Exercise 10.2.7 *Show that the three operators,* $\hat{L}_z$, $\hat{L}^2$, *and the hydrogen-like atom Hamiltonian commute with each other. Prove that these three operators have a set of joint eigenfunctions (use Eq. 10.2.32).*

Solution 10.2.7

In Ex. 3.3.1, we already sowed that $\hat{L}_z$ *and* $\hat{L}^2$ *commute:* $[\hat{L}_z, \hat{L}^2] = 0$. *To show that* $[\hat{H}, \hat{L}^2] = 0$ *we notice that the operation of the hydrogen-like atom Hamiltonian,* $\hat{H} = \frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{-KZe^2}{r} + \frac{1}{2\mu r^2}\hat{L}_{\theta,\varphi}^2$, *in the space of the variables* θ *and* φ *is limited to the term* $\frac{1}{2\mu r^2}\hat{L}_{\theta,\varphi}^2$, *which commutes with* $\hat{L}_{\theta,\varphi}^2$: $\left[\frac{1}{2\mu r^2}\hat{L}_{\theta,\varphi}^2, \hat{L}_{\theta,\varphi}^2\right] = \frac{1}{2\mu r^2}\left[\hat{L}_{\theta,\varphi}^2, \hat{L}_{\theta,\varphi}^2\right] = 0$.

To show that $[\hat{H},\hat{L}_z]=0$ *we consider the explicit form of the angular momentum operator,* $\hat{L}^2_{\theta,\varphi}=-\hbar^2(\frac{\partial^2}{\partial\theta^2}+\frac{1}{tg(\theta)}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2})$, *and we notice that the operation of the hydrogen-like atom Hamiltonian,* $\hat{H}=\frac{-\hbar^2}{2\mu}(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r})+\frac{-KZe^2}{r}+\frac{1}{2\mu r^2}\hat{L}^2_{\theta,\varphi}$, *in the space of the variable* φ *is limited to the term,* $\frac{-\hbar^2}{2\mu r^2}\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2}=\frac{1}{2\mu r^2\sin^2(\theta)}\hat{L}^2_z$, *which commutes with* $\hat{L}_z$*:*

$$\left[\frac{1}{2\mu r^2\sin^2(\theta)}\hat{L}^2_z,\hat{L}_z\right]=\frac{1}{2\mu r^2\sin^2(\theta)}\left[\hat{L}^2_z,\hat{L}_z\right]=0.$$

It is easy to verify that any eigenfunction of the hydrogen-like atom Hamiltonian (Eq. (10.2.32)), $\psi_{n,l,m}(r,\theta,\varphi)=R_{n,l}(r)Y_{l,m}(\theta,\varphi)$ *is also an eigenfunction of* $\hat{L}^2$ *(using* $\hat{L}^2Y_{l,m}(\theta,\varphi)=\hbar^2 l(l+1)Y_{l,m}(\theta,\varphi)$*) and of* $\hat{L}_z$ *(using* $\hat{L}_zY_{l,m}(\theta,\varphi)=m\hbar Y_{l,m}(\theta,\varphi)$*).*

Exercise 10.2.8 *Show that the energy levels of a hydrogen-like atom,* $E_n=-R_HZ^2/n^2$, *are* n^2*-fold degenerate. (Notice that,* $\sum_{l=0}^{n-1}(2l+1)=n^2$*.)*

Solution 10.2.8

For a given n, *the number of orthogonal* $\{\psi_{n,l,m}(r,\theta,\varphi)\}$ *corresponds to all the different combinations of the quantum numbers,* l *and* m, *associated with proper wave functions. Since* l *obtains the values,* $0,1,...,n-1$, *and since the number of different* m*-values for each* l, *is* $2l+1$, *the total number (* N *) is given by* $N=\sum_{l=0}^{n-1}(2l+1)$. *Summing the arithmetic series* $a_0,a_1,...,a_{n-1}$ *we obtain*

$$N=\sum_{l=0}^{n-1}2l+1=\frac{n}{2}(a_0+a_{n-1})=\frac{n}{2}(1+2n-1)=n^2 .$$

Exercise 10.3.1 *Use Eqs. (10.3.3) and (10.2.31) for the radial probability distribution to show that (a) the most probable relative distance between the electron and the nucleus in the ground state of a hydrogen like atom is* $r=a_0/Z$ *; (b) the probability for finding the electron and the nucleus at any* *distance in the range,* $0 < r < \gamma \frac{a_0}{Z}$*, equals* $P(\gamma) = 1 - e^{-2\gamma}(2\gamma^2 + 2\gamma + 1)$ *(you can use the identity,* $\int_x^\infty dy y^2 e^{-\alpha y} = \frac{d^2}{d\alpha^2}\int_x^\infty dy e^{-\alpha y}$*).*

Solution 10.3.1

Using Eq. (10.2.31) for the ground state ($n = 1$*,* $l = 0$*), the radial function reads,* $R_{1,0}(r) = \sqrt{\frac{4Z^3}{a_0^3}} e^{\frac{-Zr}{a_0}}$*. Using Eq. (10.3.3) for the radial probability distribution we obtain in this case,* $\rho_{1,0}(r) = \frac{4Z^3}{a_0^3} r^2 e^{\frac{-2Zr}{a_0}}$*.*

(a)

To obtain the most probable relative distance between the electron and the nucleus we search for the maximum of $\rho_{1,0}(r)$*,* $\frac{d}{dr}\rho_{1,0}(r) \propto \frac{d}{dr} r^2 e^{\frac{-2Zr}{a_0}} = (2r - 2Zr^2 / a_0) e^{-2Zr/a_0} = 0$*, which corresponds to* $r = a_0 / Z$*.*

(b)

The probability for finding the electron and the nucleus at any distance in the range, $0 < r < r_0$ *is the respective integral over the radial probability density,* $\int_0^{r_0} drr^2 \frac{4Z^3}{a_0^3} e^{-2Zr/a_0} = 1 - \int_{r_0}^\infty drr^2 \frac{4Z^3}{a_0^3} e^{-2Zr/a_0}$*.*

Defining, $\alpha = \frac{2Z}{a_0}$*, we obtain*

$$\int_{r_0}^\infty drr^2 \frac{4Z^3}{a_0^3} e^{-2Zr/a_0} = \frac{\alpha^3}{2}\int_{r_0}^\infty drr^2 e^{-\alpha r} = \frac{\alpha^3}{2}\frac{d^2}{d\alpha^2}\int_{r_0}^\infty dr e^{-\alpha r}$$
$$= \frac{\alpha^3}{2}\frac{d^2}{d\alpha^2}\frac{e^{-\alpha r_0}}{\alpha} = \frac{\alpha^3}{2} e^{-\alpha r_0}\left(\frac{r_0^2}{\alpha} + \frac{2r_0}{\alpha^2} + \frac{2}{\alpha^3}\right)$$

$$= e^{-\alpha r_0}\left(\frac{1}{2}\alpha^2 r_0^2 + \alpha r_0 + 1\right).$$

Setting $r_0 = \gamma \frac{a_0}{Z} \Rightarrow r_0\alpha = 2\gamma$*, we obtain* $\int_0^{r_0} drr^2 \frac{4Z^3}{a_0^3} e^{-2Zr/a_0} = 1 - e^{-2\gamma}(2\gamma^2 + 2\gamma + 1)$*.*

11 The Postulates of Quantum Mechanics

Exercise 11.2.1 *(a)* $\mathbf{S}$ *is a matrix whose elements are given as* $[\mathbf{S}]_{m,n} = \langle \chi_m | \varphi_n \rangle$, *where the sets* $\{|\varphi_1\rangle, |\varphi_2\rangle, |\varphi_3\rangle ...\}$ *and* $\{|\chi_1\rangle, |\chi_2\rangle, |\chi_3\rangle, ...\}$ *are two different complete orthonormal sets of vectors, which span the Hilbert space. Use Eq. (11.2.10) to show that the matrix* $\mathbf{S}$ *is unitary, namely* $\left[\mathbf{S}^\dagger \mathbf{S}\right] = \mathbf{I}$ *(or,* $\left[\mathbf{S}^\dagger \mathbf{S}\right]_{m,n} = \delta_{m,n}$*).*

Solution 11.2.1

Let us consider the matrix elements obtained by the multiplication, $\mathbf{S}^\dagger \mathbf{S}$ *:*

$$\left[\mathbf{S}^\dagger \mathbf{S}\right]_{m,n} = \sum_k \left[\mathbf{S}^\dagger\right]_{m,k} [\mathbf{S}]_{k,n} = \sum_k [\mathbf{S}]^*_{k,m} [\mathbf{S}]_{k,n} .$$

Using the definition $[\mathbf{S}]_{k,n} = \langle \chi_k | \varphi_n \rangle$, *we obtain* $[\mathbf{S}]^*_{k,m} = \langle \chi_k | \varphi_m \rangle^* = \langle \varphi_m | \chi_k \rangle$. *Therefore,*

$$\left[\mathbf{S}^\dagger \mathbf{S}\right]_{m,n} = \sum_k \langle \varphi_m | \chi_k \rangle \langle \chi_k | \varphi_n \rangle .$$

Using the expansion of the identity (Eq. (11.2.10)), $\sum_k |\chi_k\rangle\langle\chi_k| = \hat{I}$, *we obtain*

$$\left[\mathbf{S}^\dagger \mathbf{S}\right]_{m,n} = \langle \varphi_m | \chi_n \rangle = \delta_{m,n} .$$

Exercise 11.2.2 *Use Eqs. (11.2.11, 11.2.12, 11.2.16) and show that Eq. (11.2.17) holds for any states,* $|\psi\rangle$ *and* $|\chi\rangle$, *in the Hilbert space.*

Solution 11.2.2

Introducing the identity (Eq. (11.2.10), $\sum_k |\chi_k\rangle\langle\chi_k| = \hat{I}$ *), and using the matrix representation,*

$\langle \varphi_n | \hat{A}^\dagger | \varphi_{n'} \rangle = [\mathbf{A}^\dagger]_{n,n'}$ *, we obtain*

$$\langle \psi | \hat{A}^\dagger | \chi \rangle = \sum_{n,n'=1}^{\infty} \langle \psi | \varphi_n \rangle \langle \varphi_n | \hat{A}^\dagger | \varphi_{n'} \rangle \langle \varphi_{n'} | \chi \rangle = \sum_{n,n'=1}^{\infty} \langle \psi | \varphi_n \rangle [\mathbf{A}^\dagger]_{n,n'} \langle \varphi_{n'} | \chi \rangle .$$

Replacing $[\mathbf{A}^\dagger]_{n,n'} \equiv [\mathbf{A}]^*_{n',n}$ *(Eq. (11.2.16)), and using Eq. (11.2.3) we obtain Eq. (11.2.17),*

$$\langle\psi|\hat{A}^\dagger|\chi\rangle = \sum_{n,n'=1}^{\infty} \langle\psi|\varphi_n\rangle[\mathbf{A}]^*_{n',n}\langle\varphi_{n'}|\chi\rangle = [\sum_{n,n'=1}^{\infty} \langle\chi|\varphi_{n'}\rangle[\mathbf{A}]_{n',n}\langle\varphi_n|\psi\rangle]^*$$

$$= [\sum_{n,n'=1}^{\infty} \langle\chi|\varphi_{n'}\rangle\langle\varphi_{n'}|\hat{A}|\varphi_n\rangle\langle\varphi_n|\psi\rangle]^*$$

$$= \langle\chi|\hat{A}|\psi\rangle^* .$$

Exercise 11.2.3 *The Schrödinger equation for a ket reads* $\frac{\partial}{\partial t}|\psi(t)\rangle = \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle$ *, where* $\hat{H}$ *is the Hamiltonian operator. Use Eq. (11.2.18) and show that the equation of motion for the corresponding bra reads* $\frac{\partial}{\partial t}\langle\psi(t)| = \frac{-1}{i\hbar}\langle\psi(t)|\hat{H}$.

Solution 11.2.3

The equation, $\frac{\partial}{\partial t}|\psi(t)\rangle = \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle$ *, associates the time-derivative of a ket state,* $\frac{\partial}{\partial t}|\psi(t)\rangle \equiv \left|\frac{\partial}{\partial t}\psi(t)\right\rangle$*, with the ket state obtained by the Hamiltonian operation,* $\frac{1}{i\hbar}\hat{H}|\psi(t)\rangle \equiv \left|\frac{1}{i\hbar}\hat{H}\psi(t)\right\rangle$*. Consequently, the respective bra states must be equal,*

$$\left\langle\frac{\partial}{\partial t}\psi(t)\right| = \left\langle\frac{1}{i\hbar}\hat{H}\psi(t)\right|.$$

Using Eq. (11.2.18), we obtain $\left\langle\frac{1}{i\hbar}\hat{H}\psi(t)\right| = \langle\psi(t)|\left(\frac{1}{i\hbar}\hat{H}\right)^\dagger = \frac{-1}{i\hbar}\langle\psi(t)|\hat{H}$ *, and therefore,*

$$\frac{\partial}{\partial t}\langle\psi(t)| = \frac{-1}{i\hbar}\langle\psi(t)|\hat{H} .$$

Exercise 11.3.1 *One of the definitions of Dirac's delta is the limit of an infinitely narrow normalized Gaussian distribution,* $\delta(\alpha) = \lim_{\varepsilon\to 0}\sqrt{\frac{1}{4\pi\varepsilon}}e^{\frac{-\alpha^2}{4\varepsilon}}$ *. Calculate the integral explicitly and* *show that indeed* $\lim_{\varepsilon\to 0}\int_{-\infty}^{\infty}\sqrt{\frac{1}{4\pi\varepsilon}}e^{\frac{-(\alpha-\alpha')^2}{4\varepsilon}}\psi(\alpha)d\alpha=\psi(\alpha')$, *where* $\psi(\alpha)$ *is a gaussian distribution of a finite width,* $\psi(\alpha)=\sqrt{\frac{1}{2\pi\sigma^2}}e^{\frac{-(\alpha-\alpha_0)^2}{2\sigma^2}}$.

Solution 11.3.1

To demonstrate that $\int_{-\infty}^{\infty}\delta(\alpha-\alpha')\psi(\alpha)d\alpha=\psi(\alpha')$ *for the specific function,* $\psi(\alpha)=\sqrt{\frac{1}{2\pi\sigma^2}}e^{\frac{-(\alpha-\alpha_0)^2}{2\sigma^2}}$, *we consider the definition,* $\delta(\alpha-\alpha')=\lim_{\varepsilon\to 0}\sqrt{\frac{1}{4\pi\varepsilon}}e^{\frac{-(\alpha-\alpha')^2}{4\varepsilon}}$.

Let us calculate explicitly the integral $I=\int_{-\infty}^{\infty}d\alpha\sqrt{\frac{1}{4\pi\varepsilon}}e^{\frac{-(\alpha-\alpha')^2}{4\varepsilon}}\sqrt{\frac{1}{2\pi\sigma^2}}e^{\frac{-(\alpha-\alpha_0)^2}{2\sigma^2}}$:

Denoting $a_1=\frac{1}{4\varepsilon}$, $a_2=\frac{1}{2\sigma^2}$, $x_1=\alpha'$, $x_2=\alpha_0$, *we have:*

$$I=\sqrt{\frac{a_1a_2}{\pi^2}}\int_{-\infty}^{\infty}d\alpha e^{-a_1(\alpha-x_1)^2}e^{-a_2(\alpha-x_2)^2}.$$

Using,

$$a_1(\alpha-x_1)^2+a_2(\alpha-x_2)^2=\alpha^2(a_1+a_2)-\alpha(2x_1a_1+2x_2a_2)+a_1x_1^2+a_2x_2^2\equiv a\alpha^2-b\alpha+c$$

$=a(\alpha-\frac{b}{2a})^2-\frac{b^2}{4a}+c$, *we rewrite the integrand,* $I=\sqrt{\frac{a_1a_2}{\pi^2}}\int_{-\infty}^{\infty}d\alpha e^{-a(\alpha-\frac{b}{2a})^2+\frac{b^2}{4a}-c}$.

Since for noninfinite $\frac{b}{2a}$ *we have* $\int_{-\infty}^{\infty}d\alpha e^{-a(\alpha-\frac{b}{2a})^2}=\sqrt{\frac{\pi}{a}}$, *we obtain*

$$I=\sqrt{\frac{a_1a_2}{\pi a}}e^{\frac{b^2}{4a}-c}=\sqrt{\frac{a_1a_2}{\pi(a_1+a_2)}}e^{\frac{(x_1a_1+x_2a_2)^2}{(a_1+a_2)}-a_1x_1^2-a_2x_2^2}$$

$$=\sqrt{\frac{a_1a_2}{\pi(a_1+a_2)}}e^{\frac{(x_1a_1+x_2a_2)^2-a_1^2x_1^2-a_2^2x_2^2-a_2a_1(x_1^2+x_2^2)}{(a_1+a_2)}}$$

$$=\sqrt{\frac{a_1a_2}{\pi(a_1+a_2)}}e^{\frac{-a_1a_2}{a_1+a_2}(x_1-x_2)^2}$$

$$= \sqrt{\frac{1}{\pi(4\varepsilon+2\sigma^2)}} e^{\frac{-1}{4\varepsilon+2\sigma^2}(\alpha'-\alpha_0)^2} \quad .$$

Taking the limit $\varepsilon \to 0$, *we indeed obtain* $I \xrightarrow[\varepsilon\to 0]{} = \sqrt{\frac{1}{\pi 2\sigma^2}} e^{\frac{-(\alpha'-\alpha_0)^2}{2\sigma^2}} = \psi(\alpha')$.

Exercise 11.4.1 *Let* $S = \langle \chi | \psi \rangle$ *be the inner product between two normalized proper vectors,* $\langle \psi | \psi \rangle = 1$ *and* $\langle \chi | \chi \rangle = 1$. *Show that the inner product satisfies the Cauchy–Schwarz inequality, namely* $|S|^2 \le 1$, *which is consistent with the interpretation of* $|S|^2$ *as a probability. (You can use the identity,* $\int d\gamma \int d\gamma' |\psi(\gamma)\chi(\gamma') - \chi(\gamma)\psi(\gamma')|^2 \ge 0$, *which holds for any proper functions* $\psi(\gamma)$ *and* $\chi(\gamma)$*.)*

Solution 11.4.1

First, we can use different complete orthonormal systems for expanding the inner products (without loss of generality we shall use two continuous orthonormal sets $\gamma, \gamma' \in R$, *such that* $1 = \langle \psi | \psi \rangle = \int d\gamma |\psi(\gamma)|^2 = \int d\gamma' |\psi(\gamma')|^2$, $1 = \langle \chi | \chi \rangle = \int d\gamma |\chi(\gamma)|^2 = \int d\gamma' |\chi(\gamma')|^2$, *and* $\langle \psi | \chi \rangle = \int d\gamma \psi^*(\gamma)\chi(\gamma) = \int d\gamma' \psi^*(\gamma')\chi(\gamma')$. *Then, we construct a two-dimensional nonnegative integral,* $\int d\gamma \int d\gamma' |\psi(\gamma)\chi(\gamma') - \chi(\gamma)\psi(\gamma')|^2 \ge 0$, *which reads*

$$\int d\gamma \int d\gamma' |\psi(\gamma)|^2 |\chi(\gamma')|^2$$

$$-\int d\gamma \int d\gamma' \psi^*(\gamma)\chi^*(\gamma')\chi(\gamma)\psi(\gamma')$$

$$-\int d\gamma \int d\gamma' \psi^*(\gamma')\chi^*(\gamma)\chi(\gamma')\psi(\gamma)$$

$$+\int d\gamma \int d\gamma' |\chi(\gamma)|^2 |\psi(\gamma')|^2 \ge 0 \quad .$$

Identifying the one-dimensional normalization and overlap integrals, we obtain: $2 - 2|S|^2 \ge 0$, *and therefore,* $0 \le |S|^2 \le 1$.

Exercise 11.5.1 *A local operator is a function of the position operator (e.g., the scalar potential energy,* $\hat{V}_x = V(\hat{x})$, Eq. (3.4.1)). *Show that the matrix representation of a local operator in the position eigenstates is a diagonal matrix, namely* $\langle \varphi_{x'} | \hat{V} | \varphi_x \rangle = V(x)\delta(x - x')$.

Solution 11.5.1

The position eigenstates are defined as: $\hat{x}|\varphi_x\rangle = x|\varphi_x\rangle$. *For* $\hat{V} = V(\hat{x})$ *which is an analytic function of* $\hat{x}$ *we have (see Eq. (3.4.2)),* $V(\hat{x})|\varphi_x\rangle = V(x)|\varphi_x\rangle$, *and therefore:*

$$\langle \varphi_{x'} | \hat{V} | \varphi_x \rangle = \langle \varphi_{x'} | V(\hat{x}) | \varphi_x \rangle = \langle \varphi_{x'} | V(x) | \varphi_x \rangle = V(x)\langle \varphi_{x'} | \varphi_x \rangle = V(x)\delta(x - x').$$

Exercise 11.5.2 *Given a state vector,* $|\psi\rangle$, *use Eq. (11.5.4) to derive Eq. (11.5.21).*

Solution 11.5.2

The projection of the state vector $|\psi\rangle$ *on a momentum eigenstate reads* $\langle \varphi_{p_x} | \psi \rangle$. *Introducing the expansion of the identity in terms of the position operator eigenstates (Eq. (11.5.4)), we obtain* $\langle \varphi_{p_x} | \psi \rangle = \int_{-\infty}^{\infty} dx \langle \varphi_{p_x} | \varphi_x \rangle \langle \varphi_x | \psi \rangle$.

Exercise 11.5.3 *The kinetic energy of a particle is a function of the momentum operator,* $\hat{T}_x = \frac{1}{2m}(\hat{p}_x)^2$ (Eq. (3.4.3)). Show that the *matrix representation of the kinetic energy in the momentum eigenstates is a diagonal matrix, namely* $\langle \varphi_{p_x'} | \hat{T}_x | \varphi_{p_x} \rangle = \frac{{p_x}^2}{2m}\delta(p_x - p_x')$.

Solution 11.5.3

The momentum eigenstates are defined as (Eq. (11.5.12)), $\hat{p}_x |\varphi_{p_x}\rangle = p_x |\varphi_{p_x}\rangle$. *For* $\hat{T}_x = \frac{1}{2m}(\hat{p}_x)^2$, *which is an analytic function of* $\hat{p}_x$ *(see section 3.4), we have* $\frac{1}{2m}(\hat{p}_x)^2 |\varphi_{p_x}\rangle = \frac{1}{2m} p_x^2 |\varphi_{p_x}\rangle$, *and therefore,*

$$\langle \varphi_{x'} | \hat{T}_x | \varphi_{p_x} \rangle = \langle \varphi_{p_x'} | \frac{1}{2m}(\hat{p}_x)^2 | \varphi_{p_x} \rangle = \langle \varphi_{p_x'} | \frac{1}{2m} p_x^2 | \varphi_{p_x} \rangle = \frac{p_x^2}{2m}\langle \varphi_{p_x'} | \varphi_{p_x} \rangle = \frac{p_x^2}{2m}\delta(p_x - p_x').$$

Exercise 11.5.4 *Formulating the postulates in terms of wave functions, the linear momentum operator is defined as* $\hat{p}_x = -i\hbar \frac{d}{dx}$. *Use the expansions of the identity in terms of the position and momentum eigenstates, Eqs. (11.5.4 and 11.5.17), to show that* $\langle \varphi_x | \hat{p}_x | \psi \rangle = -i\hbar \frac{d}{dx}\psi(x)$ *and* $\langle \varphi_x | \frac{\hat{p}_x^2}{2m} | \psi \rangle = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)$.

Solution 11.5.4

Let us consider a matrix element of a general power of the momentum operator between position and momentum eigenstates. Using $(\hat{p}_x)^n |\varphi_{p_x}\rangle = (p_x)^n |\varphi_{p_x}\rangle$, *and introducing identity operators we obtain*

$$\langle \varphi_x | (\hat{p}_x)^n | \psi \rangle = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dp_x \langle \varphi_x | (\hat{p}_x)^n | \varphi_{p_x} \rangle \langle \varphi_{p_x} | \varphi_{x'} \rangle \langle \varphi_{x'} | \psi \rangle$$

$$= \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dp_x \cdot (p_x)^n \cdot \langle \varphi_x | \varphi_{p_x} \rangle \langle \varphi_{p_x} | \varphi_{x'} \rangle \langle \varphi_{x'} | \psi \rangle \ .$$

Recalling Eq. (11.5.16), $\langle \varphi_x | \varphi_{p_x} \rangle = \frac{e^{ip_x x/\hbar}}{\sqrt{2\pi\hbar}}$, *we obtain*

$$\langle \varphi_x | (\hat{p}_x)^n | \psi \rangle = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dp_x \cdot (p_x)^n \cdot \frac{e^{-ip_x(x'-x)/\hbar}}{2\pi\hbar} \langle \varphi_{x'} | \psi \rangle .$$

Making use of the identity, $(p_x)^n e^{-ip_x(x'-x)/\hbar} = (-i\hbar \frac{d}{dx})^n e^{-ip_x(x'-x)/\hbar}$, *we obtain*

$$\langle \varphi_x | (\hat{p}_x)^n | \psi \rangle = \int_{-\infty}^{\infty} dx' (-i\hbar \frac{d}{dx})^n \int_{-\infty}^{\infty} dp_x \frac{e^{-ip_x(x'-x)/\hbar}}{2\pi\hbar} \langle \varphi_{x'} | \psi \rangle$$

$$= (-i\hbar \frac{d}{dx})^n \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dp_x \frac{e^{-ip_x(x'-x)/\hbar}}{2\pi\hbar} \langle \varphi_{x'} | \psi \rangle \ .$$

Recalling one of the standard definitions of Dirac's delta: $\delta(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx} dx$, *we can use* $\int_{-\infty}^{\infty} dp_x \frac{e^{-ip_x(x'-x)/\hbar}}{2\pi\hbar} = \delta(x - x')$, *to obtain*

$$\langle\varphi_x|(\hat{p}_x)^n|\psi\rangle = (-i\hbar\frac{d}{dx})^n\int_{-\infty}^{\infty}dx'\delta(x-x')\langle\varphi_{x'}|\psi\rangle = (-i\hbar\frac{d}{dx})^n\langle\varphi_x|\psi\rangle = (-i\hbar\frac{d}{dx})^n\psi(x).$$

Therefore, for the momentum operator we have $\langle\varphi_x|\hat{p}_x|\psi\rangle = -i\hbar\frac{d}{dx}\psi(x)$ *, and for the kinetic energy,*

$$\frac{1}{2m}\langle\varphi_x|(\hat{p}_x)^2|\psi\rangle = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x).$$

Exercise 11.5.5 *Use Eqs. (11.5.12, 11.2.3, 11.5.17) to show that the momentum operator is Hermitian, namely* $\langle\chi|\hat{p}_x|\psi\rangle = \langle\psi|\hat{p}_x|\chi\rangle^*$.

Solution 11.5.5

Introducing identity operators in the momentum eigenstate representation, we obtain

$$\langle\chi|\hat{p}_x|\psi\rangle = \int_{-\infty}^{\infty}dp_x\int_{-\infty}^{\infty}dp_x'\langle\chi|\varphi_{p_x'}\rangle\langle\varphi_{p_x'}|\hat{p}_x|\varphi_{p_x}\rangle\langle\varphi_{p_x}|\psi\rangle$$

$$= \int_{-\infty}^{\infty}dp_x\int_{-\infty}^{\infty}dp_x'\langle\chi|\varphi_{p_x'}\rangle\, p_x\delta(p_x-p_x')\langle\varphi_{p_x}|\psi\rangle$$

$$= \int_{-\infty}^{\infty}dp_x p_x\langle\chi|\varphi_{p_x}\rangle\langle\varphi_{p_x}|\psi\rangle\ .$$

Using Eq. (11.2.3), we obtain

$$\langle\chi|\hat{p}_x|\psi\rangle = \left[\int_{-\infty}^{\infty}dp_x p_x\langle\varphi_{p_x}|\chi\rangle\langle\psi|\varphi_{p_x}\rangle\right]^*$$

$$= \left[\int_{-\infty}^{\infty}dp_x\langle\varphi_{p_x}|\chi\rangle\langle\psi|\hat{p}_x|\varphi_{p_x}\rangle\right]^*$$

$$= \left[\int_{-\infty}^{\infty}dp_x\langle\psi|\hat{p}_x|\varphi_{p_x}\rangle\langle\varphi_{p_x}|\chi\rangle\right]^*$$

$$= \langle\psi|\hat{p}_x|\chi\rangle^*\ .$$

Exercise 11.6.1 *Use the definitions in Eqs. (11.6.15-11.6.20) to prove the identities given in Eqs. (11.6.21-11.6.24).*

Solution 11.6.1

Using: $\left[\mathbf{A}\otimes\mathbf{B}\right]_{(k,l),(k',l')}\equiv a_{k,k'}b_{l,l'}$ *and* $[\mathbf{C}\otimes\mathbf{D}]_{(k,l),(k',l')}\equiv c_{k,k'}d_{l,l'}$, *we obtain*

$$[(\mathbf{A}\otimes\mathbf{B})(\mathbf{C}\otimes\mathbf{D})]_{(m,n),(m'n')}=\sum_{k,l}\ (\mathbf{A}\otimes\mathbf{B})_{(m,n),(k,l)}(\mathbf{C}\otimes\mathbf{D})_{(k,l),(m',n')}=\sum_{k,l}\ a_{m,k}b_{n,l}c_{k,m'}d_{l,n'}\,.$$

$$[\mathbf{AC}\otimes\mathbf{BD}]_{(m,n),(m',n')}=[\mathbf{AC}]_{m,m'}[\mathbf{BD}]_{n,n'}=\sum_{k}a_{m,k}c_{k,m'}\sum_{l}b_{n,l}d_{l,n'}=\sum_{k,l}a_{m,k}c_{k,m'}b_{n,l}d_{l,n'}\quad.$$

Hence, the identity (Eq. (11.6.21)) is verified: $(\mathbf{A}\otimes\mathbf{B})(\mathbf{C}\otimes\mathbf{D})=\mathbf{AC}\otimes\mathbf{BD}$.

Using: $\left[\mathbf{A}\otimes\mathbf{B}\right]_{(k,l),(k',l')}\equiv a_{k,k'}b_{l,l'}$ *and* $[\mathbf{c}\otimes\mathbf{d}]_{k,l}\equiv c_k d_l$, *we obtain*

$$[(\mathbf{A}\otimes\mathbf{B})(\mathbf{c}\otimes\mathbf{d})]_{(m,n)}=\sum_{(k,l)}\ (\mathbf{A}\otimes\mathbf{B})_{(m,n),(k,l)}(\mathbf{c}\otimes\mathbf{d})_{(k,l)}=\sum_{(k,l)}\ a_{m,k}b_{n,l}c_k d_l\,.$$

$$[\mathbf{Ac}\otimes\mathbf{Bd}]_{(m,n)}=[\mathbf{Ac}]_m[\mathbf{Bd}]_n=\sum_k a_{m,k}c_k\sum_l b_{n,l}d_l=\sum_{k,l}a_{m,k}c_k b_{n,l}d_l\,.$$

Hence, the identity (Eq. (11.6.22)) is verified: $(\mathbf{A}\otimes\mathbf{B})(\mathbf{c}\otimes\mathbf{d})=\mathbf{Ac}\otimes\mathbf{Bd}$.

Using: $[\mathbf{I}\otimes\mathbf{d}]_{(k,l),k'}\equiv i_{k,k'}d_l=\delta_{k,k'}d_l$, *we obtain*

$$[(\mathbf{A}\otimes\mathbf{B})(\mathbf{I}\otimes\mathbf{d})]_{(m,n),m'}=\sum_{k,l}\ [\mathbf{A}\otimes\mathbf{B}]_{(m,n),(k,l)}[\mathbf{I}\otimes\mathbf{d}]_{(k,l),m'}=\sum_{k,l}\ a_{m,k}b_{n,l}\delta_{k,m'}d_l=\sum_l\ a_{m,m'}b_{n,l}d_l\,.$$

$$[\mathbf{A}\otimes\mathbf{Bd}]_{(m,n),m'}=a_{m,m'}[\mathbf{Bd}]_n=a_{m,m'}\sum_l\ b_{n,l}d_l\quad.$$

Hence, the identity $(\mathbf{A}\otimes\mathbf{B})(\mathbf{I}\otimes\mathbf{d})=\mathbf{A}\otimes\mathbf{Bd}$ *in Eq. (11.6.23) is verified.*

Using: $[\mathbf{c}\otimes\mathbf{I}]_{(m,n),n'}=c_m i_{n,n'}=c_m\delta_{n,n'}$, *we obtain*

$$[(\mathbf{A}\otimes\mathbf{B})(\mathbf{c}\otimes\mathbf{I})]_{(m,n),n'}=\sum_{l,k}\ [\mathbf{A}\otimes\mathbf{B}]_{(m,n),(k,l)}[\mathbf{c}\otimes\mathbf{I}]_{(k,l),n'}=\sum_{l,k}\ a_{m,k}b_{n,l}c_k\delta_{l,n'}=\sum_k\ a_{m,k}b_{n,n'}c_k\,.$$

$$[\mathbf{Ac}\otimes\mathbf{B}]_{(m,n),n'}=[\mathbf{Ac}]_m b_{n,n'}=\sum_k\ a_{m,k}c_k b_{n,n'}\,.$$

Hence, the identity $(\mathbf{A}\otimes\mathbf{B})(\mathbf{c}\otimes\mathbf{I})=\mathbf{Ac}\otimes\mathbf{B}$ *in Eq. (11.6.23) is verified.*

Let the vectors $\mathbf{u}$ *and* $\mathbf{v}$ *be eigenvectors of the matrices* $\mathbf{A}$ *and* $\mathbf{B}$, *associated with the eigenvalues* $\lambda_{\mathbf{u}}$ *and* $\lambda_{\mathbf{v}}$, *respectively,* $\mathbf{Au}=\lambda_{\mathbf{u}}\mathbf{u}$, $\mathbf{Bv}=\lambda_{\mathbf{v}}\mathbf{v}$. *Consequently,*

$$\left(\mathbf{A}\otimes\mathbf{I}+\mathbf{I}\otimes\mathbf{B}\right)\mathbf{u}\otimes\mathbf{v}=\left(\mathbf{A}\otimes\mathbf{I}\right)\mathbf{u}\otimes\mathbf{v}+\left(\mathbf{I}\otimes\mathbf{B}\right)\mathbf{u}\otimes\mathbf{v}$$

$$=\left(\mathbf{Au}\otimes\mathbf{v}\right)+\left(\mathbf{u}\otimes\mathbf{Bv}\right)$$

$$=\left(\lambda_{\mathbf{u}}\mathbf{u}\otimes\mathbf{v}\right)+\left(\mathbf{u}\otimes\lambda_{\mathbf{v}}\mathbf{v}\right)$$

$$=\left(\lambda_{\mathbf{u}}+\lambda_{\mathbf{v}}\right)\mathbf{u}\otimes\mathbf{v}\quad ,$$

which reproduces Eq. (11.6.24).

Exercise 11.6.2 *Use Eqs. (11.6.27-11.6.29) to derive Eq. (11.6.30).*

Solution 11.6.2

From Eqs. (11.6.29, 11.6.27) we obtain $|\psi\rangle=\int d\mathbf{r}|\phi_{\mathbf{r}}\rangle\langle\phi_{\mathbf{r}}|\psi\rangle=\int d\mathbf{r}|\varphi_x\rangle\otimes|\varphi_y\rangle\otimes|\varphi_z\rangle\langle\phi_{\mathbf{r}}|\psi\rangle$*, and using Eq. (11.6.28) we identify* $\langle\phi_{\mathbf{r}}|\psi\rangle=\psi(\mathbf{r})$*, to obtain Eq. (11.6.30).*

Exercise 11.6.3 *Use the position and momentum representations of* $|\psi\rangle$ *in the three-dimensional space (Eqs. (11.6.30, 11.6.36)) and the explicit position representation of the momentum eigenstates (Eq. (11.5.16)) to show that the functions* $\psi(\mathbf{r})=\psi(x,y,z)$ *and* $\bar{\psi}(\mathbf{p})=\bar{\psi}(p_x,p_y,p_z)$*, are related to each other by the three-dimensional Fourier transforms,*

$$\bar{\psi}(\mathbf{p})=\int d\mathbf{r}\,\psi(\mathbf{r})\left(\frac{1}{\sqrt{2\pi\hbar}}\right)^3 e^{-i\mathbf{pr}/\hbar}$$
$$\psi(\mathbf{r})=\int d\mathbf{p}\,\bar{\psi}(\mathbf{p})\left(\frac{1}{\sqrt{2\pi\hbar}}\right)^3 e^{i\mathbf{pr}/\hbar}$$

(Compare to the one-dimensional case, Eqs. (11.5.22, 11.5.23)).

Solution 11.6.3

Using Eq. (11.6.30), we obtain

$$\bar{\psi}(\mathbf{p})=\bar{\psi}(p_x,p_y,p_z)=\left[\langle\varphi_{p_x}|\otimes\langle\varphi_{p_y}|\otimes\langle\varphi_{p_z}|\right]|\psi\rangle$$
$$=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz\left[\langle\varphi_{p_x}|\otimes\langle\varphi_{p_y}|\otimes\langle\varphi_{p_z}|\right]\left[|\varphi_x\rangle\otimes|\varphi_y\rangle\otimes|\varphi_z\rangle\right]\psi(x,y,z)$$

$$= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\langle \varphi_{p_x} \middle| \varphi_x \right\rangle \left\langle \varphi_{p_y} \middle| \varphi_y \right\rangle \left\langle \varphi_{p_z} \middle| \varphi_z \right\rangle \psi(x,y,z) \ ,$$

and using the explicit position representation of the momentum eigenstates (Eq. (11.5.16)), we obtain

$$\bar{\psi}(\mathbf{p}) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left(\frac{1}{\sqrt{2\pi\hbar}} \right)^3 e^{-ip_x x/\hbar} e^{-ip_y y/\hbar} e^{-ip_z z/\hbar} \psi(x,y,z) = \int d\mathbf{r} \left(\frac{1}{\sqrt{2\pi\hbar}} \right)^3 e^{-i\mathbf{pr}/\hbar} \psi(\mathbf{r}) \,.$$

Similarly,

$$\psi(\mathbf{r}) = \psi(x,y,z) = \left[\langle \varphi_x | \otimes \langle \varphi_y | \otimes \langle \varphi_z | \right] |\psi\rangle$$
$$= \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \left[\langle \varphi_x | \otimes \langle \varphi_y | \otimes \langle \varphi_z | \right] \left[\left| \varphi_{p_x} \right\rangle \otimes \left| \varphi_{p_y} \right\rangle \otimes \left| \varphi_{p_z} \right\rangle \right] \bar{\psi}(p_x, p_y, p_z)$$
$$= \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \left\langle \varphi_x \middle| \varphi_{p_x} \right\rangle \left\langle \varphi_y \middle| \varphi_{p_y} \right\rangle \left\langle \varphi_z \middle| \varphi_{p_z} \right\rangle \bar{\psi}(p_x, p_y, p_z)$$
$$= \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \left(\frac{1}{\sqrt{2\pi\hbar}} \right)^3 e^{ip_x x/\hbar} e^{ip_y y/\hbar} e^{ip_z z/\hbar} \bar{\psi}(p_x, p_y, p_z)$$

$$= \int d\mathbf{p} \left(\frac{1}{\sqrt{2\pi\hbar}} \right)^3 e^{i\mathbf{pr}/\hbar} \bar{\psi}(\mathbf{p}) \,.$$

Exercise 11.6.4 *Given that $\hat{V} = V(\hat{\mathbf{r}})$, and $T = T(\hat{\mathbf{p}})$, rederive Eq. (11.6.42) and Eq. (11.6.46) by using the Hermiticity of the corresponding operators.*

Solution 11.6.4

For the potential energy:

$$\langle \phi_{\mathbf{r}} | V(\hat{\mathbf{r}}) | \psi \rangle = \langle \psi | V(\hat{\mathbf{r}}) | \phi_{\mathbf{r}} \rangle^* = \left[\int d\mathbf{r}' \langle \psi | V(\hat{\mathbf{r}}) | \phi_{\mathbf{r}'} \rangle \langle \phi_{\mathbf{r}'} | \phi_{\mathbf{r}} \rangle \right]^*$$
$$= \left[\int d\mathbf{r}\, V(\mathbf{r}') \langle \psi | \phi_{\mathbf{r}'} \rangle \langle \phi_{\mathbf{r}'} | \phi_{\mathbf{r}} \rangle \right]^* = \left[\int d\mathbf{r}\, V(\mathbf{r}') \psi^*(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \right]^*$$

$$= \left[V(\mathbf{r}) \psi^*(\mathbf{r}) \right]^* = V(\mathbf{r}) \psi(\mathbf{r}) \quad .$$

For the kinetic energy:

$$\langle \phi_{\mathbf{p}} | \frac{\hat{\mathbf{p}}^2}{2m} | \psi \rangle = \langle \psi | \frac{\hat{\mathbf{p}}^2}{2m} | \phi_{\mathbf{p}} \rangle^* = \left[\int d\mathbf{p}' \langle \psi | \frac{\hat{\mathbf{p}}^2}{2m} | \phi_{\mathbf{p}'} \rangle \langle \phi_{\mathbf{p}'} | \phi_{\mathbf{p}} \rangle \right]^*$$

$$= \left[\int d\mathbf{p}' \frac{(\mathbf{p}')^2}{2m} \langle \psi | \phi_{\mathbf{p}'} \rangle \langle \phi_{\mathbf{p}'} | \phi_{\mathbf{p}} \rangle \right]^* = \left[\int d\mathbf{p}' \frac{(\mathbf{p}')^2}{2m} \bar{\psi}^*(\mathbf{p}') \delta(\mathbf{p} - \mathbf{p}') \right]^*$$

$$= \left[\frac{\mathbf{p}^2}{2m} \bar{\psi}^*(\mathbf{p}) \right]^* = \frac{\mathbf{p}^2}{2m} \bar{\psi}(\mathbf{p}) \quad .$$

Exercise 11.6.5 *(a) Use Eq. (11.6.46), and the explicit position representation of the momentum eigenstates (Eq. (11.5.16)) to show that* $\langle \phi_{\mathbf{r}} | \hat{T} | \psi \rangle = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} \frac{e^{i\mathbf{pr}/\hbar}}{\left(\sqrt{2\pi\hbar}\right)^3} \bar{\psi}(\mathbf{p})$.

(b) Show that $\mathbf{p}^2 e^{i\mathbf{pr}/\hbar} = -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) e^{i\mathbf{pr}/\hbar}$.

(c) Use the results of (a) and (b), as well as the Fourier expansion of $\psi(\mathbf{r})$ in *Ex. 11.6.3, to obtain Eq. (11.6.47).*

Solution 11.6.5

(a)

$$\langle \phi_{\mathbf{r}} | \hat{T} | \psi \rangle = \int d\mathbf{p} \langle \phi_{\mathbf{r}} | \hat{T} | \phi_{\mathbf{p}} \rangle \langle \phi_{\mathbf{p}} | \psi \rangle = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} \langle \phi_{\mathbf{r}} | \phi_{\mathbf{p}} \rangle \langle \phi_{\mathbf{p}} | \psi \rangle = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} \frac{e^{i\mathbf{pr}/\hbar}}{\left(\sqrt{2\pi\hbar}\right)^3} \bar{\psi}(\mathbf{p}).$$

(b)

$$-\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) e^{i\mathbf{pr}/\hbar} = -\hbar^2 \left(-\frac{1}{\hbar^2} \right) \left(p_x^2 + p_y^2 + p_z^2 \right) e^{i\mathbf{pr}/\hbar} = \mathbf{p}^2 e^{i\mathbf{pr}/\hbar} .$$

(c)

$$\langle \phi_{\mathbf{r}} | \hat{T} | \psi \rangle = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} \frac{e^{i\mathbf{pr}/\hbar}}{\left(\sqrt{2\pi\hbar}\right)^3} \bar{\psi}(\mathbf{p}) = \frac{1}{2m} \int d\mathbf{p} \left(-\hbar^2 \right) \hat{\Delta}_{\mathbf{r}} \frac{e^{i\mathbf{pr}/\hbar}}{\left(\sqrt{2\pi\hbar}\right)^3} \bar{\psi}(\mathbf{p})$$

$$= \frac{-\hbar^2}{2m} \hat{\Delta}_{\mathbf{r}} \int d\mathbf{p} \frac{e^{i\mathbf{pr}/\hbar}}{\left(\sqrt{2\pi\hbar}\right)^3} \bar{\psi}(\mathbf{p}) = \frac{-\hbar^2}{2m} \hat{\Delta}_{\mathbf{r}} \psi(\mathbf{r}) \quad .$$

Exercise 11.7.1 *Prove that the expectation value of a Hermitian operator is real-valued.*

Solution 11.7.1

For a Hermitian operator we have $\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle^*$, *hence,*

$$\langle A(t)\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle^* = \langle A(t)\rangle^*.$$

Exercise 11.7.2 *A system is found in a stationary state,* $|\psi_E(t)\rangle = e^{\frac{-iEt}{\hbar}}|\varphi_E\rangle$ *(Eq. (4.3.5)). Show that the expectation value of any operator is time-independent.*

Solution 11.7.2

$$\langle A(t)\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\varphi_E|e^{\frac{iEt}{\hbar}}\hat{A}e^{\frac{-iEt}{\hbar}}|\varphi_E\rangle = \langle\varphi_E|\hat{A}|\varphi_E\rangle.$$

Exercise 11.7.3 *Show that the expectation value of a local operator* $V(\hat{x})$ *(see Ex. 11.5.1) in a system associated with the wave function* $\psi(x,t)$ *reads* $\langle V(t)\rangle = \int\limits_{-\infty}^{\infty}\psi^*(x,t)V(x)\psi(x,t)dx$.

Solution 11.7.3

Introducing identity operators in the position eigenstate representation,

$$\langle V(t)\rangle = \langle\psi(t)|\hat{V}|\psi(t)\rangle = \int\limits_{-\infty}^{\infty}dx\int\limits_{-\infty}^{\infty}dx'\langle\psi(t)|\varphi_{x'}\rangle\langle\varphi_{x'}|\hat{V}|\varphi_x\rangle\langle\varphi_x|\psi(t)\rangle$$

$$= \int\limits_{-\infty}^{\infty}dx\int\limits_{-\infty}^{\infty}dx'\psi^*(t,x')\langle\varphi_{x'}|\hat{V}|\varphi_x\rangle\psi(t,x) \ ,$$

and using $\langle\varphi_{x'}|\hat{V}|\varphi_x\rangle = V(x)\delta(x-x')$ *(Ex. 11.5.1), we obtain*

$$\langle V(t)\rangle = \int\limits_{-\infty}^{\infty}dx\int\limits_{-\infty}^{\infty}dx'\psi^*(t,x')V(x)\delta(x-x')\psi(t,x) = \int\limits_{-\infty}^{\infty}\psi^*(x,t)V(x)\psi(x,t)dx.$$

Exercise 11.7.4 *Prove that the expectation value of the momentum operator, $\hat{p}_x$, vanishes for a system in a bound stationary state, $\psi_E(x,t)=\varphi_E(x)e^{-iEt/\hbar}$, where $\mathrm{Im}[\varphi_E^*(x)\frac{d}{dx}\varphi_E(x)]=0$.*

Solution 11.7.4

The momentum expectation value reads:

$$\langle\psi\,|\,\hat{p}_x\,|\psi\rangle=-i\hbar\int_{-\infty}^{\infty}dx\varphi_E^*(x)\frac{d}{dx}\varphi_E(x).$$

Recalling that for stationary proper (bound) states the probability flux ($\frac{\hbar}{m}\mathrm{Im}[\varphi_E^*(x)\frac{d}{dx}\varphi_E(x)]$) vanishes in the entire space (see Ex. 7.2.1), we obtain that the real value of $\langle\psi\,|\,\hat{p}\,|\psi\rangle$ vanishes in this case. However, since $\hat{p}_x$ is Hermitian, its expectation value is purely real (Ex. 11.7.1), and hence we conclude that $\langle\psi\,|\,\hat{p}_x\,|\psi\rangle$ vanishes identically in this case.

Exercise 11.7.5 *Use the time-dependent Schrödinger equation, $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle=[\frac{\hat{p}_x^2}{2m}+V(\hat{x})]|\psi(t)\rangle$, and prove the Ehrenfest theorem for a particle of mass m, in the presence of a one-dimensional potential energy, $V(x)$: $\frac{\partial}{\partial t}\langle x(t)\rangle=\frac{\langle p_x(t)\rangle}{m}$ and $\frac{\partial}{\partial t}\langle p_x(t)\rangle=-\left\langle\frac{dV}{dx}(t)\right\rangle$. Show that for a quadratic potential energy $V(x)=\alpha+\beta x+\gamma x^2$, the quantum mechanical expectation values follow the Hamilton equations of classical mechanics.*

Solution 11.7.5

First let us consider a general expectation value of a time-independent Hermitian operator $\hat{A}$:

$$\frac{\partial}{\partial t}\langle A(t)\rangle=\frac{\partial}{\partial t}\langle\psi(t)|\,\hat{A}|\psi(t)\rangle$$

$$=\left\langle\frac{\partial}{\partial t}\psi(t)\right|\hat{A}|\psi(t)\rangle+\langle\psi(t)|\,\hat{A}\left|\frac{\partial}{\partial t}\psi(t)\right\rangle$$

$$=\langle\psi(t)|\,\hat{A}\left|\frac{\partial}{\partial t}\psi(t)\right\rangle^*+\langle\psi(t)|\,\hat{A}\left|\frac{\partial}{\partial t}\psi(t)\right\rangle$$

$$= 2\,\mathrm{Re}\left\langle \psi(t) \right| \hat{A} \left| \frac{\partial}{\partial t} \psi(t) \right\rangle .$$

Using $\frac{\partial}{\partial t} \left| \psi(t) \right\rangle = \frac{-i}{\hbar} \hat{H} \left| \psi(t) \right\rangle$, *we obtain*

$$\frac{\partial}{\partial t} \left\langle A(t) \right\rangle = 2\,\mathrm{Re}\left[\frac{-i}{\hbar} \left\langle \psi(t) \right| \hat{A}\hat{H} \left| \psi(t) \right\rangle \right] = \frac{2}{\hbar} \mathrm{Im}\left[\left\langle \psi(t) \right| \hat{A}\hat{H} \left| \psi(t) \right\rangle \right]$$
$$= \frac{-i}{\hbar} \left[\left\langle \psi(t) \right| \hat{A}\hat{H} \left| \psi(t) \right\rangle - \left\langle \psi(t) \right| \hat{A}\hat{H} \left| \psi(t) \right\rangle^* \right]$$
$$= \frac{-i}{\hbar} \left[\left\langle \psi(t) \right| \hat{A}\hat{H} \left| \psi(t) \right\rangle - \left\langle \psi(t) \right| \hat{H}\hat{A} \left| \psi(t) \right\rangle \right]$$

$$= \frac{-i}{\hbar} \left\langle \psi(t) \right| [\hat{A}, \hat{H}] \left| \psi(t) \right\rangle .$$

Consequently, the time-derivative of an expectation value of $\hat{A}$ *is given as the expectation value of its commutator with the system Hamiltonian. Considering,* $\hat{H} = \frac{\hat{p}_x^2}{2m} + V(\hat{x})$, *we obtain*

$$[\hat{x}, \hat{H}] = [\hat{x}, \frac{\hat{p}_x^2}{2m}] = \frac{1}{2m} [\hat{x}, \hat{p}_x^2] = \frac{i\hbar}{m} \hat{p}_x \text{ , and}$$

$$[\hat{p}_x, \hat{H}] = [\hat{p}_x, V(\hat{x})] = -i\hbar V'(\hat{x}), \text{ where } V'(x) \equiv \frac{d}{dx} V(x).$$

Hence, we obtain the Ehrenfest equations

$$\frac{\partial}{\partial t} \left\langle x(t) \right\rangle = \frac{-i}{\hbar} \left\langle \psi(t) \right| \frac{i\hbar}{m} \hat{p}_x \left| \psi(t) \right\rangle = \frac{1}{m} \left\langle \psi(t) \right| \hat{p}_x \left| \psi(t) \right\rangle = \frac{\left\langle p_x(t) \right\rangle}{m}$$

$$\frac{\partial}{\partial t} \left\langle p_x(t) \right\rangle = \frac{-i}{\hbar} \left\langle \psi(t) \right| -i\hbar V'(\hat{x}) \left| \psi(t) \right\rangle = -\left\langle \psi(t) \right| \hat{V}' \left| \psi(t) \right\rangle = -\left\langle V'(t) \right\rangle .$$

For a quadratic potential $V(x) = \alpha + \beta x + \gamma x^2$ *we obtain*

$$\frac{\partial}{\partial t} \left\langle x(t) \right\rangle = \frac{\left\langle p_x(t) \right\rangle}{m} \text{ and } \frac{\partial}{\partial t} \left\langle p_x(t) \right\rangle = -\beta - 2\gamma \left\langle x(t) \right\rangle .$$

Considering the corresponding classical Hamilton's equations for $H(x,p_x)=\frac{1}{2m}p_x^2+\alpha+\beta x+\gamma x^2$ *:* $\dot{x}=\frac{\partial}{\partial p_x}H(x,p_x)=\frac{p_x}{m}$ *;* $\dot{p}_x=-\frac{\partial}{\partial x}H(x,p_x)=-\beta x-2\gamma x$ *,*

we can readily see that the quantum mechanical expectation values can be replaced in this case by the classical variables $x(t)$ *and* $p_x(t)$*.*

Exercise 11.7.6 *Derive Eq. (11.7.2).*

Solution 11.7.6

By definition: $\langle A(t)\rangle=\langle\psi(t)|\hat{A}|\psi(t)\rangle$*. Using the expansion of the state in terms of* $\hat{A}$ *'s eigenstates:* $\hat{A}|\varphi_n\rangle=\gamma_n|\varphi_n\rangle$*, namely,* $|\psi(t)\rangle=\sum_n a_n(t)|\varphi_n\rangle$ *and* $\langle\psi(t)|=\sum_n a_n^*(t)\langle\varphi_n|$*, we obtain*

$$\langle A(t)\rangle=\langle\psi(t)|\hat{A}|\psi(t)\rangle=\sum_{n'} a_{n'}^*(t)\langle\varphi_{n'}|\hat{A}\sum_n a_n(t)|\varphi_n\rangle$$
$$=\sum_{n,n'} a_{n'}^*(t)a_n(t)\langle\varphi_{n'}|\hat{A}|\varphi_n\rangle=\sum_{n,n'} a_{n'}^*(t)a_n(t)\gamma_n\langle\varphi_{n'}|\varphi_n\rangle$$

$$=\sum_{n,n'}a_{n'}^*(t)a_n(t)\gamma_n\delta_{n,n'}=\sum_n|a_n(t)|^2\gamma_n \qquad .$$

Exercise 11.7.7 *A system is found in a stationary state,* $|\psi_E(t)\rangle=e^{\frac{-iEt}{\hbar}}|\varphi_E\rangle$ *(Eqs. (4.3.4, 4.3.5)). Show that: (a) The probability of measuring the energy* E *is 1. (b) The standard deviation in energy measurement, as defined in Eq. (11.7.2), vanishes.*

Solution 11.7.7

For a stationary state, $|\psi_E(t)\rangle=e^{\frac{-iEt}{\hbar}}|\varphi_E\rangle$*, where* $|\varphi_E\rangle$ *is an eigenstate if the Hamiltonian,* $\hat{H}|\varphi_E\rangle=E|\varphi_E\rangle$*.*

(a)

The probability of measuring the energy E *is given by the absolute square of the projection of* $|\psi_E(t)\rangle$ *on* $|\varphi_E\rangle$*:* $p(E)=|\langle\varphi_E|\psi_E(t)\rangle|^2=|\langle\varphi_E|\varphi_E\rangle e^{-iEt/\hbar}|^2=1$*.*

(b)

The standard deviation in energy measurement reads: $\Delta H(t) = \sqrt{\langle H^2(t)\rangle - \langle H(t)\rangle^2}$ *. For a stationary state:*

$$\langle H(t)\rangle = \langle \varphi_E | e^{\frac{iEt}{\hbar}} \hat{H} e^{\frac{-iEt}{\hbar}} | \varphi_E \rangle = E$$

$$\langle H^2(t)\rangle = \langle \varphi_E | e^{\frac{iEt}{\hbar}} \hat{H}^2 e^{\frac{-iEt}{\hbar}} | \varphi_E \rangle = E^2 \quad ,$$

and therefore, the standard deviation vanishes, $\Delta H(t) = \sqrt{\langle H^2(t)\rangle - \langle H(t)\rangle^2} = \sqrt{E^2 - E^2} = 0$.

Exercise 11.7.8 *In order to prove Eq.(11.7.3): (a) Show that for any operator,* $\hat{O}$*, and its Hermitian conjugate,* $\hat{O}^\dagger$*, and for any state vector, the expectation value of* $\hat{O}^\dagger\hat{O}$ *is non-negative, namely* $\langle\psi|\hat{O}^\dagger\hat{O}|\psi\rangle \geq 0$. *(b) Given two Hermitian linear operators,* $\hat{X}$ *and* $\hat{Y}$*, and a real valued scalar,* α*, use (a) and the definition,* $\hat{O} \equiv \hat{X} - i\alpha\hat{Y}$*, to show that,* $\langle\psi|\hat{X}^2|\psi\rangle + \alpha^2\langle\psi|\hat{Y}^2|\psi\rangle - i\alpha\langle\psi|[\hat{X},\hat{Y}]|\psi\rangle \geq 0$. *(c) Since (b) holds for any real* α*, show that* $\frac{-\langle\psi|[\hat{X},\hat{Y}]|\psi\rangle^2}{4} \leq \langle\psi|\hat{X}^2|\psi\rangle\langle\psi|\hat{Y}^2|\psi\rangle$. *(d) Let* $\hat{X} \equiv \hat{A} - \langle\psi|\hat{A}|\psi\rangle$*, and* $\hat{Y} \equiv \hat{B} - \langle\psi|\hat{B}|\psi\rangle$*, where* $\hat{A}$ *and* $\hat{B}$ *are any linear Hermitian operators. Use (c) and the definition of the standard deviation (Eq. (11.7.2)) to obtain the uncertainty inequality, Eq. (11.7.3).*

Solution 11.7.8

(a)

Introducing an expansion of the identity, we obtain for any $|\psi\rangle$ *:*

$$\langle\psi|\hat{O}^\dagger\hat{O}|\psi\rangle = \sum_n \langle\psi|\hat{O}^\dagger|\varphi_n\rangle\langle\varphi_n|\hat{O}|\psi\rangle = \sum_n |\langle\varphi_n|\hat{O}|\psi\rangle|^2 \geq 0 .$$

(b)

Defining: $\hat{O} \equiv \hat{X} - i\alpha\hat{Y}$*, and hence,* $\hat{O}^\dagger \equiv \hat{X} + i\alpha\hat{Y}$ *(*$\hat{X}$ *and* $\hat{Y}$ *are Hermitian and* α *is real-valued), we obtain*

$$\langle\psi|\hat{O}^\dagger\hat{O}|\psi\rangle = \langle\psi|\left(\hat{X} + i\alpha\hat{Y}\right)\left(\hat{X} - i\alpha\hat{Y}\right)|\psi\rangle$$

$=\langle\psi|\hat{X}^2|\psi\rangle+\alpha^2\langle\psi|\hat{Y}^2|\psi\rangle-i\alpha\langle\psi|[\hat{X},\hat{Y}]|\psi\rangle\geq 0$.

(c)

In (b) we obtained a parabola in the parameter α *:* $a\alpha^2+b\alpha+c$ *, with* $a>0$ *(why?), which should be non-negative for any* α. *This means that the discriminant must be nonpositive, namely* $b^2-4ac\leq 0$ *, hence,* $\frac{-\langle\psi|[\hat{X},\hat{Y}]|\psi\rangle^2}{4}\leq\langle\psi|\hat{X}^2|\psi\rangle\langle\psi|\hat{Y}^2|\psi\rangle$.

(d)

Defining: $\hat{X}\equiv\hat{A}-\langle\psi|\hat{A}|\psi\rangle$ *and* $\hat{Y}\equiv\hat{B}-\langle\psi|\hat{B}|\psi\rangle$, *where* $\hat{A}$ *and* $\hat{B}$ *are any linear Hermitian operators, and using (c), we obtain* $\left[\hat{X},\hat{Y}\right]=[\hat{A},\hat{B}]$. *Consequently,*

$$\frac{-\langle\psi|[\hat{A},\hat{B}]|\psi\rangle^2}{4}\leq\langle\psi|\left(\hat{A}-\langle\psi|\hat{A}|\psi\rangle\right)^2|\psi\rangle\langle\psi|\left(\hat{B}-\langle\psi|\hat{B}|\psi\rangle\right)^2|\psi\rangle.$$

Recalling the definition of the standard deviations (measurement uncertainties), $\Delta A=\sqrt{\langle\psi|\left(\hat{A}-\langle\psi|\hat{A}|\psi\rangle\right)^2|\psi\rangle}$ *and* $\Delta B=\sqrt{\langle\psi|\left(\hat{B}-\langle\psi|\hat{B}|\psi\rangle\right)^2|\psi\rangle}$ *, we finally obtain for any proper* $|\psi\rangle$ *and Hermitian* $\hat{A}$ *and* $\hat{B}$ *,*

$$(\Delta A)^2(\Delta B)^2\geq\frac{-\langle\psi|[\hat{A},\hat{B}]|\psi\rangle^2}{4}.$$

Exercise 11.7.9 *Show that* $-\langle\psi(t)|[\hat{A},\hat{B}]|\psi(t)\rangle^2>0$ *for any non-commuting Hermitian operators,* $\hat{A}$ *and* $\hat{B}$ *,* $[\hat{A},\hat{B}]\neq 0$ *, and* $|\psi(t)\rangle\neq 0$. *(Show that* $\langle\psi(t)|[\hat{A},\hat{B}]|\psi(t)\rangle$ *is an imaginary number.)*

Solution 11.7.9

Using $(\hat{B}\hat{A})^\dagger=(\hat{A})^\dagger(\hat{B})^\dagger$ *, we obtain for any Hermitian* $\hat{A}$ *and* $\hat{B}$ *:*

$$\langle\psi(t)|[\hat{A},\hat{B}]|\psi(t)\rangle = \langle\psi(t)|\hat{A}\hat{B}-\hat{B}\hat{A}|\psi(t)\rangle$$
$$= \langle\psi(t)|\hat{A}\hat{B}|\psi(t)\rangle - \langle\psi(t)|\hat{B}\hat{A}|\psi(t)\rangle$$
$$= \langle\psi(t)|\hat{A}\hat{B}|\psi(t)\rangle - \langle\psi(t)|(\hat{B}\hat{A})^{\dagger}|\psi(t)\rangle^{*}$$
$$= \langle\psi(t)|\hat{A}\hat{B}|\psi(t)\rangle - \langle\psi(t)|\hat{A}\hat{B}|\psi(t)\rangle^{*}$$

$$= 2i\,\mathrm{Im}(\langle\psi(t)|\hat{A}\hat{B}|\psi(t)\rangle) \ .$$

This implies that the expectation value of the commutator of two Hermitian operator is purely imaginary, and hence $-\langle\psi(t)|[\hat{A},\hat{B}]|\psi(t)\rangle^2 > 0$ *for any proper state.*

Exercise 11.7.10 *A particle is associated at a certain time with a normalized Gaussian wave function,* $\psi(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/4} e^{\frac{-x^2}{4\sigma^2}}$. *(a) Calculate the position and momentum standard deviations as defined by Eq. (11.7.2) and verify that their multiplication satisfies Eq. (11.7.4). (You can use the following integrals:* $\int_{-\infty}^{\infty} e^{-\beta x^2}dx = \sqrt{\frac{\pi}{\beta}}$; $\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} = \frac{\sqrt{\pi}}{2}\beta^{-3/2}$ *.) (b)* ***The Gaussian wave function is sometimes referred to as the minimal uncertainty state for the particle****. Explain this term in view of the result of (a).*

Solution 11.7.10

(a)

Defining $\alpha = \frac{1}{4\sigma^2}$, *we rewrite* $\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}$.

The position uncertainty calculation:

$$\langle\hat{x}\rangle = \int_{-\infty}^{\infty} dx x\,|\psi(x)|^2 = \sqrt{\frac{2\alpha}{\pi}}\int_{-\infty}^{\infty} dx x e^{-2\alpha x^2} = 0 .$$

$$\langle\hat{x}^2\rangle = \int_{-\infty}^{\infty} dx x^2\,|\psi(x)|^2 = \sqrt{\frac{2\alpha}{\pi}}\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2}dx = \sqrt{\frac{2\alpha}{\pi}}\frac{\sqrt{\pi}}{2}\frac{1}{(2\alpha)^{3/2}} = \frac{1}{4\alpha} .$$

$$\Delta x = \sqrt{\langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2} = \sqrt{\frac{1}{4\alpha}} = \sigma .$$

The momentum uncertainty calculation:

$$\langle \hat{p}_x \rangle = -i\hbar \int_{-\infty}^{\infty} dx \psi(x) \frac{d}{dx} \psi(x) = -i\hbar \left(\frac{2\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \frac{d}{dx} e^{-\alpha x^2}$$

$$= 2\alpha i\hbar \left(\frac{2\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} dx e^{-2\alpha x^2} x = 0 \ .$$

$$\langle \hat{p}_x{}^2 \rangle = \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(-\hbar^2 \frac{d^2}{dx^2} \right) e^{-\alpha x^2} dx = -\hbar^2 \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-2\alpha x^2} \left(-2\alpha + 4\alpha^2 x^2 \right) dx$$

$$= 2\alpha\hbar^2 \sqrt{\frac{2\alpha}{\pi}} \sqrt{\frac{\pi}{2\alpha}} - \hbar^2 4\alpha^2 \frac{1}{4\alpha} = \alpha\hbar^2 = \frac{\hbar^2}{4\sigma^2} \ .$$

$$\Delta p_x = \sqrt{\langle \hat{p}_x{}^2 \rangle - \langle \hat{p}_x \rangle^2} = \sqrt{\frac{\hbar^2}{4\sigma^2}} = \frac{\hbar}{2\sigma} .$$

The product of position and momentum uncertainties therefore reads

$$\Delta p_x \Delta x = \frac{\hbar}{2\sigma} \cdot \sigma = \frac{\hbar}{2} ,$$

which complies with Eq. (11.7.4).

(b)

As one can see, the Gaussian wave function satisfies the lower bound of the uncertainty product, which generally read $\Delta p_x \Delta x \geq \frac{\hbar}{2}$. *Hence, the Gaussian wave function corresponds to a minimal uncertainty.*

12 Approximation Methods

Exercise 12.1.1 *Derive Eq. (12.1.8).*

Solution 12.1.1

Substitution of the expansions, Eq. (12.1.6) and (12.1.7), in Eq. (12.1.5) yields

$$\sum_{l=0}^{\infty}\lambda^l\hat{H}_0\left|\psi_n^{(l)}\right\rangle+\sum_{l=1}^{\infty}\lambda^l\hat{H}_1\left|\psi_n^{(l-1)}\right\rangle=\sum_{l=0}^{\infty}\lambda^l\sum_{l'=0}^{\infty}\lambda^{l'}E_n^{(l')}\left|\psi_n^{(l)}\right\rangle=\sum_{l=0}^{\infty}\ \sum_{l'=0}^{\infty}\lambda^{(l+l')}E_n^{(l')}\left|\psi_n^{(l)}\right\rangle.$$

Introducing a new index, $l''\equiv l+l'$, *the double summation in the right-hand side can be rewritten as,*

$$\sum_{l=0}^{\infty}\ \sum_{l'=0}^{\infty}\lambda^{(l+l')}E_n^{(l')}\left|\psi_n^{(l)}\right\rangle=\sum_{l''=0}^{\infty}\lambda^{l''}\sum_{l'=0}^{l''}\ E_n^{(l')}\left|\psi_n^{(l''-l')}\right\rangle=\sum_{l=0}^{\infty}\lambda^{l}\sum_{l'=0}^{l}\ E_n^{(l')}\left|\psi_n^{(l-l')}\right\rangle,\ \text{which yields}$$

$$\sum_{l=0}^{\infty}\ [\hat{H}_0\left|\psi_n^{(l)}\right\rangle+(1-\delta_{l,0})\hat{H}_1\left|\psi_n^{(l-1)}\right\rangle-\sum_{l'=0}^{l}\ E_n^{(l')}\left|\psi_n^{(l-l')}\right\rangle]\lambda^l=0.$$

Exercise 12.1.2 *(a) The projection of the vector* $\hat{H}_0\left|\psi_n^{(l)}\right\rangle$ *, appearing in the left-hand side of Eq. (12.1.9), on the vector* $\left|\psi_n^{(0)}\right\rangle$ *is the inner product,* $\left\langle\psi_n^{(0)}\right|\hat{H}_0\left|\psi_n^{(l)}\right\rangle$ *. Use the hermiticity of* $\hat{H}_0$ *and Eqs. (12.1.1, 12.1.10) to show that this projection is zero. (b) Use the result obtained in (a) to show that projection of* $\left|\psi_n^{(0)}\right\rangle$ *on the vector appearing in the right-hand side of Eq. (12.1.9) leads to Eq. (12.1.11).*

Solution 12.1.2

(a)

Using the Hermiticity of $\hat{H}_0$ *we obtain* $\left\langle\psi_n^{(0)}\right|\hat{H}_0\left|\psi_n^{(l)}\right\rangle=\left\langle\psi_n^{(l)}\right|\hat{H}_0\left|\psi_n^{(0)}\right\rangle^*$. *Using Eq. (12.1.1) we obtain* $\left\langle\psi_n^{(0)}\right|\hat{H}_0\left|\psi_n^{(l)}\right\rangle=E_n\left\langle\psi_n^{(0)}\middle|\psi_n^{(l)}\right\rangle$, *and using Eq. (12.1.10) we finally obtain* $\left\langle\psi_n^{(0)}\right|\hat{H}_0\left|\psi_n^{(l)}\right\rangle=0$.

(b)

Using Eq. (12.1.9) we obtain

$$\left\langle \psi_n^{(0)} \middle| \hat{H}_0 \middle| \psi_n^{(l)} \right\rangle = \sum_{l'=0}^{l} \left\langle \psi_n^{(0)} \middle| (E_n^{(l')} - \delta_{l',1}\hat{H}_1) \middle| \psi_n^{(l-l')} \right\rangle$$

$$\left\langle \psi_n^{(0)} \middle| E_n^{(0)} \middle| \psi_n^{(l)} \right\rangle = \left[\sum_{l'=0}^{l} E_n^{(l')} \left\langle \psi_n^{(0)} \middle| \psi_n^{(l-l')} \right\rangle \right] - \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle .$$

Using Eq. (12.1.10), this means

$$0 = E_n^{(l)} - \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle \Rightarrow E_n^{(l)} = \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle .$$

Exercise 12.1.3 *Substitute the expansion of* $\left| \psi_n^{(l)} \right\rangle$ *(Eq. (12.1.12)) into Eq. (12.1.9), and project the two sides of the resulting equation on* $\left| \psi_{n'}^{(0)} \right\rangle$ *with* $n \neq n'$. *Derive Eq. (12.1.13) for the expansion coefficients, considering that* $E_n^{(0)}$ *is a nondegenerate eigenvalue of* $\hat{H}_0$.

Solution 12.1.3

Using Eq. (12.1.9) we obtain

$$\hat{H}_0 \left| \psi_n^{(l)} \right\rangle = -\hat{H}_1 \left| \psi_n^{(l-1)} \right\rangle + \sum_{l'=0}^{l} E_n^{(l')} \left| \psi_n^{(l-l')} \right\rangle$$

$$\left\langle \psi_{n'}^{(0)} \middle| \hat{H}_0 \middle| \psi_n^{(l)} \right\rangle = -\left\langle \psi_{n'}^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle + \sum_{l'=0}^{l} E_n^{(l')} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l-l')} \right\rangle$$

$$E_{n'}^{(0)} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l)} \right\rangle = -\left\langle \psi_{n'}^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle + \sum_{l'=0}^{l} E_n^{(l')} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l-l')} \right\rangle$$

$$E_{n'}^{(0)} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l)} \right\rangle = -\left\langle \psi_{n'}^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle + E_n^{(0)} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l)} \right\rangle + \sum_{l'=1}^{l} E_n^{(l')} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l-l')} \right\rangle .$$

Using the expansion, $\left| \psi_n^{(l)} \right\rangle = \sum_{n' \neq n = 0}^{\infty} a_{n'}^{(n,l)} \left| \psi_{n'}^{(0)} \right\rangle$, *we obtain* $\left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l)} \right\rangle = a_{n'}^{(n,l)}$. *Hence,*

$$E_{n'}^{(0)} a_{n'}^{(n,l)} - E_n^{(0)} a_{n'}^{(n,l)} = -\left\langle \psi_{n'}^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle + \sum_{l'=1}^{l} E_n^{(l')} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l-l')} \right\rangle$$

$$a_{n'}^{(n,l)} = \frac{\left\langle \psi_{n'}^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(l-1)} \right\rangle}{E_n^{(0)} - E_{n'}^{(0)}} - \sum_{l'=1}^{l} \frac{E_n^{(l')} \left\langle \psi_{n'}^{(0)} \middle| \psi_n^{(l-l')} \right\rangle}{E_n^{(0)} - E_{n'}^{(0)}} ,$$

where the last step applies only or nondegenerate states, namely for $E_n^{(0)} \neq E_{n'}^{(0)}$.

Exercise 12.1.4 *(a) Use Eqs. (12.1.12, 12.1.13) to derive Eq. (12.1.14, 12.1.15). (b) Use the results of (a) and Eq. (12.1.11) to obtain Eqs. (12.1.16-12.1.18).*

Solution 12.1.4

(a)

For the first-order correction ($l=1$), Eq. (12.1.13) and the orthonormality condition (Eq. (12.1.2)) yield $a_{n'}^{(n,1)} = \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}}$. *Using this result in Eq. (12.1.12) we obtain Eq. (12.1.14),*

$$|\psi_n^{(1)}\rangle = \sum_{n'\neq n} \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} |\psi_{n'}^{(0)}\rangle .$$

For the second-order correction ($l=2$), Eq. (12.1.13) and the orthonormality condition (Eq. (12.1.2)) yield $a_{n'}^{(n,2)} = \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 - E_n^{(1)} | \psi_n^{(1)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}}$. *Using this result in Eq. (12.1.12) we obtain Eq. (12.1.15):*

$$|\psi_n^{(2)}\rangle = \sum_{n''\neq n} \frac{\langle \psi_{n''}^{(0)} | \hat{H}_1 - E_n^{(1)} | \psi_n^{(1)} \rangle}{E_n^{(0)} - E_{n''}^{(0)}} |\psi_{n''}^{(0)}\rangle$$

$$= \sum_{n''\neq n} \frac{\langle \psi_{n''}^{(0)} | (\hat{H}_1 - E_n^{(1)}) \sum_{n'\neq n} \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} |\psi_{n'}^{(0)}\rangle}{E_n^{(0)} - E_{n''}^{(0)}} |\psi_{n''}^{(0)}\rangle$$

$$= \sum_{n''\neq n} \sum_{n'\neq n} \frac{\langle \psi_{n''}^{(0)} | \hat{H}_1 | \psi_{n'}^{(0)} \rangle \langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_{n'}^{(0)})(E_n^{(0)} - E_{n''}^{(0)})} |\psi_{n''}^{(0)}\rangle$$

$$-\sum_{n''\neq n} \frac{\langle \psi_{n''}^{(0)} | E_n^{(1)} \sum_{n'\neq n} \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} |\psi_{n'}^{(0)}\rangle}{E_n^{(0)} - E_{n''}^{(0)}} |\psi_{n''}^{(0)}\rangle$$

$$= \sum_{n''\neq n} \sum_{n'\neq n} \frac{\langle \psi_{n''}^{(0)} | \hat{H}_1 | \psi_{n'}^{(0)} \rangle \langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_{n'}^{(0)})(E_n^{(0)} - E_{n''}^{(0)})} |\psi_{n''}^{(0)}\rangle$$

$$-\sum_{n''\neq n} \frac{E_n^{(1)} \langle \psi_{n''}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_{n''}^{(0)})^2} |\psi_{n''}^{(0)}\rangle$$

$$= \sum_{n''\neq n} [\left(\sum_{n'\neq n} \frac{\langle \psi_{n''}^{(0)} | \hat{H}_1 | \psi_{n'}^{(0)} \rangle \langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} \right) - \frac{E_n^{(1)} \langle \psi_{n''}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n''}^{(0)}}] \frac{1}{E_n^{(0)} - E_{n''}^{(0)}} |\psi_{n''}^{(0)}\rangle$$

$$= \sum_{n''\neq n} [\sum_{n'\neq n} \left(\frac{\langle \psi_{n''}^{(0)} | \hat{H}_1 | \psi_{n'}^{(0)} \rangle \langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} - \frac{E_n^{(1)} \delta_{n',n''} \langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} \right)] \frac{1}{E_n^{(0)} - E_{n''}^{(0)}} |\psi_{n''}^{(0)}\rangle$$

$$=\sum_{n"\neq n}\sum_{n'\neq n}\frac{\left\langle\psi_{n"}^{(0)}\left|\hat{H}_1-E_n^{(1)}\right|\psi_{n'}^{(0)}\right\rangle\left\langle\psi_{n'}^{(0)}\left|\hat{H}_1\right|\psi_n^{(0)}\right\rangle}{(E_n^{(0)}-E_{n'}^{(0)})(E_n^{(0)}-E_{n"}^{(0)})}\left|\psi_{n"}^{(0)}\right\rangle .$$

(b)

Using Eq. (12.1.11) with $l=1$ we obtain Eq. (12.1.16),

$$E_n^{(1)}=\left\langle\psi_n^{(0)}\left|\hat{H}_1\right|\psi_n^{(0)}\right\rangle.$$

For $l=2$, using Eq. (12.1.14), we obtain Eq. (12.1.17),

$$E_n^{(2)}=\left\langle\psi_n^{(0)}\left|\hat{H}_1\right|\psi_n^{(1)}\right\rangle=\sum_{n'\neq n}\frac{\left\langle\psi_{n'}^{(0)}\left|\hat{H}_1\right|\psi_n^{(0)}\right\rangle}{E_n^{(0)}-E_{n'}^{(0)}}\left\langle\psi_n^{(0)}\left|\hat{H}_1\right|\psi_{n'}^{(0)}\right\rangle$$

$$=\sum_{n'\neq n}\frac{\left|\left\langle\psi_{n'}^{(0)}\left|\hat{H}_1\right|\psi_n^{(0)}\right\rangle\right|^2}{E_n^{(0)}-E_{n'}^{(0)}} .$$

For $l=3$, using Eq. (12.1.15), we obtain Eq. (12.1.18),

$$E_n^{(3)}=\left\langle\psi_n^{(0)}\left|\hat{H}_1\right|\psi_n^{(2)}\right\rangle$$

$$=\sum_{n"\neq n}\sum_{n'\neq n}\frac{\left\langle\psi_{n"}^{(0)}\left|\hat{H}_1-E_n^{(1)}\right|\psi_{n'}^{(0)}\right\rangle\left\langle\psi_{n'}^{(0)}\left|\hat{H}_1\right|\psi_n^{(0)}\right\rangle\left\langle\psi_n^{(0)}\left|\hat{H}_1\right|\psi_{n"}^{(0)}\right\rangle}{\left(E_n^{(0)}-E_{n"}^{(0)}\right)\left(E_n^{(0)}-E_{n'}^{(0)}\right)} .$$

Exercise 12.1.5 *(a) Show that projecting Eq. (12.1.21) with $l=1$ on the orthonormal set of degenerate vectors, defined in Eq. (12.1.19), yields $\left\langle\psi_k^{(0)}\left|(E_j^{(1)}-\hat{H}_1)\right|\psi_j^{(0)}\right\rangle=0$. (b) Use the expansion, Eq. (12.1.20), to derive Eq. (12.1.23).*

Solution 12.1.5

(a)

Eq. (12.2.21) with $l=1$ reads $\hat{H}_0\left|\psi_j^{(1)}\right\rangle=E_j^{(0)}\left|\psi_j^{(1)}\right\rangle+(E_j^{(1)}-\hat{H}_1)\left|\psi_j^{(0)}\right\rangle$. Projecting on $\left|\psi_k^{(0)}\right\rangle$, associated with $\hat{H}_0\left|\psi_k^{(0)}\right\rangle=E_n^{(0)}\left|\psi_k^{(0)}\right\rangle$, yields

$$\left\langle\psi_k^{(0)}\left|\hat{H}_0\right|\psi_j^{(1)}\right\rangle=\left\langle\psi_k^{(0)}\left|E_j^{(0)}\right|\psi_j^{(1)}\right\rangle+\left\langle\psi_k^{(0)}\left|(E_j^{(1)}-\hat{H}_1)\right|\psi_j^{(0)}\right\rangle.$$

Using the orthogonality of corrections associated with different orders (Eq. (12.1.10)), we obtain

$0 = \left\langle \psi_k^{(0)} \right| (E_j^{(1)} - \hat{H}_1) \left| \psi_j^{(0)} \right\rangle .$

(b)

Using the expansion, $\left| \psi_j^{(0)} \right\rangle = \sum_{k=1}^{N} a_{k,j}^{(0)} \left| \psi_k^{(0)} \right\rangle$ *, in the result of (a) we obtain Eq. (12.1.23),*

$$\sum_{k'=1}^{N} \left\langle \psi_k^{(0)} \right| (E_j^{(1)} - \hat{H}_1) \left| \psi_{k'}^{(0)} \right\rangle a_{k',j}^{(0)} = 0 \Rightarrow \sum_{k'=1}^{N} \left\langle \psi_k^{(0)} \right| \hat{H}_1 \left| \psi_{k'}^{(0)} \right\rangle a_{k',j}^{(0)} = E_j^{(1)} a_{k,j}^{(0)} .$$

Exercise 12.1.6 *(a) Use the orthonormality of the basis states (Eq. (12.1.19)) and recall that the eigenvectors of any Hermitian matrix (e.g.,* $\mathbf{H}_1$*) can be chosen orthonormal,* $(\mathbf{a}_j^{(0)}, \mathbf{a}_{j'}^{(0)}) = \sum_{k=1}^{N} [\mathbf{a}_j^{(0)}]_k^* \cdot [\mathbf{a}_{j'}^{(0)}]_k = \delta_{j,j'}$*, to prove that the vectors defined in Eq. (12.1.25) can be chosen orthonormal, namely* $\left\langle \psi_j^{(0)} \middle| \psi_{j'}^{(0)} \right\rangle = \delta_{j,j'}$*. (b) Show that for a normalized vector defined in Eq. (12.1.25), the first-order correction to the energy can be expressed as for a non-degenerate state (Eq. (12.1.16)), namely* $E_j^{(1)} = \left\langle \psi_j^{(0)} \right| \hat{H}_1 \left| \psi_j^{(0)} \right\rangle$.

Solution 12.1.6

(a)

Using the expansion of the corrected zero-order vectors in terms of the basis states (Eq. (12.1.25)), we obtain $\left\langle \psi_{j'}^{(0)} \middle| \psi_j^{(0)} \right\rangle = \sum_{k,k'=1}^{N} [\mathbf{a}_{j'}^{(0)}]_{k'}^* [\mathbf{a}_j^{(0)}]_k \left\langle \psi_{k'}^{(0)} \middle| \psi_k^{(0)} \right\rangle$*. Using the orthonormality of the basis states (Eq. (12.1.19)), we obtain* $\left\langle \psi_{j'}^{(0)} \middle| \psi_j^{(0)} \right\rangle = \sum_{k=1}^{N} [\mathbf{a}_{j'}^{(0)}]_k^* [\mathbf{a}_j^{(0)}]_k$ *. The term on the right-hand side is identified as the scalar product of two complex-valued vectors,* $(\mathbf{a}_{j'}^{(0)}, \mathbf{a}_j^{(0)})$*. Since these vectors are eigenvectors of a Hermitian matrix (Eq. (12.1.24)), they can be chosen to be orthonormal, and therefore,* $\left\langle \psi_{j'}^{(0)} \middle| \psi_j^{(0)} \right\rangle = \delta_{j,j'}$.

(b)

Using the expansion Eq. (12.1.25), we obtain

$$\left\langle \psi_j^{(0)} \middle| \hat{H}_1 \middle| \psi_j^{(0)} \right\rangle = \sum_{k,k'=1}^{N} [\mathbf{a}_j^{(0)}]_{k'}^* \left\langle \psi_{k'}^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle [\mathbf{a}_j^{(0)}]_k .$$

Identifying the matrix elements of the perturbation, $\left\langle \psi_{k'}^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle = \left[\mathbf{H}_1\right]_{k',k}$*, the result reads*

$$\left\langle \psi_j^{(0)} \middle| \hat{H}_1 \middle| \psi_j^{(0)} \right\rangle = \sum_{k,k'=1}^{N} [\mathbf{a}_j^{(0)}]_{k'}^* \left[\mathbf{H}_1\right]_{k',k} [\mathbf{a}_j^{(0)}]_k .$$

Recalling the $\mathbf{a}_j^{(0)}$ *is an eigenvector of* $\mathbf{H}_1$*, namely* $\sum_{k=1}^{N} \left[\mathbf{H}_1\right]_{k',k} [\mathbf{a}_j^{(0)}]_k = E_j^{(1)} [\mathbf{a}_j^{(0)}]_{k'}$*, we obtain*

$$\left\langle \psi_j^{(0)} \middle| \hat{H}_1 \middle| \psi_j^{(0)} \right\rangle = \sum_{k'=1}^{N} [\mathbf{a}_j^{(0)}]_{k'}^* E_j^{(1)} [\mathbf{a}_j^{(0)}]_{k'} = E_j^{(1)} \sum_{k'=1}^{N} [\mathbf{a}_j^{(0)}]_{k'}^* [\mathbf{a}_j^{(0)}]_{k'} = E_j^{(1)} ,$$

where in the last step we used the fact that the eigenvector $\mathbf{a}_j^{(0)}$ *is normalized.*

Exercise 12.2.1 *Derive the expressions for the eigenvalues (Eq. (12.2.6)) and the eigenvectors (Eq. (12.2.8)) of the TLS Hamiltonian, as defined in Eqs. (12.2.2, 12.2.3). In order to do this, express the eigenvectors as linear combinations of the basis vectors,* $\left|\psi\right\rangle = a_1 \left|\chi_1\right\rangle + a_2 \left|\chi_2\right\rangle$*, project the corresponding eigenvalue equation* $\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$ *onto the basis vectors,* $\left|\chi_1\right\rangle$ *and* $\left|\chi_2\right\rangle$*, and obtain the algebraic eigenvalue equation,* $\begin{bmatrix} \varepsilon_1 & \gamma \\ \gamma^* & \varepsilon_2 \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = E \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$*. Then solve the equation: obtain the two eigenvalues,* $E_{\pm} = \bar{\varepsilon} \pm \sqrt{\Delta^2 + |\gamma|^2}$ *, and the corresponding eigenvector coefficients,* $a_1^{(\pm)} = \sqrt{\frac{\alpha \pm 1}{2\alpha}}$, $a_2^{(\pm)} = \pm \frac{|\gamma|}{\gamma}\sqrt{\frac{\alpha \mp 1}{2\alpha}}$, where $\bar{\varepsilon} = (\varepsilon_1 + \varepsilon_2)/2$, $\Delta = (\varepsilon_1 - \varepsilon_2)/2$ and $\alpha \equiv \sqrt{1 + |\gamma|^2/\Delta^2}$.

Solution 12.2.1

For the TLS Hamiltonian, $\hat{H} = \varepsilon_1 \left|\chi_1\right\rangle\left\langle\chi_1\right| + \varepsilon_2 \left|\chi_2\right\rangle\left\langle\chi_2\right| + \gamma \left|\chi_1\right\rangle\left\langle\chi_2\right| + \gamma^* \left|\chi_2\right\rangle\left\langle\chi_1\right|$*, we seek the solution to the equation:* $\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$*. Expanding in terms of the basis vectors,* $\left|\psi\right\rangle = a_1 \left|\chi_1\right\rangle + a_2 \left|\chi_2\right\rangle$*, we obtain*

$$\hat{H}\left|\psi\right\rangle = \varepsilon_1 a_1 \left|\chi_1\right\rangle + \varepsilon_2 a_2 \left|\chi_2\right\rangle + \gamma a_2 \left|\chi_1\right\rangle + \gamma^* a_1 \left|\chi_2\right\rangle = E a_1 \left|\chi_1\right\rangle + E a_2 \left|\chi_2\right\rangle .$$

The algebraic equations for the expansion coefficients and the energy levels therefore read,

$$\varepsilon_1 a_1 + \gamma a_2 = E a_1$$

$$\varepsilon_2 a_2 + \gamma^* a_1 = E a_2 \ ,$$

and in matrix form,

$$\begin{bmatrix} \varepsilon_1 - E & \gamma \\ \gamma^* & \varepsilon_2 - E \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Non-trivial solutions to the homogeneous equation are obtained for

$$\begin{vmatrix} \varepsilon_1 - E & \gamma \\ \gamma^* & \varepsilon_2 - E \end{vmatrix} = 0.$$

The two solutions for the energy levels are demoted E_1 *and* E_2*, and are given by*

$$E_1 = \frac{\varepsilon_1 + \varepsilon_2}{2} + \frac{\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|\gamma|^2}}{2} \quad ; \quad E_2 = \frac{\varepsilon_1 + \varepsilon_2}{2} - \frac{\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|\gamma|^2}}{2}.$$

Defining: $\bar{\varepsilon} \equiv \dfrac{\varepsilon_1 + \varepsilon_2}{2}$ *and* $\Delta \equiv \dfrac{\varepsilon_1 - \varepsilon_2}{2}$ *(Eq. (12.2.5)), we obtain Eq. (12.2.6),*

$$E_1 = \bar{\varepsilon} + \sqrt{\Delta^2 + |\gamma|^2} \quad ; \quad E_2 = \bar{\varepsilon} - \sqrt{\Delta^2 + |\gamma|^2}.$$

To calculate the eigenvector coefficients, we define, $\alpha \equiv \sqrt{1 + |\gamma|^2 / \Delta^2}$ *, where, for convenience of notation we associate the two solutions with,* $E_1 = E_+ = \bar{\varepsilon} + \Delta\alpha$ *and* $E_2 = E_- = \bar{\varepsilon} - \Delta\alpha$*. Substitution of* $E_\pm$ *in the homogeneous equation yields the coefficient ratios,*

$$(\varepsilon_1 - \bar{\varepsilon} \mp \Delta\alpha) a_1^{(\pm)} + \gamma a_2^{(\pm)} = 0 \Rightarrow \frac{a_2^{(\pm)}}{a_1^{(\pm)}} = \frac{-\varepsilon_1 + \bar{\varepsilon} \pm \Delta\alpha}{\gamma} = \frac{-\Delta(1 \mp \alpha)}{\gamma}.$$

In the most general case, γ *can be complex-valued, namely:* $\gamma \equiv |\gamma| e^{i\varphi}$*. Using the definition of* α *, we obtain* $|\gamma| = \Delta\sqrt{\alpha^2 - 1}$*, hence,* $\gamma = e^{i\varphi}\Delta\sqrt{\alpha^2 - 1}$*. Substitution in the expression for the coefficients we obtain*

$$\frac{a_2^{(\pm)}}{a_1^{(\pm)}} = \frac{-(1 \mp \alpha)}{\sqrt{\alpha^2 - 1}} e^{-i\varphi} = \pm \frac{(\alpha \mp 1)}{\sqrt{\alpha^2 - 1}} e^{-i\varphi} = \pm \sqrt{\frac{(\alpha \mp 1)(\alpha \mp 1)}{(\alpha - 1)(\alpha + 1)}} e^{-i\varphi} = \pm \sqrt{\frac{(\alpha \mp 1)}{(\alpha \pm 1)}} e^{-i\varphi}.$$

To normalize the eigenvectors, we use $|a_2^{(\pm)}|^2 = |a_1^{(\pm)}|^2 \dfrac{(\alpha \mp 1)}{(\alpha \pm 1)}$, *and therefore,*

$$1 = |a_1^{(\pm)}|^2 + |a_2^{(\pm)}|^2 = |a_1^{(\pm)}|^2 \left(1 + \frac{(\alpha \mp 1)}{(\alpha \pm 1)}\right) = |a_1^{(\pm)}|^2 \frac{2\alpha}{\alpha \pm 1}$$

$$\Rightarrow a_1^{(\pm)} = \sqrt{\frac{\alpha \pm 1}{2\alpha}} \Rightarrow a_2^{(\pm)} = \pm e^{-i\varphi}\sqrt{\frac{\alpha \mp 1}{2\alpha}} = \pm \frac{|\gamma|}{\gamma}\sqrt{\frac{\alpha \mp 1}{2\alpha}} \,,$$

namely,

$$E_\pm = \bar{\varepsilon} \pm \Delta\alpha \quad \leftrightarrow \quad \begin{bmatrix} a_1^{(\pm)} \\ a_2^{(\pm)} \end{bmatrix} = \begin{bmatrix} \sqrt{\dfrac{\alpha \pm 1}{2\alpha}} \\ \pm \dfrac{|\gamma|}{\gamma}\sqrt{\dfrac{\alpha \mp 1}{2\alpha}} \end{bmatrix}.$$

Exercise 12.2.2 *Implement perturbation theory (Eqs. (12.1.16, 12.1.17)) for the Hamiltonian defined in Eqs. (12.2.10-12.2.12). (a) Show that the first-order corrections to the energy vanish. (b) Calculate the second-order corrections to obtain Eq. (12.2.13).*

Solution 12.2.2

Using Eq. (12.2.11) for the zero-order eigenstates, $|\psi_1^{(0)}\rangle = |\chi_1\rangle$ *and* $|\psi_2^{(0)}\rangle = |\chi_2\rangle$, *and the perturbation operator (Eq. (12.2.12)),* $\hat{H}_1 = \gamma|\chi_1\rangle\langle\chi_2| + \gamma^*|\chi_2\rangle\langle\chi_1|$, *we obtain*

(a)

The first-order corrections to the two energy levels (Eq. (12.1.16)) read

$$E_1^{(1)} = \langle\psi_1^{(0)}|\hat{H}_1|\psi_1^{(0)}\rangle = \langle\chi_1|\hat{H}_1|\chi_1\rangle = 0$$

$$E_2^{(1)} = \langle\psi_2^{(0)}|\hat{H}_1|\psi_2^{(0)}\rangle = \langle\chi_2|\hat{H}_1|\chi_2\rangle = 0\,.$$

(b)

The second-order corrections to the two energy levels (Eq. (12.1.17)) read

$$E_1^{(2)} = \sum_{n'\neq 1} \frac{|\langle\psi_{n'}^{(0)}|\hat{H}_1|\psi_1^{(0)}\rangle|^2}{E_1^{(0)} - E_{n'}^{(0)}} = \frac{|\langle\chi_2|\hat{H}_1|\chi_1\rangle|^2}{E_1^{(0)} - E_2^{(0)}} = \frac{|\gamma|^2}{2\Delta}$$

$$E_2^{(2)} = \sum_{n' \neq 2} \frac{|\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_2^{(0)} \rangle|^2}{E_2^{(0)} - E_{n'}^{(0)}} = \frac{|\langle \chi_1 | \hat{H}_1 | \chi_2 \rangle|^2}{E_2^{(0)} - E_1^{(0)}} = \frac{-|\gamma|^2}{2\Delta} \ .$$

Hence, using $E_1^{(0)} = \bar{\varepsilon} + \Delta$, $E_2^{(0)} = \bar{\varepsilon} - \Delta$, *and the results of (a) and (b), we obtain Eq. (12.2.13),*

$$E_1 \cong E_1^{(0)} + \lambda E_1^{(1)} + \lambda^2 E_1^{(2)} = \bar{\varepsilon} + \Delta + \lambda^2 \frac{|\gamma|^2}{2\Delta}$$

$$E_2 \cong E_2^{(0)} + \lambda E_2^{(1)} + \lambda^2 E_2^{(2)} = \bar{\varepsilon} - \Delta - \lambda^2 \frac{|\gamma|^2}{2\Delta} \quad .$$

Exercise 12.2.3 *Implement perturbation theory (Eq. (12.1.14)) for the Hamiltonian defined in Eqs. (12.2.10-12.2.12) to obtain the first-order corrections to the eigenstates, as given in Eq. (12.2.16).*

Solution 12.2.3

Using Eq. (12.1.14), $|\psi_n^{(1)}\rangle = \sum_{n' \neq n} \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}} |\psi_{n'}^{(0)}\rangle$, *implemented for the TLS model, where,* $|\psi_1^{(0)}\rangle = |\chi_1\rangle$, $|\psi_2^{(0)}\rangle = |\chi_2\rangle$, $E_1^{(0)} = \bar{\varepsilon} + \Delta$, $E_2^{(0)} = \bar{\varepsilon} - \Delta$, *and* $\hat{H}_1 = \gamma |\chi_1\rangle\langle\chi_2| + \gamma^* |\chi_2\rangle\langle\chi_1|$, *we obtain the first-order corrections*

$$|\psi_1^{(1)}\rangle = \sum_{n' \neq 1} \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle}{E_1^{(0)} - E_{n'}^{(0)}} |\psi_{n'}^{(0)}\rangle = \frac{\langle \psi_2^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle}{E_1^{(0)} - E_2^{(0)}} |\psi_2^{(0)}\rangle = \frac{\gamma^*}{2\Delta} |\psi_2^{(0)}\rangle$$

$$|\psi_2^{(1)}\rangle = \sum_{n' \neq 2} \frac{\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_2^{(0)} \rangle}{E_2^{(0)} - E_{n'}^{(0)}} |\psi_{n'}^{(0)}\rangle = \frac{\langle \psi_1^{(0)} | \hat{H}_1 | \psi_2^{(0)} \rangle}{E_2^{(0)} - E_1^{(0)}} |\psi_1^{(0)}\rangle = -\frac{\gamma}{2\Delta} |\psi_1^{(0)}\rangle \ .$$

Hence, restricting to $\gamma = -|\gamma|$, *the corrected eigenstates up to first order read (Eq. (12.2.16))*

$$|\psi_1\rangle \approx |\psi_1^{(0)}\rangle + \lambda |\psi_1^{(1)}\rangle = |\chi_1\rangle - \lambda \frac{|\gamma|}{2\Delta} |\chi_2\rangle$$

$$|\psi_2\rangle \approx |\psi_2^{(0)}\rangle + \lambda |\psi_2^{(1)}\rangle = |\chi_2\rangle + \frac{\lambda |\gamma|}{2\Delta} |\chi_1\rangle \ .$$

Exercise 12.2.4 *(a) Derive the expressions in Eq. (12.2.17) for the exact TLS eigenstates. (b) Show that the result obtained by first-order perturbation theory (Eq. (12.2.16)) is obtained by expanding the square root function in a first-order Taylor expansion.*

Solution 12.2.4

(a)

Setting $\gamma = -|\gamma|$*, the general expressions for the TLS Hamiltonian eigenvector coefficients (obtained in Ex. 12.2.1) read (* $\alpha \equiv \sqrt{1+|\gamma|^2/\Delta^2}$ *)*

$$E_1 = \bar{\varepsilon} + \Delta\alpha \quad \leftrightarrow \quad \begin{bmatrix} a_1^{(+)} \\ a_2^{(+)} \end{bmatrix} = \begin{bmatrix} \sqrt{\dfrac{\alpha+1}{2\alpha}} \\ -\sqrt{\dfrac{\alpha-1}{2\alpha}} \end{bmatrix} \quad ; \quad E_2 = \bar{\varepsilon} - \Delta\alpha \quad \leftrightarrow \quad \begin{bmatrix} a_1^{(-)} \\ a_2^{(-)} \end{bmatrix} = \begin{bmatrix} \sqrt{\dfrac{\alpha-1}{2\alpha}} \\ \sqrt{\dfrac{\alpha+1}{2\alpha}} \end{bmatrix}.$$

Hence,

$$|\psi_1\rangle = \sqrt{\frac{\alpha+1}{2\alpha}}|\chi_1\rangle - \sqrt{\frac{\alpha-1}{2\alpha}}|\chi_2\rangle$$
$$\Rightarrow \sqrt{\frac{2\alpha}{\alpha+1}}|\psi_1\rangle = |\chi_1\rangle - \sqrt{\frac{\alpha-1}{\alpha+1}}|\chi_2\rangle$$
$$= |\chi_1\rangle - \frac{\sqrt{\alpha^2-1}}{\alpha+1}|\chi_2\rangle = |\chi_1\rangle - \frac{|\gamma|}{\Delta}\frac{(\alpha-1)}{(\alpha^2-1)}|\chi_2\rangle$$

$$= |\chi_1\rangle + \frac{\Delta}{|\gamma|}(1-\alpha)|\chi_2\rangle \ ,$$

$$|\psi_2\rangle = \sqrt{\frac{\alpha-1}{2\alpha}}|\chi_1\rangle + \sqrt{\frac{\alpha+1}{2\alpha}}|\chi_2\rangle$$
$$\Rightarrow \sqrt{\frac{2\alpha}{\alpha+1}}|\psi_2\rangle = \sqrt{\frac{\alpha-1}{\alpha+1}}|\chi_1\rangle + |\chi_2\rangle$$
$$= \frac{\alpha-1}{\sqrt{\alpha^2-1}}|\chi_1\rangle + |\chi_2\rangle = \frac{\alpha-1}{\sqrt{\alpha^2-1}}|\chi_1\rangle + |\chi_2\rangle$$

$$= \frac{\Delta}{|\gamma|}(\alpha-1)|\chi_1\rangle + |\chi_2\rangle \ .$$

Replacing γ *by* $\lambda\gamma$ *(* $\lambda \in R$ *), we obtain Eq. (12.2.17),*

$$|\psi_1\rangle \propto \left[|\chi_1\rangle + \frac{\Delta}{\lambda|\gamma|}(1-\sqrt{1+\frac{\lambda^2|\gamma|^2}{\Delta^2}})|\chi_2\rangle \right]$$

$$|\psi_2\rangle \propto \left[|\chi_2\rangle + \frac{\Delta}{\lambda|\gamma|}(\sqrt{1+\frac{\lambda^2|\gamma|^2}{\Delta^2}}-1)|\chi_1\rangle \right].$$

(b)

Approximating the square root by its first-order Taylor expansion, $\sqrt{1+\frac{\lambda^2|\gamma|^2}{\Delta^2}} \approx 1+\frac{\lambda^2|\gamma|^2}{2\Delta^2}$ *, we obtain*

$$|\psi_1\rangle \approx |\chi_1\rangle + \frac{\Delta}{\lambda|\gamma|}(-\frac{\lambda^2|\gamma|^2}{2\Delta^2})|\chi_2\rangle = |\chi_1\rangle - \lambda\frac{|\gamma|}{2\Delta}|\chi_2\rangle$$

$$|\psi_2\rangle \approx |\chi_2\rangle + \frac{\Delta}{\lambda|\gamma|}(\frac{\lambda^2|\gamma|^2}{2\Delta^2})|\chi_1\rangle = |\chi_2\rangle + \lambda\frac{|\gamma|}{2\Delta}|\chi_1\rangle \ ,$$

which coincides with the result of first-order perturbation theory (Eq. (12.2.16)).

Exercise 12.2.5 *Implement perturbation theory (Eqs. (12.1.16, 12.1.17)) for the Hamiltonian defined in Eqs. (12.2.18-12.2.20). (a) Show that the first-order corrections to the energy vanish. (b) Calculate the second-order corrections to obtain Eq. (12.2.21).*

Solution 12.2.5

Using Eq. (12.2.19) for the zero-order eigenstates, $|\psi_1^{(0)}\rangle = \sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\frac{1}{2}}|\chi_2\rangle$ *and* $|\psi_2^{(0)}\rangle = \sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\frac{1}{2}}|\chi_2\rangle$, *and the perturbation operator (Eq. (12.2.20)),* $\hat{H}_1 = \Delta|\chi_1\rangle\langle\chi_1| - \Delta|\chi_2\rangle\langle\chi_2|$, *we obtain*

(a)

The first-order corrections to the two energy levels (Eq. (12.1.16)) read

$$E_1^{(1)} = \langle\psi_1^{(0)}|\hat{H}_1|\psi_1^{(0)}\rangle$$

$$=\left(\sqrt{\frac{1}{2}}\langle\chi_1|-\sqrt{\frac{1}{2}}\langle\chi_2|\right)\left[\Delta|\chi_1\rangle\langle\chi_1|-\Delta|\chi_2\rangle\langle\chi_2|\right]\left(\sqrt{\frac{1}{2}}|\chi_1\rangle-\sqrt{\frac{1}{2}}|\chi_2\rangle\right)=0 \ .$$

$$E_2^{(1)}=\left\langle\psi_2^{(0)}\middle|\hat{H}_1\middle|\psi_2^{(0)}\right\rangle$$

$$=\left(\sqrt{\frac{1}{2}}\langle\chi_1|+\sqrt{\frac{1}{2}}\langle\chi_2|\right)\left[\Delta|\chi_1\rangle\langle\chi_1|-\Delta|\chi_2\rangle\langle\chi_2|\right]\left(\sqrt{\frac{1}{2}}|\chi_1\rangle+\sqrt{\frac{1}{2}}|\chi_2\rangle\right)=0 \ .$$

(b)

The second-order corrections to the two energy levels (Eq. (12.1.17)) read

$$E_1^{(2)}=\sum_{n'\neq 1}\frac{|\left\langle\psi_{n'}^{(0)}\middle|\hat{H}_1\middle|\psi_1^{(0)}\right\rangle|^2}{E_1^{(0)}-E_{n'}^{(0)}}=\frac{|\left\langle\psi_2^{(0)}\middle|\hat{H}_1\middle|\psi_1^{(0)}\right\rangle|^2}{E_1^{(0)}-E_2^{(0)}}=\frac{\Delta^2}{2|\gamma|}$$

$$E_2^{(2)}=\sum_{n'\neq 2}\frac{|\left\langle\psi_{n'}^{(0)}\middle|\hat{H}_1\middle|\psi_2^{(0)}\right\rangle|^2}{E_2^{(0)}-E_{n'}^{(0)}}=\frac{|\left\langle\psi_1^{(0)}\middle|\hat{H}_1\middle|\psi_2^{(0)}\right\rangle|^2}{E_2^{(0)}-E_1^{(0)}}=\frac{\Delta^2}{-2|\gamma|} \ ,$$

where we used: $E_1^{(0)}=\bar{\varepsilon}+|\gamma|$, $E_2^{(0)}=\bar{\varepsilon}-|\gamma|$, *and*

$$\left\langle\psi_2^{(0)}\middle|\hat{H}_1\middle|\psi_1^{(0)}\right\rangle$$

$$=\left(\sqrt{\frac{1}{2}}\langle\chi_1|-\sqrt{\frac{1}{2}}\langle\chi_2|\right)\left[\Delta|\chi_1\rangle\langle\chi_1|-\Delta|\chi_2\rangle\langle\chi_2|\right]\left(\sqrt{\frac{1}{2}}|\chi_1\rangle+\sqrt{\frac{1}{2}}|\chi_2\rangle\right)=\Delta \ .$$

Hence, using the results of (a) and (b) we obtain Eq. (12.2.21),

$$E_1 \cong E_1^{(0)}+\lambda E_1^{(1)}+\lambda^2 E_1^{(2)}=\bar{\varepsilon}+|\gamma|+\lambda^2\frac{\Delta^2}{2|\gamma|}$$

$$E_2 \cong E_2^{(0)}+\lambda E_2^{(1)}+\lambda^2 E_2^{(2)}=\bar{\varepsilon}-|\gamma|-\lambda^2\frac{\Delta^2}{2|\gamma|} \quad .$$

Exercise 12.2.6 *Implement perturbation theory (Eq. (12.1.14)) for the Hamiltonian defined in Eqs. (12.2.18-12.2.20) to obtain the first-order corrections to the eigenstates, as given in Eq. (12.2.24).*

Solution 12.2.6

Using Eq. (12.1.14), $\left|\psi_n^{(1)}\right\rangle = \sum_{n'\neq n} \frac{\left\langle\psi_{n'}^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{E_n^{(0)}-E_{n'}^{(0)}}\left|\psi_{n'}^{(0)}\right\rangle$*, implemented for the TLS model, where,* $\left|\psi_1^{(0)}\right\rangle = \sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\frac{1}{2}}|\chi_2\rangle$, $\left|\psi_2^{(0)}\right\rangle = \sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\frac{1}{2}}|\chi_2\rangle$, $E_1^{(0)} = \bar{\varepsilon}+|\gamma|$, $E_2^{(0)} = \bar{\varepsilon}-|\gamma|$, *and* $\hat{H}_1 = \Delta|\chi_1\rangle\langle\chi_1| - \Delta|\chi_2\rangle\langle\chi_2|$, *we obtain the first-order corrections (Eq. (12.2.24)),*

$$\left|\psi_1^{(1)}\right\rangle = \sum_{n'\neq 1} \frac{\left\langle\psi_{n'}^{(0)}\right|\hat{H}_1\left|\psi_1^{(0)}\right\rangle}{E_1^{(0)}-E_{n'}^{(0)}}\left|\psi_{n'}^{(0)}\right\rangle = \frac{\left\langle\psi_2^{(0)}\right|\hat{H}_1\left|\psi_1^{(0)}\right\rangle}{E_1^{(0)}-E_2^{(0)}}\left|\psi_2^{(0)}\right\rangle = \frac{\Delta}{2|\gamma|}\left|\psi_2^{(0)}\right\rangle .$$

$$\left|\psi_2^{(1)}\right\rangle = \sum_{n'\neq 2} \frac{\left\langle\psi_{n'}^{(0)}\right|\hat{H}_1\left|\psi_2^{(0)}\right\rangle}{E_2^{(0)}-E_{n'}^{(0)}}\left|\psi_{n'}^{(0)}\right\rangle = \frac{\left\langle\psi_1^{(0)}\right|\hat{H}_1\left|\psi_2^{(0)}\right\rangle}{E_2^{(0)}-E_1^{(0)}}\left|\psi_1^{(0)}\right\rangle = \frac{\Delta}{-2|\gamma|}\left|\psi_1^{(0)}\right\rangle .$$

Hence, the corrected eigenstates up to first order read

$$\left|\psi_1\right\rangle \cong \left|\psi_1^{(0)}\right\rangle + \lambda\left|\psi_1^{(1)}\right\rangle = \sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\frac{1}{2}}|\chi_2\rangle + \frac{\lambda\Delta}{2|\gamma|}(\sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\frac{1}{2}}|\chi_2\rangle)$$

$$= (1+\frac{\lambda\Delta}{2|\gamma|})\sqrt{\frac{1}{2}}|\chi_1\rangle - (1-\frac{\lambda\Delta}{2|\gamma|})\sqrt{\frac{1}{2}}|\chi_2\rangle .$$

$$\left|\psi_2\right\rangle \cong \left|\psi_2^{(0)}\right\rangle + \lambda\left|\psi_2^{(1)}\right\rangle = \sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\frac{1}{2}}|\chi_2\rangle - \frac{\lambda\Delta}{2|\gamma|}(\sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\frac{1}{2}}|\chi_2\rangle)$$

$$= (1-\frac{\lambda\Delta}{2|\gamma|})\sqrt{\frac{1}{2}}|\chi_1\rangle + (1+\frac{\lambda\Delta}{2|\gamma|})\sqrt{\frac{1}{2}}|\chi_2\rangle .$$

Exercise 12.2.7 *(a) Derive the expressions in Eq. (12.2.25) for the exact TLS eigenstates. (b) Show that the result obtained by first-order perturbation theory (Eq. (12.2.24)) is obtained by expanding the square root function in a first-order Taylor expansion.*

Solution 12.2.7

a)

Setting $\gamma = -|\gamma|$*, the general expressions for the TLS Hamiltonian eigenvector coefficients (obtained in Ex. 12.2.1) read (* $\alpha \equiv \sqrt{1+|\gamma|^2/\Delta^2}$ *):*

$$E_1 = \bar{\varepsilon} + \Delta\alpha \quad \leftrightarrow \quad \begin{bmatrix} a_1^{(+)} \\ a_2^{(+)} \end{bmatrix} = \begin{bmatrix} \sqrt{\dfrac{\alpha+1}{2\alpha}} \\ -\sqrt{\dfrac{\alpha-1}{2\alpha}} \end{bmatrix} \quad ; \quad E_2 = \bar{\varepsilon} - \Delta\alpha \quad \leftrightarrow \quad \begin{bmatrix} a_1^{(-)} \\ a_2^{(-)} \end{bmatrix} = \begin{bmatrix} \sqrt{\dfrac{\alpha-1}{2\alpha}} \\ \sqrt{\dfrac{\alpha+1}{2\alpha}} \end{bmatrix}.$$

Hence,

$$|\psi_1\rangle = \sqrt{\frac{\alpha+1}{2\alpha}}|\chi_1\rangle - \sqrt{\frac{\alpha-1}{2\alpha}}|\chi_2\rangle$$

$$\Rightarrow \sqrt{\alpha}|\psi_1\rangle = \sqrt{\alpha+1}\sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\alpha-1}\sqrt{\frac{1}{2}}|\chi_2\rangle$$

$$= \sqrt{\sqrt{1+\frac{|\gamma|^2}{\Delta^2}}+1}\sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\sqrt{1+\frac{|\gamma|^2}{\Delta^2}}-1}\sqrt{\frac{1}{2}}|\chi_2\rangle$$

$$= \sqrt{\frac{|\gamma|}{\Delta}\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}+1}\sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\frac{|\gamma|}{\Delta}\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}-1}\sqrt{\frac{1}{2}}|\chi_2\rangle$$

$$\propto \left(\sqrt{\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}+\frac{\Delta}{|\gamma|}}\sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}-\frac{\Delta}{|\gamma|}}\sqrt{\frac{1}{2}}|\chi_2\rangle \right) \quad ,$$

$$|\psi_2\rangle = \sqrt{\frac{\alpha-1}{2\alpha}}|\chi_1\rangle + \sqrt{\frac{\alpha+1}{2\alpha}}|\chi_2\rangle$$

$$\Rightarrow \sqrt{\alpha}|\psi_2\rangle = \sqrt{\alpha-1}\sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\alpha+1}\sqrt{\frac{1}{2}}|\chi_2\rangle$$

$$= \sqrt{\sqrt{1+\frac{|\gamma|^2}{\Delta^2}}-1}\sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\sqrt{1+\frac{|\gamma|^2}{\Delta^2}}+1}\sqrt{\frac{1}{2}}|\chi_2\rangle$$

$$= \sqrt{\frac{|\gamma|}{\Delta}\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}-1}\sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\frac{|\gamma|}{\Delta}\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}+1}\sqrt{\frac{1}{2}}|\chi_2\rangle$$

$$\propto \left(\sqrt{\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}-\frac{\Delta}{|\gamma|}}\sqrt{\frac{1}{2}}|\chi_1\rangle + \sqrt{\sqrt{1+\frac{\Delta^2}{|\gamma|^2}}+\frac{\Delta}{|\gamma|}}\sqrt{\frac{1}{2}}|\chi_2\rangle \right) \quad .$$

Replacing Δ *by* $\lambda\Delta$ *(* $\lambda \in R$ *), we obtain Eq. (12.2.25),*

$$|\psi_1\rangle \propto \left(\sqrt{\sqrt{1+\lambda^2\frac{\Delta^2}{|\gamma|^2}}+\lambda\frac{\Delta}{|\gamma|}}\sqrt{\frac{1}{2}}|\chi_1\rangle - \sqrt{\sqrt{1+\lambda^2\frac{\Delta^2}{|\gamma|^2}}-\lambda\frac{\Delta}{|\gamma|}}\sqrt{\frac{1}{2}}|\chi_2\rangle \right)$$

$$|\psi_2\rangle \propto \left(\sqrt{\sqrt{1+\lambda^2 \frac{\Delta^2}{|\gamma|^2}} - \lambda \frac{\Delta}{|\gamma|}} \sqrt{\frac{1}{2}} |\chi_1\rangle + \sqrt{\sqrt{1+\lambda^2 \frac{\Delta^2}{|\gamma|^2}} + \lambda \frac{\Delta}{|\gamma|}} \sqrt{\frac{1}{2}} |\chi_2\rangle \right) .$$

(b)

Approximating the square root functions by their first-order Taylor expansion, $\sqrt{1+x} \approx 1+\frac{x}{2}$*, we obtain*

$$|\psi_1\rangle \approx \left(\sqrt{1+\frac{\lambda^2\Delta^2}{2|\gamma|^2}+\frac{\lambda\Delta}{|\gamma|}} \sqrt{\frac{1}{2}} |\chi_1\rangle - \sqrt{1+\frac{\lambda^2\Delta^2}{2|\gamma|^2}-\frac{\lambda\Delta}{|\gamma|}} \sqrt{\frac{1}{2}} |\chi_2\rangle \right)$$

$$\approx \left(\left(1+\frac{\lambda^2\Delta^2}{4|\gamma|^2}+\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_1\rangle - \left(1+\frac{\lambda^2\Delta^2}{4|\gamma|^2}-\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_2\rangle \right)$$

$$|\psi_2\rangle \approx \left(\sqrt{1+\frac{\lambda^2\Delta^2}{2|\gamma|^2}-\frac{\lambda\Delta}{|\gamma|}} \sqrt{\frac{1}{2}} |\chi_1\rangle + \sqrt{1+\frac{\lambda^2\Delta^2}{2|\gamma|^2}+\frac{\lambda\Delta}{|\gamma|}} \sqrt{\frac{1}{2}} |\chi_2\rangle \right)$$

$$\approx \left(\left(1+\frac{\lambda^2\Delta^2}{4|\gamma|^2}-\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_1\rangle + \left(1+\frac{\lambda^2\Delta^2}{4|\gamma|^2}+\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_2\rangle \right) .$$

Keeping only the terms which are up to first order in λ*, we obtain the approximations*

$$|\psi_1\rangle \approx \left(\left(1+\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_1\rangle - \left(1-\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_2\rangle \right) = \sqrt{\frac{1}{2}} \left(|\chi_1\rangle - |\chi_2\rangle\right) + \frac{\lambda\Delta}{2|\gamma|} \sqrt{\frac{1}{2}} \left(|\chi_1\rangle + |\chi_2\rangle\right)$$

$$|\psi_2\rangle \approx \left(\left(1-\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_1\rangle + \left(1+\frac{\lambda\Delta}{2|\gamma|}\right) \sqrt{\frac{1}{2}} |\chi_2\rangle \right) = \sqrt{\frac{1}{2}} \left(|\chi_1\rangle + |\chi_2\rangle\right) - \frac{\lambda\Delta}{2|\gamma|} \sqrt{\frac{1}{2}} \left(|\chi_1\rangle - |\chi_2\rangle\right),$$

which coincide with the result of first-order perturbation theory (Eq. (12.2.24)).

Exercise 12.2.8 *To calculate the integral* $-Ke^2 q \int d\mathbf{r} \frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}_q|}$*, it is convenient to change variables to the elliptical coordinates,* (λ, μ, φ)*, defined as,*

$$\lambda \equiv \frac{r+r_q}{R_q} \quad ; \quad 1<\lambda<\infty$$

$$\mu \equiv \frac{r_q-r}{R_q} \quad ; \quad -1<\mu<1 \qquad ,$$

where $r_q \equiv |\mathbf{r}-\mathbf{R}_q|$, $R_q \equiv |\mathbf{R}_q|$, $r \equiv |\mathbf{r}|$, *and* $\mathbf{R}_q \equiv (0,0,R_q)$.

(a) Show that these definitions yield the following results:

$$x = r\sin(\theta)\cos(\varphi) = \frac{R_q}{2}\sqrt{\lambda^2+\mu^2-1-\mu^2\lambda^2}\cos(\varphi),$$

$$y = r\sin(\theta)\sin(\varphi) = \frac{R_q}{2}\sqrt{\lambda^2+\mu^2-1-\mu^2\lambda^2}\sin(\varphi)$$

and $z = r\cos(\theta) = \frac{R_q}{2}(1-\mu\lambda)$.

(b) Let $g(\lambda,\mu,\varphi) = f(x,y,z)$. *Calculate the corresponding Jacobian,* $\begin{vmatrix} \frac{\partial x}{\partial \lambda} & \frac{\partial x}{\partial \mu} & \frac{\partial x}{\partial \varphi} \\ \frac{\partial y}{\partial \lambda} & \frac{\partial y}{\partial \mu} & \frac{\partial y}{\partial \varphi} \\ \frac{\partial z}{\partial \lambda} & \frac{\partial z}{\partial \mu} & \frac{\partial z}{\partial \varphi} \end{vmatrix}$, *and show that* $\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, f(x,y,z) = \int_{0}^{2\pi} d\varphi \int_{1}^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8}(\lambda^2-\mu^2) g(\lambda,\mu,\varphi)$.

(c) Let $f(x,y,z) = -Ke^2 q \frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}_q|}$, *with* $\psi_{1s}(\mathbf{r})$ *as defined in Eq. (12.2.31) and* $\mathbf{R}_q \equiv (0,0,R_q)$. *Derive the result for* $E_1^{(1)}$ *in Eq. (12.2.32).*

(d) Show that as the distance to the point charge goes to infinity, the first-order correction to the energy approaches the Coulomb interaction energy between the remote charge and an effective point charge, in which the electron charge is subtracted from the nucleus charge, namely $E_1^{(1)} \xrightarrow[R_q\to\infty]{} \frac{Ke^2 q}{R_q}(Z-1)$.

Solution 12.2.8

(a)

Using the definitions, $r_q \equiv |\mathbf{r}-\mathbf{R}_q|$, $R_q \equiv |\mathbf{R}_q|$, $r \equiv |\mathbf{r}|$, *and*

$$\lambda \equiv \frac{r+r_q}{R_q} \quad ; \quad 1<\lambda<\infty \quad ; \quad \mu \equiv \frac{r_q-r}{R_q} \quad ; \quad -1<\mu<1,$$

we obtain $r_q = \frac{R_q}{2}(\lambda + \mu)$ *and* $r = \frac{R_q}{2}(\lambda - \mu)$. *Using the relation (the law of cosines),* $r_q^2 = r^2 + R_q^2 - 2\mathbf{R}_q\mathbf{r}$ *, we obtain*

$$\mathbf{R}_q\mathbf{r} = \frac{r^2 + R_q^2 - r_q^2}{2} = \frac{R_q^2 - (r_q - r)(r + r_q)}{2} = \frac{R_q^2 - R_q^2\mu\lambda}{2} = \frac{R_q^2}{2}(1 - \mu\lambda).$$

Setting $\mathbf{R}_q$ *along the z direction in a three-dimensional cartesian coordinate system,* $\mathbf{R}_q \equiv (0,0,R_q) \equiv 0\mathbf{i} + 0\mathbf{j} + R_q\mathbf{k}$, *and transforming to spherical coordinates, we obtain* $\mathbf{R}_q\mathbf{r} = (0,0,R_q)\cdot(x,y,z) = R_q z = R_q r\cos(\theta)$. *Consequently,*

$$r\cos(\theta) = \frac{R_q}{2}(1 - \mu\lambda)$$

$$r\sin(\theta) = \sqrt{r^2 - r^2\cos^2(\theta)} = \frac{R_q}{2}\sqrt{(\lambda - \mu)^2 - (1 - \mu\lambda)^2} = \frac{R_q}{2}\sqrt{\lambda^2 + \mu^2 - 1 - \mu^2\lambda^2}\ ,$$

and therefore,

$$z = r\cos(\theta) = \frac{R_q}{2}(1 - \mu\lambda)$$

$$x = r\sin(\theta)\cos(\varphi) = \frac{R_q}{2}\sqrt{\lambda^2 + \mu^2 - 1 - \mu^2\lambda^2}\cos(\varphi)$$

$$y = r\sin(\theta)\sin(\varphi) = \frac{R_q}{2}\sqrt{\lambda^2 + \mu^2 - 1 - \mu^2\lambda^2}\sin(\varphi)\ .$$

(b)

Using (a), the Jacobian reads

$$\begin{vmatrix} \frac{\partial x}{\partial \lambda} & \frac{\partial x}{\partial \mu} & \frac{\partial x}{\partial \varphi} \\ \frac{\partial y}{\partial \lambda} & \frac{\partial y}{\partial \mu} & \frac{\partial y}{\partial \varphi} \\ \frac{\partial z}{\partial \lambda} & \frac{\partial z}{\partial \mu} & \frac{\partial z}{\partial \varphi} \end{vmatrix} = \begin{vmatrix} \frac{R_q^2}{4}\frac{\left(\lambda-\mu^2\lambda\right)}{x}\cos^2(\varphi) & \frac{R_q^2}{4}\frac{\left(\mu-\lambda^2\mu\right)}{x}\cos^2(\varphi) & -x\tan(\varphi) \\ \frac{R_q^2}{4}\frac{\left(\lambda-\mu^2\lambda\right)}{y}\sin^2(\varphi) & \frac{R_q^2}{4}\frac{\left(\mu-\lambda^2\mu\right)}{y}\sin^2(\varphi) & y\cot(\varphi) \\ -\frac{R_q}{2}\mu & -\frac{R_q}{2}\lambda & 0 \end{vmatrix}$$

$$= \frac{R_q}{2}\lambda\left(\frac{R_q^2}{4}\frac{\left(\lambda-\mu^2\lambda\right)}{x}\cos^2(\varphi)y\cot(\varphi) + \frac{R_q^2}{4}\frac{\left(\lambda-\mu^2\lambda\right)}{y}\sin^2(\varphi)x\tan(\varphi)\right)$$

$$-\frac{R_q}{2}\mu\left(\frac{R_q^2}{4}\frac{\left(\mu-\lambda^2\mu\right)}{x}\cos^2(\varphi)y\cot(\varphi) + \frac{R_q^2}{4}\frac{\left(\mu-\lambda^2\mu\right)}{y}\sin^2(\varphi)x\tan(\varphi)\right)$$

$$= \frac{R_q^3}{8}\left(\left(\lambda^2-\mu^2\right)\cos^2(\varphi) + \left(\lambda^2-\mu^2\right)\sin^2(\varphi)\right)$$

$$= \frac{R_q^3}{8}\left(\lambda^2-\mu^2\right) .$$

Therefore, $\int\limits_{-\infty}^{\infty} dx \int\limits_{-\infty}^{\infty} dy \int\limits_{-\infty}^{\infty} dz\, f(x,y,z) = \int\limits_0^{2\pi} d\varphi \int\limits_1^{\infty} d\lambda \int\limits_{-1}^{1} d\mu \frac{R_q^3}{8}(\lambda^2-\mu^2) g(\lambda,\mu,\varphi)$.

(c)

We are interested in calculating the integral, $Ke^2 q\int d\mathbf{r}\frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}_q|}$, *for* $\psi_{1s}(x,y,z) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Z\sqrt{x^2+y^2+z^2}/a_0}$ *. Changing variables to elliptical coordinates,* (λ,μ,φ), *and recalling that,* $|\mathbf{r}-\mathbf{R}_q| = r_q = \frac{R_q}{2}(\lambda+\mu)$, *we obtain*

$$Ke^2 q\int d\mathbf{r}\frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}_q|} = \frac{Z^3 Ke^2 q}{\pi a_0^3}\int d\vec{r}\frac{1}{|\mathbf{r}-\mathbf{R}_q|} e^{-2Zr/a_0}$$

$$= \frac{Z^3 Ke^2 q}{\pi a_0^3}\frac{R_q^2}{4}\int\limits_0^{2\pi} d\varphi \int\limits_1^{\infty} d\lambda \int\limits_{-1}^{1} d\mu (\lambda^2-\mu^2)\frac{1}{(\lambda+\mu)} e^{-ZR_q(\lambda-\mu)/a_0}$$

$$= \frac{Z^3 Ke^2 q}{\pi a_0^3}\frac{R_q^2}{4}\int\limits_0^{2\pi} d\varphi \int\limits_1^{\infty} d\lambda \int\limits_{-1}^{1} d\mu (\lambda-\mu) e^{-ZR_q(\lambda-\mu)/a_0} .$$

Defining, $\frac{ZR_q / a_0}{a_0} = \beta$ *, we obtain*

$$Ke^2 q \int d\mathbf{r} \frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}_q|} = \frac{-Ke^2 q \beta^3}{R_q 2} \frac{d}{d\beta} \int_1^\infty d\lambda \int_{-1}^{1} d\mu e^{-\beta(\lambda-\mu)}$$

$$= \frac{-Ke^2 q \beta^3}{R_q 2} 2 \frac{(\beta+1)e^{-2\beta}-1}{\beta^3} = \frac{-Ke^2 q}{R_q}[(\beta+1)e^{-2\beta}-1] \ ,$$

and finally, we obtain the first-order correction to the energy (Eq. (12.2.32)),

$$E_1^{(1)} = \frac{KZqe^2}{R_q} - Ke^2 q \int d\mathbf{r} \frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}_q|} = \frac{KZqe^2}{R_q} + \frac{Ke^2 q}{R_q}[(\beta+1)e^{-2\beta}-1]$$

$$= \frac{Kqe^2}{R_q}\left[Z - 1 + (\frac{ZR_q}{a_0}+1)e^{\frac{-2ZR_q}{a_0}} \right].$$

(d)

Using the expression in (c) we can see that $E_1^{(1)} \xrightarrow[R_q \to \infty]{} \frac{Ke^2 q}{R_q}(Z-1)$.

Exercise 12.2.9 *Calculate the first-order correction to the ground state energy (Eq. (12.1.16)), owing to a remote point charge, using the approximation for the perturbation, Eq. (12.2.34). Compare the result to the exact calculation, Eq. (12.2.32), in the limit,* $R_q >> \frac{a_0}{Z}$.

Solution 12.2.9

We are interested in calculating $\left\langle \psi_{1s}^{(0)} \middle| \hat{H}_1 \middle| \psi_{1s}^{(0)} \right\rangle$ *with* $\psi_{1s}(x,y,z) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Z\sqrt{x^2+y^2+z^2}/a_0}$ *, for the approximated perturbation operator,* $\hat{H}_1 = \frac{Ke^2 Zq}{R_q} + \frac{-Ke^2 q}{R_q}(1 + \frac{x_q x}{R_q^2} + \frac{y_q y}{R_q^2} + \frac{z_q z}{R_q^2})$ *, namely*

$$\left\langle \psi_{1s}^{(0)} \middle| \hat{H}_1 \middle| \psi_{1s}^{(0)} \right\rangle = \frac{Ke^2Zq}{R_q} + \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-2Z\sqrt{x^2+y^2+z^2}/a_0} \frac{(-Ke^2q)}{R_q}\left(1+\frac{x_q x}{R_q^2}+\frac{y_q y}{R_q^2}+\frac{z_q z}{R_q^2}\right).$$

Since integrals of the type $\int_{-\infty}^{\infty} xe^{-\alpha x^2}dx$ *vanish, and since* $\psi_{1s}(x,y,z)$ *is normalized, we readily obtain* $\left\langle \psi_{1s}^{(0)} \middle| \hat{H}_1 \middle| \psi_{1s}^{(0)} \right\rangle = \frac{Ke^2Zq}{R_q} - \frac{Ke^2q}{R_q}$. *This result is indeed consistent with the calculation of the matrix element for the perturbation,* $\hat{H}_1 = \frac{Ke^2Zq}{|\mathbf{R}_q|} + \frac{-Ke^2q}{|\mathbf{r}-\mathbf{R}_q|}$, *(Eq. (12.2.32)) in the limit* $R_q >> \frac{a_0}{Z}$, *namely*

$$\frac{Kqe^2}{R_q}\left[Z-1+\left(\frac{ZR_q}{a_0}+1\right)e^{\frac{-2ZR_q}{a_0}}\right] \xrightarrow[\frac{ZR_q}{a_0}\to\infty]{} \frac{Ke^2Zq}{R_q} - \frac{-Ke^2q}{R_q}.$$

Exercise 12.2.10 *Using the explicit set of degenerate wave functions (Eq. (12.2.35)), calculate the matrix elements of the operator* $\frac{-Ke^2q}{|\mathbf{r}-\mathbf{R}_q|}$, *for* $\mathbf{R}_q \equiv (0,0,R_q)$, *and verify the results given in Eqs. (12.2.36, 12.2.37) (including the vanishing entries). For this purpose, it is recommended to change variables to the elliptical coordinates,* (λ,μ,φ), *following the practice of Ex. 12.2.8.*

Solution 12.2.10

It is helpful to calculate some relevant integrals first:

$$\int_1^{\infty} d\lambda e^{-\beta\lambda} = \frac{e^{-\beta}}{\beta}$$

$$\int_1^{\infty} \lambda d\lambda e^{-\beta\lambda} = \frac{e^{-\beta}(\beta+1)}{\beta^2}$$

$$\int_1^{\infty} \lambda^2 d\lambda e^{-\beta\lambda} = \frac{\beta^2 e^{-\beta}+2e^{-\beta}(\beta+1)}{\beta^3}$$

$$I_1 = \int_1^\infty d\lambda \int_{-1}^1 d\mu e^{-\beta(\lambda-\mu)} = \frac{1-e^{-2\beta}}{\beta^2}$$

$$\frac{d}{d\beta} I_1 = 2\frac{(\beta+1)e^{-2\beta}-1}{\beta^3}$$

$$\frac{d^2}{d\beta^2} I_1 = 2\frac{3-(2\beta^2+4\beta+3)e^{-2\beta}}{\beta^4}$$

$$\frac{d^3}{d\beta^3} I_1 = 2\frac{(4\beta^3+12\beta^2+18\beta+12)e^{-2\beta}-12}{\beta^5}$$

$$I_2 = \int_1^\infty d\lambda \lambda e^{-\beta\lambda} \int_{-1}^1 d\mu \mu e^{\beta\mu} = \frac{\beta^2-1+[\beta^2+2\beta+1]e^{-2\beta}}{\beta^4}$$

$$\frac{d}{d\beta} I_2 = \frac{-2\beta^2-2e^{-2\beta}\beta^3+4-6\beta^2 e^{-2\beta}-8\beta e^{-2\beta}-4e^{-2\beta}}{\beta^5}$$

$$\frac{d^2}{d\beta^2} I_2 = \frac{6\beta^2-20+[4\beta^4+16\beta^3+34\beta^2+40\beta+20]e^{-2\beta}}{\beta^6}$$

$$I_3 = \int_1^\infty d\lambda \int_{-1}^1 d\mu (\lambda^2-1)(1-\mu^2) e^{-\beta(\lambda-\mu)} = \frac{4}{\beta^6}\left((\beta^2+2\beta+1)e^{-2\beta}+\beta^2-1\right)$$

$$\frac{d}{d\beta} I_3 = \frac{4}{\beta^7}\left((-2\beta^3-8\beta^2-12\beta-6)e^{-2\beta}-4\beta^2+6\right).$$

We now turn to the calculation of matrix elements of the perturbation operator, $\frac{-Ke^2 q}{|\mathbf{r}-\mathbf{R}_q|}$, *between the selected basis functions for the degenerate subspace:*

$$\left\langle \mathbf{r} \middle| \psi_{2s}^{(0)} \right\rangle = \psi_{2s}(x,y,z) = \frac{1}{8}\sqrt{\frac{2Z^3}{\pi a_0^3}}\left(2-\frac{Z}{a_0}\sqrt{x^2+y^2+z^2}\right) e^{-\sqrt{x^2+y^2+z^2}Z/2a_0}$$

$$\left\langle \mathbf{r} \middle| \psi_{2p_z}^{(0)} \right\rangle = \psi_{2p_z}(x,y,z) = \frac{1}{8}\sqrt{\frac{2Z^5}{\pi a_0^5}} z e^{-\sqrt{x^2+y^2+z^2}Z/2a_0}$$

$$\left\langle \mathbf{r} \middle| \psi_{2p_y}^{(0)} \right\rangle = \psi_{2p_y}(x,y,z) = \frac{1}{8}\sqrt{\frac{2Z^5}{\pi a_0^5}} y e^{-\sqrt{x^2+y^2+z^2}Z/2a_0}$$

$$\left\langle \mathbf{r} \middle| \psi_{2p_x}^{(0)} \right\rangle = \psi_{2p_x}(x,y,z) = \frac{1}{8}\sqrt{\frac{2Z^5}{\pi a_0^5}} x e^{-\sqrt{x^2+y^2+z^2}Z/2a_0} \quad .$$

Denoting, $r=\sqrt{x^2+y^2+z^2}$ *, and using,* $|\mathbf{r}-\mathbf{R}_q|=r_q$ *, the relevant integrals read*

$$\left\langle \psi_{2s}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2s}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^3}{\pi a_0^3} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr/a_0)^2}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2p_z}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{z^2}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2p_x}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_x}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{x^2}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2p_y}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_y}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{y^2}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2s}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr/a_0)z}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2s}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_x}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr/a_0)x}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2s}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_y}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr/a_0)y}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2p_x}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{xz}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2p_y}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{yz}{r_q} e^{-rZ/a_0}$$

$$\left\langle \psi_{2p_y}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_x}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{yx}{r_q} e^{-rZ/a_0} \quad .$$

Transforming to elliptical coordinates, $\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \to \int_{0}^{2\pi} d\varphi \int_{1}^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2)$ *, with*

$$z = r\cos(\theta) = \frac{R_q}{2}(1 - \mu\lambda)$$

$$x = r\sin(\theta)\cos(\varphi) = \frac{R_q}{2}\sqrt{\lambda^2 + \mu^2 - 1 - \mu^2\lambda^2}\cos(\varphi)$$

$$y = r\sin(\theta)\sin(\varphi) = \frac{R_q}{2}\sqrt{\lambda^2 + \mu^2 - 1 - \mu^2\lambda^2}\sin(\varphi) \ ,$$

$R_q = |\mathbf{R}_q|$, $r_q = \frac{R_q}{2}(\lambda + \mu)$, $r = \frac{R_q}{2}(\lambda - \mu)$, *and defining,* $\frac{R_q Z}{2a_0} \equiv \beta$ *, we obtain*

$$\left\langle \psi_{2s}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}}-\mathbf{R}_q|} \left| \psi_{2s}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^3}{\pi a_0^3} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr/a_0)^2}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^3}{\pi a_0^3} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) \frac{(2 - \frac{Z}{a_0}\frac{R_q}{2}(\lambda-\mu))^2}{\frac{R_q}{2}(\lambda+\mu)} e^{-\frac{R_q}{2}(\lambda-\mu)Z/a_0}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^2 \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda-\mu)(2-\beta(\lambda-\mu))^2 e^{-\beta(\lambda-\mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^2 \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu [4(\lambda-\mu) - 4\beta(\lambda-\mu)^2 + \beta^2(\lambda-\mu)^3] e^{-\beta(\lambda-\mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^2 [-4\frac{d}{d\beta} - 4\beta \frac{d^2}{d\beta^2} - \beta^2 \frac{d^3}{d\beta^3}] \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu e^{-\beta(\lambda-\mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^2 [-4\frac{d}{d\beta} I_1 - 4\beta \frac{d^2}{d\beta^2} I_1 - \beta^2 \frac{d^3}{d\beta^3} I_1]$$

$$= \frac{-Ke^2 q}{4} \frac{Z}{a_0 \beta^3} [2\beta^2 + e^{-2\beta}[-2\beta^2 - 3\beta^3 - 2\beta^5 - 2\beta^4]]$$

$$\left\langle \psi_{2p_z}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}}-\mathbf{R}_q|} \left| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{z^2}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2)(r^2 - (x^2+y^2)) \frac{1}{\frac{R_q}{2}(\lambda+\mu)} e^{-\frac{R_q}{2}(\lambda-\mu)Z/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^2}{4} (\lambda-\mu)[\frac{R_q^2}{4}(\lambda-\mu)^2 - \frac{R_q^2}{4}(\lambda^2-1)(1-\mu^2)] e^{-\frac{R_q}{2}(\lambda-\mu)Z/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \frac{R_q^4}{16} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda-\mu)[(\lambda-\mu)^2 - (\lambda^2-1)(1-\mu^2)] e^{-\frac{R_q Z}{2a_0}(\lambda-\mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^4 \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu [(\lambda-\mu)^3 - (\lambda-\mu)(\lambda^2-1)(1-\mu^2)] e^{-\beta(\lambda-\mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^4 [-\frac{d^3}{d\beta^3} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu e^{-\beta(\lambda-\mu)} + \frac{d}{d\beta} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2-1)(1-\mu^2) e^{-\beta(\lambda-\mu)}]$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^4 [-\frac{d^3}{d\beta^3} I_1 + \frac{d}{d\beta} I_3]$$

$$= \frac{-Ke^2 q}{4} \frac{Z}{a_0 \beta^3} [(-2\beta^5 - 6\beta^4 - 11\beta^3 - 14\beta^2 - 12\beta - 6) e^{-2\beta} + 2\beta^2 + 6]$$

$$\left\langle \psi^{(0)}_{2p_x} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi^{(0)}_{2p_x} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{x^2}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) \frac{1}{\frac{R_q}{2}(\lambda + \mu)} \frac{R_q^2}{4} (\lambda^2 - 1)(1 - \mu^2) e^{-\frac{R_q Z}{2a_0}(\lambda - \mu)} \cos^2(\varphi)$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{a_0^5} \frac{R_q^4}{16} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) \frac{1}{(\lambda + \mu)} (\lambda^2 - 1)(1 - \mu^2) e^{-\frac{R_q Z}{2a_0}(\lambda - \mu)}$$

$$= \frac{-Ke^2 q}{32} \frac{Z}{a_0} \beta^4 \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda - \mu)(\lambda^2 - 1)(1 - \mu^2) e^{-\beta(\lambda - \mu)}$$

$$= \frac{-Ke^2 q}{32} \frac{Z}{a_0} \beta^4 \frac{-d}{d\beta} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2 - 1)(1 - \mu^2) e^{-\beta(\lambda - \mu)}$$

$$= \frac{-Ke^2 q}{32} \frac{Z}{a_0} \beta^4 \frac{-d}{d\beta} I_3$$

$$= \frac{-Ke^2 q}{4} \frac{Z}{a_0 \beta^3} \left((\beta^3 + 4\beta^2 + 6\beta + 3) e^{-2\beta} + 2\beta^2 - 3 \right)$$

$$\left\langle \psi^{(0)}_{2p_y} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi^{(0)}_{2p_y} \right\rangle$$

$$= \frac{-Ke^2 q}{4} \frac{Z}{a_0 \beta^3} \left((\beta^3 + 4\beta^2 + 6\beta + 3) e^{-2\beta} + 2\beta^2 - 3 \right)$$

$$\left\langle \psi_{2s}^{(0)} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr / a_0) z}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) \frac{1}{\frac{R_q}{2}(\lambda + \mu)} e^{-\frac{R_q}{2}(\lambda - \mu) Z/a_0} \frac{R_q}{2} (1 - \mu\lambda)(2 - \frac{Z}{a_0} \frac{R_q}{2} (\lambda - \mu))$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^3 \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda - \mu)(1 - \mu\lambda)(2 - \frac{Z}{a_0} \frac{R_q}{2} (\lambda - \mu)) e^{-\beta(\lambda - \mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^3 \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu [(\lambda - \mu)(1 - \mu\lambda) 2 e^{-\beta(\lambda - \mu)} - \beta (1 - \mu\lambda)(\lambda - \mu)^2 e^{-\beta(\lambda - \mu)}]$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^3 [-2 \frac{d}{d\beta} - \beta \frac{d^2}{d\beta^2}] \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (1 - \mu\lambda) e^{-\beta(\lambda - \mu)}$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^3 ([-2 \frac{d}{d\beta} - \beta \frac{d^2}{d\beta^2}] \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu e^{-\beta(\lambda - \mu)} + [2 \frac{d}{d\beta} + \beta \frac{d^2}{d\beta^2}] \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \mu\lambda e^{-\beta(\lambda - \mu)})$$

$$= \frac{-Ke^2 q}{16} \frac{Z}{a_0} \beta^3 (-2 \frac{d}{d\beta} I_1 - \beta \frac{d^2}{d\beta^2} I_1 + 2 \frac{d}{d\beta} I_2 + \beta \frac{d^2}{d\beta^2} I_2)$$

$$= \frac{-Ke^2 q}{4} \frac{Z}{a_0 \beta^3} (-3\beta + [2\beta^5 + 4\beta^4 + 6\beta^3 + 6\beta^2 + 3\beta] e^{-2\beta})$$

$$\left\langle \psi_{2s}^{(0)} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi_{2p_x}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr / a_0) x}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) f(\lambda, \mu) \cos(\varphi) = 0$$

$$\left\langle \psi_{2s}^{(0)} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi_{2p_y}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{(2 - Zr / a_0) y}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^4}{\pi a_0^4} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) f(\lambda, \mu) \sin(\varphi) = 0$$

$$\left\langle \psi_{2p_x}^{(0)} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{xz}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) g(\lambda, \mu) \cos(\varphi) = 0$$

$$\left\langle \psi_{2p_y}^{(0)} \left| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \right| \psi_{2p_z}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{yz}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) g(\lambda, \mu) \sin(\varphi) = 0$$

$$\left\langle \psi_{2p_y}^{(0)} \right| \frac{-Ke^2 q}{|\hat{\mathbf{r}} - \mathbf{R}_q|} \left| \psi_{2p_x}^{(0)} \right\rangle = \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{xy}{r_q} e^{-rZ/a_0}$$

$$= \frac{-Ke^2 q}{32} \frac{Z^5}{\pi a_0^5} \int_0^{2\pi} d\varphi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R_q^3}{8} (\lambda^2 - \mu^2) h(\lambda, \mu) \sin(2\varphi) = 0 \ .$$

Exercise 12.2.11 *Use the explicit form of* $\left|\psi_{2s}^{(0)}\right\rangle$ *and* $\left|\psi_{2p_z}^{(0)}\right\rangle$ *in Eq. (12.2.35), and show that far from the nucleus (* $r > 2a_0 / Z$ *) the probability density associated with* $\left|\psi_{2s}^{(0)}\right\rangle - \left|\psi_{2p_z}^{(0)}\right\rangle$ *is larger above the* (x, y) *plane, namely* $\rho(x, y, |z|) \geq \rho(x, y, -|z|)$*, and the result is reversed for* $\left|\psi_{2s}^{(0)}\right\rangle + \left|\psi_{2p_z}^{(0)}\right\rangle$*.*

Solution 12.2.11

Using Eq. (12.2.35) we obtain $\rho_{\pm} = \left| \left\langle \mathbf{r} \middle| \psi_{2s}^{(0)} \right\rangle \pm \left\langle \mathbf{r} \middle| \psi_{2p_z}^{(0)} \right\rangle \right|^2 \propto \left| 2 - \frac{Z}{a_0} r \pm \frac{Z}{a_0} z \right|^2$.

For, $Zr / a_0 > 2$*, we have* $a \equiv 2 - \frac{Z}{a_0} r < 0$*, hence,* $\rho_{\pm} \propto \left| -|a| \pm \frac{Z}{a_0} z \right|^2$.

Consequently,

$$\rho_+(|z|) \propto \left| -|a| + \frac{Z}{a_0} |z| \right|^2 < \left| -|a| - \frac{Z}{a_0} |z| \right|^2 = \rho_+(-|z|)$$

$$\rho_-(|z|) \propto \left| -|a| - \frac{Z}{a_0} |z| \right|^2 > \left| -|a| + \frac{Z}{a_0} |z| \right|^2 = \rho_-(-|z|) \ .$$

Exercise 12.2.12 *(a) Use the explicit form of the hydrogen-like orbitals (Eq. (12.2.35)) to show that* $\left\langle \psi_{2s}^{(0)} \middle| \hat{z} \middle| \psi_{2p_z}^{(0)} \right\rangle = \left\langle \psi_{2s}^{(0)} \middle| \hat{x} \middle| \psi_{2p_x}^{(0)} \right\rangle = \left\langle \psi_{2s}^{(0)} \middle| \hat{y} \middle| \psi_{2p_y}^{(0)} \right\rangle = -3a_0 / Z$*. (b) Diagonalize the matrix* $\mathbf{H}_1$ *for* $\alpha = 1/3^{1/4}$ *to show that the eigenvalues are* $C(\mathbf{R}_1, \mathbf{R}_2) + \frac{-Ke^2 q}{R_q}(1 + 3^{1/4})$*;* $C(\mathbf{R}_1, \mathbf{R}_2) + \frac{-Ke^2 q}{R_q}(1 + 3^{1/4} \pm \frac{6a_0}{ZR_q})$*. (c) Obtain the corresponding first-order corrected atomic orbitals.*

Solution 12.2.12

(a)

$$\left\langle \psi_{2s}^{(0)} \middle| \hat{z} \middle| \psi_{2p_z}^{(0)} \right\rangle = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \int_0^{\infty} dr \, \frac{1}{64} \frac{2Z^4}{\pi a_0^4} (2 - \frac{rZ}{a_0}) e^{-Zr/a_0} r^4 \cos^2(\theta) \sin(\theta)$$

$$= \frac{1}{64} \frac{2Z^4}{\pi a_0^4} \left(\int_0^{2\pi} d\varphi \right) \left(\int_0^{\pi} d\theta \cos^2(\theta) \sin(\theta) \right) \int_0^{\infty} dr (2 - \frac{rZ}{a_0}) e^{-Zr/a_0} r^4$$

$$= \frac{1}{64} \frac{2Z^4}{\pi a_0^4} (2\pi) \left(\frac{2}{3} \right) \int_0^{\infty} dr (2 - \frac{rZ}{a_0}) e^{-Zr/a_0} r^4$$

Using, $\int_0^{\infty} dr r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$ *, we obtain*

$$\left\langle \psi_{2s}^{(0)} \middle| \hat{z} \middle| \psi_{2p_z}^{(0)} \right\rangle = \frac{1}{64} \frac{2Z^4}{\pi a_0^4} (2\pi) \left(\frac{2}{3} \right) \left(2 \cdot 24 (\frac{a_0}{Z})^5 - 120 (\frac{a_0}{Z})^5 \right) = -3 \frac{a_0}{Z} \, .$$

(b)

Denoting: $1 + \frac{1}{\alpha} = a$ *,* $-\frac{3a_0}{ZR_q} = b$ *and* $-\frac{3a_0}{\alpha^2 ZR_q} = c$ *, the matrix reads*

$$\mathbf{H}_1 = C(\mathbf{R}_1, \mathbf{R}_2) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ c & 0 & 0 & 1 \end{bmatrix} + \frac{-Ke^2 q}{R_q} \begin{bmatrix} 1 + \frac{1}{\alpha} & -\frac{3a_0}{ZR_q} & 0 & -\frac{3a_0}{\alpha^2 ZR_q} \\ -\frac{3a_0}{ZR_q} & 1 + \frac{1}{\alpha} & 0 & 0 \\ 0 & 0 & 1 + \frac{1}{\alpha} & 0 \\ -\frac{3a_0}{\alpha^2 ZR_q} & 0 & 0 & 1 + \frac{1}{\alpha} \end{bmatrix}$$

$$= \left(C(\mathbf{R}_1, \mathbf{R}_2) - a \frac{Ke^2 q}{R_q} \right) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} - b \frac{Ke^2 q}{R_q} \begin{bmatrix} 0 & 1 & 0 & c/b \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ c/b & 0 & 0 & 0 \end{bmatrix} \, .$$

The first term is diagonal. To obtain the eigenvalues of the second term we solve,

$$\begin{vmatrix} 0 & 1 & 0 & c/b \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ c/b & 0 & 0 & 0 \end{vmatrix} = 0 \Rightarrow \lambda = 0, 0, +\sqrt{1 + c^2 / b^2}, -\sqrt{1 + c^2 / b^2} \, .$$

Using $\alpha = 1/3^{1/4}$, *we obtain* $c/b = \sqrt{3}$, *hence the eigenvalues are* $\lambda = 0, 0, 2, -2$. *Adding the diagonal of the first term, we obtain the first-order corrections to the energy:*

$$\left(E_2^{(1)}\right)_1 = \left(E_2^{(1)}\right)_2 = C(\mathbf{R}_1, \mathbf{R}_2) + \frac{-Ke^2 q}{R_q}(1 + 3^{1/4})$$

$$\left(E_2^{(1)}\right)_3 = C(\mathbf{R}_1, \mathbf{R}_2) + \frac{-Ke^2 q}{R_q}(1 + 3^{1/4} - \frac{6a_0}{ZR_q})$$

$$\left(E_2^{(1)}\right)_4 = C(\mathbf{R}_1, \mathbf{R}_2) + \frac{-Ke^2 q}{R_q}(1 + 3^{1/4} + \frac{6a_0}{ZR_q}) \ .$$

(c) Solving the secular equation for the atomic orbital coefficients,

$$\begin{bmatrix} -\lambda & 1 & 0 & c/b \\ 1 & -\lambda & 0 & 0 \\ 0 & 0 & -\lambda & 0 \\ c/b & 0 & 0 & -\lambda \end{bmatrix} \begin{bmatrix} a_s \\ a_{p_z} \\ a_{p_y} \\ a_{p_x} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad ,$$

we obtain for $\lambda = 0$: $\sqrt{\frac{3}{4}}\left|\psi_{2p_z}^{(0)}\right\rangle - \frac{1}{2}\left|\psi_{2p_x}^{(0)}\right\rangle$, *or* $\left|\psi_{2p_y}^{(0)}\right\rangle$,

for $\lambda = 2$: $\frac{1}{\sqrt{2}}\left|\psi_{2s}^{(0)}\right\rangle + \frac{1}{\sqrt{8}}\left|\psi_{2p_z}^{(0)}\right\rangle + \sqrt{\frac{3}{8}}\left|\psi_{2p_x}^{(0)}\right\rangle$,

and for $\lambda = -2$: $\frac{1}{\sqrt{2}}\left|\psi_{2s}^{(0)}\right\rangle - \frac{1}{\sqrt{8}}\left|\psi_{2p_z}^{(0)}\right\rangle - \sqrt{\frac{3}{8}}\left|\psi_{2p_x}^{(0)}\right\rangle$.

Exercise 12.2.13 *Use the explicit form of the particle-in-a-box eigenstates (Eq. (12.2.48)) and the perturbation operator, Eq. (12.2.49), to show the following: (a) For any* $n, n' > 0$, $\left\langle \psi_{n'} \middle| \hat{H}_1 \middle| \psi_n \right\rangle = \frac{\alpha}{2}\begin{cases} \delta_{n',n+2k} - \delta_{n',2k-n} & ; \quad 2k > n \\ \delta_{n',n+2k} + \delta_{n',n-2k} & ; \quad 2k \le n \end{cases}$. *(b) The first-order corrections to the energy vanish, unless* $n = k$ *(Eq. (12.2.50)). (c) The second-order correction to the energy is given in terms of Eq. (12.2.51). (d) The first-order correction to the function is given in terms of Eq. (12.2.52).*

Solution 12.2.13

(a)

For any $0 < n, n'$,

$$\frac{2}{L}\int_0^L dx \sin(\frac{n'\pi x}{L})\cos(\frac{2k\pi x}{L})\sin(\frac{n\pi x}{L})$$
$$= \frac{1}{L}\int_0^L dx \sin(\frac{n'\pi x}{L})\{\sin[\frac{(n+2k)\pi x}{L}] + \sin[\frac{(n-2k)\pi x}{L}]\}$$

$$= \begin{cases} 2k > n \quad ; \quad (\delta_{n',n+2k} - \delta_{n',2k-n})/2 \\ 2k \le n \quad ; \quad (\delta_{n',n+2k} + \delta_{n',n-2k})/2 \end{cases} ,$$

where in the last step we used the orthonormality of the particle-in-a-box eigenstates.

(b)

From the result (a) it follows that for $n = n'$ *the integral must vanish, unless* $k = n = n'$, *where it obtains a finite value,* $\frac{2}{L}\int_0^L dx \sin(\frac{n\pi x}{L})\cos(\frac{2k\pi x}{L})\sin(\frac{n\pi x}{L}) = -\frac{1}{2}$.

(c)

Using Eq. (12.2.48) for the zero-order energy levels, and the result (a) for the perturbation matrix elements, we obtain

$$E_n^{(2)} = \sum_{n' \ne n = 1}^{\infty} \frac{|\langle \psi_{n'}^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}}$$
$$= \frac{\alpha^2}{4}\frac{2mL^2}{\hbar^2\pi^2}\begin{cases} n \ne (k, 2k) \quad ; \quad \dfrac{1}{n^2 - (2k+n)^2} + \dfrac{1}{n^2 - (2k-n)^2} \\ \qquad n = (k, 2k) \quad ; \quad \dfrac{1}{n^2 - (2k+n)^2} \end{cases}$$

$$= \frac{-\alpha^2}{16k}\frac{2mL^2}{\hbar^2\pi^2}\begin{cases} \dfrac{1}{k+n} + \dfrac{1}{k-n} \quad ; \quad n \ne (k, 2k) \\ \qquad \dfrac{1}{k+n} \quad ; \quad n = (k, 2k) \end{cases} .$$

(d)

Using Eq. (12.2.48) for the zero-order functions, and the result (a) for the perturbation matrix elements, we obtain

$$\left\langle x \middle| \psi^{(1)}_{n=k,2k} \right\rangle = \sum_{n'\neq n=1}^{\infty} \frac{\left\langle \psi^{(0)}_{n'} \middle| \hat{H}_1 \middle| \psi^{(0)}_{n} \right\rangle}{E^{(0)}_{n} - E^{(0)}_{n'}} \left\langle x \middle| \psi^{(0)}_{n'} \right\rangle$$
$$= \frac{\alpha}{2}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{1}{n^2-(n+2k)^2}\sin\left(\frac{(n+2k)\pi x}{L}\right)]$$
$$= \frac{\alpha}{2}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{1}{-4nk-4k^2}\sin\left(\frac{(n+2k)\pi x}{L}\right)]$$
$$= \frac{\alpha}{2}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{1}{-4nk-4k^2}\sin\left(\frac{(n+2k)\pi x}{L}\right)]$$

$$= \frac{\alpha}{8k}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{-1}{n+k}\sin\left(\frac{(n+2k)\pi x}{L}\right)] \ ,$$

$$\left\langle x \middle| \psi^{(1)}_{n\neq k,2k} \right\rangle = \sum_{n'\neq n=1}^{\infty} \frac{\left\langle \psi^{(0)}_{n'} \middle| \hat{H}_1 \middle| \psi^{(0)}_{n} \right\rangle}{E^{(0)}_{n} - E^{(0)}_{n'}} \left\langle x \middle| \psi^{(0)}_{n'} \right\rangle$$
$$= \frac{\alpha}{2}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{1}{n^2-(n+2k)^2}\sin\left(\frac{(n+2k)\pi x}{L}\right)+\frac{1}{n^2-(n-2k)^2}\sin\left(\frac{(n-2k)\pi x}{L}\right)]$$
$$= \frac{\alpha}{2}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{1}{-4nk-4k^2}\sin\left(\frac{(n+2k)\pi x}{L}\right)+\frac{1}{4nk-4k^2}\sin\left(\frac{(n-2k)\pi x}{L}\right)]$$
$$= \frac{\alpha}{2}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{1}{-4nk-4k^2}\sin\left(\frac{(n+2k)\pi x}{L}\right)+\frac{1}{4nk-4k^2}\sin\left(\frac{(n-2k)\pi x}{L}\right)]$$

$$= \frac{\alpha}{8k}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{-1}{n+k}\sin\left(\frac{(n+2k)\pi x}{L}\right)+\frac{1}{n-k}\sin\left(\frac{(n-2k)\pi x}{L}\right)] \ .$$

Exercise 12.2.14 *Derive Eq. (12.2.53) from Eq. (12.2.52) in the limit* $n << k$.

Solution 12.2.14

For $n << k$ *we start from the general case,* $n \neq k, 2k$,

$$\langle x|\psi_n^{(1)}\rangle = \frac{\alpha}{8k}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)[\frac{-1}{n+k}\sin\left(\frac{(n+2k)\pi x}{L}\right)+\frac{1}{n-k}\sin\left(\frac{(n-2k)\pi x}{L}\right)]$$

$$=\frac{\alpha}{8k}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)\{\frac{-1}{n+k}[\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{2k\pi x}{L}\right)+\cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{2k\pi x}{L}\right)]$$

$$+\frac{1}{n-k}[\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{2k\pi x}{L}\right)-\cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{2k\pi x}{L}\right)]\}$$

$$=\frac{\alpha}{8k}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)\frac{1}{n^2-k^2}\{\frac{k-n}{1}[\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{2k\pi x}{L}\right)+\cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{2k\pi x}{L}\right)]$$

$$+\frac{k+n}{1}[\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{2k\pi x}{L}\right)-\cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{2k\pi x}{L}\right)]\}$$

$$=\frac{\alpha}{8k}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)\frac{1}{n^2-k^2}\{2k\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{2k\pi x}{L}\right)-2n\cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{2k\pi x}{L}\right)\} \ .$$

Taking the limit, $n << k$ *, we obtain*

$$\langle x|\psi_n^{(1)}\rangle \xrightarrow[n<<k]{} \frac{-\alpha}{4}\sqrt{\frac{2}{L}}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)\frac{1}{k^2}\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{2k\pi x}{L}\right).$$

Adding the correction to the zero-order wave function, we obtain the corrected function to first-order in the perturbation in this limit,

$$\langle x|\psi_n^{(0)}\rangle+\langle x|\psi_n^{(1)}\rangle=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)[1-\frac{\alpha}{4k^2}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)\cos\left(\frac{2k\pi x}{L}\right)]$$

$$=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)[1-\frac{\alpha}{E_{2k}^{(0)}}\cos(\frac{2k\pi x}{L})] \ .$$

Exercise 12.2.15 *Use the explicit form of the zero-order solutions (Eq. (12.2.54)) and the perturbation matrix elements, Eq. (12.2.56), to derive the results of Eqs. (12.2.59, 12.2.61).*

Solution 12.2.15

Using the fact that the matrix elements of the perturbation are products of one-dimensional integrals (Eq. (12.2.56)), we can use the result of Ex. 12.2.13 (a). For the energy corrections this yields

$$E^{(2)}_{n_x,n_y} = \sum_{\substack{n'_x=1\\ n'_x\neq n_x}}^{\infty} \sum_{\substack{n'_y=1\\ n'_y\neq n_y}}^{\infty} \frac{\alpha^2}{4}\frac{2m}{\hbar^2\pi^2} \frac{|(\delta_{n'_x,n_x+2k}-\delta_{n'_x,2k_x-n_x})(\delta_{n'_y,n_y+2k_y}-\delta_{n'_y,2k_y-n_y})|^2}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n,_x,n'_y})}$$

$$= \sum_{\substack{n'_x=1\\ n'_x\neq n_x}}^{\infty} \sum_{\substack{n'_y=1\\ n'_y\neq n_y}}^{\infty} \frac{\alpha^2}{4}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{\delta_{n'_x,n_x+2k_x}\delta_{n'_y,n_y+2k_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n,_x,n'_y})}+\frac{\delta_{n'_x,2k_x-n_x}\delta_{n'_y,n_y+2k_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n,_x,n'_y})}$$

$$+\frac{\delta_{n'_x,n_x+2k_x}\delta_{n'_y,2k_y-n_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n,_x,n'_y})}+\frac{\delta_{n'_x,2k_x-n_x}\delta_{n'_y,2k_y-n_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n,_x,n'_y})}\Bigg)$$

$$=\frac{\alpha^2}{4}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x+2k_x)^2}{L_x^2}-\frac{(n_y+2k_y)^2}{L_y^2}}+\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x-2k_x)^2}{L_x^2}-\frac{(n_y+2k_y)^2}{L_y^2}}$$

$$+\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x+2k_x)^2}{L_x^2}-\frac{(n_y-2k_y)^2}{L_y^2}}+\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x-2k_x)^2}{L_x^2}-\frac{(n_y-2k_y)^2}{L_y^2}}\Bigg)$$

$$=\frac{\alpha^2}{4}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{1}{-\frac{4n_xk_x+4k_x{}^2}{L_x^2}-\frac{4n_yk_y+4k_y{}^2}{L_y^2}}+\frac{1}{-\frac{-4n_xk_x+4k_x{}^2}{L_x^2}-\frac{4n_yk_y+4k_y{}^2}{L_y^2}}$$

$$+\frac{1}{-\frac{4n_xk_x+4k_x{}^2}{L_x^2}-\frac{-4n_yk_y+4k_y{}^2}{L_y^2}}+\frac{1}{-\frac{-4n_xk_x+4k_x{}^2}{L_x^2}-\frac{-4n_yk_y+4k_y{}^2}{L_y^2}}\Bigg)$$

$$=-\frac{\alpha^2}{16}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{1}{\frac{n_xk_x+k_x{}^2}{L_x^2}+\frac{n_yk_y+k_y{}^2}{L_y^2}}+\frac{1}{\frac{-n_xk_x+k_x{}^2}{L_x^2}+\frac{n_yk_y+k_y{}^2}{L_y^2}}$$

$$+\frac{1}{\frac{n_xk_x+k_x{}^2}{L_x^2}+\frac{-n_yk_y+k_y{}^2}{L_y^2}}+\frac{1}{\frac{-n_xk_x+k_x{}^2}{L_x^2}+\frac{-n_yk_y+k_y{}^2}{L_y^2}}\Bigg)$$

$$\xrightarrow[n_x,n_y\ll k_x,k_y]{}-\frac{\alpha^2}{16}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{1}{\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}}+\frac{1}{\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}}+\frac{1}{\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}}+\frac{1}{\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}}\Bigg)$$

$$=-\frac{\alpha^2}{4}\frac{2m}{\hbar^2\pi^2}\frac{1}{\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}}.$$

For the first-order corrections to the wave functions we similarly obtain,

$$\left|\psi^{(1)}_{n_x,n_y}\right\rangle = \sum_{\substack{n'_x=1\\ n'_x\neq n_x}}^{\infty}\sum_{\substack{n'_y=1\\ n'_y\neq n_y}}^{\infty}\frac{\alpha}{2}\frac{2m}{\hbar^2\pi^2}\frac{(\delta_{n'_x,n_x+2k_x}-\delta_{n'_x,2k_x-n_x})(\delta_{n'_y,n_y+2k_y}-\delta_{n'_y,2k_y-n_y})}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n'_x,n'_y})}\left|\psi^{(0)}_{n'_x,n'_y}\right\rangle$$

$$=\sum_{\substack{n'_x=1\\ n'_x\neq n_x}}^{\infty}\sum_{\substack{n'_y=1\\ n'_y\neq n_y}}^{\infty}\frac{\alpha}{2}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{\delta_{n'_x,n_x+2k_x}\delta_{n'_y,n_y+2k_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n'_x,n'_y})}\left|\psi^{(0)}_{n'_x,n'_y}\right\rangle-\frac{\delta_{n'_x,2k_x-n_x}\delta_{n'_y,n_y+2k_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n'_x,n'_y})}\left|\psi^{(0)}_{n'_x,n'_y}\right\rangle$$

$$-\frac{\delta_{n'_x,n_x+2k_x}\delta_{n'_y,2k_y-n_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n'_x,n'_y})}\left|\psi^{(0)}_{n'_x,n'_y}\right\rangle+\frac{\delta_{n'_x,2k_x-n_x}\delta_{n'_y,2k_y-n_y}}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-(E^{(0)}_{n'_x,n'_y})}\left|\psi^{(0)}_{n'_x,n'_y}\right\rangle$$

$$=\frac{\alpha}{2}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x+2k_x)^2}{L_x^2}-\frac{(n_y+2k_y)^2}{L_y^2}}\left|\psi^{(0)}_{n_x+2k_x,n_y+2k_y}\right\rangle$$

$$-\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x-2k_x)^2}{L_x^2}-\frac{(n_y+2k_y)^2}{L_y^2}}\left|\psi^{(0)}_{2k_x-n_x,n_y+2k_y}\right\rangle$$

$$-\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x+2k_x)^2}{L_x^2}-\frac{(n_y-2k_y)^2}{L_y^2}}\left|\psi^{(0)}_{n_x+2k_x,2k_y-n_y}\right\rangle+\frac{1}{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}-\frac{(n_x-2k_x)^2}{L_x^2}-\frac{(n_y-2k_y)^2}{L_y^2}}\left|\psi^{(0)}_{2k_x-n_x,2k_y-n_y}\right\rangle\Bigg)$$

$$=-\frac{\alpha}{8}\frac{2m}{\hbar^2\pi^2}\Bigg(\frac{1}{\frac{n_xk_x+k_x{}^2}{L_x^2}+\frac{n_yk_y+k_y{}^2}{L_y^2}}\left|\psi^{(0)}_{n_x+2k_x,n_y+2k_y}\right\rangle-\frac{1}{\frac{-n_xk_x+k_x{}^2}{L_x^2}+\frac{n_yk_y+k_y{}^2}{L_y^2}}\left|\psi^{(0)}_{2k_x-n_x,n_y+2k_y}\right\rangle$$

$$-\frac{1}{\frac{n_xk_x+k_x{}^2}{L_x^2}+\frac{-n_yk_y+k_y{}^2}{L_y^2}}\left|\psi^{(0)}_{n_x+2k_x,2k_y-n_y}\right\rangle+\frac{1}{\frac{-n_xk_x+k_x{}^2}{L_x^2}+\frac{-n_yk_y+k_y{}^2}{L_y^2}}\left|\psi^{(0)}_{2k_x-n_x,2k_y-n_y}\right\rangle\Bigg)$$

$$\xrightarrow[n_x,n_y<<k_x,k_y]{}-\frac{\alpha}{8}\frac{2m}{\hbar^2\pi^2}\left(\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}\right)^{-1}\left(\left|\psi^{(0)}_{n_x+2k_x,n_y+2k_y}\right\rangle-\left|\psi^{(0)}_{2k_x-n_x,n_y+2k_y}\right\rangle-\left|\psi^{(0)}_{n_x+2k_x,2k_y-n_y}\right\rangle+\left|\psi^{(0)}_{2k_x-n_x,2k_y-n_y}\right\rangle\right)$$

, and in the position representation,

$$\psi^{(1)}_{n_x,n_y}(x,y)=-\frac{\alpha}{8}\frac{2m}{\hbar^2\pi^2}\left(\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}\right)^{-1}\cdot$$

$$\sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\left[\sin\left(\frac{(n_x+2k_x)\pi x}{L_x}\right)-\sin\left(\frac{(2k_x-n_x)\pi x}{L_x}\right)\right]\cdot\left[\sin\left(\frac{(n_y+2k_y)\pi y}{L_y}\right)-\sin\left(\frac{(2k_y-n_y)\pi y}{L_y}\right)\right]$$

$$=-\frac{\alpha}{2}\frac{2m}{\hbar^2\pi^2}\left(\frac{k_x{}^2}{L_x^2}+\frac{k_y{}^2}{L_y^2}\right)^{-1}\sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)\cos\left(\frac{2k_x\pi x}{L_x}\right)\cos\left(\frac{2k_y\pi y}{L_y}\right)$$

$$= -\frac{2\alpha}{E^{(0)}_{2k_x,2k_y}}\sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)\cos\left(\frac{2k_x\pi x}{L_x}\right)\cos\left(\frac{2k_y\pi y}{L_y}\right).$$

Finally,

$$\psi^{(0)}_{n_x,n_y}(x,y)+\psi^{(1)}_{n_x,n_y}(x,y)$$

$$\approx \sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)[1-\frac{2\alpha}{E^{(0)}_{2k_x,2k_y}}\cos\left(\frac{2k_x\pi x}{L_x}\right)\cos\left(\frac{2k_y\pi y}{L_y}\right)] .$$

Exercise 12.3.1 *(a) Show that for* $\left|\delta\tilde{\psi}\right\rangle \equiv \left|\frac{\partial}{\partial\sigma}\tilde{\psi}\right\rangle d\sigma$*, the general condition for the optimal trial function (Eq. (12.3.4)) obtains the form* $\left\langle \frac{\partial}{\partial\sigma}\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\tilde{\psi}\right\rangle = 0$*. (b) Use the Hermiticity of* $\hat{H}$ *to show that this condition leads to* $\frac{\partial}{\partial\sigma}\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle = \tilde{\varepsilon}\frac{\partial}{\partial\sigma}\langle\tilde{\psi}|\tilde{\psi}\rangle$*. (c) Use the result of (b) and the definition of the variational energy (Eq. (12.3.1)) to obtain Eq. (12.3.6).*

Solution 12.3.1

(a)

Using $\left|\delta\tilde{\psi}\right\rangle \equiv \left|\frac{d}{d\sigma}\tilde{\psi}\right\rangle d\sigma$*, the respective bra state reads* $\left\langle\delta\tilde{\psi}\right| \equiv \left\langle\frac{d}{d\sigma}\tilde{\psi}\right| d\sigma^*$*. Hence, the general condition for the optimal solution reads* $\left\langle \frac{d}{d\sigma}\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\tilde{\psi}\right\rangle d\sigma^* = 0$ *for any* $d\sigma$*, namely* $\left\langle \frac{d}{d\sigma}\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\tilde{\psi}\right\rangle 0.$

(b)

The Hermiticity of the Hamiltonian means that $\left\langle \frac{d}{d\sigma}\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\tilde{\psi}\right\rangle = \left\langle\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\frac{d}{d\sigma}\tilde{\psi}\right\rangle^*$*. Given the result (a), we have for the optimal solution,* $\left\langle\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\frac{d}{d\sigma}\tilde{\psi}\right\rangle^* = 0 \Rightarrow \left\langle\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}\left|\frac{d}{d\sigma}\tilde{\psi}\right\rangle = 0$*.*

Therefore,

$$\left\langle \frac{d}{d\sigma}\tilde{\psi}\right|\hat{H}-\tilde{\varepsilon}|\tilde{\psi}\rangle+\langle\tilde{\psi}|\hat{H}-\tilde{\varepsilon}\left|\frac{d}{d\sigma}\tilde{\psi}\right\rangle=0\Rightarrow\frac{d}{d\sigma}\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle-\tilde{\varepsilon}\frac{d}{d\sigma}\langle\tilde{\psi}|\tilde{\psi}\rangle=0.$$

(c)

Using the definition of the variational energy (Eq. (12.3.1)), $\tilde{\varepsilon}\equiv\frac{\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle}$, *the result of (b) can be written as*

$$\frac{d}{d\sigma}\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle-\frac{\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle}\frac{d}{d\sigma}\langle\tilde{\psi}|\tilde{\psi}\rangle=0$$

$$\Rightarrow\frac{\langle\tilde{\psi}|\tilde{\psi}\rangle\frac{d}{d\sigma}\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle-\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle\frac{d}{d\sigma}\langle\tilde{\psi}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle}=0$$

$$\Rightarrow\frac{\langle\tilde{\psi}|\tilde{\psi}\rangle\frac{d}{d\sigma}\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle-\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle\frac{d}{d\sigma}\langle\tilde{\psi}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle^2}=0$$

$$\Rightarrow\frac{d}{d\sigma}\frac{\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle}=0$$

$$\Rightarrow\frac{d}{d\sigma}\tilde{\varepsilon}=0\ .$$

Exercise 12.3.2 *A trial function is defined as* $|\tilde{\psi}\rangle=|\tilde{\varphi}\rangle-\sum_{n=0}^{N}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle$, *where* $|\psi_n\rangle$ *are all the orthonormal eigenstates of the corresponding system Hamiltonian,* $\hat{H}|\psi_n\rangle=E_n|\psi_n\rangle$, *with energy smaller than* E_{N+1} *. (a) Show that* $|\tilde{\psi}\rangle$ *is orthogonal to {*$|\psi_n\rangle$*}, for* $n=0,1,..,N$ *. (b) Use the definition of the variational energy (Eq. (12.3.1)) and follow Eq. (12.3.8) to show that* $\tilde{\varepsilon}\geq E_{N+1}$ *.*

Solution 12.3.2

(a)

Let, $|\psi_{n'}\rangle\in\{|\psi_n\rangle\}$, *then*

$$\langle\psi_{n'}|\tilde{\psi}\rangle = \langle\psi_{n'}|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\psi_{n'}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle$$

$$= \langle\psi_{n'}|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \delta_{n,n'}\langle\psi_n|\tilde{\varphi}\rangle$$

$$= \langle\psi_{n'}|\tilde{\varphi}\rangle - \langle\psi_{n'}|\tilde{\varphi}\rangle = 0 \ .$$

(b)

Given, $|\tilde{\psi}\rangle = |\tilde{\varphi}\rangle - \sum_{n=0}^{N} |\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle$*, we obtain*

$$\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle = \langle\tilde{\varphi}|\hat{H}|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\tilde{\varphi}|\hat{H}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\tilde{\varphi}|\psi_n\rangle\langle\psi_n|\hat{H}|\tilde{\varphi}\rangle$$

$$+ \sum_{n,n'=0}^{N} \langle\tilde{\varphi}|\psi_{n'}\rangle\langle\psi_{n'}|\hat{H}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle$$

$$= \sum_{n=0}^{\infty} |\langle\psi_n|\tilde{\varphi}\rangle|^2 E_n - \sum_{n=0}^{N} E_n |\langle\psi_n|\tilde{\varphi}\rangle|^2 - \sum_{n=0}^{N} E_n |\langle\psi_n|\tilde{\varphi}\rangle|^2 + \sum_{n=0}^{N} E_n |\langle\psi_n|\tilde{\varphi}\rangle|^2$$

$$= \sum_{n=0}^{\infty} |\langle\psi_n|\tilde{\varphi}\rangle|^2 E_n - \sum_{n=0}^{N} E_n |\langle\psi_n|\tilde{\varphi}\rangle|^2$$

$$= \sum_{n\geq N+1}^{\infty} |\langle\psi_n|\tilde{\varphi}\rangle|^2 E_n \ ,$$

and,

$$\langle\tilde{\psi}|\tilde{\psi}\rangle = \langle\tilde{\varphi}|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\tilde{\varphi}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\tilde{\varphi}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle + \sum_{n,n'=0}^{N} \langle\tilde{\varphi}|\psi_{n'}\rangle\langle\psi_{n'}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle$$

$$= \langle\tilde{\varphi}|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\tilde{\varphi}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle - \sum_{n=0}^{N} \langle\tilde{\varphi}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle + \sum_{n=0}^{N} \langle\tilde{\varphi}|\psi_n\rangle\langle\psi_n|\tilde{\varphi}\rangle]$$

$$= \langle\tilde{\varphi}|\tilde{\varphi}\rangle - \sum_{n=0}^{N} |\langle\tilde{\varphi}|\psi_n\rangle|^2$$

$$= \sum_{n=N+1}^{\infty} |\langle\tilde{\varphi}|\psi_n\rangle|^2 \ .$$

According to the definition of the variation energy (Eq. (12.3.1)), we obtain in this case

$$\tilde{\varepsilon} = \frac{\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\sum_{n=N+1}^{\infty} E_n |\langle\tilde{\varphi}|\psi_n\rangle|^2}{\sum_{n=N+1}^{\infty} |\langle\tilde{\varphi}|\psi_n\rangle|^2} \geq \frac{\sum_{n=N+1}^{\infty} E_{N+1} |\langle\tilde{\varphi}|\psi_n\rangle|^2}{\sum_{n=N+1}^{\infty} |\langle\tilde{\varphi}|\psi_n\rangle|^2} = E_{N+1}.$$

Exercise 12.3.3 *(a) Show that the exact expression for the variational energy, as defined in Eq. (12.3.12), reads* $\tilde{\varepsilon}(\Delta) = \frac{\hbar^2\pi^2}{2m(L+\Delta)^2} + \frac{V_0\Delta}{L+\Delta} + \frac{V_0}{2\pi}\sin[2\pi(1-\frac{\Delta}{L+\Delta})]$. *(b) Obtain the approximation, Eq. (12.3.13). by expanding the result for* $\Delta << L+\Delta$.

Solution 12.3.3

(a)

Dividing the Hamiltonian expectation value to potential end kinetic energy terms, $\tilde{\varepsilon}(\Delta) = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle$, *we obtain:*

$$< T >= \frac{2}{L+\Delta}\int_0^{L+\Delta} \sin(\frac{\pi x}{L+\Delta})\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\sin(\frac{\pi x}{L+\Delta})dx = \frac{\hbar^2\pi^2}{2m(L+\Delta)^2}.$$

Using the definition of the potential energy function (Eq. (12.3.9)), and denoting $b = L$ *and* $a = L+\Delta$ *, we obtain*

$$< V >= V_0 \frac{2}{a}\int_b^a \sin^2(\frac{\pi x}{a})dx = V_0\left[\frac{a-b}{a} + \frac{1}{2\pi}\sin(\frac{2\pi b}{a})\right]$$
$$= V_0\left(\frac{a-b}{a} + \frac{1}{2\pi}\sin[2\pi(1-\frac{(a-b)}{a})]\right)$$

$$= V_0\left[\frac{\Delta}{L+\Delta} + \frac{1}{2\pi}\sin[2\pi(1-\frac{\Delta}{L+\Delta})]\right].$$

Hence, $\tilde{\varepsilon}(\Delta) = \frac{\hbar^2\pi^2}{2m(L+\Delta)^2} + \frac{V_0\Delta}{L+\Delta} + \frac{V_0}{2\pi}\sin[2\pi(1-\frac{\Delta}{L+\Delta})]$.

(b)

Using the Taylor expansion for $x << 1$, *we obtain* $\sin[2\pi(1-x)] \approx -2\pi x + 8\pi^3\frac{x^3}{6}$. *Therefore,*

$$\langle \hat{V} \rangle = \frac{V_0\Delta}{L+\Delta} + \frac{V_0}{2\pi}\sin[2\pi(1-\frac{\Delta}{L+\Delta})] \approx \frac{V_0}{2\pi}\cdot 8\pi^3\frac{1}{6}\frac{\Delta^3}{(L+\Delta)^3} = \frac{2V_0}{3}\pi^2\frac{\Delta^3}{(L+\Delta)^3}$$ *, and finally,*

$$\tilde{\varepsilon}(\Delta) \cong \frac{\hbar^2\pi^2}{2m(L+\Delta)^2} + V_0\frac{2\pi^2}{3}\frac{\Delta^3}{(L+\Delta)^3}.$$

Exercise 12.3.4 *Obtain the optimal value of the box extension parameter, Δ_{opt} (Eq. (12.3.14)) according to the variation principle. (Recall that $\Delta \geq 0$.)*

Solution 12.3.4

The variational energy is given by Eq. (12.3.13), $\tilde{\varepsilon}(\Delta) = \frac{\hbar^2\pi^2}{2m(L+\Delta)^2} + V_0 \frac{2\pi^2}{3} \frac{\Delta^3}{(L+\Delta)^3}$.

The optimal value of the parameter Δ is obtained by the stationarity condition (Eq. (12.3.6)),

$$\frac{d\tilde{\varepsilon}}{d\Delta} = \frac{\hbar^2\pi^2}{2m}\frac{-2}{(L+\Delta)^3} + \frac{2V_0\pi^2}{3}\frac{3\Delta^2}{(L+\Delta)^3} - \frac{2V_0\pi^2}{3}\frac{3\Delta^3}{(L+\Delta)^4} = 0$$

$$\Rightarrow \frac{\hbar^2}{2mV_0}\frac{-1}{(L+\Delta)^3} + \frac{\Delta^2}{(L+\Delta)^3} - \frac{\Delta^3}{(L+\Delta)^4} = 0$$

$$\Rightarrow -\frac{\hbar^2}{2mV_0}(L+\Delta) + \Delta^2 L + \Delta^3 - \Delta^3 = 0$$

$$\Rightarrow \Delta^2 - \frac{\hbar^2}{2mLV_0}\Delta - \frac{\hbar^2}{2mV_0} = 0.$$

Defining $\alpha = 2mL^2V_0/\hbar^2$, *we obtain* $\Delta^2 - \frac{L}{\alpha}\Delta - \frac{L^2}{\alpha} = 0$. *Therefore,*

$\Delta = \frac{L}{2\alpha} \pm \frac{1}{2}\sqrt{\frac{L^2}{\alpha^2} + \frac{4\alpha L^2}{\alpha^2}} = \frac{L}{2\alpha} \pm \frac{L}{2\alpha}\sqrt{1+4\alpha} = \frac{L}{2\alpha}(1 \pm \sqrt{1+4\alpha})$, *where the relevant optimal value is* $\Delta = \frac{L}{2\alpha}(1+\sqrt{1+4\alpha})$.

Exercise 12.3.5 *Recall the definition of the penetration length, Eq. (6.2.4), for a particle in a finite potential well,* $\gamma = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$, *and show that when the ground-state energy is much smaller than V_0, the optimal value, Δ_{opt}, increases with the penetration length (as might be expected).*

Solution 12.3.5

For $E << V_0$ *we can approximate,* $\gamma = \frac{\hbar}{\sqrt{2m(V_0 - E)}} \approx \frac{\hbar}{\sqrt{2mV_0}}$. *Therefore,* $\alpha \equiv V_0 2mL^2 / \hbar^2 \cong L^2 / \gamma^2$, *and as we can see, the optimal value,* Δ_{opt}, *is a monotonically increasing function of the penetration length:*

$$\Delta_{opt} = \frac{\gamma^2}{2L}(1+\sqrt{1+4\frac{L^2}{\gamma^2}}) = \frac{\gamma^2}{2L} + \sqrt{\frac{\gamma^2}{4L^2}(1+4\frac{L^2}{\gamma^2})} = \frac{\gamma^2}{2L} + \sqrt{1+\frac{\gamma^2}{4L^2}}.$$

Exercise 12.3.6 *Calculate numerically the exact ground state energies for a particle in a semi-infinite potential energy well, corresponding to* $V_0 / E_1^{(\infty)} = 10, 100, 1000, 10000$ *(Eq. (12.3.9)), using the approach described in section 6.3. Show that the respective ground state energies are 0.823310, 0.939163, 0.980165, 0.993664, in units of* $E_1^{(\infty)} = \hbar^2\pi^2 / (2mL^2)$.

Solution 12.3.6

Given the potential energy function given in Eq. (12.3.9), the boundary conditions for a proper stationary state at energy ($E << V_0$*) are* $\psi(0) = 0$ *and* $\psi(x) \xrightarrow[x\to\infty]{} 0$, *from which follows,*

$$\psi(x) = \begin{cases} 0 & ; \quad x < 0 \\ a_1 \sin(kx) & ; \quad 0 \le x < L \\ a_2 e^{-\gamma x} & ; \quad L \le x \end{cases}, \text{ where, } \gamma \equiv \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \text{ and } k \equiv \sqrt{\frac{2mE}{\hbar^2}}.$$

The continuity conditions at $x = L$ *require,*

$$\begin{bmatrix} \sin(kL) & -e^{-\gamma L} \\ k\cos(kL) & \gamma e^{-\gamma L} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Consequently, a non-trivial solution is obtained for $\begin{vmatrix} \sin(kL) & -e^{-\gamma L} \\ k\cos(kL) & \gamma e^{-\gamma L} \end{vmatrix} = 0 \Rightarrow \gamma tg(kL) + k = 0$, *which holds for a discrete set of energies, the smallest of which is the ground state energy.*

Exercise 12.3.7 *Generalize the derivation of the optimization condition for a single variation parameter, Ex. 12.3.1, to the case of several variation parameters and show that Eq. (12.3.17) is obtained from Eq. (12.3.16).*

Solution 12.3.7

For a variation function that depends on a set of parameters, $|\tilde{\psi}(c_1, c_2, ..., c_N)\rangle$*, the conditions for the optimal parameters read (Eq. (12.3.16))*

$$\left\langle \frac{\partial}{\partial c_n}\tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} |\tilde{\psi}\rangle \right|_{\mathbf{c}^{(opt)}} = 0 \qquad ; \qquad n = 1, 2, ..., N \ .$$

Using the Hermiticity of the Hamiltonian we obtain, $\left\langle \frac{\partial}{\partial c_n}\tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} |\tilde{\psi}\rangle = \left\langle \tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} \middle| \frac{\partial}{\partial c_n}\tilde{\psi} \right\rangle^*$*, and using* $\left\langle \frac{\partial}{\partial c_n}\tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} |\tilde{\psi}\rangle = 0$ *we obtain:* $\left\langle \tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} \middle| \frac{\partial}{\partial c_n}\tilde{\psi} \right\rangle = 0$*. Consequently:*

$$\left\langle \frac{\partial}{\partial c_n}\tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} |\tilde{\psi}\rangle + \left\langle \tilde{\psi} \middle| \hat{H} - \tilde{\varepsilon} \middle| \frac{\partial}{\partial c_n}\tilde{\psi} \right\rangle = 0 \Rightarrow \frac{\partial}{\partial c_n}\langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle - \tilde{\varepsilon}\frac{\partial}{\partial c_n}\langle \tilde{\psi} | \tilde{\psi}\rangle = 0 .$$

Rewriting the last result, we obtain for each $n \in 1, 2, ..., N$*,*

$$\frac{\partial}{\partial c_n}\langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle - \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle}{\langle \tilde{\psi} | \tilde{\psi}\rangle}\frac{\partial}{\partial c_n}\langle \tilde{\psi} | \tilde{\psi}\rangle = 0$$

$$\Rightarrow \frac{\langle \tilde{\psi} | \tilde{\psi}\rangle \frac{\partial}{\partial c_n}\langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle - \langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle \frac{\partial}{\partial c_n}\langle \tilde{\psi} | \tilde{\psi}\rangle}{\langle \tilde{\psi} | \tilde{\psi}\rangle} = 0$$

$$\Rightarrow \frac{\langle \tilde{\psi} | \tilde{\psi}\rangle \frac{\partial}{\partial c_n}\langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle - \langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle \frac{\partial}{\partial c_n}\langle \tilde{\psi} | \tilde{\psi}\rangle}{\langle \tilde{\psi} | \tilde{\psi}\rangle^2} = 0$$

$$\Rightarrow \frac{\partial}{\partial c_n}\frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi}\rangle}{\langle \tilde{\psi} | \tilde{\psi}\rangle} = 0$$

$$\Rightarrow \frac{\partial}{\partial c_n}\tilde{\varepsilon} = 0 \ .$$

Exercise 12.3.8 *A two-dimensional coordinate system is associated with an identity operator,* $\hat{I} = \hat{I}_1 \otimes \hat{I}_2 = \sum_{n_1} |\alpha_{n_1}\rangle\langle\alpha_{n_1}| \otimes \sum_{n_2} |\beta_{n_2}\rangle\langle\beta_{n_2}|$*, where* $\{|\alpha_{n_1}\rangle\}$ *and* $\{|\beta_{n_2}\rangle\}$ *are complete orthonormal systems in the respective spaces. A general operator in the full space reads (see Eq.*

(11.6.14)) $\hat{A}=\sum_{n_1,n_1'}\sum_{n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|\otimes\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|$. *Given two vectors in the respective one-dimensional coordinated spaces,* $\left|\tilde{\varphi}\right\rangle=\sum_{n_1}\tilde{\varphi}_{n_1}\left|\alpha_{n_1}\right\rangle$ *and* $\left|\tilde{\chi}\right\rangle=\sum_{n_2}\tilde{\chi}_{n_2}\left|\beta_{n_2}\right\rangle$, *show that:*

(a) $\langle\tilde{\chi}|\hat{A}|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle=\hat{A}_1^{(\tilde{\chi})}|\tilde{\varphi}\rangle$, *where,*

$$\hat{A}_1^{(\tilde{\chi})}=\sum_{n_1,n_1',n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left\langle\tilde{\chi}\middle|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\middle|\tilde{\chi}\right\rangle\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|=\langle\tilde{\chi}|\hat{A}|\tilde{\chi}\rangle.$$

(b) $\langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle=\hat{A}_2^{(\tilde{\varphi})}|\tilde{\chi}\rangle$, *where*

$$\hat{A}_2^{(\tilde{\varphi})}=\sum_{n_1,n_1',n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left\langle\tilde{\varphi}\middle|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\middle|\tilde{\varphi}\right\rangle\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|=\langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle.$$

(c) Use the results of (a) and (b) to show that $\langle\tilde{\chi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle=0\Rightarrow\hat{H}_1^{(\tilde{\chi})}|\tilde{\varphi}\rangle=\tilde{\varepsilon}|\tilde{\varphi}\rangle$ *and* $\langle\tilde{\varphi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle=0\Rightarrow\hat{H}_2^{(\tilde{\varphi})}|\tilde{\chi}\rangle=\tilde{\varepsilon}|\tilde{\chi}\rangle$.

Solution 12.3.8

(a)

Using $\hat{A}=\sum_{n_1,n_1'}\sum_{n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|\otimes\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|$, *we obtain*

$$\langle\tilde{\chi}|\hat{A}|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle=\langle\tilde{\chi}|\left[\sum_{n_1,n_1'}\sum_{n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|\otimes\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|\right]|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle$$

$$=\left[\sum_{n_1,n_1'}\sum_{n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|\left\langle\tilde{\chi}\middle|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\middle|\tilde{\chi}\right\rangle\right]|\tilde{\varphi}\rangle\ .$$

The result can be identified as $\langle\tilde{\chi}|\hat{A}|\tilde{\varphi}\rangle\otimes|\tilde{\chi}\rangle\equiv\hat{A}_1^{(\tilde{\chi})}|\tilde{\varphi}\rangle$, *where,*

$$\hat{A}_1^{(\tilde{\chi})}=\sum_{n_1,n_1'}\sum_{n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|\left\langle\tilde{\chi}\middle|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\middle|\tilde{\chi}\right\rangle$$
$$=\langle\tilde{\chi}|\left[\sum_{n_1,n_1'}\sum_{n_2,n_2'}A_{n_1,n_1',n_2,n_2'}\left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right|\otimes\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|\right]|\tilde{\chi}\rangle$$

$$=\langle\tilde{\chi}|\hat{A}|\tilde{\chi}\rangle\quad .$$

(b)

Using: $\hat{A} = \sum_{n_1,n_1'} \sum_{n_2,n_2'} A_{n_1,n_1',n_2,n_2'} \left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right| \otimes \left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|$ *we obtain:*

$$\langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = \langle\tilde{\varphi}|\left[\sum_{n_1,n_1'} \sum_{n_2,n_2'} A_{n_1,n_1',n_2,n_2'} \left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right| \otimes \left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|\right]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle$$

$$= \left[\sum_{n_1,n_1'} \sum_{n_2,n_2'} A_{n_1,n_1',n_2,n_2'} \left\langle\tilde{\varphi}\middle|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\middle|\tilde{\varphi}\right\rangle\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|\right]|\tilde{\chi}\rangle \ .$$

The result can be identified as $\langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = \hat{A}_2^{(\tilde{\varphi})}|\tilde{\chi}\rangle$, *where,*

$$\hat{A}_2^{(\tilde{\varphi})} = \sum_{n_1,n_1'} \sum_{n_2,n_2'} A_{n_1,n_1',n_2,n_2'} \left\langle\tilde{\varphi}\middle|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\middle|\tilde{\varphi}\right\rangle\left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|$$
$$= \langle\tilde{\varphi}|\left[\sum_{n_1,n_1'} \sum_{n_2,n_2'} A_{n_1,n_1',n_2,n_2'} \left|\alpha_{n_1}\right\rangle\left\langle\alpha_{n_1'}\right| \otimes \left|\beta_{n_2}\right\rangle\left\langle\beta_{n_2'}\right|\right]|\tilde{\varphi}\rangle$$

$$= \langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle \ .$$

(c)

In (a) we saw that, $\langle\tilde{\chi}|\hat{A}|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle \equiv \hat{A}_1^{(\tilde{\chi})}|\tilde{\varphi}\rangle$, *where,* $\hat{A}_1^{(\tilde{\chi})} = \langle\tilde{\chi}|\hat{A}|\tilde{\chi}\rangle$. *Therefore,* $\langle\tilde{\chi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = [\hat{H}-\tilde{\varepsilon}]_1^{(\tilde{\chi})}|\tilde{\varphi}\rangle$, *where,* $[\hat{H}-\tilde{\varepsilon}]_1^{(\tilde{\chi})} = \langle\tilde{\chi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\chi}\rangle = \hat{H}_1^{(\tilde{\chi})} - \tilde{\varepsilon}$.

Consequently, $\langle\tilde{\chi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = \left(\hat{H}_1^{(\tilde{\chi})} - \tilde{\varepsilon}\right)|\tilde{\varphi}\rangle$, *and the requirement* $\langle\tilde{\chi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = 0$, *therefore means that,* $\hat{H}_1^{(\tilde{\chi})}|\tilde{\varphi}\rangle = \tilde{\varepsilon}|\tilde{\varphi}\rangle$.

Similarly, in (b) we saw that, $\langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = \hat{A}_2^{(\tilde{\varphi})}|\tilde{\chi}\rangle$, *where,* $\hat{A}_2^{(\tilde{\varphi})} = \langle\tilde{\varphi}|\hat{A}|\tilde{\varphi}\rangle$. *Therefore,* $\langle\tilde{\varphi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = [\hat{H}-\tilde{\varepsilon}]_2^{(\tilde{\varphi})}|\tilde{\chi}\rangle$, *where,* $[\hat{H}-\tilde{\varepsilon}]_2^{(\tilde{\varphi})} = \langle\tilde{\varphi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle = \hat{H}_2^{(\tilde{\varphi})} - \tilde{\varepsilon}$.

Consequently, $\langle\tilde{\varphi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = \left(\hat{H}_2^{(\tilde{\varphi})} - \tilde{\varepsilon}\right)|\tilde{\chi}\rangle$, *and the requirement* $\langle\tilde{\varphi}|[\hat{H}-\tilde{\varepsilon}]|\tilde{\varphi}\rangle \otimes |\tilde{\chi}\rangle = 0$, *therefore means that* $\hat{H}_2^{(\tilde{\varphi})}|\tilde{\chi}\rangle = \tilde{\varepsilon}|\tilde{\chi}\rangle$.

Exercise 12.3.9 *Use Eq. (12.3.41) to derive the relation in Eq. (12.3.44).*

Solution 12.3.9

Starting from the definition of the variational energy, we obtain

$$\tilde{\varepsilon} = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle = \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{H}_1 + \hat{H}_2 + \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle$$
$$= \langle \tilde{\varphi}_{opt} | \hat{H}_1 | \tilde{\varphi}_{opt} \rangle + \langle \tilde{\chi}_{opt} | \hat{H}_2 | \tilde{\chi}_{opt} \rangle + \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle$$
$$= \langle \tilde{\varphi}_{opt} | \hat{H}_1 | \tilde{\varphi}_{opt} \rangle + \langle \tilde{\chi}_{opt} | \hat{H}_2 | \tilde{\chi}_{opt} \rangle + \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle$$
$$+ \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle - \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle$$
$$= \langle \tilde{\varphi}_{opt} | \left[\hat{H}_1 + \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\chi}_{opt} \rangle \right] | \tilde{\varphi}_{opt} \rangle + \langle \tilde{\chi}_{opt} | \left[\hat{H}_2 + \langle \tilde{\varphi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle \right] | \tilde{\chi}_{opt} \rangle$$
$$- \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle \ .$$

Using Eq. (12.3.41), we obtain

$$\tilde{\varepsilon} = \tilde{\varepsilon}_{\tilde{\varphi}_{opt}} + \tilde{\varepsilon}_{\tilde{\chi}_{opt}} - \langle \tilde{\varphi}_{opt} | \langle \tilde{\chi}_{opt} | \hat{V}_{1,2} | \tilde{\varphi}_{opt} \rangle | \tilde{\chi}_{opt} \rangle = \tilde{\varepsilon}_{\tilde{\varphi}_{opt}} + \tilde{\varepsilon}_{\tilde{\chi}_{opt}} - \langle \tilde{\psi}_{opt} | \hat{V}_{1,2} | \tilde{\psi}_{opt} \rangle .$$

Exercise 12.3.10 *Show that in the absence of coupling, namely, when* $\hat{V}_{1,2,...,N} = 0$, *the variational energy equals the sum of independent variational energies in the one-dimensional coordinate subspaces, namely* $\tilde{\varepsilon} = \sum_{n=1}^{N} \tilde{\varepsilon}_{\tilde{\varphi}_{opt},n} = \sum_{n=1}^{N} \langle \tilde{\varphi}_{opt,n} | \hat{H}_n | \tilde{\varphi}_{opt,n} \rangle$.

Solution 12.3.10

In the absence of coupling, the different SCF equations (Eq. (12.3.47)) are decoupled, namely $\hat{H}_n | \tilde{\varphi}_{opt,n} \rangle = \tilde{\varepsilon}_{\tilde{\varphi}_{opt,n}} | \tilde{\varphi}_{opt,n} \rangle$ *for* $n = 1, 2, ..., N$. *The variational energy reads*

$$\tilde{\varepsilon} = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle = \langle \tilde{\varphi}_{opt,1} | \otimes \langle \tilde{\varphi}_{opt,2} | \otimes \cdots \otimes \langle \tilde{\varphi}_{opt,N} | \sum_{n=1}^{N} \hat{H}_n | \tilde{\varphi}_{opt,1} \rangle \otimes | \tilde{\varphi}_{opt,1} \rangle \otimes \cdots \otimes | \tilde{\varphi}_{opt,N} \rangle$$

$$= \sum_{n=1}^{N} \langle \tilde{\varphi}_{opt,n} | \hat{H}_n | \tilde{\varphi}_{opt,n} \rangle = \sum_{n=1}^{N} \langle \tilde{\varphi}_{opt,n} | \hat{H}_n | \tilde{\varphi}_{opt,n} \rangle = \sum_{n=1}^{N} \tilde{\varepsilon}_{\tilde{\varphi}_{opt},n} ,$$

where we notice that the product form of the multi-dimensional state becomes exact in this case.

Exercise 12.3.11 *(a) Use the identity operator in the full space,* $\int d\mathbf{r}'_1 \int d\mathbf{r}'_2 | \phi_{\mathbf{r}'_1} \rangle \langle \phi_{\mathbf{r}'_1} | \otimes | \phi_{\mathbf{r}'_2} \rangle \langle \phi_{\mathbf{r}'_2} |$, *and the definition of* $\hat{V}_{1,2}$ *according to Eq. (12.3.52) to show that*

$$\langle \phi_{\mathbf{r}_1} | \otimes \langle \tilde{\chi}_{opt} | \hat{H}_{1,2} | \tilde{\varphi}_{opt} \rangle \otimes | \tilde{\chi}_{opt} \rangle = \int d\mathbf{r}_2 \, | \tilde{\chi}_{opt}(\mathbf{r}_2) |^2 \frac{Ke^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tilde{\varphi}_{opt}(\mathbf{r}_1)$$

$$\left\langle\tilde{\varphi}_{opt}\right|\otimes\left\langle\phi_{\mathbf{r}_2}\right|\hat{H}_{1,2}\left|\tilde{\varphi}_{opt}\right\rangle\otimes\left|\tilde{\chi}_{opt}\right\rangle=\int d\mathbf{r}_1\,|\tilde{\varphi}_{opt}(\mathbf{r}_1)|^2\,\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\tilde{\chi}_{opt}(\mathbf{r}_2)\,.$$

(b) Use the definitions of $\hat{H}_1$ and $\hat{H}_2$ according to Eq. (12.3.52), and the coordinate representation of the kinetic energy operator ($\left\langle\phi_{\mathbf{r}}\right|\hat{T}_{\mathbf{r}}\left|\psi\right\rangle=\frac{-\hbar^2}{2m}\Delta\psi(\mathbf{r})$; see Ex. 11.5.4) to show that

$$\left\langle\phi_{\mathbf{r}_2}\right|\hat{H}_1\left|\tilde{\varphi}_{opt}\right\rangle=\left[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}_1}+\frac{-KZe^2}{|\mathbf{r}_1|}\right]\tilde{\varphi}_{opt}(\mathbf{r}_1)$$

$$\left\langle\phi_{\mathbf{r}_2}\right|\hat{H}_2\left|\tilde{\chi}_{opt}\right\rangle=\left[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}_2}+\frac{-KZe^2}{|\mathbf{r}_2|}\right]\tilde{\chi}_{opt}(\mathbf{r}_2)\,.$$

(c) Use the results of (a) and (b) to show that the generic mean field equations translate to Eq. (12.3.54) in the case of the He atom Hamiltonian (Eq. (12.3.52)).

Solution 12.3.11

(a)

Using $\hat{H}_{1,2}=\frac{Ke^2}{|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2|}=V(\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2)$*, and introducing the identity, we obtain*

$$\begin{aligned}
&\left\langle\phi_{\mathbf{r}_1}\right|\otimes\left\langle\tilde{\chi}_{opt}\right|\hat{H}_{1,2}\left|\tilde{\varphi}_{opt}\right\rangle\otimes\left|\tilde{\chi}_{opt}\right\rangle\\
&=\left\langle\phi_{\mathbf{r}_1}\right|\otimes\left\langle\tilde{\chi}_{opt}\right|\left[\int d\mathbf{r}_1'\int d\mathbf{r}_2'\left|\phi_{\mathbf{r}_1'}\right\rangle\left\langle\phi_{\mathbf{r}_1'}\right|\otimes\left|\phi_{\mathbf{r}_2'}\right\rangle\left\langle\phi_{\mathbf{r}_2'}\right|\hat{H}_{1,2}\int d\mathbf{r}_1''\int d\mathbf{r}_2''\left|\phi_{\mathbf{r}_1''}\right\rangle\left\langle\phi_{\mathbf{r}_1''}\right|\otimes\left|\phi_{\mathbf{r}_2''}\right\rangle\left\langle\phi_{\mathbf{r}_2''}\right|\right]\left|\tilde{\chi}_{opt}\right\rangle\otimes\left|\tilde{\varphi}_{opt}\right\rangle\\
&=\int d\mathbf{r}_1'\int d\mathbf{r}_2'\int d\mathbf{r}_1''\int d\mathbf{r}_2''\tilde{\chi}_{opt}^{*}(\mathbf{r}_2')\delta(\mathbf{r}_1-\mathbf{r}_1')\left\langle\phi_{\mathbf{r}_1'}\right|\otimes\left\langle\phi_{\mathbf{r}_2'}\right|\hat{H}_{1,2}\left|\phi_{\mathbf{r}_1''}\right\rangle\otimes\left|\phi_{\mathbf{r}_2''}\right\rangle\tilde{\chi}_{opt}(\mathbf{r}_2'')\tilde{\varphi}_{opt}(\mathbf{r}_1'')\\
&=\int d\mathbf{r}_1'\int d\mathbf{r}_2'\int d\mathbf{r}_1''\int d\mathbf{r}_2''\tilde{\chi}_{opt}^{*}(\mathbf{r}_2')\delta(\mathbf{r}_1-\mathbf{r}_1')V(\mathbf{r}_1'-\mathbf{r}_2')\delta(\mathbf{r}_1'-\mathbf{r}_1'')\delta(\mathbf{r}_2'-\mathbf{r}_2'')\tilde{\chi}_{opt}(\mathbf{r}_2'')\tilde{\varphi}_{opt}(\mathbf{r}_1'')\\
&=\int d\mathbf{r}_2'\tilde{\chi}_{opt}^{*}(\mathbf{r}_2')V(\mathbf{r}_1-\mathbf{r}_2')\tilde{\chi}_{opt}(\mathbf{r}_2')\tilde{\varphi}_{opt}(\mathbf{r}_1)\\
&=\int d\mathbf{r}_2'\,|\tilde{\chi}_{opt}(\mathbf{r}_2')|^2\,V(\mathbf{r}_1-\mathbf{r}_2')\tilde{\varphi}_{opt}(\mathbf{r}_1)
\end{aligned}$$

$$\begin{aligned}
&\left\langle\tilde{\varphi}_{opt}\right|\otimes\left\langle\phi_{\mathbf{r}_2}\right|\hat{H}_{1,2}\left|\tilde{\varphi}_{opt}\right\rangle\otimes\left|\tilde{\chi}_{opt}\right\rangle\\
&=\left\langle\tilde{\varphi}_{opt}\right|\otimes\left\langle\phi_{\mathbf{r}_2}\right|\left[\int d\mathbf{r}_1'\int d\mathbf{r}_2'\left|\phi_{\mathbf{r}_1'}\right\rangle\left\langle\phi_{\mathbf{r}_1'}\right|\otimes\left|\phi_{\mathbf{r}_2'}\right\rangle\left\langle\phi_{\mathbf{r}_2'}\right|\hat{H}_{1,2}\int d\mathbf{r}_1''\int d\mathbf{r}_2''\left|\phi_{\mathbf{r}_1''}\right\rangle\left\langle\phi_{\mathbf{r}_1''}\right|\otimes\left|\phi_{\mathbf{r}_2''}\right\rangle\left\langle\phi_{\mathbf{r}_2''}\right|\right]\left|\tilde{\chi}_{opt}\right\rangle\otimes\left|\tilde{\varphi}_{opt}\right\rangle\\
&=\int d\mathbf{r}_1'\int d\mathbf{r}_2'\int d\mathbf{r}_1''\int d\mathbf{r}_2''\tilde{\varphi}_{opt}^{*}(\mathbf{r}_1')\delta(\mathbf{r}_2-\mathbf{r}_2')\left\langle\phi_{\mathbf{r}_1'}\right|\otimes\left\langle\phi_{\mathbf{r}_2'}\right|\hat{H}_{1,2}\left|\phi_{\mathbf{r}_1''}\right\rangle\otimes\left|\phi_{\mathbf{r}_2''}\right\rangle\tilde{\chi}_{opt}(\mathbf{r}_2'')\tilde{\varphi}_{opt}(\mathbf{r}_1'')\\
&=\int d\mathbf{r}_1'\int d\mathbf{r}_2'\int d\mathbf{r}_1''\int d\mathbf{r}_2''\tilde{\varphi}_{opt}^{*}(\mathbf{r}_1')\delta(\mathbf{r}_2-\mathbf{r}_2')V(\mathbf{r}_1'-\mathbf{r}_2')\delta(\mathbf{r}_1'-\mathbf{r}_1'')\delta(\mathbf{r}_2'-\mathbf{r}_2'')\tilde{\chi}_{opt}(\mathbf{r}_2'')\tilde{\varphi}_{opt}(\mathbf{r}_1'')\\
&=\int d\mathbf{r}_1'\tilde{\varphi}_{opt}^{*}(\mathbf{r}_1')V(\mathbf{r}_1'-\mathbf{r}_2)\tilde{\chi}_{opt}(\mathbf{r}_2)\tilde{\varphi}_{opt}(\mathbf{r}_1')\\
&=\int d\mathbf{r}_1'\,|\tilde{\varphi}_{opt}(\mathbf{r}_1')|^2\,V(\mathbf{r}_1'-\mathbf{r}_2)\tilde{\chi}_{opt}(\mathbf{r}_2)
\end{aligned}$$

(b)

The single particle Hamiltonian reads $\hat{H}_1 = \frac{-\hbar^2}{2m_e}\hat{\mathbf{p}}_1^2 + \frac{-KZe^2}{|\hat{\mathbf{r}}_1|}$. *Introducing the identity in the position representation, we obtain for the potential energy,*

$$\left\langle \phi_{\mathbf{r}_1} \middle| \frac{-KZe^2}{|\hat{\mathbf{r}}_1|} \middle| \tilde{\varphi}_{opt} \right\rangle = \int d\mathbf{r}_1' \int d\mathbf{r}_1'' \left\langle \phi_{\mathbf{r}_1} \middle| \phi_{\mathbf{r}_1'} \right\rangle \left\langle \phi_{\mathbf{r}_1'} \middle| \frac{-KZe^2}{|\hat{\mathbf{r}}_1|} \middle| \phi_{\mathbf{r}_1''} \right\rangle \left\langle \phi_{\mathbf{r}_1''} \middle| \tilde{\varphi}_{opt} \right\rangle$$
$$= \int d\mathbf{r}_1' \int d\mathbf{r}_1'' \delta(\mathbf{r}_1 - \mathbf{r}_1') \frac{-KZe^2}{|\mathbf{r}_1''|} \delta(\mathbf{r}_1' - \mathbf{r}_1'') \left\langle \phi_{\mathbf{r}_1''} \middle| \tilde{\varphi}_{opt} \right\rangle$$

$$= \frac{-KZe^2}{|\mathbf{r}_1|} \tilde{\varphi}_{opt}(\mathbf{r}_1) \ .$$

For the kinetic energy, we use the result of Ex. 11.5.4 to obtain

$$\left\langle \varphi_x \middle| \frac{\hat{p}_x^2}{2m} \middle| \psi \right\rangle = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) \Rightarrow \left\langle \phi_{\mathbf{r}_1} \middle| \frac{\hat{\mathbf{p}}_1^2}{2m} \middle| \psi \right\rangle = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^{\ 2}} + \frac{\partial^2}{\partial y_1^{\ 2}} + \frac{\partial^2}{\partial z_1^{\ 2}} \right) \psi(\mathbf{r}_1),$$

and therefore: $\left\langle \phi_{\mathbf{r}_1} \middle| \hat{H}_1 \middle| \tilde{\varphi}_{opt} \right\rangle = \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}_1} + \frac{-KZe^2}{|\mathbf{r}_1|} \right] \tilde{\varphi}_{opt}(\mathbf{r}_1)$.

Similarly, for $\hat{H}_2 = \frac{-\hbar^2}{2m_e}\hat{\mathbf{p}}_2^2 + \frac{-KZe^2}{|\hat{\mathbf{r}}_2|}$, *we obtain*

$$\left\langle \phi_{\mathbf{r}_2} \middle| \hat{H}_2 \middle| \tilde{\chi}_{opt} \right\rangle = \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}_2} + \frac{-KZe^2}{|\mathbf{r}_2|} \right] \tilde{\chi}_{opt}(\mathbf{r}_2).$$

(c)

The generic mean-field equations read (Eq. (12.3.41)),

$$[\hat{H}_1 + \left\langle \tilde{\chi}_{opt} \middle| \hat{V}_{1,2} \middle| \tilde{\chi}_{opt} \right\rangle] \left| \tilde{\varphi}_{opt} \right\rangle = \tilde{\varepsilon}_{\tilde{\varphi}_{opt}} \left| \tilde{\varphi}_{opt} \right\rangle$$

$$[\hat{H}_2 + \left\langle \tilde{\varphi}_{opt} \middle| \hat{V}_{1,2} \middle| \tilde{\varphi}_{opt} \right\rangle] \left| \tilde{\chi}_{opt} \right\rangle = \tilde{\varepsilon}_{\tilde{\chi}_{opt}} \left| \tilde{\chi}_{opt} \right\rangle \ .$$

In the coordinate representation, these equations obtain the form,

$$\left\langle \phi_{\mathbf{r}_1} \middle| \hat{H}_1 \middle| \tilde{\varphi}_{opt} \right\rangle + \left\langle \phi_{\mathbf{r}_1} \right| \otimes \left\langle \tilde{\chi}_{opt} \middle| \hat{V}_{1,2} \middle| \tilde{\varphi}_{opt} \right\rangle \otimes \left| \tilde{\chi}_{opt} \right\rangle = \tilde{\varepsilon}_{\tilde{\varphi}_{opt}} \left\langle \phi_{\mathbf{r}_1} \middle| \tilde{\varphi}_{opt} \right\rangle$$

$$\left\langle \phi_{\mathbf{r}_2} \middle| \hat{H}_2 \middle| \tilde{\chi}_{opt} \right\rangle + \left\langle \tilde{\varphi}_{opt} \right| \otimes \left\langle \phi_{\mathbf{r}_2} \middle| \hat{V}_{1,2} \middle| \tilde{\varphi}_{opt} \right\rangle \otimes \left| \tilde{\chi}_{opt} \right\rangle = \tilde{\varepsilon}_{\tilde{\chi}_{opt}} \left\langle \phi_{\mathbf{r}_2} \middle| \tilde{\chi}_{opt} \right\rangle \ .$$

Using the results of (a) and (b), we obtain,

$$\left[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}_1}+\frac{-KZe^2}{|\mathbf{r}_1|}\right]\tilde{\varphi}_{opt}(\mathbf{r}_1)+\int d\mathbf{r}_2\,|\,\tilde{\chi}_{opt}(\mathbf{r}_2)|^2\,V(\mathbf{r}_1-\mathbf{r}_2)\tilde{\varphi}_{opt}(\mathbf{r}_1)=\tilde{\varepsilon}_{\tilde{\varphi}_{opt}}\tilde{\varphi}_{opt}(\mathbf{r}_1)$$

$$\left[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}_2}+\frac{-KZe^2}{|\mathbf{r}_2|}\right]\tilde{\chi}_{opt}(\mathbf{r}_2)+\int d\mathbf{r}_1\,|\,\tilde{\varphi}_{opt}(\mathbf{r}_1)|^2\,V(\mathbf{r}_1-\mathbf{r}_2)\tilde{\chi}_{opt}(\mathbf{r}_2)=\tilde{\varepsilon}_{\tilde{\chi}_{opt}}\tilde{\chi}_{opt}(\mathbf{r}_1)\,.$$

Exercise 12.3.12 *Let us define the permutation operator,* $\hat{P}_{1,2}f(\mathbf{r}_1,\mathbf{r}_2)=f(\mathbf{r}_2,\mathbf{r}_1)$. *(a) Show that any eigenfunction of this operator must satisfy* $\psi(\mathbf{r}_2,\mathbf{r}_1)=\alpha\psi(\mathbf{r}_1,\mathbf{r}_2)$, *where* α *is a scalar. (b) Show that if an eigen function of* $\hat{P}_{1,2}$ *is a product,* $\psi(\mathbf{r}_1,\mathbf{r}_2)=g(\mathbf{r}_1)h(\mathbf{r}_2)$, *then,* $g(\mathbf{r})\propto h(\mathbf{r})$.

Solution 12.3.12

(a)

For any $f(\mathbf{r}_1,\mathbf{r}_2)$, *by definition, we have* $\hat{P}_{1,2}f(\mathbf{r}_1,\mathbf{r}_2)=f(\mathbf{r}_2,\mathbf{r}_1)$. *If* $f(\mathbf{r}_1,\mathbf{r}_2)$ *is an eigenfunction of* $\hat{P}_{1,2}$, *then* $\hat{P}_{1,2}f(\mathbf{r}_1,\mathbf{r}_2)=\alpha f(\mathbf{r}_1,\mathbf{r}_2)$, *where* α *is a scalar. Consequently, if* $f(\mathbf{r}_1,\mathbf{r}_2)$ *is an eigenfunction of* $\hat{P}_{1,2}$ *we must have* $f(\mathbf{r}_2,\mathbf{r}_1)=\alpha f(\mathbf{r}_1,\mathbf{r}_2)$.

(b)

Given an eigenfunction of $\hat{P}_{1,2}$ *which is a product,* $\psi(\mathbf{r}_1,\mathbf{r}_2)=g(\mathbf{r}_1)h(\mathbf{r}_2)$, *then from (a) we know that* $g(\mathbf{r}_1)h(\mathbf{r}_2)=\alpha h(\mathbf{r}_1)g(\mathbf{r}_2)$. *Fixing the value of one of the variables, e.g.* $\mathbf{r}_2$, *we obtain* $g(\mathbf{r}_1)\propto h(\mathbf{r}_1)$ *for any* $\mathbf{r}_1$.

Exercise 12.3.13 *Calculate the exact ground state energy of the Hamiltonian,*

$$\hat{H}=\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}_1}+\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}_2}+\frac{-KZe^2}{|\mathbf{r}_1|}+\frac{-KZe^2}{|\mathbf{r}_2|}\,,$$

which corresponds to the He atom, when the electron-electron interaction is completely ignored. Refer as needed to Ex. 4.3.4 and to the known solution for a hydrogen-like atom (see chapter 10).

Solution 12.3.13

Notice that the Hamiltonian is a sum of two operators associated with two different single-particle spaces. Consequently, its eigenvalues are sums of the single-particle Hamiltonian eigenvalues. The single-particle Hamiltonians are readily identified as hydrogen-like Hamiltonians, whose ground state energy equals $-R_H Z^2$. *The ground state energy of the two-electron Hamiltonian is therefore,* $E_g = \left(-R_H Z^2\right) + \left(-R_H Z^2\right) = -2R_H Z^2$. *For* $Z = 2$, *we obtain* $E_g = -8 \cdot 13.6 = -108.8$ *eV.*

13 Many-Electron Systems

Exercise 13.1.1 *The spin states* $|\alpha\rangle$ *and* $|\beta\rangle$ *are common eigenstates of* $\hat{S}^2$ *and* $\hat{S}_z$ *(see Eq. (13.1.8)). Denoting the common eigenstates by the respective quantum numbers,* $|s,m_s\rangle$*, one can identify,* $|\alpha\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle$*, and* $|\beta\rangle = \left|\frac{1}{2},\frac{-1}{2}\right\rangle$.

(a) Use the definition of the spin ladder operators ($\hat{S}_\pm$*, Eq. (13.1.6)) and their commutation relations (Eq. (1.3.7)) to show that* $\hat{S}_\pm|s,m_s\rangle \propto |s,m_s \pm 1\rangle$*. Particularly, show that* $\hat{S}_+|\beta\rangle \propto |\alpha\rangle$*, and* $\hat{S}_-|\alpha\rangle \propto |\beta\rangle$.

(b) Use the commutation relation (Eq. (13.1.7)) to show that $\hat{S}_+|\alpha\rangle = 0$ *and* $\hat{S}_-|\beta\rangle = 0$*. (Show that* $\langle\alpha|\hat{S}_-\hat{S}_+|\alpha\rangle = \langle\beta|\hat{S}_+\hat{S}_-|\beta\rangle = 0$*.)*

(c) Normalize the vectors $\hat{S}_+|\beta\rangle$ *and* $\hat{S}_-|\alpha\rangle$*, and show that the normalized vectors satisfy the relations* $\hat{S}_+|\beta\rangle = \hbar|\alpha\rangle$ *and* $\hat{S}_-|\alpha\rangle = \hbar|\beta\rangle$.

Solution 13.1.1

(a)

Using $[\hat{S}_z,\hat{S}_\pm] = \pm\hbar\hat{S}_\pm$ *and* $\hat{S}_z|s,m_s\rangle = m_s\hbar|s,m_s\rangle$*, we obtain*

$$\hat{S}_z\left(\hat{S}_\pm|s,m_s\rangle\right) = \hat{S}_z\hat{S}_\pm|s,m_s\rangle = \hat{S}_\pm(\hat{S}_z \pm \hbar)|s,m_s\rangle = \hat{S}_\pm\hbar(m_s \pm 1)|s,m_s\rangle = \hbar(m_s \pm 1)\left(\hat{S}_\pm|s,m_s\rangle\right).$$

Specifically, for $|\alpha\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle$ *and* $|\beta\rangle = \left|\frac{1}{2},\frac{-1}{2}\right\rangle$*, we obtain*

$$\hat{S}_z\left(\hat{S}_-\left|\frac{1}{2},\frac{1}{2}\right\rangle\right) = \hbar(\frac{1}{2}-1)\left(\hat{S}_-\left|\frac{1}{2},\frac{1}{2}\right\rangle\right) = -\frac{1}{2}\hbar\left(\hat{S}_-\left|\frac{1}{2},\frac{1}{2}\right\rangle\right)$$

$$\Rightarrow \hat{S}_z\left(\hat{S}_-|\alpha\rangle\right) = -\frac{1}{2}\hbar\left(\hat{S}_-|\alpha\rangle\right),$$

$$\hat{S}_z\left(\hat{S}_+\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right) = \hbar(-\frac{1}{2}+1)\left(\hat{S}_+\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right) = \frac{1}{2}\hbar\left(\hat{S}_+\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right)$$

$$\Rightarrow \hat{S}_z\left(\hat{S}_+|\beta\rangle\right)=\frac{1}{2}\hbar\left(\hat{S}_+|\beta\rangle\right).$$

Since $\hat{S}_z|\alpha\rangle=\frac{1}{2}\hbar|\alpha\rangle$ *and* $\hat{S}_z|\beta\rangle=-\frac{1}{2}\hbar|\beta\rangle$*, we must identify*

$\hat{S}_-|\alpha\rangle\propto|\beta\rangle$ *and* $\hat{S}_+|\beta\rangle\propto|\alpha\rangle$.

(b)

Using $[\hat{S}_+,\hat{S}_-]=2\hbar\hat{S}_z$ *we obtain*

$$\langle\alpha|\hat{S}_-\hat{S}_+|\alpha\rangle=\langle\alpha|\hat{S}_+\hat{S}_- -2\hbar\hat{S}_z|\alpha\rangle\Rightarrow 2\langle\alpha|\hat{S}_-\hat{S}_+|\alpha\rangle=\langle\alpha|\hat{S}_+\hat{S}_- +\hat{S}_-\hat{S}_+ -2\hbar\hat{S}_z|\alpha\rangle,$$

$$\langle\beta|\hat{S}_+\hat{S}_-|\beta\rangle=\langle\beta|\hat{S}_-\hat{S}_+ +2\hbar\hat{S}_z|\beta\rangle\Rightarrow 2\langle\beta|\hat{S}_+\hat{S}_-|\beta\rangle=\langle\beta|\hat{S}_+\hat{S}_- +\hat{S}_-\hat{S}_+ +2\hbar\hat{S}_z|\beta\rangle.$$

Using: $\hat{S}^2-\hat{S}_z^2=\frac{1}{2}(\hat{S}_+\hat{S}_- +\hat{S}_-\hat{S}_+)$*, we obtain*

$$2\langle\alpha|\hat{S}_-\hat{S}_+|\alpha\rangle=\langle\alpha|2\hat{S}^2-2\hat{S}_z^2-2\hbar\hat{S}_z|\alpha\rangle=\langle\alpha|\frac{3}{2}\hbar^2-\frac{1}{2}\hbar^2-\hbar^2|\alpha\rangle=0,$$

$$2\langle\beta|\hat{S}_+\hat{S}_-|\beta\rangle=\langle\beta|2\hat{S}^2-2\hat{S}_z^2+2\hbar\hat{S}_z|\beta\rangle=\langle\beta|\frac{3}{2}\hbar^2-\frac{1}{2}\hbar^2-\hbar^2|\beta\rangle=0.$$

Noticing that $\langle\alpha|\hat{S}_-\hat{S}_+|\alpha\rangle$ *is the norm of* $\hat{S}_+|\alpha\rangle$*, and* $\langle\beta|\hat{S}_+\hat{S}_-|\beta\rangle$ *is the norm of* $\hat{S}_-|\beta\rangle$*, we must conclude that* $\hat{S}_+|\alpha\rangle=0$ *and* $\hat{S}_-|\beta\rangle=0$.

(c)

The norms of $\hat{S}_+|\beta\rangle$ *and* $\hat{S}_-|\alpha\rangle$ *read*

$$\langle\beta|\hat{S}_-\hat{S}_+|\beta\rangle=\langle\beta|2\hat{S}^2-2\hat{S}_z^2-\hat{S}_+\hat{S}_-|\beta\rangle=\langle\beta|2\frac{3\hbar^2}{4}-2\frac{\hbar^2}{4}-0|\beta\rangle=\hbar^2\langle\beta|\beta\rangle,$$

$$\langle\alpha|\hat{S}_+\hat{S}_-|\alpha\rangle=\langle\alpha|2\hat{S}^2-2\hat{S}_z^2-\hat{S}_-\hat{S}_+|\alpha\rangle=\langle\alpha|2\frac{3\hbar^2}{4}-2\frac{\hbar^2}{4}-0|\alpha\rangle=\hbar^2\langle\alpha|\alpha\rangle.$$

Since in (a) we saw that $\hat{S}_-|\alpha\rangle\propto|\beta\rangle$ *and* $\hat{S}_+|\beta\rangle\propto|\alpha\rangle$*, and since* $\langle\beta|\beta\rangle=\langle\alpha|\alpha\rangle=1$*, we can identify the proportion coefficients, namely* $\hat{S}_+|\beta\rangle=\hbar|\alpha\rangle$ *and* $\hat{S}_-|\alpha\rangle=\hbar|\beta\rangle$.

Exercise 13.1.2 *Use the properties of the spin eigenstates in Eqs. (13.1.8, 13.1.10) and derive the matrix representations of the spin operators in Eq. (13.1.16).*

Solution 13.1.2

The orthonormal spin states $|\alpha\rangle$ *and* $|\beta\rangle$ *satisfy the following equations:*

$$\hat{S}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle \quad ; \quad \hat{S}_z|\beta\rangle = \frac{-\hbar}{2}|\beta\rangle \quad ; \quad \hat{S}_x|\alpha\rangle = \frac{\hbar}{2}|\beta\rangle \quad ; \quad \hat{S}_x|\beta\rangle = \frac{\hbar}{2}|\alpha\rangle \quad ;$$

$$\hat{S}_y|\alpha\rangle = i\frac{\hbar}{2}|\beta\rangle \quad ; \quad \hat{S}_y|\beta\rangle = -i\frac{\hbar}{2}|\alpha\rangle \quad .$$

Hence,

$$S_{z_{\alpha,\alpha}} = \langle\alpha|\hat{S}_z|\alpha\rangle = \langle\alpha|\frac{\hbar}{2}|\alpha\rangle = \frac{\hbar}{2}$$

$$S_{z_{\beta,\alpha}} = \langle\beta|\hat{S}_z|\alpha\rangle = \langle\beta|\frac{\hbar}{2}|\alpha\rangle = 0$$

$$S_{z_{\alpha,\beta}} = \langle\alpha|\hat{S}_z|\beta\rangle = \langle\alpha|\frac{\hbar}{2}|\beta\rangle = 0$$

$$S_{z_{\beta,\beta}} = \langle\beta|\hat{S}_z|\beta\rangle = \langle\beta|\frac{-\hbar}{2}|\beta\rangle = \frac{-\hbar}{2}$$

$$\Rightarrow \mathbf{S}_z = \begin{bmatrix} S_{z_{\alpha,\alpha}} & S_{z_{\alpha,\beta}} \\ S_{z_{\beta,\alpha}} & S_{z_{\beta,\beta}} \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

$$S_{x_{\alpha,\alpha}} = \langle\alpha|\hat{S}_x|\alpha\rangle = \langle\alpha|\frac{\hbar}{2}|\beta\rangle = 0$$

$$S_{x_{\beta,\alpha}} = \langle\beta|\hat{S}_x|\alpha\rangle = \langle\beta|\frac{\hbar}{2}|\beta\rangle = \frac{\hbar}{2}$$

$$S_{x_{\alpha,\beta}} = \langle\alpha|\hat{S}_x|\beta\rangle = \langle\alpha|\frac{\hbar}{2}|\alpha\rangle = \frac{\hbar}{2}$$

$$S_{x_{\beta,\beta}} = \langle\beta|\hat{S}_x|\beta\rangle = \langle\beta|\frac{\hbar}{2}|\alpha\rangle = 0$$

$$\Rightarrow \mathbf{S}_x = \begin{bmatrix} S_{x_{\alpha,\alpha}} & S_{x_{\alpha,\beta}} \\ S_{x_{\beta,\alpha}} & S_{x_{\beta,\beta}} \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},$$

$$S_{y_{\alpha,\alpha}} = \langle\alpha|\hat{S}_y|\alpha\rangle = \langle\alpha|\frac{i\hbar}{2}|\beta\rangle = 0$$

$$S_{y_{\beta,\alpha}} = \langle\beta|\hat{S}_y|\alpha\rangle = \langle\beta|\frac{i\hbar}{2}|\beta\rangle = \frac{i\hbar}{2}$$

$$S_{y_{\alpha,\beta}} = \langle\alpha|\hat{S}_y|\beta\rangle = \langle\alpha|\frac{-i\hbar}{2}|\alpha\rangle = \frac{-i\hbar}{2}$$

$$S_{y_{\beta,\beta}} = \langle\beta|\hat{S}_y|\beta\rangle = \langle\beta|\frac{-i\hbar}{2}|\alpha\rangle = 0$$

$$\Rightarrow \mathbf{S}_y = \begin{bmatrix} S_{y_{\alpha,\alpha}} & S_{y_{\alpha,\beta}} \\ S_{y_{\beta,\alpha}} & S_{y_{\beta,\beta}} \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad .$$

Exercise 13.1.3 *(a) Verify that the commutation relations between the spin operators (Eqs. (13.1.5-13.1.7)) are satisfied by the spin matrices (Eqs. (13.1.16-13.1.17)). (b) Verify that the results in Eqs. (13.1.8, 13.1.10) are obtained by matrix-vector multiplications of the appropriate spin matrices (Eqs. (13.1.16-13.1.17)) on the basis vectors* $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ *and* $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$*, corresponding to the states* $|\alpha\rangle$ *and* $|\beta\rangle$*, respectively.*

Solution 13.1.3

(a)

The commutation relations for the spin operators read

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$$

$$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$$

$$[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x$$

$$[\hat{S}^2, \hat{S}_j] = 0 \qquad \text{for} \qquad j = x, y, z$$

$$[\hat{S}_+, \hat{S}_-] = 2\hbar\hat{S}_z$$

$$[\hat{S}_z, \hat{S}_\pm] = \pm\hbar\hat{S}_\pm$$

$$[\hat{S}^2, \hat{S}_\pm] = 0 \quad .$$

The respective commutation relations between the spin matrices are

$$[\mathbf{S}_x,\mathbf{S}_y]=\frac{\hbar^2}{4}(\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}0&-i\\i&0\end{bmatrix}-\begin{bmatrix}0&-i\\i&0\end{bmatrix}\begin{bmatrix}0&1\\1&0\end{bmatrix})$$

$$=\frac{\hbar^2}{4}(\begin{bmatrix}i&0\\0&-i\end{bmatrix}-\begin{bmatrix}-i&0\\0&i\end{bmatrix})=i\hbar\frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}=i\hbar\mathbf{S}_z\ ,$$

$$[\mathbf{S}_z,\mathbf{S}_x]=\frac{\hbar^2}{4}(\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}0&1\\1&0\end{bmatrix}-\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}1&0\\0&-1\end{bmatrix})$$

$$=\frac{\hbar^2}{4}(\begin{bmatrix}0&1\\-1&0\end{bmatrix}-\begin{bmatrix}0&-1\\1&0\end{bmatrix})=i\hbar\frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}=i\hbar\mathbf{S}_y\,,$$

$$[\mathbf{S}_y,\mathbf{S}_z]=\frac{\hbar^2}{4}(\begin{bmatrix}0&-i\\i&0\end{bmatrix}\begin{bmatrix}1&0\\0&-1\end{bmatrix}-\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}0&-i\\i&0\end{bmatrix})$$

$$=\frac{\hbar^2}{4}(\begin{bmatrix}0&i\\i&0\end{bmatrix}-\begin{bmatrix}0&-i\\-i&0\end{bmatrix})=i\hbar\frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}=i\hbar\mathbf{S}_x\ .$$

Notice that $\mathbf{S}^2$ *is proportional to an identity matrix,*

$$\mathbf{S}^2=\left[\mathbf{S}_x\right]^2+\left[\mathbf{S}_y\right]^2+\left[\mathbf{S}_z\right]^2$$

$$=\frac{\hbar^2}{4}(\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}1&0\\0&-1\end{bmatrix}+\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}0&1\\1&0\end{bmatrix}+\begin{bmatrix}0&-i\\i&0\end{bmatrix}\begin{bmatrix}0&-i\\i&0\end{bmatrix})=\frac{3\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}\ ,$$

and therefore, it commutes with any 2 by 2 matrix. In particular, $[\mathbf{S}^2,\mathbf{S}_j]=0$, *for* $j=x,y,z$.

Defining,

$$\mathbf{S}_+=\mathbf{S}_x+i\mathbf{S}_y=\frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}+i\frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}=\hbar\begin{bmatrix}0&1\\0&0\end{bmatrix}$$

$$\mathbf{S}_-=\mathbf{S}_x-i\mathbf{S}_y=\frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}-i\frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}=\hbar\begin{bmatrix}0&0\\1&0\end{bmatrix}\ ,$$

we obtain

$$[\mathbf{S}_+,\mathbf{S}_-]=\hbar^2\begin{bmatrix}0&1\\0&0\end{bmatrix}\begin{bmatrix}0&0\\1&0\end{bmatrix}-\hbar^2\begin{bmatrix}0&0\\1&0\end{bmatrix}\begin{bmatrix}0&1\\0&0\end{bmatrix}=\hbar^2\begin{bmatrix}1&0\\0&-1\end{bmatrix}=2\hbar\mathbf{S}_z\,,$$

$$[\mathbf{S}_z,\mathbf{S}_+]=\frac{\hbar^2}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}0&1\\0&0\end{bmatrix}-\frac{\hbar^2}{2}\begin{bmatrix}0&1\\0&0\end{bmatrix}\begin{bmatrix}1&0\\0&-1\end{bmatrix}$$

$$=\frac{\hbar^2}{2}\begin{bmatrix}0&1\\0&0\end{bmatrix}-\frac{\hbar^2}{2}\begin{bmatrix}0&-1\\0&0\end{bmatrix}=\hbar^2\begin{bmatrix}0&1\\0&0\end{bmatrix}=\hbar\mathbf{S}_+\ ,$$

$$[\mathbf{S}_z,\mathbf{S}_-]=\frac{\hbar^2}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}0&0\\1&0\end{bmatrix}-\frac{\hbar^2}{2}\begin{bmatrix}0&0\\1&0\end{bmatrix}\begin{bmatrix}1&0\\0&-1\end{bmatrix}$$

$$=\frac{\hbar^2}{2}\begin{bmatrix}0&0\\-1&0\end{bmatrix}-\frac{\hbar^2}{2}\begin{bmatrix}0&0\\1&0\end{bmatrix}=-\hbar^2\begin{bmatrix}0&0\\1&0\end{bmatrix}=-\hbar\mathbf{S}_- \ ,$$

$$[\mathbf{S}^2,\mathbf{S}_\pm]=[\frac{3\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix},\mathbf{S}_\pm]=0.$$

(b)

Using the matrices defined in (a), and the vectors, $\boldsymbol{\alpha}=\begin{pmatrix}1\\0\end{pmatrix}$ *and* $\boldsymbol{\beta}=\begin{pmatrix}0\\1\end{pmatrix}$, *we obtain*

$$\mathbf{S}_z\boldsymbol{\alpha}=\frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\frac{\hbar}{2}\begin{pmatrix}1\\0\end{pmatrix}=\frac{\hbar}{2}\boldsymbol{\alpha} \quad ,$$

$$\mathbf{S}_z\boldsymbol{\beta}=\frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{pmatrix}0\\1\end{pmatrix}=-\frac{\hbar}{2}\begin{pmatrix}0\\1\end{pmatrix}=-\frac{\hbar}{2}\boldsymbol{\beta} \quad ,$$

$$\mathbf{S}^2\boldsymbol{\alpha}=\frac{3\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\frac{3\hbar^2}{4}\begin{pmatrix}1\\0\end{pmatrix}=\frac{3\hbar^2}{4}\boldsymbol{\alpha} \ ,$$

$$\mathbf{S}^2\boldsymbol{\beta}=\frac{3\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\frac{3\hbar^2}{4}\begin{pmatrix}0\\1\end{pmatrix}=\frac{3\hbar^2}{4}\boldsymbol{\beta} \ ,$$

$$\mathbf{S}_+\boldsymbol{\beta}=\hbar\begin{bmatrix}0&1\\0&0\end{bmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\hbar\begin{pmatrix}1\\0\end{pmatrix}=\hbar\boldsymbol{\alpha} \ ,$$

$$\mathbf{S}_+\boldsymbol{\alpha}=\hbar\begin{bmatrix}0&1\\0&0\end{bmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix} \ ,$$

$$\mathbf{S}_-\boldsymbol{\beta}=\hbar\begin{bmatrix}0&0\\1&0\end{bmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix},$$

$$\mathbf{S}_-\boldsymbol{\alpha}=\hbar\begin{bmatrix}0&0\\1&0\end{bmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\hbar\begin{pmatrix}0\\1\end{pmatrix}=\hbar\boldsymbol{\beta} \ ,$$

$$\mathbf{S}_x\boldsymbol{\alpha}=\frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\frac{\hbar}{2}\begin{pmatrix}0\\1\end{pmatrix}=\frac{\hbar}{2}\boldsymbol{\beta} \ ,$$

$$\mathbf{S}_x\boldsymbol{\beta}=\frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\frac{\hbar}{2}\begin{pmatrix}1\\0\end{pmatrix}=\frac{\hbar}{2}\boldsymbol{\alpha} \ ,$$

$$\mathbf{S}_y\boldsymbol{\alpha} = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = i\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = i\frac{\hbar}{2}\boldsymbol{\beta} \ ,$$

$$\mathbf{S}_y\boldsymbol{\beta} = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -i\frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = -i\frac{\hbar}{2}\boldsymbol{\alpha} \ .$$

Exercise 13.2.1 *Consider a system of three identical particles. The three particle space is spanned by the complete set of products of singe particle states,* $|\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes |\varphi_{n_3}\rangle$*, associated with the quantum numbers* n_1, n_2, n_3*, respectively for the particle indexes 1,2, and 3. The permutation between particles 1 and 2 is associated with the operator* $\hat{P}_{1,2}$*, defined as,* $\hat{P}_{1,2}|\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes |\varphi_{n_3}\rangle = |\varphi_{n_2}\rangle \otimes |\varphi_{n_1}\rangle \otimes |\varphi_{n_3}\rangle$*. Show that:*

(a) The operator $\hat{P}_{1,2}$ *is Hermitian, namely* $\langle \chi | \hat{P}_{1,2} | \psi \rangle = \langle \psi | \hat{P}_{1,2} | \chi \rangle^*$*, for any three-particle states,* $|\psi\rangle = \sum_{n_1,n_2,n_3} \psi_{n_1,n_2,n_3} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes |\varphi_{n_3}\rangle$*, and* $|\chi\rangle = \sum_{n_1,n_2,n_3} \chi_{n_1,n_2,n_3} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes |\varphi_{n_3}\rangle$.

(b) The operator $\hat{P}_{1,2}$ *is unitary, namely,* $\left(\hat{P}_{1,2}\right)^\dagger \hat{P}_{1,2} = \hat{I}$.

Solution 13.2.1

(a)

For any two three-particle states, $|\psi\rangle = \sum_{n_1,n_2,n_3} \psi_{n_1,n_2,n_3} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes |\varphi_{n_3}\rangle$*, and* $|\chi\rangle = \sum_{n_1,n_2,n_3} \chi_{n_1,n_2,n_3} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes |\varphi_{n_3}\rangle$*, we obtain*

$$\langle \chi | \hat{P}_{1,2} | \psi \rangle = \sum_{n_1',n_2',n_3'} \chi_{n_1',n_2',n_3'}^* \sum_{n_1,n_2,n_3} \psi_{n_1,n_2,n_3} \langle \varphi_{n_1'} | \otimes \langle \varphi_{n_2'} | \otimes \langle \varphi_{n_3'} | \hat{P}_{1,2} | \varphi_{n_1} \rangle \otimes | \varphi_{n_2} \rangle \otimes | \varphi_{n_3} \rangle$$
$$= \sum_{n_1',n_2',n_3'} \chi_{n_1',n_2',n_3'}^* \sum_{n_1,n_2,n_3} \psi_{n_1,n_2,n_3} \left(\left(\langle \varphi_{n_1'} | \otimes \langle \varphi_{n_2'} | \otimes \langle \varphi_{n_3'} | \right) \left(| \varphi_{n_2} \rangle \otimes | \varphi_{n_1} \rangle \otimes | \varphi_{n_3} \rangle \right) \right)$$
$$= \sum_{n_1',n_2',n_3'} \chi_{n_1',n_2',n_3'}^* \sum_{n_1,n_2,n_3} \psi_{n_1,n_2,n_3} \delta_{n_1',n_2} \delta_{n_2',n_1} \delta_{n_3',n_3}$$

$$= \sum_{n_1,n_2,n_3} \chi_{n_2,n_1,n_3}^* \psi_{n_1,n_2,n_3} \ .$$

Similarly,

$$\langle\psi|\hat{P}_{1,2}|\chi\rangle=\sum_{n_1',n_2',n_3'}\psi_{n_1',n_2',n_3'}{}^*\sum_{n_1,n_2,n_3}\chi_{n_1,n_2,n_3}\left\langle\varphi_{n_1'}\right|\otimes\left\langle\varphi_{n_2'}\right|\otimes\left\langle\varphi_{n_3'}\right|\hat{P}_{1,2}\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle$$
$$=\sum_{n_1,n_2,n_3}\psi_{n_2,n_1,n_3}{}^*\chi_{n_1,n_2,n_3}=\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}{}^*\chi_{n_2,n_1,n_3}$$

$$=\left(\sum_{n_1,n_2,n_3}\chi_{n_2,n_1,n_3}{}^*\psi_{n_1,n_2,n_3}\right)^*.$$

Hence, $\langle\chi|\hat{P}_{1,2}|\psi\rangle=\langle\psi|\hat{P}_{1,2}|\chi\rangle^*$ *(*$\hat{P}_{1,2}$ *is Hermitian) for any* $|\psi\rangle$ *and* $|\chi\rangle$.

(b)

Using (a) we obtain: $\left(\hat{P}_{1,2}\right)^\dagger=\hat{P}_{1,2}\Rightarrow\left(\hat{P}_{1,2}\right)^\dagger\hat{P}_{1,2}=(\hat{P}_{1,2})^2$. *One can readily see that, by definition,* $(\hat{P}_{1,2})^2=\hat{I}$, *and hence* $\left(\hat{P}_{1,2}\right)^\dagger\hat{P}_{1,2}=\hat{I}$,

$$(\hat{P}_{1,2})^2\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle=\hat{P}_{1,2}\hat{P}_{1,2}\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle=\hat{P}_{1,2}\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle$$

$$\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\Rightarrow(\hat{P}_{1,2})^2=\hat{I}\ .$$

Exercise 13.2.2 *A symmetry of a many-particle observable,* $\hat{O}$, *to exchange of particle indexes,* $\hat{O}_{1,\ldots i,\ldots,j,\ldots,N}=\hat{O}_{1,\ldots j,\ldots,i,\ldots,N}$, *means that the following identity holds for any two tensor product basis states:*

$$\begin{aligned}&\left\langle\varphi_{n_1'}\right|\cdots\otimes\left\langle\varphi_{n_i'}\right|\otimes\cdots\otimes\left\langle\varphi_{n_j'}\right|\otimes\cdots\left\langle\varphi_{n_N'}\right|\hat{O}\left|\varphi_{n_1}\right\rangle\cdots\otimes\left|\varphi_{n_i}\right\rangle\otimes\cdots\otimes\left|\varphi_{n_j}\right\rangle\otimes\cdots\left|\varphi_{n_N}\right\rangle\\&=\left\langle\varphi_{n_1'}\right|\cdots\otimes\left\langle\varphi_{n_j'}\right|\otimes\cdots\otimes\left\langle\varphi_{n_i'}\right|\otimes\cdots\left\langle\varphi_{n_N'}\right|\hat{O}\left|\varphi_{n_1}\right\rangle\cdots\otimes\left|\varphi_{n_j}\right\rangle\otimes\cdots\otimes\left|\varphi_{n_i}\right\rangle\otimes\cdots\left|\varphi_{n_N}\right\rangle\end{aligned}.$$

Use the definition of the permutation operator, Eq. (13.2.13), to show that such an observable commutes with any permutation operator, namely $[\hat{P}_{i,j},\hat{O}_{1,\ldots i,\ldots,j,\ldots,N}]=0$.

Solution 13.2.2

Using a generic representation of the operator,

$$\hat{O}_{1,\ldots i,\ldots,j,\ldots,N} = \sum_{\mathbf{n},\mathbf{n}'} O_{\mathbf{n},\mathbf{n}'} \left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right|,$$

and the definition of the permutation operator (Eq. (13.2.13)),

$\hat{P}_{i,j} \left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle = \left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle$*, we obtain*

$$
\begin{aligned}
&[\hat{P}_{i,j}, \hat{O}_{1,\ldots i,\ldots,j,\ldots,N}] \\
&= \sum_{\mathbf{n},\mathbf{n}'} O_{\mathbf{n},\mathbf{n}'} \hat{P}_{i,j} \left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \\
&- \sum_{\mathbf{n},\mathbf{n}'} O_{\mathbf{n},\mathbf{n}'} \left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \hat{P}_{i,j} \\
&= \sum_{\mathbf{n},\mathbf{n}'} O_{n_1,\ldots,n_i,\ldots,n_j,\ldots n_N, n_1',\ldots,n_i',\ldots,n_j',\ldots n_N'} \\
&\left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \\
&- \sum_{\mathbf{n},\mathbf{n}'} O_{n_1,\ldots,n_i,\ldots,n_j,\ldots n_N, n_1',\ldots,n_i',\ldots,n_j',\ldots n_N'} \\
&\left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \quad .
\end{aligned}
$$

Changing indexes in the first summation, we obtain

$$
\begin{aligned}
&[\hat{P}_{i,j}, \hat{O}_{1,\ldots i,\ldots,j,\ldots,N}] = \\
&\sum_{\mathbf{n},\mathbf{n}'} O_{n_1,\ldots,n_j,\ldots,n_i,\ldots n_N, n_1',\ldots,n_j',\ldots,n_i',\ldots n_N'} \\
&\left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \\
&- \sum_{\mathbf{n},\mathbf{n}'} O_{n_1,\ldots,n_i,\ldots,n_j,\ldots n_N, n_1',\ldots,n_i',\ldots,n_j',\ldots n_N'} \\
&\left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \quad .
\end{aligned}
$$

Given the symmetry of $\hat{O}_{1,\ldots i,\ldots,j,\ldots,N}$ *with respect to permutation, namely*

$O_{n_1,\ldots,n_j,\ldots,n_i,\ldots n_N, n_1',\ldots,n_j',\ldots,n_i',\ldots n_N'} = O_{n_1,\ldots,n_i,\ldots,n_j,\ldots n_N, n_1',\ldots,n_i',\ldots,n_j',\ldots n_N'}$*, we obtain*

$$
\begin{aligned}
&[\hat{P}_{i,j}, \hat{O}_{1,\ldots i,\ldots,j,\ldots,N}] = \\
&O_{n_1,\ldots,n_i,\ldots,n_j,\ldots n_N, n_1',\ldots,n_i',\ldots,n_j',\ldots n_N'} \\
&\left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| \\
&- \sum_{\mathbf{n},\mathbf{n}'} O_{n_1,\ldots,n_i,\ldots,n_j,\ldots n_N, n_1',\ldots,n_i',\ldots,n_j',\ldots n_N'} \\
&\left|\varphi_{n_1}\right\rangle \cdots \otimes \left|\varphi_{n_i}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_j}\right\rangle \otimes \cdots \left|\varphi_{n_N}\right\rangle \left\langle\varphi_{n_1'}\right| \cdots \otimes \left\langle\varphi_{n_j'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_i'}\right| \otimes \cdots \left\langle\varphi_{n_N'}\right| = 0 \quad .
\end{aligned}
$$

Exercise 13.2.3 *The operator $\hat{R}_n = \prod_{i,j>i=1}^{N} \left(\hat{P}_{i,j}\right)^{p_{i,j}^{(n)}}$ is a sequence of permutation operators, defined by a specific vector of scalars ($p_{1,2}^{(n)}, p_{1,3}^{(n)}, p_{2,3}^{(n)}, \ldots$) with entries 0 or 1. Each $\hat{R}_n$ corresponds to one of the N! unique arrangements of the particle indexes. The symmetrizer and the anti-symmetrizer operators are defined as sums over all possible arrangements with appropriate coefficients, as follows: $\hat{S}\left|\psi\right\rangle \equiv \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}\hat{R}_n\left|\psi\right\rangle$, and, $\hat{A}\left|\psi\right\rangle \equiv \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}(-1)^{\sum_{i=1}^{N}\sum_{j>i}^{N}p_{i,j}^{(n)}}\hat{R}_n\left|\psi\right\rangle$, respectively. Show that $\hat{P}_{i,j}\hat{S}\left|\psi\right\rangle \equiv \hat{S}\left|\psi\right\rangle$ and $\hat{P}_{i,j}\hat{A}\left|\psi\right\rangle \equiv -\hat{A}\left|\psi\right\rangle$ by showing that the following holds for any tensor product basis vector:*

$$\left\langle \varphi_{n_1}\right|\otimes\left\langle \varphi_{n_2}\right|\otimes\cdots\otimes\left\langle \varphi_{n_N}\right|\hat{P}_{i,j}\hat{S}\left|\psi\right\rangle = \left\langle \varphi_{n_1}\right|\otimes\left\langle \varphi_{n_2}\right|\otimes\cdots\otimes\left\langle \varphi_{n_N}\right|\hat{S}\left|\psi\right\rangle$$

$$\left\langle \varphi_{n_1}\right|\otimes\left\langle \varphi_{n_2}\right|\otimes\cdots\otimes\left\langle \varphi_{n_N}\right|\hat{P}_{i,j}\hat{A}\left|\psi\right\rangle = -\left\langle \varphi_{n_1}\right|\otimes\left\langle \varphi_{n_2}\right|\otimes\cdots\otimes\left\langle \varphi_{n_N}\right|\hat{A}\left|\psi\right\rangle .$$

Solution 13.2.3

A pair permutation, $\hat{P}_{i,j}$, replaces each term $\hat{R}_n\left|\psi\right\rangle$ by $\hat{P}_{i,j}\hat{R}_n\left|\psi\right\rangle$. Since the arrangement of the particle indexes associated with $\hat{P}_{i,j}\hat{R}_n\left|\psi\right\rangle$ is already included in the summation over all possible arrangements, we have: $\hat{P}_{i,j}\hat{R}_n\left|\psi\right\rangle = \hat{R}_{n'}\left|\psi\right\rangle$, where $\hat{R}_{n'} = \prod_{i,j>i=1}^{N}\left(\hat{P}_{i,j}\right)^{p_{i,j}^{(n')}}$.

In the case of the symmetrizer, $\hat{S}\left|\psi\right\rangle \equiv \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}\hat{R}_n\left|\psi\right\rangle$, the different terms in the summation over n are associated with the same coefficient. Since the pair permutation maps the sum over $N!$ arrangements on itself, the total sum is not changed, hence we obtain: $\hat{P}_{i,j}\hat{S}\left|\psi\right\rangle = \hat{S}\left|\psi\right\rangle$.

In the case of the anti-symmetrizer, $\hat{A}\left|\psi\right\rangle \equiv \frac{1}{\sqrt{N!}}\sum_{n=1}^{N!}(-1)^{\sum_{i=1}^{N}\sum_{j>i}^{N}p_{i,j}^{(n)}}\hat{R}_n\left|\psi\right\rangle$, the coefficients of the different terms in the summation are the same only up to their signs, determined by the vectors, $p_{1,2}^{(n)}, p_{1,3}^{(n)}, p_{2,3}^{(n)}, \ldots$, namely: $(-1)^{\sum_{i=1}^{N}\sum_{j>i}^{N}p_{i,j}^{(n)}}$. A permutation $\hat{P}_{i,j}$ maps each arrangement in the summation onto a different arrangement: $\hat{P}_{i,j}\hat{R}_n\left|\psi\right\rangle = \hat{R}_{n'}\left|\psi\right\rangle$. However, the additional permutation *means that the number of non-zero elements in the vector* $p_{1,2}^{(n')}, p_{1,3}^{(n')}, p_{2,3}^{(n')}, \ldots$ *differs by one (can be plus or minus 1) from the number of non-zero elements in the vector* $p_{1,2}^{(n)}, p_{1,3}^{(n)}, p_{2,3}^{(n)}, \ldots$*. Consequently, the coefficient associated with* $\hat{P}_{i,j}\hat{R}_n|\psi\rangle = \hat{R}_{n'}|\psi\rangle$*, namely* $(-1)^{\sum_{i=1}^{N}\sum_{j>i}^{N} p_{i,j}^{(n')}}$*, has an opposite sign from the coefficient associated with* $\hat{R}_n|\psi\rangle$*. Since this applies to all terms in the summation, the pair permutation maps the summation over the* $N!$ *arrangements onto itself, up to a global inverse sign, hence:* $\hat{P}_{i,j}\hat{A}|\psi\rangle = -\hat{A}|\psi\rangle$.

Exercise 13.2.4 *The symmetrizer and antisymmetrizer operators applied to a generic two-particle state,* $|\psi\rangle = \sum_{n_1,n_2} \psi_{n_1,n_2} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle$*, yield,*

$$|\psi_S\rangle = \hat{S}|\psi\rangle = \frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle + \frac{1}{\sqrt{2}}\hat{P}_{1,2}\sum_{n_1,n_2}\psi_{n_1,n_2}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle$$
$$= \frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle + |\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\right)$$

and

$$|\psi_A\rangle = \hat{A}|\psi\rangle = \frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle - \frac{1}{\sqrt{2}}\hat{P}_{1,2}\sum_{n_1,n_2}\psi_{n_1,n_2}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle$$
$$= \frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle - |\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\right) .$$

Show that $\hat{S}|\psi\rangle$ *and* $\hat{A}|\psi\rangle$ *are indeed eigenstates of the permutation operator,* $\hat{P}_{1,2}$ *(Eq. (13.2.23)). What are the corresponding eigenvalues?*

Solution 13.2.4

For $|\psi\rangle = \sum_{n_1,n_2} \psi_{n_1,n_2} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle$ *we have*

$$\hat{S}|\psi\rangle = \frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle + |\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\right),$$

$$\hat{A}|\psi\rangle = \frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle - |\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\right).$$

Applying the permutation, $\hat{P}_{1,2}$, *we obtain*

$$\hat{P}_{1,2}\left(\hat{S}|\psi\rangle\right)=\frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle+|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\right)=\hat{S}|\psi\rangle ,$$

$$\hat{P}_{1,2}\left(\hat{A}|\psi\rangle\right)=\frac{1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle-|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\right)$$

$$=\frac{-1}{\sqrt{2}}\sum_{n_1,n_2}\psi_{n_1,n_2}\left(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle-|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\right)=-\left(\hat{A}|\psi\rangle\right) .$$

Hence, $\hat{P}_{1,2}\left(\hat{S}|\psi\rangle\right)=\hat{S}|\psi\rangle$ *and* $\hat{P}_{1,2}\left(\hat{A}|\psi\rangle\right)=-\left(\hat{A}|\psi\rangle\right)$.

$\hat{S}|\psi\rangle$ *and* $\hat{A}|\psi\rangle$ *are eigenstates of* $\hat{P}_{1,2}$ *with the eigenvalues* 1 *and* -1, *respectively.*

Exercise 13.2.5 *The symmetrizer and antisymmetrizer operators applied to a generic three-particle state,* $|\psi\rangle=\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle$, *yield*

$$\hat{S}|\psi\rangle=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle+|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\otimes|\varphi_{n_3}\rangle+|\varphi_{n_1}\rangle\otimes|\varphi_{n_3}\rangle\otimes|\varphi_{n_2}\rangle$$
$$+|\varphi_{n_3}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle+|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle\otimes|\varphi_{n_1}\rangle+|\varphi_{n_3}\rangle\otimes|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle)$$

$$\hat{A}|\psi\rangle=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle-|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\otimes|\varphi_{n_3}\rangle-|\varphi_{n_1}\rangle\otimes|\varphi_{n_3}\rangle\otimes|\varphi_{n_2}\rangle$$
$$-|\varphi_{n_3}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle+|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle\otimes|\varphi_{n_1}\rangle+|\varphi_{n_3}\rangle\otimes|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle) .$$

Show that $\hat{S}|\psi\rangle$ *and* $\hat{A}|\psi\rangle$ *are indeed eigenstates of the two particle permutation operators,* $\hat{P}_{1,2}$, $\hat{P}_{2,3}$ *and* $\hat{P}_{1,3}$ *(Eq. (13.2.23)). What are the corresponding eigenvalues?*

Solution 13.2.5

For $|\psi\rangle=\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle$ *we have*

$$\hat{S}|\psi\rangle=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes|\varphi_{n_3}\rangle+|\varphi_{n_2}\rangle\otimes|\varphi_{n_1}\rangle\otimes|\varphi_{n_3}\rangle+|\varphi_{n_1}\rangle\otimes|\varphi_{n_3}\rangle\otimes|\varphi_{n_2}\rangle$$

$$+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle) \ ,$$

$$\hat{A}\left|\psi\right\rangle=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle-\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle-\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle$$

$$-\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle) \ .$$

Applying the permutation, $\hat{P}_{1,2}$, $\hat{P}_{2,3}$ *and* $\hat{P}_{1,3}$, *we obtain*

$$\hat{P}_{1,2}\left(\hat{S}\left|\psi\right\rangle\right)=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle$$
$$\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle)=\left(\hat{S}\left|\psi\right\rangle\right)$$

$$\hat{P}_{2,3}\left(\hat{S}\left|\psi\right\rangle\right)=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle$$
$$\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle)=\left(\hat{S}\left|\psi\right\rangle\right)$$

$$\hat{P}_{1,3}\left(\hat{S}\left|\psi\right\rangle\right)=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle$$
$$+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle)=\left(\hat{S}\left|\psi\right\rangle\right)$$

$$\hat{P}_{1,2}\left(\hat{A}\left|\psi\right\rangle\right)=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle-\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle-\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle$$
$$-\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle)=-\left(\hat{A}\left|\psi\right\rangle\right)$$

$$\hat{P}_{2,3}\left(\hat{A}\left|\psi\right\rangle\right)=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle-\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle-\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle$$
$$-\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle+\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle)=-\left(\hat{A}\left|\psi\right\rangle\right)$$

$$\hat{P}_{1,3}\left(\hat{A}\left|\psi\right\rangle\right)=\frac{1}{\sqrt{6}}\sum_{n_1,n_2,n_3}\psi_{n_1,n_2,n_3}(\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle-\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle-\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle$$

$$-\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle+\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle+\left|\varphi_{n_2}\right\rangle\otimes\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_3}\right\rangle)=-\left(\hat{A}\left|\psi\right\rangle\right) \ .$$

As we can see, both $\hat{S}\left|\psi\right\rangle$ *and* $\hat{A}\left|\psi\right\rangle$ *are eigenstates of the permutation operators* $\hat{P}_{1,2}$, $\hat{P}_{2,3}$ *and* $\hat{P}_{1,3}$ *, where* $\hat{S}\left|\psi\right\rangle$ *and* $\hat{A}\left|\psi\right\rangle$ *are associated with the eigenvalues* 1 *and* -1, *respectively.*

Exercise 13.3.1 *The antisymmetrizer $\hat{A}$ is defined in Eq. (13.2.21). (a) Show that $\hat{A}=\hat{A}^{\dagger}$. (b) Given the symmetry of the many-electron Hamiltonian to permutations (Eqs. 13.2.16, 13.2.17), show that the antisymmetrizer commutes with the Hamiltonian, $[\hat{A},\hat{H}_{1,\ldots i,\ldots,j,\ldots,N}]=0$. (c) Show that $\hat{A}^2=\sqrt{N!}\hat{A}$.*

Solution 13.3.1

(a)

To show that $\langle\chi|\hat{A}|\psi\rangle^*=\langle\psi|\hat{A}|\chi\rangle$ for any $|\psi\rangle$ and $|\chi\rangle$, let us expand the many-particle states in a complete orthonormal set of tensor products of orthonormal single particle states (Eq. (13.2.12)),

$$|\psi\rangle=\sum_{n_1,n_2,\ldots,n_N}\psi_{n_1,n_2,\ldots,n_N}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes\cdots\otimes|\varphi_{n_N}\rangle,$$

$$|\chi\rangle=\sum_{n_1,n_2,\ldots,n_N}\chi_{n_1,n_2,\ldots,n_N}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes\cdots\otimes|\varphi_{n_N}\rangle.$$

In this representation,

$$\langle\chi|\hat{A}|\psi\rangle=\sum_{n_1,n_2,\ldots,n_N}\sum_{n_1',n_2',\ldots,n_N'}\chi^*_{n_1',n_2',\ldots,n_N'}\psi_{n_1,n_2,\ldots,n_N}$$
$$\langle\varphi_{n_1'}|\otimes\langle\varphi_{n_2'}|\otimes\cdots\otimes\langle\varphi_{n_N'}|\hat{A}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes\cdots\otimes|\varphi_{n_N}\rangle\ .$$

By its definition, the anti-symmetrizer maps each product state, $|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes\cdots\otimes|\varphi_{n_N}\rangle$, onto a determinant, $\hat{A}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes\cdots\otimes|\varphi_{n_N}\rangle$, which is a normalized linear combination of $N!$ product states, each associated with a different arrangement of the single particle indexes. Using the orthonormality of the single-particle basis, the matrix elements of $\hat{A}$ obtain the form

$$\langle\varphi_{n_1'}|\otimes\langle\varphi_{n_2'}|\otimes\cdots\otimes\langle\varphi_{n_N'}|\hat{A}|\varphi_{n_1}\rangle\otimes|\varphi_{n_2}\rangle\otimes\cdots\otimes|\varphi_{n_N}\rangle$$
$$=\frac{(-1)^p}{\sqrt{N!}}\begin{cases}\delta_{\{n_1,n_2,\ldots,n_N\},\{n_1',n_2',\ldots,n_N'\}} & ;\quad i\neq j\Rightarrow n_i\neq n_j\\ 0 & ;\quad otherwise\end{cases}.$$

Namely, the result is zero unless the indexes $n_1, n_2, ..., n_N$ *are all different from one another, and the sets of indexes* $\{ n_1, n_2, ..., n_N \}$ *and* $\{ n_1', n_2', ..., n_N' \}$ *are identical. When these conditions hold, the determinant,* $\hat{A}\left|\varphi_{n_1}\right\rangle \otimes \left|\varphi_{n_2}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N}\right\rangle$, *contains a product term which corresponds precisely to the state,* $\left|\varphi_{n_1'}\right\rangle \otimes \left|\varphi_{n_2'}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N'}\right\rangle$. *The non-zero contribution is therefore either* $1/\sqrt{N!}$ *or* $-1/\sqrt{N!}$ *, depending on the parity of the permutation which maps* $\left|\varphi_{n_1}\right\rangle \otimes \left|\varphi_{n_2}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N}\right\rangle$ *onto* $\left|\varphi_{n_1'}\right\rangle \otimes \left|\varphi_{n_2'}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N'}\right\rangle$. *Given this result, we can see that*

$$\left\langle\varphi_{n_1'}\right| \otimes \left\langle\varphi_{n_2'}\right| \otimes \cdots \otimes \left\langle\varphi_{n_N'}\right| \hat{A} \left|\varphi_{n_1}\right\rangle \otimes \left|\varphi_{n_2}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N}\right\rangle$$

$$= \left\langle\varphi_{n_1}\right| \otimes \left\langle\varphi_{n_2}\right| \otimes \cdots \otimes \left\langle\varphi_{n_N}\right| \hat{A} \left|\varphi_{n_1'}\right\rangle \otimes \left|\varphi_{n_2'}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N'}\right\rangle ,$$

where we use the fact that the permutation operators are unitary (Ex. 13.2.1 (b)), and therefore, the permutation that maps $\left|\varphi_{n_1'}\right\rangle \otimes \left|\varphi_{n_2'}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N'}\right\rangle$ *onto* $\left|\varphi_{n_1}\right\rangle \otimes \left|\varphi_{n_2}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N}\right\rangle$ *is the Hermitian conjugate of the permutation that maps* $\left|\varphi_{n_1}\right\rangle \otimes \left|\varphi_{n_2}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N}\right\rangle$ *onto* $\left|\varphi_{n_1'}\right\rangle \otimes \left|\varphi_{n_2'}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N'}\right\rangle$ *(a reversed sequence of pair permutations), which implies that the parity of these two permutations is the same. Substitution in the expression for* $\langle \chi | \hat{A} | \psi \rangle$ *we readily obtain,*

$$\langle \chi | \hat{A} | \psi \rangle^* = \sum_{n_1, n_2, ..., n_N} \sum_{n_1', n_2', ..., n_N'} \chi_{n_1', n_2', ..., n_N'} \psi^*_{n_1, n_2, ..., n_N}$$

$$\left\langle\varphi_{n_1}\right| \otimes \left\langle\varphi_{n_2}\right| \otimes \cdots \otimes \left\langle\varphi_{n_N}\right| \hat{A} \left|\varphi_{n_1'}\right\rangle \otimes \left|\varphi_{n_2'}\right\rangle \otimes \cdots \otimes \left|\varphi_{n_N'}\right\rangle = \langle \psi | \hat{A} | \chi \rangle .$$

Hence, the anti-symmetrizer ($\hat{A}$ *) is Hermitian.*

(b)

Using the representation of the anti-symmetrizer as a linear combination of sequences of pair permutations (Eq. (13.2.21)) and the commutativity of each pair permutation with the Hamiltonian of a system of identical articles (Eqs. (13.2.16, 13.2.17)), $[\hat{P}_{i,j}, \hat{H}_{1,...i,...,j,...,N}] = 0$, *we readily obtain* $\hat{A}\hat{H}_{1,...i,...,j,...,N} \left|\psi\right\rangle = \hat{H}_{1,...i,...,j,...,N} \hat{A} \left|\psi\right\rangle$, *and hence,* $[\hat{A}, \hat{H}_{1,...i,...,j,...,N}] = 0$.

(c)

Considering again a generic expansion of any many-particle state in tensor products of the single particle basis states (Eq. (13.2.12)): $|\psi\rangle = \sum_{n_1,n_2,...,n_N} \psi_{n_1,n_2,...,n_N} |\varphi_{n_1}\rangle \otimes |\varphi_{n_2}\rangle \otimes \cdots \otimes |\varphi_{n_N}\rangle$*, it is sufficient to consider a single product state. By its definition the anti-symmetrizer maps a product state onto a normalized linear combination of* $N!$ *product states, each associated with a different arrangement of the single particle indexes, namely* $\hat{A}|\psi\rangle = \frac{1}{\sqrt{N!}}\left[N!\ \ products\right]$*. A consecutive operation of* $\hat{A}$ *onto each one of these* $N!$ *product states would map it onto a normalized linear combination of* $N!$ *product states. However, these linear combinations would be identical copies, such that the outcome of* $\hat{A}\hat{A}|\psi\rangle$ *reads*

$$\hat{A}\hat{A}|\psi\rangle = \frac{1}{\sqrt{N!}}\hat{A}\left[N!\ \ products\right] = \frac{1}{\sqrt{N!}}N!\cdot\left(\frac{1}{\sqrt{N!}}\left[N!\ \ products\right]\right) = \left[N!\ \ products\right].$$

Comparing to $\hat{A}|\psi\rangle$*, we obtain the relation,* $\hat{A}\hat{A}|\psi\rangle = \sqrt{N!}\hat{A}|\psi\rangle$.

Exercise 13.3.2 *Given the antisymmetrizer,* $\hat{A}$, the single particle operators in the j th particle subspaces, $\{\hat{h}_j\}$, and the pair interactions $\{\hat{w}_{j,j'}\}$ in the subspace of the j th and j'th particles, prove the following identities*:*

(a)

$$\left(\langle\tilde{\Phi}_1|\otimes\cdots\otimes\langle\delta\tilde{\Phi}_k|\otimes\cdots\otimes\langle\tilde{\Phi}_N|\right)\hat{A}\left(|\tilde{\Phi}_1\rangle\otimes|\tilde{\Phi}_2\rangle\otimes\cdots\otimes|\tilde{\Phi}_N\rangle\right) = \frac{1}{\sqrt{N!}}\langle\delta\tilde{\Phi}_k|\tilde{\Phi}_k\rangle$$

(b)

$$\left(\langle\tilde{\Phi}_1|\otimes\cdots\otimes\langle\delta\tilde{\Phi}_j|\otimes\cdots\otimes\langle\tilde{\Phi}_N|\right)\sum_{j'=1}^{N}\hat{h}_{j'}\hat{A}\left(|\tilde{\Phi}_1\rangle\otimes|\tilde{\Phi}_2\rangle\otimes\cdots\otimes|\tilde{\Phi}_N\rangle\right)$$
$$= \frac{1}{\sqrt{N!}}[\sum_{\substack{j'=1\\(j'\neq j)}}^{N}\langle\tilde{\Phi}_{j'}|\hat{h}_{j'}|\tilde{\Phi}_{j'}\rangle]\langle\delta\tilde{\Phi}_j|\tilde{\Phi}_j\rangle + \frac{1}{\sqrt{N!}}\langle\delta\tilde{\Phi}_j|\hat{h}_j|\tilde{\Phi}_j\rangle$$

(c)

$$\left(\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\right)\sum_{j'>j"=1}^{N}\hat{w}_{j',j"}\hat{A}\left(\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle\right)$$
$$=\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_j\middle|\tilde{\Phi}_j\right\rangle[\sum_{\substack{j'>j"=1\\ j',j"\neq j}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j"}\right|\hat{w}_{j',j"}\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_{j"}\right\rangle-\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j"}\right|\hat{w}_{j',j"}\left|\tilde{\Phi}_{j"}\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle]$$
$$+\frac{1}{\sqrt{N!}}\sum_{j'\neq j=1}^{N}[\left\langle\delta\tilde{\Phi}_j\right|\otimes\left\langle\tilde{\Phi}_{j'}\right|\hat{w}_{j,j'}\left|\tilde{\Phi}_j\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle-\left\langle\delta\tilde{\Phi}_j\right|\otimes\left\langle\tilde{\Phi}_{j'}\right|\hat{w}_{j,j'}\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_j\right\rangle]$$

Use the identities, (a), (b) and (c), and Eqs. (13.3.8, 13.3.12) to show that

$$\left\langle\delta\tilde{\Phi}_k\right|\hat{h}_k\left|\tilde{\Phi}_k\right\rangle+\sum_{j=1}^{N}[\left\langle\delta\tilde{\Phi}_k\right|\otimes\left\langle\tilde{\Phi}_j\right|\hat{w}_{k,j}\left[\left|\tilde{\Phi}_k\right\rangle\otimes\left|\tilde{\Phi}_j\right\rangle-\left|\tilde{\Phi}_j\right\rangle\otimes\left|\tilde{\Phi}_k\right\rangle\right]=\varepsilon_k\left\langle\delta\tilde{\Phi}_k\middle|\tilde{\Phi}_k\right\rangle,\ \textit{where,}$$

$$\varepsilon_k=\varepsilon-\sum_{j'\neq k=1}^{N}\left\langle\tilde{\Phi}_{j'}\right|\hat{h}_{j'}\left|\tilde{\Phi}_{j'}\right\rangle$$
$$-\sum_{\substack{j'>j"=1\\ j',j"\neq k}}^{N}[\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j"}\right|\hat{w}_{j',j"}\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_{j"}\right\rangle-\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j"}\right|\hat{w}_{j',j"}\left|\tilde{\Phi}_{j"}\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle]$$

Solution 13.3.2

(a)

By its definition, the anti-symmetrizer $\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$ *maps the product state onto a normalized linear combination of* $N!$ *product states, each associated with a different arrangement of the single particle indexes. The orthonormality of the single-particle basis,* $\left\langle\tilde{\Phi}_n\middle|\tilde{\Phi}_{n'}\right\rangle=\delta_{n,n'}$ *means that all the arrangements have zero overlap with the state* $\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_k\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|$, *except for the term,* $\frac{1}{\sqrt{N!}}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$, *which yields*

$$\left(\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_k\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\right)\hat{A}\left(\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle\right)=\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_k\middle|\tilde{\Phi}_k\right\rangle.$$

(b)

Considering again the $N!$ *products expansion obtained by the anti-symmetrizer operation on a product state,* $\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$, *and the orthonormality of the single-particle basis states,* $\left\langle\tilde{\Phi}_k\middle|\tilde{\Phi}_{k'}\right\rangle=\delta_{k,k'}$; $\left.\left\langle\delta\tilde{\Phi}_k\middle|\tilde{\Phi}_{k'}\right\rangle\right|_{k\neq k'}=0$, *we notice that the only arrangement in the expansion*

$\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$ *that gives non-zero overlap with the bra,* $\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\hat{h}_{j'}$, *is,* $\frac{1}{\sqrt{N!}}\left|\tilde{\Phi}_1\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_{j'}\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$.

For $j = j'$, *the result is*

$$\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\hat{h}_j\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle=\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_j\right|\hat{h}_j\left|\tilde{\Phi}_j\right\rangle,$$

whereas for $j \neq j'$, *the result is*

$$\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\hat{h}_{j'}\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle=\frac{1}{\sqrt{N!}}\left\langle\tilde{\Phi}_{j'}\right|\hat{h}_{j'}\left|\tilde{\Phi}_{j'}\right\rangle\left\langle\delta\tilde{\Phi}_j\right|\tilde{\Phi}_j\right\rangle.$$

Consequently, we obtain

$$\left(\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\right)\sum_{j'=1}^{N}\hat{h}_{j'}\hat{A}\left(\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle\right)$$

$$=\frac{1}{\sqrt{N!}}[\sum_{\substack{j'=1\\(j'\neq j)}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\hat{h}_{j'}\left|\tilde{\Phi}_{j'}\right\rangle]\left\langle\delta\tilde{\Phi}_j\right|\tilde{\Phi}_j\right\rangle+\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_j\right|\hat{h}_j\left|\tilde{\Phi}_j\right\rangle .$$

(c)

Considering again the $N!$ *products expansion obtained by the anti-symmetrizer operation* $\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$, *and the orthonormality of the single-particle basis states,* $\left\langle\tilde{\Phi}_k\middle|\tilde{\Phi}_{k'}\right\rangle=\delta_{k,k'}$; $\left\langle\delta\tilde{\Phi}_k\middle|\tilde{\Phi}_{k'}\right\rangle\Big|_{k\neq k'}=0$, *we notice that there are only two arrangements in the expansion* $\hat{A}\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle$ *that give non-zero overlap with the bra* $\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\hat{w}_{j',j''}$. *Their sum is:*

$$\frac{1}{\sqrt{N!}}(\left|\tilde{\Phi}_1\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_{j'}\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_{j''}\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle-\left|\tilde{\Phi}_1\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_{j''}\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_{j'}\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle)$$

. (Notice that these arrangements differ by a single permutation and therefore their coefficients are of opposite signs.)

If $j \neq j'$ *and* $j \neq j''$, *we obtain in this case*

$$\langle\tilde\Phi_1|\otimes\cdots\otimes\langle\delta\tilde\Phi_j|\otimes\cdots\otimes\langle\tilde\Phi_N|\hat w_{j',j''}\hat A|\tilde\Phi_1\rangle\otimes|\tilde\Phi_2\rangle\otimes\cdots\otimes|\tilde\Phi_N\rangle$$

$$\frac{1}{\sqrt{N!}}\langle\delta\tilde\Phi_j|\tilde\Phi_j\rangle[\langle\tilde\Phi_{j'}|\otimes\langle\tilde\Phi_{j''}|\hat w_{j',j''}|\tilde\Phi_{j'}\rangle\otimes|\tilde\Phi_{j''}\rangle-\langle\tilde\Phi_{j'}|\otimes\langle\tilde\Phi_{j''}|\hat w_{j',j''}|\tilde\Phi_{j''}\rangle\otimes|\tilde\Phi_{j'}\rangle] \ .$$

If j coincides with j', we obtain:

$$\langle\tilde\Phi_1|\otimes\cdots\otimes\langle\delta\tilde\Phi_j|\otimes\cdots\otimes\langle\tilde\Phi_N|\hat w_{j,j''}\hat A|\tilde\Phi_1\rangle\otimes|\tilde\Phi_2\rangle\otimes\cdots\otimes|\tilde\Phi_N\rangle$$

$$=\frac{1}{\sqrt{N!}}\langle\delta\tilde\Phi_j|\otimes\langle\tilde\Phi_{j''}|\hat w_{j,j''}|\tilde\Phi_j\rangle\otimes|\tilde\Phi_{j''}\rangle-\frac{1}{\sqrt{N!}}\langle\delta\tilde\Phi_j|\otimes\langle\tilde\Phi_{j''}|\hat w_{j,j''}|\tilde\Phi_{j''}\rangle\otimes|\tilde\Phi_j\rangle \ ,$$

and if j coincides with j'', we obtain:

$$\langle\tilde\Phi_1|\otimes\cdots\otimes\langle\delta\tilde\Phi_j|\otimes\cdots\otimes\langle\tilde\Phi_N|\hat w_{j',j}\hat A|\tilde\Phi_1\rangle\otimes|\tilde\Phi_2\rangle\otimes\cdots\otimes|\tilde\Phi_N\rangle$$
$$=\frac{1}{\sqrt{N!}}\langle\tilde\Phi_{j'}|\otimes\langle\delta\tilde\Phi_j|\hat w_{j',j}|\tilde\Phi_{j'}\rangle\otimes|\tilde\Phi_j\rangle-\frac{1}{\sqrt{N!}}\langle\tilde\Phi_{j'}|\otimes\langle\delta\tilde\Phi_j|\hat w_{j',j}|\tilde\Phi_j\rangle\otimes|\tilde\Phi_{j'}\rangle$$
$$=\frac{1}{\sqrt{N!}}\langle\delta\tilde\Phi_j|\otimes\langle\tilde\Phi_{j'}|\hat w_{j,j'}|\tilde\Phi_j\rangle\otimes|\tilde\Phi_{j'}\rangle-\frac{1}{\sqrt{N!}}\langle\delta\tilde\Phi_j|\otimes\langle\tilde\Phi_{j'}|\hat w_{j,j'}|\tilde\Phi_{j'}\rangle\otimes|\tilde\Phi_j\rangle \ ,$$

where in the last step we changed the ordering of the two single-particle subspaces.

Consequently, we obtain

$$\left(\langle\tilde\Phi_1|\otimes\cdots\otimes\langle\delta\tilde\Phi_j|\otimes\cdots\otimes\langle\tilde\Phi_N|\right)\sum_{j''>j'=1}^{N}\hat w_{j',j''}\hat A\left(|\tilde\Phi_1\rangle\otimes|\tilde\Phi_2\rangle\otimes\cdots\otimes|\tilde\Phi_N\rangle\right)$$
$$=\frac{1}{\sqrt{N!}}\langle\delta\tilde\Phi_j|\tilde\Phi_j\rangle[\sum_{\substack{j''>j'=1\\ j',j''\neq j}}^{N}\langle\tilde\Phi_{j'}|\otimes\langle\tilde\Phi_{j''}|\hat w_{j',j''}|\tilde\Phi_{j'}\rangle\otimes|\tilde\Phi_{j''}\rangle-\langle\tilde\Phi_{j'}|\otimes\langle\tilde\Phi_{j''}|\hat w_{j',j''}|\tilde\Phi_{j''}\rangle\otimes|\tilde\Phi_{j'}\rangle]$$
$$+\frac{1}{\sqrt{N!}}\sum_{\substack{j'=1\\ j'\neq j}}^{N}[\langle\delta\tilde\Phi_j|\otimes\langle\tilde\Phi_{j'}|\hat w_{j,j'}|\tilde\Phi_j\rangle\otimes|\tilde\Phi_{j'}\rangle-\langle\delta\tilde\Phi_j|\otimes\langle\tilde\Phi_{j'}|\hat w_{j,j'}|\tilde\Phi_{j'}\rangle\otimes|\tilde\Phi_j\rangle] \ .$$

Using $\hat H=\sum_{j=1}^{N}\hat h_j+\sum_{j'>j=1}^{N}\hat w_{j,j'}$, *Eq. (13.3.12) yields*

$$\left(\langle\tilde\Phi_1|\otimes\cdots\otimes\langle\delta\tilde\Phi_k|\otimes\cdots\otimes\langle\tilde\Phi_N|\right)(\sum_{j=1}^{N}\hat h_j+\sum_{j'>j=1}^{N}\hat w_{j,j'}-\varepsilon)\hat A\left(|\tilde\Phi_1\rangle\otimes|\tilde\Phi_2\rangle\otimes\cdots\otimes|\tilde\Phi_N\rangle\right)=0 \,.$$

Using the identities, (a), (b) and (c), we obtain

$$\left(\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\right)\sum_{j'=1}^{N}\hat{h}_{j'}\hat{A}\left(\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle\right)$$
$$+\left(\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\right)\sum_{j''>j'=1}^{N}\hat{w}_{j',j''}\hat{A}\left(\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle\right)$$
$$-\varepsilon\left(\left\langle\tilde{\Phi}_1\right|\otimes\cdots\otimes\left\langle\delta\tilde{\Phi}_j\right|\otimes\cdots\otimes\left\langle\tilde{\Phi}_N\right|\right)\hat{A}\left(\left|\tilde{\Phi}_1\right\rangle\otimes\left|\tilde{\Phi}_2\right\rangle\otimes\cdots\otimes\left|\tilde{\Phi}_N\right\rangle\right)$$
$$=\frac{1}{\sqrt{N!}}[\sum_{\substack{j'=1\\(j'\neq j)}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\hat{h}_{j'}\left|\tilde{\Phi}_{j'}\right\rangle]\left\langle\delta\tilde{\Phi}_j\middle|\tilde{\Phi}_j\right\rangle+\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_j\right|\hat{h}_j\left|\tilde{\Phi}_j\right\rangle$$
$$+\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_j\middle|\tilde{\Phi}_j\right\rangle[\sum_{\substack{j''>j'=1\\j',j''\neq j}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j''}\right|\hat{w}_{j',j''}\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_{j''}\right\rangle-\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j''}\right|\hat{w}_{j',j''}\left|\tilde{\Phi}_{j''}\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle]$$
$$+\frac{1}{\sqrt{N!}}\sum_{\substack{j'=1\\j'\neq j}}^{N}[\left\langle\delta\tilde{\Phi}_j\right|\otimes\left\langle\tilde{\Phi}_{j'}\right|\hat{w}_{j,j'}\left|\tilde{\Phi}_j\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle-\left\langle\delta\tilde{\Phi}_j\right|\otimes\left\langle\tilde{\Phi}_{j'}\right|\hat{w}_{j,j'}\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_j\right\rangle]$$
$$-\varepsilon\frac{1}{\sqrt{N!}}\left\langle\delta\tilde{\Phi}_j\middle|\tilde{\Phi}_j\right\rangle=0\ .$$

Therefore,

$$\left\{\left[\sum_{\substack{j'=1\\(j'\neq j)}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\hat{h}_{j'}\left|\tilde{\Phi}_{j'}\right\rangle\right]+\left[\sum_{\substack{j''>j'=1\\j',j''\neq j}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j''}\right|\hat{w}_{j',j''}\left(\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_{j''}\right\rangle-\left|\tilde{\Phi}_{j''}\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle\right)\right]-\varepsilon\right\}\left\langle\delta\tilde{\Phi}_j\middle|\tilde{\Phi}_j\right\rangle$$
$$+\left\langle\delta\tilde{\Phi}_j\right|\hat{h}_j\left|\tilde{\Phi}_j\right\rangle+\sum_{\substack{j'=1\\j'\neq j}}^{N}[\left\langle\delta\tilde{\Phi}_j\right|\otimes\left\langle\tilde{\Phi}_{j'}\right|\hat{w}_{j,j'}\left(\left|\tilde{\Phi}_j\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle-\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_j\right\rangle\right)]=0.$$

Defining, $\varepsilon_j\equiv\varepsilon-\sum_{\substack{j'=1\\(j'\neq j)}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\hat{h}_{j'}\left|\tilde{\Phi}_{j'}\right\rangle-\sum_{\substack{j''>j'=1\\j',j''\neq j}}^{N}\left\langle\tilde{\Phi}_{j'}\right|\otimes\left\langle\tilde{\Phi}_{j''}\right|\hat{w}_{j',j''}\left(\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_{j''}\right\rangle-\left|\tilde{\Phi}_{j''}\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle\right)$,

we obtain

$$\left\langle\delta\tilde{\Phi}_j\right|\hat{h}_j\left|\tilde{\Phi}_j\right\rangle+\sum_{\substack{j'=1\\j'\neq j}}^{N}[\left\langle\delta\tilde{\Phi}_j\right|\otimes\left\langle\tilde{\Phi}_{j'}\right|\hat{w}_{j,j'}\left(\left|\tilde{\Phi}_j\right\rangle\otimes\left|\tilde{\Phi}_{j'}\right\rangle-\left|\tilde{\Phi}_{j'}\right\rangle\otimes\left|\tilde{\Phi}_j\right\rangle\right)]=\varepsilon_j\left\langle\delta\tilde{\Phi}_j\middle|\tilde{\Phi}_j\right\rangle.$$

Exercise 13.3.3 *Use the product form of each spin-orbital (Eq. (13.3.16)) to obtain Eq. (13.3.17) from Eq. (13.3.15).*

Solution 13.3.3

Using $\left|\tilde{\Phi}_j\right\rangle \equiv \left|\tilde{\varphi}_j\right\rangle \otimes \left|m_{s,j}\right\rangle$ *for the single-particle states in Eq. (13.3.17), we obtain*

$$\begin{aligned}&\left\langle \delta\tilde{\varphi}_k\right|\left\langle m_{s,k}\right|\{\ \hat{h}_k-\varepsilon_k\\&+\sum_{j=1}^{N}\ [\hat{I}\otimes\left\langle\tilde{\varphi}_j\right|\left\langle m_{s,j}\right|]\hat{w}_{k,j}[\hat{I}\otimes\left|\tilde{\varphi}_j\right\rangle\left|m_{s,j}\right\rangle]-[\hat{I}\otimes\left\langle\tilde{\varphi}_j\right|\left\langle m_{s,j}\right|]\hat{w}_{k,j}[\left|\tilde{\varphi}_j\right\rangle\left|m_{s,j}\right\rangle\otimes\hat{I}]\ \}\left|\tilde{\varphi}_k\right\rangle\left|m_{s,k}\right\rangle=0\,.\end{aligned}$$

Using the fact that $\hat{w}_{k,j}$ *does not operate in the spin space and using the orthonormality of the spin functions in each single particle space, we obtain*

$$\begin{aligned}&\left\langle \delta\tilde{\varphi}_k\right|\left\langle m_{s,k}\right|\hat{h}_k-\varepsilon_k\left|\tilde{\varphi}_k\right\rangle\left|m_{s,k}\right\rangle\\&+\sum_{j=1}^{N}\ \left\langle \delta\tilde{\varphi}_k\right|\left\langle m_{s,k}\right|[\hat{I}\otimes\left\langle\tilde{\varphi}_j\right|\left\langle m_{s,j}\right|]\hat{w}_{k,j}[\hat{I}\otimes\left|\tilde{\varphi}_j\right\rangle\left|m_{s,j}\right\rangle]\left|\tilde{\varphi}_k\right\rangle\left|m_{s,k}\right\rangle\\&-\left\langle \delta\tilde{\varphi}_k\right|\left\langle m_{s,k}\right|[\hat{I}\otimes\left\langle\tilde{\varphi}_j\right|\left\langle m_{s,j}\right|]\hat{w}_{k,j}[\left|\tilde{\varphi}_j\right\rangle\left|m_{s,j}\right\rangle\otimes\hat{I}]\left|\tilde{\varphi}_k\right\rangle\left|m_{s,k}\right\rangle=0\\&\Rightarrow\\&\left\langle \delta\tilde{\varphi}_k\right|\hat{h}_k-\varepsilon_k\left|\tilde{\varphi}_k\right\rangle\\&+\sum_{j=1}^{N}\ (\left[\left\langle \delta\tilde{\varphi}_k\right|\left\langle m_{s,k}\right|\otimes\left\langle\tilde{\varphi}_j\right|\left\langle m_{s,j}\right|\right]\hat{w}_{k,j}\left[\left|\tilde{\varphi}_k\right\rangle\left|m_{s,k}\right\rangle\otimes\left|\tilde{\varphi}_j\right\rangle\left|m_{s,j}\right\rangle\right]\\&-\left[\left\langle \delta\tilde{\varphi}_k\right|\left\langle m_{s,k}\right|\otimes\left\langle\tilde{\varphi}_j\right|\left\langle m_{s,j}\right|\right]\hat{w}_{k,j}\left[\left|\tilde{\varphi}_j\right\rangle\left|m_{s,j}\right\rangle\otimes\left|\tilde{\varphi}_k\right\rangle\left|m_{s,k}\right\rangle\right])=0\\&\Rightarrow\\&\left\langle \delta\tilde{\varphi}_k\right|\hat{h}_k-\varepsilon_k\left|\tilde{\varphi}_k\right\rangle\\&+\sum_{j=1}^{N}\ (\left[\left\langle \delta\tilde{\varphi}_k\right|\otimes\left\langle\tilde{\varphi}_j\right|\right]\hat{w}_{k,j}\left[\left|\tilde{\varphi}_k\right\rangle\otimes\left|\tilde{\varphi}_j\right\rangle\right]\\&-\delta_{m_{s,j},m_{s,k}}\left[\left\langle \delta\tilde{\varphi}_k\right|\otimes\left\langle\tilde{\varphi}_j\right|\right]\hat{w}_{k,j}\left[\left|\tilde{\varphi}_j\right\rangle\otimes\left|\tilde{\varphi}_k\right\rangle\right])=0\end{aligned}$$

$$\Rightarrow\left\langle \delta\tilde{\varphi}_k\right|\left[\hat{h}_k-\varepsilon_k+\sum_{j=1}^{N}\ \left[\hat{I}\otimes\left\langle\tilde{\varphi}_j\right|\right]\hat{w}_{k,j}\left[\hat{I}\otimes\left|\tilde{\varphi}_j\right\rangle\right]-\delta_{m_{s,j},m_{s,k}}\left[\hat{I}\otimes\left\langle\tilde{\varphi}_j\right|\right]\hat{w}_{k,j}\left[\left|\tilde{\varphi}_j\right\rangle\otimes\hat{I}\right]\right]\left|\tilde{\varphi}_k\right\rangle=0\,.$$

Exercise 13.3.4 *The operator* $\hat{w}_{k,j}$ *is a two-particle operator confined to the subspace of the* k *th and* j *th particles, which is diagonal in the two-particle coordinate representation, namely*

$$\left[\left\langle\phi_{\mathbf{r}}\right|\right]_k\otimes\left[\left\langle\phi_{\mathbf{r}'}\right|\right]_j\cdot\hat{w}_{k,j}\cdot\left[\left|\phi_{\mathbf{r}''}\right\rangle\right]_k\otimes\left[\left|\phi_{\mathbf{r}'''}\right\rangle\right]_j=\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}\delta(\mathbf{r}-\mathbf{r}'')\delta(\mathbf{r}'-\mathbf{r}''')\,.$$

Introducing identity operators in the corresponding single-particle subspaces, $\left[\hat{I}_{\mathbf{r}}\right]_k \otimes \left[\hat{I}_{\mathbf{r}}\right]_j \cdot \hat{w}_{k,j} \cdot \left[\hat{I}_{\mathbf{r}}\right]_k \otimes \left[\hat{I}_{\mathbf{r}}\right]_j$*, derive Eq. (13.3.21) for* $\hat{w}_{k,j}$*.*

Solution 13.3.4

Using the short notation $|\phi_{\mathbf{r}}\rangle \equiv |\mathbf{r}\rangle$ *for a position eigenstate, an identity in the single particle space reads* $\hat{I}_r = \int d\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}|$*. Introducing identity operators in the single particle subspaces we obtain*

$$\begin{aligned}\hat{w}_{k,j} &= \left[\hat{I}_{\mathbf{r}}\right]_k \otimes \left[\hat{I}_{\mathbf{r}}\right]_j \cdot \hat{w}_{k,j} \cdot \left[\hat{I}_{\mathbf{r}}\right]_k \otimes \left[\hat{I}_{\mathbf{r}}\right]_j \\ &= \int d\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}| \otimes \int d\mathbf{r}'|\mathbf{r}'\rangle\langle\mathbf{r}'|\hat{w}_{k,j}\int d\mathbf{r}''|\mathbf{r}''\rangle\langle\mathbf{r}''| \otimes \int d\mathbf{r}'''|\mathbf{r}'''\rangle\langle\mathbf{r}'''| \\ &= \int d\mathbf{r}\int d\mathbf{r}'\int d\mathbf{r}''\int d\mathbf{r}'''|\mathbf{r}\rangle\otimes|\mathbf{r}'\rangle\left[\langle\mathbf{r}|\otimes\langle\mathbf{r}'|\hat{w}_{k,j}|\mathbf{r}''\rangle\otimes|\mathbf{r}'''\rangle\right]\langle\mathbf{r}''|\otimes\langle\mathbf{r}'''| \ .\end{aligned}$$

Using the representation of the Coulomb interaction in the position representation,

$$\langle\mathbf{r}|\otimes\langle\mathbf{r}'|\hat{w}_{k,j}|\mathbf{r}''\rangle\otimes|\mathbf{r}'''\rangle = \langle\mathbf{r}|\otimes\langle\mathbf{r}'|\frac{Ke^2}{|\hat{\mathbf{r}}-\hat{\mathbf{r}}'|}|\mathbf{r}''\rangle\otimes|\mathbf{r}'''\rangle = \frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}\delta(\mathbf{r}-\mathbf{r}'')\delta(\mathbf{r}'-\mathbf{r}'''),$$

we obtain Eq. (13.3.21),

$$\hat{w}_{k,j} = \int d\mathbf{r}\int d\mathbf{r}'|\mathbf{r}\rangle\otimes|\mathbf{r}'\rangle\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}\langle\mathbf{r}|\otimes\langle\mathbf{r}'| = \int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\langle\mathbf{r}|\otimes|\mathbf{r}'\rangle\langle\mathbf{r}'|.$$

Exercise 13.3.5 *The single particle operators,* $\hat{J}_k$ *and* $\hat{K}_k$*, are defined in Eq. (13.3.19) and Eq. (13.3.20), respectively. Use Eq. (13.3.21) to derive the explicit coordinate representations of these operators, (Eq. (13.3.22) and Eq. (13.3.23), respectively).*

Solution 13.3.5

Using the notation, $|\phi_{\mathbf{r}}\rangle \equiv |\mathbf{r}\rangle$*, for a position eigenstate, the operator* $\hat{J}_k$ *reads*

$$\begin{aligned}\hat{J}_k &= \sum_{j=1}^{N} [\hat{I}\otimes\langle\tilde{\varphi}_j|]\hat{w}_{k,j}[\hat{I}\otimes|\tilde{\varphi}_j\rangle] \\ &= \sum_{j=1}^{N} [\hat{I}\otimes\langle\tilde{\varphi}_j|]\int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\langle\mathbf{r}|\otimes|\mathbf{r}'\rangle\langle\mathbf{r}'|[\hat{I}\otimes|\tilde{\varphi}_j\rangle] \\ &= \sum_{j=1}^{N} \int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\langle\mathbf{r}|\otimes\langle\tilde{\varphi}_j|\mathbf{r}'\rangle\langle\mathbf{r}'|\tilde{\varphi}_j\rangle \\ &= \sum_{j=1}^{N} \int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\langle\mathbf{r}||\tilde{\varphi}_j(\mathbf{r}')|^2\end{aligned}$$

$$=\sum_{j=1}^{N}\int d\mathbf{r}'\frac{Ke^2}{|\hat{\mathbf{r}}-\mathbf{r}'|}|\tilde{\varphi}_j(\mathbf{r}')|^2 .$$

For the operator $\hat{K}_k$, *we obtain*

$$\hat{K}_k=\sum_{j=1}^{N}\delta_{m_{s,j},m_{s,k}}[\hat{I}\otimes\langle\tilde{\varphi}_j|]\hat{w}_{k,j}[|\tilde{\varphi}_j\rangle\otimes\hat{I}]$$
$$=\sum_{j=1}^{N}\delta_{m_{s,j},m_{s,k}}[\hat{I}\otimes\langle\tilde{\varphi}_j|]\int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\langle\mathbf{r}|\otimes|\mathbf{r}'\rangle\langle\mathbf{r}'|[|\tilde{\varphi}_j\rangle\otimes\hat{I}]$$
$$=\sum_{j=1}^{N}\delta_{m_{s,j},m_{s,k}}\int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{\varphi}_j\rangle\otimes\langle\tilde{\varphi}_j|\mathbf{r}'\rangle\langle\mathbf{r}'|$$
$$=\sum_{j=1}^{N}\delta_{m_{s,j},m_{s,k}}\int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\mathbf{r}\rangle\tilde{\varphi}_j(\mathbf{r})\otimes\tilde{\varphi}_j^*(\mathbf{r}')\langle\mathbf{r}'|$$
$$=\sum_{j=1}^{N}\delta_{m_{s,j},m_{s,k}}\int d\mathbf{r}\int d\mathbf{r}'\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}\tilde{\varphi}_j(\mathbf{r})\tilde{\varphi}_j^*(\mathbf{r}')|\mathbf{r}\rangle\otimes\langle\mathbf{r}'|$$

$$=\int d\mathbf{r}\int d\mathbf{r}'\sum_{j=1}^{N}\delta_{m_{s,j},m_{s,k}}\tilde{\varphi}_j^*(\mathbf{r}')\tilde{\varphi}_j(\mathbf{r})\frac{Ke^2}{|\mathbf{r}-\mathbf{r}'|}|\phi_{\mathbf{r}}\rangle\langle\phi_{\mathbf{r}'}| \; .$$

Notice that this single particle operator is non-local in the single particle spaces, where it maps a single particle state from the j *th space onto the* k *th space.*

Exercise 13.3.6 *Using the properties of the antisymmetrizer (Eq. (13.3.10), and* $\hat{A}^2=\sqrt{N!}\hat{A}$ *), derive Eq. (13.3.28).*

Solution 13.3.6

For the normalized slater determinant, $|\tilde{\Psi}\rangle=\hat{A}|\tilde{\Phi}_1\rangle\otimes|\tilde{\Phi}_2\rangle\otimes\cdots\otimes|\tilde{\Phi}_N\rangle$, *the variational energy reads* $\varepsilon=\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle=\langle\tilde{\Phi}_1|\otimes\langle\tilde{\Phi}_2|\otimes\cdots\otimes\langle\tilde{\Phi}_N|\hat{A}\hat{H}\hat{A}|\tilde{\Phi}_1\rangle\otimes|\tilde{\Phi}_2\rangle\otimes\cdots\otimes|\tilde{\Phi}_N\rangle$.

Using the properties, $\hat{A}^2=\sqrt{N!}\hat{A}$; $[\hat{A},\hat{H}]=0$, *we obtain*

$$\varepsilon = \left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{A}\hat{H}\hat{A} \left| \tilde{\Phi}_1 \right\rangle \otimes \left| \tilde{\Phi}_2 \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_N \right\rangle$$
$$\left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{H}\hat{A}\hat{A} \left| \tilde{\Phi}_1 \right\rangle \otimes \left| \tilde{\Phi}_2 \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_N \right\rangle$$
$$= \sqrt{N!} \left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{H} \left| \tilde{\Psi} \right\rangle$$
$$= \sqrt{N!} \sum_{j=1}^{N} \left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{h}_j \left| \tilde{\Psi} \right\rangle$$
$$+ \sqrt{N!} \sum_{j'>j=1}^{N} \left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{w}_{j,j'} \left| \tilde{\Psi} \right\rangle \ .$$

The determinant $\left| \tilde{\Psi} \right\rangle$ *is a normalized linear combination of* $N!$ *product states, each corresponding to a unique arrangement of the spin-orbitals in the single particle spaces. Using the orthonormality of the single-particle states, there is only one arrangement that gives non-zero overlap with the state,* $\left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{h}_j$*. Therefore,*

$$\begin{aligned} &\sqrt{N!} \sum_{j=1}^{N} \left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{h}_j \left| \tilde{\Psi} \right\rangle \\ &= \sqrt{N!} \sum_{j=1}^{N} \frac{1}{\sqrt{N!}} \left\langle \tilde{\Phi}_1 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_j \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{h}_j \left| \tilde{\Phi}_1 \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_j \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_N \right\rangle \end{aligned} = \left\langle \tilde{\Phi}_j \right| \hat{h}_j \left| \tilde{\Phi}_j \right\rangle .$$

Similarly, there are only two arrangements in the expansion, $\hat{A} \left| \tilde{\Phi}_1 \right\rangle \otimes \left| \tilde{\Phi}_2 \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_N \right\rangle$*, that give non-zero overlap with the state,* $\left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{w}_{j,j'}$*. Therefore,*

$$\sqrt{N!} \sum_{j'>j=1}^{N} \left\langle \tilde{\Phi}_1 \right| \otimes \left\langle \tilde{\Phi}_2 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_N \right| \hat{w}_{j,j'} \left| \tilde{\Psi} \right\rangle$$
$$= \sqrt{N!} \sum_{j'>j=1}^{N} \left\langle \tilde{\Phi}_1 \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_j \right| \otimes \cdots \otimes \left\langle \tilde{\Phi}_{j'} \right| \otimes \cdots \left\langle \tilde{\Phi}_N \right| \hat{w}_{j,j'} \frac{1}{\sqrt{N!}} \cdot$$
$$\left(\left| \tilde{\Phi}_1 \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_j \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_{j'} \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_N \right\rangle - \left| \tilde{\Phi}_1 \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_{j'} \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_j \right\rangle \otimes \cdots \otimes \left| \tilde{\Phi}_N \right\rangle \right)$$
$$= \sum_{j'>j=1}^{N} \left\langle \tilde{\Phi}_j \right| \otimes \left\langle \tilde{\Phi}_{j'} \right| \hat{w}_{j,j'} \left(\left| \tilde{\Phi}_j \right\rangle \otimes \left| \tilde{\Phi}_{j'} \right\rangle - \left| \tilde{\Phi}_{j'} \right\rangle \otimes \left| \tilde{\Phi}_j \right\rangle \right).$$

Consequently,

$$\varepsilon = \sum_{j=1}^{N} \left\langle \tilde{\Phi}_j \right| \hat{h}_j \left| \tilde{\Phi}_j \right\rangle + \sum_{j'>j=1}^{N} [\left\langle \tilde{\Phi}_j \right| \left\langle \tilde{\Phi}_{j'} \right| \hat{w}_{j,j'} \left(\left| \tilde{\Phi}_j \right\rangle \left| \tilde{\Phi}_{j'} \right\rangle - \left| \tilde{\Phi}_{j'} \right\rangle \left| \tilde{\Phi}_j \right\rangle \right)$$
$$= \sum_{j=1}^{N} \left\langle \tilde{\Phi}_j \right| \hat{h}_j \left| \tilde{\Phi}_j \right\rangle + \frac{1}{2} \sum_{j',j=1}^{N} [\left\langle \tilde{\Phi}_j \right| \left\langle \tilde{\Phi}_{j'} \right| \hat{w}_{j,j'} \left(\left| \tilde{\Phi}_j \right\rangle \left| \tilde{\Phi}_{j'} \right\rangle - \left| \tilde{\Phi}_{j'} \right\rangle \left| \tilde{\Phi}_j \right\rangle \right) ,$$

where in the last step we introduced double counting of all pairs. Considering that the single particle states are spin-orbitals of the type, $\left|\tilde{\Phi}_j\right\rangle = \left|\tilde{\varphi}_j\right\rangle \otimes \left|m_{s,j}\right\rangle$ *(which differ from each either by either* $m_{s,j}$*, or* $\tilde{\varphi}_j$*, or both), we obtain*

$$\varepsilon = \sum_{j=1}^{N} \left\langle \tilde{\varphi}_j \left| \hat{h}_j \right| \tilde{\varphi}_j \right\rangle + \frac{1}{2} \sum_{j',j=1}^{N} [\left\langle \tilde{\varphi}_j \right| \left\langle \tilde{\varphi}_{j'} \right| \hat{w}_{j,j'} \left(\left| \tilde{\varphi}_j \right\rangle \left| \tilde{\varphi}_{j'} \right\rangle - \delta_{m_{s,j},m_{s,j'}} \left| \tilde{\varphi}_{j'} \right\rangle \left| \tilde{\varphi}_j \right\rangle \right).$$

Exercise 13.4.1 *For each determinant in Eq. (13.4.2): (a) calculate the appropriate energy* $\varepsilon = \langle \Psi | \hat{H} | \Psi \rangle$ *in Eq. (13.4.4) by expressing it in terms of the integrals given in Eqs. (13.4.5-13.4.7). (b) Calculate the orbital energy for each of the relevant spin orbitals,* $\varphi_1(\mathbf{r}_i)\alpha(i)$, $\varphi_2(\mathbf{r}_i)\alpha(i)$, $\varphi_1(\mathbf{r}_i)\beta(i)$ *or* $\varphi_2(\mathbf{r}_i)\beta(i)$*, using Eq. (13.3.29). (c) Verify that the relation between the total energy and the sum over orbital energies (Eq. (13.3.31)) holds.*

Solution 13.4.1

(a)

Since the Hamiltonian ($\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{w}_{1,2}$*) does not operate in the spin space, and since the spin functions are orthonormal, we only need to consider the spatial integrals. Using the definition of the two-electron states in Eq. (13.4.2), the orthonormality of the spatial orbitals, and the notations in Eqs. (13.4.5-13.4.7), we obtain*

$$\varepsilon_{1\alpha,1\beta} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \varphi_1^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\left[\hat{h}_1 + \hat{h}_2 + \hat{w}_{1,2}\right]\varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$$
$$= \int d\mathbf{r}_1 \varphi_1^*(\mathbf{r}_1)\left[\hat{h}_1\right]\varphi_1(\mathbf{r}_1) + \int d\mathbf{r}_2 \varphi_1^*(\mathbf{r}_2)\left[\hat{h}_2\right]\varphi_1(\mathbf{r}_2)$$
$$+ \int d\mathbf{r}_1 \int d\mathbf{r}_2 \,|\varphi_1(\mathbf{r}_1)|^2 |\varphi_1(\mathbf{r}_2)|^2 \left[\frac{Ke^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]$$

$$= 2E_1 + J_{1,1} \;,$$

$$\varepsilon_{2\alpha,2\beta} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \varphi_2^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\left[\hat{h}_1 + \hat{h}_2 + \hat{w}_{1,2}\right]\varphi_2(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)$$
$$= \int d\mathbf{r}_1 \varphi_2^*(\mathbf{r}_1)\left[\hat{h}_1\right]\varphi_2(\mathbf{r}_1) + \int d\mathbf{r}_2 \varphi_2^*(\mathbf{r}_2)\left[\hat{h}_2\right]\varphi_2(\mathbf{r}_2)$$
$$+ \int d\mathbf{r}_1 \int d\mathbf{r}_2 \,|\varphi_2(\mathbf{r}_1)|^2 |\varphi_2(\mathbf{r}_2)|^2 \left[\frac{Ke^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]$$

$$= 2E_2 + J_{2,2} \,,$$

$$\varepsilon_{1\alpha,2\alpha}=\varepsilon_{1\beta,2\beta}=\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)-\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)]\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right][\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)-\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)]$$

$$=\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right]\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)$$

$$+\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right]\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$$

$$-\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right]\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$$

$$-\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right]\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)$$

$$=\frac{1}{2}\int d\mathbf{r}_1\varphi_1^*(\mathbf{r}_1)\left[\hat{h}_1\right]\varphi_1(\mathbf{r}_1)+\frac{1}{2}\int d\mathbf{r}_2\varphi_2^*(\mathbf{r}_2)\left[\hat{h}_2\right]\varphi_2(\mathbf{r}_2)+\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\varphi_1(\mathbf{r}_1)|^2|\varphi_2(\mathbf{r}_2)|^2\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]$$

$$+\frac{1}{2}\int d\mathbf{r}_1\varphi_2^*(\mathbf{r}_1)\left[\hat{h}_1\right]\varphi_2(\mathbf{r}_1)+\frac{1}{2}\int d\mathbf{r}_2\varphi_1^*(\mathbf{r}_2)\left[\hat{h}_2\right]\varphi_1(\mathbf{r}_2)+\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\varphi_2(\mathbf{r}_1)|^2|\varphi_1(\mathbf{r}_2)|^2\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]$$

$$-\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$$

$$-\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)$$

$$=E_1+E_2+J_{1,2}-K_{1,2},$$

$$\varepsilon_{1\alpha,2\beta}=\varepsilon_{1\beta,2\alpha}=\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right]\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)$$

$$+\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\left[\hat{h}_1+\hat{h}_2+\hat{w}_{1,2}\right]\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$$

$$=\frac{1}{2}\int d\mathbf{r}_1\varphi_1^*(\mathbf{r}_1)\left[\hat{h}_1\right]\varphi_1(\mathbf{r}_1)+\frac{1}{2}\int d\mathbf{r}_2\varphi_2^*(\mathbf{r}_2)\left[\hat{h}_2\right]\varphi_2(\mathbf{r}_2)+\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\varphi_1(\mathbf{r}_1)|^2|\varphi_2(\mathbf{r}_2)|^2\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$$+\frac{1}{2}\int d\mathbf{r}_1\varphi_2^*(\mathbf{r}_1)\left[\hat{h}_1\right]\varphi_2(\mathbf{r}_1)+\frac{1}{2}\int d\mathbf{r}_2\varphi_1^*(\mathbf{r}_2)\left[\hat{h}_2\right]\varphi_1(\mathbf{r}_2)+\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\varphi_2(\mathbf{r}_1)|^2|\varphi_1(\mathbf{r}_2)|^2\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$$=E_1+E_2+J_{1,2}.$$

Consequently,

$$\varepsilon_{1\alpha,1\beta}=2E_1+J_{1,1}$$
$$\varepsilon_{2\alpha,2\beta}=2E_2+J_{2,2}$$
$$\varepsilon_{1\alpha,2\alpha}=\varepsilon_{1\beta,2\beta}=E_1+E_2+J_{1,2}-K_{1,2}$$

$$\varepsilon_{1\alpha,2\beta}=\varepsilon_{1\beta,2\alpha}=E_1+E_2+J_{1,2}.$$

(b)

Eq. (13.3.29) for the orbital energies reads

$$\varepsilon_k = \langle\tilde{\varphi}_k|\hat{h}_k|\tilde{\varphi}_k\rangle + \sum_{j=1}^{2}\langle\tilde{\varphi}_k|\otimes\langle\tilde{\varphi}_j|\hat{w}_{1,2}[|\tilde{\varphi}_k\rangle\otimes|\tilde{\varphi}_j\rangle - \delta_{m_{s,j},m_{s,k}}|\tilde{\varphi}_j\rangle\otimes|\tilde{\varphi}_k\rangle].$$

For $\Psi_{1\alpha,1\beta}$*, we have,* $k, j \in (1\alpha, 1\beta)$*. Therefore*

$$\varepsilon_{1\alpha} = \varepsilon_{1\beta} = \langle\tilde{\varphi}_1|\hat{h}_1|\tilde{\varphi}_1\rangle + \langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_1\rangle = E_1 + J_{1,1}.$$

For $\Psi_{2\alpha,2\beta}$*, we have,* $k, j \in (2\alpha, 2\beta)$*. Therefore,*

$$\varepsilon_{2\alpha} = \varepsilon_{2\beta} = \langle\tilde{\varphi}_2|\hat{h}_2|\tilde{\varphi}_2\rangle + \langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_2\rangle = E_2 + J_{2,2}.$$

For $\Psi_{1\alpha,2\alpha}$*, we have,* $k, j \in (1\alpha, 2\alpha)$*. Therefore,*

$$\varepsilon_{1\alpha} = \langle\tilde{\varphi}_1|\hat{h}_1|\tilde{\varphi}_1\rangle + \langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}[|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_2\rangle - |\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_1\rangle] = E_1 + J_{1,2} - K_{1,2},$$

$$\varepsilon_{2\alpha} = \langle\tilde{\varphi}_2|\hat{h}_2|\tilde{\varphi}_2\rangle + \langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}[|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_1\rangle - |\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_2\rangle] = E_2 + J_{1,2} - K_{1,2}.$$

Similarly, for $\Psi_{1\beta,2\beta}$*,*

$$\varepsilon_{1\beta} = E_1 + J_{1,2} - K_{1,2},$$

$$\varepsilon_{2\beta} = E_2 + J_{1,2} - K_{1,2}.$$

For $\Psi_{1\alpha,2\beta}$*, we have,* $k, j \in (1\alpha, 2\beta)$*. Therefore,*

$$\varepsilon_{1\alpha} = \langle\tilde{\varphi}_1|\hat{h}_1|\tilde{\varphi}_1\rangle + \langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_2\rangle = E_1 + J_{1,2},$$

$$\varepsilon_{2\beta} = \langle\tilde{\varphi}_2|\hat{h}_2|\tilde{\varphi}_2\rangle + \langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_1\rangle = E_2 + J_{1,2}.$$

Similarly, for $\Psi_{1\beta,2\alpha}$*,*

$$\varepsilon_{1\beta} = E_1 + J_{1,2},$$

$$\varepsilon_{2\alpha} = E_2 + J_{1,2}.$$

(c)

Eq. (13.3.31) for the difference between the sum of orbital energies and the HF energy (namely, for the over-counted interaction) reads

$$\sum_{k=1}^{2}\varepsilon_k-\varepsilon=\frac{1}{2}\sum_{k=1}^{2}\sum_{j=1}^{2}\langle\tilde{\varphi}_k|\otimes\langle\tilde{\varphi}_j|\hat{w}_{1,2}[|\tilde{\varphi}_k\rangle\otimes|\tilde{\varphi}_j\rangle-\delta_{m_{s,j},m_{s,k}}|\tilde{\varphi}_j\rangle\otimes|\tilde{\varphi}_k\rangle].$$

For $\Psi_{1\alpha,1\beta}$, *we have,* $k,j\in(1\alpha,1\beta)$. *Therefore,*

$$\varepsilon_{1\alpha}+\varepsilon_{1\beta}-\varepsilon_{1\alpha,1\beta}=\frac{1}{2}\langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_1\rangle+\frac{1}{2}\langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_1\rangle=J_{1,1},$$

which is consistent with the results in (a) and (b).

For $\Psi_{2\alpha,2\beta}$, *we have,* $k,j\in(2\alpha,2\beta)$. *Therefore,*

$$\varepsilon_{2\alpha}+\varepsilon_{2\beta}-\varepsilon_{2\alpha,2\beta}=\frac{1}{2}\langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_2\rangle+\frac{1}{2}\langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_2\rangle=J_{2,2},$$

which is consistent with the results in (a) and (b).

For $\Psi_{1\alpha,2\alpha}$, *we have,* $k,j\in(1\alpha,2\alpha)$. *Therefore,*

$$\varepsilon_{1\alpha}+\varepsilon_{2\alpha}-\varepsilon_{1\alpha,2\alpha}=\frac{1}{2}\langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}[|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_2\rangle-|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_1\rangle]$$
$$+\frac{1}{2}\langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}[|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_1\rangle-|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_2\rangle]$$

$$=\frac{1}{2}\left(2J_{1,2}-2K_{1,2}\right)=J_{1,2}-K_{1,2},$$

which is consistent with the result in (a) and (b).

Similarly, for $\Psi_{1\beta,2\beta}$,

$$\varepsilon_{1\beta}+\varepsilon_{2\beta}-\varepsilon_{1\beta,2\beta}=J_{1,2}-K_{1,2},$$

which is consistent with (a) and (b).

For $\Psi_{1\alpha,2\beta}$, *we have,* $k,j\in(1\alpha,2\beta)$. *Therefore,*

$$\varepsilon_{1\alpha}+\varepsilon_{2\beta}-\varepsilon_{1\alpha,2\beta}=\frac{1}{2}\langle\tilde{\varphi}_1|\otimes\langle\tilde{\varphi}_2|\hat{w}_{1,2}|\tilde{\varphi}_1\rangle\otimes|\tilde{\varphi}_2\rangle+\frac{1}{2}\langle\tilde{\varphi}_2|\otimes\langle\tilde{\varphi}_1|\hat{w}_{1,2}|\tilde{\varphi}_2\rangle\otimes|\tilde{\varphi}_1\rangle=J_{1,2},$$

which is consistent with (a) and (b).

Similarly, for $\Psi_{1\beta,2\alpha}$,

$$\varepsilon_{1\beta}+\varepsilon_{2\alpha}-\varepsilon_{1\beta,2\alpha}=J_{1,2},$$

which is consistent with (a) and (b).

Exercise 13.4.2 *Show that the following four spin states of two electrons,*

$$\begin{aligned}&\alpha(1)\alpha(2)\\&\beta(1)\beta(2)\\&\alpha(1)\beta(2)+\beta(1)\alpha(2)\,,\\&\alpha(1)\beta(2)-\beta(1)\alpha(2)\end{aligned}$$

are eigenfunctions of the two-electrons spin operators:

$$\begin{aligned}&\hat{S}_z=\hat{S}_{z,1}+\hat{S}_{z,2}\\&\hat{S}^2=(\hat{S}_{x,1}+\hat{S}_{x,2})^2+(\hat{S}_{y,1}+\hat{S}_{y,2})^2+(\hat{S}_{z,1}+\hat{S}_{z,2})^2\,.\end{aligned}$$

What are the respective eigenvalues and spin quantum numbers for each of the spin states?

Solution 13.4.2

Using Eq. (13.1.8) for the single particle spin operators, $\hat{S}_z|\alpha\rangle=\frac{\hbar}{2}|\alpha\rangle$ *and* $\hat{S}_z|\beta\rangle=\frac{-\hbar}{2}|\beta\rangle$,

we obtain for $\hat{S}_z$,

$$\begin{aligned}&\hat{S}_z\alpha(1)\alpha(2)=(\hat{S}_{z,1}+\hat{S}_{z,2})\alpha(1)\alpha(2)=(\frac{\hbar}{2}+\frac{\hbar}{2})\alpha(1)\alpha(2)=\hbar\alpha(1)\alpha(2)\\&\hat{S}_z\beta(1)\beta(2)=(\hat{S}_{z,1}+\hat{S}_{z,2})\beta(1)\beta(2)=(\frac{-\hbar}{2}+\frac{-\hbar}{2})\beta(1)\beta(2)=-\hbar\beta(1)\beta(2)\\&\hat{S}_z\alpha(1)\beta(2)=(\hat{S}_{z,1}+\hat{S}_{z,2})\alpha(1)\beta(2)=(\frac{\hbar}{2}-\frac{\hbar}{2})\alpha(1)\beta(2)=0\\&\hat{S}_z\beta(1)\alpha(2)=(\hat{S}_{z,1}+\hat{S}_{z,2})\beta(1)\alpha(2)=(\frac{-\hbar}{2}+\frac{\hbar}{2})\beta(1)\alpha(2)=0\quad.\end{aligned}$$

Therefore,

$$\begin{aligned}&\hat{S}_z\left[\alpha(1)\alpha(2)\right]=\hbar\left[\alpha(1)\alpha(2)\right]\\&\hat{S}_z\left[\beta(1)\beta(2)\right]=-\hbar\left[\beta(1)\beta(2)\right]\\&\hat{S}_z\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]=0\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]\\&\hat{S}_z\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]=0\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\,.\end{aligned}$$

To test $\hat{S}^2$, *we first rewrite it using Eq. (13.1.7),*

$$\hat{S}^2 = (\hat{S}_{x,1} + \hat{S}_{x,2})^2 + (\hat{S}_{y,1} + \hat{S}_{y,2})^2 + (\hat{S}_{z,1} + \hat{S}_{z,2})^2$$
$$= (\hat{S}_{x,1})^2 + (\hat{S}_{y,1})^2 + (\hat{S}_{x,2})^2 + (\hat{S}_{y,2})^2 + 2(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2}) + (\hat{S}_z)^2$$
$$= \frac{1}{2}(\hat{S}_{+,1}\hat{S}_{-,1} + \hat{S}_{-,1}\hat{S}_{+,1} + \hat{S}_{+,2}\hat{S}_{-,2} + \hat{S}_{-,2}\hat{S}_{+,2}) + 2(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2}) + (\hat{S}_z)^2 .$$

Using the following identities (Eq. (13.1.10)),

$$\hat{S}_x|\alpha\rangle = \frac{\hbar}{2}|\beta\rangle \quad ; \quad \hat{S}_x|\beta\rangle = \frac{\hbar}{2}|\alpha\rangle \quad ; \quad \hat{S}_y|\alpha\rangle = i\frac{\hbar}{2}|\beta\rangle \quad ; \quad \hat{S}_y|\beta\rangle = -i\frac{\hbar}{2}|\alpha\rangle$$

$$\hat{S}_+|\beta\rangle = \hbar|\alpha\rangle \quad ; \quad \hat{S}_-|\alpha\rangle = \hbar|\beta\rangle \quad ; \quad \hat{S}_+|\alpha\rangle = 0 \quad ; \quad \hat{S}_-|\beta\rangle = 0$$

we obtain

$$\hat{S}^2\alpha(1)\alpha(2)$$
$$= \frac{1}{2}(\hat{S}_{+,1}\hat{S}_{-,1} + \hat{S}_{-,1}\hat{S}_{+,1} + \hat{S}_{+,2}\hat{S}_{-,2} + \hat{S}_{-,2}\hat{S}_{+,2})\alpha(1)\alpha(2)$$
$$+2(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2})\alpha(1)\alpha(2) + (\hat{S}_z)^2\alpha(1)\alpha(2)$$
$$= \hbar^2\alpha(1)\alpha(2) + 2\frac{\hbar^2}{4}\beta(1)\beta(2) - 2\frac{\hbar^2}{4}\beta(1)\beta(2) + \hbar^2\alpha(1)\alpha(2)$$
$$= 2\hbar^2\alpha(1)\alpha(2)$$

$$\hat{S}^2\beta(1)\beta(2)$$
$$= \frac{1}{2}(\hat{S}_{+,1}\hat{S}_{-,1} + \hat{S}_{-,1}\hat{S}_{+,1} + \hat{S}_{+,2}\hat{S}_{-,2} + \hat{S}_{-,2}\hat{S}_{+,2})\beta(1)\beta(2) + 2(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2})\beta(1)\beta(2) + (\hat{S}_z)^2\beta(1)\beta(2)$$
$$= \hbar^2\beta(1)\beta(2) + 2\frac{\hbar^2}{4}\alpha(1)\alpha(2) - 2\frac{\hbar^2}{4}\alpha(1)\alpha(2) + \hbar^2\beta(1)\beta(2)$$
$$= 2\hbar^2\beta(1)\beta(2)$$

$$\hat{S}^2\alpha(1)\beta(2)$$
$$= \frac{1}{2}(\hat{S}_{+,1}\hat{S}_{-,1} + \hat{S}_{-,1}\hat{S}_{+,1} + \hat{S}_{+,2}\hat{S}_{-,2} + \hat{S}_{-,2}\hat{S}_{+,2})\alpha(1)\beta(2) + 2(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2})\alpha(1)\beta(2) + (\hat{S}_z)^2\alpha(1)\beta(2)$$
$$= \hbar^2\alpha(1)\beta(2) + 2\frac{\hbar^2}{4}\beta(1)\alpha(2) + 2\frac{\hbar^2}{4}\beta(1)\alpha(2) + 0$$
$$= \hbar^2(\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

$$\hat{S}^2\beta(1)\alpha(2)$$
$$= \frac{1}{2}(\hat{S}_{+,1}\hat{S}_{-,1} + \hat{S}_{-,1}\hat{S}_{+,1} + \hat{S}_{+,2}\hat{S}_{-,2} + \hat{S}_{-,2}\hat{S}_{+,2})\beta(1)\alpha(2) + 2(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2})\beta(1)\alpha(2) + (\hat{S}_z)^2\beta(1)\alpha(2)$$
$$= \hbar^2\beta(1)\alpha(2) + 2\frac{\hbar^2}{4}\alpha(1)\beta(2) + 2\frac{\hbar^2}{4}\alpha(1)\beta(2) + 0$$
$$= \hbar^2(\alpha(1)\beta(2) + \beta(1)\alpha(2)) .$$

Therefore,

$$\hat{S}^2\left[\alpha(1)\alpha(2)\right]=2\hbar^2\left[\alpha(1)\alpha(2)\right]$$
$$\hat{S}^2\left[\beta(1)\beta(2)\right]=2\hbar^2\left[\beta(1)\beta(2)\right]$$
$$\hat{S}^2\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]=2\hbar^2\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$
$$\hat{S}^2\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]=0\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right] \quad .$$

These results can be summarized as follows,

$$\hat{S}^2\begin{cases}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \alpha(1)\beta(2)+\beta(1)\alpha(2)\end{cases}=2\hbar^2\begin{cases}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \alpha(1)\beta(2)+\beta(1)\alpha(2)\end{cases}$$
$$\hat{S}^2(\alpha(1)\beta(2)-\beta(1)\alpha(2))=0(\alpha(1)\beta(2)-\beta(1)\alpha(2))$$

$$\hat{S}_z\begin{cases}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \alpha(1)\beta(2)+\beta(1)\alpha(2)\end{cases}=\begin{cases}+1\alpha(1)\alpha(2)\\ -1\beta(1)\beta(2)\\ 0(\alpha(1)\beta(2)+\beta(1)\alpha(2))\end{cases}$$
$$\hat{S}_z(\alpha(1)\beta(2)-\beta(1)\alpha(2))=0(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \quad .$$

The "triplet" states, $\left\{\begin{matrix}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \alpha(1)\beta(2)+\beta(1)\alpha(2)\end{matrix}\right\}$, *are associated with the spin quantum numbers* $s=1$ *(the eigenvalue of* $\hat{S}^2$ *equals* $s(s+1)\hbar^2=2\hbar^2$*), and* $m_s=-1,0,1$*(corresponding to the different eigenvalues of* $\hat{S}_z$*, namely,* $-\hbar,0,\hbar$*).*

The "singlet" state, $\alpha(1)\beta(2)-\beta(1)\alpha(2)$*, is associated with* $s=0$ *and* $m_s=0$.

Exercise 13.4.3 *Substitute the relevant determinants, defined in Eq. (13.4.2), in Eq. (13.4.8) to derive Eq. (13.4.9).*

Solution 13.4.3

Substituting the determinants from Eq. (13.4.2) in Eq. (13.4.8) we obtain

$$\Psi_\pm = \frac{1}{2}[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\alpha(1)\beta(2) - \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\beta(1)\alpha(2)]$$
$$\pm\frac{1}{2}[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\beta(1)\alpha(2) - \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\alpha(1)\beta(2)]$$
$$= \frac{1}{2}\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\alpha(1)\beta(2) - \frac{1}{2}\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\beta(1)\alpha(2)$$
$$\pm\frac{1}{2}\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\beta(1)\alpha(2) \mp \frac{1}{2}\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\alpha(1)\beta(2)$$
$$= \frac{1}{2}\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \mp \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right]\alpha(1)\beta(2) - \frac{1}{2}\left[\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2) \mp \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\right]\beta(1)\alpha(2)$$
$$= \frac{1}{2}\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \mp \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right]\left[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)\right] \ .$$

Exercise 13.4.4 *Express the energy $\varepsilon = \langle\Psi|\hat{H}|\Psi\rangle$ of Ψ_+ and Ψ_-, as defined in Eq.(13.4.9), in terms of the integrals defined in Eq. (13.4.5-13.4.7) (obtain Eq. (13.4.10)).*

Solution 13.4.4

Since the Hamiltonian ($\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{w}_{1,2}$) does not operate in the spin space, and since the spin functions are orthonormal, we only need to consider the spatial integrals. Using the definition of the two-electron states $\Psi_\pm$ (Eq. (13.4.9)), the orthonormality of the spatial orbitals, and the notations in Eqs. (13.4.5-13.4.7), we obtain

$$\varepsilon_\pm = \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\left[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2) \mp \varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\right]\left[\hat{h}_1 + \hat{h}_2 + \hat{w}_{1,2}\right]\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \mp \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right]$$
$$= \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\left[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2) \mp \varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\right]\left[\hat{h}_1\right]\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \mp \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right]$$
$$+ \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\left[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2) \mp \varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\right]\left[\hat{h}_2\right]\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \mp \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right]$$
$$+ \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\left[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2) \mp \varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\right]\left[\hat{w}_{1,2}\right]\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \mp \varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right]$$

$$
\begin{aligned}
&= \frac{1}{2}\int d\mathbf{r}_1 \varphi_1^*(\mathbf{r}_1)\hat{h}_1\varphi_1(\mathbf{r}_1) + \frac{1}{2}\int d\mathbf{r}_1 \varphi_2^*(\mathbf{r}_1)\hat{h}_1\varphi_2(\mathbf{r}_1) \\
&+ \frac{1}{2}\int d\mathbf{r}_2 \varphi_2^*(\mathbf{r}_2)\hat{h}_2\varphi_2(\mathbf{r}_2) + \frac{1}{2}\int d\mathbf{r}_2 \varphi_1^*(\mathbf{r}_2)\hat{h}_2\varphi_1(\mathbf{r}_2) \\
&+ \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \left[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\right]\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\right] \\
&\mp \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \left[\varphi_1^*(\mathbf{r}_1)\varphi_2^*(\mathbf{r}_2)\right]\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\left[\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right] \\
&+ \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \left[\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\right]\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\left[\varphi_2(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\right] \\
&\mp \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2 \left[\varphi_2^*(\mathbf{r}_1)\varphi_1^*(\mathbf{r}_2)\right]\left[\frac{Ke^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\left[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\right]
\end{aligned}
$$

$$
= E_1 + E_2 + J_{1,2} \mp K_{1,2} \ .
$$

14 Many-Atom Systems

Exercise 14.2.1 *Obtain Eqs. (4.2.10, 4.2.11) from Eq. (4.2.9) by multiplying from the left by* $\phi_m^*(\mathbf{R},\mathbf{r})$ *and integrating over the electronic coordinates. Use the fact that the electronic functions, {* $\phi_l(\mathbf{R},\mathbf{r})$ *}, are the orthonormal (Eq. 14.2.7)) eigenfunctions of the electronic Hamiltonian (Eq. 14.2.6).*

Solution 14.2.1

Starting from Eq. (14.2.9), multiplying from the left by $\phi_m^*(\mathbf{R},\mathbf{r})$, *and integrating over the electronic coordinates, we obtain*

$$\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\left[\hat{H}_{elec}(\mathbf{R})+\hat{T}_{\mathbf{R}}\right]\sum_l \chi_l(\mathbf{R})\phi_l(\mathbf{R},\mathbf{r})=\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})E\sum_l \chi_l(\mathbf{R})\phi_l(\mathbf{R},\mathbf{r}).$$

Using, $\hat{H}_{elec}(\mathbf{R})\chi_l(\mathbf{R})\phi_l(\mathbf{R},\mathbf{r})=\varepsilon_l(\mathbf{R})$ *we obtain*

$$\sum_l \int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\left[\varepsilon_l(\mathbf{R})+\hat{T}_{\mathbf{R}}\right]\chi_l(\mathbf{R})\phi_l(\mathbf{R},\mathbf{r})=E\sum_l \chi_l(\mathbf{R})\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\phi_l(\mathbf{R},\mathbf{r}),$$

and using the orthonormality of the electronic functions,

$$\varepsilon_m(\mathbf{R})\chi_m(\mathbf{R})+\sum_l \int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\left[\hat{T}_{\mathbf{R}}\right]\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})=E\chi_m(\mathbf{R}).$$

Therefore, $\sum_l \left[\hat{H}_{\mathbf{R}}\right]_{m,l}\chi_l(\mathbf{R})=E\chi_m(\mathbf{R})$, *where,*

$$\left[\hat{H}_{\mathbf{R}}\right]_{m,l}=\varepsilon_m(\mathbf{R})\delta_{m,l}+\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\left[\hat{T}_{\mathbf{R}}\right]\phi_l(\mathbf{R},\mathbf{r})=\varepsilon_m(\mathbf{R})\delta_{m,l}+\left[\hat{T}_{\mathbf{R}}\right]_{m,l}.$$

Exercise 14.2.2 *(a) Use the definition of the gradient operator,* $\nabla_{\mathbf{R}_\alpha}\equiv\left(\frac{\partial}{\partial x_\alpha},\frac{\partial}{\partial y_\alpha},\frac{\partial}{\partial z_\alpha}\right)^t$ *to show that* $\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}[\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})]=2[\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})+\phi_l(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})$ $+[\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})$.

(b) Use the definition of the nuclear kinetic energy operator in Eq. (14.2.4), the result of (a), and the orthonormality of the electronic functions (Eq. (14.2.7)) to show that

$$\left[\hat{T}_{\mathbf{R}}\right]_{m,l}\chi_l(\mathbf{R})=\sum_{\alpha=1}^{n}\frac{-\hbar^2}{m_\alpha}[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})+$$

$$\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})+\delta_{m,l}\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R}).$$

(c) Use the result of (b) and the definition of $\nabla_{\tilde{\mathbf{R}}}$ to obtain Eq. (14.2.13).

Solution 14.2.2

(a)

Taking the derivatives of the product functions, we obtain

$$\left[\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})\right]=\begin{bmatrix}\frac{\partial\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})}{\partial x_\alpha}\\ \frac{\partial\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})}{\partial y_\alpha}\\ \frac{\partial\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})}{\partial z_\alpha}\end{bmatrix}=\begin{bmatrix}\frac{\partial\phi_l(\mathbf{R},\mathbf{r})}{\partial x_\alpha}\\ \frac{\partial\phi_l(\mathbf{R},\mathbf{r})}{\partial y_\alpha}\\ \frac{\partial\phi_l(\mathbf{R},\mathbf{r})}{\partial z_\alpha}\end{bmatrix}\chi_l(\mathbf{R})+\phi_l(\mathbf{R},\mathbf{r})\begin{bmatrix}\frac{\partial\chi_l(\mathbf{R})}{\partial x_\alpha}\\ \frac{\partial\chi_l(\mathbf{R})}{\partial y_\alpha}\\ \frac{\partial\chi_l(\mathbf{R})}{\partial z_\alpha}\end{bmatrix}$$

$$=\left[\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})\right]\chi_l(\mathbf{R})+\phi_l(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R}) .$$

Consequently,

$$\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}[\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})]=\nabla_{\mathbf{R}_\alpha}\cdot\left\{\left[\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})\right]\chi_l(\mathbf{R})+\phi_l(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})\right\}$$

$$=2[\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})+[\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})+\phi_l(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R}) .$$

(b)

Using the definition of the nuclear kinetic energy operator, $\hat{T}_{\mathbf{R}}=\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}$ *, in the expression for* $\left[\hat{T}_{\mathbf{R}}\right]_{m,l}$ *(Eq. (14.2.11)), we obtain*

$$\left[\hat{T}_{\mathbf{R}}\right]_{m,l}\chi_l(\mathbf{R})=\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\hat{T}_{\mathbf{R}}\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})=\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R}) .$$

Using the result of (a) we obtain,

$$\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})$$
$$=2[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})$$
$$+[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})$$
$$+\delta_{m,l}\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R}).$$

Hence,

$$\left[\hat{T}_{\mathbf{R}}\right]_{m,l}\chi_l(\mathbf{R})=\sum_{\alpha=1}^{n}\frac{-\hbar^2}{m_\alpha}[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R})$$
$$+\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})$$
$$+\delta_{m,l}\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\chi_l(\mathbf{R}).$$

(c)

Changing variables: $\tilde{\mathbf{R}}_\alpha=\sqrt{\frac{2m_\alpha}{\hbar^2}}\mathbf{R}_\alpha$ *and* $\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\equiv-\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}$*, the kinetic energy matrix elements are rewritten as,*

$$\left[\hat{T}_{\mathbf{R}}\right]_{m,l}=\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\sum_{\alpha=1}^{n}\frac{-\hbar^2}{2m_\alpha}\nabla_{\mathbf{R}_\alpha}\cdot\nabla_{\mathbf{R}_\alpha}\phi_l(\mathbf{R},\mathbf{r})=-\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r}).$$

Following (b), we obtain

$$\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})\chi_l(\mathbf{R})= 2[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\tilde{\mathbf{R}}}\chi_l(\mathbf{R}) +[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})+\delta_{m,l}\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\chi_l(\mathbf{R}),$$

and hence,

$$\left[\hat{T}_{\mathbf{R}}\right]_{m,l}\chi_l(\mathbf{R})=-2[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})]\cdot\nabla_{\tilde{\mathbf{R}}}\chi_l(\mathbf{R})$$
$$-[\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})]\chi_l(\mathbf{R})$$
$$+\delta_{m,l}\hat{T}_{\mathbf{R}}\chi_l(\mathbf{R}),$$

from which we conclude (Eq. (14.2.13)),

$$\left[\hat{T}_{\mathbf{R}}\right]_{m,l} = \delta_{m,l}\hat{T}_{\mathbf{R}} - 2\left(\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})\right)\cdot\nabla_{\tilde{\mathbf{R}}} - \left(\int d\mathbf{r}\phi_m^*(\mathbf{R},\mathbf{r})\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R},\mathbf{r})\right)$$
$$\equiv \delta_{m,l}\hat{T}_{\mathbf{R}} - 2\left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle\cdot\nabla_{\tilde{\mathbf{R}}} - \left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle.$$

Exercise 14.2.3 *The non-adiabatic terms in the nuclear Hamiltonian are given by* $\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l}$ *in Eq. (14.2.16). Follow (a-d) to show that a sufficient condition for the vanishing of* $\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l}$ *is the vanishing of the non-adiabatic coupling vector,* $\mathbf{D}_{i,j}(\mathbf{R}) = \left\langle\phi_i(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_j(\mathbf{R})\right\rangle$, *for any* i *and* j.

(a) Show that $\left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle = \left[\nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R})\right] - \left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\cdot\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle$.

(b) For any $\mathbf{R}$, *introduce a complete orthonormal system of electronic functions and show that* $\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\cdot\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle = \sum_k \left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle\cdot\mathbf{D}_{k,l}(\mathbf{R})$.

(c) Use Eq. (14.2.7) to prove that $\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle = -\mathbf{D}_{m,k}(\mathbf{R})$.

(d) Show that $\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l} = -2\mathbf{D}_{m,l}(\mathbf{R})\cdot\nabla_{\tilde{\mathbf{R}}} - \left[\nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R})\right] - \sum_k \mathbf{D}_{m,k}(\mathbf{R})\cdot\mathbf{D}_{k,l}(\mathbf{R})$.

Solution 14.2.3

(a)

The divergence of the vector $\mathbf{D}_{i,j}(\mathbf{R}) = \left\langle\phi_i(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_j(\mathbf{R})\right\rangle$ *reads*

$$\nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R}) = \nabla_{\tilde{\mathbf{R}}}\cdot\left\langle\phi_i(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_j(\mathbf{R})\right\rangle = \left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\cdot\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle + \left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle.$$

Therefore, $\left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle = \nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R}) - \left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\cdot\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle$.

(b)

Introducing a complete orthonormal system of electronic functions, we obtain

$$\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\cdot\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle = \sum_k \left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle\cdot\left\langle\phi_k(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle$$
$$= \sum_k \left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle\cdot\mathbf{D}_{k,l}(\mathbf{R})$$
.

(c)

Using Eq. (14.2.7), we have $\left\langle\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle = \delta_{m,k}$. *Therefore,*

$$\nabla_{\tilde{\mathbf{R}}}\left\langle\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle=\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle+\left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_k(\mathbf{R})\right\rangle=0$$
$$\Rightarrow\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle+\mathbf{D}_{m,k}(\mathbf{R})=0$$
$$\Rightarrow\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle=-\mathbf{D}_{m,k}(\mathbf{R}).$$

(d)

According to Eq. (14.2.16), the non-adiabatic terms obtain the form,

$$\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l}=-2\left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle\cdot\nabla_{\tilde{\mathbf{R}}}-\left\langle\phi_m(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\cdot\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle.$$

Using (a), we obtain

$$\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l}=-2\mathbf{D}_{m,l}(\mathbf{R})\cdot\nabla_{\tilde{\mathbf{R}}}-\nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R})+\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\cdot\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle,$$

using (b) we obtain

$$\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l}=-2\mathbf{D}_{m,l}(\mathbf{R})\cdot\nabla_{\tilde{\mathbf{R}}}-\nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R})+\sum_k\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\phi_k(\mathbf{R})\right\rangle\cdot\mathbf{D}_{k,l}(\mathbf{R}),$$

and using (c) we finally obtain

$$\left[\hat{H}_{\mathbf{R}}^{(1)}\right]_{m,l}=-2\mathbf{D}_{m,l}(\mathbf{R})\cdot\nabla_{\tilde{\mathbf{R}}}-\nabla_{\tilde{\mathbf{R}}}\cdot\mathbf{D}_{m,l}(\mathbf{R})-\sum_k\mathbf{D}_{m,k}(\mathbf{R})\cdot\mathbf{D}_{k,l}(\mathbf{R}).$$

Exercise 14.2.4 *Derive Eq. (14.2.25) by calculating* $\nabla_{\tilde{\mathbf{R}}}\left\langle\phi_m(\mathbf{R})\middle|\hat{H}_{elec}(\mathbf{R})\middle|\phi_l(\mathbf{R})\right\rangle$*, using the properties of the electronic functions, Eqs. (14.2.6, 14.2.7).*

Solution 14.2.4

The gradient of the matrix element $\left\langle\phi_m(\mathbf{R})\middle|\hat{H}_{elec}(\mathbf{R})\middle|\phi_l(\mathbf{R})\right\rangle$ *reads*

$$\nabla_{\tilde{\mathbf{R}}}\left\langle\phi_m(\mathbf{R})\middle|\hat{H}_{elec}(\mathbf{R})\middle|\phi_l(\mathbf{R})\right\rangle$$

$$=\left\langle\nabla_{\tilde{\mathbf{R}}}\phi_m(\mathbf{R})\middle|\hat{H}_{elec}(\mathbf{R})\middle|\phi_l(\mathbf{R})\right\rangle+\left\langle\phi_m(\mathbf{R})\middle|\left[\nabla_{\tilde{\mathbf{R}}}\hat{H}_{elec}(\mathbf{R})\right]\middle|\phi_l(\mathbf{R})\right\rangle$$

$$+\left\langle\phi_m(\mathbf{R})\middle|\hat{H}_{elec}(\mathbf{R})\middle|\nabla_{\tilde{\mathbf{R}}}\phi_l(\mathbf{R})\right\rangle.$$

Using $\hat{H}_{elec}(\mathbf{R})\left|\phi_l(\mathbf{R})\right\rangle=\varepsilon_l(\mathbf{R})\left|\phi_l(\mathbf{R})\right\rangle$*, we obtain*

$$\nabla_{\tilde{\mathbf{R}}} \left\langle \phi_m(\mathbf{R}) \middle| \hat{H}_{elec}(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle$$

$$= \varepsilon_l(\mathbf{R}) \left\langle \nabla_{\tilde{\mathbf{R}}} \phi_m(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle + \varepsilon_m(\mathbf{R}) \left\langle \phi_m(\mathbf{R}) \middle| \nabla_{\tilde{\mathbf{R}}} \phi_l(\mathbf{R}) \right\rangle + \left\langle \phi_m(\mathbf{R}) \middle| \left[\nabla_{\tilde{\mathbf{R}}} \hat{H}_{elec}(\mathbf{R}) \right] \middle| \phi_l(\mathbf{R}) \right\rangle.$$

Since $\left\langle \phi_l(\mathbf{R}) \middle| \phi_{l'}(\mathbf{R}) \right\rangle = \delta_{l,l'}$, *we have*

$$\nabla_{\tilde{\mathbf{R}}} \left\langle \phi_m(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle = \left\langle \nabla_{\tilde{\mathbf{R}}} \phi_m(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle + \left\langle \phi_m(\mathbf{R}) \middle| \nabla_{\tilde{\mathbf{R}}} \phi_l(\mathbf{R}) \right\rangle = 0$$

$$\Rightarrow \left\langle \nabla_{\tilde{\mathbf{R}}} \phi_m(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle = -\left\langle \phi_m(\mathbf{R}) \middle| \nabla_{\tilde{\mathbf{R}}} \phi_l(\mathbf{R}) \right\rangle,$$

and therefore,

$$\nabla_{\tilde{\mathbf{R}}} \left\langle \phi_m(\mathbf{R}) \middle| \hat{H}_{elec}(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle$$

$$= \left[\varepsilon_m(\mathbf{R}) - \varepsilon_l(\mathbf{R}) \right] \left\langle \phi_m(\mathbf{R}) \middle| \nabla_{\tilde{\mathbf{R}}} \phi_l(\mathbf{R}) \right\rangle + \left\langle \phi_m(\mathbf{R}) \middle| \left[\nabla_{\tilde{\mathbf{R}}} \hat{H}_{elec}(\mathbf{R}) \right] \middle| \phi_l(\mathbf{R}) \right\rangle.$$

On the other hand, since $\left\langle \phi_m(\mathbf{R}) \middle| \hat{H}_{elec}(\mathbf{R}) \middle| \phi_l(\mathbf{R}) \right\rangle = \varepsilon_l(\mathbf{R}) \delta_{m,l}$, *for* $l \neq m$ *we have,* $\nabla_{\tilde{\mathbf{R}}} \left\langle \phi_m(\mathbf{R}) \middle| \hat{H}_{elec}(\mathbf{R}) \middle| \phi_{l\neq m}(\mathbf{R}) \right\rangle = 0$, *which leads to Eq. (14.2.25),*

$$\left\langle \phi_m(\mathbf{R}) \middle| \nabla_{\tilde{\mathbf{R}}} \phi_l(\mathbf{R}) \right\rangle = \frac{\left\langle \phi_m(\mathbf{R}) \middle| \left[\nabla_{\tilde{\mathbf{R}}} \hat{H}_{elec}(\mathbf{R}) \right] \middle| \phi_l(\mathbf{R}) \right\rangle}{\varepsilon_l(\mathbf{R}) - \varepsilon_m(\mathbf{R})}.$$

Exercise 14.3.1 *Solve the secular equation, Eq. (14.3.7): (a) Express the eigenvalues as functions of* $H_{\alpha,\alpha}(R), H_{\beta,\alpha}(R), S(R)$ *(use Eqs. (14.3.8, 14.39)) by calculating the roots of the determinant,*

$$\begin{vmatrix} H_{\alpha,\alpha}(R) - \tilde{\varepsilon}(R) S_{\alpha,\alpha}(R) & H_{\alpha,\beta}(R) - \tilde{\varepsilon}(R) S_{\alpha,\beta}(R) \\ H_{\beta,\alpha}(R) - \tilde{\varepsilon}(R) S_{\beta,\alpha}(R) & H_{\beta,\beta}(R) - \tilde{\varepsilon}(R) S_{\beta,\beta}(R) \end{vmatrix} = 0.$$

(b) For each eigenvalue obtain the ratio between the elements $c_\beta(R)$ *and* $c_\alpha(R)$ *of the respective eigen vector (Eq. (14.3.11)).*

Solution 14.3.1

(a)

Using the simplifying assumptions, Eqs. (14.3.8, 14.39), we need to solve

$$\begin{bmatrix} H_{\alpha,\alpha}(R)-\tilde{\varepsilon}(R) & H_{\beta,\alpha}(R)-\tilde{\varepsilon}(R)S(R) \\ H_{\beta,\alpha}(R)-\tilde{\varepsilon}(R)S(R) & H_{\alpha,\alpha}(R)-\tilde{\varepsilon}(R) \end{bmatrix}\begin{bmatrix} c_{\alpha}(R) \\ c_{\beta}(R) \end{bmatrix}=\begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

The equation for the eigenvalues reads

$$\begin{vmatrix} H_{\alpha,\alpha}(R)-\tilde{\varepsilon}(R) & H_{\beta,\alpha}(R)-\tilde{\varepsilon}(R)S(R) \\ H_{\beta,\alpha}(R)-\tilde{\varepsilon}(R)S(R) & H_{\alpha,\alpha}(R)-\tilde{\varepsilon}(R) \end{vmatrix}=0,$$

and the solution is

$$\begin{aligned} &\left(H_{\alpha,\alpha}(R)-\tilde{\varepsilon}(R)\right)^2-\left(H_{\beta,\alpha}(R)-\tilde{\varepsilon}(R)S(R)\right)^2=0 \\ &\Rightarrow H_{\alpha,\alpha}(R)-\tilde{\varepsilon}(R)=\pm H_{\beta,\alpha}(R)\mp\tilde{\varepsilon}(R)S(R) \\ &\Rightarrow H_{\alpha,\alpha}(R)\mp H_{\beta,\alpha}(R)=\tilde{\varepsilon}(R)(1\mp S(R)) \end{aligned}$$

$$\Rightarrow \tilde{\varepsilon}_{\pm}(R)=\frac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)}.$$

(b)

For each one of the two eigenvalues, $\tilde{\varepsilon}_{\pm}(R)$, *we obtain*

$$\begin{bmatrix} H_{\alpha,\alpha}(R)-\tilde{\varepsilon}_{\pm}(R) & H_{\beta,\alpha}(R)-\tilde{\varepsilon}_{\pm}(R)S(R) \\ H_{\beta,\alpha}(R)-\tilde{\varepsilon}_{\pm}(R)S(R) & H_{\alpha,\alpha}(R)-\tilde{\varepsilon}_{\pm}(R) \end{bmatrix}\begin{bmatrix} c_{\alpha}^{\pm}(R) \\ c_{\beta}^{\pm}(R) \end{bmatrix}=\begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\Rightarrow \begin{bmatrix} H_{\alpha,\alpha}(R)-\dfrac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)} & H_{\beta,\alpha}(R)-\dfrac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)}S(R) \\ H_{\beta,\alpha}(R)-\dfrac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)}S(R) & H_{\alpha,\alpha}(R)-\dfrac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)} \end{bmatrix}\begin{bmatrix} c_{\alpha}^{\pm}(R) \\ c_{\beta}^{\pm}(R) \end{bmatrix}=\begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Since the two linear equations are linearly dependent, it is sufficient to consider the first row,

$$\begin{aligned} &\left(H_{\alpha,\alpha}(R)-\frac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)}\right)c_{\alpha}^{\pm}(R)+\left(H_{\beta,\alpha}(R)-\frac{H_{\alpha,\alpha}(R)\pm H_{\beta,\alpha}(R)}{1\pm S(R)}S(R)\right)c_{\beta}^{\pm}(R)=0 \\ &\Rightarrow \left(H_{\alpha,\alpha}(R)\pm H_{\alpha,\alpha}(R)S(R)-H_{\alpha,\alpha}(R)\mp H_{\beta,\alpha}(R)\right)c_{\alpha}^{\pm}(R) \\ &+\left(H_{\beta,\alpha}(R)\pm H_{\beta,\alpha}(R)S(R)-H_{\alpha,\alpha}(R)S(R)\mp H_{\beta,\alpha}(R)S(R)\right)c_{\beta}^{\pm}(R)=0 \\ &\Rightarrow \left(\mp H_{\alpha,\alpha}(R)S(R)\pm H_{\beta,\alpha}(R)\right)c_{\alpha}^{\pm}(R)=\left(H_{\beta,\alpha}(R)-H_{\alpha,\alpha}(R)S(R)\right)c_{\beta}^{\pm}(R) \end{aligned}$$

$$\Rightarrow \frac{c_{\beta}^{\pm}(R)}{c_{\alpha}^{\pm}(R)}=\frac{\mp H_{\alpha,\alpha}(R)S(R)\pm H_{\beta,\alpha}(R)}{H_{\beta,\alpha}(R)-H_{\alpha,\alpha}(R)S(R)}=\pm 1.$$

In conclusion, for $\tilde{\varepsilon}_+(R)$ *we have* $c^+_\beta(R) = c^+_\alpha(R)$, *and for* $\tilde{\varepsilon}_-(R)$ *we have,* $c^-_\beta(R) = -c^-_\alpha(R)$.

Exercise 14.3.2 *The variational approximations for the two lowest eigenfunctions of the electronic Hamiltonian are expressed as linear combinations of atomic orbitals, according to Eq. (14.3.6). Using the result, Eq. (14.3.11), for the corresponding relations between the expansion coefficients, show that the normalized wave functions,* $\tilde{\phi}_\pm(R,\mathbf{r})$, *are given by Eq. (14.3.12).*

Solution 14.3.2

Using Dirac's notations, $\left|\tilde{\phi}_\pm(R)\right\rangle = \left|\varphi_\alpha(R)\right\rangle \pm \left|\varphi_\beta(R)\right\rangle$, *the norm of* $\left|\tilde{\phi}(R)\right\rangle$ *reads*

$$\left\langle\tilde{\phi}_\pm(R)\middle|\tilde{\phi}_\pm(R)\right\rangle = \left\langle\varphi_\alpha(R)\middle|\varphi_\alpha(R)\right\rangle + \left\langle\varphi_\beta(R)\middle|\varphi_\beta(R)\right\rangle \pm \left\langle\varphi_\alpha(R)\middle|\varphi_\beta(R)\right\rangle \pm \left\langle\varphi_\beta(R)\middle|\varphi_\alpha(R)\right\rangle.$$

For normalized atomic orbitals, $\left\langle\varphi_\alpha(R)\middle|\varphi_\alpha(R)\right\rangle = \left\langle\varphi_\beta(R)\middle|\varphi_\beta(R)\right\rangle = 1$, *and defining,* $\left\langle\varphi_\alpha(R)\middle|\varphi_\beta(R)\right\rangle = S(R)$, *we obtain* $\left\langle\tilde{\phi}_\pm(R)\middle|\tilde{\phi}_\pm(R)\right\rangle = 2 \pm 2S(R)$. *Hence, the normalized states are*

$$\left|\tilde{\phi}_\pm(R)\right\rangle = \frac{1}{\sqrt{2[1 \pm S(R)]}}\left(\left|\varphi_\alpha(R)\right\rangle \pm \left|\varphi_\beta(R)\right\rangle\right).$$

Exercise 14.3.3 *Obtain the expressions in Eqs. (14.3.13, 14.3.14) for the integrals,* $H_{\alpha,\alpha}(R)$ *and* $H_{\beta,\alpha}(R)$, *as defined in Eq. (14.3.8). Use Eq. (14.3.5) and Fig. 10.2.2 for the explicit form of the atomic orbitals, and Eq. (14.3.2) for the electronic Hamiltonian. Change integration variables to comply with the definitions of the integrals in Eq. (14.3.14).*

Solution 14.3.3

The matrix elements of the electronic Hamiltonian, as defined in Eq. (14.3.8), read

$$H_{\beta,\beta}(R) = H_{\alpha,\alpha}(R) = \left\langle\varphi_\alpha(R)\middle|\hat{H}_{elec}(R)\middle|\varphi_\alpha(R)\right\rangle \quad H_{\alpha,\beta}(R) = H_{\beta,\alpha}(R) = \left\langle\varphi_\beta(R)\middle|\hat{H}_{elec}(R)\middle|\varphi_\alpha(R)\right\rangle.$$

Introducing explicitly the electronic Hamiltonian (Eq. (14.3.2)), namely,

$$\hat{H}_{elec}(R) = \frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}} + \frac{Ke^2}{R} - \frac{Ke^2}{|\mathbf{r} + \boldsymbol{k}R/2|} - \frac{Ke^2}{|\mathbf{r} - \boldsymbol{k}R/2|},$$ *we obtain*

$$H_{\alpha,\alpha}(R) = \langle \varphi_\alpha(R) | \hat{H}_{elec}(R) | \varphi_\alpha(R) \rangle$$
$$= \frac{Ke^2}{R} \langle \varphi_\alpha(R) | \varphi_\alpha(R) \rangle + \langle \varphi_\alpha(R) | \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r} + \boldsymbol{k}R/2|} \right] | \varphi_\alpha(R) \rangle + \langle \varphi_\alpha(R) | \frac{-Ke^2}{|\mathbf{r} - \boldsymbol{k}R/2|} | \varphi_\alpha(R) \rangle$$

$$H_{\beta,\alpha}(R) = \langle \varphi_\beta(R) | \hat{H}_{elec}(R) | \varphi_\alpha(R) \rangle$$
$$= \frac{Ke^2}{R} \langle \varphi_\beta(R) | \varphi_\alpha(R) \rangle + \langle \varphi_\beta(R) | \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r} + \boldsymbol{k}R/2|} \right] | \varphi_\alpha(R) \rangle + \langle \varphi_\beta(R) | \frac{-Ke^2}{|\mathbf{r} - \boldsymbol{k}R/2|} | \varphi_\alpha(R) \rangle .$$

Identifying the atomic orbitals with normalized (real-valued) $\psi_{1,0,0}$ *states, associated with the two nuclei (Eq. (14.3.5), Fig. 10.2.2), namely,* $\varphi_\alpha(R,\mathbf{r}) \equiv \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2)$ *and* $\varphi_\beta(R,\mathbf{r}) \equiv \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R/2)$*, we obtain*

$$H_{\alpha,\alpha}(R) = \frac{Ke^2}{R} + \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2) \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r} + \boldsymbol{k}R/2|} \right] \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2)$$
$$+ \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2) \frac{-Ke^2}{|\mathbf{r} - \boldsymbol{k}R/2|} \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2),$$

$$H_{\beta,\alpha}(R) = \frac{Ke^2}{R} \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R/2) \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2)$$
$$+ \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R/2) \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r} + \boldsymbol{k}R/2|} \right] \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2)$$
$$+ \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R/2) \frac{-Ke^2}{|\mathbf{r} - \boldsymbol{k}R/2|} \psi_{1,0,0}(\mathbf{r} + \boldsymbol{k}R/2) \quad .$$

Changing integration variables, we obtain

$$H_{\alpha,\alpha}(R) = \frac{Ke^2}{R} + \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r}) \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r}|} \right] \psi_{1,0,0}(\mathbf{r}) + \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r}) \frac{-Ke^2}{|\mathbf{r} - \boldsymbol{k}R|} \psi_{1,0,0}(\mathbf{r}),$$

$$H_{\beta,\alpha}(R) = \frac{Ke^2}{R} \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R) \psi_{1,0,0}(\mathbf{r}) + \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R) \left[\frac{-\hbar^2}{2m_e} \Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r}|} \right] \psi_{1,0,0}(\mathbf{r})$$
$$+ \int d\mathbf{r} \psi_{1,0,0}(\mathbf{r} - \boldsymbol{k}R) \frac{-Ke^2}{|\mathbf{r} - \boldsymbol{k}R|} \psi_{1,0,0}(\mathbf{r}) .$$

Introducing the following notations for the different integrals (Eq. (14.3.14)),

$$E_{1s} = \int d\mathbf{r}\psi_{1,0,0}(\mathbf{r})[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r}|}]\psi_{1,0,0}(\mathbf{r})$$

$$C(R) = -Ke^2\int d\mathbf{r}\frac{|\psi_{1,0,0}(\mathbf{r})|^2}{|\mathbf{r}-\boldsymbol{k}R|}$$

$$A(R) = -Ke^2\int d\mathbf{r}\frac{\psi_{1,0,0}(\mathbf{r}-\boldsymbol{k}R)\psi_{1,0,0}(\mathbf{r})}{|\mathbf{r}-\boldsymbol{k}R|}$$

$$S(R) = \int d\mathbf{r}\psi_{1,0,0}(\mathbf{r}-\boldsymbol{k}R)\psi_{1,0,0}(\mathbf{r}),$$

and using, $[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}} - \frac{Ke^2}{|\mathbf{r}|}]\psi_{1,0,0}(\mathbf{r}) = E_{1s}\psi_{1,0,0}(\mathbf{r})$, *we finally obtain*

$$H_{\alpha,\alpha}(R) = \frac{Ke^2}{R} + E_{1s} + C(R) \quad ; \quad H_{\beta,\alpha}(R) = \left(\frac{Ke^2}{R} + E_{1s}\right)S(R) + A(R) \quad .$$

Exercise 14.3.4 *To derive the results, Eqs. (14.3.15-14.3.17), for the integrals defined in Eq. (14.3.14), first follow steps (a) and (b) of Ex. 12.2.8. Then:*

(a) Set $f(x,y,z) = -Ke^2\frac{|\psi_{1,0,0}(\mathbf{r})|^2}{|\mathbf{r}-\boldsymbol{k}R|}$ *and obtain the result for* $C(R)$ *in Eq. (14.3.16). (This amounts to setting the charge to* $q=1$ *in the result of Ex. 12.2.8.)*

(b) Set $f(x,y,z) = -Ke^2\frac{\psi_{1,0,0}(\mathbf{r}-\boldsymbol{k}R)\psi_{1,0,0}(\mathbf{r})}{|\mathbf{r}-\boldsymbol{k}R|}$ *and obtain the result for* $A(R)$ *in Eq. (14.3.17).*

(c) Set $f(x,y,z) = \psi_{1,0,0}(\mathbf{r}-\boldsymbol{k}R)\psi_{1,0,0}(\mathbf{r})$ *and obtain the result for* $S(R)$ *in Eq. (14.3.15).*

(d) Show that $H_{\alpha,\alpha}(R) = -R_H + 2R_H(1+\frac{a_0}{R})e^{-2R/a_0}$

and $H_{\alpha,\beta}(R) = R_H(\frac{2a_0}{R} - 1 - \frac{7R}{3a_0} - \frac{R^2}{3a_0^2})e^{-R/a_0}$

(e) Show that as the interatomic distance exceeds the size of a single atom, that is, for $R > a_0$, *the coupling matrix element is negative, namely,* $H_{\alpha,\beta}(R) = -|H_{\alpha,\beta}(R)|$.

Solution 14.3.4

Following Ex. 12.2.8, we transform the integrals to elliptical coordinates,

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, f(x,y,z) = \int_{0}^{2\pi} d\varphi \int_{1}^{\infty} d\lambda \int_{-1}^{1} d\mu \frac{R^3}{8}(\lambda^2-\mu^2) g(\lambda,\mu,\varphi)\,,$$

where,

$$z = r\cos(\theta) = \frac{R}{2}(1-\mu\lambda)$$
$$x = r\sin(\theta)\cos(\varphi) = \frac{R}{2}\sqrt{\lambda^2+\mu^2-1-\mu^2\lambda^2}\cos(\varphi)$$
$$y = r\sin(\theta)\sin(\varphi) = \frac{R}{2}\sqrt{\lambda^2+\mu^2-1-\mu^2\lambda^2}\sin(\varphi)\ .$$

The elliptical coordinates are related to the inter-nuclear distance, $\mathbf{R} \equiv \mathbf{k}R = (0,0,R)$, *as follows:*

$\lambda \equiv \frac{r+r_q}{R}$; $1<\lambda<\infty$; $\mu \equiv \frac{r_q - r}{R}$; $-1<\mu<1$, *where,* $r_q \equiv |\mathbf{r}-\mathbf{R}|$, *and* $r \equiv |\mathbf{r}|$

.

(a)

In Ex. 12.2.8 we calculated the integral $Ke^2 q\int d\mathbf{r}\frac{|\psi_{1s}(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{R}|} = \frac{Kqe^2}{R}\left[1-(\frac{ZR}{a_0}+1)e^{\frac{-2ZR}{a_0}}\right]$. *Setting* $q=1$ *and* $Z=1$, *we obtain Eq. (14.3.16),*

$$C(R) = -Ke^2\int d\mathbf{r}\frac{|\psi_{1,0,0}(\mathbf{r})|^2}{|\mathbf{r}-\boldsymbol{k}R|} = \frac{-Ke^2}{R}\left[1-(\frac{R}{a_0}+1)e^{\frac{-2R}{a_0}}\right].$$

(b)

Using the explicit form of $\psi_{1,0,0}(\mathbf{r})$ *(Fig. 10.2.2), we obtain*

$$A(R) = -Ke^2\int d\mathbf{r}\frac{\psi_{1,0,0}(\mathbf{r}-\mathbf{k}R)\psi_{1,0,0}(\mathbf{r})}{|\mathbf{r}-\mathbf{k}R|} = \frac{-Z^3Ke^2}{\pi a_0^3}\int d\mathbf{r}\frac{1}{r_q}e^{-Zr/a_0}e^{-Zr_q/a_0}\,.$$

Changing to elliptical coordinates, we obtain

$$A(R) = \frac{-Z^3Ke^2}{\pi a_0^3}\int d\mathbf{r}\frac{1}{r_q}e^{-Zr/a_0}e^{-Zr_q/a_0}$$
$$= \frac{-Z^3Ke^2}{\pi a_0^3}\frac{R^3}{8}\int_0^{2\pi}d\varphi\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda(\lambda^2-\mu^2)\frac{1}{\frac{R}{2}(\lambda+\mu)}e^{\frac{-ZR}{2}(\lambda+\mu)/a_0}e^{\frac{-ZR}{2}(\lambda-\mu)/a_0}$$
$$= \frac{-Z^3Ke^2}{\pi a_0^3}\frac{R^2}{4}\int_0^{2\pi}d\varphi\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda(\lambda-\mu)e^{-ZR\,\lambda/a_0}$$
$$= \frac{-Z^3Ke^2}{a_0^3}\frac{R^2}{2}\left[\left(\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda\lambda e^{-ZR\,\lambda/a_0}\right)-\left(\int_{-1}^{1}\mu d\mu\int_1^{\infty}d\lambda e^{-ZR\,\lambda/a_0}\right)\right]$$
$$= \frac{-Z^3Ke^2R^2}{a_0^3}\int_1^{\infty}d\lambda\lambda e^{-ZR\,\lambda/a_0} \quad .$$

Defining, $\beta = \frac{ZR}{a_0}$*, we obtain*

$$A(R) = \frac{-ZKe^2}{a_0}\beta^2\int_1^{\infty}d\lambda\lambda e^{-\beta\lambda} = \frac{-ZKe^2}{a_0}\beta^2(-\frac{d}{d\beta}\int_1^{\infty}d\lambda e^{-\beta\lambda}) = \frac{-ZKe^2}{a_0}e^{-\beta}(1+\beta)$$

$$= \frac{-ZKe^2}{a_0}e^{\frac{-ZR}{a_0}}(1+\frac{ZR}{a_0}) \ ,$$

which yields Eq. (14.3.17) for $Z=1$.

(c)

Using the explicit form of $\psi_{1,0,0}(\mathbf{r})$ *(Fig. 10.2.2), we obtain*

$$S(R) = \int d\mathbf{r}\psi_{1,0,0}(\mathbf{r}-\boldsymbol{k}R)\psi_{1,0,0}(\mathbf{r}) = \frac{Z^3}{\pi a_0^3}\int d\mathbf{r}e^{-Zr/a_0}e^{-Zr_q/a_0} \ .$$

Changing to elliptical coordinates, we obtain

$$S(R) = \frac{Z^3}{\pi a_0^3}\int d\mathbf{r}e^{-Zr/a_0}e^{-Zr_q/a_0}$$
$$= \frac{Z^3}{\pi a_0^3}\frac{R^3}{8}\int_0^{2\pi}d\varphi\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda(\lambda^2-\mu^2)e^{\frac{-ZR}{2}(\lambda+\mu)/a_0}e^{\frac{-ZR}{2}(\lambda-\mu)/a_0}$$
$$= \frac{Z^3}{\pi a_0^3}\frac{R^3}{8}\int_0^{2\pi}d\varphi\int_{-1}^{1}d\mu\int_1^{\infty}d\lambda(\lambda^2-\mu^2)e^{-ZR\,\lambda/a_0} \ .$$

Defining, $\beta = \frac{ZR}{a_0}$*, we obtain*

$$S(R) = \frac{\beta^3}{8\pi}\int_0^{2\pi} d\varphi \int_{-1}^{1} d\mu \int_1^{\infty} d\lambda (\lambda^2 - \mu^2) e^{-\beta\lambda}$$

$$= \frac{1}{4}\beta^3 \int_{-1}^{1} d\mu \int_1^{\infty} d\lambda (\lambda^2 - \mu^2) e^{-\beta\lambda} = \frac{-1}{4}\beta^3 [\int_{-1}^{1} d\mu \int_1^{\infty} d\lambda \mu^2 e^{-\beta\lambda} - \int_{-1}^{1} d\mu \int_1^{\infty} d\lambda \lambda^2 e^{-\beta\lambda}]$$

$$= \frac{-1}{4}\beta^3 [\frac{2}{3}\int_1^{\infty} d\lambda e^{-\beta\lambda} - 2\frac{d^2}{d\beta^2}\int_1^{\infty} d\lambda e^{-\beta\lambda}] = \frac{-1}{4}\beta^3 [\frac{2}{3}\frac{e^{-\beta}}{\beta} - 2\frac{d^2}{d\beta^2}\frac{e^{-\beta}}{\beta}]$$

$$= \frac{-1}{4}\beta^3 [\frac{2}{3}\frac{e^{-\beta}}{\beta} + 2\frac{d}{d\beta}\frac{(\beta+1)e^{-\beta}}{\beta^2}] = \frac{-1}{4}\beta^3 [\frac{2}{3}\frac{e^{-\beta}}{\beta} + 2\frac{-(\beta+1)e^{-\beta}\beta^2 + e^{-\beta}\beta^2 - 2\beta(\beta+1)e^{-\beta}}{\beta^4}]$$

$$= \frac{-1}{4}\beta^3 [\frac{2}{3}\frac{e^{-\beta}}{\beta} + 2e^{-\beta}\frac{-\beta^2 - 2\beta - 2}{\beta^3}] = \frac{-1}{4}[\frac{2}{3}\beta^2 e^{-\beta} - 2e^{-\beta}(\beta^2 + 2\beta + 2)]$$

$$= -e^{-\beta}[\frac{1}{6}\beta^2 - (\frac{\beta^2}{2} + \beta + 1)] = e^{-\beta}[\frac{\beta^2}{3} + \beta + 1]$$

$$= e^{\frac{-ZR}{a_0}}[\frac{Z^2R^2}{3a_0^2} + \frac{ZR}{a_0} + 1],$$

which yields Eq. (14.3.15) for $Z = 1$.

(d)

Using Eq. (14.3.13), the Rydberg constant (see Chapter 10), $R_H = \frac{Ke^2}{2a_0} = -E_{1s}$*, and the results (a-c), we obtain*

$$H_{\alpha,\alpha}(R) = \frac{Ke^2}{R} + E_{1s} + \frac{-Ke^2}{R}\left[1 - (\frac{R}{a_0} + 1)e^{\frac{-2R}{a_0}}\right]$$

$$= R_H\frac{2a_0}{R} - R_H + R_H\frac{2a_0}{R}\left[(\frac{R}{a_0} + 1)e^{\frac{-2R}{a_0}} - 1\right] = 2R_H(1 + \frac{a_0}{R})e^{\frac{-2R}{a_0}} - R_H \quad ,$$

$$H_{\beta,\alpha}(R) = \left(\frac{Ke^2}{R} + E_{1s}\right)S(R) + A(R)$$

$$= \left(R_H\frac{2a_0}{R} - R_H\right)e^{\frac{-R}{a_0}}[\frac{R^2}{3a_0^2} + \frac{R}{a_0} + 1] - 2R_H e^{\frac{-R}{a_0}}(1 + \frac{R}{a_0}) = -R_H e^{\frac{-R}{a_0}}\left[\frac{R^2}{3a_0^2} + \frac{7}{3}\frac{R}{a_0} + 1 - \frac{2a_0}{R}\right].$$

(e)

Using the result of (d), $H_{\beta,\alpha}(R) = -R_H e^{\frac{-R}{a_0}} \left[\frac{R^2}{3a_0^2} + \frac{7}{3}\frac{R}{a_0} + 1 - \frac{2a_0}{R} \right]$, *we obtain*

$\frac{R}{a_0} > 1 \Rightarrow \left[\frac{R^2}{3a_0^2} + \frac{7}{3}\frac{R}{a_0} + 1 - \frac{2a_0}{R} \right] > 0$, *and therefore,* $R > a_0 \Rightarrow H_{\beta,\alpha}(R) < 0$.

Exercise 14.3.5 *(a) Use Eqs. (14.3.13, 14.3.15-14.3.17) to show that as the interatomic distance goes to zero, the electronic energies reflect the classical electrostatic repulsion between the nuclei,* $\tilde{\varepsilon}_\pm(R) \xrightarrow[R\to 0]{} \frac{Ke^2}{R}$. *(show that* $H_{\alpha,\alpha}(R) = R_H(-3 + \frac{2a_0}{R} + o(R^2))$, $H_{\beta,\alpha}(R) = R_H(-3 + \frac{2a_0}{R} - \frac{R}{3a_0} + o(R^2))$, $S(R) = 1 - \frac{R^2}{6a_0^2} + o(R^3)$ *). (b) Show that as the interatomic distance becomes infinite, the electronic energies converge to the ground state energy of an isolated hydrogen atom,* $\tilde{\varepsilon}_\pm(R) \xrightarrow[R\to\infty]{} -R_H$.

Solution 14.3.5

(a)

Based on Eqs. (14.3.13, 14.3.15, 14.3.16, 14.3.17), and using the results of Ex. 14.3.4, we obtain

$S(R) = e^{-R/a_0}[\frac{R^2}{3a_0^2} + \frac{R}{a_0} + 1]$, $H_{\alpha,\alpha}(R) = 2R_H(1 + \frac{a_0}{R})e^{\frac{-2R}{a_0}} - R_H$, *and*

$H_{\beta,\alpha}(R) = R_H e^{\frac{-R}{a_0}} \left[-\frac{R^2}{3a_0^2} - \frac{7}{3}\frac{R}{a_0} - 1 + \frac{2a_0}{R} \right]$.

Defining: $\bar{R} = R/a_0$, *and expanding the exponential function to the lowest orders in* $\bar{R}$, *we obtain*

$$\frac{H_{\alpha,\alpha}(\bar{R})}{R_H} = -1 + 2(1 + \frac{1}{\bar{R}})e^{-2\bar{R}} = -1 + (2 + \frac{2}{\bar{R}})(1 - 2\bar{R} + 2\bar{R}^2)$$

$$= -1 + (2 + \frac{2}{\bar{R}})(1 - 2\bar{R} + 2\bar{R}^2 + ...) = -1 + 2 - 4\bar{R} + \frac{2}{\bar{R}} - 4 + 4\bar{R} + o(\bar{R}^2) = -3 + \frac{2}{\bar{R}} + o(\bar{R}^2) ,$$

$$\frac{H_{\beta,\alpha}(R)}{R_H} = \left[-\frac{\bar{R}^2}{3} - \frac{7}{3}\bar{R} - 1 + \frac{2}{\bar{R}} \right] e^{\frac{-R}{a_0}} = \left[-\frac{\bar{R}^2}{3} - \frac{7}{3}\bar{R} - 1 + \frac{2}{\bar{R}} \right](1 - \bar{R} + \frac{\bar{R}^2}{2} + ...)$$

$$= -3 + \frac{2}{\bar{R}} - \frac{\bar{R}}{3} + o(\bar{R}^2),$$

$$S(R) = e^{-\bar{R}}[\frac{\bar{R}^2}{3} + \bar{R} + 1] = [\frac{\bar{R}^2}{3} + \bar{R} + 1]\left[1 - \bar{R} + \frac{\bar{R}^2}{2} + ...\right]$$

$$= 1 - \frac{\bar{R}^2}{6} + o(\bar{R}^3) \quad .$$

Consequently, the variational energy levels in the limit $\bar{R} \to 0$ *reproduce the classical electrostatic repulsion between the nuclei,*

$$\varepsilon_+(\bar{R}) = \frac{H_{\alpha,\alpha}(\bar{R}) + H_{\beta,\alpha}(\bar{R})}{1 + S(\bar{R})} = R_H \frac{-6 + \frac{4}{\bar{R}} - \frac{\bar{R}}{3} + o(\bar{R}^2)}{2 - \frac{\bar{R}^2}{6} + o(\bar{R}^3)} \xrightarrow[\bar{R}\to 0]{} R_H \frac{\frac{4}{\bar{R}}}{2} = R_H \frac{2}{\bar{R}} = \frac{Ke^2}{2a_0}\frac{2a_0}{R} = \frac{Ke^2}{R}$$

$$\varepsilon_-(\bar{R}) = \frac{H_{\alpha,\alpha}(\bar{R}) - H_{\beta,\alpha}(\bar{R})}{1 - S(\bar{R})} = R_H \frac{\frac{\bar{R}}{3} + o(\bar{R}^2)}{\frac{\bar{R}^2}{6} + o(\bar{R}^3)} = \xrightarrow[\bar{R}\to 0]{} R_H \frac{\frac{\bar{R}}{3}}{\frac{\bar{R}^2}{6}} = R_H \frac{2}{\bar{R}} = \frac{Ke^2}{R} .$$

(b)

Considering the limit $\bar{R} \to \infty$ *:*

$$\frac{H_{\alpha,\alpha}(\bar{R})}{R_H} = -1 + 2(1 + \frac{1}{\bar{R}})e^{-2\bar{R}} \xrightarrow[\bar{R}\to\infty]{} -1 \ ,$$

$$\frac{H_{\beta,\alpha}(\bar{R})}{R_H} = \left[-\frac{\bar{R}^2}{3} - \frac{7}{3}\bar{R} - 1 + \frac{2}{\bar{R}}\right]e^{\frac{-R}{a_0}} \xrightarrow[\bar{R}\to\infty]{} 0 \quad ,$$

$$\bar{S}(\bar{R}) = e^{-\bar{R}}[\frac{\bar{R}^2}{3} + \bar{R} + 1] \xrightarrow[\bar{R}\to\infty]{} 0 \ ,$$

and therefore, $\dfrac{H_{\alpha,\alpha}(\bar{R}) \pm H_{\beta,\alpha}(\bar{R})}{1 \pm S} \xrightarrow[\bar{R}\to 0]{} -R_H$.

Exercise 14.3.6 *(a) Use Eqs. (14.3.10, 14.3.13) to show that the difference between the two electronic energies reads* $\tilde{\varepsilon}_+(R) - \tilde{\varepsilon}_-(R) = 2\dfrac{A(R) - S(R)C(R)}{1 - S(R)^2}$. *(b) Use Eqs. (14.3.15-14.3.17) to* *show that as the internuclear distance becomes large in comparison to atomic sizes,* $R >> a_0$*, the energy splitting between the electronic states,* $\tilde{\varepsilon}_+(R) - \tilde{\varepsilon}_-(R)$ *decays exponentially, as* $\propto \frac{R}{a_0} \mathrm{e}^{-R/a_0}$*, and becomes proportional to the exchange integral,* $A(R)$.

Solution 14.3.6

(a)

Using $\tilde{\varepsilon}_\pm(R) = \frac{H_{\alpha,\alpha}(R) \pm H_{\beta,\alpha}(R)}{1 \pm S(R)}$ *(Eq. (14.3.10)), we obtain*

$$\tilde{\varepsilon}_+(R) - \tilde{\varepsilon}_-(R) = \frac{H_{\alpha,\alpha}(R) + H_{\beta,\alpha}(R)}{1+S(R)} - \frac{H_{\alpha,\alpha}(R) - H_{\beta,\alpha}(R)}{1-S(R)}$$
$$= \frac{\left(H_{\alpha,\alpha}(R) + H_{\beta,\alpha}(R)\right)\left(1-S(R)\right) - \left(H_{\alpha,\alpha}(R) - H_{\beta,\alpha}(R)\right)\left(1+S(R)\right)}{1-S^2(R)}$$
$$= 2\frac{H_{\beta,\alpha}(R) - S(R)H_{\alpha,\alpha}(R)}{1-S^2(R)} \quad .$$

Using additionally (Eq. (14.3.13)) $H_{\alpha,\alpha}(R) = \frac{Ke^2}{R} + E_{1s} + C(R)$ *and* $H_{\beta,\alpha}(R) = \left(\frac{Ke^2}{R} + E_{1s}\right) S(R) + A(R)$*, we obtain*

$$\tilde{\varepsilon}_+(R) - \tilde{\varepsilon}_-(R) = 2\frac{A(R) - S(R)C(R)}{1-S^2(R)} \, .$$

(b)

Introducing the Rydberg constant, $R_H = \frac{Ke^2}{2a_0} = -E_{1s}$*, and* $\bar{R} = R / a_0$*, Eqs. (14.3.15-14.3.17) yield in the limit* $\bar{R} >> 1$,

$$\bar{C}(\bar{R}) = -2[\frac{1}{\bar{R}} - (1+\frac{1}{\bar{R}})e^{-2\bar{R}}] \xrightarrow[\bar{R}>>1]{} \frac{-2}{\bar{R}} \, ,$$

$$\bar{A}(\bar{R}) = -2(\bar{R}+1)e^{-\bar{R}} \xrightarrow[\bar{R}>>1]{} -2\bar{R}e^{-\bar{R}} \, ,$$

$$\bar{S}(\bar{R}) = e^{-\bar{R}}[\frac{\bar{R}^2}{3} + \bar{R} + 1] \xrightarrow[\bar{R}>>1]{} \frac{\bar{R}^2}{3} e^{-\bar{R}} \, .$$

Therefore, the difference between the variational energies in this limit reads

$$\tilde{\varepsilon}_+(R)-\tilde{\varepsilon}_-(R)=2\frac{A(R)-S(R)C(R)}{1-S^2(R)}$$

$$\xrightarrow[\bar{R}>>1]{} 2\frac{-2\bar{R}-\frac{\bar{R}^2}{3}\frac{-2}{\bar{R}}}{1-\frac{\bar{R}^4}{9}e^{-2\bar{R}}}e^{-\bar{R}}=2\frac{-2\bar{R}+\frac{2\bar{R}}{3}}{1}e^{-\bar{R}}=\frac{-8\bar{R}}{3}e^{-\bar{R}}\xrightarrow[\bar{R}\to\infty]{}\frac{4}{3}A(\bar{R}).$$

Exercise 14.4.1 *Let the operator $\hat{H}$ commute with the Hermitian operator $\hat{A}$, and let $|\varphi_1\rangle$ and $|\varphi_2\rangle$ be two eigenvectors of $\hat{A}$, associated with two different eigenvalues, $\hat{A}|\varphi_1\rangle=\alpha_1|\varphi_1\rangle$, $\hat{A}|\varphi_2\rangle=\alpha_2|\varphi_2\rangle$, $\alpha_1\neq\alpha_2$. (a) Show that the vectors $\hat{H}|\varphi_1\rangle$ and $\hat{H}|\varphi_2\rangle$ are eigenvectors of $\hat{A}$, corresponding to the eigenvalue, α_1 and α_2, respectively. (b) Use the Hermiticity of $\hat{A}$ to prove that $H_{1,2}=\langle\varphi_2|\hat{H}|\varphi_1\rangle=0$.*

Solution 14.4.1

(a)

Let: $\hat{A}|\varphi_1\rangle=\alpha_1|\varphi_1\rangle$ and $\hat{A}|\varphi_2\rangle=\alpha_2|\varphi_2\rangle$ with $\alpha_1\neq\alpha_2$, and let $\left[\hat{H},\hat{A}\right]=0$. Consequently,

$$\hat{A}\left[\hat{H}|\varphi_1\rangle\right]=\hat{H}\left[\hat{A}|\varphi_1\rangle\right]=\hat{H}\alpha_1|\varphi_1\rangle=\alpha_1\left[\hat{H}|\varphi_1\rangle\right]$$
$$\hat{A}\left[\hat{H}|\varphi_2\rangle\right]=\hat{H}\left[\hat{A}|\varphi_2\rangle\right]=\hat{H}\alpha_2|\varphi_2\rangle=\alpha_2\left[\hat{H}|\varphi_2\rangle\right],$$

namely, the vectors $\hat{H}|\varphi_1\rangle$ and $\hat{H}|\varphi_2\rangle$ are eigenvectors of $\hat{A}$, corresponding to the eigenvalues α_1 and α_2, respectively.

(b)

Since $\hat{A}$ is Hermitian, its eigenvectors that correspond to different eigenvalues are orthogonal. Since $\hat{A}|\varphi_2\rangle=\alpha_2|\varphi_2\rangle$ (given) and $\hat{A}\left[\hat{H}|\varphi_1\rangle\right]=\alpha_1\left[\hat{H}|\varphi_1\rangle\right]$ (see (a)), and since $\alpha_1\neq\alpha_2$, we obtain $H_{1,2}=\langle\varphi_2|\hat{H}|\varphi_1\rangle=0$.

Exercise 14.4.2 *Use the condition for "energy matching",* $2|H_{\alpha,\beta}|>>\left|H_{\alpha,\alpha}-H_{\beta,\beta}\right|$*, in Eqs. (14.4.9, 14.4.10) to obtain the approximations for the orbital energies and coefficients in Eqs. (14.4.12, 14.4.13).*

Solution 14.4.2

The condition for "energy matching" reads $2|H_{\alpha,\beta}|>>\left|H_{\alpha,\alpha}-H_{\beta,\beta}\right|$*, which means that*

$$1+\frac{4|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}\approx\frac{4|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}.$$

Consequently Eq. (14.4.9) yields

$$\varepsilon_1\approx\frac{H_{\alpha,\alpha}+H_{\beta,\beta}}{2}+\frac{H_{\alpha,\alpha}-H_{\beta,\beta}}{2}\sqrt{\frac{4|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}}=\frac{H_{\alpha,\alpha}+H_{\beta,\beta}}{2}+\left|H_{\alpha,\beta}\right|$$

$$\varepsilon_2\approx\frac{H_{\alpha,\alpha}+H_{\beta,\beta}}{2}-\frac{H_{\alpha,\alpha}-H_{\beta,\beta}}{2}\sqrt{\frac{4|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}}=\frac{H_{\alpha,\alpha}+H_{\beta,\beta}}{2}-\left|H_{\alpha,\beta}\right|.$$

Since $\xi=\sqrt{1+4|H_{\alpha,\beta}|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}\approx\sqrt{4H_{\alpha,\beta}{}^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}>>1$*, Eq. (14.4.10) yields*

$$\left|\phi_1\right\rangle\approx\sqrt{\frac{\xi}{2\xi}}\left|\varphi_\alpha\right\rangle-\sqrt{\frac{\xi}{2\xi}}\left|\varphi_\beta\right\rangle=\sqrt{\frac{1}{2}}\left|\varphi_\alpha\right\rangle-\sqrt{\frac{1}{2}}\left|\varphi_\beta\right\rangle$$

$$\left|\phi_2\right\rangle\approx\sqrt{\frac{\xi}{2\xi}}\left|\varphi_\alpha\right\rangle+\sqrt{\frac{\xi}{2\xi}}\left|\varphi_\beta\right\rangle=\sqrt{\frac{1}{2}}\left|\varphi_\alpha\right\rangle+\sqrt{\frac{1}{2}}\left|\varphi_\beta\right\rangle.$$

Exercise 14.4.3 *Use the condition for "energy mismatching",* $2|H_{\alpha,\beta}|<<|H_{\alpha,\alpha}-H_{\beta,\beta}|$*, in Eqs. (14.4.9, 14.4.10) to obtain the approximations for the orbital energies and coefficients in Eqs. (14.4.14, 14.4.15).*

Solution 14.4.3

The condition for "energy mismatching" reads $2|H_{\alpha,\beta}|<<|H_{\alpha,\alpha}-H_{\beta,\beta}|$*, which means that*

$$\sqrt{1+\frac{4|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}} \approx 1+\frac{2|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2} .$$

Consequently, Eq. (14.4.9) yields

$$\varepsilon_1 \approx \frac{H_{\alpha,\alpha}+H_{\beta,\beta}}{2}+\frac{H_{\alpha,\alpha}-H_{\beta,\beta}}{2}(1+\frac{2|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}) = H_{\alpha,\alpha}+\frac{|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)}$$

$$\varepsilon_2 = \frac{H_{\alpha,\alpha}+H_{\beta,\beta}}{2}-\frac{H_{\alpha,\alpha}-H_{\beta,\beta}}{2}(1+\frac{2|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}) = H_{\beta,\beta}-\frac{|H_{\alpha,\beta}|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)} .$$

Since $\xi \equiv \sqrt{1+4\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2} \approx 1+2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2$, *Eq. (14.4.10) yields*

$$\left|\phi_1\right\rangle = \sqrt{\frac{\xi+1}{2\xi}}\left|\varphi_\alpha\right\rangle - \sqrt{\frac{\xi-1}{2\xi}}\left|\varphi_\beta\right\rangle$$

$$\cong \sqrt{\frac{2+2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}{2(1+2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2)}}\left|\varphi_\alpha\right\rangle - \sqrt{\frac{2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}{2(1+2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2)}}\left|\varphi_\beta\right\rangle$$

$$\cong \left|\varphi_\alpha\right\rangle - \sqrt{\frac{\left|H_{\alpha,\beta}\right|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}}\left|\varphi_\beta\right\rangle = \left|\varphi_\alpha\right\rangle - \frac{\left|H_{\alpha,\beta}\right|}{H_{\alpha,\alpha}-H_{\beta,\beta}}\left|\varphi_\beta\right\rangle \cong \left|\varphi_\alpha\right\rangle \quad ,$$

$$\left|\phi_2\right\rangle = \sqrt{\frac{\xi-1}{2\xi}}\left|\varphi_\alpha\right\rangle + \sqrt{\frac{\xi+1}{2\xi}}\left|\varphi_\beta\right\rangle$$

$$\cong \sqrt{\frac{2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}{2}}\left|\varphi_\alpha\right\rangle + \sqrt{\frac{2+2\left|H_{\alpha,\beta}\right|^2/\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}{2\xi}}\left|\varphi_\beta\right\rangle$$

$$\left|\phi_2\right\rangle \cong \sqrt{\frac{\left|H_{\alpha,\beta}\right|^2}{\left(H_{\alpha,\alpha}-H_{\beta,\beta}\right)^2}}\left|\varphi_\alpha\right\rangle + \left|\varphi_\beta\right\rangle = \frac{\left|H_{\alpha,\beta}\right|^2}{H_{\alpha,\alpha}-H_{\beta,\beta}}\left|\varphi_\alpha\right\rangle + \left|\varphi_\beta\right\rangle \cong \left|\varphi_\beta\right\rangle \ .$$

Exercise 14.4.4 *(a) Show that solutions to the secular equation, Eq. (14.4.16), which are perfectly delocalized (defined in Eq. (14.4.18)), correspond to the orbital energies,* $\varepsilon_\pm$ *, as given in Eq. (14.4.19). (b) Show that the orbital energies in Eq. (14.4.19) are not equally displaces in energy with respect to* $H_{\alpha,\alpha}$ *(*$H_{\beta,\beta}$*), namely* $|\varepsilon_+ - H_{\alpha,\alpha}| < |\varepsilon_- - H_{\alpha,\alpha}|$.

Solution 14.4.4

(a)

Using $c_{\alpha}^{(k)} = \pm c_{\beta}^{(k)}$ *in the secular equation (Eq. (14.4.16)), we obtain*

$$\left(H_{\alpha,\alpha} - \varepsilon_k\right) = \mp\left(H_{\alpha,\beta} - \varepsilon_k s\right)$$

$$H_{\alpha,\beta} - \varepsilon_k s = \mp\left(H_{\beta,\beta} - \varepsilon_k\right).$$

Consequently, the corresponding eigenvalues (denoted $\varepsilon_{\pm}$ *) read*

$$\varepsilon_{\pm} = \frac{H_{\alpha,\alpha} \pm H_{\alpha,\beta}}{1 \pm s} = \frac{H_{\beta,\beta} \pm H_{\alpha,\beta}}{1 \pm s} \quad .$$

b)

Using the expression in (a) for $\varepsilon_{\pm}$*, we obtain*

$$\varepsilon_{+} - H_{\alpha,\alpha} = \frac{H_{\alpha,\alpha} + H_{\alpha,\beta}}{1+s} - H_{\alpha,\alpha} = \frac{H_{\alpha,\beta} - sH_{\alpha,\alpha}}{1+s} = \frac{\left(H_{\alpha,\beta} - sH_{\alpha,\alpha}\right)(1-s)}{1-s^2}$$

$$\varepsilon_{-} - H_{\alpha,\alpha} = \frac{H_{\alpha,\alpha} - H_{\alpha,\beta}}{1-s} - H_{\alpha,\alpha} = \frac{-H_{\alpha,\beta} + sH_{\alpha,\alpha}}{1-s} = -\frac{\left(H_{\alpha,\beta} - sH_{\alpha,\alpha}\right)(1+s)}{1-s^2} \quad .$$

Since for $0 < s < 1$ *we have,* $\left|\frac{\left(H_{\alpha,\beta} - sH_{\alpha,\alpha}\right)(1-s)}{1-s^2}\right| < \left|-\frac{\left(H_{\alpha,\beta} - sH_{\alpha,\alpha}\right)(1+s)}{1-s^2}\right|$*, we conclude that* $\left|\varepsilon_{+} - H_{\alpha,\alpha}\right| < \left|\varepsilon_{-} - H_{\alpha,\alpha}\right|$*. This means the in the case of finite overlap between the two atomic orbitals, the molecular orbital energies (Eq. (14.4.19)) are not equally displaces in energy with respect to the atomic orbital energies* $H_{\alpha,\alpha}$ *(*$= H_{\beta,\beta}$*), where the "energy gain" in* ε_{+} *is not compensated for by the "energy loss" in* ε_{-}*.*

Exercise 14.4.5

(a) The secular equation for the Huckel model for a uniform linear chain reads (see Fig. 14.4.7)

$$\begin{cases} (\varepsilon_\alpha - \varepsilon_k)c_1^{(k)} + \beta c_2^{(k)} = 0 & ; \quad n=1 \\ \beta c_{n-1}^{(k)} + (\varepsilon_\alpha - \varepsilon_k)c_n^{(k)} + \beta c_{n+1}^{(k)} = 0 & ; \quad 1<n<N \\ \beta c_{N-1}^{(k)} + (\varepsilon_\alpha - \varepsilon_k)c_N^{(k)} = 0 & ; \quad n=N \end{cases}.$$

Show that the orbital energies (Eq. (14.4.25)) and coefficients (Eq. (14.4.26)) satisfy these secular equations. Show that $\sum_{n=1}^{N}\left(c_n^{(k)}\right)^2 = 1$.

(b) The secular equation for the Huckel model for a uniform cyclic chain reads (see Fig. 14.4.7)

$$\begin{cases} (\varepsilon_\alpha - \varepsilon_k)c_1^{(k)} + \beta c_2^{(k)} + \beta c_N^{(k)} = 0 & ; \quad n=1 \\ \beta c_{n-1}^{(k)} + (\varepsilon_\alpha - \varepsilon_k)c_n^{(k)} + \beta c_{n+1}^{(k)} = 0 & ; \quad 1<n<N \\ \beta c_1^{(k)} + \beta c_{N-1}^{(k)} + (\varepsilon_\alpha - \varepsilon_k)c_N^{(k)} = 0 & ; \quad n=N \end{cases}.$$

Show that the orbital energies (Eq. (14.4.27)) and coefficients (Eq. (14.4.28)) satisfy these secular equations. Show that $\sum_{n=1}^{N}\left(c_n^{(k)}\right)^2 = 1$.

Solution 14.4.5

(a)

Substitution of the orbital energies (Eq. (14.4.25)) and coefficients (Eq. (14.4.26)) in the secular equation,

$$\begin{cases} (\varepsilon_\alpha - \varepsilon_k)c_1^{(k)} + \beta c_2^{(k)} = 0 & ; \quad n=1 \\ \beta c_{n-1}^{(k)} + (\varepsilon_\alpha - \varepsilon_k)c_n^{(k)} + \beta c_{n+1}^{(k)} = 0 & ; \quad 1<n<N \\ \beta c_{N-1}^{(k)} + (\varepsilon_\alpha - \varepsilon_k)c_N^{(k)} = 0 & ; \quad n=N \end{cases},$$

yields

$$\begin{cases} -2\beta\cos(\frac{\pi k}{(N+1)})\sin(\frac{\pi k}{(N+1)}) + \beta\sin(\frac{2\pi k}{(N+1)}) = 0 & ; \quad n=1 \\ \beta\sin(\frac{(n-1)\pi k}{(N+1)}) - 2\beta\cos(\frac{\pi k}{(N+1)})\sin(\frac{n\pi k}{(N+1)}) + \beta\sin(\frac{(n+1)\pi k}{(N+1)}) = 0 & ; \quad 1<n<N \\ \beta\sin(\frac{(N-1)\pi k}{(N+1)}) - 2\beta\cos(\frac{\pi k}{(N+1)})\sin(\frac{N\pi k}{(N+1)}) = 0 & ; \quad n=N \end{cases}.$$

Using the identity, $\sin(\theta-\varphi)+\sin(\theta+\varphi) = 2\cos(\varphi)\sin(\theta)$, *these equations are shown to hold.*

To verify the normalization, $\sum_{n=1}^{N}\left(c_n^{(k)}\right)^2=1$, *we notice that*

$$\sum_{n=1}^{N}\sin^2\left(\frac{n\pi k}{(N+1)}\right)=\sum_{n=1}^{N+1}\sin^2\left(\frac{n\pi k}{(N+1)}\right)=\frac{N+1}{2}-\frac{1}{2}\sum_{n=1}^{N+1}\cos\left(\frac{2n\pi k}{(N+1)}\right)=\frac{N+1}{2}.$$

(b)

Substitution of the orbital energies (Eq. (14.4.27)) and coefficients (Eq. (14.4.28)) in the secular equation,

$$\begin{cases}(\varepsilon_\alpha-\varepsilon_k)c_1^{(k)}+\beta c_2^{(k)}+\beta c_N^{(k)}=0 & ; \quad n=1\\ \beta c_{n-1}^{(k)}+(\varepsilon_\alpha-\varepsilon_k)c_n^{(k)}+\beta c_{n+1}^{(k)}=0 & ; \quad 1<n<N\\ \beta c_1^{(k)}+\beta c_{N-1}^{(k)}+(\varepsilon_\alpha-\varepsilon_k)c_N^{(k)}=0 & ; \quad n=N\end{cases},$$

yields

$$\begin{cases}-2\beta\cos\left(\frac{2\pi k}{N}\right)\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k}{N}}+\beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k2}{N}}+\beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi kN}{N}}=0 & ; \quad n=1\\ \beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k(n-1)}{N}}-2\beta\cos\left(\frac{2\pi k}{N}\right)\frac{1}{\sqrt{N}}e^{-i\frac{2\pi kn}{N}}+\beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k(n+1)}{N}}=0 & ; \quad 1<n<N\\ \beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k}{N}}+\beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k(N-1)}{N}}-2\beta\cos\left(\frac{2\pi k}{N}\right)\frac{1}{\sqrt{N}}e^{-i\frac{2\pi kN}{N}}=0 & ; \quad n=N\end{cases},$$

which is equivalent to:

$$\begin{cases}-\beta\left(e^{-i\frac{4\pi k}{N}}+1\right)\frac{1}{\sqrt{N}}+\beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k2}{N}}+\beta\frac{1}{\sqrt{N}}1=0 & ; \quad n=1\\ \beta\frac{1}{\sqrt{N}}e^{i\frac{2\pi k}{N}}-2\beta\cos\left(\frac{2\pi k}{N}\right)\frac{1}{\sqrt{N}}+\beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k}{N}}=0 & ; \quad 1<n<N\\ \beta\frac{1}{\sqrt{N}}e^{-i\frac{2\pi k}{N}}+\beta\frac{1}{\sqrt{N}}e^{i\frac{2\pi k}{N}}-2\beta\cos\left(\frac{2\pi k}{N}\right)\frac{1}{\sqrt{N}}1=0 & ; \quad n=N\end{cases}.$$

Using $2\cos(\theta)=e^{i\theta}+e^{-i\theta}$, *these equations are shown to hold.*

To verify the normalization, $\sum_{n=1}^{N}\left(c_n^{(k)}\right)^2=1$, *we notice that,* $\sum_{n=1}^{N}|e^{i\frac{2\pi kn}{N}}|^2=N$.

Exercise 14.4.6 *Prove the asymptotic results in Eqs. (14.4.29, 14.4.30).*

Solution 14.4.6

For the linear chain we obtain

$$\varepsilon^{(k+1)}-\varepsilon^{(k)}=2\beta\{\cos[\frac{(k+1)\pi}{(N+1)}]-\cos[\frac{k\pi}{(N+1)}]\}=-4\beta\sin[\frac{(2k+1)\pi}{2(N+1)}]\sin[\frac{\pi}{2(N+1)}]\xrightarrow[N\to\infty]{}0 \quad .$$

For the cyclic chain we obtain

$$\varepsilon^{(k+1)}-\varepsilon^{(k)}=2\beta\{\cos[\frac{2(k+1)\pi}{N}]-\cos[\frac{2k\pi}{N}]\}$$
$$=2\beta\{\cos[\frac{2k\pi}{N}]\cos[\frac{2\pi}{N}]-\sin[\frac{2k\pi}{N}]\sin[\frac{2\pi}{N}]-\cos[\frac{2k\pi}{N}]\}$$
$$\xrightarrow[N\to\infty]{}2\beta\{[\cos[\frac{2\pi}{N}]-1]]\cos[\frac{2k\pi}{N}]\}\xrightarrow[N\to\infty]{}0\,.$$

Exercise 14.5.1

(a) *Derive Eq. (14.5.4) by substituting the plane wave expansion of* $\psi(x)$ *in the Schrödinger equation with a periodic potential, Eqs. (14.5.1,14.5.2), projecting the result on the plane wave,* e^{ikx}*, and using the representation of the delta function,* $\delta(k)=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}e^{ikx}dx$.

(b) *Derive Eq. (14.5.5) by substituting the plane wave expansion of* $\psi(x)$ *in the Schrödinger equation with a periodic potential, Eqs. (14.5.1,14.5.2), projecting the result on the plane wave,* $e^{i(k-\frac{2\pi}{a}n)x}$*, and using the representation of the delta function,* $\delta(k)=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}e^{ikx}dx$.

(c) *Use the definition,* $u_k(x)\equiv e^{-ikx}\psi_k(x)$*, and Eq. (14.5.7) to derive Eq. (14.5.8).*

(d) *Obtain Eq. (14.5.10) by substituting Eqs. (14.5.8, 14.5.9) in Eq. (14.5.6).*

(e) *Use the general form of the solutions to the Schrödinger equation for a periodic potential (Eq. (14.5.7)) and prove Eq. (14.5.11).*

Solution 14.5.1

(a)

Substitution of the expansion, $\psi(x)=\frac{1}{\sqrt{2\pi}}\int\limits_{-\infty}^{\infty}e^{ik'x}\overline{\psi}(k')dk'$*, in Eq. (14.5.1) with a periodic potential energy, (Eq. (14.5.2)) yields*

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\sum_{n=-\infty}^{\infty}V_n e^{\frac{i2\pi n}{a}x}-E\right]\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{ik'x}\bar{\psi}(k')dk'=0 .$$

projecting on the plane wave, $\frac{1}{\sqrt{2\pi}}e^{ikx}$*, we obtain*

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}dxe^{-ikx}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\sum_{n=-\infty}^{\infty}V_n e^{\frac{i2\pi n}{a}x}-E\right]\int_{-\infty}^{\infty}e^{ik'x}\bar{\psi}(k')dk'=0 .$$

We now take the second derivative with respect to x*, and change the order of integration to obtain*

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}dk'\int_{-\infty}^{\infty}dx\left[\sum_{n=-\infty}^{\infty}V_n e^{i(k'+\frac{2\pi n}{a}-k)x}+\left(\frac{\hbar^2k'^2}{2m}-E\right)e^{i(k'-k)x}\right]\bar{\psi}(k')=0 .$$

Using the definition of Dirac's delta, $\delta(k)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ikx}dx$*, we obtain*

$$\int_{-\infty}^{\infty}dk'\left[\sum_{n=-\infty}^{\infty}V_n\delta(k'+\frac{2\pi n}{a}-k)+\left(\frac{\hbar^2k'^2}{2m}-E\right)\delta(k'-k)\right]\bar{\psi}(k')=0 ,$$

and finally, the integral over dk' *yields*

$$\left[\sum_{n=-\infty}^{\infty}V_n\bar{\psi}(k-\frac{2\pi n}{a})\right]+\left(\frac{\hbar^2k^2}{2m}-E\right)\bar{\psi}(k)=0 ,$$

which can also be written as Eq. (14.5.4),

$$\sum_{n=-\infty}^{\infty}\left[V_n+\delta_{n,0}\left(\frac{\hbar^2k^2}{2m}-E\right)\right]\bar{\psi}(k-\frac{2\pi}{a}n)=0 .$$

(b)

As in (a), the Schrödinger equation with a periodic potential energy can be written as

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\sum_{n=-\infty}^{\infty}V_n e^{\frac{i2\pi n}{a}x}-E\right]\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{ik'x}\bar{\psi}(k')dk'=0 .$$

Projecting on a plane wave, $\frac{1}{\sqrt{2\pi}}e^{i(k-\frac{2\pi n}{a})x}$*, for any* $-\infty<n<\infty$*, and following the steps in (a) we obtain*

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}dxe^{-i(k-\frac{2\pi n}{a})x}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\sum_{n'=-\infty}^{\infty}V_{n'}e^{\frac{i2\pi n'}{a}x}-E\right]\int_{-\infty}^{\infty}e^{ik'x}\bar{\psi}(k')dk'=0$$

$$\Rightarrow\int_{-\infty}^{\infty}dk'\int_{-\infty}^{\infty}dx\left[\sum_{n'=-\infty}^{\infty}V_{n'}e^{i(k'+\frac{2\pi(n'+n)}{a}-k)x}+\left(\frac{\hbar^2k'^2}{2m}-E\right)e^{i(k'-k+\frac{2\pi n}{a})x}\right]\bar{\psi}(k')=0$$

$$\Rightarrow \int_{-\infty}^{\infty} dk' \left[\sum_{n'=-\infty}^{\infty} V_{n'} \delta(k' + \frac{2\pi(n+n')}{a} - k) + \left(\frac{\hbar^2 k'^2}{2m} - E \right) \delta(k' - k + \frac{2\pi n}{a}) \right] \bar{\psi}(k') = 0$$

$$\Rightarrow \left[\sum_{n'=-\infty}^{\infty} V_{n'} \bar{\psi}(k - \frac{2\pi(n+n')}{a}) \right] + \left(\frac{\hbar^2}{2m} (k - \frac{2\pi n}{a})^2 - E \right) \bar{\psi}(k - \frac{2\pi n}{a}) = 0 .$$

Changing the summation index, we obtain Eq. (14.5.5),

$$\left[\sum_{n'=-\infty}^{\infty} V_{n'-n} \bar{\psi}(k - \frac{2\pi n'}{a}) \right] + \left(\frac{\hbar^2}{2m} (k - \frac{2\pi n}{a})^2 - E \right) \bar{\psi}(k - \frac{2\pi n}{a}) = 0$$

$$\Rightarrow \sum_{n'=-\infty}^{\infty} \left[V_{n'-n} + \delta_{n,n'} \left(\frac{\hbar^2}{2m} (k - \frac{2\pi}{a} n)^2 - E \right) \right] \bar{\psi}(k - \frac{2\pi}{a} n') = 0 .$$

(c)

Given, $\psi_k(x+a) = e^{ika}\psi_k(x)$, *and* $u_k(x) = e^{-ikx}\psi_k(x)$, *we readily obtain*

$$u_k(x+a) = e^{-ik(x+a)}\psi_k(x+a) = e^{-ik(x+a)}e^{ika}\psi_k(x) = e^{-ikx}\psi_k(x) = u_k(x) .$$

(d)

By Eq. (14.5.6) we obtain $\bar{\psi}(k - \frac{2\pi n}{a}) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} e^{i\frac{2\pi}{a}nx} \psi_k(x) dx$.

Using the Bloch theorem (Eq. (14.5.8)) we identify, $e^{-ikx}\psi_k(x) = u_k(x)$, *and using Eq. (14.5.9), we obtain*

$$\bar{\psi}(k - \frac{2\pi n}{a}) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\frac{2\pi}{a}nx} u_k(x) dx = \frac{1}{\sqrt{2\pi}} \sum_{n'=-\infty}^{\infty} u_{n'}^{(k)} \int_{-\infty}^{\infty} e^{i\frac{2\pi}{a}(n+n')x} dx = \sqrt{2\pi} u_{-n}^{(k)}$$

$$\Rightarrow u_n^{(k)} = \frac{1}{\sqrt{2\pi}} \bar{\psi}(k + \frac{2\pi n}{a}) .$$

(e)

Using Eqs. (14.5.7) the solutions to the Schrödinger equation with a periodic potential energy have a generic form, $\psi(x+a) = e^{ika}\psi(x)$. *Each solution satisfying this relation is denoted by a wave vector* k', *where* $\psi_{k'}(x+a) = e^{ik'a}\psi_{k'}(x)$. *Choosing* $k' = k + 2\pi n / a$ *(for any integer* n*) we obtain*

$$\psi_{k+2\pi n/a}(x+a) = e^{i(k+2\pi n/a)a}\psi_{k+2\pi n/a}(x) = e^{ika}\psi_{k+2\pi n/a}(x) .$$

On the other hand, by definition, $\psi_k(x+a) = e^{ika}\psi_k(x)$. *Hence,* $\psi_{k+2\pi n/a}(x)$ *and* $\psi_k(x)$ *cannot be distinguished,*

$\psi_{k+2\pi n/a}(x) = \psi_k(x)$.

Notice that the functions $u_k(x) = e^{-ikx}\psi_k(x)$ *and* $u_{k+2\pi n/a}(x) = e^{-i(k+2\pi n/a)x}\psi_{k+2\pi n/a}(x)$ *are both periodic,* $u_{k+2\pi n/a}(x+a) = e^{-i(k+2\pi n/a)(x+a)}\psi_{k+2\pi n/a}(x+a) = e^{-i(k+2\pi n/a)x}\psi_{k+2\pi n/a}(x) = u_{k+2\pi n/a}(x)$,

and $u_k(x+a) = e^{-ik(x+a)}\psi_k(x+a) = e^{-ikx}\psi_k(x) = u_k(x)$. *Using* $\psi_k(x) = \psi_{k+2\pi n/a}(x)$, *we obtain* $u_{k+2\pi n/a}(x) = e^{-i2\pi nx/a}u_k(x)$, *which compensates for the difference in the wavevector between* $\psi_k(x)$ *and* $\psi_{k+2\pi n/a}(x)$.

Exercise 14.5.2

(a) *Defining the "unit cell" coefficient vector,* $\mathbf{c}_n^{(l)} = (c_{1,n}^{(l)}, c_{2,n}^{(l)}, ..., c_{M,n}^{(l)})$ *and using Eq. (14.5.18) for the matrix* $\mathbf{S}$ *and Eq. (14.5.21) for the Hamiltonian,* $\mathbf{H}$*, show that the secular equation (Eq. (14.5.17)) reads* $\boldsymbol{\beta}^t\mathbf{c}_{n-1}^{(l)} + [\boldsymbol{\alpha} - \varepsilon_l\mathbf{I}]\mathbf{c}_n^{(l)} + \boldsymbol{\beta}\mathbf{c}_{n+1}^{(l)} = 0$.

(b) *Use the ansatz* $\mathbf{c}_n^{(l)} = \mathbf{u}^{(l,\tilde{k})}e^{i\tilde{k}n}$*, where,* $\mathbf{u}^{(l,\tilde{k})} \equiv (u_1^{(l,\tilde{k})}, u_2^{(l,\tilde{k})}, ..., u_M^{(l,\tilde{k})})$*, to show that the unit cell vectors,* $\{\mathbf{u}^{(l,\tilde{k})}\}$*, are the eigenvectors of a finite dimensional Hermitian matrix,* $\left[\boldsymbol{\alpha} + \boldsymbol{\beta}^t e^{-i\tilde{k}} + \boldsymbol{\beta}e^{i\tilde{k}}\right]\mathbf{u}^{(l,\tilde{k})} = \varepsilon_l(\tilde{k})\mathbf{u}^{(l,\tilde{k})}$, *for* $l = 1, 2, ..., M$.

Solution 14.5.2

(a)

In block matrix form, the infinite secular equation which involves the n *th unit cell and the neighboring cells reads*

$$\begin{bmatrix} \ddots & \boldsymbol{\beta} & & & \\ \boldsymbol{\beta}^t & \boldsymbol{\alpha}-\varepsilon_l\mathbf{I} & \boldsymbol{\beta} & & \\ & \boldsymbol{\beta}^t & \boldsymbol{\alpha}-\varepsilon_l\mathbf{I} & \boldsymbol{\beta} & \\ & & \boldsymbol{\beta}^t & \boldsymbol{\alpha}-\varepsilon_l\mathbf{I} & \boldsymbol{\beta} \\ & & & \boldsymbol{\beta}^t & \ddots \end{bmatrix} \begin{bmatrix} \vdots \\ \mathbf{c}_{n-1}^{(l)} \\ \mathbf{c}_n^{(l)} \\ \mathbf{c}_{n+1}^{(l)} \\ \vdots \end{bmatrix} = \begin{bmatrix} \vdots \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \vdots \end{bmatrix}.$$

The n *th row of this equation therefore reads* $\boldsymbol{\beta}^t\mathbf{c}_{n-1}^{(l)} + [\boldsymbol{\alpha} - \varepsilon_l\mathbf{I}]\mathbf{c}_n^{(l)} + \boldsymbol{\beta}\mathbf{c}_{n+1}^{(l)} = 0$.

(b)

Defining $\mathbf{c}_n^{(l)} = \mathbf{u}^{(l,\tilde{k})} e^{i\tilde{k}n}$ *and substituting in the equation obtained in (a), we obtain*

$$\boldsymbol{\beta}^t \mathbf{u}^{(l,\tilde{k})} e^{i\tilde{k}n} e^{-i\tilde{k}} + \left[\boldsymbol{\alpha} - \varepsilon_l \mathbf{I}\right] \mathbf{u}^{(l,\tilde{k})} e^{i\tilde{k}n} + \boldsymbol{\beta} \mathbf{u}^{(l,\tilde{k})} e^{i\tilde{k}n} e^{i\tilde{k}} = 0 \quad ; \quad -\infty < l < \infty .$$

This equation is still of infinite dimension since it applies to all the unit cells (any integer value of n *). Noticing that the equation is independent on* n *, (* $e^{i\tilde{k}n}$ *is a common factor in all terms) we obtain an equation of dimension* M *for a single (any) unit cell:*

$$\Rightarrow \left[\boldsymbol{\alpha} + \boldsymbol{\beta} e^{i\tilde{k}} + \boldsymbol{\beta}^t e^{-i\tilde{k}} - \varepsilon_l(\tilde{k}) \mathbf{I}\right] \mathbf{u}^{(l,\tilde{k})} = 0 \quad ; \quad 1 < l < M .$$

Exercise 14.5.3 *Calculate the eigenvalues,* $\varepsilon_l(\tilde{k})$ *, of the secular equation, Eq. (14.5.27), and obtain the results in Eq. (14.5.28).*

Solution 14.5.3

The secular equation reads

$$\begin{bmatrix} \Delta - \varepsilon_l(\tilde{k}) & \beta(1+e^{i\tilde{k}}) \\ \beta(1+e^{-i\tilde{k}}) & -\Delta - \varepsilon_l(\tilde{k}) \end{bmatrix} \begin{bmatrix} u_1^{(l,\tilde{k})} \\ u_2^{(l,\tilde{k})} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} .$$

Non-trivial solutions are obtained for vanishing determinant,

$$\begin{vmatrix} \Delta - \varepsilon_l(\tilde{k}) & \beta(1+e^{i\tilde{k}}) \\ \beta(1+e^{-i\tilde{k}}) & -\Delta - \varepsilon_l(\tilde{k}) \end{vmatrix} = 0$$

$$\Rightarrow \left(\Delta - \varepsilon_l(\tilde{k})\right)\left(-\Delta - \varepsilon_l(\tilde{k})\right) - 2\beta^2(1+\cos(\tilde{k})) = 0$$

$$\Rightarrow \left[\varepsilon_l(\tilde{k})\right]^2 = \Delta^2 + 2\beta^2(1+\cos(\tilde{k})) .$$

Consequently, the two eigenvalues (as functions of $\tilde{k}$ *) read*

$$\varepsilon_1(\tilde{k}) = \sqrt{\Delta^2 + 2\beta^2(1+\cos(\tilde{k}))}$$

$$\varepsilon_2(\tilde{k}) = -\sqrt{\Delta^2 + 2\beta^2(1+\cos(\tilde{k}))} ,$$

or using, $\cos(\tilde{k}) = 2\cos^2(\tilde{k}/2) - 1$,

$$\varepsilon_1(\tilde{k}) = \sqrt{\Delta^2 + 4\beta^2 \cos^2(\tilde{k}/2)}$$

$$\varepsilon_2(\tilde{k}) = -\sqrt{\Delta^2 + 4\beta^2 \cos^2(\tilde{k}/2)} .$$

Exercise 14.5.4 *(a) Use Eq. (14.5.30) for the band energies (corresponding to $\Delta = 0$) in the secular equation for the unit cell coefficients (Eq. (14.5.27)) to obtain the relation between the coefficients as given in Eq. (14.5.31) (recall that $\tilde{k}/2 = \tilde{\tilde{k}}$). (b) Use Eq. (14.5.34) for the two band energies (corresponding to $\Delta >> |\beta|$) in the secular equation for the unit cell coefficients (Eq. (14.5.27)) to obtain the relations between the coefficients, as given in Eq. (14.5.35).*

Solution 14.5.4

(a)

The secular equation for a single unit cell (Eq. (14.5.27)) reads

$$\begin{bmatrix} \Delta - \varepsilon_l(\tilde{k}) & \beta(1+e^{i\tilde{k}}) \\ \beta(1+e^{-i\tilde{k}}) & -\Delta - \varepsilon_l(\tilde{k}) \end{bmatrix} \begin{bmatrix} u_1^{(l,\tilde{k})} \\ u_2^{(l,\tilde{k})} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

For $\Delta = 0$, and using Eq. (14.5.30) for the eigenvalues (where $\tilde{k} \equiv 2\tilde{\tilde{k}}$), we obtain

$$\begin{bmatrix} -2\beta\cos(\tilde{\tilde{k}}) & \beta(1+e^{i2\tilde{\tilde{k}}}) \\ \beta(1+e^{-i2\tilde{\tilde{k}}}) & -2\beta\cos(\tilde{\tilde{k}}) \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Consequently, we obtain Eq. (14.5.31),

$$2\beta\cos(\tilde{\tilde{k}})u_1 = e^{i\tilde{\tilde{k}}}\beta(e^{-i\tilde{\tilde{k}}} + e^{i\tilde{\tilde{k}}})u_2$$
$$\Rightarrow 2\beta\cos(\tilde{\tilde{k}})u_1 = e^{i\tilde{\tilde{k}}}2\beta\cos(\tilde{\tilde{k}})u_2$$

$$\Rightarrow u_2 = e^{-i\tilde{\tilde{k}}}u_1 .$$

(b)

The secular equation for a single unit cell (Eq. (14.5.27)) reads

$$\begin{bmatrix} \Delta - \varepsilon_l(\tilde{k}) & \beta(1+e^{i\tilde{k}}) \\ \beta(1+e^{-i\tilde{k}}) & -\Delta - \varepsilon_l(\tilde{k}) \end{bmatrix} \begin{bmatrix} u_1^{(l,\tilde{k})} \\ u_2^{(l,\tilde{k})} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Using Eq. (14.5.34) for the eigenvalues in the limit $\Delta >> |\beta|$*, namely* $\varepsilon_{\pm}(\tilde{k}) \approx \pm\Delta\left(1+\frac{2\beta^2}{\Delta^2}\cos^2(\tilde{k}/2)\right)$*, we obtain*

$$\begin{bmatrix} \Delta\left(1\mp 1\mp \frac{2\beta^2}{\Delta^2}\cos^2(\tilde{k}/2)\right) & \beta(1+e^{i\tilde{k}}) \\ \beta(1+e^{-i\tilde{k}}) & \Delta\left(-1\mp 1\mp \frac{2\beta^2}{\Delta^2}\cos^2(\tilde{k}/2)\right) \end{bmatrix}\begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

For $\varepsilon_+(\tilde{k})$ *we obtain*

$$\left(-\frac{2\beta^2}{\Delta}\cos^2(\tilde{k}/2)\right)u_1 + \beta(1+e^{i\tilde{k}})u_2 = 0$$
$$\Rightarrow \left(-\frac{2\beta^2}{\Delta}\cos^2(\tilde{k}/2)\right)u_1 + e^{i\tilde{k}/2}2\beta\cos(\tilde{k}/2)u_2 = 0$$
$$\Rightarrow \frac{2\beta^2}{\Delta}\cos^2(\tilde{k}/2)u_1 = e^{i\tilde{k}/2}2\beta\cos(\tilde{k}/2)u_2$$
$$\Rightarrow \frac{\beta}{\Delta}\cos(\tilde{k}/2)u_1 = e^{i\tilde{k}/2}u_2$$

$$\Rightarrow \frac{u_2}{u_1} = \frac{\beta}{\Delta}e^{-i\tilde{k}/2}\cos(\tilde{k}/2),$$

and for $\varepsilon_-(\tilde{k})$ *we obtain*

$$2\Delta\left(1+\frac{\beta^2}{\Delta^2}\cos^2(\tilde{k}/2)\right)u_1 + \beta(1+e^{i\tilde{k}})u_2 = 0,$$

which can be approximated in the limit $\Delta >> |\beta|$*, as* $2\Delta u_1 + \beta(1+e^{i\tilde{k}})u_2 \approx 0$.

Consequently,

$$2\Delta u_1 + e^{i\tilde{k}/2}2\beta\cos(\tilde{k}/2)u_2 = 0$$
$$\Rightarrow 2\Delta u_1 = -e^{i\tilde{k}/2}2\beta\cos(\tilde{k}/2)u_2$$

$$\Rightarrow \frac{u_1}{u_2} = -\frac{\beta}{\Delta}e^{i\tilde{k}/2}\cos(\tilde{k}/2),$$

hence,

$$\frac{u_2^{(+,\tilde{k})}}{u_1^{(+,\tilde{k})}} = \frac{\beta}{\Delta} e^{-i\tilde{k}/2} \cos(\tilde{k}/2) \quad ; \quad \frac{u_1^{(-,\tilde{k})}}{u_2^{(-,\tilde{k})}} = -\frac{\beta}{\Delta} e^{i\tilde{k}/2} \cos(\tilde{k}/2) \quad .$$

Exercise 14.5.5 *Consider a tight binding model Hamiltonian for two degenerate atomic orbitals coupled indirectly through a third, nondegenerate atomic orbital,*

$$H = \begin{bmatrix} \Delta & \beta & 0 \\ \beta & -\Delta & \beta \\ 0 & \beta & \Delta \end{bmatrix}.$$

In the case $\Delta >> |\beta|$ *the corrections to the energy of the two degenerate states can be calculated using perturbation theory, where* $H = H_0 + V$ *:*

$$H_0 = \begin{bmatrix} \Delta & 0 & 0 \\ 0 & -\Delta & 0 \\ 0 & 0 & \Delta \end{bmatrix} \quad ; \quad V = \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix}.$$

Denoting the local atomic orbitals as {$|\varphi_n\rangle$*, n=1,2,3}, we chose a symmetric and an antisymmetric linear combinations as two degenerate zero-order vectors,* $|\psi_s^{(0)}\rangle = (|\varphi_1\rangle + |\varphi_3\rangle)/\sqrt{2}$*,* $|\psi_a^{(0)}\rangle = (|\varphi_1\rangle - |\varphi_3\rangle)/\sqrt{2}$*, and a third, localized eigenvector,* $|\psi_2^{(0)}\rangle = |\varphi_2\rangle$*.*

(a) Show that the first order corrections to the two degenerate state energies vanish.

(b) Show that the second order correction to the antisymmetric state energy vanishes.

(c) Show that the second order correction to the symmetric state reads $E_s^{(2)} = \frac{\beta^2}{\Delta}$*.*

(d) Show that the resulting energy splitting between $|\psi_s^{(0)}\rangle$ *and* $|\psi_a^{(0)}\rangle$*, induced by the coupling to* $|\psi_2^{(0)}\rangle$ *, is equivalent to the spitting induced by a direct coupling matrix element,* $\beta_{eff} = \frac{\beta^2}{2\Delta}$ *, within an effective two-state Hamiltonian,* $H_{eff} = \begin{bmatrix} 0 & \beta_{eff} \\ \beta_{eff} & 0 \end{bmatrix}$*.*

Solution 14.5.5

Considering the vector representations of the three zero-order Hamiltonian eigenstates:

$$\begin{bmatrix} \langle\varphi_1|\psi_s^{(0)}\rangle \\ \langle\varphi_2|\psi_s^{(0)}\rangle \\ \langle\varphi_3|\psi_s^{(0)}\rangle \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{bmatrix} \quad ; \quad \begin{bmatrix} \langle\varphi_1|\psi_a^{(0)}\rangle \\ \langle\varphi_2|\psi_a^{(0)}\rangle \\ \langle\varphi_3|\psi_a^{(0)}\rangle \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{bmatrix} \quad ; \quad \begin{bmatrix} \langle\varphi_1|\psi_2^{(0)}\rangle \\ \langle\varphi_2|\psi_2^{(0)}\rangle \\ \langle\varphi_3|\psi_2^{(0)}\rangle \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix},$$

the matrix representation of the perturbation,

$$V = \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix},$$

and using perturbation theory (Eqs. (12.1.16, 12.1.17)), we obtain

(a)

The first-order corrections to the energy levels read:

$$E_s^{(1)} = \begin{bmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{bmatrix} = 0$$

$$E_a^{(1)} = \begin{bmatrix} 1/\sqrt{2} & 0 & -1/\sqrt{2} \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{bmatrix} = 0$$

$$E_2^{(1)} = \begin{bmatrix} 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = 0 \quad .$$

(b)+(c)

The second-order corrections to the energy levels read

$$E_s^{(2)} = \frac{1}{E_s^{(0)} - E_2^{(0)}} \left| \begin{bmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \right|^2 = \frac{1}{2\Delta} \left| \sqrt{2}\beta \right|^2 = \frac{|\beta|^2}{\Delta}$$

$$E_a^{(2)} = \frac{1}{E_a^{(0)} - E_2^{(0)}} \left| \begin{bmatrix} 1/\sqrt{2} & 0 & -1/\sqrt{2} \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \right|^2 = \frac{1}{2\Delta} |0|^2 = 0$$

$$E_2^{(2)} = \frac{1}{E_2^{(0)} - E_s^{(0)}} \left| \begin{bmatrix} 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{bmatrix} \right|^2$$

$$+ \frac{1}{E_2^{(0)} - E_a^{(0)}} \left| \begin{bmatrix} 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{bmatrix} \right|^2 = \frac{-1}{2\Delta} \left| \sqrt{2}\beta \right|^2 = \frac{-|\beta|^2}{\Delta} \quad .$$

(d)

Using (b) and (c), we can see that up to second order in perturbation theory, the energy splitting between $\left|\psi_s^{(0)}\right\rangle$ *and* $\left|\psi_a^{(0)}\right\rangle$, *induced by the coupling to* $\left|\psi_2^{(0)}\right\rangle$, *reads* $E_s^{(2)} - E_a^{(2)} = \dfrac{|\beta|^2}{\Delta}$.

This splitting is equivalent to the spitting induced by a direct coupling between two degenerate states, associated witan effective two-level system Hamiltonian, $H_{eff} = \begin{bmatrix} 0 & \dfrac{|\beta|^2}{2\Delta} \\ \dfrac{|\beta|^2}{2\Delta} & 0 \end{bmatrix}$, *whose energy levels are,* $E = \pm\dfrac{|\beta|^2}{2\Delta}$.

15 Quantum Dynamics

Exercise 15.1.1 *A stationary solution to the time-dependent Schrödinger equation is defined as $|\psi_n(t)\rangle = e^{\frac{-i\varepsilon_n t}{\hbar}}|\varphi_n\rangle$, where $|\varphi_n\rangle$ is an eigenstate of the system Hamiltonian, $\hat{H}|\varphi_n\rangle = \varepsilon_n|\varphi_n\rangle$ (see section 4.3). Show that any linear combination of stationary solutions is also a solution to the time-dependent Shroedinger equation with the same time-independent Hamiltonian, $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$*

.

Solution 15.1.1

Let $|\psi(t)\rangle$ be a linear combination (superposition) of stationary solutions, $|\psi(t)\rangle = \sum_n a_n e^{\frac{-iE_n t}{\hbar}}|\varphi_n\rangle$, where $\hat{H}|\varphi_n\rangle = \varepsilon_n|\varphi_n\rangle$. Then,

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\sum_n a_n e^{\frac{-iE_n t}{\hbar}}|\varphi_n\rangle = i\hbar\sum_n a_n\left(\frac{-iE_n}{\hbar}\right)e^{\frac{-iE_n t}{\hbar}}|\varphi_n\rangle$$
$$= \sum_n a_n e^{\frac{-iE_n t}{\hbar}}E_n|\varphi_n\rangle = \sum_n a_n e^{\frac{-iE_n t}{\hbar}}\hat{H}|\varphi_n\rangle$$

$$= \hat{H}\sum_n a_n e^{\frac{-iE_n t}{\hbar}}|\varphi_n\rangle = \hat{H}|\psi(t)\rangle ,$$

which means that the linear combination (superposition) of stationary solutions is also a solution to the equation.

Exercise 15.1.2 *Given a complete orthonormal system of the Hamiltonian eigenstates, $\hat{H}|\varphi_n\rangle = \varepsilon_n|\varphi_n\rangle$, any operator in the system's Hilbert space can be represented according to Eq. (15.1.12), and any state of the system, $|\psi(t)\rangle$, can be expended as in Eq. (15.1.6). (a) Show that the time-dependence of any observable obtains the form of Eq. (15.1.14) with $\gamma_{n,m}$ as defined in Eq. (15.1.15). (b) Show that $\gamma_{n,m} = \gamma^*_{m,n}$.*

Solution 15.1.2

(a)

Using Eq. (15.1.12) we obtain $\langle\psi(t)|\hat{O}|\psi(t)\rangle = \sum_{n,m} o_{m,n}\langle\psi(t)|\varphi_m\rangle\langle\varphi_n|\psi(t)\rangle$. *Using the expansion of any state in terms of the Hamiltonian eigenstates (Eq. (15.1.6)),* $|\psi(t)\rangle = \sum_n a_n(0)|\psi_n(t)\rangle = \sum_n a_n(0)e^{-i\varepsilon_n t/\hbar}|\varphi_n\rangle$, *we obtain*

$$\langle\psi(t)|\hat{O}|\psi(t)\rangle = \sum_{n,m} o_{m,n}a_m^*(0)e^{i\varepsilon_m t/\hbar}a_n(0)e^{-i\varepsilon_n t/\hbar} = \sum_{n,m} o_{m,n}a_m^*(0)a_n(0)e^{-i(\varepsilon_n-\varepsilon_m)t/\hbar} \equiv \sum_{n,m}\gamma_{m,n}e^{-i\omega_{n,m}t/\hbar},$$

where, $\gamma_{n,m} \equiv a_m^*(0)a_n(0)o_{m,n}$ *and* $\omega_{n,m} \equiv \frac{\varepsilon_n-\varepsilon_m}{\hbar}$.

(b)

Using the Hermiticity of the operator $\hat{O}$, *we obtain*

$$\begin{aligned}
&\left(\gamma_{n,m}\right)^* = \left(a_m^*(0)a_n(0)o_{m,n}\right)^* \\
&= a_m(0)a_n^*(0)o_{m,n}^* = a_n^*(0)a_m(0)\langle\varphi_m|\hat{O}|\varphi_n\rangle^* = a_n^*(0)a_m(0)\langle\varphi_n|\hat{O}|\varphi_m\rangle \\
&= a_n^*(0)a_m(0)o_{n,m} \\
&= \gamma_{m,n} \quad .
\end{aligned}$$

Exercise 15.1.3 *(a) Given the expansion of the state of a TLS,* $|\psi(t)\rangle$, *in terms of its stationary states (Eq. (15.1.21)) and the expansion of the stationary states in terms of the basis states (Eq. 15.1.18), derive Eqs. (15.1.22, 15.1.23). (b) Use the explicit expressions for the projections of the TLS stationary states on the basis states in terms of the TLS Hamiltonian parameters (Eqs. (15.1.18, 15.1.19)) to derive Eq. (15.1.25).*

Solution 15.1.3

(a)

Starting from the expansion of the TLS state associated with $|\psi(0)\rangle = |\chi_1\rangle$,

$$|\psi(t)\rangle = \langle\varphi_+|\chi_1\rangle \mathrm{e}^{\frac{-iE_+t}{\hbar}}|\varphi_+\rangle + \langle\varphi_-|\chi_1\rangle \mathrm{e}^{\frac{-iE_-t}{\hbar}}|\varphi_-\rangle,$$

and using Eq. (15.1.18), we obtain

$$\left|\psi(t)\right\rangle = \left\langle\varphi_+\middle|\chi_1\right\rangle e^{\frac{-iE_+t}{\hbar}}\left(a_1^{(+)}\left|\chi_1\right\rangle + a_2^{(+)}\left|\chi_2\right\rangle\right) + \left\langle\varphi_-\middle|\chi_1\right\rangle e^{\frac{-iE_-t}{\hbar}}\left(a_1^{(-)}\left|\chi_1\right\rangle + a_2^{(-)}\left|\chi_2\right\rangle\right)$$

$$= \left(\left\langle\varphi_+\middle|\chi_1\right\rangle a_1^{(+)} e^{\frac{-iE_+t}{\hbar}} + \left\langle\varphi_-\middle|\chi_1\right\rangle a_1^{(-)} e^{\frac{-iE_-t}{\hbar}}\right)\left|\chi_1\right\rangle + \left(\left\langle\varphi_+\middle|\chi_1\right\rangle a_2^{(+)} e^{\frac{-iE_+t}{\hbar}} + \left\langle\varphi_-\middle|\chi_1\right\rangle a_2^{(-)} e^{\frac{-iE_-t}{\hbar}}\right)\left|\chi_2\right\rangle.$$

Identifying the coefficients with the projections of the stationary states on the basis states,

$$\left|\varphi_\pm\right\rangle = a_1^{(\pm)}\left|\chi_1\right\rangle + a_2^{(\pm)}\left|\chi_2\right\rangle \Rightarrow \begin{cases} a_1^{(\pm)} = \left\langle\chi_1\middle|\varphi_\pm\right\rangle \\ a_2^{(\pm)} = \left\langle\chi_2\middle|\varphi_\pm\right\rangle \end{cases},$$

we obtain

$$\left|\psi(t)\right\rangle$$

$$= \left(\left\langle\varphi_+\middle|\chi_1\right\rangle\left\langle\chi_1\middle|\varphi_+\right\rangle e^{\frac{-iE_+t}{\hbar}} + \left\langle\varphi_-\middle|\chi_1\right\rangle\left\langle\chi_1\middle|\varphi_-\right\rangle e^{\frac{-iE_-t}{\hbar}}\right)\left|\chi_1\right\rangle$$

$$+ \left(\left\langle\varphi_+\middle|\chi_1\right\rangle\left\langle\chi_2\middle|\varphi_+\right\rangle e^{\frac{-iE_+t}{\hbar}} + \left\langle\varphi_-\middle|\chi_1\right\rangle\left\langle\chi_2\middle|\varphi_-\right\rangle e^{\frac{-iE_-t}{\hbar}}\right)\left|\chi_2\right\rangle$$

$$= \left(\left|\left\langle\chi_1\middle|\varphi_+\right\rangle\right|^2 e^{\frac{-iE_+t}{\hbar}} + \left|\left\langle\chi_1\middle|\varphi_-\right\rangle\right|^2 e^{\frac{-iE_-t}{\hbar}}\right)\left|\chi_1\right\rangle$$

$$+ \left(\left\langle\varphi_+\middle|\chi_1\right\rangle\left\langle\chi_2\middle|\varphi_+\right\rangle e^{\frac{-iE_+t}{\hbar}} + \left\langle\varphi_-\middle|\chi_1\right\rangle\left\langle\chi_2\middle|\varphi_-\right\rangle e^{\frac{-iE_-t}{\hbar}}\right)\left|\chi_2\right\rangle \quad ,$$

which reproduces Eqs. (15.1.22, 15.1.23).

(b)

Starting from Eqs. (15.1.22, 15.1.23), the TLS state associated with $\left|\psi(0)\right\rangle = \left|\chi_1\right\rangle$ *is expressed as,*

$\left|\psi(t)\right\rangle = c_1(t)\left|\chi_1\right\rangle + c_2(t)\left|\chi_2\right\rangle$ *with* $c_1(t) = \left|\left\langle\varphi_+\middle|\chi_1\right\rangle\right|^2 e^{\frac{-iE_+t}{\hbar}} + \left|\left\langle\varphi_-\middle|\chi_1\right\rangle\right|^2 e^{\frac{-iE_-t}{\hbar}}$ *and* $c_2(t) = \left\langle\varphi_+\middle|\chi_1\right\rangle\left\langle\chi_2\middle|\varphi_+\right\rangle e^{\frac{-iE_+t}{\hbar}} + \left\langle\varphi_-\middle|\chi_1\right\rangle\left\langle\chi_2\middle|\varphi_-\right\rangle e^{\frac{-iE_-t}{\hbar}}$.

Using Eqs. (15.1.18, 15.1.19), $\left\langle\varphi_\pm\middle|\chi_1\right\rangle = \sqrt{\frac{\alpha\pm1}{2\alpha}}$ *and* $\left\langle\varphi_\pm\middle|\chi_2\right\rangle = \pm\frac{\gamma}{|\gamma|}\sqrt{\frac{\alpha\mp1}{2\alpha}}$, *we obtain Eq. (15.1.25),*

$$c_1(t) = \frac{\alpha+1}{2\alpha}e^{\frac{-iE_+t}{\hbar}} + \frac{\alpha-1}{2\alpha}e^{\frac{-iE_-t}{\hbar}} = e^{\frac{-iE_+t}{\hbar}}\left(\frac{\alpha+1}{2\alpha} + \frac{\alpha-1}{2\alpha}e^{\frac{i(E_+-E_-)t}{\hbar}}\right),$$

and,

$$c_2(t) = \frac{|\gamma|}{\gamma}\left(\sqrt{\frac{\alpha+1}{2\alpha}}\sqrt{\frac{\alpha-1}{2\alpha}}\,\mathrm{e}^{\frac{-iE_+t}{\hbar}} - \sqrt{\frac{\alpha-1}{2\alpha}}\sqrt{\frac{\alpha+1}{2\alpha}}\,\mathrm{e}^{\frac{-iE_-t}{\hbar}}\right) = \frac{|\gamma|}{\gamma}\frac{\sqrt{\alpha^2-1}}{2\alpha}\left(\mathrm{e}^{\frac{-iE_+t}{\hbar}} - \mathrm{e}^{\frac{-iE_-t}{\hbar}}\right)$$
$$= \frac{|\gamma|}{\gamma}\mathrm{e}^{\frac{-iE_+t}{\hbar}}\frac{\sqrt{\alpha^2-1}}{2\alpha}\left(1-\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right).$$

Exercise 15.1.4 *Given the time-dependent expansion coefficients for the TLS state, Eqs. (15.1.22, 15.1.25), and the general expansion of a TLS observable, Eq. (15.1.27), show that the TLS observables are either time-independent, or oscillating at a single frequency,* $\omega = \frac{E_+ - E_-}{\hbar}$.

Solution 15.1.4

Using the explicit expressions for $c_1(t)$ *and* $c_2(t)$*, as given in Eq. (Eq. (15.1.25), and focusing on their time-dependence, we obtain*

$$|c_1(t)|^2 = \left(\frac{\alpha+1}{2\alpha} + \frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)\left(\frac{\alpha+1}{2\alpha} + \frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}\right)$$
$$\equiv A + \frac{\alpha+1}{2\alpha}\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}} + \frac{\alpha+1}{2\alpha}\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}$$
$$= A + \frac{\alpha+1}{2\alpha}\frac{\alpha-1}{2\alpha}2\cos\left(\frac{(E_+-E_-)t}{\hbar}\right) ,$$

$$|c_2(t)|^2 \equiv C\left(1-\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)\left(1-\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}\right) = 2C - 2C\cos\left(\frac{(E_+-E_-)t}{\hbar}\right) ,$$

$$2\,\mathrm{Re}[o_{1,2}c_1^*(t)c_2(t)]$$
$$= 2\,\mathrm{Re}[o_{1,2}\,\mathrm{e}^{\frac{iE_+t}{\hbar}}\left(\frac{\alpha+1}{2\alpha} + \frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}\right)\frac{|\gamma|}{\gamma}\mathrm{e}^{\frac{-iE_+t}{\hbar}}\frac{\sqrt{\alpha^2-1}}{2\alpha}\left(1-\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)$$
$$= 2\,\mathrm{Re}[o_{1,2}\frac{|\gamma|}{\gamma}\frac{\sqrt{\alpha^2-1}}{2\alpha}\left(\frac{\alpha+1}{2\alpha} + \frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}\right)\left(1-\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)]$$
$$= 2\,\mathrm{Re}[o_{1,2}\frac{|\gamma|}{\gamma}\frac{\sqrt{\alpha^2-1}}{2\alpha}\left(\frac{\alpha+1}{2\alpha} + \frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}} - \frac{\alpha+1}{2\alpha}\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}} - \frac{\alpha-1}{2\alpha}\right)]$$

$$\equiv A+B\left(\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}-\frac{\alpha+1}{2\alpha}\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)$$

$$=A+B\frac{\alpha}{2\alpha}\left(\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}-\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)+B\frac{-1}{2\alpha}\left(\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}+\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right) .$$

$$=A-iB\sin(\frac{(E_+-E_-)t}{\hbar})-\frac{B}{\alpha}\cos(\frac{(E_+-E_-)t}{\hbar})$$

Substitution of these expressions in Eq. (15.1.27) shows that any TLS observable, $O(t)$, is either time-independent, or oscillating at a single frequency, $\omega=\frac{E_+-E_-}{\hbar}$.

Exercise 15.1.5 *Use Eq. (15.1.25) for $c_1(t)$, and the definition $\alpha\equiv\sqrt{1+|\gamma|^2/\Delta^2}$ to derive Eq. (15.1.30).*

Solution 15.1.5

Using the explicit expressions for $c_1(t)$, as given in Eq. (15.1.25), we obtain

$$|c_1(t)|^2=\left(\frac{\alpha+1}{2\alpha}+\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)\left(\frac{\alpha+1}{2\alpha}+\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}\right)$$

$$=\left(\frac{\alpha+1}{2\alpha}\right)^2+\left(\frac{\alpha-1}{2\alpha}\right)^2+\frac{\alpha+1}{2\alpha}\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}+\frac{\alpha+1}{2\alpha}\frac{\alpha-1}{2\alpha}\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}$$

$$=\frac{\alpha^2+1}{2\alpha^2}+\frac{\alpha^2-1}{4\alpha^2}\left(\mathrm{e}^{\frac{-i(E_+-E_-)t}{\hbar}}+\mathrm{e}^{\frac{i(E_+-E_-)t}{\hbar}}\right)=\frac{\alpha^2+1}{2\alpha^2}+\frac{\alpha^2-1}{2\alpha^2}\cos(\frac{(E_+-E_-)t}{\hbar})$$

$$=\frac{\alpha^2+1}{2\alpha^2}+\frac{\alpha^2-1}{2\alpha^2}[1-2\sin^2(\frac{(E_+-E_-)t}{2\hbar})]=\frac{\alpha^2+1}{2\alpha^2}+\frac{\alpha^2-1}{2\alpha^2}-2\frac{\alpha^2-1}{2\alpha^2}\sin^2(\frac{(E_+-E_-)t}{2\hbar})$$

$$=1-\frac{\alpha^2-1}{\alpha^2}\sin^2(\frac{(E_+-E_-)t}{2\hbar}) .$$

Recalling the definition of α in terms of the TLS Hamiltonian parameters, $\alpha\equiv\sqrt{1+|\gamma|^2/\Delta^2}$, where $\Delta\equiv(\varepsilon_1-\varepsilon_2)/2$ (see Eq. (15.1.17)), and the expressions for the TLS Hamiltonian eigenvalues in terms of these parameters (Eq. (15.1.18)), we obtain Eq. (15.1.30),

$$P(t) = |c_1(t)|^2 = 1 - \frac{|\gamma|^2/\Delta^2}{1+|\gamma|^2/\Delta^2}\sin^2\left(\frac{(E_+ - E_-)t}{2\hbar}\right)$$

$$= 1 - \frac{4|\gamma|^2}{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}\sin^2\left(\frac{t\sqrt{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}}{2\hbar}\right).$$

Exercise 15.1.6 *Use Eqs. (15.1.18, 15.1.19) for the stationary states of the TLS to show that in the strong interaction limit,* $|\gamma| >> |\varepsilon_1 - \varepsilon_2|$, *the states are approximated as* $|\varphi_\pm\rangle \approx \frac{1}{\sqrt{2}}|\chi_1\rangle \pm \frac{|\gamma|}{\gamma}\frac{1}{\sqrt{2}}|\chi_2\rangle$ *(recall the definition,* $\alpha \equiv \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2}$ *).*

Solution 15.1.6

Using $\alpha \equiv \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2}$ *in the limit* $|\gamma| >> |\varepsilon_1 - \varepsilon_2|$, *we obtain*

$$\alpha = \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2} \xrightarrow[|\gamma|>>|\varepsilon_1-\varepsilon_2|]{} \frac{2|\gamma|}{|\varepsilon_1-\varepsilon_2|} >> 1.$$

Using $\alpha >> 1$ *in Eq. (15.1.19) for the coefficients we obtain*

$a_1^{(\pm)} = \sqrt{\frac{\alpha \pm 1}{2\alpha}} \approx \sqrt{\frac{\alpha}{2\alpha}} = \sqrt{\frac{1}{2}}$; $a_2^{(\pm)} = \pm\frac{|\gamma|}{\gamma}\sqrt{\frac{\alpha \mp 1}{2\alpha}} \approx \pm\frac{|\gamma|}{\gamma}\sqrt{\frac{\alpha}{2\alpha}} = \pm\frac{|\gamma|}{\gamma}\sqrt{\frac{1}{2}}$, *and using these results in Eq. (15.1.18), we finally obtain* $|\varphi_\pm\rangle \approx \frac{1}{\sqrt{2}}|\chi_1\rangle \pm \frac{|\gamma|}{\gamma}\frac{1}{\sqrt{2}}|\chi_2\rangle$.

Exercise 15.1.7 *Use Eqs. (15.1.18, 15.1.19) for the stationary states of the TLS and show that in the weak interaction limit,* $|\gamma| << |\varepsilon_1 - \varepsilon_2|$, *the states are approximated as* $|\varphi_+\rangle \approx |\chi_1\rangle$ and $|\varphi_-\rangle \approx |\chi_2\rangle$ *(recall the definition,* $\alpha \equiv \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2}$ *).*

Solution 15.1.7

Using $\alpha \equiv \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2}$ *in the limit* $|\gamma| << |\varepsilon_1 - \varepsilon_2|$, *we obtain*

$$\alpha = \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2} \xrightarrow[|\gamma|<<|\varepsilon_1-\varepsilon_2|]{} 1.$$

Using $\alpha \approx 1$ *in Eq. (15.1.19) for the coefficients, we obtain*

$$a_1^{(+)} = \sqrt{\frac{\alpha+1}{2\alpha}} \approx \sqrt{\frac{2}{2}} = 1 \quad ; \quad a_2^{(+)} = \frac{|\gamma|}{\gamma}\sqrt{\frac{\alpha-1}{2\alpha}} \approx \frac{|\gamma|}{\gamma}\sqrt{\frac{0}{2}} = 0$$

$$a_1^{(-)} = \sqrt{\frac{\alpha-1}{2\alpha}} \approx \sqrt{\frac{0}{2}} = 0 \quad ; \quad a_2^{(-)} = -\frac{|\gamma|}{\gamma}\sqrt{\frac{\alpha+1}{2\alpha}} \approx -\frac{|\gamma|}{\gamma}\sqrt{\frac{2}{2}} = -\frac{|\gamma|}{\gamma},$$

and using these results in Eq. (15.1.18), we finally obtain

$$|\varphi_+\rangle \approx |\chi_1\rangle \text{ and } |\varphi_-\rangle \approx -\frac{|\gamma|}{\gamma}|\chi_2\rangle \propto |\chi_2\rangle.$$

Exercise 15.2.1 *Use Eqs. (15.2.4, 15.2.7) for the time-derivative of the time evolution operator to show that* $\frac{\partial}{\partial t}\hat{U}^\dagger(t,t')\hat{U}(t,t') = 0$.

Solution 15.2.1

Using Eqs. (15.2.4, 15.2.7),

$$\frac{\partial}{\partial t}\hat{U}(t,t') = \frac{-i}{\hbar}\hat{H}(t)\hat{U}(t,t') \quad ; \quad \frac{\partial}{\partial t}\hat{U}^\dagger(t,t') = \frac{i}{\hbar}\hat{U}^\dagger(t,t')\hat{H}(t),$$

we readily obtain

$$\frac{\partial}{\partial t}\hat{U}^\dagger(t,0)\hat{U}(t,0) = \hat{U}^\dagger(t,0)[\frac{\partial}{\partial t}\hat{U}(t,0)] + [\frac{\partial}{\partial t}\hat{U}^\dagger(t,0)]\hat{U}(t,0)$$

$$= \frac{-i}{\hbar}[\hat{U}^\dagger(t,0)\hat{H}\hat{U}(t,0) - \hat{U}^\dagger(t,0)\hat{H}\hat{U}(t,0)] = 0 \ .$$

Exercise 15.3.1 *The state of the system,* $|\psi(t)\rangle$, *is associated with a solution to the time-dependent Schrödinger equation,* $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$. *A transformed state,* $|\tilde{\psi}(t)\rangle$, *is related to* $|\psi(t)\rangle$ *via a unitary transformation, as defined in Eq. (15.3.1). Express the time-derivative of* $|\tilde{\psi}(t)\rangle$ *in terms of the operation of a transformed Hamiltonian on* $|\tilde{\psi}(t)\rangle$, *as defined in Eq. (15.3.2).*

Solution 15.3.1

Using the definition, $|\tilde{\psi}(t)\rangle = \hat{S}(t)|\psi(t)\rangle$, *the time-derivative of* $|\tilde{\psi}(t)\rangle$ *reads*

$$i\hbar\frac{\partial}{\partial t}|\tilde{\psi}(t)\rangle = i\hbar\frac{\partial}{\partial t}\hat{S}(t)|\psi(t)\rangle = i\hbar\left(\frac{\partial}{\partial t}\hat{S}(t)\right)|\psi(t)\rangle + i\hbar\hat{S}(t)\frac{\partial}{\partial t}|\psi(t)\rangle .$$

Since $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$, *we obtain* $i\hbar\frac{\partial}{\partial t}|\tilde{\psi}(t)\rangle = i\hbar\left(\frac{\partial}{\partial t}\hat{S}(t)\right)|\psi(t)\rangle + \hat{S}(t)\hat{H}(t)|\tilde{\psi}(t)\rangle$.

Using the unitarity of $\hat{S}(t)$, *namely* $\hat{S}(t)\hat{S}^{\dagger}(t) = \hat{I}$, *we obtain*

$|\psi(t)\rangle = \left[\hat{S}(t)\right]^{-1}|\tilde{\psi}(t)\rangle = \hat{S}^{\dagger}(t)|\tilde{\psi}(t)\rangle$, *and*

$$\frac{\partial}{\partial t}\hat{S}(t)\hat{S}^{\dagger}(t) = 0 \Rightarrow \left[\frac{\partial}{\partial t}\hat{S}(t)\right]\hat{S}^{\dagger}(t) = -\hat{S}(t)\left[\frac{\partial}{\partial t}\hat{S}^{\dagger}(t)\right].$$

Consequently,

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}|\tilde{\psi}(t)\rangle &= i\hbar\left(\frac{\partial}{\partial t}\hat{S}(t)\right)|\psi(t)\rangle + \hat{S}(t)\hat{H}(t)|\tilde{\psi}(t)\rangle \\
&= i\hbar\left(\frac{\partial}{\partial t}\hat{S}(t)\right)\hat{S}^{\dagger}(t)|\tilde{\psi}(t)\rangle + \hat{S}(t)\hat{H}(t)\hat{S}^{\dagger}(t)|\tilde{\psi}(t)\rangle \\
&= -i\hbar\hat{S}(t)\left(\frac{\partial}{\partial t}\hat{S}^{\dagger}(t)\right)|\tilde{\psi}(t)\rangle + \hat{S}(t)\hat{H}(t)\hat{S}^{\dagger}(t)|\tilde{\psi}(t)\rangle \\
&= \left[-i\hbar\hat{S}(t)\left(\frac{\partial}{\partial t}\hat{S}^{\dagger}(t)\right) + \hat{S}(t)\hat{H}(t)\hat{S}^{\dagger}(t)\right]|\tilde{\psi}(t)\rangle \\
&\equiv \hat{\tilde{H}}(t)|\tilde{\psi}(t)\rangle .
\end{aligned}$$

Exercise 15.3.2 *The state of the system,* $|\psi(t)\rangle$, *is associated with a solution to the time-dependent Schrödinger equation,* $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$, *where* $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$. *A transformed state,* $|\psi_I(t)\rangle$, *is related to* $|\psi(t)\rangle$ *via a unitary transformation, as defined in Eq. (15.3.7). Express the time-derivative of* $|\psi_I(t)\rangle$ *in terms of the operation of the transformed interaction operator, as defined in Eq. (15.3.8).*

Solution 15.3.2

Starting from the result for a general unitary transformation (Ex. 15.3.1),

$$i\hbar\frac{\partial}{\partial t}\left|\tilde{\psi}(t)\right\rangle=\left[-i\hbar\hat{S}(t)\left(\frac{\partial}{\partial t}\hat{S}^{\dagger}(t)\right)+\hat{S}(t)\left[\hat{H}_0+\hat{V}(t)\right]\hat{S}^{\dagger}(t)\right]\left|\tilde{\psi}(t)\right\rangle,$$

and specifying, $\left|\tilde{\psi}(t)\right\rangle=\left|\psi_I(t)\right\rangle$ *and* $\hat{S}(t)=e^{\frac{i}{\hbar}\hat{H}_0t}$ *, we obtain the interaction picture representation of the Schrödinger equation,*

$$i\hbar\frac{\partial}{\partial t}\left|\psi_I(t)\right\rangle=\left[-i\hbar e^{\frac{i}{\hbar}\hat{H}_0t}\left(\frac{\partial}{\partial t}e^{\frac{-i}{\hbar}\hat{H}_0t}\right)+e^{\frac{i}{\hbar}\hat{H}_0t}\left[\hat{H}_0+\hat{V}(t)\right]e^{\frac{-i}{\hbar}\hat{H}_0t}\right]\left|\psi_I(t)\right\rangle.$$

Using, $\frac{\partial}{\partial t}e^{\frac{-i}{\hbar}\hat{H}_0t}=\frac{-i}{\hbar}\hat{H}_0e^{\frac{-i}{\hbar}\hat{H}_0t}$ *, we readily obtain Eq. (15.3.8),*

$$i\hbar\frac{\partial}{\partial t}\left|\psi_I(t)\right\rangle=\left[-\hat{H}_0+\hat{H}_0+e^{\frac{i}{\hbar}\hat{H}_0t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0t}\right]\left|\psi_I(t)\right\rangle\Rightarrow i\hbar\frac{\partial}{\partial t}\left|\psi_I(t)\right\rangle=\left[e^{\frac{i}{\hbar}\hat{H}_0t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0t}\right]\left|\psi_I(t)\right\rangle.$$

Exercise 15.3.3 *Use Eqs. (15.2.4,15.2.7) to derive Eq. (15.3.17) from Eq. (15.3.16).*

Solution 15.3.3

Starting from the definition of the Heisenberg operator (Eq. (15.3.16)) and using Eqs. (15.2.4, 15.2.7), we obtain

$$\begin{aligned}
&\frac{\partial}{\partial t}\hat{O}_H(t)=\frac{\partial}{\partial t}\hat{U}^{\dagger}(t,0)\hat{O}(t)\hat{U}(t,0)\\
&=\left(\frac{\partial}{\partial t}\hat{U}^{\dagger}(t,0)\right)\hat{O}(t)\hat{U}(t,0)+\hat{U}^{\dagger}(t,0)\hat{O}(t)\left(\frac{\partial}{\partial t}\hat{U}(t,0)\right)+\hat{U}^{\dagger}(t,0)\left[\frac{\partial}{\partial t}\hat{O}(t)\right]\hat{U}(t,0)\\
&=\left(\frac{i}{\hbar}\hat{U}^{\dagger}(t,0)\hat{H}(t)\right)\hat{O}(t)\hat{U}(t,0)+\hat{U}^{\dagger}(t,0)\hat{O}(t)\left(\frac{-i}{\hbar}\hat{H}(t)\hat{U}(t,0)\right)+\hat{U}^{\dagger}(t,0)\left[\frac{\partial}{\partial t}\hat{O}(t)\right]\hat{U}(t,0)\\
&=\frac{i}{\hbar}\hat{U}^{\dagger}(t,0)[\hat{H}(t),\hat{O}(t)]\hat{U}(t,0)+\hat{U}^{\dagger}(t,0)\left[\frac{\partial}{\partial t}\hat{O}(t)\right]\hat{U}(t,0)\ .
\end{aligned}$$

Using the unitarity of the time evolution operator ($\hat{U}(t,0)\hat{U}^{\dagger}(t,0)=\hat{I}$ *, see Eq. (15.2.5)), we obtain*

$$\frac{\partial}{\partial t}\hat{O}_H(t) = \frac{i}{\hbar}\hat{U}^\dagger(t,0)[\hat{H}(t),\hat{O}(t)]\hat{U}(t,0) + \hat{U}^\dagger(t,0)\left[\frac{\partial}{\partial t}\hat{O}(t)\right]\hat{U}(t,0)$$
$$= \frac{i}{\hbar}\left(\hat{U}^\dagger(t,0)\hat{H}(t)\hat{U}(t,0)\hat{U}^\dagger(t,0)\hat{O}(t)\hat{U}(t,0) - \hat{U}^\dagger(t,0)\hat{O}(t)\hat{U}(t,0)\hat{U}^\dagger(t,0)\hat{H}(t)\hat{U}(t,0)\right)$$
$$+\hat{U}^\dagger(t,0)\left[\frac{\partial}{\partial t}\hat{O}(t)\right]\hat{U}(t,0),$$

which can be rewritten in terms of the Heisenberg operator definitions,

$$\frac{\partial}{\partial t}\hat{O}_H(t) = \frac{i}{\hbar}\left(\hat{H}_H(t)\hat{O}_H(t) - \hat{O}_H(t)\hat{H}_H(t)\right) + \left[\frac{\partial}{\partial t}\hat{O}(t)\right]_H = \frac{i}{\hbar}[\hat{H}_H(t),\hat{O}_H(t)] + \left[\frac{\partial}{\partial t}\hat{O}(t)\right]_H .$$

Exercise 15.4.1 *(a) Given the commutation relation,* $[\hat{x},\frac{\partial}{\partial x}] = -1$, *prove that,* $[\hat{x}^n,\frac{\partial}{\partial x}] = -n\hat{x}^{n-1}$. *(b) Given the definitions of the canonical position and momentum operators, Eqs. (3.2.1, 3.2.2), and using the solution to (a), derive the results in Eq. (15.4.3).*

Solution 15.4.1

(a)

For $n = 1$ *we have,*

$$[\hat{x},\frac{\partial}{\partial x}] = -1 = -1\cdot\hat{x}^0 .$$

For $n = 2$ *we have,*

$$[\hat{x}^2,\frac{\partial}{\partial x}] = \hat{x}^2\frac{\partial}{\partial x} - \frac{\partial}{\partial x}\hat{x}\hat{x} = \hat{x}\hat{x}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial x}\hat{x} - \hat{x} = \hat{x}[\hat{x},\frac{\partial}{\partial x}] - \hat{x} = -2\hat{x} = -2\hat{x}^1 .$$

If we assume that $[\hat{x}^n,\frac{\partial}{\partial x}] = -n\hat{x}^{n-1}$ *holds for a given* n, *we obtain that it holds also for* $n+1$,

$$[\hat{x}^{n+1},\frac{\partial}{\partial x}] = \hat{x}^{n+1}\frac{\partial}{\partial x} - \frac{\partial}{\partial x}\hat{x}^{n+1} = \hat{x}^n\hat{x}\frac{\partial}{\partial x} - \frac{\partial}{\partial x}\hat{x}^n\hat{x} = \hat{x}^n\frac{\partial}{\partial x}\hat{x} - \hat{x}^n - \frac{\partial}{\partial x}\hat{x}^n\hat{x} = [\hat{x}^n,\frac{\partial}{\partial x}]\hat{x} - \hat{x}^n$$
$$= -n\hat{x}^{n-1}\hat{x} - \hat{x}^n = -(n+1)\hat{x}^n \quad .$$

Therefore, we conclude by induction that the identity $[\hat{x}^n,\frac{\partial}{\partial x}] = -n\hat{x}^{n-1}$ *holds for any* n .

(b)

For the Hamiltonian, $\hat{H}=\dfrac{\hat{p}^2}{2m}+V(\hat{x})$ *with* $V(\hat{x})=\sum_{n=0}^{\infty}a_n\hat{x}^n$*, we have*

$[V(\hat{x}),\hat{x}]=0$*, and* $[\dfrac{\hat{p}^2}{2m},\hat{p}]=0$.

Using also

$$[\hat{H},\hat{x}_H]=e^{\frac{i}{\hbar}\hat{H}t}\hat{H}e^{\frac{-i}{\hbar}\hat{H}t}e^{\frac{i}{\hbar}\hat{H}t}\hat{x}e^{\frac{-i}{\hbar}\hat{H}t}-e^{\frac{i}{\hbar}\hat{H}t}\hat{x}e^{\frac{-i}{\hbar}\hat{H}t}e^{\frac{i}{\hbar}\hat{H}t}\hat{H}e^{\frac{-i}{\hbar}\hat{H}t}=e^{\frac{i}{\hbar}\hat{H}t}[\hat{H}\hat{x}-\hat{x}\hat{H}]e^{\frac{-i}{\hbar}\hat{H}t}=[\hat{H},\hat{x}]_H\,,$$

and

$$[\hat{H},\hat{p}_H]=e^{\frac{i}{\hbar}\hat{H}t}\hat{H}e^{\frac{-i}{\hbar}\hat{H}t}e^{\frac{i}{\hbar}\hat{H}t}\hat{p}e^{\frac{-i}{\hbar}\hat{H}t}-e^{\frac{i}{\hbar}\hat{H}t}\hat{p}e^{\frac{-i}{\hbar}\hat{H}t}e^{\frac{i}{\hbar}\hat{H}t}\hat{H}e^{\frac{-i}{\hbar}\hat{H}t}=e^{\frac{i}{\hbar}\hat{H}t}[\hat{H}\hat{p}-\hat{p}\hat{H}]e^{\frac{-i}{\hbar}\hat{H}t}=[\hat{H},\hat{p}]_H\,,$$

we obtain

$$\begin{aligned}\dot{\hat{x}}_H&=\frac{i}{\hbar}[\hat{H},\hat{x}_H]=\frac{i}{\hbar}[\hat{H},\hat{x}]_H=\frac{i}{\hbar}[\frac{\hat{p}^2}{2m},\hat{x}]_H=\frac{i}{2m\hbar}[\hat{p}^2,\hat{x}]_H=\frac{i}{2m\hbar}[\hat{p}\hat{p}\hat{x}-\hat{x}\hat{p}\hat{p}]_H\\&=\frac{i}{2m\hbar}[\hat{p}\hat{p}\hat{x}-\hat{p}\hat{x}\hat{p}+\hat{p}\hat{x}\hat{p}-\hat{x}\hat{p}\hat{p}]_H=\frac{i}{2m\hbar}\left(\hat{p}[\hat{p},\hat{x}]+[\hat{p},\hat{x}]\hat{p}\right)_H=\frac{1}{2m}\left(2\hat{p}\right)_H=\frac{1}{m}\hat{p}_H\end{aligned}$$

$$\begin{aligned}\dot{\hat{p}}_H&=\frac{i}{\hbar}[\hat{H},\hat{p}_H]=\frac{i}{\hbar}[\hat{H},\hat{p}]_H=\frac{i}{\hbar}[V(\hat{x}),\hat{p}]_H=\frac{i}{\hbar}\sum_{n=0}^{\infty}a_n[\hat{x}^n,\hat{p}]_H\\&=\sum_{n=0}^{\infty}a_n[\hat{x}^n,\frac{\partial}{\partial x}]_H=-\sum_{n=0}^{\infty}a_n n[\hat{x}^{n-1}]_H=-[V'(\hat{x})]_H=-V'(\hat{x}_H)\,,\end{aligned}$$

where in the last step we used the identity

$$[\hat{x}^n]_H=e^{\frac{i}{\hbar}\hat{H}t}\underbrace{\hat{x}\cdot\hat{x}\cdots\hat{x}}_{n\ times}e^{\frac{-i}{\hbar}\hat{H}t}=\underbrace{e^{\frac{i}{\hbar}\hat{H}t}\hat{x}e^{\frac{-i}{\hbar}\hat{H}t}\cdot e^{\frac{i}{\hbar}\hat{H}t}\hat{x}e^{\frac{-i}{\hbar}\hat{H}t}\cdots e^{\frac{i}{\hbar}\hat{H}t}\hat{x}e^{\frac{-i}{\hbar}\hat{H}t}}_{n\ times}=[\hat{x}_H]^n\,,$$

which means that for any analytic function we have, $[f(\hat{x})]_H=f(\hat{x}_H)$.

Exercise 15.4.2 *In Eq. (15.4.19) the time-dependent Heisenberg operators,* $\hat{x}_H(t)$ *and* $\hat{p}_H(t)$*, are expressed in terms of the operators,* $\hat{x}^2$, $\hat{p}^2$, $\hat{x}\hat{p}$ *and* $\hat{p}\hat{x}$. *(a) Express the expectation values of* $\hat{x}^2$, $\hat{p}^2$, $\hat{x}\hat{p}$ *and* $\hat{p}\hat{x}$ *in terms of the parameters* x_0, p_0, σ *of the Gaussian wave packet (Eq. (15.4.11)).*

(b) Obtain the expressions for the quantum mechanical expectation values, $x^2(t) = \langle \psi_0 | \hat{x}_H^2(t) | \psi_0 \rangle$ *and* $p^2(t) = \langle \psi_0 | \hat{p}_H^2(t) | \psi_0 \rangle$*, in Eq. (15.4.20).*

Solution 15.4.2

(a)

Using the Gaussian integrals,

$$\int_{-\infty}^{\infty} e^{-\alpha y^2} dy = \sqrt{\frac{\pi}{\alpha}} \quad ; \quad \int_{-\infty}^{\infty} y^{2n+1} e^{-\alpha y^2} dy = 0 \quad ; \quad \int_{-\infty}^{\infty} y^{2n} e^{-\alpha y^2} dy = \left(-\frac{\partial}{\partial \alpha}\right)^n \sqrt{\frac{\pi}{\alpha}},$$

we obtain for the Gaussian wave packet (Eq. (15.4.11)),

$$\langle \hat{x} \rangle = x_0 \ ; \ \langle \hat{p} \rangle = p_0 \ ; \ \langle \hat{x}^2 \rangle = x_0{}^2 + \sigma^2 \ ; \ \langle \hat{p}^2 \rangle = p_0^2 + \frac{\hbar^2}{4\sigma^2} \ ; \ \langle \hat{x}\hat{p} \rangle = p_0 x_0 + \frac{i\hbar}{2} \ ; \ \langle \hat{p}\hat{x} \rangle = p_0 x_0 - \frac{i\hbar}{2}$$

(see the following calculations),

$$\langle \hat{x} \rangle = \langle \psi_0 | \hat{x} | \psi_0 \rangle = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} x e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} (x-x_0) e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx + x_0 \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx$$
$$= 0 + x_0 \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^2\right)^{1/2} = x_0$$

$$\langle \hat{p} \rangle = \langle \psi_0 | \hat{p} | \psi_0 \rangle$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{-ip_0 x/\hbar} \left(-i\hbar \frac{\partial}{\partial x}\right) e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0 x/\hbar} dx$$
$$= -i\hbar \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{-ip_0 x/\hbar} \left(\frac{ip_0}{\hbar} - \frac{1}{2\sigma^2}(x-x_0)\right) e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0 x/\hbar} dx$$
$$= -i\hbar \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{2\sigma^2}} \left(\frac{ip_0}{\hbar} - \frac{1}{2\sigma^2}(x-x_0)\right) dx$$
$$= p_0 \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^2\right)^{1/2} = p_0$$

$$\left\langle \hat{x}^2 \right\rangle = \langle \psi_0 | \hat{x}^2 | \psi_0 \rangle$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} (x-x_0)^2 e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx + \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} 2xx_0 e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx - \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} x_0^{\ 2} e^{\frac{-(x-x_0)^2}{2\sigma^2}} dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^6\right)^{1/2} + 0 + x_0^{\ 2}$$
$$= x_0^{\ 2} + \sigma^2$$

$$\left\langle \hat{p}^2 \right\rangle = \langle \psi_0 | \hat{p}^2 | \psi_0 \rangle$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{-ip_0x/\hbar} \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0x/\hbar} dx$$
$$= -\hbar^2 \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{-ip_0x/\hbar} \left(\frac{-p_0^2}{\hbar^2} - \frac{2ip_0}{2\hbar\sigma^2}(x-x_0) + \frac{1}{4\sigma^4}(x-x_0)^2 - \frac{1}{2\sigma^2}\right) e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0x/\hbar} dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{2\sigma^2}} \left(p_0^2 + i\hbar\frac{p_0}{\sigma^2}(x-x_0) + \frac{-\hbar^2}{4\sigma^4}(x-x_0)^2 + \frac{\hbar^2}{2\sigma^2}\right) dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^2\right)^{1/2} \left(p_0^2 + \frac{\hbar^2}{2\sigma^2}\right) + \frac{-\hbar^2}{4\sigma^4} \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^6\right)^{1/2}$$
$$= p_0^2 + \frac{\hbar^2}{4\sigma^2}$$

$$\left\langle \hat{x}\hat{p} \right\rangle = \langle \psi_0 | \hat{x}\hat{p} | \psi_0 \rangle$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{-ip_0x/\hbar} \left(-i\hbar x \frac{\partial}{\partial x}\right) e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0x/\hbar} dx$$
$$= -i\hbar \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{2\sigma^2}} \left(x\frac{ip_0}{\hbar} - x\frac{1}{2\sigma^2}(x-x_0)\right) dx$$
$$= -i\hbar \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{2\sigma^2}} \left((x-x_0)\frac{ip_0}{\hbar} + \frac{ip_0x_0}{\hbar} - \frac{1}{2\sigma^2}(x-x_0)^2 - x_0\frac{1}{2\sigma^2}(x-x_0)\right) dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{\frac{-(x-x_0)^2}{2\sigma^2}} \left(p_0x_0 - \frac{-i\hbar}{2\sigma^2}(x-x_0)^2\right) dx$$
$$= \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^2\right)^{1/2} p_0x_0 + \frac{i\hbar}{2\sigma^2} \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \left(2\pi\sigma^6\right)^{1/2}$$
$$= p_0x_0 + \frac{i\hbar}{2}$$

$$\langle \hat{p}\hat{x}\rangle = \langle \psi_0 | \hat{p}\hat{x} | \psi_0 \rangle = \langle \psi_0 | (\hat{p}\hat{x})^\dagger | \psi_0 \rangle^*$$

$$= \langle \psi_0 | \hat{x}\hat{p} | \psi_0 \rangle^* = \langle \hat{x}\hat{p}\rangle^* = p_0 x_0 - \frac{i\hbar}{2} \; .$$

(b)

Using Eq. (5.4.19), $\hat{x}_H^2(t) = \hat{x}^2 + \frac{\hat{p}^2}{m^2}t^2 + \frac{\hat{x}\hat{p}+\hat{p}\hat{x}}{m}t$, *and* $\hat{p}_H^2(t) = \hat{p}^2$, *and the results of (a), the corresponding expectation values for a free particle associated with the Gaussian wave packet read*

$$x^2(t) = \langle \psi_0 | \hat{x}_H^2(t) | \psi_0 \rangle = \langle \psi_0 | (\hat{x} + \frac{\hat{p}}{m}t)^2 | \psi_0 \rangle$$

$$= \langle \psi_0 | \hat{x}^2 | \psi_0 \rangle + \langle \psi_0 | \frac{\hat{p}^2 t^2}{m^2} | \psi_0 \rangle + \frac{t}{m} \langle \psi_0 | \hat{x}\hat{p} + \hat{p}\hat{x} | \psi_0 \rangle$$

$$= \langle \hat{x}^2 \rangle + \frac{t^2}{m^2} \langle \hat{p}^2 \rangle + \frac{t}{m} (\langle \hat{x}\hat{p}\rangle + \langle \hat{p}\hat{x}\rangle)$$

$$= x_0^2 + \sigma^2 + \frac{t^2}{m^2}\frac{\hbar^2}{4\sigma^2} + \frac{t^2}{m^2}p_0^2 + \frac{2t}{m}x_0 p_0 \, ,$$

and

$$p^2(t) = \langle \psi_0 | \hat{p}_H^2(t) | \psi_0 \rangle = \langle \psi_0 | \hat{p}^2 | \psi_0 \rangle = p_0^2 + \frac{\hbar^2}{4\sigma^2} .$$

Exercise 15.4.3 *Use Eqs. (15.4.18, 15.4.20) to derive Eq. (*15.4.21*).*

Solution 15.4.3

Using Eqs. (15.4.18, 15.4.20) we obtain

$$x^2(t) - x(t)^2 = \sigma^2 + x_0^2 + \frac{t^2}{m^2}\frac{\hbar^2}{4\sigma^2} + \frac{t^2}{m^2}p_0^2 + \frac{2t}{m}x_0 p_0 - \left(x_0 + \frac{p_0}{m}t \right)^2$$

$$= \sigma^2 + x_0^2 + \frac{t^2}{m^2}\frac{\hbar^2}{4\sigma^2} + \frac{t^2}{m^2}p_0^2 + \frac{2t}{m}x_0 p_0 - x_0^{\,2} - \frac{p_0^2}{m^2}t^2 - 2x_0\frac{p_0}{m}t$$

$$= \sigma^2 + \frac{t^2}{m^2}\frac{\hbar^2}{4\sigma^2} \quad ,$$

and

$$p^2(t) - \left(p(t)\right)^2 = p_0^2 + \frac{\hbar^2}{4\sigma^2} - p_0^2 = \frac{\hbar^2}{4\sigma^2}.$$

Therefore, $\sqrt{x^2(t) - [x(t)]^2} = \sigma\sqrt{1 + \frac{t^2}{m^2}\frac{\hbar^2}{4\sigma^4}}$ *, and* $\sqrt{p^2(t) - [p(t)]^2} = \frac{\hbar}{2\sigma}$.

Exercise 15.4.4 *Use the momentum space representation of the time-dependent Gaussian wave packet, Eq. (15.4.24), change the integration variable,* $p' = p - p_0$*, and use the identity,* $\int_{-\infty}^{\infty} dp' e^{-zp'^2} e^{ip'x} = \sqrt{\frac{\pi}{z}} e^{\frac{-x^2}{4z}}$ *for a complex valued* z *to obtain and explicit expression for the time-evolution of the Gaussian wave packet for a free particle,* $\langle x|\psi(t)\rangle = (e^{\frac{-ip_0^2 t}{2m\hbar}} e^{ip_0 x/\hbar})\sqrt{\frac{\hbar}{2\pi}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\sqrt{\frac{\pi}{[\sigma^2 + \frac{i\hbar t}{2m}]}}\, e^{\frac{-(x - x_0 - \frac{p_0 t}{m})^2}{4[\sigma^2 + \frac{i\hbar t}{2m}]}}$ *, and the corresponding probability density, Eq. (15.4.25).*

Solution 15.4.4

Starting from Eq. (15.4.24), we obtain

$$\langle x|\psi(t)\rangle = \psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty} dp\, e^{\frac{-(p-p_0)^2}{(\hbar/\sigma)^2}} e^{-i(p-p_0)x_0/\hbar} e^{ipx/\hbar} e^{\frac{-ip^2 t}{2m\hbar}}$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty} dp\, e^{ip_0 x_0/\hbar} e^{\frac{-(p-p_0)^2}{(\hbar/\sigma)^2}} e^{ip(x-x_0)/\hbar} e^{\frac{-ip^2 t}{2m\hbar}}$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty} dp\, e^{ip_0 x/\hbar} e^{\frac{-(p-p_0)^2}{(\hbar/\sigma)^2}} e^{i(p-p_0)(x-x_0)/\hbar} e^{\frac{-ip^2 t}{2m\hbar}}.$$

Changing integration variable, $p' = p - p_0$*, we obtain*

$$\psi(x,t)=\frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty}dp'e^{ip_0x/\hbar}e^{\frac{-(p')^2}{(\hbar/\sigma)^2}}e^{ip'(x-x_0)/\hbar}e^{\frac{-i(p'+p_0)^2t}{2m\hbar}}$$

$$=\frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty}dp'e^{ip_0x/\hbar}e^{\frac{-(p')^2}{(\hbar/\sigma)^2}}e^{ip'(x-x_0)/\hbar}e^{\frac{-i(p')^2t}{2m\hbar}}e^{\frac{-ip_0{}^2t}{2m\hbar}}e^{\frac{-ip'p_0t}{m\hbar}}$$

$$=e^{\frac{-ip_0{}^2t}{2m\hbar}}e^{ip_0x/\hbar}\frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty}dp'e^{-(p')^2[\frac{\sigma^2}{\hbar^2}+\frac{it}{2m\hbar}]}e^{ip'(x-x_0-\frac{p_0t}{m})/\hbar},$$

and using the identity, $\int_{-\infty}^{\infty}dke^{-zk^2}e^{ikx}=\sqrt{\frac{\pi}{z}}e^{\frac{-x^2}{4z}}$ *, we have*

$$\psi(x,t)=e^{\frac{-ip_0{}^2t}{2m\hbar}}e^{ip_0x/\hbar}\frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int_{-\infty}^{\infty}dp'e^{-(p')^2[\frac{\sigma^2}{\hbar^2}+\frac{it}{2m\hbar}]}e^{ip'(x-x_0-\frac{p_0t}{m})/\hbar}$$

$$=e^{\frac{-ip_0{}^2t}{2m\hbar}}e^{ip_0x/\hbar}\sqrt{\frac{\hbar}{2\pi}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\sqrt{\frac{\pi}{[\sigma^2+\frac{i\hbar t}{2m}]}}e^{\frac{-(x-x_0-\frac{p_0t}{m})^2}{4[\sigma^2+\frac{i\hbar t}{2m}]}}$$

$$=e^{\frac{-ip_0{}^2t}{2m\hbar}}e^{ip_0x/\hbar}\left(\frac{\sigma^2}{2\pi}\right)^{1/4}\sqrt{\frac{1}{[\sigma^2+\frac{i\hbar t}{2m}]}}e^{\frac{-(x-x_0-\frac{p_0t}{m})^2}{4[\sigma^2+\frac{i\hbar t}{2m}]}}.$$

The corresponding probability density therefore reads

$$\left|\langle x|\psi(t)\rangle\right|^2=\sqrt{\frac{\sigma^2}{2\pi}}\sqrt{\frac{1}{[\sigma^2-\frac{i\hbar t}{2m}]}\frac{1}{[\sigma^2+\frac{i\hbar t}{2m}]}}e^{\frac{-(x-x_0-\frac{p_0t}{m})^2}{4[\sigma^2-\frac{i\hbar t}{2m}]}+\frac{-(x-x_0-\frac{p_0t}{m})^2}{4[\sigma^2+\frac{i\hbar t}{2m}]}}$$

$$=\sqrt{\frac{\sigma^2}{2\pi[\sigma^4+\frac{\hbar^2t^2}{4m^2}]}}e^{\frac{-(x-x_0-\frac{p_0t}{m})^2}{4}\left[\frac{1}{[\sigma^2+\frac{i\hbar t}{2m}]}+\frac{1}{[\sigma^2-\frac{i\hbar t}{2m}]}\right]}$$

$$=\sqrt{\frac{1}{2\pi[\sigma^2+\frac{\hbar^2t^2}{4\sigma^2m^2}]}}e^{\frac{-2\sigma^2(x-x_0-\frac{p_0t}{m})^2}{4[\sigma^4+\frac{\hbar^2t^2}{4m^2}]}}=\sqrt{\frac{1}{2\pi[\sigma^2+\frac{\hbar^2t^2}{4\sigma^2m^2}]}}e^{\frac{-(x-x_0-\frac{p_0t}{m})^2}{2[\sigma^2+\frac{\hbar^2t^2}{4\sigma^2m^2}]}}.$$

Exercise 15.4.5 *Obtain the time-dependent Heisenberg operators for the Harmonic oscillator (Eq. (15.4.28)) by solving Eq. (15.4.27) for the initial conditions,* $\hat{x}_H(0)=\hat{x}$, $\hat{p}_H(0)=\hat{p}$.

Solution 15.4.5

The equations of motion for the Heisenberg operators for the Harmonic oscillator read

$$\frac{\partial}{\partial t}\hat{x}_H(t)=\frac{1}{m}\hat{p}_H(t) \quad ; \quad \frac{\partial}{\partial t}\hat{p}_H=-m\omega^2\hat{x}_H \text{, which yields } \frac{\partial^2}{\partial t^2}\hat{x}_H=-\omega^2\hat{x}_H .$$

The general solution for this equation is

$$\hat{x}_H(t)=\hat{A}\cos(\omega t)+\hat{B}\sin(\omega t) \text{, and } \hat{p}_H(t)=-m\omega\hat{A}\sin(\omega t)+m\omega\hat{B}\cos(\omega t) .$$

The operators $\hat{A}$ *and* $\hat{B}$ *are related to the initial conditions,* $\hat{x}_H(0)=\hat{A}$ *and* $\hat{p}_H(0)=m\omega\hat{B}$. *For the initial conditions* $\hat{x}_H(0)=\hat{x}$ *and* $\hat{p}_H(0)=\hat{p}$, *the operators* $\hat{A}$ *and* $\hat{B}$ *are given explicitly as,*

$\hat{A}=\hat{x}_H(0)=\hat{x}$, *and* $\hat{B}=\frac{1}{m\omega}\hat{p}_H(0)=\frac{1}{m\omega}\hat{p}$. *Therefore, we obtain Eq. (15.4.28),*

$$\hat{x}_H(t)=\hat{x}\cos(\omega t)+\frac{\hat{p}}{m\omega}\sin(\omega t) \quad ; \quad \hat{p}_H(t)=-m\omega\hat{x}\sin(\omega t)+\hat{p}\cos(\omega t) .$$

Exercise 15.4.6 *Use the results of Ex. 15.4.2(a) for the expectation values of* $\hat{x}^2$, $\hat{p}^2$, $\hat{x}\hat{p}$ *and* $\hat{p}\hat{x}$ *as functions of the parameters* x_0, p_0, σ *of the Gaussian wave packet to obtain the expressions for the quantum mechanical expectation values,* $x^2(t)=\langle\psi_0|\hat{x}_H^2(t)|\psi_0\rangle$ *and* $p^2(t)=\langle\psi_0|\hat{p}_H^2(t)|\psi_0\rangle$ *, in Eq. (15.4.31). (b) Obtain the expressions for the standard deviations of the momentum and position distributions in Eq. (15.4.32).*

Solution 15.4.6

(a)

Taking the expectation values of the Heisenberg operators $\hat{x}_H^2(t)$ *and* $\hat{p}_H^2(t)$ *with respect to the Gaussian eave packet (Eq. (15.4.11)),* $\psi(x,0)=\langle x|\psi_0\rangle=\left(\frac{1}{2\pi\sigma^2}\right)^{1/4} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0x/\hbar}$, *using Eq.*

(15.4.30), and the results of Ex. 15.4.2(a), $\langle \hat{x}^2 \rangle = x_0{}^2 + \sigma^2$, $\langle \hat{p}^2 \rangle = p_0^2 + \frac{\hbar^2}{4\sigma^2}$, $\langle \hat{x}\hat{p} \rangle = p_0 x_0 + \frac{i\hbar}{2}$ *and* $\langle \hat{p}\hat{x} \rangle = p_0 x_0 - \frac{i\hbar}{2}$, *we obtain (Eq. (15.4.31))*

$$x^2(t) = \langle \hat{x}^2 \rangle \cos^2(\omega t) + \frac{\langle \hat{p}^2 \rangle}{m^2\omega^2}\sin^2(\omega t) + \frac{\langle \hat{x}\hat{p} \rangle + \langle \hat{p}\hat{x} \rangle}{m\omega}\cos(\omega t)\sin(\omega t)$$

$$= (x_0{}^2 + \sigma^2)\cos^2(\omega t) + \frac{\left(p_0^2 + \frac{\hbar^2}{4\sigma^2}\right)}{m^2\omega^2}\sin^2(\omega t) + \frac{2x_0 p_0}{m\omega}\cos(\omega t)\sin(\omega t) \;,$$

and

$$p^2(t) = m^2\omega^2 \langle \hat{x}^2 \rangle \sin^2(\omega t) + \langle \hat{p}^2 \rangle \cos^2(\omega t) - m\omega(\langle \hat{x}\hat{p} \rangle + \langle \hat{p}\hat{x} \rangle)\cos(\omega t)\sin(\omega t)$$

$$= m^2\omega^2 \left(x_0^2 + \sigma^2\right)\sin^2(\omega t) + \left(p_0^2 + \frac{\hbar^2}{4\sigma^2}\right)\cos^2(\omega t) - 2m\omega x_0 p_0 \sin(\omega t)\cos(\omega t) .$$

(b)

Taking the expectation values of the Heisenberg operators $\hat{x}_H(t)$ *and* $\hat{p}_H(t)$ *with respect to the Gaussian eave packet (Eq. (15.4.11)),* $\psi(x,0) = \langle x | \psi_0 \rangle = \left(\frac{1}{2\pi\sigma^2}\right)^{1/4} e^{\frac{-(x-x_0)^2}{4\sigma^2}} e^{ip_0 x/\hbar}$, *using Eq. (15.4.28), and the results of Ex. 15.4.2(a):* $\langle \hat{x} \rangle = x_0$ *and* $\langle \hat{p} \rangle = p_0$, *we obtain (Eq. (15.4.29))*

$$x(t) = x_0 \cos(\omega t) + \frac{p_0}{m\omega}\sin(\omega t) \text{, and } p(t) = -m\omega x_0 \sin(\omega t) + p_0 \cos(\omega t) .$$

Consequently,

$$\left[x(t)\right]^2 = x_o{}^2 \cos^2(\omega t) + \frac{p_0{}^2}{m^2\omega^2}\sin^2(\omega t) + \frac{2x_o p_0}{m\omega}\cos(\omega t)\sin(\omega t) ,$$

and

$$\left[p(t)\right]^2 = m^2\omega^2 x_0^2 \sin^2(\omega t) + p_0{}^2 \cos^2(\omega t) - 2m\omega x_0 p_0 \sin(\omega t)\cos(\omega t) .$$

Using these results along with $x^2(t)$ *and* $p^2(t)$ *obtained in (a), we obtain for the position and momentum standard deviations,*

$$x^2(t)-[x(t)]^2$$
$$=(x_0{}^2+\sigma^2)\cos^2(\omega t)+\frac{\left(p_0^2+\frac{\hbar^2}{4\sigma^2}\right)}{m^2\omega^2}\sin^2(\omega t)+\frac{2x_0p_0}{m\omega}\cos(\omega t)\sin(\omega t)$$
$$-x_o{}^2\cos^2(\omega t)-\frac{p_0{}^2}{m^2\omega^2}\sin^2(\omega t)-\frac{2x_op_0}{m\omega}\cos(\omega t)\sin(\omega t)$$
$$=\sigma^2\cos^2(\omega t)+\frac{\hbar^2}{4m^2\omega^2\sigma^2}\sin^2(\omega t)$$

and

$$p^2(t)-\left[p(t)\right]^2$$
$$=m^2\omega^2\left(x_0^2+\sigma^2\right)\sin^2(\omega t)+\left(p_0^2+\frac{\hbar^2}{4\sigma^2}\right)\cos^2(\omega t)-2m\omega x_0p_0\sin(\omega t)\cos(\omega t)$$
$$-m^2\omega^2x_0^2\sin^2(\omega t)-p_0{}^2\cos^2(\omega t)+2m\omega x_0p_0\sin(\omega t)\cos(\omega t)$$
$$=m^2\omega^2\sigma^2\sin^2(\omega t)+\frac{\hbar^2}{4\sigma^2}\cos^2(\omega t)\ .$$

Hence, we obtain Eq. (15.4.32),

$$\sqrt{x^2(t)-\left[x(t)\right]^2}=\sqrt{\sigma^2\cos^2(\omega t)+\frac{\hbar^2}{4\sigma^2m^2\omega^2}\sin^2(\omega t)}$$

$$\sqrt{p^2(t)-[p(t)]^2}=\sqrt{m^2\omega^2\sigma^2\sin^2(\omega t)+\left(\frac{\hbar^2}{4\sigma^2}\right)\cos^2(\omega t)}\ .$$

Exercise 15.4.7 *Use the position representation of the annihilation operator,* $\hat{a}=\sqrt{\frac{m\omega}{2\hbar}}x+\sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}$*, and of the coherent state,* $\psi(x,0)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{\frac{-m\omega(\mathrm{x}-\mathrm{x}_0)^2}{2\hbar}}e^{ip_0x/\hbar}$ *, to show that the coherent state is an eigenstate of the annihilation operator, Eq. (15.4.35).*

Solution 15.4.7

In the position representation, we can use, $\langle x|\hat{a}|\psi_0\rangle=\left(\sqrt{\frac{m\omega}{2\hbar}}x+\sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}\right)\psi(x,0)$. *For the coherent state,* $\psi(x,0)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{\frac{-m\omega(\mathrm{x}-\mathrm{x}_0)^2}{2\hbar}}e^{ip_0x/\hbar}$*, we then obtain*

$$\begin{aligned}
&\langle x|\hat{a}|\psi_0\rangle \\
&=\sqrt{\frac{m\omega}{2\hbar}}x\psi(x,0)+\sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{\frac{-m\omega(x-x_0)^2}{2\hbar}} e^{ip_0x/\hbar} \\
&=\sqrt{\frac{m\omega}{2\hbar}}x\psi(x,0)+\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\sqrt{\frac{\hbar}{2m\omega}}\left(\frac{-m\omega(x-x_0)}{\hbar}+\frac{ip_0}{\hbar}\right)e^{\frac{-m\omega(x-x_0)^2}{2\hbar}} e^{ip_0x/\hbar} \\
&=\sqrt{\frac{m\omega}{2\hbar}}x\psi(x,0)+\sqrt{\frac{m\omega}{2\hbar}}\left(-x+x_0+\frac{ip_0}{m\omega}\right)\psi(x,0) \\
&=\sqrt{\frac{m\omega}{2\hbar}}\left(x_0+\frac{ip_0}{m\omega}\right)\psi(x,0) \\
&=\sqrt{\frac{m\omega}{2\hbar}}\left(x_0+\frac{ip_0}{m\omega}\right)\langle x|\psi_0\rangle \; .
\end{aligned}$$

Hence, the coherent state, $\psi(x,0)=\left(\frac{1}{2\pi\sigma^2}\right)^{1/4} e^{\frac{-m\omega(x-x_0)^2}{2\hbar}} e^{ip_0x/\hbar}$, *is shown to be an eigenstate of the annihilation operator,* $\hat{a}=\sqrt{\frac{m\omega}{2\hbar}}x+\sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}$, *with the eigenvalue* $\sqrt{\frac{m\omega}{2\hbar}}\left(x_0+\frac{ip_0}{m\omega}\right)$.

Exercise 15.4.8 *Derive the expansion of the coherent state in terms of the Harmonic oscillator eigenstates, Eq. (15.4.37). Apply the annihilation operator to the formal expansion,* $\hat{a}|\alpha\rangle=\sum_{n=0}^{\infty}\gamma_n\hat{a}|\varphi_n\rangle$, *recalling that* $\hat{a}|\varphi_n\rangle=\sqrt{n}|\varphi_{n-1}\rangle$ *(Eq. (8.5.3)). Then show that* $\gamma_{m+1}\sqrt{m+1}=\alpha\gamma_m$. *Use the normalization condition* $\langle\alpha|\alpha\rangle=1$ *to show that* $\left|\langle\varphi_0|\alpha\rangle\right|^2=e^{-|\alpha|^2}$, *and prove the identity, Eq. (15.4.37).*

Solution 15.4.8

We start from the formal expansion of the coherent state in terms of the harmonic oscillator Hamiltonian eigenstates, $|\alpha\rangle=\sum_{n=0}^{\infty}\gamma_n|\varphi_n\rangle$, *where we wish to identify the expansion coefficients. Using the property of the annihilation operator,* $\hat{a}|\varphi_n\rangle=\sqrt{n}|\varphi_{n-1}\rangle$, *we obtain* $\hat{a}|\alpha\rangle=\sum_{n=0}^{\infty}\gamma_n\hat{a}|\varphi_n\rangle=\sum_{n=0}^{\infty}\gamma_n\sqrt{n}|\varphi_{n-1}\rangle$, *and projecting on the* m *th eigenstate,* $|\varphi_m\rangle$, *we obtain* $\langle\varphi_m|\hat{a}|\alpha\rangle=\sum_{n=0}^{\infty}\gamma_n\sqrt{n}\delta_{n-1,m}=\gamma_{m+1}\sqrt{m+1}$. *Considering that* $|\alpha\rangle$ *is an eigenstate of* $\hat{a}$, *namely,*

$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$, *we have* $\langle\varphi_m|\hat{a}|\alpha\rangle = \alpha\gamma_m = \gamma_{m+1}\sqrt{m+1}$, *and consequently,* $\gamma_{m+1} = \dfrac{\alpha}{\sqrt{m+1}}\gamma_m$. *Using the last result recursively, we obtain,* $\gamma_n = \dfrac{\alpha^n}{\sqrt{n!}}\gamma_0$, *namely* $|\alpha\rangle = \sum_{n=0}^{\infty}\dfrac{\alpha^n}{\sqrt{n!}}\gamma_0$. *The value of* γ_0 *is subject to normalization. Requiring* $\langle\alpha|\alpha\rangle = 1 \Rightarrow \sum_{n=0}^{\infty}|\langle\varphi_n|\alpha\rangle|^2 = 1$, *we obtain* $1 = |\gamma_0|^2\sum_{n=0}^{\infty}\dfrac{|\alpha|^{2n}}{n!} = |\gamma_0|^2 e^{|\alpha|^2}$, *and therefore,* $|\gamma_0|^2 = |\langle\varphi_0|\alpha\rangle|^2 = e^{-|\alpha|^2}$. *Consequently,* $\gamma_0 = e^{i\Phi}e^{-|\alpha|^2/2}$, *where* Φ *is a real valued number. Substitution* $\gamma_n = \dfrac{\alpha^n}{\sqrt{n!}}\gamma_0$ *and* $\gamma_0 = e^{i\Phi}e^{-|\alpha|^2/2}$ *in the expansion,* $|\alpha\rangle = \sum_{n=0}^{\infty}\gamma_n|\varphi_n\rangle$, *yields Eq. (15.4.37),* $|\alpha\rangle = e^{i\Phi}e^{\frac{-|\alpha^2|}{2}}\sum_{n=0}^{\infty}\dfrac{\alpha^n}{\sqrt{n!}}|\varphi_n\rangle$.

Exercise 15.4.9 *Using the identity* $e^{-i\omega nt} = (e^{-i\omega t})^n$, *rewrite Eq. (15.4.38) as Eq. (15.4.39).*

Solution 15.4.9

Starting from the time-evolution of a coherent state (Eq. (15.4.38)), we obtain

$$|\psi(t)\rangle \equiv e^{\frac{-it}{\hbar}\hbar\omega(\hat{a}^\dagger\hat{a}+1/2)}|\alpha\rangle = e^{\frac{-it}{\hbar}\hbar\omega(\hat{a}^\dagger\hat{a}+1/2)}e^{i\Phi}e^{\frac{-|\alpha^2|}{2}}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|\varphi_n\rangle$$
$$= e^{i\Phi}e^{\frac{-|\alpha^2|}{2}}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}e^{\frac{-it}{\hbar}\hbar\omega(n+1/2)}|\varphi_n\rangle$$
$$= e^{i\Phi}e^{\frac{-i\omega t}{2}}e^{\frac{-|\alpha^2|}{2}}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}e^{-i\omega nt}|\varphi_n\rangle$$
$$= e^{i\Phi}e^{\frac{-i\omega t}{2}}e^{\frac{-|\alpha^2|}{2}}\sum_{n=0}^{\infty}\frac{(\alpha e^{-i\omega t})^n}{\sqrt{n!}}|\varphi_n\rangle .$$

Identifying, $\alpha(t) \equiv \alpha e^{-i\omega t}$, *the result can be rewritten as,* $|\psi(t)\rangle = e^{i\Phi}e^{\frac{-i\omega t}{2}}e^{\frac{-|\alpha(t)|^2}{2}}\sum_{n=0}^{\infty}\dfrac{[\alpha(t)]^n}{\sqrt{n!}}|\varphi_n\rangle$.

Recalling the expansion (Ex. 15.4.8), $|\alpha\rangle = e^{i\Phi}e^{\frac{-|\alpha^2|}{2}}\sum_{n=0}^{\infty}\dfrac{\alpha^n}{\sqrt{n!}}|\varphi_n\rangle$, *we can identify the last result as,*

$$|\psi(t)\rangle = e^{\frac{-i\omega t}{2}}|\alpha(t)\rangle = e^{\frac{-i\omega t}{2}}|\alpha e^{-i\omega t}\rangle .$$

Finally, realizing that the normalized coherent state (Eq. (15.4.37)) is defined up to a global phase $e^{i\Phi(t)}$ *at any time, the most general expression for the time evolution of* $|\alpha\rangle$ *reads (Eq. (15.4.39)):*

$$|\psi(t)\rangle = e^{\frac{-i\omega t}{2}} e^{i\Phi(t)} |\alpha(t)\rangle = e^{\frac{-i\omega t}{2}} e^{i\Phi(t)} |\alpha e^{-i\omega t}\rangle .$$

Exercise 15.4.10 *Use Eqs. (15.4.36, 15.4.40) to derive the quantum mechanical position and momentum expectation values for the coherent state. Show that these results identify with a classical trajectory of a corresponding particle.*

Solution 15.4.10

According to Eq. (15.4.36) and the related discussion, a coherent state is identified with a Gaussian wave packet. Replacing $|\alpha\rangle$ *by* $|\alpha e^{-i\omega t}\rangle$, x_0 *by* $x(t)$, *and* p_0 *by* $p(t)$, *Eq. (15.4.36) can be rewritten as,* $|\psi(t)\rangle \equiv |\alpha e^{-i\omega t}\rangle$, *with* $\alpha e^{-i\omega t} \equiv \sqrt{\frac{1}{2}}\left(\sqrt{\frac{m\omega}{\hbar}}x(t) + i\frac{p(t)}{\sqrt{\hbar m\omega}}\right)$, *where, in the position representation,* $\langle x|\alpha e^{-i\omega t}\rangle = \psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{\frac{-m\omega(x-x(t))^2}{2\hbar}} e^{ip(t)x/\hbar}$. *The quantum mechanical expectation values associated with this state (see Ex. 15.4.2) are readily identified as* $\langle \hat{x}(t)\rangle = x(t)$, *and* $\langle \hat{p}(t)\rangle = p(t)$. *These can be expressed explicitly according to their relation to* $\alpha e^{-i\omega t}$ *(Eq. (15.4.40)). Recalling that* $\alpha \equiv \sqrt{\frac{1}{2}}\left(\sqrt{\frac{m\omega}{\hbar}}x_0 + i\frac{p_0}{\sqrt{\hbar m\omega}}\right)$, *we obtain*

$$x(t) = \sqrt{\frac{2\hbar}{m\omega}}\,\mathrm{Re}[\alpha e^{-i\omega t}] = \sqrt{\frac{2\hbar}{m\omega}}\,\mathrm{Re}[\sqrt{\frac{1}{2}}\left(\sqrt{\frac{m\omega}{\hbar}}x_0 + i\frac{p_0}{\sqrt{\hbar m\omega}}\right)e^{-i\omega t}]$$
$$= \mathrm{Re}[\left(x_0 + i\frac{p_0}{m\omega}\right)e^{-i\omega t}]$$
$$= x_0\cos(\omega t) + \frac{p_0}{m\omega}\sin(\omega t)$$

and

$$p(t) = \sqrt{2m\omega\hbar}\,\mathrm{Im}[\alpha e^{-i\omega t}] = \sqrt{2m\omega\hbar}\,\mathrm{Im}[\sqrt{\frac{1}{2}}\left(\sqrt{\frac{m\omega}{\hbar}}x_0 + i\frac{p_0}{\sqrt{\hbar m\omega}}\right)e^{-i\omega t}]$$
$$= \mathrm{Im}[\left(m\omega x_0 + ip_0\right)e^{-i\omega t}]$$
$$= p_0\cos(\omega t) - m\omega x_0\sin(\omega t) .$$

These results coincide with the explicit calculation of the expectation values for a Gaussian wave packet in a harmonic potential energy well (see Eq. (15.4.29)), as well as with the solution of the classical equations of motion for a harmonic oscillator:

$$\frac{\partial}{\partial t}x(t)=\frac{1}{m}p(t) \qquad ; \qquad \frac{\partial}{\partial t}p(t)=-m\omega^2 x(t),$$

for the initial conditions $x(0)=x_0$ *and* $p(0)=p_0$, *as can be readily verified.*

Exercise 15.4.11 *Show that* $\psi(x,t)$, *as defined in Eq. (15.4.41), is a solution of the time-dependent Schrödinger equation for the harmonic oscillator,* $i\hbar\frac{\partial}{\partial t}\psi(x,t)=\hbar\omega\left[\hat{a}^\dagger\hat{a}+\frac{1}{2}\right]\psi(x,t)$, *where* $\hat{a}=\sqrt{\frac{m\omega}{2\hbar}}x+\sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}$.

Solution 15.4.11

Starting from Eq. (15.4.41), $\psi(x,t)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{\frac{-m\omega(x-x(t))^2}{2\hbar}} e^{ip(t)x/\hbar}e^{i\bar{\Phi}(t)}$, *we obtain*

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=i\left[m\omega(x-x(t))\dot{x}(t)+ix\dot{p}(t)\right]\psi(x,t)-\hbar\dot{\bar{\Phi}}\psi(x,t)$$
$$=\left[im\omega(x-x(t))\dot{x}(t)-x\dot{p}(t)\right]\psi(x,t)-\hbar\dot{\bar{\Phi}}\psi(x,t).$$

Using the relations (Eqs. (15.4.27-15.4.29)), $\dot{x}(t)=\frac{p(t)}{m}$ *and* $\dot{p}(t)=-m\omega^2 x(t)$, *we obtain*

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=m\omega^2\left[i(x-x(t))\frac{p(t)}{m\omega}+xx(t)\right]\psi(x,t)-\hbar\dot{\bar{\Phi}}\psi(x,t)$$
$$=m\omega^2\left[x[x(t)+\frac{ip(t)}{m\omega}]-x(t)\frac{ip(t)}{m\omega}\right]\psi(x,t)-\hbar\dot{\bar{\Phi}}\psi(x,t).$$

To obtain the result of the Hamiltonian operation ($\hat{H}=\hbar\omega\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)$*) on* $\psi(x,t)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{\frac{-m\omega(x-x(t))^2}{2\hbar}} e^{ip(t)x/\hbar}e^{i\bar{\Phi}(t)}$, *we first notice that*

$$\langle x|\hat{a}|\psi(t)\rangle = \left(\sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}\right)\psi(x,t)$$
$$= \sqrt{\frac{m\omega}{2\hbar}}x\psi(x,t) + \sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}\psi(x,t)$$
$$= \sqrt{\frac{m\omega}{2\hbar}}x\psi(x,t) + \sqrt{\frac{\hbar}{2m\omega}}\left(\frac{-m\omega(x-x(t))}{\hbar} + \frac{ip(t)}{\hbar}\right)\psi(x,t)$$
$$= \sqrt{\frac{m\omega}{2\hbar}}x\psi(x,t) + \sqrt{\frac{m\omega}{2\hbar}}\left(-x + x(t) + \frac{ip(t)}{m\omega}\right)\psi(x,t)$$

$$= \sqrt{\frac{m\omega}{2\hbar}}\left(x(t) + \frac{ip(t)}{m\omega}\right)\psi(x,t) \ ,$$

and

$$\langle x|\hat{a}^\dagger|\psi(t)\rangle = \left(\sqrt{\frac{m\omega}{2\hbar}}x - \sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}\right)\psi(x,t)$$
$$= \sqrt{\frac{m\omega}{2\hbar}}x\psi(x,t) - \sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x}\psi(x,t)$$
$$= \sqrt{\frac{m\omega}{2\hbar}}x\psi(x,t) - \sqrt{\frac{\hbar}{2m\omega}}\left(\frac{-m\omega(x-x(t))}{\hbar} + \frac{ip(t)}{\hbar}\right)\psi(x,t)$$
$$= \sqrt{\frac{m\omega}{2\hbar}}x\psi(x,t) - \sqrt{\frac{m\omega}{2\hbar}}\left(-x + x(t) + \frac{ip(t)}{m\omega}\right)\psi(x,t)$$

$$= \sqrt{\frac{m\omega}{2\hbar}}2x\psi(x,t) - \sqrt{\frac{m\omega}{2\hbar}}\left(x(t) + \frac{ip(t)}{m\omega}\right)\psi(x,t) \ .$$

Therefore,

$$\hbar\omega\langle x|\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)|\psi(t)\rangle = \hbar\omega\left[\sqrt{\frac{m\omega}{2\hbar}}2x - \sqrt{\frac{m\omega}{2\hbar}}\left(x(t) + \frac{ip(t)}{m\omega}\right)\right]$$
$$\left[\sqrt{\frac{m\omega}{2\hbar}}\left(x(t) + \frac{ip(t)}{m\omega}\right)\right]\psi(x,t) + \frac{\hbar\omega}{2}\psi(x,t)$$
$$= m\omega^2\left[x - \frac{1}{2}\left(x(t) + \frac{ip(t)}{m\omega}\right)\right]\left[\left(x(t) + \frac{ip(t)}{m\omega}\right)\right]\psi(x,t) + \frac{\hbar\omega}{2}\psi(x,t)$$
$$= m\omega^2\left[x\left(x(t) + \frac{ip(t)}{m\omega}\right) - \frac{1}{2}\left(x(t) + \frac{ip(t)}{m\omega}\right)^2\right]\psi(x,t) + \frac{\hbar\omega}{2}\psi(x,t)$$
$$= m\omega^2\left[x\left(x(t) + \frac{ip(t)}{m\omega}\right) - \frac{ix(t)p(t)}{m\omega} - \frac{1}{2}\left(x(t)^2 - \frac{p(t)^2}{m^2\omega^2}\right)\right]\psi(x,t) + \frac{\hbar\omega}{2}\psi(x,t) \ .$$

Using the above results, the coherent state is identified as a solution to the Schrodinger equation,

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=\hat{H}\psi(x,t)=\hbar\omega\langle x|\left(\hat{a}^{\dagger}\hat{a}+\frac{1}{2}\right)|\psi(t)\rangle,$$

only if the following condition holds,

$$\begin{aligned}&m\omega^2\left[x[x(t)+\frac{ip(t)}{m\omega}]-x(t)\frac{ip(t)}{m\omega}\right]-\hbar\dot{\bar{\Phi}}\\&=m\omega^2\left[x\left(x(t)+\frac{ip(t)}{m\omega}\right)-\frac{ix(t)p(t)}{m\omega}-\frac{1}{2}\left(x(t)^2-\frac{p(t)^2}{m^2\omega^2}\right)\right]+\frac{\hbar\omega}{2}\end{aligned}\Rightarrow\dot{\bar{\Phi}}=\frac{m\omega^2x(t)^2}{2\hbar}-\frac{p(t)^2}{2m\hbar}-\frac{\omega}{2}.$$

Using the relations, $x(t)=x_0\cos(\omega t)+\frac{p_0}{m\omega}\sin(\omega t)$ *and* $p(t)=p_0\cos(\omega t)-m\omega x_0\sin(\omega t)$ *(Eqs. (15.4.27-15.4.29)), the equation for the appropriate phase,* $\bar{\Phi}(t)$*, reads*

$$\begin{aligned}\dot{\bar{\Phi}}&=\frac{m\omega^2x(t)^2}{2\hbar}-\frac{p(t)^2}{2m\hbar}-\frac{\omega}{2}\\&=\frac{m\omega^2}{2\hbar}\left(x_0\cos(\omega t)+\frac{p_0}{m\omega}\sin(\omega t)\right)^2-\frac{1}{2m\hbar}\left(p_0\cos(\omega t)-m\omega x_0\sin(\omega t)\right)^2-\frac{\omega}{2}\\&=\frac{m\omega^2x_0^2}{2\hbar}\cos^2(\omega t)+\frac{p_0^2}{2\hbar m}\sin^2(\omega t)+\frac{\omega x_0p_0}{\hbar}\sin(\omega t)\cos(\omega t)\\&-\frac{p_0^2}{2m\hbar}\cos^2(\omega t)-\frac{m\omega^2x_0^2}{2\hbar}\sin^2(\omega t)+\frac{p_0\omega x_0}{\hbar}\cos(\omega t)\sin(\omega t)-\frac{\omega}{2}\\&=[\frac{m\omega^2x_0^2}{2\hbar}-\frac{p_0^2}{2m\hbar}]\cos(2\omega t)+\frac{\omega x_0p_0}{\hbar}\sin(2\omega t)-\frac{\omega}{2}.\end{aligned}$$

This is readily shown to hold for $\bar{\Phi}(t)=\left[\frac{m\omega x_0{}^2}{4\hbar}-\frac{p_0^2}{4\hbar m\omega}\right]\sin(2\omega t)-\frac{x_0p_0}{2\hbar}\cos(2\omega t)-\frac{\omega t}{2}$,

which complies with the definition of the coherent state in Eq. (15.4.41).

Exercise 15.5.1 *Using the definition of the trace of an operator, Eq. (15.5.3), (a) prove the following identities:* $tr\{\hat{A}\hat{B}\}=tr\{\hat{B}\hat{A}\}$, $tr\{\hat{A}^{\dagger}\}=tr\{\hat{A}\}^*$, $tr\{[\hat{A},\hat{B}]\}=0$. *(b) Show that the trace of an operator is invariant to a similarity transformation of the operator,* $tr\{\hat{S}^{-1}\hat{A}\hat{S}\}=tr\{\hat{A}\}$. *(c) Show that the trace of an operator is invariant to a unitary transformation of the operator,*

$tr\left\{\hat{U}^{\dagger}\hat{A}\hat{U}\right\} = tr\left\{\hat{A}\right\}$. *(d) Show that the trace of an operator is independent of the basis in which the operator is represented,* $tr\left\{\hat{A}\right\} \equiv \sum_{n}\langle\varphi_n|\hat{A}|\varphi_n\rangle = \sum_{m}\langle\chi_m|\hat{A}|\chi_m\rangle$*, where,* $\{|\varphi_n\rangle\}$*, and* $\{|\chi_m\rangle\}$ *are complete orthonormal systems in the relevant Hilbert space,* $\hat{I} = \sum_{n}|\varphi_n\rangle\langle\varphi_n| = \sum_{m}|\chi_m\rangle\langle\chi_m|$. *(e) Show that the trace of a tensor product of operators in a multidimensional space,* $\hat{A}_1 \otimes \hat{A}_2 \otimes \cdots \otimes \hat{A}_N$*, is a product of traces over the subspaces,* $tr\left\{\hat{A}_1 \otimes \hat{A}_2 \otimes \cdots \otimes \hat{A}_N\right\} = tr\left\{\hat{A}_1\right\}\cdot tr\left\{\hat{A}_2\right\}\cdots tr\left\{\hat{A}_N\right\}$ *(recall that the multidimensional space is spanned by a complete set of tensor product states (Eq. (11.6.12)).*

Solution 15.5.1

(a)

Using the definition (Eq. (15.5.3)), $tr\left\{\hat{O}\right\} \equiv \sum_{n}\langle\varphi_n|\hat{O}|\varphi_n\rangle$*, and introducing identity operators,* $\hat{I} = \sum_{n}|\varphi_n\rangle\langle\varphi_n|$*, we obtain*

$$tr\left\{\hat{A}\hat{B}\right\} \equiv \sum_{n}\langle\varphi_n|\hat{A}\hat{B}|\varphi_n\rangle = \sum_{n,m}\langle\varphi_n|\hat{A}|\varphi_m\rangle\langle\varphi_m|\hat{B}|\varphi_n\rangle$$

$$= \sum_{n,m}\langle\varphi_m|\hat{B}|\varphi_n\rangle\langle\varphi_n|\hat{A}|\varphi_m\rangle = \sum_{m}\langle\varphi_m|\hat{B}\hat{A}|\varphi_m\rangle = tr\left\{\hat{B}\hat{A}\right\} .$$

$$tr\left\{[\hat{A},\hat{B}]\right\} = tr\left\{\hat{A}\hat{B}\right\} - tr\left\{\hat{B}\hat{A}\right\} = 0 .$$

$$tr\left\{\hat{A}^{\dagger}\right\} = \sum_{n}\langle\varphi_n|\hat{A}^{\dagger}|\varphi_n\rangle = \sum_{n}\langle\varphi_n|\hat{A}|\varphi_n\rangle^{*} = \left(\sum_{n}\langle\varphi_n|\hat{A}|\varphi_n\rangle\right)^{*} = \left(tr\left\{\hat{A}\right\}\right)^{*} .$$

(b)

Using $tr\left\{\hat{A}\hat{B}\right\} = tr\left\{\hat{B}\hat{A}\right\}$*, we obtain*

$$tr\left\{\hat{S}^{-1}\hat{A}\hat{S}\right\} = tr\left\{\left[\hat{S}^{-1}\hat{A}\right]\hat{S}\right\} = tr\left\{\hat{S}\left[\hat{S}^{-1}\hat{A}\right]\right\} = tr\left\{\hat{S}\hat{S}^{-1}\hat{A}\right\} = tr\left\{\hat{A}\right\}.$$

(c)

Since for a unitary operator we have, $\hat{U}^{\dagger} = \hat{U}^{-1}$*, using the result of (b) we obtain*

$$tr\left\{\hat{U}^{\dagger}\hat{A}\hat{U}\right\} = tr\left\{\hat{U}^{-1}\hat{A}\hat{U}\right\} = tr\left\{\hat{A}\right\}.$$

(d)

$$tr\left\{\hat{A}\right\} \equiv \sum_{n}\langle\varphi_n|\hat{A}|\varphi_n\rangle = \sum_{n,m}\langle\varphi_n|\chi_m\rangle\langle\chi_m|\hat{A}|\varphi_n\rangle = \sum_{n,m}\langle\chi_m|\hat{A}|\varphi_n\rangle\langle\varphi_n|\chi_m\rangle = \sum_{m}\langle\chi_m|\hat{A}|\chi_m\rangle .$$

(e) Using product of states, $\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\cdots\otimes\left|\varphi_{n_N}\right\rangle$*, as an orthonormal basis for the multidimensional tensor product space (see, e.g., Eq. (11.6.6)), the trace of a product* $\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N$*, reads*

$$
\begin{aligned}
& tr\left\{\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N\right\} \\
&=\sum_{n_1,n_2,\ldots,n_N}\left\langle\varphi_{n_1}\right|\otimes\left\langle\varphi_{n_2}\right|\otimes\cdots\otimes\left\langle\varphi_{n_N}\right|\left[\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N\right]\left|\varphi_{n_1}\right\rangle\otimes\left|\varphi_{n_2}\right\rangle\otimes\cdots\otimes\left|\varphi_{n_N}\right\rangle \\
&=\sum_{n_1,n_2,\ldots,n_N}\left\langle\varphi_{n_1}\right|\otimes\left\langle\varphi_{n_2}\right|\otimes\cdots\otimes\left\langle\varphi_{n_N}\right|\cdot\left|\hat{A}_1\varphi_{n_1}\right\rangle\otimes\left|\hat{A}_2\varphi_{n_2}\right\rangle\otimes\cdots\otimes\left|\hat{A}_N\varphi_{n_N}\right\rangle \\
&=\sum_{n_1,n_2,\ldots,n_N}\left\langle\varphi_{n_1}\right|\hat{A}_1\left|\varphi_{n_1}\right\rangle\cdot\left\langle\varphi_{n_2}\right|\hat{A}_2\left|\varphi_{n_2}\right\rangle\cdots\left\langle\varphi_{n_N}\right|\hat{A}_N\left|\varphi_{n_N}\right\rangle \\
&=\sum_{n_1}\left\langle\varphi_{n_1}\right|\hat{A}_1\left|\varphi_{n_1}\right\rangle\cdot\sum_{n_2}\left\langle\varphi_{n_2}\right|\hat{A}_2\left|\varphi_{n_2}\right\rangle\cdots\sum_{n_N}\left\langle\varphi_{n_N}\right|\hat{A}_N\left|\varphi_{n_N}\right\rangle \\
&=\sum_{n_1}\left\langle\varphi_{n_1}\right|\hat{A}_1\left|\varphi_{n_1}\right\rangle\cdot\sum_{n_2}\left\langle\varphi_{n_2}\right|\hat{A}_2\left|\varphi_{n_2}\right\rangle\cdots tr\left\{\hat{A}_N\right\} \\
&=\sum_{n_1}\left\langle\varphi_{n_1}\right|\hat{A}_1\left|\varphi_{n_1}\right\rangle tr\left\{\hat{A}_2\right\}\cdots tr\left\{\hat{A}_N\right\} \\
&=tr\left\{\hat{A}_1\right\}\cdot tr\left\{\hat{A}_2\right\}\cdots tr\left\{\hat{A}_N\right\} \quad .
\end{aligned}
$$

Exercise 15.5.2 *Use Eqs. (15.5.2, 15.5.3) and the identity operator* $\hat{I}=\sum_n|\varphi_n\rangle\langle\varphi_n|$ *to derive Eq. (15.5.4).*

Solution 15.5.2

Starting from the definition of the transition probability, we obtain

$$P_{i\to f}(t)=\left|\left\langle\chi_f\left|\hat{U}(t,0)\right|\chi_i\right\rangle\right|^2=\left\langle\chi_i\left|\hat{U}^\dagger(t,0)\right|\chi_f\right\rangle\left\langle\chi_f\left|\hat{U}(t,0)\right|\chi_i\right\rangle .$$

Introducing an identity operator, changing the multiplication order, and using the definition of the trace, we obtain

$$
\begin{aligned}
P_{i\to f}(t)&=\left\langle\chi_i\left|\hat{U}^\dagger(t,0)\right|\chi_f\right\rangle\left\langle\chi_f\left|\hat{U}(t,0)\right|\chi_i\right\rangle \\
&=\left\langle\chi_i\right|\sum_n|\varphi_n\rangle\left\langle\varphi_n\left|\hat{U}^\dagger(t,0)\right|\chi_f\right\rangle\left\langle\chi_f\left|\hat{U}(t,0)\right|\chi_i\right\rangle \\
&=\sum_n\left\langle\varphi_n\left|\hat{U}^\dagger(t,0)\right|\chi_f\right\rangle\left\langle\chi_f\left|\hat{U}(t,0)\right|\chi_i\right\rangle\langle\chi_i|\varphi_n\rangle
\end{aligned}
$$

$$= tr\left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}.$$

Exercise 15.5.3 *Use Eqs. (15.5.4, 15.5.6) to derive Eqs. (15.5.8, 15.5.9).*

Solution 15.5.3

Starting from Eq. (15.5.4) for the transition probability, $P_{i\to f}(t) = tr\left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}$, *we obtain*

$$\frac{d}{dt}P_{i\to f}(t) = tr\left\{\left[\frac{d}{dt}\hat{U}^{\dagger}(t,0)\right]\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}$$
$$+ tr\left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\left[\frac{d}{dt}\hat{U}(t,0)\right]\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}.$$

Using cyclic permutation under the trace (see Ex. 15.5.1(a)), we can rewrite the first term as, $tr\left\{\left[\frac{d}{dt}\hat{U}^{\dagger}(t,0)\right]\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\} = tr\left\{\left|\chi_i\right\rangle\left\langle\chi_i\right|\left[\frac{d}{dt}\hat{U}^{\dagger}(t,0)\right]\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\right\}$.

Noticing that

$$\left\{\left|\chi_i\right\rangle\left\langle\chi_i\right|\left[\frac{d}{dt}\hat{U}^{\dagger}(t,0)\right]\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\right\} = \left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\left[\frac{d}{dt}\hat{U}(t,0)\right]\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}^{\dagger},$$

and recalling that $tr\left\{\hat{A}^{\dagger}\right\} == \left(tr\left\{\hat{A}\right\}\right)^{*}$, *we obtain Eq. (15.5.8),*

$$\frac{d}{dt}P_{i\to f}(t) = tr\left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\left[\frac{d}{dt}\hat{U}(t,0)\right]\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}^{*}$$
$$+ tr\left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\left[\frac{d}{dt}\hat{U}(t,0)\right]\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}$$
$$= 2\,\mathrm{Re}\,tr\left\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\left[\frac{d}{dt}\hat{U}(t,0)\right]\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}.$$

Starting from Eq. (15.5.6), $P_{i\to f}(t) = tr\left\{\hat{P}_H^{(f)}(t)\hat{P}_H^{(i)}(0)\right\}$, *we immediately obtain Eq. (15.5.9),*

$$\frac{d}{dt}P_{i\to f}(t) = tr\left\{\frac{d}{dt}\hat{P}_H^{(f)}(t)\hat{P}_H^{(i)}(0)\right\}.$$

An alternative derivation of the last result can be obtained directly from Eq. (15.5.8), by using the Schrodinger equation for the time-evolution operator (Eq. (15.2.4)):

$$\frac{d}{dt}P_{i\to f}(t) = 2\,\mathrm{Re}\,tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\left[\frac{d}{dt}\hat{U}(t,0)\right]\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}$$
$$= 2\,\mathrm{Re}\,tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\frac{-i}{\hbar}\hat{H}(t)\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}$$
$$= \frac{2}{\hbar}\mathrm{Im}\,tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{H}(t)\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}$$
$$= \frac{-i}{\hbar}\left[tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{H}(t)\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\} - tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{H}(t)\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}^*\right]$$
$$= \frac{-i}{\hbar}\left[tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{H}(t)\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\} - tr\left\{\left|\chi_i\right\rangle\left\langle\chi_i\right|\hat{U}^\dagger(t,0)\hat{H}(t)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\right\}\right]$$
$$= \frac{-i}{\hbar}\left[tr\left\{\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{H}(t)\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\} - tr\left\{\hat{U}^\dagger(t,0)\hat{H}(t)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}\right]$$
$$= tr\left\{\hat{U}^\dagger(t,0)\frac{i}{\hbar}\left[\hat{H}(t),\left|\chi_f\right\rangle\left\langle\chi_f\right|\right]\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\right\}.$$

Identifying the derivative of the Heisenberg operator (Eq. (15.3.18)), $\hat{U}^\dagger(t,0)\frac{i}{\hbar}\left[\hat{H}(t),\left|\chi_f\right\rangle\left\langle\chi_f\right|\right]\hat{U}(t,0) = \frac{d}{dt}\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)$,

and denoting, $\hat{U}^\dagger(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0) = \hat{P}_H^{(f)}(t)$ *and* $\left|\chi_i\right\rangle\left\langle\chi_i\right| = \hat{P}_H^{(i)}(0)$, *the result reads,* $\frac{d}{dt}P_{i\to f}(t) = tr\{\frac{d}{dt}\hat{P}_H^{(f)}(t)\hat{P}_H^{(i)}(0)\}$.

Exercise 15.5.4 *Let the time-dependent state of a system be* $\left|\psi(t)\right\rangle \equiv \hat{U}(t,0)\left|\chi_i\right\rangle$. *(a) Use the transformation of the state to the interaction picture,* $\left|\psi_I(t)\right\rangle \equiv e^{\frac{i}{\hbar}\hat{H}_0 t}\left|\psi(t)\right\rangle$ *(Eq. (15.3.7)), and the definition of the interaction picture propagator,* $\left|\psi_I(t)\right\rangle \equiv \hat{U}^{(I)}(t,0)\left|\chi_i\right\rangle$, *(Eq. (15.3.9)), to show that* $\left|\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\right|^2 = \left|\left\langle\chi_f\right|e^{\frac{-it}{\hbar}\hat{H}_0}\hat{U}^{(I)}(t,0)\left|\chi_i\right\rangle\right|^2$. *(b) Given that* $\left|\chi_f\right\rangle$ *is an eigenvector of* $\hat{H}_0$, *show* *that* $\left|\left\langle \chi_f \left| \hat{U}(t,0) \right| \chi_i \right\rangle\right|^2 = \left|\left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2$. *(c) Given the definitions* $\hat{P}_i = |\chi_i\rangle\langle\chi_i|$ *and* $\hat{P}_f = |\chi_f\rangle\langle\chi_f|$, *and using the trace definition (Eq. (15.5.3)), derive Eq. (15.5.12) from Eq. (15.5.11).*

Solution 15.5.4

(a)

For the state, $|\psi(t)\rangle \equiv \hat{U}(t,0)|\chi_i\rangle$, *the transition probability reads* $\left|\left\langle \chi_f \left| \hat{U}(t,0) \right| \chi_i \right\rangle\right|^2 = \left|\left\langle \chi_f | \psi(t) \right\rangle\right|^2$. *Transforming to the interaction picture representation,* $|\psi_I(t)\rangle \equiv e^{\frac{i}{\hbar}\hat{H}_0 t}|\psi(t)\rangle$, *we obtain* $\left|\left\langle \chi_f | \psi(t) \right\rangle\right|^2 = \left|\left\langle \chi_f \left| e^{\frac{-i}{\hbar}\hat{H}_0 t} \right| \psi_I(t) \right\rangle\right|^2$, *or, in terms of the interaction picture propagator,* $\left|\left\langle \chi_f \left| e^{\frac{-i}{\hbar}\hat{H}_0 t} \right| \psi_I(t) \right\rangle\right|^2 = \left|\left\langle \chi_f \left| e^{\frac{-it}{\hbar}\hat{H}_0} \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2$.

(b)

If the final state is an eigenvector of $\hat{H}_0$, *namely,* $\hat{H}_0|\chi_f\rangle = \varepsilon_f|\chi_f\rangle$, *we obtain*

$$\left|\left\langle \chi_f \left| \hat{U}(t,0) \right| \chi_i \right\rangle\right|^2 = \left|\left\langle \chi_f \left| e^{\frac{-it}{\hbar}\hat{H}_0} \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2 = \left|\left\langle \chi_f \left| e^{\frac{-it}{\hbar}\varepsilon_f} \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2$$

$$= \left| e^{\frac{-it}{\hbar}\varepsilon_f} \right|^2 \left|\left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2 = \left|\left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2.$$

(c)

Using $P_{i\to f}(t) = \left|\left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle\right|^2$, *we obtain*

$$P_{i\to f}(t) = \left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle^* \left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle = \left\langle \chi_i \left| \hat{U}^{\dagger(I)}(t,0) \right| \chi_f \right\rangle \left\langle \chi_f \left| \hat{U}^{(I)}(t,0) \right| \chi_i \right\rangle .$$

Introducing an identity operator in the relevant Hilbert space, $\hat{I} = \sum_n |\varphi_n\rangle\langle\varphi_n|$, *and recalling the definition of the trace (Eq. (15.5.3)), the transition probability can be expressed as*

$$= \sum_n \langle \chi_i | \varphi_n \rangle \langle \varphi_n | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$= \sum_n \langle \varphi_n | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle \langle \chi_i | \varphi_n \rangle = tr\{\hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle \langle \chi_i |\}$$

.

Finally, introducing the projection operators, $\hat{P}_i = |\chi_i\rangle\langle\chi_i|$ *and* $\hat{P}_f = |\chi_f\rangle\langle\chi_f|$, *we obtain Eq. (15.5.12),* $P_{i\to f}(t) = tr\{\hat{U}^{\dagger(I)}(t,0)\hat{P}_f\hat{U}^{(I)}(t,0)\hat{P}_i\}$.

Exercise 15.5.5 *(a) Take the time-derivative of the transition probability, Eq. (15.5.11),* $P_{i\to f}(t) = \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle$, *using Eq. (15.3.9) for the time derivative of* $\hat{U}^{(I)}(t,0)$, *to show that*

$$\frac{\partial}{\partial t} P_{i\to f}(t) = \frac{-1}{i\hbar} \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) e^{\frac{it}{\hbar}\hat{H}_0} \hat{V}(t) e^{\frac{-it}{\hbar}\hat{H}_0} | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$+ \frac{1}{i\hbar} \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{it}{\hbar}\hat{H}_0} \hat{V}(t) e^{\frac{-it}{\hbar}\hat{H}_0} \hat{U}^{(I)}(t,0) | \chi_i \rangle.$$

(b) Recall that for a Hermitian operator, $\langle \chi_i | \hat{A} | \chi_i \rangle = \langle \chi_i | \hat{A}^\dagger | \chi_i \rangle^*$ *and show that*

$$\frac{\partial}{\partial t} P_{i\to f}(t) = \frac{2}{\hbar} \mathrm{Im} \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{it}{\hbar}\hat{H}_0} \hat{V}(t) e^{\frac{-it}{\hbar}\hat{H}_0} \hat{U}^{(I)}(t,0) | \chi_i \rangle.$$

Solution 15.5.5

(a)

Starting from the transition probability to an $\hat{H}_0$*-eigenstate,* $\hat{H}_0 | \chi_f \rangle = \varepsilon_f | \chi_f \rangle$,

$$P_{i\to f}(t) = \left| \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle \right|^2 = \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle,$$

the time-derivative reads

$$\frac{d}{dt} P_{i\to f}(t) = \langle \chi_i | \left[\frac{d}{dt} \hat{U}^{\dagger(I)}(t,0) \right] | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$+ \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \left[\frac{d}{dt} \hat{U}^{(I)}(t,0) \right] | \chi_i \rangle.$$

Using the equation for the time-evolution of $\hat{U}^{(I)}(t,0)$ *(Eq. (15.3.9)), we obtain*

$$\frac{d}{dt}P_{i\to f}(t) = \langle \chi_i | \frac{-1}{i\hbar}\hat{U}^{\dagger(I)}(t,0)\hat{H}^{(I)}(t) | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$+ \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \frac{1}{i\hbar}\hat{H}^{(I)}(t)\hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$= \frac{-1}{i\hbar}\langle \chi_i | \hat{U}^{\dagger(I)}(t,0) e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0 t} | \chi_f \rangle \langle \chi_f | \hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$+ \frac{1}{i\hbar}\langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0 t}\hat{U}^{(I)}(t,0) | \chi_i \rangle \ .$$

(b)

Using $\langle \chi_i | \hat{A} | \chi_i \rangle = \langle \chi_i | \hat{A}^\dagger | \chi_i \rangle^*$*, the result of (a) can be rewritten as*

$$\frac{d}{dt}P_{i\to f}(t) = \left[\frac{1}{i\hbar}\langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0 t}\hat{U}^{(I)}(t,0) | \chi_i \rangle \right]^*$$
$$+ \frac{1}{i\hbar}\langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0 t}\hat{U}^{(I)}(t,0) | \chi_i \rangle$$
$$= 2\,\mathrm{Re}\left\{ \frac{1}{i\hbar}\langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0 t}\hat{U}^{(I)}(t,0) | \chi_i \rangle \right\}$$
$$= \frac{2}{\hbar}\,\mathrm{Im}\left\{ \langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}(t)e^{\frac{-i}{\hbar}\hat{H}_0 t}\hat{U}^{(I)}(t,0) | \chi_i \rangle \right\} \ .$$

Exercise 15.6.1 *Use the definition of the first-order propagator in the interaction representation,* $g^{(1)}_{f,i}(t) = \frac{-i}{\hbar}\int_0^t dt_0 \langle \chi_f | \hat{V}_I(t_0) | \chi_i \rangle$ *(Eqs. (15.6.6, 15.6.8)), and Eq. (15.6.2) for the states* $|\chi_i\rangle$ *and* $|\chi_f\rangle$*, to show that* $g^{(1)}_{f,i}(t) = \frac{-i}{\hbar}\int_0^t d\tau \langle \chi_f | e^{\frac{i}{\hbar}\varepsilon_f \tau}\hat{V}(\tau)e^{\frac{-i}{\hbar}\varepsilon_i \tau} | \chi_i \rangle$.

Solution 15.6.1

Starting from $g_{f,i}^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt_0 \left\langle \chi_f \left| \hat{V}_I(t_0) \right| \chi_i \right\rangle$, *and using the definition of the interaction,* $\hat{V}_I(\tau) \equiv e^{\frac{i}{\hbar}\hat{H}_0\tau}\hat{V}(\tau)e^{\frac{-i}{\hbar}\hat{H}_0\tau}$ *(Eq. (15.6.6)), we obtain* $g_{f,i}^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt_0 \left\langle \chi_f \left| e^{\frac{i}{\hbar}\hat{H}_0 t_0}\hat{V}(t_0)e^{\frac{-i}{\hbar}\hat{H}_0 t_0} \right| \chi_i \right\rangle$. *For initial and final states that are eigenstates of* $\hat{H}_0$ *(Eq. (15.6.2)), we therefore obtain*

$$g_{f,i}^{(1)}(t) = \frac{-i}{\hbar}\int_0^t d\tau \left\langle \chi_f \left| e^{\frac{i}{\hbar}\varepsilon_f\tau}\hat{V}(\tau)e^{\frac{-i}{\hbar}\varepsilon_i\tau} \right| \chi_i \right\rangle .$$

Exercise 15.6.2 *Use the orthogonality of the initial and final states (Eq. (15.6.3)) and the result of Ex. 15.6.1 to derive the first order transition probability,* $P_{i\to f}^{(1)}(t)$ *(Eq. 15.6.10), from Eq. (15.6.9).*

Solution 15.6.2

For orthogonal initial and final states, we have $P_{i\to f}^{(1)}(t) \cong \left|\lambda g_{f,i}^{(1)}(t)\right|^2$ *(Eq. (15.6.9)). Using* $g_{f,i}^{(1)}(t) = \frac{-i}{\hbar}\int_0^t d\tau \left\langle \chi_f \left| e^{\frac{i}{\hbar}\varepsilon_f\tau}\hat{V}(\tau)e^{\frac{-i}{\hbar}\varepsilon_i\tau} \right| \chi_i \right\rangle$ *(Ex. 15.6.1), we obtain Eq. (15.6.10),*

$$P_{i\to f}^{(1)}(t) = \left| \frac{-i\lambda}{\hbar}\int_0^t d\tau \left\langle \chi_f \left| e^{\frac{i}{\hbar}\varepsilon_f\tau}\hat{V}(\tau)e^{\frac{-i}{\hbar}\varepsilon_i\tau} \right| \chi_i \right\rangle \right|^2 = \frac{\lambda^2}{\hbar^2}\left| \int_0^t d\tau e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)\tau} \left\langle \chi_f \left| \hat{V}(\tau) \right| \chi_i \right\rangle \right|^2 .$$

Exercise 15.6.3 *Follow the steps given here as an alternative derivation of the expression for the first-order transition probability, Eq. (15.6.10): Any solution to the time-dependent Schrödinger equation can be expanded at any time in the basis of the eigenstates of the zero order Hamiltonian,* $\left\{ \hat{H}_0 \left|\varphi_n\right\rangle = \varepsilon_n \left|\varphi_n\right\rangle \right\}$, *namely* $\left|\psi(t)\right\rangle = \sum_n b_n(t)\left|\varphi_n\right\rangle \equiv \sum_n a_n(t)\mathrm{e}^{\frac{-i\varepsilon_n t}{\hbar}}\left|\varphi_n\right\rangle$, *where the projection of the system state on any eigenstate,* $\left|\varphi_m\right\rangle$, *is given as* $P_m(t) = \left|\left\langle \varphi_m \middle| \psi(t)\right\rangle\right|^2 = \left|b_m(t)\right|^2 = \left|a_m(t)\right|^2$. *Show that substitution of this expansion in the time-dependent Schrödinger equation,* $i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}\left|\psi(t)\right\rangle$, *yields coupled equations for the expansion coefficients,* $\{a_n(t)\}$*:* $i\hbar\sum_n \dot{a}_n(t)\mathrm{e}^{\frac{-i\varepsilon_n t}{\hbar}}\left|\varphi_n\right\rangle = \lambda\sum_n \hat{V}(t)a_n(t)\mathrm{e}^{\frac{-i\varepsilon_n t}{\hbar}}\left|\varphi_n\right\rangle$. *Project this equation on the bra state* $\left\langle \varphi_m \right|$, *multiply* *by* $e^{\frac{i\varepsilon_m t}{\hbar}}$, *and integrate over time from* 0 *to* t, *to obtain* $a_m(t) = a_m(0) + \frac{\lambda}{i\hbar}\sum_n \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_n \rangle e^{\frac{-i(\varepsilon_n - \varepsilon_m)t'}{\hbar}} a_n(t')$. *Since this result means that* $a_n(t') = a_n(0) + o(\lambda)$ *, the expression for the probability amplitude,* $a_m(t)$*, to first order in* λ*, reads,* $a_m(t) \cong a_m(0) + \frac{\lambda}{i\hbar}\sum_n \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_n \rangle e^{\frac{-i(\varepsilon_n - \varepsilon_m)t'}{\hbar}} a_n(0)$. *Choose the initial state as the* i *th eigenstate of* $\hat{H}_0$*, namely* $a_m(0) = \delta_{m,i}$. *Substitute this condition in the approximated expression for the probability amplitude and show that the probability to find the system in any other eigenstate (*$m \neq i$ *) at time* t *reads* $P_{i\to m}(t) = | a_m(t) |^2 \cong \frac{\lambda^2}{\hbar^2} | \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_i \rangle e^{\frac{-i(\varepsilon_i - \varepsilon_m)t'}{\hbar}} |^2$, *which reproduces the result, Eq. (15.6.10).*

Solution 15.6.3

Using a time-dependent expansion of the state vector $|\psi(t)\rangle$ *in terms of the zero Hamiltonian eigenstates,* $|\psi(t)\rangle = \sum_n b_n(t)|\varphi_n\rangle \equiv \sum_n a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle$, *where* $\{\hat{H}_0|\varphi_n\rangle = \varepsilon_n|\varphi_n\rangle\}$, *and* $b_n(t) \equiv a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}}$*, we obtain*

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\sum_n a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle = \sum_n \varepsilon_n a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle + i\hbar\sum_n \dot{a}_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle,$$

and

$$[\hat{H}_0 + \lambda\hat{V}(t)]|\psi(t)\rangle = [\hat{H}_0 + \lambda\hat{V}(t)]\sum_n a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle$$

$$= \sum_n \varepsilon_n a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle + \lambda\sum_n \hat{V}(t) a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle \ .$$

For $|\psi(t)\rangle$ *to be a solution of the Schrodinger equation,* $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$, *the following condition must therefore be satisfied,* $i\hbar\sum_n \dot{a}_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle = \lambda\sum_n \hat{V}(t) a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle$.

To obtain the expression for any of the coefficients, e.g., $a_m(t)$*, we project* $|\psi(t)\rangle$ *on the respective* $\hat{H}_0$*-eigenstate,* $|\varphi_m\rangle$*, and use the orthonormality of the set* $\{|\varphi_n\rangle\}$*,*

$$i\hbar \dot{a}_m(t) e^{\frac{-i\varepsilon_m t}{\hbar}} = \lambda \sum_n \langle \varphi_m | \hat{V}(t) a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} | \varphi_n \rangle$$
$$\Rightarrow \dot{a}_m(t) = \frac{\lambda}{i\hbar} \sum_n \langle \varphi_m | \hat{V}(t) | \varphi_n \rangle a_n(t) e^{\frac{-i(\varepsilon_n - \varepsilon_m)t}{\hbar}}$$
$$\Rightarrow a_m(t) = a_m(0) + \frac{\lambda}{i\hbar} \sum_n \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_n \rangle e^{\frac{-i(\varepsilon_n - \varepsilon_m)t'}{\hbar}} a_n(t') \ .$$

Since this result applies to any $a_m(t)$*, we can rewrite is also for* $a_n(t')$ *under the time-integral:*

$$a_n(t') = a_n(0) + \frac{\lambda}{i\hbar} \sum_{n'} \int_0^{t'} dt'' \langle \varphi_m | \hat{V}(t'') | \varphi_{n'} \rangle e^{\frac{-i(\varepsilon_{n'} - \varepsilon_n)t''}{\hbar}} a_n(t'') = a_n(0) + o(\lambda) \, .$$

Substitution in the equation for $a_m(t)$*, and keeping only terms up to first order in* λ*, we obtain*

$$a_m(t) = a_m(0) + \frac{\lambda}{i\hbar} \sum_n \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_n \rangle e^{\frac{-i(\varepsilon_n - \varepsilon_m)t'}{\hbar}} a_n(0) + o(\lambda^2) \, .$$

Associating the initial state with the i *th eigenstate of* $\hat{H}_0$*, namely* $|\psi(0)\rangle = |\varphi_i\rangle = \sum_n \delta_{n,i} |\varphi_n\rangle$*, or* $a_n(0) = \delta_{n,i}$*, we obtain*

$$a_m(t) \cong a_m(0) + \frac{\lambda}{i\hbar} \sum_n \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_n \rangle e^{\frac{-i(\varepsilon_n - \varepsilon_m)t'}{\hbar}} \delta_{n,i} = a_m(0) + \frac{\lambda}{i\hbar} \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_i \rangle e^{\frac{-i(\varepsilon_i - \varepsilon_m)t'}{\hbar}} \, .$$

Recalling that, $|\psi(t)\rangle = \sum_n b_n(t) |\varphi_n\rangle \equiv \sum_n a_n(t) e^{\frac{-i\varepsilon_n t}{\hbar}} |\varphi_n\rangle$*, the probability of finding the system at a state* $|\varphi_m\rangle$ *at time* t *reads:* $|\langle \varphi_m | \psi(t) \rangle|^2 = |a_m(t)|^2$*. Using the expression for* $a_m(t)$ *to first order in* λ *, we obtain for* $m \neq i$ *(namely, for a final state that is orthogonal to the initial state such that* $a_m(0) = 0$ *),*

$$P_{i \to m}(t) = |a_m(t)|^2 \cong \frac{\lambda^2}{\hbar^2} \left| \int_0^t dt' \langle \varphi_m | \hat{V}(t') | \varphi_i \rangle e^{\frac{-i(\varepsilon_i - \varepsilon_m)t'}{\hbar}} \right|^2 ,$$

which reproduces Eq. (15.6.10).

Exercise 15.6.4 *Prove that in the short time limit ($t \to 0$), the exact transition probability increases quadratically in time: Start from the Dyson expansion (15.6.5, 15.6.6) of the probability amplitude for $|\chi_i\rangle \neq |\chi_f\rangle$ (where, $V_{m,n}(\tau) \equiv \langle \chi_m | \hat{V}(\tau) | \chi_n \rangle$),*

$$g_{f,i}(\lambda,t) = \frac{-i\lambda}{\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f-\varepsilon_i)t'}{\hbar}} V_{f,i}(t') + \sum_j \left(\frac{-i\lambda}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' e^{\frac{i(\varepsilon_f-\varepsilon_j)t'}{\hbar}} V_{f,j}(t') e^{\frac{i(\varepsilon_j-\varepsilon_i)t''}{\hbar}} V_{j,i}(t'') + \dots .$$

Expand the exponential functions and the interaction to their lowest order in time, for example,

$e^{\frac{i(\varepsilon_f-\varepsilon_i)t'}{\hbar}} \approx \left[1 + \frac{i(\varepsilon_f - \varepsilon_i)t'}{\hbar}\right]$ *and* $V_{f,i}(t') \approx \left[V_{f,i}(0) + t'V'_{f,i}(0)\right]$, *and show that*

$\lim_{t\to 0}[g_{f,i}(\lambda,t)] = \frac{-i\lambda}{\hbar} V_{f,i}(0)t + o(t^2)$ *and therefore* $\lim_{t\to 0} P_{i\to f}(t) = \frac{\lambda^2}{\hbar^2}\left|\langle \chi_f | \hat{V}(0) | \chi_i \rangle\right|^2 t^2$.

Solution 15.6.4

Considering the exact Dyson expansion for the propagator (for $|\chi_i\rangle \neq |\chi_f\rangle$),

$$g_{f,i}(\lambda,t) = \frac{-i\lambda}{\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f-\varepsilon_i)t'}{\hbar}} V_{f,i}(t') + \sum_j \left(\frac{-i\lambda}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' e^{\frac{i(\varepsilon_f-\varepsilon_j)t'}{\hbar}} V_{f,j}(t') e^{\frac{i(\varepsilon_j-\varepsilon_i)t''}{\hbar}} V_{j,i}(t'') + \dots ,$$

we are interested in the short time limit, where $t' << \frac{\hbar}{|\varepsilon_f - \varepsilon_i|}$ *and* $V_{f,i}(t') \approx V_{f,i}(0) + t' \left.\frac{dV_{f,i}(t)}{dt}\right|_{t=0}$.

Expanding the exponential functions and the interaction to their lowest order in time: $e^{\frac{i(\varepsilon_f-\varepsilon_i)t'}{\hbar}} \approx \left[1 + \frac{i(\varepsilon_f - \varepsilon_i)t'}{\hbar}\right]$ *and* $V_{f,i}(t') \approx \left[V_{f,i}(0) + t'V'_{f,i}(0)\right]$, *we obtain for the first term,*

$$\frac{-i\lambda}{\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f-\varepsilon_i)t'}{\hbar}} V_{f,i}(t') \approx \frac{-i\lambda}{\hbar}\int_0^t dt' \left[1 + \frac{i(\varepsilon_f - \varepsilon_i)t'}{\hbar}\right]\left[V_{f,i}(0) + t'V'_{f,i}(0)\right] = \frac{-i\lambda t}{\hbar} V_{f,i}(0) + o(t^2) .$$

Using this result in the second term, we obtain

$$\sum_j \left(\frac{-i\lambda}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' e^{\frac{i(\varepsilon_f-\varepsilon_j)t'}{\hbar}} V_{f,j}(t') e^{\frac{i(\varepsilon_j-\varepsilon_i)t''}{\hbar}} V_{j,i}(t'')$$
$$\approx \sum_j \left(\frac{-i\lambda}{\hbar}\right)^2 \int_0^t dt' e^{\frac{i(\varepsilon_f-\varepsilon_j)t'}{\hbar}} V_{f,j}(t')\left[V_{j,i}(0)t' + o((t')^2)\right]$$
$$\approx \sum_j \left(\frac{-i\lambda}{\hbar}\right)^2 \int_0^t dt' \left[1+\frac{i(\varepsilon_f-\varepsilon_i)t'}{\hbar}\right]\left[V_{f,j}(0)+t'V'_{f,j}(0)\right]\left[V_{j,i}(0)t'+o((t')^2)\right] = o(t^2).$$

Similarly, the higher orders in the Dyson expansion are associated with $o(t^3)$, $o(t^4)$, *and so forth. We can therefore conclude that in the short time limit,* $g_{f,i}(\lambda,t) \approx \frac{-i\lambda}{\hbar} V_{f,i}(0)\cdot t + o(t^2)$. *Consequently, the transition probability (for* $|\chi_i\rangle \neq |\chi_f\rangle$ *) in this limit is quadratic in time,* $P_{i\to f}(t) = |g_{f,i}(\lambda,t)|^2 \approx \frac{\lambda^2}{\hbar^2}\left|\langle\chi_f|\hat{V}(0)|\chi_i\rangle\right|^2 t^2$.

Exercise 15.6.5 *Obtain Eq. (15.6.14) for the transition probability amplitude from the general expression, Eq. (15.6.10), in the case where the interaction operator is constant through the propagation time,* $\hat{V}(t)\big|_{t\geq 0} \mapsto \hat{V}$.

Solution 15.6.5

Considering a time-independent perturbation, $\hat{V}(t)\big|_{t\geq 0} \mapsto \hat{V}$, *the general expression (Eq. (15.6.10)) reads* $P^{(1)}_{i\to f}(t) = \frac{\lambda^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t'} \langle\chi_f|\hat{V}|\chi_i\rangle\right|^2$. *Integrating over time, we obtain Eq. (15.6.14),*

$$P_{i\to f}^{(1)}(t)=\frac{\lambda^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t'}\left\langle\chi_f\left|\hat{V}\right|\chi_i\right\rangle\right|^2$$

$$=\frac{\lambda^2\left|\left\langle\chi_f\left|\hat{V}\right|\chi_i\right\rangle\right|^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t'}\right|^2$$

$$=\frac{\lambda^2\left|\left\langle\chi_f\left|\hat{V}\right|\chi_i\right\rangle\right|^2}{\hbar^2}\left|\frac{e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t}-1}{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)}\right|^2=\frac{\lambda^2\left|\left\langle\chi_f\left|\hat{V}\right|\chi_i\right\rangle\right|^2}{\hbar^2}\left|e^{\frac{i}{2\hbar}(\varepsilon_f-\varepsilon_i)t}\right|^2\left|\frac{e^{\frac{i}{2\hbar}(\varepsilon_f-\varepsilon_i)t}-e^{\frac{-i}{2\hbar}(\varepsilon_f-\varepsilon_i)t}}{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)}\right|^2$$

$$=\lambda^2\left|\left\langle\chi_f\left|\hat{V}\right|\chi_i\right\rangle\right|^2\left|\frac{2\sin[(\varepsilon_f-\varepsilon_i)t/(2\hbar)]}{(\varepsilon_f-\varepsilon_i)}\right|^2$$

$$=\frac{4\lambda^2\left|\left\langle\chi_f\left|\hat{V}\right|\chi_i\right\rangle\right|^2}{\left|\varepsilon_f-\varepsilon_i\right|^2}\sin^2\left(\frac{(\varepsilon_f-\varepsilon_i)t}{2\hbar}\right)\ .$$

Exercise 15.6.6 *Show that for times much shorter than the oscillation period, both the exact and the approximate expressions for the TLS transition probability (Eq. (15.6.19), and Eq. (15.6.20), respectively) converge to quadratic time-dependence of Eq. (15.6.21).*

Solution 15.6.6

For the exact expression (Eq. (15.6.19)), we have (recalling that $\frac{\sin(x)}{x}\xrightarrow[x<<1]{}1$*)*

$$P_{1\to2}(t)=\frac{4|\gamma|^2}{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}\sin^2\left(\frac{t\sqrt{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}}{2\hbar}\right)$$

$$=\frac{4|\gamma|^2\,t^2\hbar^2}{(\varepsilon_1-\varepsilon_2)^2t^2\hbar^2+4|\gamma|^2\,t^2\hbar^2}\sin^2\left(\frac{t\sqrt{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}}{2\hbar}\right)$$

$$=\frac{|\gamma|^2\,t^2}{\hbar^2}\left[\frac{\sin\left(\frac{t\sqrt{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}}{2\hbar}\right)}{\frac{t\sqrt{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}}{2\hbar}}\right]^2\xrightarrow[t<<2\hbar/\sqrt{(\varepsilon_1-\varepsilon_2)^2+4|\gamma|^2}]{}\frac{|\gamma|^2\,t^2}{\hbar^2}\ .$$

Similarly, for the approximate expression (Eq. (15.6.20)), we have

$$P_{1\to2}^{(1)}(t) = \frac{4|\gamma|^2}{|\varepsilon_2-\varepsilon_1|^2}\sin^2(\frac{(\varepsilon_2-\varepsilon_1)t}{2\hbar})$$
$$= \frac{4|\gamma|^2\hbar^2t^2}{|\varepsilon_2-\varepsilon_1|^2\hbar^2t^2}\sin^2(\frac{(\varepsilon_2-\varepsilon_1)t}{2\hbar}) \qquad ,$$
$$= \frac{|\gamma|^2t^2}{\hbar^2}\left[\frac{\sin(\frac{(\varepsilon_2-\varepsilon_1)t}{2\hbar})}{\frac{(\varepsilon_2-\varepsilon_1)t}{2\hbar}}\right]^2 \xrightarrow[t<<2\hbar/(\varepsilon_1-\varepsilon_2)]{} \frac{|\gamma|^2t^2}{\hbar^2}$$

where Eq. (15.6.21) is reproduced in both cases.

Exercise 15.6.7 *The approximate and the exact expressions for the TLS transition probability are given by Eqs. (15.6.20) and (15.6.19), respectively. (a) Show that* $P_{1\to2}^{(1)}(t) = \frac{1}{2}(\alpha^2-1)\left[1-\cos(\omega t)\right]$ and $P_{1\to2}(t) = \frac{\alpha^2-1}{2\alpha^2}[1-\cos(\omega\alpha t)]$, *where* $\omega = \frac{|\varepsilon_1-\varepsilon_2|}{\hbar}$ *and* $\alpha \equiv \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2}$ *.(b) The oscillation frequencies of the approximate and the exact expressions are* ω *and* $\omega\alpha$ *, respectively. At a certain time,* t_c *, the approximate solution completes* n *oscillation periods, whereas the exact solution completes* $n+1$ *periods. Show that* $t_c = \frac{2\pi}{\omega\alpha-\omega}$ *.*

Solution 15.6.7

(a)

Using the definitions, $\omega \equiv \frac{|\varepsilon_1-\varepsilon_2|}{\hbar}$, $\alpha \equiv \sqrt{1+4|\gamma|^2/(\varepsilon_1-\varepsilon_2)^2}$ *, and the identity,* $\sin^2(x) = \frac{1-\cos(2x)}{2}$ *, we readily obtain*

$$P_{1\to2}^{(1)}(t) = \frac{4|\gamma|^2}{(\varepsilon_1-\varepsilon_2)^2}\sin^2(t\frac{(\varepsilon_1-\varepsilon_2)}{2\hbar}) \equiv \frac{1}{2}(\alpha^2-1)\left[1-\cos(\omega t)\right],$$

and

$$P_{1\to2}(t) = \frac{\frac{4|\gamma|^2}{(\varepsilon_1-\varepsilon_2)^2}}{1+\frac{4|\gamma|^2}{(\varepsilon_1-\varepsilon_2)^2}}\sin^2(t\frac{(\varepsilon_1-\varepsilon_2)}{2\hbar}\sqrt{1+\frac{4|\gamma|^2}{(\varepsilon_1-\varepsilon_2)^2}}) \equiv \frac{\alpha^2-1}{2\alpha^2}[1-\cos(\omega\alpha t)].$$

(b)

The time for completing n *periods at a frequency* ω *is* $\frac{2\pi}{\omega}n$. *Similarly, the time for completing* $n+1$ *periods at a frequency* $\alpha\omega$ *is* $\frac{2\pi}{\alpha\omega}(n+1)$. *For these to coincide at a certain time* t_c, *we must have,*

$$t_c = \frac{2\pi}{\alpha\omega}(n+1) = \frac{2\pi}{\omega}n \Rightarrow \frac{2\pi}{\alpha\omega} = 2\pi n\left(\frac{1}{\omega} - \frac{1}{\alpha\omega}\right) \Rightarrow n = \frac{\frac{1}{\alpha\omega}}{\left(\frac{1}{\omega} - \frac{1}{\alpha\omega}\right)} = \frac{1}{\alpha - 1}.$$

Hence, $t_c = \frac{2\pi}{\omega(\alpha-1)}$, *or, in terms of the TLS parameters,*

$$t_c = \frac{h}{|\varepsilon_1 - \varepsilon_2|(\alpha - 1)} = \frac{h}{\sqrt{(\varepsilon_1-\varepsilon_2)^2 + 4|\gamma|^2} - |\varepsilon_1 - \varepsilon_2|}.$$

Exercise 15.6.8 *Show that for an interaction term,* $\hat{V} = \hat{\mu}\sin(\Omega t)$, *the transition probability to first order in* λ *(Eq. (15.6.10)) reads as Eq. (15.6.24).*

Solution 15.6.8

Starting from the general expression (Eq. (15.6.10)) with $\hat{V}(t) = \hat{\mu}\sin(\Omega t)$, *we obtain*

$$P^{(1)}_{i\to f}(t) = \frac{\lambda^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)t'} \left\langle \chi_f \middle| \hat{V}(t') \middle| \chi_i \right\rangle\right|^2$$

$$= \frac{\lambda^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)t'} \sin(\Omega t')\left\langle \chi_f \middle| \hat{\mu} \middle| \chi_i \right\rangle\right|^2$$

$$= \frac{\lambda^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)t'} \frac{e^{i\Omega t'} - e^{-i\Omega t'}}{2i}\left\langle \chi_f \middle| \hat{\mu} \middle| \chi_i \right\rangle\right|^2$$

$$= \frac{\lambda^2\left|\left\langle \chi_f \middle| \hat{\mu} \middle| \chi_i \right\rangle\right|^2}{4\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)t'} \left(e^{i\Omega t'} - e^{-i\Omega t'}\right)\right|^2 .$$

Introducing the definition, $\omega_{f,i} \equiv \frac{\varepsilon_f - \varepsilon_i}{\hbar}$, *we obtain Eq. (15.6.24),*

$$P^{(1)}_{i\to f}(t) = \frac{\lambda^2 \left|\left\langle \chi_f \left| \hat{\mu} \right| \chi_i \right\rangle\right|^2}{4\hbar^2} \left| \int_0^t dt' e^{i\omega_{f,i}t'} \left(e^{i\Omega t'} - e^{-i\Omega t'} \right) \right|^2$$

$$= \frac{\lambda^2 \left|\left\langle \chi_f \left| \hat{\mu} \right| \chi_i \right\rangle\right|^2}{4\hbar^2} \left| \int_0^t dt' \left(e^{i(\omega_{f,i}+\Omega)t'} - e^{i(\omega_{f,i}-\Omega)t'} \right) \right|^2$$

$$= \frac{\lambda^2 \left|\left\langle \chi_f \left| \hat{\mu} \right| \chi_i \right\rangle\right|^2}{4\hbar^2} \left| \frac{e^{i(\omega_{f,i}+\Omega)t} - 1}{\omega_{f,i} + \Omega} - \frac{e^{i(\omega_{f,i}-\Omega)t} - 1}{\omega_{f,i} - \Omega} \right|^2 .$$

Exercise 15.6.9 *Derive Eq. (15.6.26) from Eq. (15.6.24) for* $|\Delta| << \Omega$.

Solution 15.6.9

In the case of energy absorption by the system we have, $\omega_{f,i} \equiv \frac{\varepsilon_f - \varepsilon_i}{\hbar} > 0$, *where* $\Delta = \Omega - \omega_{f,i}$. *In this case, the resonance (small detuning) condition,* $|\Delta| << \Omega$, *means that* $|\Omega - \omega_{f,i}| << \Omega$, *and hence* $|\Omega - \omega_{f,i}| << |\Omega + \omega_{f,i}|$.

In the case of energy emission by the system we have, $\omega_{f,i} \equiv \frac{\varepsilon_f - \varepsilon_i}{\hbar} < 0$, *where* $\Delta = \Omega + \omega_{f,i}$. *In this case, the resonance (small detuning) condition,* $|\Delta| << \Omega$, *means that* $|\Omega + \omega_{f,i}| << \Omega$, *and hence* $|\Omega + \omega_{f,i}| << |\Omega - \omega_{f,i}|$.

Considering now the first order transition probability (Eq. (15.6.24)),

$$P^{(1)}_{i\to f}(t) = \frac{\lambda^2 \left|\left\langle \chi_f \left| \hat{\mu} \right| \chi_i \right\rangle\right|^2}{4\hbar^2} \left| \frac{e^{i(\omega_{f,i}+\Omega)t} - 1}{\omega_{f,i} + \Omega} - \frac{e^{i(\omega_{f,i}-\Omega)t} - 1}{\omega_{f,i} - \Omega} \right|^2 ,$$

we notice that for small detuning one of the two denominators is much smaller in absolute value than the other: $|\Omega - \omega_{f,i}| << |\Omega + \omega_{f,i}|$ *for resonant absorption, and* $|\Omega + \omega_{f,i}| << |\Omega - \omega_{f,i}|$ *for resonant emission. Since the numerators are similarly bounded, the term with the smaller denominator dominates, and we can neglect the other one. This is often referred to as the "rotating wave approximation", which yields*

$$P^{(1)}_{i\to f}(t) \cong \frac{\lambda^2 \left|\left\langle \chi_f \left| \hat{\mu} \right| \chi_i \right\rangle\right|^2}{4\hbar^2} \left| \frac{e^{i(\omega_{f,i}\pm\Omega)t} - 1}{\omega_{f,i} \pm \Omega} \right|^2 ,$$

where the plus and minus signs correspond to emission and absorption probabilities, respectively.

Introducing the detuning parameter (Eq. (15.6.27)), $\Delta \equiv \Omega - |\omega_{f,i}|$, *we obtain in both cases Eq. (15.6.26),*

$$P^{(1)}_{i\to f}(t) \cong \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2}{4\hbar^2} \left| \frac{e^{i\Delta t} - 1}{\Delta} \right|^2 = \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2}{\hbar^2} \left| \frac{e^{i\Delta t/2} - e^{-i\Delta t/2}}{2i\Delta} \right|^2$$

$$= \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2}{\hbar^2} \left| \frac{\sin(\Delta t/2)}{\Delta} \right|^2 = \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2 t^2}{4\hbar^2} \left| \frac{\sin(\Delta t/2)}{\Delta t/2} \right|^2 .$$

Exercise 15.6.10 *Derive Eq. (15.6.28) for the transition rate by taking the time-derivative of the transition probability as given in Eq. (15.6.26).*

Solution 15.6.10

Starting from Eq. (15.6.26), $P^{(1)}_{i\to f}(t) \cong \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2 t^2}{4\hbar^2} \left[\frac{\sin[\Delta t/2]}{\Delta t/2} \right]^2$ *, the transition rate reads*

$$\frac{d}{dt} P^{(1)}_{i\to f}(t) = \frac{d}{dt} \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2}{\hbar^2} \left[\frac{\sin[\Delta t/2]}{\Delta} \right]^2$$

$$= \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2}{\hbar^2 \Delta^2} 2\sin[\Delta t/2]\cos[\Delta t/2] \frac{\Delta}{2} = \frac{\lambda^2 |\langle \chi_f | \hat{\mu} | \chi_i \rangle|^2}{\hbar^2 2\Delta} \sin[\Delta t] \quad .$$

16 Incoherent States

Exercise 16.1.1 *(a) A mixed state corresponds to an ensemble of non-interacting spin-half particles, of which half are in a spin state* $|\alpha\rangle$*, and the other half in a spin state* $|\beta\rangle$*, where,* $w_\alpha = w_\beta = 0.5$*. Use Eqs. (13.1.9, 13.1.10) to compute the expectation value of the three different components of the single particle spin vector in this state,* $S_i = w_\alpha \langle\alpha|\hat{S}_i|\alpha\rangle + w_\beta \langle\beta|\hat{S}_i|\beta\rangle$ $(i \in x, y, z)$*, and show that the spin vector orientation in this state is random,* $S_x = S_y = S_z = 0$*. (b) Repeat the calculation of the spin vector components for a pure state in which all the particles are associated with a superposition state,* $|\Psi\rangle = \frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle$*. Show that in this case* $S_y = S_z = 0$*,* $S_x = \hbar/2$*, namely, the spin is polarized along the* x *axis. (c) Repeat the calculation of the spin vector components for a pure state in which all the particles are associated with another superposition state,* $|\Psi\rangle = \frac{1}{\sqrt{2}}|\alpha\rangle + i\frac{1}{\sqrt{2}}|\beta\rangle$*. Show that in this case* $S_x = S_z = 0$*,* $S_y = \hbar/2$*, namely, the spin is polarized along the* y *axis.*

Solution 16.1.1

Given: $\hat{S}_z|\alpha\rangle = \hbar\frac{1}{2}|\alpha\rangle$; $\hat{S}_z|\beta\rangle = -\hbar\frac{1}{2}|\beta\rangle$; $\hat{S}_x|\alpha\rangle = \frac{\hbar}{2}|\beta\rangle$; $\hat{S}_x|\beta\rangle = \frac{\hbar}{2}|\alpha\rangle$; $\hat{S}_y|\alpha\rangle = i\frac{\hbar}{2}|\beta\rangle$; $\hat{S}_y|\beta\rangle = -i\frac{\hbar}{2}|\alpha\rangle$*, and the orthonormality of the spin states,* $\langle\beta|\beta\rangle = \langle\alpha|\alpha\rangle = 1$; $\langle\alpha|\beta\rangle = 0$*, we obtain*

(a)

For a mixed state with $w_\alpha = w_\beta = 1/2$*, the expectation values of the spin components read*

$$S_z = 0.5\langle\alpha|\hat{S}_z|\alpha\rangle + 0.5\langle\beta|\hat{S}_z|\beta\rangle = 0$$
$$S_x = 0.5\langle\alpha|\hat{S}_x|\alpha\rangle + 0.5\langle\beta|\hat{S}_x|\beta\rangle = 0$$
$$S_y = 0.5\langle\alpha|\hat{S}_y|\alpha\rangle + 0.5\langle\beta|\hat{S}_y|\beta\rangle = 0.$$

(b)

For the pure state, $|\Psi\rangle = \frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle$, *the expectation values read*

$$S_z = \frac{1}{2}\left(\langle\alpha| + \langle\beta|\right)\hat{S}_z\left(|\alpha\rangle + |\beta\rangle\right) = 0$$

$$S_x = \frac{1}{2}\left(\langle\alpha| + \langle\beta|\right)\hat{S}_x\left(|\alpha\rangle + |\beta\rangle\right) = \frac{1}{2}\left(\langle\alpha|\hat{S}_x|\beta\rangle + \langle\beta|\hat{S}_x|\alpha\rangle\right) = \frac{\hbar}{2}$$

$$S_y = \frac{1}{2}\left(\langle\alpha| + \langle\beta|\right)\hat{S}_y\left(|\alpha\rangle + |\beta\rangle\right) = \frac{1}{2}\left(\langle\alpha|\hat{S}_y|\beta\rangle + \langle\beta|\hat{S}_y|\alpha\rangle\right) = 0\,.$$

(c)

For the pure state, $|\Psi\rangle = \frac{1}{\sqrt{2}}|\alpha\rangle + i\frac{1}{\sqrt{2}}|\beta\rangle$, *the expectation values read*

$$S_z = \frac{1}{2}\left(\langle\alpha| - i\langle\beta|\right)\hat{S}_z\left(|\alpha\rangle + i|\beta\rangle\right) = 0$$

$$S_x = \frac{1}{2}\left(\langle\alpha| - i\langle\beta|\right)\hat{S}_x\left(|\alpha\rangle + i|\beta\rangle\right) = \frac{1}{2}\left(i\langle\alpha|\hat{S}_x|\beta\rangle - i\langle\beta|\hat{S}_x|\alpha\rangle\right) = 0$$

$$S_y = \frac{1}{2}\left(\langle\alpha| - i\langle\beta|\right)\hat{S}_y\left(|\alpha\rangle + i|\beta\rangle\right) = \frac{1}{2}\left(i\langle\alpha|\hat{S}_y|\beta\rangle - i\langle\beta|\hat{S}_y|\alpha\rangle\right) = \frac{\hbar}{2}.$$

Exercise 16.2.1 *Introduce the identity operator,* $\hat{I} = \sum_n |\varphi_n\rangle\langle\varphi_n|$, *into the general definition of a measurable quantity (Eq. (16.1.3)), and use the definition of the trace of an operator Eq. (15.5.3), to show that* $\sum_i w_i \langle\psi_i(t)|\hat{O}|\psi_i(t)\rangle = tr\{\sum_i w_i |\psi_i(t)\rangle\langle\psi_i(t)|\hat{O}\} = tr\{\hat{\rho}(t)\hat{O}\}$.

Solution 16.2.1

Starting from Eq. (16.1.3), we obtain

$$\sum_i w_i \langle\psi_i(t)|\hat{O}|\psi_i(t)\rangle = \sum_i w_i \langle\psi_i(t)|\hat{O}\sum_n |\varphi_n\rangle\langle\varphi_n|\psi_i(t)\rangle$$
$$= \sum_n \sum_i w_i \langle\varphi_n|\psi_i(t)\rangle\langle\psi_i(t)|\hat{O}|\varphi_n\rangle$$
$$= \sum_n \langle\varphi_n|\sum_i w_i |\psi_i(t)\rangle\langle\psi_i(t)|\hat{O}|\varphi_n\rangle = tr\{\sum_i w_i |\psi_i(t)\rangle\langle\psi_i(t)|\hat{O}\} \quad .$$

Using the definition $\hat{\rho}(t) \equiv \sum_i w_i |\psi_i(t)\rangle\langle\psi_i(t)|$ *(Eq. (16.2.3)), we obtain*

$$\sum_i w_i \langle\psi_i(t)|\hat{O}|\psi_i(t)\rangle = tr\{\hat{\rho}(t)\hat{O}\}.$$

Exercise 16.2.2 *Use the generic structure of the density operator, Eq. (16.2.3), to show that its eigenvalues are non-negative; namely, if* $\hat{\rho}(t)|\phi\rangle = \eta|\phi\rangle$ *(where* $\langle\phi|\phi\rangle = 1$*), than,* $\eta \geq 0$.

Solution 16.2.2

Let $|\phi\rangle$ *be a normalized eigenstate of the density operator, associated with the eigenvalue,* η *, namely,* $\eta = \langle\phi|\hat{\rho}(t)|\phi\rangle$. *Using the definition of the density operator, Eqs. (16.2.3, 16.1.2), we obtain* $\eta = \langle\phi|\hat{\rho}(t)|\phi\rangle = \hat{\rho}(t) \equiv \sum_i w_i \langle\phi|\psi_i(t)\rangle\langle\psi_i(t)|\phi\rangle = \sum_i w_i |\langle\phi|\psi_i(t)\rangle|^2 \geq 0$.

Exercise 16.2.3 *In Ex. 16.1.1 we discussed the difference between two ensembles of spin-half particles. The first corresponded to a random spin orientation, where half of the particles are found in a spin state* $|\alpha\rangle$*, and the other half in a spin state* $|\beta\rangle$*. The other ensemble corresponded to spin polarization along the x direction, where all the particles are in a superposition state,* $|\Psi\rangle = \frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle$*. The density operators corresponding to the two ensembles are* $\hat{\rho}_R = 0.5|\alpha\rangle\langle\alpha| + 0.5|\beta\rangle\langle\beta|$ *and* $\hat{\rho}_P = |\Psi\rangle\langle\Psi|$*. (a) Show that the density matrices corresponding to these two ensembles in the basis of the two spin states are* $\boldsymbol{\rho}_R = \begin{bmatrix} 0.5 & 0 \\ 0 & 0.5 \end{bmatrix}$ *and* $\boldsymbol{\rho}_P = \begin{bmatrix} 0.5 & 0.5 \\ 0.5 & 0.5 \end{bmatrix}$*, respectively. (b) Change the basis from* $|\alpha\rangle$ *and* $|\beta\rangle$ *(*$\hat{S}_z$*-eigenstates) into the two eigenstates of* $\hat{S}_x$*, namely,* $\frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle$ *and* $\frac{1}{\sqrt{2}}|\alpha\rangle - \frac{1}{\sqrt{2}}|\beta\rangle$*. Show that the matrix representation of the random ensemble is invariant to the transformation, whereas the matrix representation of the pure state becomes diagonal in this basis,* $\boldsymbol{\rho}_P = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$.

Solution 16.2.3

(a)

The matrix elements of the density operators in the orthonormal set, $|\alpha\rangle$ *and* $|\beta\rangle$*, read*

$$\left.\begin{array}{l}\langle\alpha|\hat{\rho}_R|\alpha\rangle=\langle\alpha|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\alpha\rangle=0.5\\ \langle\beta|\hat{\rho}_R|\beta\rangle=\langle\beta|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\beta\rangle=0.5\\ \langle\alpha|\hat{\rho}_R|\beta\rangle=\langle\alpha|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\beta\rangle=0\\ \langle\beta|\hat{\rho}_R|\alpha\rangle=\langle\beta|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\alpha\rangle=0\end{array}\right\}\Rightarrow\boldsymbol{\rho}_R=\begin{bmatrix}0.5 & 0\\ 0 & 0.5\end{bmatrix},$$

$$\left.\begin{array}{l}\langle\alpha|\hat{\rho}_P|\alpha\rangle=\langle\alpha|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\alpha\rangle=0.5\\ \langle\beta|\hat{\rho}_P|\beta\rangle=\langle\beta|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\beta\rangle=0.5\\ \langle\alpha|\hat{\rho}_P|\beta\rangle=\langle\alpha|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\beta\rangle=0.5\\ \langle\beta|\hat{\rho}_P|\alpha\rangle=\langle\beta|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\alpha\rangle=0.5\end{array}\right\}\Rightarrow\boldsymbol{\rho}_P=\begin{bmatrix}0.5 & 0.5\\ 0.5 & 0.5\end{bmatrix}.$$

(b)

The matrix elements of the density operators in the orthonormal set, $|\psi_+\rangle=\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle$ *and* $|\psi_-\rangle=\frac{1}{\sqrt{2}}|\alpha\rangle-\frac{1}{\sqrt{2}}|\beta\rangle$*, read:*

$$\left.\begin{array}{l}\langle\psi_+|\hat{\rho}_R|\psi_+\rangle=\langle\psi_+|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\psi_+\rangle=0.5\\ \langle\psi_-|\hat{\rho}_R|\psi_-\rangle=\langle\psi_-|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\psi_-\rangle=0.5\\ \langle\psi_+|\hat{\rho}_R|\psi_-\rangle=\langle\psi_+|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\psi_-\rangle=0\\ \langle\psi_-|\hat{\rho}_R|\psi_+\rangle=\langle\psi_-|\big[0.5|\alpha\rangle\langle\alpha|+0.5|\beta\rangle\langle\beta|\big]|\psi_+\rangle=0\end{array}\right\}\Rightarrow\boldsymbol{\rho}_R=\begin{bmatrix}0.5 & 0\\ 0 & 0.5\end{bmatrix},$$

$$\left.\begin{array}{l}\langle\psi_+|\hat{\rho}_P|\psi_+\rangle=\langle\psi_+|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\psi_+\rangle=1\\ \langle\psi_-|\hat{\rho}_P|\psi_-\rangle=\langle\psi_-|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\psi_-\rangle=0\\ \langle\psi_+|\hat{\rho}_P|\psi_-\rangle=\langle\psi_+|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\psi_-\rangle=0\\ \langle\psi_-|\hat{\rho}_P|\psi_+\rangle=\langle\psi_-|\left(\frac{1}{\sqrt{2}}|\alpha\rangle+\frac{1}{\sqrt{2}}|\beta\rangle\right)\left(\frac{1}{\sqrt{2}}\langle\alpha|+\frac{1}{\sqrt{2}}\langle\beta|\right)|\psi_+\rangle=0\end{array}\right\}\Rightarrow\boldsymbol{\rho}_P=\begin{bmatrix}1 & 0\\ 0 & 0\end{bmatrix}.$$

(Notice that $\hat{\rho}_P = |\psi_+\rangle\langle\psi_+|$ *.)*

Exercise 16.3.1 *Let the set of vectors,* $\{|\varphi_n\rangle\}$ *be a complete orthonormal system spanning a Hilbert space, where,* $\langle\varphi_m|\varphi_n\rangle = \delta_{m,n}$ *. The outer products between these vectors,* $\{\hat{\varphi}_{m,n} = |\varphi_m\rangle\langle\varphi_n|\}$*, are operators in that space. (a) Associating each operator,* $\hat{\varphi}_{m,n}$ *, with a vector in a (Liouville) vector space with an inner product,* $(\hat{A},\hat{B}) = tr\{\hat{A}^\dagger\hat{B}\}$ *, show that* $\{\hat{\varphi}_{m,n}\}$ *is an orthonormal set, namely* $(\hat{\varphi}_{m,n},\hat{\varphi}_{m',n'}) = \delta_{m,m'}\delta_{n,n'}$ *. (b) Show that any operator in the original Hilbert space can be expanded as a linear combination of the set* $\{\hat{\varphi}_{m,n}\}$ *,* $\hat{A} = \sum_{m,n} A_{m,n}\hat{\varphi}_{m,n}$ *, where* $A_{m,n}$ *is the inner product of* $\hat{A}$ *with* $\hat{\varphi}_{m,n}$ *,* $A_{m,n} = (\hat{\varphi}_{m,n},\hat{A}) = tr\{\hat{\varphi}^\dagger_{m,n}\hat{A}\}$ *.*

Solution 16.3.1

(a)

Let $\hat{\varphi}_{m,n} \equiv |\varphi_m\rangle\langle\varphi_n|$ *, where* $\langle\varphi_m|\varphi_n\rangle = \delta_{m,n}$ *. Therefore,*

$$tr\{\hat{\varphi}_{m,n}{}^\dagger\hat{\varphi}_{m',n'}\} = tr\{\hat{\varphi}_{n,m}\hat{\varphi}_{m',n'}\} = tr\{|\varphi_n\rangle\langle\varphi_m|\varphi_{m'}\rangle\langle\varphi_{n'}|\} = \sum_k \langle\varphi_k|\varphi_n\rangle\langle\varphi_m|\varphi_{m'}\rangle\langle\varphi_{n'}|\varphi_k\rangle\}$$

$$= \langle\varphi_m|\varphi_{m'}\rangle\langle\varphi_{n'}|\varphi_n\rangle = \delta_{m,m'}\delta_{n,n'} \ .$$

(b)

Any operator in the system Hilbert space can be expanded as

$$\hat{A} = \sum_m |\varphi_m\rangle\langle\varphi_m|\hat{A}\sum_n |\varphi_n\rangle\langle\varphi_n|\} = \sum_{m,n} A_{m,n}|\varphi_m\rangle\langle\varphi_n| = \sum_{m,n} A_{m,n}\hat{\varphi}_{m,n} \ .$$

Using the result (a), the expansion coefficients can be readily identified as $A_{m,n} = tr\{\hat{\varphi}^\dagger_{m,n}\hat{A}\}$ *,*

$$tr\{\hat{\varphi}^\dagger_{m,n}\hat{A}\} = tr\{\hat{\varphi}^\dagger_{m,n}\sum_{m',n'} A_{m',n'}\hat{\varphi}_{m',n'}\} = \sum_{m',n'} A_{m',n'}tr\{\hat{\varphi}^\dagger_{m,n}\hat{\varphi}_{m',n'}\} = \sum_{m',n'} A_{m',n'}\delta_{m,m'}\delta_{n,n'} = A_{m,n} \ .$$

Exercise 16.3.2 *Consider the space of two-dimensional matrices,* $\begin{bmatrix} x & y \\ z & w \end{bmatrix}$*, where* x, y, z *and* w *are complex valued numbers. (a) Show that the set of Pauli matrices (Eq. (13.1.17)) and the identity matrix,*

$$\boldsymbol{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad ; \quad \mathbf{I} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

compose an orthogonal set of vectors in this space, under the inner product, $(\mathbf{A}, \mathbf{B}) = tr\{\mathbf{A}^\dagger \mathbf{B}\}$. *(b) Show that the corresponding normalized basis vectors under this inner product read*

$$\boldsymbol{\sigma}_z = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_y = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad ; \quad \mathbf{I} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} .$$

(c) Show that any two-by-two matrix $\begin{bmatrix} x & y \\ z & w \end{bmatrix}$ *can be written as a linear combination of these matrices, with expansion coefficients given by its inner product with the basis vectors in (b).*

Solution 16.3.2

Given the Pauli matrices:

$$\boldsymbol{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad ; \quad \mathbf{I} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad ,$$

(a)

We can readily verify that these matrices are orthogonal under the inner product, $(\mathbf{A}, \mathbf{B}) = tr\{\mathbf{A}^\dagger \mathbf{B}\}$*:*

$$(\boldsymbol{\sigma}_z, \boldsymbol{\sigma}_x) = tr\{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\} = tr\{\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}\} = 0$$

$$(\boldsymbol{\sigma}_z, \boldsymbol{\sigma}_y) = tr\{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\} = tr\{\begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}\} = 0$$

$$(\boldsymbol{\sigma}_z, \mathbf{I}) = tr\{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\} = 0$$

$$(\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y) = tr\{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\} = tr\{\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}\} = 0$$

$$(\boldsymbol{\sigma}_x, \mathbf{I}) = tr\{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\} = 0$$

$$(\boldsymbol{\sigma}_y, \mathbf{I}) = tr\{\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\} = 0 \quad .$$

(b)

To normalize, we consider the inner product of each matrix with itself, $(\mathbf{A}, \mathbf{A}) = tr\{\mathbf{A}^\dagger \mathbf{A}\}$,

$$(\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_x) = tr\{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\} = tr\{\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\} = 2$$
$$(\boldsymbol{\sigma}_y, \boldsymbol{\sigma}_y) = tr\{\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\} = tr\{\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\} = 2$$
$$(\boldsymbol{\sigma}_z, \boldsymbol{\sigma}_z) = tr\{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\} = tr\{\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\} = 2$$

$$(\mathbf{I}, \mathbf{I}) = tr\{\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\} = 2 \ .$$

Hence, the normalized matrices are

$$\boldsymbol{\sigma}_z = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_x = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad ; \quad \boldsymbol{\sigma}_y = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad ; \quad \mathbf{I} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

(c)

For a general matrix, $\begin{bmatrix} x & y \\ z & w \end{bmatrix}$, *the inner products with the normalized Pauli matrices read,*

$$(\mathbf{I}, \begin{bmatrix} x & y \\ z & w \end{bmatrix}) = tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\} = \frac{x+w}{\sqrt{2}}$$
$$(\boldsymbol{\sigma}_x, \begin{bmatrix} x & y \\ z & w \end{bmatrix}) = tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\} = \frac{z+y}{\sqrt{2}}$$
$$(\boldsymbol{\sigma}_y, \begin{bmatrix} x & y \\ z & w \end{bmatrix}) = tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\} = i\,\frac{y-z}{\sqrt{2}}$$
$$(\boldsymbol{\sigma}_z, \begin{bmatrix} x & y \\ z & w \end{bmatrix}) = tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\} = \frac{x-w}{\sqrt{2}}.$$

The latter are readily shown to be the expansion coefficients in the representation of the matrix, $\begin{bmatrix} x & y \\ z & w \end{bmatrix}$, *as a linear combination of the Pauli matrices,*

$$\begin{bmatrix} x & y \\ z & w \end{bmatrix} = tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\}\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\}\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$
$$+tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\}\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} + tr\{\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} x & y \\ z & w \end{bmatrix}\}\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$
$$= \begin{bmatrix} \frac{x+w}{2} & 0 \\ 0 & \frac{x+w}{2} \end{bmatrix} + \begin{bmatrix} 0 & \frac{z+y}{2} \\ \frac{z+y}{2} & 0 \end{bmatrix} + \begin{bmatrix} 0 & \frac{y-z}{2} \\ \frac{z-y}{2} & 0 \end{bmatrix} + \begin{bmatrix} \frac{x-w}{2} & 0 \\ 0 & \frac{w-x}{2} \end{bmatrix} .$$

Exercise 16.4.1 *Use the Schrödinger equation for the coherent states,* $i\hbar\frac{\partial}{\partial t}|\psi_i(t)\rangle = \hat{H}(t)|\psi_i(t)\rangle$*, and the Hermitian conjugated equation to show that the time-derivative of the density operator (Eq. (16.2.3)) is given by Eq. (16.4.1).*

Solution 16.4.1

Given the time-dependent Schrodinger equation, $i\hbar\frac{\partial}{\partial t}|\psi_i(t)\rangle = \hat{H}(t)|\psi_i(t)\rangle$*, and its Hermitian conjugate,* $-i\hbar\frac{\partial}{\partial t}\langle\psi_i(t)| = \langle\psi_i(t)|\hat{H}(t)$*, and using the definition of the density operator, Eq. (16.2.3), we obtain the Liouville-Von Neumann equation,*

$$\frac{\partial}{\partial t}\hat{\rho}(t) = \frac{\partial}{\partial t}\sum_{i=1}^{N} w_i|\psi_i(t)\rangle\langle\psi_i(t)| = \sum_{i=1}^{N} w_i\left|\frac{\partial}{\partial t}\psi_i(t)\right\rangle\langle\psi_i(t)| + \sum_{i=1}^{N} w_i|\psi_i(t)\rangle\left\langle\frac{\partial}{\partial t}\psi_i(t)\right|$$
$$= \sum_{i=1}^{N} w_i\frac{-i}{\hbar}\hat{H}|\psi_i(t)\rangle\langle\psi_i(t)| + \sum_{i=1}^{N} w_i|\psi_i(t)\rangle\langle\psi_i(t)|\frac{i}{\hbar}\hat{H}$$
$$= \frac{-i}{\hbar}[\hat{H}, \hat{\rho}(t)] .$$

Exercise 16.4.2 *(a) Show that by its definition, the density operator (Eq. (16.2.3)) can be formulated using the time evolution operator (Eq. (15.2.2)),* $\hat{\rho}(t) = \hat{U}(t,0)\hat{\rho}(0)\hat{U}^{\dagger}(t,0)$*. (b) Show that the Heisenberg picture representation (Eq. (15.3.16)) of the density operator,* $\hat{\rho}_H(t)$*, is time-independent. (c) Use Eq. (15.3.17) to show that the time derivative of* $\hat{\rho}_H(t)$ *vanishes at all times.*

Solution 16.4.2

(a)

Using Eq. (15.2.2) we have, $|\psi_i(t)\rangle = \hat{U}(t,0)|\psi_i(0)\rangle$ *, and* $\langle\psi_i(t)| = \langle\psi_i(0)|\hat{U}^\dagger(t,0)$ *.*

Consequently,

$$\hat{\rho}(t) \equiv \sum_{i=1}^{N} w_i |\psi_i(t)\rangle\langle\psi_i(t)| = \sum_{i=1}^{N} w_i \hat{U}(t,0)|\psi_i(0)\rangle\langle\psi_i(0)|\hat{U}^\dagger(t,0)$$

$$= \hat{U}(t,0)\left[\sum_{i=1}^{N} w_i |\psi_i(0)\rangle\langle\psi_i(0)|\right]\hat{U}^\dagger(t,0) = \hat{U}(t,0)\hat{\rho}(0)\hat{U}^\dagger(t,0) \ .$$

(b)

The Heisenberg picture representation (Eq. (15.3.16)) of the density operator reads $\hat{\rho}_H(t) \equiv \hat{U}^\dagger(t,0)\hat{\rho}(t)\hat{U}(t,0)$*. Using the result of (a) we have,* $\hat{\rho}(t) = \hat{U}(t,0)\hat{\rho}(0)\hat{U}^\dagger(t,0)$*, and therefore,* $\hat{\rho}_H(t) = \hat{U}^\dagger(t,0)\hat{U}(t,0)\hat{\rho}(0)\hat{U}^\dagger(t,0)\hat{U}(t,0)$*. Using the unitarity of the time-evolution operator (Eq. (15.2.5)),* $\hat{U}^\dagger(t,0)\hat{U}(t,0) = \hat{I}$ *, we obtain* $\hat{\rho}_H(t) = \hat{\rho}(0)$*.*

(c)

Using Eq. (15.3.17), the time-derivative of the Heisenberg operator $\hat{\rho}_H(t)$ *reads*

$$\frac{\partial}{\partial t}\hat{\rho}_H(t) = \frac{i}{\hbar}[\hat{H}_H(t),\hat{\rho}_H(t)] + \left[\frac{\partial}{\partial t}\hat{\rho}(t)\right]_H = \frac{i}{\hbar}[\hat{H}(t),\hat{\rho}(t)]_H + \left[\frac{\partial}{\partial t}\hat{\rho}(t)\right]_H \ .$$

Using the Liouville-Von Neumann equation (Eq. (16.4.1)) for the second term, we obtain

$$\frac{\partial}{\partial t}\hat{\rho}_H(t) = \frac{i}{\hbar}[\hat{H}(t),\hat{\rho}(t)]_H + \left[\frac{\partial}{\partial t}\hat{\rho}(t)\right]_H = \frac{i}{\hbar}[\hat{H}(t),\hat{\rho}(t)]_H + \left[\frac{-i}{\hbar}[\hat{H}(t),\hat{\rho}(t)]\right]_H = 0 \ .$$

Exercise 16.4.3 *Given a finite basis for the system's Hilbert space, where operators are represented as* $N \times N$ *matrices, Use Eqs. (16.3.6, 16.3.8) to show that the Liouville super operator can be represented as a matrix of dimensions* $N^2 \times N^2$, $\mathbf{L} = \mathbf{H}\otimes\mathbf{I} - \mathbf{I}\otimes\mathbf{H}^t$ *, where* $\mathbf{H}$ *and* $\mathbf{I}$ *are, respectively, the matrix representation of the Hamiltonian and the identity (use the matrix tensor product definition, Eqs. (11.6.17, 11.6.18), to show that* $\left[\hat{H}\hat{\rho} - \hat{\rho}\hat{H}\right]_{n',m'} = \sum_{m,n} \left(\mathbf{H}\otimes\mathbf{I} - \mathbf{I}\otimes\mathbf{H}^t\right)_{(n',m'),(n,m)} \rho_{n,m}$*).*

Solution 16.4.3

Using the general relations (Eqs. (16.3.6, 16.3.8)), $\left[\hat{B}\hat{A}\right]_{n',m'} = \sum_{m,n} B_{n',n}\delta_{m',m}A_{n,m}$ *and* $\left[\hat{A}\hat{B}\right]_{n',m'} = \sum_{m,n} \delta_{n',n}B_{m,m'}A_{n,m}$, *we obtain* $\left[\hat{H}\hat{\rho}\right]_{n',m'} = \sum_{m,n} H_{n',n}\delta_{m',m}\rho_{n,m}$ *and* $\left[\hat{\rho}\hat{H}\right]_{n',m'} = \sum_{m,n} \delta_{n',n}H_{m,m'}\rho_{n,m}$.

Consequently, we obtain $\left[\hat{H}\hat{\rho}-\hat{\rho}\hat{H}\right]_{n',m'} = \sum_{m,n} \left(H_{n',n}\delta_{m',m} - \delta_{n',n}H_{m,m'}\right)\rho_{n,m}$. *Using Eq. (11.6.18) we can identify the matrix elements,* $H_{n',n}\delta_{m',m} = \left[\mathbf{H}\otimes\mathbf{I}\right]_{(n',m'),(n,m)}$ *and* $\delta_{n',n}H_{m,m'} = \left[\mathbf{I}\otimes\mathbf{H}^t\right]_{(n',m'),(n,m)}$, *to obtain*

$$\left[\hat{H}\hat{\rho}-\hat{\rho}\hat{H}\right]_{n',m'} = \sum_{m,n} \left(H_{n',n}\delta_{m',m} - \delta_{n',n}H_{m,m'}\right)\rho_{n,m} = \sum_{m,n} \left(\mathbf{H}\otimes\mathbf{I} - \mathbf{I}\otimes\mathbf{H}^t\right)_{(n',m'),(n,m)} \rho_{n,m}.$$

Exercise 16.5.1 *Given a time-independent system Hamiltonian, any pure state can be expanded in terms of the stationary solutions (Eq. (15.1.5)),* $\left|\psi_i(t)\right\rangle = \sum_n a_n^{(i)} e^{\frac{-it}{\hbar}\varepsilon_n}\left|\varphi_n\right\rangle$, *where* $\left|\varphi_n\right\rangle$ *are the Hamiltonian eigenstates,* $\hat{H}\left|\varphi_n\right\rangle = \varepsilon_n\left|\varphi_n\right\rangle$. *(a) Use this expansion and the definition of the system's density operator, Eq. (16.2.3), to show that the matrix representation of the density operator in the basis of the Hamiltonian eigenstates reads* $\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle = \sum_i w_i a_{m'}^{(i)}\left(a_m^{(i)}\right)^* e^{\frac{-it}{\hbar}(\varepsilon_{m'}-\varepsilon_m)}$. *(b) Show that the equilibrium requirement,* $\frac{\partial}{\partial t}\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle = 0$, *means that off-diagonal matrix elements between non-degenerate Hamiltonian eigenstates (*$\varepsilon_m \neq \varepsilon_{m'}$*) must vanish identically. (c) Show that any density matrix that is diagonal in the basis of stationary states,* $\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle \propto \delta_{m',m}$, *must be time-independent. (d) Given the diagonal representation of the equilibrium density operator in the basis of Hamiltonian eigenstates {*$\left|\varphi_n\right\rangle$*} (Eq. (16.5.4)), show that* $\hat{\rho}^{(eq)}\left|\varphi_n\right\rangle = w_n\left|\varphi_n\right\rangle$.

Solution 16.5.1

(a)

Using the expansions of state vectors in term of stationary states, $\left|\psi_j(t)\right\rangle = \sum_n a_n^{(j)} e^{\frac{-it}{\hbar}\varepsilon_n} \left|\varphi_n\right\rangle$*, the density operator reads* $\hat{\rho}(t) \equiv \sum_j w_j \left|\psi_j(t)\right\rangle\left\langle\psi_j(t)\right| = \sum_{j,n,n'} w_j a_n^{(j)} e^{\frac{-it}{\hbar}\varepsilon_n} \left(a_{n'}^{(j)}\right)^* e^{\frac{it}{\hbar}\varepsilon_{n'}} \left|\varphi_n\right\rangle\left\langle\varphi_{n'}\right|$.

The matrix elements in the basis of stationary states are therefore,

$$\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle \equiv \left\langle\varphi_{m'}\right|\left[\sum_j w_j \left|\psi_j(t)\right\rangle\left\langle\psi_j(t)\right|\right]\left|\varphi_m\right\rangle = \sum_{j,n,n'} w_j a_n^{(j)} e^{\frac{-it}{\hbar}\varepsilon_n} \left(a_{n'}^{(j)}\right)^* e^{\frac{it}{\hbar}\varepsilon_{n'}} \delta_{m',n}\delta_{n',m}$$

$$= \sum_j w_j a_{m'}^{(j)} e^{\frac{-it}{\hbar}\varepsilon_{m'}} \left(a_m^{(j)}\right)^* e^{\frac{it}{\hbar}\varepsilon_m} = \sum_j w_j a_{m'}^{(j)} \left(a_m^{(j)}\right)^* e^{\frac{-it}{\hbar}(\varepsilon_{m'}-\varepsilon_m)} \quad .$$

(b)

Using the result of (a), the time-derivative of any matrix element reads

$$\frac{\partial}{\partial t}\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle = \frac{-i}{\hbar}[\varepsilon_{m'}-\varepsilon_m] e^{\frac{-it}{\hbar}(\varepsilon_{m'}-\varepsilon_m)} \sum_j w_j a_{m'}^{(j)} \left(a_m^{(j)}\right)^* .$$

For the equilibrium density we have, $\frac{\partial}{\partial t}\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle \equiv 0$*, and therefore,*

$$\frac{-i}{\hbar}[\varepsilon_{m'}-\varepsilon_m] e^{\frac{-it}{\hbar}(\varepsilon_{m'}-\varepsilon_m)} \sum_j w_j a_{m'}^{(j)} \left(a_m^{(j)}\right)^* = 0 .$$

If $\left|\varphi_m\right\rangle$ *and* $\left|\varphi_{m'}\right\rangle$ *are non-degenerate eigenstates of the system Hamiltonian, namely* $\varepsilon_{m'}-\varepsilon_m \neq 0$*, the equilibrium condition means that* $\sum_j w_j a_{m'}^{(j)} \left(a_m^{(j)}\right)^* = 0$*. Consequently, the respective matrix element vanishes at any time,* $\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle = \sum_j w_j a_{m'}^{(j)} \left(a_m^{(j)}\right)^* e^{\frac{-it}{\hbar}(\varepsilon_{m'}-\varepsilon_m)} = 0$.

(c)

Using the result of (a) for the matrix representation of $\hat{\rho}(t)$ *in the basis of stationary states,* $\left\langle\varphi_{m'}\right|\hat{\rho}(t)\left|\varphi_m\right\rangle = \sum_j w_j a_{m'}^{(j)} \left(a_m^{(j)}\right)^* e^{\frac{-it}{\hbar}(\varepsilon_{m'}-\varepsilon_m)}$*, we readily notice that the diagonal matrix elements are time-independent. Hence, if all the off-diagonal matrix elements vanish identically, the entire matrix is time-independent.*

(d)

Given $\hat{\rho}^{(eq)} = \sum_{n'} w_{n'} |\varphi_{n'}\rangle\langle\varphi_{n'}|$ *(Eq. (16.5.4)), we readily obtain*

$$\hat{\rho}^{(eq)}|\varphi_n\rangle = \sum_{n'} w_{n'} |\varphi_{n'}\rangle\langle\varphi_{n'}|\varphi_n\rangle = w_n|\varphi_n\rangle.$$

Exercise 16.5.2 *Show that the von Neumann equilibrium entropy, Eq. (16.5.11) vanishes for a pure state, namely when the weights are either* $w_n \to 0$ *or* $w_n \to 1$.

Solution 16.5.2

For $w_n \to 0$ *we obtain* $\lim_{w_n \to 0}\left[w_n \ln(w_n)\right] = \lim_{w_n \to 0}\left[\frac{\ln(w_n)}{1/w_n}\right] = \lim_{w_n \to 0}\left[\frac{1/w_n}{-1/w_n^2}\right] = 0$.

For $w_n \to 1$ *we obtain* $\lim_{w_n \to 1}\left[w_n \ln(w_n)\right] = 0$.

Therefore, if $\{w_n\} \in (0,1)$, *then* $S^{(eq)} = -\sum_n w_n \ln(w_n) = 0$.

Exercise 16.5.3 *The statistical weights at equilibrium are obtained by maximizing the von Neumann entropy, subject to constraints. For a random ensemble the only constraint is the normalization,* $\sum_{n=1}^{N} w_n = 1$, *which can be imposed in terms of a Lagrange multiplier* λ. *The function to be maximized in this case is* $F(w_1, w_2, ...) = S^{(eq)}(w_1, w_2, ...) - \lambda\left[\sum_{n=1}^{N} w_n - 1\right]$. *Apply the necessary condition for a maximum,* $\left\{\frac{\partial}{\partial w_n} F(w_1, w_2, ...) = 0\right\}$, *and show that the maximum is obtained when the weight is uniform for all the stationary states, namely,* $w_n = e^{-(1+\lambda)}$. *Determine the value of* λ *by the normalization constraint to show that the equilibrium weights in this case read* $w_n = \frac{1}{N}$.

Solution 16.5.3

To maximize the entropy, $-\sum_{n'=1}^{N} w_{n'} \ln(w_{n'})$, *under the normalization constraint,* $\sum_{n=1}^{N} w_n = 1$, *we set to zero the derivative of* $F(w_1, w_2, ...) = -\sum_{n'=1}^{N} w_{n'} \ln(w_{n'}) - \lambda\left[\sum_{n=1}^{N} w_n - 1\right]$, *with respect to {* w_n *},*

$$F(w_1, w_2, ...) = -\sum_{n'=1}^{N} w_{n'} \ln(w_{n'}) - \lambda \left[\sum_{n'=1}^{N} w_{n'} - 1 \right]$$
$$\Rightarrow \frac{\partial}{\partial w_n} F(w_1, w_2, ...) = -\ln(w_n) - 1 - \lambda = 0$$
$$\Rightarrow \ln(w_n) = -(1+\lambda)$$
$$\Rightarrow w_n = e^{-(1+\lambda)} \ .$$

To determine the value of the Lagrange multiplier, λ *, we normalize,*

$$\sum_{n=1}^{N} w_n = 1 \Rightarrow Ne^{-(1+\lambda)} = 1 \Rightarrow \lambda = \ln(N) - 1 .$$

Therefore, $w_n = e^{-(1+\lambda)} = e^{-\ln(N)} = \frac{1}{N}$.

Exercise 16.5.4 *For a canonical ensemble, the weights of the stationary states are constrained, such that* $\sum_{n=1}^{N} w_n = 1$ *and* $\sum_{n=1}^{N} w_n \varepsilon_n = U$. *(a) Derive Eq. (16.5.14) by maximizing the von Neuman entropy subject to these constraints. Determine the value of* λ *by the normalization constraint to show that the equilibrium weights are given in this case by Eq. (16.5.15).*

Solution 16.5.4

To maximize the entropy, $-\sum_{n'=1}^{N} w_{n'} \ln(w_{n'})$ *, under the constraints* $\sum_{n=1}^{N} w_n = 1$ *and* $\sum_{n=1}^{N} w_n \varepsilon_n = U$ *, we set to zero the derivative of*

$$F(w_1, w_2, ...) = -\sum_{n'=1}^{N} w_{n'} \ln(w_{n'}) - \lambda \left[\sum_{n=1}^{N} w_n - 1 \right] - \beta \left[\sum_{n=1}^{N} \varepsilon_n w_n - U \right],$$

with respect to { w_n *},*

$$\frac{\partial}{\partial w_n} F(w_1, w_2, ...) = -\ln(w_n) - 1 - \lambda - \beta\varepsilon_n = 0$$
$$\ln(w_n) = -(1+\lambda+\beta\varepsilon_n)$$
$$w_n = e^{-(1+\lambda+\beta\varepsilon_n)} \ .$$

To determine the value of the Lagrange multiplier λ *, we normalize,*

$$\sum_{n=1}^{N} w_n = \sum_{n=1}^{N} e^{-(1+\lambda+\beta\varepsilon_n)} = e^{-(1+\lambda)} \sum_{n=1}^{N} e^{-\beta\varepsilon_n} = 1 \Rightarrow e^{-(1+\lambda)} = \frac{1}{\sum_n e^{-\beta\varepsilon_n}}.$$

Therefore, $w_n = \dfrac{e^{-\beta\varepsilon_n}}{\sum_n e^{-\beta\varepsilon_n}}$.

Exercise 16.5.5 *Derive Eq. (16.5.18) by substitution of the result, Eq. (16.5.17), for the canonical ensemble in the general expression for the density matrix, Eq. (16.5.4), and by using Eq. (16.5.5).*

Solution 16.5.5

Using $w_n = \dfrac{e^{\frac{-\varepsilon_n}{k_B T}}}{Z}$ *with* $Z = \sum_{n=1}^{N} e^{\frac{-\varepsilon_n}{k_B T}}$ *(Eq. (16.5.17)), the general expression for the equilibrium density (Eq. (16.5.4)) yields,* $\hat{\rho}^{(eq)} = \sum_{n=1}^{N} w_n |\varphi_n\rangle\langle\varphi_n| = \sum_{n=1}^{N} \dfrac{e^{\frac{-\varepsilon_n}{k_B T}}}{Z} |\varphi_n\rangle\langle\varphi_n|$. *Since* $|\varphi_n\rangle$ *are the Hamiltonian eigenstates,* $\hat{H}|\varphi_n\rangle = \varepsilon_n |\varphi_n\rangle$, *we obtain,*

$$\hat{\rho}^{(eq)} = \sum_{n=1}^{N} \frac{e^{\frac{-\varepsilon_n}{k_B T}}}{Z} |\varphi_n\rangle\langle\varphi_n| = \sum_{n=1}^{N} \frac{1}{Z} e^{\frac{-\hat{H}}{k_B T}} |\varphi_n\rangle\langle\varphi_n| = \frac{1}{Z} e^{\frac{-\hat{H}}{k_B T}} \sum_{n=1}^{N} |\varphi_n\rangle\langle\varphi_n| = \frac{1}{Z} e^{\frac{-\hat{H}}{k_B T}} .$$

Similarly, $Z = \sum_{n=1}^{N} e^{\frac{-\varepsilon_n}{k_B T}} = \sum_{n=1}^{N} \langle\varphi_n| e^{\frac{-\hat{H}}{k_B T}} |\varphi_n\rangle = tr\{e^{\frac{-\hat{H}}{k_B T}}\}$. *Consequently, we obtain,*

$$\hat{\rho}^{(eq)} = \frac{e^{\frac{-\hat{H}}{k_B T}}}{tr\{e^{\frac{-\hat{H}}{k_B T}}\}}.$$

Exercise 16.5.6 *For a grand canonical ensemble, the weights of the stationary states are constrained, such that* $\sum_{n=1}^{N} w_n = 1$, $\sum_{n=1}^{N} w_n\varepsilon_n = U$, *and* $\sum_{n=1}^{N} w_n N_n = N_0$. *Derive Eq. (16.5.22) by maximizing the von Neuman entropy subject to these constraints.*

Solution 16.5.6

To maximize the entropy, $-\sum_{n'=1}^{N} w_{n'} \ln(w_{n'})$, *under the constraints* $\sum_{n=1}^{N} w_n = 1$, $\sum_{n=1}^{N} w_n \varepsilon_n = U$, *and* $\sum_{n=1}^{N} w_n N_n = N_0$, *we set to zero the derivative of*

$$F(w_1, w_2, ...) = -\sum_{n'=1}^{N} w_{n'} \ln(w_{n'}) - \lambda \left[\sum_{n=1}^{N} w_n - 1\right] - \beta \left[\sum_{n=1}^{N} \varepsilon_n w_n - U\right] - \eta \left[\sum_{n=1}^{N} N_n w_n - N_0\right],$$

with respect to { w_n *},*

$$\frac{\partial}{\partial w_n} F(w_1, w_2, ...) = -\ln(w_n) - 1 - \lambda - \beta\varepsilon_n - \eta N_n = 0$$

$$\ln(w_n) = -(1 + \lambda + \beta\varepsilon_n + \eta N_n)$$

$$w_n = e^{-(1+\lambda+\beta\varepsilon_n+\eta N_n)}.$$

To determine the value of the Lagrange multiplier λ, *we normalize,*

$$\sum_{n=1}^{N} e^{-(1+\lambda+\beta\varepsilon_n+\eta N_n)} = 1 \Rightarrow e^{-(1+\lambda)} \sum_{n=1}^{N} e^{-\beta\varepsilon_n - \eta N_n} = 1 \Rightarrow e^{-(1+\lambda)} = \frac{1}{\sum_{n=1}^{N} e^{-\beta\varepsilon_n - \eta N_n}}.$$

Therefore, $w_n = \dfrac{e^{-\beta\varepsilon_n - \eta N_n}}{\sum_{n=1}^{N} e^{-\beta\varepsilon_n - \eta N_n}}$.

Exercise 16.5.7 *Derive Eq. (16.5.25) by substitution of the result, Eq. (16.5.24), for the grand canonical ensemble in the general expression for the density matrix, Eq. (16.5.4), and by using Eqs. (16.5.5, 16.5.19).*

Solution 16.5.7

Using $w_n = \dfrac{1}{Z} e^{\frac{-1}{k_B T}(\varepsilon_n - \mu N_n)}$ *with* $Z = \sum_{n=1}^{N} e^{\frac{-1}{k_B T}(\varepsilon_n - \mu N_n)}$ *(Eq. (16.5.24)), the general expression for the equilibrium density (Eq. (16.5.4)) yields,* $\hat{\rho}^{(eq)} = \sum_{n=1}^{N} w_n |\varphi_n\rangle\langle\varphi_n| = \sum_{n=1}^{N} \dfrac{e^{\frac{-1}{k_B T}(\varepsilon_n - \mu N_n)}}{Z} |\varphi_n\rangle\langle\varphi_n|$.

Since $|\varphi_n\rangle$ *are eigenstates of the system Hamiltonian,* $\hat{H}|\varphi_n\rangle = \varepsilon_n|\varphi_n\rangle$ *(Eq. (16.5.5)), and of the number operator,* $\hat{N}|\varphi_n\rangle = N_n|\varphi_n\rangle$ *(Eq. (16.5.19)), we obtain*

$$\hat{\rho}^{(eq)} = \sum_{n=1}^{N} w_n |\varphi_n\rangle\langle\varphi_n| = \sum_{n=1}^{N} \frac{e^{\frac{-1}{k_B T}(\varepsilon_n - \mu N_n)}}{Z} |\varphi_n\rangle\langle\varphi_n| = \sum_{n=1}^{N} \frac{e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})}}{Z} |\varphi_n\rangle\langle\varphi_n|$$

$$= \frac{e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})}}{Z} \sum_{n=1}^{N} |\varphi_n\rangle\langle\varphi_n| = \frac{e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})}}{Z} \ .$$

Similarly, $Z = \sum_{n=1}^{N} e^{\frac{-1}{k_B T}(\varepsilon_n - \mu N_n)} = \sum_{n=1}^{N} \langle\varphi_n| \sum_{n=1}^{N} e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})} |\varphi_n\rangle = tr\{e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})}\}$. *Consequently, we obtain,* $\hat{\rho}^{(eq)} = \dfrac{e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})}}{tr\{e^{\frac{-1}{k_B T}(\hat{H} - \mu\hat{N})}\}}$.

17 Quantum Rate Processes

Exercise 17.1.1 *(a) Use the first-order Dyson expansion,* $\hat{U}^{(I)}(t,0) \cong \hat{I} + \frac{-i}{\hbar}\int_0^t dt' V_I(t')$ *, in the exact expression for the transition rate (Eq. (15.5.13)) to obtain the first order approximation for the rate, Eq. (17.1.1). (b) Show that when the initial and final states are eigenstates of* $\hat{H}_0$ *the first order approximation for the rate is given by Eq. (17.1.2).*

Solution 17.1.1

(a)

Starting from Eq. (15.5.13), $k_{i\to f}(t) = \frac{1}{\hbar} 2\,\mathrm{Im}\langle \chi_i | \hat{U}^{\dagger(I)}(t,0) | \chi_f \rangle \langle \chi_f | \hat{V}_I(t)\hat{U}^{(I)}(t,0) | \chi_i \rangle$*, and using the first order Dyson expansion of the time-evolution operator,* $\hat{U}^{(I)}(t,0) \cong \hat{I} + \frac{-i}{\hbar}\int_0^t dt' V_I(t')$ *, we obtain*

$$k^{(1)}_{i\to f}(t) = \frac{1}{\hbar} 2\,\mathrm{Im}\langle \chi_i | \left[\hat{I} + \frac{i}{\hbar}\int_0^t dt' V_I(t') \right] | \chi_f \rangle \langle \chi_f | \hat{V}_I(t) \left[\hat{I} + \frac{-i}{\hbar}\int_0^t dt' V_I(t') \right] | \chi_i \rangle .$$

For $\langle \chi_f | \chi_i \rangle = 0$ *, keeping only terms up to second order in the interaction, we obtain*

$$k^{(1)}_{i\to f}(t) \approx \frac{1}{\hbar} 2\,\mathrm{Im}\langle \chi_i | \left[\hat{I} + \frac{i}{\hbar}\int_0^t dt' V_I(t') \right] | \chi_f \rangle \langle \chi_f | \hat{V}_I(t) \left[\hat{I} + \frac{-i}{\hbar}\int_0^t dt' V_I(t') \right] | \chi_i \rangle$$
$$\approx \frac{1}{\hbar} 2\,\mathrm{Im}\langle \chi_i | \left[\frac{i}{\hbar}\int_0^t dt' V_I(t') \right] | \chi_f \rangle \langle \chi_f | \hat{V}_I(t) \left[\hat{I} \right] | \chi_i \rangle$$
$$\approx \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' \langle \chi_i | V_I(t') | \chi_f \rangle \langle \chi_f | \hat{V}_I(t) | \chi_i \rangle \; .$$

(b)

Using $\hat{V}_I(t) = e^{\frac{it}{\hbar}\hat{H}_0}\hat{V}(t)e^{\frac{-it}{\hbar}\hat{H}_0}$ *, we have*

$$k^{(1)}_{i\to f}(t) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^t dt' \langle \chi_i | e^{\frac{it'}{\hbar}\hat{H}_0}\hat{V}(t')e^{\frac{-it'}{\hbar}\hat{H}_0} | \chi_f \rangle \langle \chi_f | e^{\frac{it}{\hbar}\hat{H}_0}\hat{V}(t)e^{\frac{-it}{\hbar}\hat{H}_0} | \chi_i \rangle .$$

Using $\hat{H}_0|\chi_i\rangle = \varepsilon_i|\chi_i\rangle$ *and* $\hat{H}_0|\chi_f\rangle = \varepsilon_f|\chi_f\rangle$, *we obtain*

$$k^{(1)}_{i\to f}(t) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^t dt'\langle\chi_i|e^{\frac{it'}{\hbar}\hat{H}_0}\hat{V}(t')e^{\frac{-it'}{\hbar}\hat{H}_0}|\chi_f\rangle\langle\chi_f|e^{\frac{it}{\hbar}\hat{H}_0}\hat{V}(t)e^{\frac{-it}{\hbar}\hat{H}_0}|\chi_i\rangle$$

$$= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t dt'\langle\chi_i|e^{\frac{it'}{\hbar}\varepsilon_i}\hat{V}(t')e^{\frac{-it'}{\hbar}\varepsilon_f}|\chi_f\rangle\langle\chi_f|e^{\frac{it}{\hbar}\varepsilon_f}\hat{V}(t)e^{\frac{-it}{\hbar}\varepsilon_i}|\chi_i\rangle$$

$$= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)(t-t')}\langle\chi_i|\hat{V}(t')|\chi_f\rangle\langle\chi_f|\hat{V}(t)|\chi_i\rangle \quad .$$

Changing integration variable, $t-t'=\tau$ *, we obtain Eq. (17.1.2),*

$$k^{(1)}_{i\to f}(t) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^t d\tau e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)\tau}\langle\chi_i|\hat{V}(t-\tau)|\chi_f\rangle\langle\chi_f|\hat{V}(t)|\chi_i\rangle .$$

Exercise 17.1.2 *The first order approximation for the transition probability is given by Eq. (15.6.10). Show that the rate expression, Eq. (17.1.2), is indeed the time derivative of the transition probability.*

Solution 17.1.2

Starting from the first order approximation to the transition probability (for $\hat{H}(\lambda,t) = \hat{H}_0 + \lambda\hat{V}(t)$ *, Eqs. (15.6.1, 15.6.10)),*

$$P^{(1)}_{i\to f}(t) = \frac{\lambda^2}{\hbar^2}\left|\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t'}\langle\chi_f|\hat{V}(t')|\chi_i\rangle\right|^2$$

$$= \frac{\lambda^2}{\hbar^2}\left(\int_0^t dt' e^{\frac{-i}{\hbar}(\varepsilon_f-\varepsilon_i)t'}\langle\chi_i|\hat{V}(t')|\chi_f\rangle\right)\left(\int_0^t dt'' e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t''}\langle\chi_f|\hat{V}(t'')|\chi_i\rangle\right) .$$

Taking the derivative with respect to t *, we reproduce Eq. (17.1.2) for* $\lambda = 1$ *,*

$$\frac{\partial}{\partial t}P^{(1)}_{i\to f}(t) = 2\,\mathrm{Re}\frac{\lambda^2}{\hbar^2}\int_0^t dt' e^{\frac{-i}{\hbar}(\varepsilon_f-\varepsilon_i)t'}\langle\chi_i|\hat{V}(t')|\chi_f\rangle e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t}\langle\chi_f|\hat{V}(t)|\chi_i\rangle$$

$$= 2\,\mathrm{Re}\frac{\lambda^2}{\hbar^2}e^{\frac{i}{\hbar}(\varepsilon_f-\varepsilon_i)t}\int_0^t dt' e^{\frac{-i}{\hbar}(\varepsilon_f-\varepsilon_i)t'}\langle\chi_i|\hat{V}(t')|\chi_f\rangle\langle\chi_f|\hat{V}(t)|\chi_i\rangle$$

$$= \frac{2\lambda^2}{\hbar^2} \mathrm{Re}\left[\int_0^t dt' e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)(t-t')} \langle \chi_i | \hat{V}(t') | \chi_f \rangle \langle \chi_f | \hat{V}(t) | \chi_i \rangle \right]$$

$$= \frac{2\lambda^2}{\hbar^2} \mathrm{Re}\left[\int_0^t d\tau e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)\tau} \langle \chi_i | \hat{V}(t-\tau) | \chi_f \rangle \langle \chi_f | \hat{V}(t) | \chi_i \rangle \right].$$

Exercise 17.1.3 *Derive the expression for the time-dependent transition rate, Eq. (17.1.3), from Eq. (17.1.2) for a time-independent interaction operator,* $\hat{V}(\tau) \mapsto \hat{V}$.

Solution 17.1.3

When the interaction term in the Hamiltonian is time-independent, namely $\hat{V}(\tau) \mapsto \hat{V}$ *, Eq. (17.1.2) reads*

$$k_{i \to f}^{(1)}(t) = \frac{2}{\hbar^2} \mathrm{Re} \int_0^t d\tau e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)\tau} \langle \chi_i | \hat{V} | \chi_f \rangle \langle \chi_f | \hat{V} | \chi_i \rangle .$$

Carrying out the time-integration, we obtain Eq. (17.1.3),

$$k_{i \to f}^{(1)}(t) = \frac{2}{\hbar^2} \mathrm{Re} \int_0^t d\tau e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)\tau} \langle \chi_i | \hat{V} | \chi_f \rangle \langle \chi_f | \hat{V} | \chi_i \rangle$$

$$= \frac{2 \left| \langle \chi_f | \hat{V} | \chi_i \rangle \right|^2}{\hbar^2} \mathrm{Re} \int_0^t e^{\frac{i}{\hbar}(\varepsilon_f - \varepsilon_i)\tau} d\tau = \frac{2 \left| \langle \chi_f | \hat{V} | \chi_i \rangle \right|^2}{\hbar^2} \int_0^t \cos((\varepsilon_f - \varepsilon_i)\tau / \hbar) d\tau$$

$$= \frac{2 \left| \langle \chi_f | \hat{V} | \chi_i \rangle \right|^2}{\hbar(\varepsilon_f - \varepsilon_i)} \sin(\frac{(\varepsilon_f - \varepsilon_i)t}{\hbar}) .$$

Exercise 17.2.1 *One of the representations of Dirac's delta reads* $\delta(\varepsilon_i - \varepsilon_f) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} d\tau \exp(\frac{-i(\varepsilon_f - \varepsilon_i)\tau}{\hbar}) d\tau$ *. Use this representation to calculate the infinite time limit of the first-order rate, Eq. (17.2.11), as given in Eq. (17.2.12) (notice that the integrand in Eq. (17.2.11) is an even function of time).*

Solution 17.2.1

Replacing the upper limit of the time integral by infinity, the expression for the first-order rate (Eq. (17.2.11)) reads

$$k^{(1)}_{i\to\{f\}}(t)=\frac{1}{\pi\hbar^2}\int_0^t d\tau\int d\varepsilon J_{i,\{f\}}(\varepsilon)\cos((\varepsilon-\varepsilon_i)\tau/\hbar)\cong\frac{1}{\pi\hbar^2}\int_0^\infty d\tau\int d\varepsilon J_{i,\{f\}}(\varepsilon)\cos((\varepsilon-\varepsilon_i)\tau/\hbar).$$

Noticing that the integrand is an even function of τ *, we obtain,*

$$\frac{1}{\pi\hbar^2}\int_0^\infty d\tau\int d\varepsilon J_{i,\{f\}}\cos((\varepsilon-\varepsilon_i)\tau/\hbar)=\frac{1}{2\pi\hbar^2}\mathrm{Re}\int_{-\infty}^\infty d\tau\int d\varepsilon J_{i,\{f\}}(\varepsilon)e^{-i(\varepsilon-\varepsilon_i)\tau/\hbar}.$$

Using this result and the identity, $\delta(\varepsilon_i-\varepsilon_f)=\frac{1}{2\pi\hbar}\int_{-\infty}^\infty d\tau\exp(\frac{-i(\varepsilon_f-\varepsilon_i)\tau}{\hbar})d\tau$ *, in the rate expression, we obtain Eq. (17.2.12),*

$$k^{(1)}_{i\to\{f\}}\cong\frac{1}{2\pi\hbar^2}\mathrm{Re}\int_{-\infty}^\infty d\tau\int d\varepsilon J_{i,\{f\}}e^{-i(\varepsilon-\varepsilon_i)\tau/\hbar}=\frac{1}{\hbar}\int d\varepsilon J_{i,\{f\}}(\varepsilon)\delta(\varepsilon-\varepsilon_i)=\frac{1}{\hbar}J_{i,\{f\}}(\varepsilon_i).$$

Exercise 17.2.2 *The spectral density for a discretely resolved density of states reads* $J_{i,\{f\}}(\varepsilon)\equiv\sum_f 2\pi\lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)$. *(a) Show that Eq. (17.2.13) is obtained directly from Eq. (17.2.12) in this case. (b) Derive Eq. (17.2.13) by substituting the given spectral density in Eq. (17.2.11), and taking the infinite time limit of the integral.*

Solution 17.2.2

(a)

Using $J_{i,\{f\}}(\varepsilon)\equiv\sum_f 2\pi\lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)$ *in Eq. (17.2.12) for the transition rate, we readily obtain,*

$$k_{i\to\{f\}}=\frac{J_{i,\{f\}}(\varepsilon_i)}{\hbar}=\frac{2\pi}{\hbar}\sum_f\lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon_i-\varepsilon_f).$$

(b)

Starting from $k^{(1)}_{i\to\{f\}}(t)=\frac{1}{\pi\hbar^2}\int_0^t d\tau\int d\varepsilon J_{i,\{f\}}(\varepsilon)\cos((\varepsilon-\varepsilon_i)\tau/\hbar)$, *with the spectral density,* $J_{i,\{f\}}(\varepsilon)\equiv\sum_f 2\pi\lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)$, *we obtain*

$$k^{(1)}_{i\to\{f\}}(t) = \frac{1}{\pi\hbar^2}\int_0^t d\tau \int d\varepsilon J_{i,\{f\}}(\varepsilon)\cos((\varepsilon-\varepsilon_i)\tau/\hbar)$$

$$= \frac{2}{\hbar^2}\int_0^t d\tau \int d\varepsilon \sum_f \lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)\cos((\varepsilon-\varepsilon_i)\tau/\hbar) \ .$$

Replacing the upper limit of the time integral by infinity, noticing that the time-integrand is an even function of time, and using, $\int_{-\infty}^{\infty} d\tau \exp(\frac{i(\varepsilon-\varepsilon_i)\tau}{\hbar})d\tau = 2\pi\hbar\delta(\varepsilon-\varepsilon_i)$ *, we obtain*

$$k^{(1)}_{i\to\{f\}}(t) \cong \frac{1}{\hbar^2}\int_{-\infty}^{\infty} d\tau \int d\varepsilon \sum_f \lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)\cos((\varepsilon-\varepsilon_i)\tau/\hbar)$$

$$= \mathrm{Re}\frac{1}{\hbar^2}\int_{-\infty}^{\infty} d\tau \int d\varepsilon \sum_f \lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)\exp(i(\varepsilon-\varepsilon_i)\tau/\hbar) \qquad = \frac{2\pi}{\hbar}\sum_f \lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon_i-\varepsilon_f) \ .$$

$$= \frac{2\pi}{\hbar}\int d\varepsilon \sum_f \lambda^2_{i,\{f\}}(\varepsilon_f)\delta(\varepsilon-\varepsilon_f)\delta(\varepsilon-\varepsilon_i)$$

Exercise 17.2.3 *The energy integral in Eq. (17.2.11) is related to the Fourier transform of the spectral density,* $\int d\varepsilon J_{i,\{f\}}(\varepsilon)\cos((\varepsilon-\varepsilon_i)\tau/\hbar) = \mathrm{Re}\, e^{-i\varepsilon_i\tau/\hbar}\int d\varepsilon J_{i,\{f\}}(\varepsilon)e^{i\varepsilon\tau/\hbar}$*. Show that for the "square window" spectral density function, given in Eq. (17.2.14), the energy-integral reads* $2J_0\varepsilon_0 \,\mathrm{Re}\, e^{\frac{-i\varepsilon_i\tau}{\hbar}}\frac{\sin(\varepsilon_0\tau/\hbar)}{\varepsilon_0\tau/\hbar}$.

Solution 17.2.3

For a "square window" spectral density function,

$$J_{i,\{f\}}(\varepsilon) = \begin{cases} J_0 & ; \ |\varepsilon| \le \varepsilon_0 \\ 0 & ; \ |\varepsilon| > \varepsilon_0 \end{cases},$$

we have

$$\int d\varepsilon J_{i,\{f\}}(\varepsilon)\cos((\varepsilon-\varepsilon_i)\tau/\hbar) = J_0\int_{-\varepsilon_0}^{\varepsilon_0} d\varepsilon\cos((\varepsilon-\varepsilon_i)\tau/\hbar)$$

$$= J_0\,\mathrm{Re}\int_{-\varepsilon_0}^{\varepsilon_0} d\varepsilon e^{\frac{i(\varepsilon-\varepsilon_i)\tau}{\hbar}} = J_0\hbar\,\mathrm{Re}\,e^{\frac{-i\varepsilon_i\tau}{\hbar}}\frac{e^{\frac{i\varepsilon_0\tau}{\hbar}}-e^{\frac{-i\varepsilon_0\tau}{\hbar}}}{i\tau} = 2J_0\hbar\,\mathrm{Re}\,e^{\frac{-i\varepsilon_i\tau}{\hbar}}\frac{\sin(\varepsilon_0\tau/\hbar)}{\tau}$$

$$= 2J_0\varepsilon_0\,\mathrm{Re}\,e^{\frac{-i\varepsilon_i\tau}{\hbar}}\frac{\sin(\varepsilon_0\tau/\hbar)}{\varepsilon_0\tau/\hbar}\ .$$

Exercise 17.2.4 *(a) One of the representations of Dirac's delta reads* $\delta(x)=\lim_{\alpha\to\infty}\frac{\sin(\alpha x)}{\pi x}$*. Use it to show that the infinite bandwidth limit of the transition rate in Eq. (17.2.17) is* $k_{i\to\{f\}}=\frac{J_0}{\hbar}$.

(b) In Fig. 17.2.2 numerical results are presented for a discrete model, in which the initial state energy is set to zero, $\varepsilon_i=0$*, and the final ensemble includes* N *states in the energy range,* $-\varepsilon_0<\varepsilon_f<\varepsilon_0$*, with a constant coupling matrix element,* $\left|\langle\chi_f|\hat{V}|\chi_i\rangle\right|\equiv V$ *and a constant nearest level spacing,* Δ*. As* N *increases (at a constant level spacing), the rates calculated by Eq. (17.2.3) are shown to converge to* $k^{(1)}_{i\to\{f\}}\xrightarrow[N\to\infty]{}2\pi V^2/(\hbar\Delta)$*. Obtain this result analytically by replacing the discrete summation over final states by an integral with a constant density of states,* $\rho=1/\Delta$*. Show that the discrete model coincides with the result of the continuous model (a) by identifying the spectral density,* $J_0=2\pi V^2/\Delta$.

Solution 17.2.4

(a)

Considering Eq. (17.2.17),

$$k_{i\to\{f\}}=\frac{2J_0\varepsilon_0}{\pi\hbar^2}\int_0^t d\tau\cos(\varepsilon_i\tau/\hbar)\frac{\sin(\varepsilon_0\tau/\hbar)}{(\varepsilon_0\tau/\hbar)}=\frac{2J_0}{\pi\hbar^2}\int_0^t d\tau\cos(\varepsilon_i\tau/\hbar)\frac{\sin(\varepsilon_0\tau/\hbar)}{\tau/\hbar},$$

and using, $\frac{\sin(\varepsilon_0\tau/\hbar)}{\tau/\hbar}\xrightarrow[\varepsilon_0\to\infty]{}\pi\delta(\tau/\hbar)=\pi\hbar\delta(\tau)$*, we obtain in the infinite band limit,*

$$k_{i\to\{f\}}\xrightarrow[\varepsilon_0\to\infty]{}=\frac{2J_0}{\pi\hbar^2}\int_0^t d\tau\cos(\varepsilon_i\tau/\hbar)\pi\hbar\delta(\tau)=\frac{J_0}{\hbar}\int_{-t}^t d\tau\delta(\tau)=\frac{J_0}{\hbar}.$$

(b)

Eq. (17.2.3), $k^{(1)}_{i\to\{f\}}(t) = \frac{2}{\hbar^2}\int\limits_0^t \sum\limits_{f\in\{f\}} \left|\langle \chi_f|\hat{V}|\chi_i\rangle\right|^2 \cos(\omega_{f,i}\tau)d\tau$ *, obtains a simple form when applied to a uniform band mode with* $\left|\langle \chi_f|\hat{V}|\chi_i\rangle\right| \equiv V$ *. Using dimensionless variables,* $\tilde{\omega}_{f,i} = \omega_{f,i}\frac{\hbar}{V} = \frac{\varepsilon_f - \varepsilon_i}{V}$ *,* $\tilde{t} = t\frac{V}{\hbar}$ *and* $\tilde{k}^{(1)}_{i\to\{f\}}(\tilde{t}) = \frac{\hbar}{V}k^{(1)}_{i\to\{f\}}(t)$ *, we obtain,*

$$k^{(1)}_{i\to\{f\}}(t) = \frac{2V^2}{\hbar^2}\int\limits_0^t \sum\limits_{f\in\{f\}} \cos(\omega_{f,i}\tau)d\tau \;\Rightarrow\; \tilde{k}^{(1)}_{i\to\{f\}}(\tilde{t}) = 2\int\limits_0^{\tilde{t}} \sum\limits_{f=1}^{N} \cos(\tilde{\omega}_{f,i}\tilde{\tau})d\tilde{\tau}.$$

Replacing the discrete states with a continuous finite band, $-\tilde{\omega}_{\max} \le \tilde{\omega}_{f,i} \le \tilde{\omega}_{\max}$ *, we obtain:*

$$\tilde{k}^{(1)}_{i\to\{f\}}(\tilde{t}) = 2\int\limits_0^{\tilde{t}} \sum\limits_{f=1}^{N} \cos(\tilde{\omega}_{f,i}\tilde{\tau})d\tilde{\tau} \to 2\int\limits_0^{\tilde{t}} \int\limits_{-\tilde{\omega}_{\max}}^{\tilde{\omega}_{\max}} \tilde{\rho}(\tilde{\omega})d\tilde{\omega}\cos(\tilde{\omega}\tilde{\tau})d\tilde{\tau}.$$

For a constant density of states, $\rho(\omega) = 1/\Delta$ *, we define,* $\tilde{\rho}(\tilde{\omega}) = 1/\tilde{\Delta} = V/\Delta$ *. Hence,*

$$\tilde{k}^{(1)}_{i\to\{f\}}(\tilde{t}) \to \frac{2}{\tilde{\Delta}}\int\limits_0^{\tilde{t}} \int\limits_{-\tilde{\omega}_{\max}}^{\tilde{\omega}_{\max}} d\tilde{\omega}\cos(\tilde{\omega}\tilde{\tau})d\tilde{\tau} = \frac{4}{\tilde{\Delta}}\int\limits_0^{\tilde{t}} \frac{\sin(\tilde{\omega}_{\max}\tilde{\tau})}{\tilde{\tau}}d\tilde{\tau}.$$

To obtain the rate in the infinite band limit, $\tilde{\omega}_{\max} \to \infty$*, we make use of the identity,* $\int\limits_0^t d\tau \frac{\sin(x\tau)}{(\tau)} \xrightarrow[x\to\infty]{} \frac{\pi}{2}$ *, and therefore,* $\tilde{k}^{(1)}_{i\to\{f\}}(\tilde{t}) \to \frac{4}{\tilde{\Delta}}\frac{\pi}{2} = \frac{2\pi}{\tilde{\Delta}}$ *. Returning to the original variables, we obtain* $k^{(1)}_{i\to\{f\}}(\tilde{t}) = \frac{V}{\hbar}\tilde{k}^{(1)}_{i\to\{f\}}(\tilde{t}) \to \frac{V^2}{\hbar}\frac{2\pi}{\Delta}$ *. Comparing to the general result for an infinite uniform band* $k_{i\to\{f\}} \to \frac{J_0}{\hbar}$ *(see (a)), the spectral density for this model is identified as* $J_0 = \frac{2\pi V^2}{\Delta} = 2\pi V^2\rho$ *.*

Exercise 17.3.1 *Use Eq. (15.5.8) for the exact state-to-state transition rate,* $k_{i\to f}(t)$*, and derive Eq. (17.3.8).*

Solution 17.3.1

Starting from Eq. (15.5.8),

$$k_{i\to f}(t) = 2\,\mathrm{Re}\, tr\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\frac{d}{dt}\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\}$$

$$= tr\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\frac{d}{dt}\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\} + tr\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\frac{d}{dt}\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\}^{*} ,$$

and using $tr\{\hat{A}\}^{*} = tr\{\hat{A}^{\dagger}\}$, *and* $tr\{\hat{A}\hat{B}\} = tr\{\hat{B}\hat{A}\}$, *we obtain Eq. (17.3.8),*

$$k_{i\to f}(t) = tr\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\frac{d}{dt}\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right| + \left|\chi_i\right\rangle\left\langle\chi_i\right|\frac{d}{dt}\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\}$$
$$= \frac{d}{dt} tr\{\hat{U}^{\dagger}(t,0)\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\}$$
$$= \frac{d}{dt} tr\{\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\hat{U}^{\dagger}(t,0)\}.$$

Exercise 17.3.2 *(a) Substitute Eqs. (17.3.6, 17.3.8) in Eq. (17.3.7), and use the definition of the projection operators to the initial and final ensembles,* $\hat{P}_{\{i\}}$ *and* $\hat{P}_{\{f\}}$ *(use Eqs. (17.3.1-17.3.3), and recall that* $\sum_{i\in\{i\}}\left\langle\chi_i\right|\hat{A}\left|\chi_i\right\rangle = tr\{\hat{A}\hat{P}_{\{i\}}\}$*) to derive the result for the transition rate between the two ensembles,* $k_{\{i\}\to\{f\}}(t) = \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{U}(t,0)\hat{\rho}_{\{i\}}(0)\hat{U}^{\dagger}(t,0)\}$. *(b) Use this result and the definition of the time-dependent density operator (Ex. 16.4.2) to show that,* $k_{\{i\}\to\{f\}}(t) = \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{\rho}_{\{i\}}(t)\}$. *(c) Use the result of (a) and the definition of the Heisenberg picture representation of* $\hat{P}_{\{f\}}$ *(Eq. (15.3.16)) to show that* $k_{\{i\}\to\{f\}}(t) = tr\{\frac{i}{\hbar}[\hat{H}, \hat{P}_{H}^{\{f\}}(t)]\hat{\rho}_{\{i\}}(0)\}$.

Solution 17.3.2

(a)

Substituting Eqs. (17.3.6, 17.3.8) in Eq. (17.3.7) we obtain

$$\begin{aligned}
k_{\{i\}\to\{f\}}(t) &\cong \sum_{i\in\{i\}} P_i(0) \sum_{f\in\{f\}} k_{i\to f}(t) \\
&= \sum_{i\in\{i\}} \frac{e^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}} \sum_{f\in\{f\}} \frac{d}{dt} tr\{\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\left|\chi_i\right\rangle\left\langle\chi_i\right|\hat{U}^\dagger(t,0)\} \\
&= \frac{d}{dt}\sum_{i\in\{i\}}\sum_{f\in\{f\}} tr\{\left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\frac{e^{-\hat{H}_0/(k_BT)}}{Z_{\{i\}}}\left|\chi_i\right\rangle\left\langle\chi_i\right|\hat{U}^\dagger(t,0)\} \\
&= \frac{d}{dt} tr\{\sum_{f\in\{f\}} \left|\chi_f\right\rangle\left\langle\chi_f\right|\hat{U}(t,0)\frac{e^{-\hat{H}_0/(k_BT)}}{Z_{\{i\}}}\sum_{i\in\{i\}} \left|\chi_i\right\rangle\left\langle\chi_i\right|\hat{U}^\dagger(t,0)\} \\
&= \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{U}(t,0)\frac{e^{-\hat{H}_0/(k_BT)}}{Z_{\{i\}}}\hat{P}_{\{i\}}\hat{U}^\dagger(t,0)\} \ .
\end{aligned}$$

Identifying $Z_{\{i\}} \equiv \sum_{i\in\{i\}} e^{-\varepsilon_i/(k_BT)}$ *(Eq. (17.3.5)) as,* $Z_{\{i\}} = \sum_{i\in\{i\}}\left\langle\chi_i\right|e^{-\hat{H}_0/(k_BT)}\left|\chi_i\right\rangle = tr\{e^{-\hat{H}_0/(k_BT)}\hat{P}_{\{i\}}\}$,

and using the definition of $\hat{\rho}_{\{i\}}(0)$ *(see Eq. (17.3.10)),* $\hat{\rho}_{\{i\}}(0) \equiv \dfrac{e^{-\hat{H}_0/(k_BT)}\hat{P}_{\{i\}}}{tr\{e^{-\hat{H}_0/(k_BT)}\hat{P}_{\{i\}}\}}$ *, we obtain*

$$k_{\{i\}\to\{f\}}(t) \cong \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{U}(t,0)\hat{\rho}_{\{i\}}(0)\hat{U}^\dagger(t,0)\}.$$

(b)

Using $k_{\{i\}\to\{f\}}(t) \cong \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{U}(t,0)\hat{\rho}_{\{i\}}(0)\hat{U}^\dagger(t,0)\}$ *and the definition* $\hat{\rho}(t) = \hat{U}(t,0)\hat{\rho}(0)\hat{U}^\dagger(t,0)$

, we obtain $k_{\{i\}\to\{f\}}(t) \cong tr\{\hat{P}_{\{f\}}\frac{d}{dt}\hat{\rho}_{\{i\}}(t)\}$.

(c)

Using $k_{\{i\}\to\{f\}}(t) \cong \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{U}(t,0)\hat{\rho}_{\{i\}}(0)\hat{U}^\dagger(t,0)\}$ *and the definition of the Heisenberg operators (Eqs. (15.3.16, 15.3.18)),* $\hat{O}_H(t) \equiv \hat{U}^\dagger(t,0)\hat{O}(t)\hat{U}(t,0)$, *where* $\frac{\partial}{\partial t}\hat{O}_H(t) = \frac{i}{\hbar}[\hat{H}_H(t),\hat{O}_H(t)]$, *we obtain*

$$\begin{aligned}
k_{\{i\}\to\{f\}}(t) &= \frac{d}{dt} tr\{\hat{P}_{\{f\}}\hat{U}(t,0)\hat{\rho}_{\{i\}}(0)\hat{U}^\dagger(t,0)\} \\
&= \frac{d}{dt} tr\{\hat{U}^\dagger(t,0)\hat{P}_{\{f\}}\hat{U}(t,0)\hat{\rho}_{\{i\}}(0)\}
\end{aligned}
= tr\{\frac{d}{dt}\hat{P}_H^{\{f\}}(t)\hat{\rho}_{\{i\}}(0)\} = tr\{\frac{i}{\hbar}[\hat{H},\hat{P}_H^{\{f\}}(t)]\hat{\rho}_{\{i\}}(0)\} \ .$$

Exercise 17.3.3 *Use Eq. (17.2.3) for $k^{(1)}_{i\to\{f\}}(t)$, and Eq. (17.3.6) for the thermal weights ({ $P_i(0)$ }), to derive Eq. (17.3.12).*

Solution 17.3.3

Using Eq. (17.3.11) for the approximate transition rates, with the initial thermal weights (Eq. (17.3.6)), and the state-specific rates (Eq. (17.2.3)), we obtain

$$k^{(1)}_{\{i\}\to\{f\}}(t) \cong \sum_{i\in\{i\}} P_i(0) k^{(1)}_{i\to\{f\}}(t)$$

$$= \sum_{i\in\{i\}} \frac{\mathrm{e}^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \sum_{f\in\{f\}} \left|\langle \chi_f | \hat{V} | \chi_i \rangle\right|^2 e^{\frac{i(\varepsilon_f-\varepsilon_i)\tau}{\hbar}} d\tau$$

$$= \sum_{i\in\{i\}} \frac{\mathrm{e}^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \sum_{f\in\{f\}} \langle \chi_i | \hat{V} | \chi_f \rangle \langle \chi_f | \hat{V} | \chi_i \rangle e^{\frac{i(\varepsilon_f-\varepsilon_i)\tau}{\hbar}} d\tau$$

$$= \frac{1}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \sum_{i\in\{i\}} \sum_{f\in\{f\}} \langle \chi_i | \hat{V} | \chi_f \rangle \langle \chi_f | e^{\frac{i\varepsilon_f\tau}{\hbar}} \hat{V} e^{\frac{-i\varepsilon_i\tau}{\hbar}} \mathrm{e}^{-\varepsilon_i/(k_BT)} | \chi_i \rangle d\tau$$

$$= \frac{1}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \sum_{i\in\{i\}} \sum_{f\in\{f\}} \langle \chi_i | \hat{V} | \chi_f \rangle \langle \chi_f | e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{V} e^{\frac{-i\hat{H}_0\tau}{\hbar}} \mathrm{e}^{-\hat{H}_0/(k_BT)} | \chi_i \rangle d\tau .$$

Introducing the projection operators to the initial and final ensembles (Eqs. (17.3.1-17.3.3)), and identifying the initial density operator (Eq. (17.3.10)), the result reads

$$k^{(1)}_{\{i\}\to\{f\}}(t) \cong \frac{1}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \sum_{i\in\{i\}} \langle \chi_i | \hat{V}\hat{P}_{\{f\}} e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{V} e^{\frac{-i\hat{H}_0\tau}{\hbar}} \mathrm{e}^{-\hat{H}_0/(k_BT)} \hat{P}_{\{i\}} | \chi_i \rangle d\tau$$

$$= \frac{1}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t tr\{\hat{V}\hat{P}_{\{f\}} e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{V} e^{\frac{-i\hat{H}_0\tau}{\hbar}} \mathrm{e}^{-\hat{H}_0/(k_BT)} \hat{P}_{\{i\}}\} d\tau$$

$$= \frac{2}{\hbar^2} \mathrm{Re} \int_0^t tr\{\hat{V}\hat{P}_{\{f\}} e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{V} e^{\frac{-i\hat{H}_0\tau}{\hbar}} \frac{\mathrm{e}^{-\hat{H}_0/(k_BT)} \hat{P}_{\{i\}}}{Z_{\{i\}}}\} d\tau$$

$$= \frac{2}{\hbar^2} \mathrm{Re} \int_0^t tr\{\hat{V}\hat{P}_{\{f\}} e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{P}_{\{f\}}\hat{V}\hat{P}_{\{i\}} e^{\frac{-i\hat{H}_0\tau}{\hbar}} \hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\} d\tau$$

$$= \frac{2}{\hbar^2} \mathrm{Re} \int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}} e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{P}_{\{f\}}\hat{V}\hat{P}_{\{i\}} e^{\frac{-i\hat{H}_0\tau}{\hbar}}\} d\tau$$

$$= \frac{2}{\hbar^2} \mathrm{Re} \int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}} e^{\frac{i\hat{H}_0\tau}{\hbar}} \hat{V} e^{\frac{-i\hat{H}_0\tau}{\hbar}}\} d\tau .$$

Exercise 17.3.4 *Use the definition* $\hat{V}_{\{i\},\{f\}} \equiv \hat{P}_{\{f\}}\hat{V}\hat{P}_{\{i\}}$ *and the properties of the projection operators,* $\hat{P}_{\{i\}}$ *and* $\hat{P}_{\{f\}}$ *(Eqs. (17.3.1-17.3.3)), to derive Eq. (17.3.13) from Eq. (17.3.12).*

Solution 17.3.4

Starting from Eq. (17.3.12), and using the properties of the projection operators, $\hat{P}_{\{i\}}$ *and* $\hat{P}_{\{f\}}$ *(Eqs. (17.3.1-17.3.3)), we readily obtain*

$$k^{(1)}_{\{i\}\to\{f\}}(t) \cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}\hat{P}_{\{f\}}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{\{f\}}\hat{V}\hat{P}_{\{i\}}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\left[\hat{V}^{\dagger}_{\{i\},\{f\}}(0)\right]_I\left[\hat{V}_{\{i\},\{f\}}(\tau)\right]_I\}d\tau\,.$$

Exercise 17.3.5 *Use Eq. (17.1.1) for* $k^{(1)}_{i\to f}(t)$*, and Eq. (17.3.6) for the thermal weights (\{* $P_i(0)$ *\}), to derive Eq. (17.3.15) from Eq. (17.3.11).*

Solution 17.3.5

Starting from Eq. (17.3.11), $k_{\{i\}\to\{f\}}(t) \cong \sum_{i\in\{i\}} P_i(0)k^{(1)}_{i\to\{f\}}(t)$*, with the thermal weights,*

$P_i(0) = \frac{\mathrm{e}^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}}$*, we obtain* $k_{\{i\}\to\{f\}}(t) \cong \sum_{i\in\{i\}}\sum_{f\in\{f\}}\frac{\mathrm{e}^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}}k^{(1)}_{i\to f}(t)$*. Using the general expression, Eq. (17.1.1), which applies also for time-dependent interactions,*

$k^{(1)}_{i\to f}(t) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^t dt'\langle\chi_i|\hat{V}_I(t')|\chi_f\rangle\langle\chi_f|\hat{V}_I(t)|\chi_i\rangle$*, we obtain*

$$k_{\{i\}\to\{f\}}(t) \cong \sum_{i\in\{i\}} \sum_{f\in\{f\}} \frac{e^{-\varepsilon_i/(k_B T)}}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' \langle \chi_i | V_I(t') | \chi_f \rangle \langle \chi_f | \hat{V}_I(t) | \chi_i \rangle$$

$$= \sum_{i\in\{i\}} \frac{e^{-\varepsilon_i/(k_B T)}}{Z_{\{i\}}} \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' \langle \chi_i | V_I(t') \sum_{f\in\{f\}} | \chi_f \rangle \langle \chi_f | \hat{V}_I(t) | \chi_i \rangle$$

$$= \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' \sum_{i\in\{i\}} \langle \chi_i | \frac{e^{-\varepsilon_i/(k_B T)}}{Z_{\{i\}}} V_I(t') \hat{P}_{\{f\}} \hat{V}_I(t) \hat{P}_{\{i\}} | \chi_i \rangle$$

$$= \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' tr\{ \frac{e^{-\hat{H}_0/(k_B T)}}{Z_{\{i\}}} V_I(t') \hat{P}_{\{f\}} \hat{V}_I(t) \hat{P}_{\{i\}} \} \ .$$

Using, $\hat{V}_I(t) = e^{\frac{iH_0 t}{\hbar}} \hat{V}(t) e^{\frac{-iH_0 t}{\hbar}}$ *we obtain*

$$k_{\{i\}\to\{f\}}(t) \cong \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' tr\{ \frac{e^{-\hat{H}_0/(k_B T)}}{Z_{\{i\}}} e^{\frac{iH_0 t'}{\hbar}} \hat{V}(t') e^{\frac{-iH_0 t'}{\hbar}} \hat{P}_{\{f\}} e^{\frac{iH_0 t}{\hbar}} \hat{V}(t) e^{\frac{-iH_0 t}{\hbar}} \hat{P}_{\{i\}} \} ,$$

and using the properties of the projection operators (Eqs. (17.3.1-17.3.3)), we obtain

$$k_{\{i\}\to\{f\}}(t) \cong \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' tr\{ \frac{e^{-\hat{H}_0/(k_B T)}}{Z_{\{i\}}} e^{\frac{iH_0 t'}{\hbar}} \hat{P}_{\{i\}} \hat{V}(t') \hat{P}_{\{f\}} e^{\frac{-iH_0 t'}{\hbar}} e^{\frac{iH_0 t}{\hbar}} \hat{P}_{\{f\}} \hat{V}(t) \hat{P}_{\{i\}} e^{\frac{-iH_0 t}{\hbar}} \} .$$

Denoting: $\left[\hat{V}_{\{i\},\{f\}}(t)\right]_I \equiv e^{\frac{iH_0 t}{\hbar}} \hat{P}_{\{f\}} \hat{V}(t) \hat{P}_{\{i\}} e^{\frac{-iH_0 t}{\hbar}}$ *, we finally obtain*

$$k_{\{i\}\to\{f\}}(t) \cong \frac{2}{\hbar^2} \mathrm{Re}\int_0^t dt' tr\{ \frac{e^{-\hat{H}_0/(k_B T)}}{Z_{\{i\}}} \left[\hat{V}^\dagger_{\{i\},\{f\}}(t')\right]_I \left[\hat{V}_{\{i\},\{f\}}(t)\right]_I \} .$$

Exercise 17.3.6 *Replacing the role of the initial and final states, the rate of transition from the thermal ensemble* $\{f\}$ *to the ensemble* $\{i\}$ *is given by Eq. (17.3.18). Use the symmetry of the coupling function (Eq. (17.3.19)) to derive Eq. (17.3.20).*

Solution 17.3.6

Using the expressions for the backward rate (Eq. (17.3.18)) we obtain

$$k_{\{f\}\to\{i\}}(T) = \frac{2\pi}{\hbar} \int d\varepsilon_f \int d\varepsilon_i \frac{e^{-\varepsilon_f/(k_B T)}}{Z_{\{f\}}} \lambda^2_{\{f\},\{i\}}(\varepsilon_i, \varepsilon_f) \rho_{\{f\}}(\varepsilon_f) \rho_{\{i\}}(\varepsilon_i) \delta(\varepsilon_i - \varepsilon_f)$$

$$= \frac{2\pi}{\hbar} \int d\varepsilon_i \frac{e^{-\varepsilon_i/(k_B T)}}{Z_{\{f\}}} \lambda^2_{\{f\},\{i\}}(\varepsilon_i, \varepsilon_i) \rho_{\{f\}}(\varepsilon_i) \rho_{\{i\}}(\varepsilon_i) \ .$$

Similarly, for the forward rate we (Eq. (17.3.16)) we obtain

$$k_{\{i\}\to\{f\}}(T)=\frac{2\pi}{\hbar}\int d\varepsilon_i\int d\varepsilon_f\,\frac{\mathrm{e}^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}}\lambda^2_{\{i\},\{f\}}(\varepsilon_f,\varepsilon_i)\rho_{\{i\}}(\varepsilon_i)\rho_{\{f\}}(\varepsilon_f)\delta(\varepsilon_f-\varepsilon_i)$$

$$=\frac{2\pi}{\hbar}\int d\varepsilon_i\,\frac{\mathrm{e}^{-\varepsilon_i/(k_BT)}}{Z_{\{i\}}}\lambda^2_{\{i\},\{f\}}(\varepsilon_i,\varepsilon_i)\rho_{\{i\}}(\varepsilon_i)\rho_{\{f\}}(\varepsilon_i)\ .$$

Using the symmetry of the coupling function (Eq. (17.3.19)),

$$\lambda^2_{\{f\},\{i\}}(\varepsilon_i,\varepsilon_f)=\left|\langle\chi_i(\varepsilon_i)|\hat{V}|\chi_f(\varepsilon_f)\rangle\right|^2=\left|\langle\chi_f(\varepsilon_f)|\hat{V}|\chi_i(\varepsilon_i)\rangle\right|^2=\lambda^2_{\{i\},\{f\}}(\varepsilon_f,\varepsilon_i)\,,$$

we obtain Eq. (1.3.20),

$$\frac{k_{\{i\}\to\{f\}}(T)}{k_{\{f\}\to\{i\}}(T)}=\frac{Z_{\{f\}}}{Z_{\{i\}}}\,.$$

Exercise 17.3.7 *Let us associate the relative populations of the two ensembles,* $P_{\{i\}}(t)$ *and* $P_{\{f\}}(t)$, *with generic probability-conserving kinetic equations (see Eq. (17.2.1)),*

$$\begin{aligned}\dot{P}_{\{i\}}(t)&=-k_{\{i\}\to\{f\}}P_{\{i\}}(t)+k_{\{f\}\to\{i\}}P_{\{f\}}(t)\\ \dot{P}_{\{f\}}(t)&=-k_{\{f\}\to\{i\}}P_{\{f\}}(t)+k_{\{i\}\to\{f\}}P_{\{i\}}(t)\end{aligned},$$

where, $P_{\{i\}}(t)+P_{\{f\}}(t)=1$. *Show that* $P_{\{i\}}(t)=P_{\{i\}}(0)\,\mathrm{e}^{-(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t}$ $+\dfrac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}}}(1-\mathrm{e}^{-(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t})$, *where* $\lim_{t\to\infty}\dfrac{P_{\{i\}}(t)}{P_{\{f\}}(t)}=\dfrac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}}}$.

Solution 17.3.7

Using $P_{\{i\}}(t)+P_{\{f\}}(t)=1$ *in the kinetic equation, we obtain*

$$\dot{P}_{\{i\}}(t) = -k_{\{i\}\to\{f\}}P_{\{i\}}(t) + k_{\{f\}\to\{i\}}(1 - P_{\{i\}}(t))$$
$$\Rightarrow \dot{P}_{\{i\}}(t) = -(k_{\{i\}\to\{f\}} + k_{\{f\}\to\{i\}})P_{\{i\}}(t) + k_{\{f\}\to\{i\}}$$
$$\Rightarrow \frac{d}{dt}e^{(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t}P_{\{i\}}(t) = k_{\{f\}\to\{i\}}e^{(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t}$$
$$\Rightarrow e^{(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t}P_{\{i\}}(t) = P_{\{i\}}(0) + \frac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}} + k_{\{f\}\to\{i\}}}[e^{(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t} - 1]$$
$$\Rightarrow P_{\{i\}}(t) = P_{\{i\}}(0)e^{-(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t} + \frac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}} + k_{\{f\}\to\{i\}}}[1 - e^{-(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t}] \ .$$

In the infinite time limit,

$$P_{\{i\}}(t) = P_{\{i\}}(0)e^{-(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t} + \frac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}} + k_{\{f\}\to\{i\}}}[1 - e^{-(k_{\{i\}\to\{f\}}+k_{\{f\}\to\{i\}})t}] \xrightarrow[t\to\infty]{} \frac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}} + k_{\{f\}\to\{i\}}} \ ,$$

and therefore $P_{\{f\}}(t) = 1 - P_{\{i\}}(t) \xrightarrow[t\to\infty]{} \dfrac{k_{\{i\}\to\{f\}}}{k_{\{i\}\to\{f\}} + k_{\{f\}\to\{i\}}}$.

Consequently,

$$\frac{P_{\{i\}}(t)}{P_{\{f\}}(t)} \xrightarrow[t\to\infty]{} \frac{k_{\{f\}\to\{i\}}}{k_{\{i\}\to\{f\}}} .$$

18 Thermal Rates in a Bosonic Environment

Exercise 18.1.1 *Use the matrix representations of the spin operators (Eq. (13.1.17)) to identify the explicit form of the nuclear space Hamiltonians (Eq. (18.1.3)), as the diagonal elements of the spin-boson model Hamiltonian (Eq. (18.1.1)).*

Solution 18.1.1

Using Eq. (13.1.17), the matrix representation of the spin-boson model Hamiltonian (Eq. (18.1.1)) in the spin states reads

$$\hat{H} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \sum_{j=1}^{N_\omega} \frac{\hbar\omega_j}{2} (\hat{P}_j^{\,2} + \hat{Q}_j^{\,2}) + \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \gamma \hat{I}_{\mathbf{Q}} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \Delta_E \hat{I}_{\mathbf{Q}} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \sum_{j=1}^{N_\omega} \hbar\omega_j \Delta_j \hat{Q}_j .$$

Denoting the diagonal parts in the spin space as $\begin{bmatrix} \hat{H}_{1,Q} & 0 \\ 0 & \hat{H}_{2,Q} \end{bmatrix}$*, we can readily identify,*

$$\hat{H}_{1,Q} = \Delta_E + \sum_{j=1}^{N_\omega} \hbar\omega_j [\frac{1}{2}(\hat{P}_j^{\,2} + \hat{Q}_j^{\,2}) + \Delta_j \hat{Q}_j] = \Delta_E + \sum_{j=1}^{N_\omega} [\frac{\hbar\omega_j}{2}(\hat{P}_j^{\,2} + \hat{Q}_j^{\,2}) + \hbar\omega_j \Delta_j \hat{Q}_j]$$

$$\hat{H}_{2,Q} = -\Delta_E + \sum_{j=1}^{N_\omega} \hbar\omega_j [\frac{1}{2}(\hat{P}_j^{\,2} + \hat{Q}_j^{\,2}) - \Delta_j \hat{Q}_j] = -\Delta_E + \sum_{j=1}^{N_\omega} [\frac{\hbar\omega_j}{2}(\hat{P}_j^{\,2} + \hat{Q}_j^{\,2}) - \hbar\omega_j \Delta_j \hat{Q}_j],$$

which can also be written as

$$\hat{H}_{1,Q} = \Delta_E + \sum_{j=1}^{N_\omega} \hbar\omega_j [\frac{1}{2}\hat{P}_j^{\,2} + \frac{1}{2}(\hat{Q}_j + \Delta_j)^2] - \sum_{j=1}^{N_\omega} \frac{\hbar\omega_j \Delta_j^2}{2}$$

$$\hat{H}_{2,Q} = -\Delta_E + \sum_{j=1}^{N_\omega} \hbar\omega_j [\frac{1}{2}\hat{P}_j^{\,2} + \frac{1}{2}(\hat{Q}_j - \Delta_j)^2] - \sum_{j=1}^{N_\omega} \frac{\hbar\omega_j \Delta_j^2}{2} .$$

Exercise 18.2.1 *(a) Use Eqs. (18.2.12, 18.2.13, 18.2.15) to rewrite Eq. (18.2.11) as*

$$\hat{H}_{D,\mathbf{q}} = \Delta_E + \frac{\varepsilon_D^0 + \varepsilon_A^0}{2} + \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \left(\frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}\hat{Q}_j^2 + \hbar\omega_j \Delta_j \hat{Q}_j \right)$$

$$\hat{H}_{A,\mathbf{q}} = -\Delta_E + \frac{\varepsilon_D^0 + \varepsilon_A^0}{2} + \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \left(\frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}\hat{Q}_j^2 - \hbar\omega_j \Delta_j \hat{Q}_j \right)$$

(b) Show that Eq. (18.2.14) is obtained by setting the zero of energy to $\frac{\varepsilon_D^0+\varepsilon_A^0}{2}+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2$.

Solution 18.2.1

(a)

Starting from Eq. (18.2.11): $\hat{H}_{D,\mathbf{q}}=\varepsilon_D^0+\sum_j \frac{\hat{p}_j^2}{2m_j}+\frac{1}{2}m_j\omega_j^2(\hat{q}_j-q_{j,D})^2$, *and using the definitions*

(Eq. (18.2.12)): $\hat{Q}_j\equiv\sqrt{\frac{m_j\omega_j}{\hbar}}\left(\hat{q}_j-\frac{q_{j,D}+q_{j,A}}{2}\right)$ *and* $\hat{P}_j\equiv\sqrt{\frac{1}{m_j\hbar\omega_j}}\hat{p}_j$, *we obtain*

$$\hat{H}_{D,\mathbf{q}}=\varepsilon_D^0+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{1}{2}m_j\omega_j^2\left(\sqrt{\frac{\hbar}{m_j\omega_j}}\hat{Q}_j+\frac{\hat{q}_{j,A}-\hat{q}_{j,D}}{2}\right)^2$$

$$=\varepsilon_D^0+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{1}{2}m_j\omega_j^2\frac{\hbar}{m_j\omega_j}\left(\hat{Q}_j+\sqrt{\frac{m_j\omega_j}{\hbar}}\frac{\hat{q}_{j,A}-\hat{q}_{j,D}}{2}\right)^2 .$$

Introducing (Eq. (18.2.15)), $\Delta_j\equiv\sqrt{\frac{m_j\omega_j}{\hbar}}\left(\frac{q_{j,A}-q_{j,D}}{2}\right)$, *we obtain*

$$\hat{H}_{D,\mathbf{q}}=\varepsilon_D^0+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}(\hat{Q}_j+\Delta_j)^2=\varepsilon_D^0+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2+\hbar\omega_j\Delta_j\hat{Q}_j ,$$

and using Eq. (18.2.13), $\varepsilon_D^0-\varepsilon_A^0\equiv 2\Delta_E$, *we finally obtain*

$$\hat{H}_{D,\mathbf{q}}=\frac{\varepsilon_D^0-\varepsilon_A^0}{2}+\frac{\varepsilon_A^0-\varepsilon_D^0}{2}+\varepsilon_D^0+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2+\hbar\omega_j\Delta_j\hat{Q}_j$$

$$=\Delta_E+\frac{\varepsilon_A^0+\varepsilon_D^0}{2}+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2+\hbar\omega_j\Delta_j\hat{Q}_j .$$

Similarly,

$$\hat{H}_{A,\mathbf{q}}=\frac{\varepsilon_D^0-\varepsilon_A^0}{2}+\frac{\varepsilon_A^0-\varepsilon_D^0}{2}+\varepsilon_A^0+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2-\hbar\omega_j\Delta_j\hat{Q}_j$$

$$=-\Delta_E+\frac{\varepsilon_D^0+\varepsilon_A^0}{2}+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2-\hbar\omega_j\Delta_j\hat{Q}_j .$$

(b)

Setting $\frac{\varepsilon_D^0+\varepsilon_A^0}{2}+\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2=0$, *the results of (a) read*

$$\hat{H}_{D,\mathbf{q}}=\Delta_E+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2+\hbar\omega_j\Delta_j\hat{Q}_j$$

$$\hat{H}_{A,\mathbf{q}}=-\Delta_E+\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+\frac{\hbar\omega_j}{2}\hat{Q}_j^2-\hbar\omega_j\Delta_j\hat{Q}_j\ ,$$

or, as in Eq. (18.2.14),

$$\hat{H}_{D,\mathbf{Q}}=\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+E_D(\hat{\mathbf{Q}}) \quad ; \quad E_D(\hat{\mathbf{Q}})=\Delta_E+\sum_j \frac{\hbar\omega_j}{2}\hat{Q}_j^2+\hbar\omega_j\Delta_j\hat{Q}_j$$

$$\hat{H}_{A,\mathbf{Q}}=\sum_j \frac{\hbar\omega_j}{2}\hat{P}_j^2+E_A(\hat{\mathbf{Q}}) \quad ; \quad E_A(\hat{\mathbf{Q}})=-\Delta_E+\sum_j \frac{\hbar\omega_j}{2}\hat{Q}_j^2-\hbar\omega_j\Delta_j\hat{Q}_j\ .$$

Exercise 18.2.2 *For the zero-order Hamiltonian,* $\hat{H}_0$, *as defined in Eqs. (18.2.14, 18.2.16), show that the eigenvectors and eigenvalues are given by Eqs. (18.2.17-18.2.21).*

Solution 18.2.2

The general solution to the Schrodinger equation, $\hat{H}_0|\Psi\rangle=E|\Psi\rangle$, *with the zero order Hamiltonian as defined in Eq. (18.2.14),* $\hat{H}_0=\hat{H}_{D,\mathbf{Q}}\otimes|D\rangle\langle D|+\hat{H}_{A,\mathbf{Q}}\otimes|A\rangle\langle A|$, *can be formally expressed as a sum over all product states in the electronic and the medium degrees of freedom, namely* $|\Psi\rangle=\sum_n d_n|\psi_n\rangle\otimes|D\rangle+\sum_n a_n|\psi_n\rangle\otimes|A\rangle=|\psi_D\rangle\otimes|D\rangle+|\psi_A\rangle\otimes|A\rangle$, *where* $|\psi_D\rangle$ *and* $|\psi_A\rangle$ *are states of the medium. Using* $\langle A|D\rangle=0$, *we obtain*

$$\hat{H}_0|\Psi\rangle=\left[\hat{H}_{D,\mathbf{Q}}\otimes|D\rangle\langle D|+\hat{H}_{A,\mathbf{Q}}\otimes|A\rangle\langle A|\right]\left[|\psi_D\rangle\otimes|D\rangle+|\psi_A\rangle\otimes|A\rangle\right]$$

$$=\left[\hat{H}_{D,\mathbf{Q}}|\psi_D\rangle\right]\otimes|D\rangle+\left[\hat{H}_{A,\mathbf{Q}}|\psi_A\rangle\right]\otimes|A\rangle,$$

where the Schrodinger equation reads

$$\left[\hat{H}_{D,\mathbf{Q}}|\psi_D\rangle\right]\otimes|D\rangle+\left[\hat{H}_{A,\mathbf{Q}}|\psi_A\rangle\right]\otimes|A\rangle=E|\psi_D\rangle\otimes|D\rangle+E|\psi_A\rangle\otimes|A\rangle\ .$$

Projecting on either one of the two orthogonal electronic states $|A\rangle$ *or* $|D\rangle$*, the reduced equation for the medium degrees of freedom is either* $\hat{H}_{D,\mathbf{Q}}|\psi_D\rangle = E|\psi_D\rangle$*, or* $\hat{H}_{A,\mathbf{Q}}|\psi_A\rangle = E|\psi_A\rangle$*, which correspond to the* $\hat{H}_0$*-eigenstates,* $|\psi_D\rangle \otimes |D\rangle$ *or* $|\psi_A\rangle \otimes |A\rangle$*, respectively.*

To express explicitly the eigenstates and eigenvalues for the medium degrees of freedom we use the fact that (up to additive constant) $\hat{H}_{D,\mathbf{Q}}$ *and* $\hat{H}_{A,\mathbf{Q}}$ *(Eq. (18.2.14)) are sums of single Harmonic oscillator Hamiltonians,*

$$\hat{H}_{D,\mathbf{Q}} = \Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j + \Delta_j)^2]$$

$$\hat{H}_{A,\mathbf{Q}} = -\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j - \Delta_j)^2].$$

Consequently (see Ex. 4.3.4), the eigenstates of these Hamiltonians are products of single Hamonic oscillator eigenstates, namely

$$|\psi_D\rangle = |\varphi_{D,n_1}\rangle \otimes |\varphi_{D,n_2}\rangle \otimes \cdots \otimes |\varphi_{D,n_j}\rangle \otimes \cdots \equiv |\chi_{D,\mathbf{n}}\rangle$$

$$|\psi_A\rangle = |\varphi_{A,n_1}\rangle \otimes |\varphi_{A,n_2}\rangle \otimes \cdots \otimes |\varphi_{A,n_j}\rangle \otimes \cdots \equiv |\chi_{A,\mathbf{n}}\rangle.$$

Here, $\langle Q_j | \varphi_{D,n_j}\rangle = \varphi_{n_j}(\hat{Q}_j + \Delta_j)$ *and* $\langle Q_j | \varphi_{A,n_j}\rangle = \varphi_{n_j}(\hat{Q}_j - \Delta_j)$ *are eigenfunctions of the displaced Harmonic oscillators. Each function is associated with a quantum number* n_j *(see chapter 8), where* $\mathbf{n} = n_1, n_2, ...$ *is the vector of quantum numbers associated with all the oscillators in the medium, and the corresponding eigenvalues are sums over the harmonic oscillator eigenvalues,*

$$\varepsilon_{D,\mathbf{n}} = \Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \hbar\omega_j\left(n_j + \frac{1}{2}\right)$$

$$\varepsilon_{A,\mathbf{n}} = -\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \hbar\omega_j\left(n_j + \frac{1}{2}\right).$$

In summary, we obtain Eqs. (18.2.17, 18.2.18),

$$\hat{H}_{D,\mathbf{Q}}|\chi_{D,\mathbf{n}}\rangle = \varepsilon_{D,\mathbf{n}}|\chi_{D,\mathbf{n}}\rangle \quad ; \quad \hat{H}_{A,\mathbf{Q}}|\chi_{A,\mathbf{m}}\rangle = \varepsilon_{A,\mathbf{m}}|\chi_{A,\mathbf{m}}\rangle$$

$$\hat{H}_0|D\rangle \otimes |\chi_{D,\mathbf{n}}\rangle = \varepsilon_{D,\mathbf{n}}|D\rangle \otimes |\chi_{D,\mathbf{n}}\rangle$$

$\hat{H}_0 |A\rangle \otimes |\chi_{A,\mathbf{m}}\rangle = \varepsilon_{A,\mathbf{m}} |A\rangle \otimes |\chi_{A,\mathbf{m}}\rangle$.

Exercise 18.2.3 *(a) Use the explicit expressions for the zero-order Hamiltonian (Eq. (18.2.16)) to show that* $f(\hat{H}_0)|D\rangle = f(\hat{H}_{D,\mathbf{Q}})|D\rangle$ *and* $f(\hat{H}_0)|A\rangle = f(\hat{H}_{A,\mathbf{Q}})|A\rangle$, *where* f *is an analytic function of its argument. (b) Use the results of (a), the interaction operator (Eq. (18.2.16)), and the definitions of the initial and final ensembles (Eqs. (18.2.22, 18.2.24)) to derive Eq. (18.2.26) from Eq. (18.2.25). Notice that the trace over the full electronic and nuclear space can be expressed as* $tr\{\hat{O}\} = tr_{\mathbf{Q}}\{\langle D|\hat{O}|D\rangle + \langle A|\hat{O}|A\rangle\}$.

Solution 18.2.3

(a)

Noticing that $\hat{H}_0 |D\rangle = \left[\hat{H}_{D,\mathbf{Q}}|D\rangle\langle D| + \hat{H}_{A,\mathbf{Q}}|A\rangle\langle A|\right]|D\rangle = \left[\hat{H}_{D,\mathbf{Q}} \otimes |D\rangle\langle D|\right]|D\rangle$,

and that $\left[\hat{H}_{D,\mathbf{Q}}|D\rangle\langle D| + \hat{H}_{A,\mathbf{Q}}|A\rangle\langle A| \;,\; \hat{H}_{D,\mathbf{Q}}|D\rangle\langle D|\right] = 0$, *we obtain (for* $n > 0$*)*

$$\hat{H}_0^n |D\rangle = \hat{H}_0^{n-1}\left[\hat{H}_{D,\mathbf{Q}}|D\rangle\langle D| + \hat{H}_{A,\mathbf{Q}}|A\rangle\langle A|\right]|D\rangle$$
$$= \hat{H}_0^{n-1}\left[\hat{H}_{D,\mathbf{Q}}|D\rangle\langle D|\right]|D\rangle = \left[\hat{H}_{D,\mathbf{Q}}|D\rangle\langle D|\right]\hat{H}_0^{n-1}|D\rangle .$$

Consequently, for $n \geq 0$, $\hat{H}_0^n |D\rangle = \left[\hat{H}_{D,\mathbf{Q}} \otimes |D\rangle\langle D|\right]^n |D\rangle = \left[\hat{H}_{D,\mathbf{Q}}\right]^n |D\rangle$, *and therefore, for any analytic function,* $f(\hat{H}_0) = \sum_{n=0}^{\infty} f_n \hat{H}_0^n$, *we obtain*

$$f(\hat{H}_0)|D\rangle \equiv \sum_{n=0}^{\infty} f_n \hat{H}_0^n |D\rangle = \sum_{n=0}^{\infty} f_n \hat{H}_{D,\mathbf{Q}}^n |D\rangle = f(\hat{H}_{D,\mathbf{Q}})|D\rangle .$$

Similarly,

$$f(\hat{H}_0)|A\rangle \equiv \sum_{n=0}^{\infty} f_n \hat{H}_0^n |A\rangle = \sum_{n=0}^{\infty} f_n \hat{H}_{A,\mathbf{Q}}^n |A\rangle = f(\hat{H}_{A,\mathbf{Q}})|A\rangle .$$

(b)

Starting from Eq. (18.2.25) with $\hat{\rho}_D(0) = \dfrac{\mathrm{e}^{-\hat{H}_0/(k_B T)}\,\hat{P}_D}{tr\{\mathrm{e}^{-\hat{H}_0/(k_B T)}\,\hat{P}_D\}} = \dfrac{\mathrm{e}^{-\hat{H}_0/(k_B T)}\,\hat{P}_D}{Z_D}$, *we obtain*

$$k^{(1)}_{D\to A}(t) \cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_D(0)\hat{P}_D\hat{V}\hat{P}_A e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$= \frac{2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{P}_D\, \mathrm{e}^{-\hat{H}_0/(k_BT)}\, \hat{P}_D\hat{V}\hat{P}_A e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau \ .$$

Using $\hat{P}_D = |D\rangle\langle D|$ *and* $\hat{P}_A = |A\rangle\langle A|$ *as the projection operators, and* $tr\{\hat{O}\} = tr_{\mathbf{Q}}\{\langle D|\hat{O}|D\rangle + \langle A|\hat{O}|A\rangle\}$*, we obtain*

$$\frac{2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{P}_D\, \mathrm{e}^{-\hat{H}_0/(k_BT)}\, \hat{P}_D\hat{V}\hat{P}_A e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$
$$= \frac{2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}}\{\langle D|\mathrm{e}^{-\hat{H}_0/(k_BT)}|D\rangle\langle D|\hat{V}|A\rangle\langle A|e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}|D\rangle\}d\tau$$
$$= \frac{2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}}\{\langle D|\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}|D\rangle\langle D|\hat{V}|A\rangle\langle A|e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}|D\rangle\}d\tau \ ,$$

where in the last step we used the result from (a).

For the interaction term, as defined in Eq. (18.2.16), $\hat{V} = V_{D,A}\left(|D\rangle\langle A| + |A\rangle\langle D|\right)$*, we obtain*

$$k^{(1)}_{D\to A}(t) \cong \frac{2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}}\{\langle D|\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}|D\rangle\langle D|\hat{V}|A\rangle\langle A|e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}|D\rangle\}d\tau$$
$$= \frac{2|V_{D,A}|^2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}}\{\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}\, e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}\}d\tau$$
$$= \frac{2|V_{D,A}|^2}{Z_D\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}}\{\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}\, e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\}d\tau \ ,$$

where in the last step we used a permutation under the trace.

Exercise 18.2.4 *Derive Eq. (18.2.27) from Eq. (18.2.26) by evaluating the trace over the nuclear space using a complete set of eigenstates of the multidimensional Hamiltonian,* $\hat{H}_{D,\mathbf{Q}}$*, and an identity operator, expressed in terms of* $\hat{H}_{A,\mathbf{Q}}$*-eigenstates (Eq. (18.2.18)).*

Solution 18.2.4

Starting from Eq. (18.2.26) and introducing complete orthonormal sets of $\hat{H}_{D,\mathbf{Q}}$ *and* $\hat{H}_{A,\mathbf{Q}}$ *eigenstates,* $\hat{H}_{D,\mathbf{Q}}|\chi_{D,\mathbf{n}}\rangle = \varepsilon_{D,\mathbf{n}}|\chi_{D,\mathbf{n}}\rangle$ *and* $\hat{H}_{A,\mathbf{Q}}|\chi_{A,\mathbf{m}}\rangle = \varepsilon_{A,\mathbf{m}}|\chi_{A,\mathbf{m}}\rangle$, *we obtain Eq. (18.2.27),*

$$k_{D\to A}^{(1)}(t) = \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}}{Z_D}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\}d\tau$$

$$= \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n}}\langle\chi_{D,\mathbf{n}}|\frac{\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}}{Z_D}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}\sum_{\mathbf{m}}|\chi_{A,\mathbf{m}}\rangle\langle\chi_{A,\mathbf{m}}|e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}|\chi_{D,\mathbf{n}}\rangle d\tau$$

$$= \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n}}\langle\chi_{D,\mathbf{n}}|\frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D}e^{\frac{-i\varepsilon_{D,\mathbf{n}}\tau}{\hbar}}\sum_{\mathbf{m}}|\chi_{A,\mathbf{m}}\rangle\langle\chi_{A,\mathbf{m}}|e^{\frac{i\varepsilon_{A,\mathbf{m}}}{\hbar}}|\chi_{D,\mathbf{n}}\rangle d\tau$$

$$= \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n},\mathbf{m}}\frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D}e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}}\left|\langle\chi_{D,\mathbf{n}}|\chi_{A,\mathbf{m}}\rangle\right|^2 d\tau\ .$$

Exercise 18.2.5 *(a) The donor partition function is defined as* $Z_D = \sum_{\mathbf{n}}\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}$. *Use the definition of* $\hat{H}_{D,\mathbf{Q}}$ *(Eq. (18.2.14)) to show that* $Z_D = \mathrm{e}^{-\Delta_E/(k_BT)}\mathrm{e}^{\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2/(k_BT)}Z_{D,1}Z_{D,2}Z_{D,3}\cdots$, *where the* j *th mode partition function reads* $Z_{D,j} \equiv \sum_{n_j}\mathrm{e}^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})} = \frac{\mathrm{e}^{\frac{-\hbar\omega_j}{2k_BT}}}{1-\mathrm{e}^{\frac{-\hbar\omega_j}{k_BT}}}$. *(b) Show that* $e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}} = \mathrm{e}^{\frac{-i\tau}{\hbar}\Delta_E}\mathrm{e}^{\frac{i\tau}{\hbar}\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2}\prod_j\mathrm{e}^{\frac{-i\tau}{\hbar}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}$; $e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}} = \mathrm{e}^{\frac{-i\tau}{\hbar}\Delta_E}\mathrm{e}^{\frac{-i\tau}{\hbar}\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2}\prod_j\mathrm{e}^{\frac{i\tau}{\hbar}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2+(\hat{Q}_j-\Delta_j)^2\right)}$. *(c) Use the results of (a) and (b), and the definitions in Eq. (18.2.30) to derive Eq. (18.2.29) from Eq. (18.2.26). Recall that the trace of a tensor product of operators in a multidimensional space,* $\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N$, *is a product,* $tr\left\{\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N\right\} = tr\left\{\hat{A}_1\right\}\cdot tr\left\{\hat{A}_2\right\}\cdots tr\left\{\hat{A}_N\right\}$ *(Ex. 15.5.1).*

Solution 18.2.5

(a)

Using the explicit expressions for the eigenvalues of $\hat{H}_{D,\mathbf{Q}}$ *(Eqs. (18.2.18, 18.2.21)),*

$\varepsilon_{D,\mathbf{n}} = \Delta_E - \sum_j\frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j\hbar\omega_j\left(n_j+\frac{1}{2}\right)$, *the donor partition function reads*

$$Z_D = \sum_{\mathbf{n}} \mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)} = \sum_{\mathbf{n}} \mathrm{e}^{-[\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \hbar\omega_j \left(n_j+\frac{1}{2}\right)]/(k_BT)}$$

$$= \mathrm{e}^{-[\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2]/(k_BT)} \sum_{n_1,n_2,n_3,\ldots} \mathrm{e}^{-\hbar\omega_1\left(n_1+\frac{1}{2}\right)/(k_BT)} \mathrm{e}^{-\hbar\omega_2\left(n_2+\frac{1}{2}\right)/(k_BT)} \mathrm{e}^{-\hbar\omega_3\left(n_3+\frac{1}{2}\right)/(k_BT)} \cdots$$

$$= \mathrm{e}^{-[\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2]/(k_BT)} \sum_{n_1} \mathrm{e}^{-\hbar\omega_1\left(n_1+\frac{1}{2}\right)/(k_BT)} \sum_{n_2} \mathrm{e}^{-\hbar\omega_2\left(n_2+\frac{1}{2}\right)/(k_BT)} \sum_{n_3} \mathrm{e}^{-\hbar\omega_3\left(n_3+\frac{1}{2}\right)/(k_BT)} \cdots .$$

Defining a single-oscillator partition function,

$$Z_{D,j} = \sum_{n_j} \mathrm{e}^{-\hbar\omega_j\left(n_j+\frac{1}{2}\right)/(k_BT)} = \mathrm{e}^{\frac{-\hbar\omega_j}{2k_BT}} \sum_{n_j} (\mathrm{e}^{\frac{-\hbar\omega_j}{k_BT}})^{n_j} = \frac{\mathrm{e}^{\frac{-\hbar\omega_j}{2k_BT}}}{1-\mathrm{e}^{\frac{-\hbar\omega_j}{k_BT}}}$$ *, we obtain*

$$Z_D = \mathrm{e}^{\frac{-\Delta_E}{k_BT}} \mathrm{e}^{\sum_j \frac{\hbar\omega_j \Delta_j^2}{2k_BT}} Z_{D,1} \cdot Z_{D,2} \cdot Z_{D,3} \cdots .$$

(b)

Using Eq. (18.2.14),

$$\hat{H}_{D,\mathbf{Q}} = \Delta_E + \sum_j \frac{\hbar\omega_j}{2}\left(\hat{P}_j^2 + \hat{Q}_j^2\right) + \hbar\omega_j\Delta_j\hat{Q}_j = \Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j + \Delta_j)^2]$$

$$\hat{H}_{A,\mathbf{Q}} = -\Delta_E + \sum_j \frac{\hbar\omega_j}{2}\left(\hat{P}_j^2 + \hat{Q}_j^2\right) - \hbar\omega_j\Delta_j\hat{Q}_j = -\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j - \Delta_j)^2],$$

we obtain

$$e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}} = \mathrm{e}^{\frac{-i\tau}{\hbar}(\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j+\Delta_j)^2])} = \mathrm{e}^{\frac{-i\tau}{\hbar}\Delta_E} \mathrm{e}^{\frac{i\tau}{\hbar}\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2} \mathrm{e}^{\frac{-i\tau}{\hbar}\sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j+\Delta_j)^2]}$$

$$= \mathrm{e}^{\frac{-i\tau}{\hbar}\Delta_E} \mathrm{e}^{\frac{i\tau}{\hbar}\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2} \prod_j \mathrm{e}^{\frac{-i\tau}{\hbar}\frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j+\Delta_j)^2]} .$$

Similarly,

$$e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}} = \mathrm{e}^{\frac{i\tau}{\hbar}(-\Delta_E - \sum_j \frac{\hbar\omega_j}{2}\Delta_j^2 + \sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j-\Delta_j)^2])} = \mathrm{e}^{\frac{-i\tau}{\hbar}\Delta_E} \mathrm{e}^{\frac{-i\tau}{\hbar}\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2} \mathrm{e}^{\frac{i\tau}{\hbar}\sum_j \frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j-\Delta_j)^2]}$$

$$= \mathrm{e}^{\frac{-i\tau}{\hbar}\Delta_E} \mathrm{e}^{\frac{-i\tau}{\hbar}\sum_j \frac{\hbar\omega_j}{2}\Delta_j^2} \prod_j \mathrm{e}^{\frac{i\tau}{\hbar}\frac{\hbar\omega_j}{2}[\hat{P}_j^2 + (\hat{Q}_j-\Delta_j)^2]} .$$

(c)

Using (a) and (b) we obtain

$$tr_{\mathbf{Q}}\{\frac{e^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}}{Z_D}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\}=tr_{\mathbf{Q}}\{\frac{e^{-\Delta_E/(k_BT)}e^{\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2/(k_BT)}\prod_j e^{\frac{-\hbar\omega_j}{2(k_BT)}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}}{e^{-\Delta_E/(k_BT)}e^{\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2/(k_BT)}\prod_j Z_{D,j}}$$

$$e^{\frac{-i\tau}{\hbar}\Delta_E}e^{\frac{i\tau}{\hbar}\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2}\prod_{j'}e^{\frac{-i\tau}{\hbar}\frac{\hbar\omega_{j'}}{2}\left(\hat{P}_{j'}^2+(\hat{Q}_{j'}+\Delta_{j'})^2\right)}e^{\frac{-i\tau}{\hbar}\Delta_E}e^{\frac{-i\tau}{\hbar}\sum_j\frac{\hbar\omega_j}{2}\Delta_j^2}\prod_{j''}e^{\frac{i\tau}{\hbar}\frac{\hbar\omega_{j''}}{2}\left(\hat{P}_{j''}^2+(\hat{Q}_{j''}-\Delta_{j''})^2\right)}\}$$

$$=e^{\frac{-i\tau}{\hbar}2\Delta_E}\;tr_{\mathbf{Q}}\{\prod_j\frac{1}{Z_{D,j}}e^{\frac{-\hbar\omega_j}{2(k_BT)}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}\prod_{j'}e^{\frac{-i\tau}{\hbar}\frac{\hbar\omega_{j'}}{2}\left(\hat{P}_{j'}^2+(\hat{Q}_{j'}+\Delta_{j'})^2\right)}\prod_{j''}e^{\frac{i\tau}{\hbar}\frac{\hbar\omega_{j''}}{2}\left(\hat{P}_{j''}^2+(\hat{Q}_{j''}-\Delta_{j''})^2\right)}\}$$

$$=e^{\frac{-i\tau}{\hbar}2\Delta_E}\;tr_{\mathbf{Q}}\{\prod_j\frac{1}{Z_{D,j}}e^{\frac{-\hbar\omega_j}{2(k_BT)}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}e^{\frac{-i\tau}{\hbar}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}e^{\frac{i\tau}{\hbar}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2+(\hat{Q}_j-\Delta_j)^2\right)}\}\;,$$

where in the last step we used the fact that the operators associated with different oscillators are associated with different spaces, hence, $\left(\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N\right)\left(\hat{B}_1\otimes\hat{B}_2\otimes\cdots\otimes\hat{B}_3\right)$ $=\left(\hat{A}_1\otimes\hat{B}_1\right)\left(\hat{A}_2\otimes\hat{B}_2\right)\cdots\left(\hat{A}_N\otimes\hat{B}_N\right)$.

Using, $tr\left\{\hat{A}_1\otimes\hat{A}_2\otimes\cdots\otimes\hat{A}_N\right\}=tr\left\{\hat{A}_1\right\}\cdot tr\left\{\hat{A}_2\right\}\cdots tr\left\{\hat{A}_N\right\}$*, we obtain*

$$tr_{\mathbf{Q}}\{\frac{e^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}}{Z_D}e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}}e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\}$$

$$=e^{\frac{-i\tau}{\hbar}2\Delta_E}\prod_j\;tr_{Q_j}\{\frac{1}{Z_{D,j}}e^{\frac{-\hbar\omega_j}{2(k_BT)}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}e^{\frac{-i\tau}{\hbar}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2+(\hat{Q}_j+\Delta_j)^2\right)}e^{\frac{i\tau}{\hbar}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2+(\hat{Q}_j-\Delta_j)^2\right)}\}\;,$$

and therefore, we obtain Eq. (18.2.29),

$$k_{D\to A}^{(1)}(t)=\frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t e^{\frac{-i\tau}{\hbar}2\Delta_E}\prod_j\;c_{D,j}(\tau)d\tau\qquad;\qquad c_{D,j}(\tau)\equiv tr_{Q_j}\{\frac{e^{\frac{-1}{k_BT}\hat{h}_{D,j}}}{Z_{D,j}}e^{\frac{-i\tau}{\hbar}\hat{h}_{D,j}}e^{\frac{i\tau}{\hbar}\hat{h}_{A,j}}\}\,.$$

Exercise 18.2.6 *To prove the identity in Eq. (18.2.31), you can follow these steps: (a) Let* $f(x)$ *be an analytic function of* x*. Prove the identity:* $e^{-\lambda\frac{\partial}{\partial x}}f(x)e^{\lambda\frac{\partial}{\partial x}}=f(x-\lambda)$*. (b) Use the result of (a) to show that the single-mode Hamiltonians at the donor and acceptor states, as defined by Eq. (18.2.30),* *are transformations of a reference Hamiltonian,* $\hat{h}_j = \frac{\hbar\omega_j}{2}\left(\hat{P}_j^2 + \hat{Q}_j^2\right)$*, that is,* $\hat{h}_{D,j} = e^{i\Delta_j \hat{P}_j}\hat{h}_j e^{-i\Delta_j \hat{P}_j}$*, and* $\hat{h}_{A,j} = e^{-i\Delta_j \hat{P}_j}\hat{h}_j e^{i\Delta_j \hat{P}_j}$*. (c) Let* $f(x)$ *be an analytic function of* x*. Show that* $f(\hat{h}_{D,j}) = e^{i\Delta_j \hat{P}_j} f(\hat{h}_j) e^{-i\Delta_j \hat{P}_j}$ *and* $f(\hat{h}_{A,j}) = e^{-i\Delta_j \hat{P}_j} f(\hat{h}_j) e^{i\Delta_j \hat{P}_j}$*. (d) Expressing the dimensionless momentum operator in terms of Dirac's ladder operator,* $\hat{P}_j = \frac{-i}{\sqrt{2}}(\hat{b}_j - \hat{b}_j^\dagger)$*, and defining,* $\hat{b}_j(\tau) = \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\,\hat{b}_j\,\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}$*, show that* $\hat{b}_j(\tau) = \mathrm{e}^{-i\tau\omega_j}\,\hat{b}_j$*. (e) Use the results of (c) and (d) to show that* $c_{D,j}(\tau) = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_B T}\hat{h}_{D,j}}}{Z_{D,j}}\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_{D,j}}\mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_{A,j}}\} = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_B T}\hat{h}_j}}{Z_{D,j}} e^{-\sqrt{2}\Delta_j[\hat{b}_j - \hat{b}_j^\dagger]} e^{\sqrt{2}\Delta_j[\mathrm{e}^{-i\tau\omega_j}\hat{b}_j - \hat{b}_j^\dagger \mathrm{e}^{i\tau\omega_j}]}\}$*. (f) The Baker-Campbell-Hausdorff formula for two operators,* $\hat{A}$ *and* $\hat{B}$*, that commute with their commutator (* $[\hat{A},[\hat{A},\hat{B}]] = [\hat{B},[\hat{A},\hat{B}]] = 0$ *) reads* $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-[\hat{A},\hat{B}]/2}$*. Use it and the commutator,* $\left[\hat{b},\hat{b}^\dagger\right] = 1$*, to show that* $c_{D,j}(\tau) = e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})} tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_B T}\hat{h}_j}}{Z_{D,j}} e^{\sqrt{2}\Delta_j \hat{b}_j^\dagger(1-\mathrm{e}^{i\tau\omega_j})} e^{-\sqrt{2}\Delta_j \hat{b}_j(1-\mathrm{e}^{-i\tau\omega_j})}\}$*. (g) To evaluate the trace over the single-mode space, use a complete set of* $\hat{h}_j$ *-eigenstates,* $\hat{h}_j|\varphi_m\rangle = \hbar\omega_j(m+1/2)|\varphi_m\rangle$*. Recalling that* $\hat{b}_j|\varphi_m\rangle = \sqrt{m}|\varphi_{m-1}\rangle$*, show that* $c_{D,j}(\tau)$ $= \frac{e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})}}{Z_{D,j}}\sum_{m=0}\mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}(m+1/2)}\sum_{n=0}^{m}\left[-2\Delta_j^2|(1-\mathrm{e}^{i\tau\omega_j})|^2\right]^n\frac{m!}{(n!)^2(m-n)!}$*. (h) The Laguerre polynomials of order* m *are defined as* $L_m(x) = \sum_{k=0}^{m}\binom{m}{k}\frac{(-1)^k}{k!}x^k$*, and their generating functions reads* $\sum_{m=0}^{\infty}t^m L_m(x) = \frac{1}{1-t}e^{-tx/(1-t)}$*. Use it to show that* $c_{D,j}(\tau) = e^{2i\Delta_j^2\sin(\omega_j\tau)}e^{-2\Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))}$*, where* $n(\omega_j) = \frac{1}{e^{\hbar\omega_j/(k_B T)}-1}$.

Solution 18.2.6

(a)

Using the Taylor series expansion for $e^{\pm\lambda\frac{\partial}{\partial x}}$*, we obtain* $e^{\pm\lambda\frac{\partial}{\partial x}}f(x) = \sum_{n=0}^{\infty}\frac{(\pm\lambda)^n}{n!}\frac{\partial^n f(x)}{\partial x^n} = f(x\pm\lambda)$*, where we identify the Taylor series expansion of* $f(x\pm\lambda)$*. Consequently,*

$e^{-\lambda\frac{\partial}{\partial x}} f(x) e^{\lambda\frac{\partial}{\partial x}} g(x) = e^{-\lambda\frac{\partial}{\partial x}} f(x) g(x+\lambda) = f(x-\lambda) g(x)$. *Since this holds for any analytic* $g(x)$, *we conclude that* $e^{-\lambda\frac{\partial}{\partial x}} f(x) e^{\lambda\frac{\partial}{\partial x}} = f(x-\lambda)$.

(b)

To express explicitly $e^{\pm i\Delta_j \hat{P}_j}$ *, we recall the definitions of the dimensionless position and momentum operators (Eqs. (18.2.12, 18.2.15)),*

$$\hat{Q}_j \equiv \sqrt{\frac{m_j\omega_j}{\hbar}}\left(\hat{q}_j - \frac{q_{j,D}+q_{j,A}}{2}\right) \Rightarrow \hat{q}_j = \hat{Q}_j\sqrt{\frac{\hbar}{m_j\omega_j}} + \frac{q_{j,D}+q_{j,A}}{2}$$

$$\hat{P}_j \equiv \sqrt{\frac{1}{m_j\hbar\omega_j}}\hat{p}_j = \sqrt{\frac{1}{m_j\hbar\omega_j}}\left(-i\hbar\right)\frac{\partial}{\partial q_j} = \left(-i\hbar\right)\sqrt{\frac{1}{m_j\hbar\omega_j}}\frac{\partial}{\partial q_j}$$

$$= \left(-i\hbar\right)\sqrt{\frac{1}{m_j\hbar\omega_j}}\frac{\partial}{\sqrt{\frac{\hbar}{m_j\omega_j}}\partial Q_j} = -i\frac{\partial}{\partial Q_j} \quad .$$

Consequently, we identify, $e^{\pm i\Delta_j \hat{P}_j} = e^{\pm\Delta_j\frac{\partial}{\partial Q_j}}$.

Given $\hat{h}_j = \frac{\hbar\omega_j}{2}\left(\hat{P}_j^2 + \hat{Q}_j^2\right)$ *and using (a), we obtain*

$$e^{i\Delta_j\hat{P}_j}\hat{h}_j e^{-i\Delta_j\hat{P}_j} = e^{i\Delta_j\hat{P}_j}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2 + \hat{Q}_j^2\right)e^{-i\Delta_j\hat{P}_j}$$

$$= \frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}e^{i\Delta_j\hat{P}_j}\hat{Q}_j^2 e^{-i\Delta_j\hat{P}_j} = \frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}e^{\Delta_j\frac{\partial}{\partial Q_j}}\hat{Q}_j^2 e^{-\Delta_j\frac{\partial}{\partial Q_j}}$$

$$= \frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}(\hat{Q}_j + \Delta_j)^2 = \hat{h}_{D,j}$$

$$e^{-i\Delta_j\hat{P}_j}\hat{h}_j e^{i\Delta_j\hat{P}_j} = e^{-i\Delta_j\hat{P}_j}\frac{\hbar\omega_j}{2}\left(\hat{P}_j^2 + \hat{Q}_j^2\right)e^{i\Delta_j\hat{P}_j}$$

$$= \frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}e^{-i\Delta_j\hat{P}_j}\hat{Q}_j^2 e^{i\Delta_j\hat{P}_j} = \frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}e^{-\Delta_j\frac{\partial}{\partial Q_j}}\hat{Q}_j^2 e^{\Delta_j\frac{\partial}{\partial Q_j}}$$

$$= \frac{\hbar\omega_j}{2}\hat{P}_j^2 + \frac{\hbar\omega_j}{2}(\hat{Q}_j - \Delta_j)^2 = \hat{h}_{A,j} \; .$$

(c)

First, we notice that for analytic $f(\hat{A})=\sum_{n=0}^{\infty} f_n \hat{A}^n$ *, we have,* $\hat{O}^{-1} f(\hat{A})\hat{O} = f(\hat{O}^{-1}\hat{A}\hat{O})$. *This can be readily verified by considering any power,* $\hat{A}^n$ *,*

$$\hat{O}^{-1}\left(\hat{A}\right)^n \hat{O} = \underbrace{\left(\hat{O}^{-1}\hat{A}\hat{O}\right)\left(\hat{O}^{-1}\hat{A}\hat{O}\right)\cdots\left(\hat{O}^{-1}\hat{A}\hat{O}\right)}_{n \;\; times} = \left(\hat{O}^{-1}\hat{A}\hat{O}\right)^n \cdot$$

Particularly:

$$e^{i\Delta_j \hat{P}_j}\left(\hat{h}_j\right)^n e^{-i\Delta_j \hat{P}_j} = \underbrace{\left(e^{i\Delta_j \hat{P}_j}\hat{h}_j e^{-i\Delta_j \hat{P}_j}\right)\left(e^{i\Delta_j \hat{P}_j}\hat{h}_j e^{-i\Delta_j \hat{P}_j}\right)\cdots\left(e^{i\Delta_j \hat{P}_j}\hat{h}_j e^{-i\Delta_j \hat{P}_j}\right)}_{n \;\; times} = \left(\hat{h}_{D,j}\right)^n$$

$$e^{-i\Delta_j \hat{P}_j}\left(\hat{h}_j\right)^n e^{i\Delta_j \hat{P}_j} = \underbrace{\left(e^{-i\Delta_j \hat{P}_j}\hat{h}_j e^{i\Delta_j \hat{P}_j}\right)\left(e^{-i\Delta_j \hat{P}_j}\hat{h}_j e^{i\Delta_j \hat{P}_j}\right)\cdots\left(e^{-i\Delta_j \hat{P}_j}\hat{h}_j e^{i\Delta_j \hat{P}_j}\right)}_{n \;\; times} = \left(\hat{h}_{A,j}\right)^n \;,$$

and therefore, $f(\hat{h}_{D,j}) = e^{i\Delta_j \hat{P}_j} f(\hat{h}_j) e^{-i\Delta_j \hat{P}_j}$ *, and* $f(\hat{h}_{D,j}) = e^{i\Delta_j \hat{P}_j} f(\hat{h}_j) e^{-i\Delta_j \hat{P}_j}$.

(d)

We start from $\hat{b}_j(\tau) \equiv \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\,\hat{b}_j\,\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}$ *, and introduce an identity, expanded in terms of the harmonic oscillator eigenstates,* $\mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\,\hat{b}_j\,\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j} = \sum_n \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\,\hat{b}_j\left|n\right\rangle\left\langle n\right|\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}$. *Recalling Eq. (8.5.3) for the harmonic oscillator annihilation operator,* $\hat{b}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle$ *, we obtain*

$$\hat{b}_j(\tau) = \sum_n \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\,\hat{b}_j\left|n\right\rangle\left\langle n\right|\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j} = \sum_n \sqrt{n}\,\mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\left|n-1\right\rangle\left\langle n\right|\mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}$$
$$= \sum_n \mathrm{e}^{\frac{i\tau}{\hbar}\hbar\omega_j(n-1/2)}\sqrt{n}\left|n-1\right\rangle\left\langle n\right|\mathrm{e}^{\frac{-i\tau}{\hbar}\hbar\omega_j(n+1/2)} = \mathrm{e}^{-i\tau\omega_j}\sum_n \sqrt{n}\left|n-1\right\rangle\left\langle n\right| = \mathrm{e}^{-i\tau\omega_j}\sum_n \hat{b}_j\left|n\right\rangle\left\langle n\right|$$
$$= \mathrm{e}^{-i\tau\omega_j}\,\hat{b}_j \,,$$

and similarly (or by Hermitian conjugation), we obtain

$$\hat{b}_j^\dagger(\tau) = \mathrm{e}^{i\tau\omega_j}\,\hat{b}_j^\dagger .$$

(e)

Using the results of (c), we obtain

$$c_{D,j}(\tau) \equiv tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_{D,j}}}{Z_{D,j}} \mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_{D,j}} \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_{A,j}}\} = tr_{Q_j}\{e^{i\Delta_j\hat{P}_j} \frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} \mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j} e^{-i\Delta_j\hat{P}_j} e^{-i\Delta_j\hat{P}_j} \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j} e^{i\Delta_j\hat{P}_j}\}$$

$$= tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} \mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j} e^{-2i\Delta_j\hat{P}_j} \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j} e^{2i\Delta_j\hat{P}_j}\} = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-2i\Delta_j\hat{P}_j} \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j} e^{2i\Delta_j\hat{P}_j} \mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}\}$$

$$= tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-i2\Delta_j\hat{P}_j} e^{2i\Delta_j \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\hat{P}_j \mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}}\} \ ,$$

where in the last step we used again the general property for analytic $f(\hat{A})$, $\hat{O}^{-1}f(\hat{A})\hat{O} = f(\hat{O}^{-1}\hat{A}\hat{O})$. *Using* $\hat{P}_j = \frac{-i}{\sqrt{2}}(\hat{b}_j - \hat{b}_j^\dagger)$ *and the results of (d) we obtain,*

$$c_{D,j}(\tau) = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-i2\Delta_j\hat{P}_j} e^{2i\Delta_j \mathrm{e}^{\frac{i\tau}{\hbar}\hat{h}_j}\hat{P}_j \mathrm{e}^{\frac{-i\tau}{\hbar}\hat{h}_j}}\}$$

$$= tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-2i\Delta_j\frac{-i}{\sqrt{2}}(\hat{b}_j-\hat{b}_j^\dagger)} e^{2i\Delta_j\frac{-i}{\sqrt{2}}(\hat{b}_j(\tau)-\hat{b}_j^\dagger(\tau))}\} = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-\sqrt{2}\Delta_j[\hat{b}_j-\hat{b}_j^\dagger]} e^{\sqrt{2}\Delta_j[\hat{b}_j(\tau)-\hat{b}_j^\dagger(\tau)]}\}$$

$$= tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-\sqrt{2}\Delta_j[\hat{b}_j-\hat{b}_j^\dagger]} e^{\sqrt{2}\Delta_j[\mathrm{e}^{-i\tau\omega_j}\hat{b}_j-\hat{b}_j^\dagger \mathrm{e}^{i\tau\omega_j}]}\}.$$

(f)

Using the Baker-Campbell-Hausdorff formula, for $[\hat{A},[\hat{A},\hat{B}]] = [\hat{B},[\hat{A},\hat{B}]] = 0$, *we have,* $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-[\hat{A},\hat{B}]/2}$, *or* $e^{\hat{A}+\hat{B}} = e^{\hat{B}}e^{\hat{A}}e^{[\hat{A},\hat{B}]/2}$, *and therefore also* $e^{\hat{A}}e^{\hat{B}} = e^{\hat{B}}e^{\hat{A}}e^{[\hat{A},\hat{B}]}$. *Using additionally,* $\left[\hat{b},\hat{b}^\dagger\right] = 1$, *we obtain* $e^{-\sqrt{2}\Delta_j[\hat{b}_j-\hat{b}_j^\dagger]} = e^{-\sqrt{2}\Delta_j\hat{b}_j}e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger}e^{\Delta_j^2}$ *and* $e^{-\sqrt{2}\Delta_j[\hat{b}_j^\dagger \mathrm{e}^{i\tau\omega_j}-\mathrm{e}^{-i\tau\omega_j}\hat{b}_j]} = e^{-\sqrt{2}\Delta_j\hat{b}_j^\dagger \mathrm{e}^{i\tau\omega_j}} e^{\sqrt{2}\Delta_j \mathrm{e}^{-i\tau\omega_j}\hat{b}_j} e^{-\Delta_j^2}$. *Consequently,*

$$c_{D,j}(\tau) = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-\sqrt{2}\Delta_j[\hat{b}_j-\hat{b}_j^\dagger]} e^{\sqrt{2}\Delta_j[\mathrm{e}^{-i\tau\omega_j}\hat{b}_j-\hat{b}_j^\dagger \mathrm{e}^{i\tau\omega_j}]}\} = tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-\sqrt{2}\Delta_j\hat{b}_j} e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-\mathrm{e}^{i\tau\omega_j})} e^{\sqrt{2}\Delta_j \mathrm{e}^{-i\tau\omega_j}\hat{b}_j}\}$$

$$= tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})} e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-\mathrm{e}^{i\tau\omega_j})} e^{-\sqrt{2}\Delta_j\hat{b}_j} e^{\sqrt{2}\Delta_j \mathrm{e}^{-i\tau\omega_j}\hat{b}_j}\}$$

$$= e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})} tr_{Q_j}\{\frac{\mathrm{e}^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-\mathrm{e}^{i\tau\omega_j})} e^{-\sqrt{2}\Delta_j\hat{b}_j(1-\mathrm{e}^{-i\tau\omega_j})}\} \ .$$

(g)

Calculating the trace explicitly, using a complete set of $\hat{h}_j$ *-eigenstates, we obtain*

$$c_{D,j}(\tau) = e^{-2\Delta_j^2(1-e^{i\tau\omega_j})} tr_{Q_j}\{\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_{D,j}} e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-e^{i\tau\omega_j})} e^{-\sqrt{2}\Delta_j\hat{b}_j(1-e^{-i\tau\omega_j})}\}$$

$$= \frac{e^{-2\Delta_j^2(1-e^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0}^{\infty} e^{\frac{-\hbar\omega_j}{k_BT}(m+1/2)} \langle m | e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-e^{i\tau\omega_j})} e^{-\sqrt{2}\Delta_j\hat{b}_j(1-e^{-i\tau\omega_j})} | m \rangle$$

$$= \frac{e^{-2\Delta_j^2(1-e^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0}^{\infty} e^{\frac{-\hbar\omega_j}{k_BT}(m+1/2)} \langle m | e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-e^{i\tau\omega_j})} \sum_{n=0}^{m} \frac{\left[-\sqrt{2}\Delta_j(1-e^{-i\tau\omega_j})\right]^n}{n!} \hat{b}_j^n | m \rangle ,$$

where in the last step we consider that $\hat{b}_j | m \rangle = \sqrt{m} | m-1 \rangle$, *and consequently* $\hat{b}_j^n | m \rangle$ *vanishes for* $n > m$. *Similarly,*

$$c_{D,j}(\tau) = \frac{e^{-2\Delta_j^2(1-e^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0}^{\infty} e^{\frac{-\hbar\omega_j}{k_BT}(m+1/2)} \langle m | e^{\sqrt{2}\Delta_j\hat{b}_j^\dagger(1-e^{i\tau\omega_j})} \sum_{n=0}^{m} \frac{\left[-\sqrt{2}\Delta_j(1-e^{-i\tau\omega_j})\right]^n}{n!} \hat{b}_j^n | m \rangle$$

$$= \frac{e^{-2\Delta_j^2(1-e^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0}^{\infty} e^{\frac{-\hbar\omega_j}{k_BT}(m+1/2)} \sum_{n',n=0}^{m} \langle m | \left(\hat{b}_j^\dagger\right)^{n'} \frac{\left[\sqrt{2}\Delta_j(1-e^{i\tau\omega_j})\right]^{n'}}{n'!} \frac{\left[-\sqrt{2}\Delta_j(1-e^{-i\tau\omega_j})\right]^n}{n!} \hat{b}_j^n | m \rangle$$

$$= \frac{e^{-2\Delta_j^2(1-e^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0}^{\infty} e^{\frac{-\hbar\omega_j}{k_BT}(m+1/2)}$$

$$\sum_{n',n=0}^{m} \langle m-n' | \sqrt{\frac{m!}{(m-n')!}} \frac{\left[\sqrt{2}\Delta_j(1-e^{i\tau\omega_j})\right]^{n'}}{n'!} \frac{\left[-\sqrt{2}\Delta_j(1-e^{-i\tau\omega_j})\right]^n}{n!} \sqrt{\frac{m!}{(m-n)!}} | m-n \rangle$$

$$= \frac{e^{-2\Delta_j^2(1-e^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0}^{\infty} e^{\frac{-\hbar\omega_j}{k_BT}(m+1/2)} \sum_{n=0}^{m} \left[-2\Delta_j^2 |(1-e^{i\tau\omega_j})|^2\right]^n \frac{m!}{(n!)^2 (m-n)!} \quad .$$

(h)

Using their definition, $L_m(x) = \sum_{k=0}^{m} \binom{m}{k} \frac{(-1)^k}{k!} x^k$, *we can identify the Laguerre polynomials of order* m *in the expression for* $c_{D,j}(\tau)$,

$$c_{D,j}(\tau) = \frac{e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})}}{Z_{D,j}} \sum_{m=0} \mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}(m+1/2)} \sum_{n=0}^{m} \left[-2\Delta_j^2 |(1-\mathrm{e}^{i\tau\omega_j})|^2\right]^n \frac{m!}{(n!)^2 (m-n)!}$$

$$= \frac{e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})}}{Z_{D,j}} \mathrm{e}^{\frac{-\hbar\omega_j}{2k_B T}} \sum_{m=0} \left(\mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}}\right)^m L_m(2\Delta_j^2 |(1-\mathrm{e}^{i\tau\omega_j})|^2) \ .$$

Using the identity, $\sum_{m=0}^{\infty} t^m L_m(x) = \frac{1}{1-t} e^{-tx/(1-t)}$*, we obtain*

$$c_{D,j}(\tau) = \frac{e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})}}{Z_{D,j}} \frac{\mathrm{e}^{\frac{-\hbar\omega_j}{2k_B T}}}{1-\mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}}} e^{-2\Delta_j^2 |(1-\mathrm{e}^{i\tau\omega_j})|^2 \frac{\mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}}}{1-\mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}}}} \ .$$

Recalling the definition of the harmonic oscillator partition function (Ex. 18.2.5), $Z_{D,j} = \mathrm{e}^{\frac{-\hbar\omega_j}{2k_B T}} / (1-\mathrm{e}^{\frac{-\hbar\omega_j}{k_B T}})$*, and introducing,* $n(\omega_j) = \frac{1}{e^{\hbar\omega_j/(k_B T)} - 1}$*, we finally obtain:*

$$c_{D,j}(\tau) = e^{-2\Delta_j^2(1-\mathrm{e}^{i\tau\omega_j})} e^{-2\Delta_j^2 |(1-\mathrm{e}^{i\tau\omega_j})|^2 n(\omega_j)} = e^{-2\Delta_j^2(1-\cos(\omega_j\tau)-i\sin(\omega_j\tau))} e^{-4\Delta_j^2(1-\cos(\omega_j\tau))n(\omega_j)}$$
$$= e^{2i\Delta_j^2 \sin(\omega_j\tau)} e^{-2\Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))} \ .$$

Exercise 18.2.7 *The averaged occupation number of a harmonic mode at a frequency,* ω_j*, and a temperature,* T*, is defined as* $n(\omega_j) = \frac{1}{Z}\sum_{n=0}^{\infty} n e^{-\hbar\omega_j n/(k_B T)}$*, where* $Z = \sum_{n'=0}^{\infty} e^{-\hbar\omega_j n'/(k_B T)}$*. Show that* $n(\omega_j) = \frac{e^{-\hbar\omega_j/(k_B T)}}{1-e^{-\hbar\omega_j/(k_B T)}}$.

Solution 18.2.7

Using $\beta = 1/(k_B T)$,

$$n(\omega_j) = \frac{1}{\sum_{n'=0}^{\infty} e^{-\beta\hbar\omega_j n'}} \sum_{n=0}^{\infty} n e^{-\beta\hbar\omega_j n} = \frac{1}{\sum_{n'=0}^{\infty} e^{-\beta\hbar\omega_j n'}} \frac{-\partial}{\partial(\beta\hbar\omega_j)} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_j n}$$

$$= \left(1-e^{-\beta\hbar\omega_j}\right) \frac{-\partial}{\partial(\beta\hbar\omega_j)} \frac{1}{1-e^{-\beta\hbar\omega_j}} = \left(1-e^{-\beta\hbar\omega_j}\right) \frac{e^{-\beta\hbar\omega_j}}{\left(1-e^{-\beta\hbar\omega_j}\right)^2} = \frac{e^{-\beta\hbar\omega_j}}{1-e^{-\beta\hbar\omega_j}} \ .$$

Exercise 18.2.8 *Derive Eq. (18.2.34) by taking the upper limit of the time-integral in Eq. (18.2.27) to infinity and using a suitable definition of Dirac's delta. Use the fact that the real part of the integrand is an even function of time.*

Solution 18.2.8

Starting from Eq. (18.2.27) and replacing the upper integration limit by infinity, we obtain

$$k^{(1)}_{D\to A}(t) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{m},\mathbf{n}} \frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D} e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}} \left|V_{D,A}\left\langle \chi_{D,\mathbf{n}} \middle| \chi_{A,\mathbf{m}}\right\rangle\right|^2 d\tau$$

$$\cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty \sum_{\mathbf{m},\mathbf{n}} \frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D} e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}} \left|V_{D,A}\left\langle \chi_{D,\mathbf{n}} \middle| \chi_{A,\mathbf{m}}\right\rangle\right|^2 d\tau$$

$$= \frac{1}{\hbar^2}\mathrm{Re}\int_{-\infty}^\infty \sum_{\mathbf{m},\mathbf{n}} \frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D} e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}} \left|V_{D,A}\left\langle \chi_{D,\mathbf{n}} \middle| \chi_{A,\mathbf{m}}\right\rangle\right|^2 d\tau \quad .$$

Using the identity, $\int_{-\infty}^{\infty} d\tau e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}} = 2\pi\hbar\delta(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})$, *we obtain*

$$k^{(1)}_{D\to A}(t) \approx \frac{1}{\hbar^2}\mathrm{Re}\int_{-\infty}^\infty \sum_{\mathbf{m},\mathbf{n}} \frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D} e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}} \left|V_{D,A}\left\langle \chi_{D,\mathbf{n}} \middle| \chi_{A,\mathbf{m}}\right\rangle\right|^2 d\tau$$

$$= \frac{1}{\hbar^2}\mathrm{Re}\sum_{\mathbf{m},\mathbf{n}} \frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D} \left|V_{D,A}\left\langle \chi_{D,\mathbf{n}} \middle| \chi_{A,\mathbf{m}}\right\rangle\right|^2 \int_{-\infty}^\infty e^{\frac{-i(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}})\tau}{\hbar}} d\tau$$

$$= \frac{2\pi}{\hbar}\sum_{\mathbf{m},\mathbf{n}} \frac{\mathrm{e}^{-\varepsilon_{D,\mathbf{n}}/(k_BT)}}{Z_D} \left|V_{D,A}\left\langle \chi_{D,\mathbf{n}} \middle| \chi_{A,\mathbf{m}}\right\rangle\right|^2 \delta(\varepsilon_{D,\mathbf{n}}-\varepsilon_{A,\mathbf{m}}) \quad .$$

Exercise 18.2.9 *Use Eqs. (18.2.36, 18.2.38) in Eq. (18.2.33) to express the rate, Eq. (18.2.39), in terms of the reorganization energy, defined in Eq. (18.2.40).*

Solution 18.2.9

Substitution of the approximations, $n(\omega_j) \approx \frac{k_BT}{\hbar\omega_j} >> 1$, $\sin(\omega_j\tau) \approx \omega_j\tau$, *and* $\cos(\omega_j\tau) \approx 1-\omega_j^2\tau^2/2$

, *in Eq. (18.2.33), we obtain*

$$k^{(1)}_{D\to A}(t) = \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}2\Delta_E} e^{2i\sum_j \Delta_j^2 \sin(\omega_j\tau)} e^{-2\sum_j \Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))} d\tau$$

$$\cong \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}2\Delta_E} e^{2i\sum_j \Delta_j^2 \sin(\omega_j\tau)} e^{-2\sum_j \Delta_j^2(1-\cos(\omega_j\tau))\frac{2k_BT}{\hbar\omega_j}} d\tau$$

$$\cong \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}2\Delta_E} e^{2i\sum_j \Delta_j^2 \omega_j\tau} e^{-2\sum_j \Delta_j^2\omega_j\tau^2\frac{k_BT}{\hbar}} d\tau \ .$$

Using the definition of the reorganization energy, $E_\lambda = \sum_j 2\Delta_j^2\omega_j\hbar$, *we obtain Eq. (18.2.39),*

$$k^{(1)}_{D\to A}(t) \cong \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}2\Delta_E} e^{2i\sum_j \Delta_j^2 \omega_j\tau} e^{-2\sum_j \Delta_j^2\omega_j\tau^2\frac{k_BT}{\hbar}} d\tau$$

$$= \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}2\Delta_E} e^{iE_\lambda\tau/\hbar} e^{\frac{-E_\lambda k_BT\tau^2}{\hbar^2}} d\tau$$

$$= \frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E - E_\lambda)} e^{\frac{-E_\lambda k_BT\tau^2}{\hbar^2}} d\tau \ .$$

Exercise 18.2.10 *Show that Eq. (18.2.41) reproduces the reorganization energy as defined in Eq. (18.2.40), where* $E_D(\hat{\mathbf{Q}})$ *and* $E_A(\hat{\mathbf{Q}})$ *are the donor and acceptor potential energy surfaces, defined in Eq. (18.2.14).*

Solution 18.2.10

The definitions of E_λ *in terms of the donor or acceptor potential energy functions (Eq. (18.2.41)) read* $E_\lambda = E_D(\mathbf{\Delta}) - E_D(-\mathbf{\Delta})$, *or* $E_\lambda = E_A(-\mathbf{\Delta}) - E_A(\mathbf{\Delta})$, *respectively. Using the explicit expressions (Eq. (18.2.14)),* $E_D(\hat{\mathbf{Q}}) = \Delta_E + \sum_j \frac{\hbar\omega_j}{2}\hat{Q}_j^2 + \hbar\omega_j\Delta_j\hat{Q}_j$ *and* $E_A(\hat{\mathbf{Q}}) = -\Delta_E + \sum_j \frac{\hbar\omega_j}{2}\hat{Q}_j^2 - \hbar\omega_j\Delta_j\hat{Q}_j$, *we obtain*

$$E_\lambda = E_D(\mathbf{\Delta}) - E_D(-\mathbf{\Delta}) = \Delta_E + \sum_j \left(\frac{\hbar\omega_j}{2}\Delta_j^2 + \hbar\omega_j\Delta_j\Delta_j\right) - \Delta_E - \sum_j \left(\frac{\hbar\omega_j}{2}\Delta_j^2 - \hbar\omega_j\Delta_j\Delta_j\right)$$

$$= \left(\sum_j \hbar\omega_j\Delta_j\Delta_j\right) - \left(\sum_j -\hbar\omega_j\Delta_j\Delta_j\right) = \sum_j 2\hbar\omega_j\Delta_j^2 \ ,$$

$$E_\lambda = E_A(-\mathbf{\Delta}) - E_A(\mathbf{\Delta}) = -\Delta_E + \sum_j \left(\frac{\hbar\omega_j}{2}\Delta_j^2 + \hbar\omega_j\Delta_j\Delta_j\right) + \Delta_E - \sum_j \left(\frac{\hbar\omega_j}{2}\Delta_j^2 - \hbar\omega_j\Delta_j\Delta_j\right)$$

$$= \left(\sum_j \hbar\omega_j\Delta_j\Delta_j\right) - \left(\sum_j -\hbar\omega_j\Delta_j\Delta_j\right) = \sum_j 2\hbar\omega_j\Delta_j^2 \ ,$$

in consistency with Eq. (18.2.40).

Exercise 18.2.11 *Change the time limit in Eq. (18.2.39) to infinity (notice that the real part of the integrand is an even function of time) to obtain the result in Eq. (18.2.43). Use the identity,* $\int_{-\infty}^{\infty} dk e^{-zk^2} e^{ikx} = \sqrt{\frac{\pi}{z}} e^{\frac{-x^2}{4z}}$.

Solution 18.2.11

Starting from Eq. (18.2.39), and replacing the upper integration limit by infinity, we obtain

$$k_{D\to A}^{(1)}(t) = \frac{2|V_{D,A}|^2}{\hbar^2} \mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E - E_\lambda)} e^{\frac{-E_\lambda k_B T \tau^2}{\hbar^2}} d\tau$$

$$\cong \frac{2|V_{D,A}|^2}{\hbar^2} \mathrm{Re}\int_0^\infty \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E - E_\lambda)} e^{\frac{-E_\lambda k_B T \tau^2}{\hbar^2}} d\tau$$

$$= \frac{|V_{D,A}|^2}{\hbar^2} \mathrm{Re}\int_{-\infty}^\infty \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E - E_\lambda)} e^{\frac{-E_\lambda k_B T \tau^2}{\hbar^2}} d\tau \ .$$

Using $\int_{-\infty}^{\infty} dk e^{-zk^2} e^{ikx} = \sqrt{\frac{\pi}{z}} e^{\frac{-x^2}{4z}}$ *, we obtain Eq. (18.2.43),*

$$k_{D\to A}^{(1)}(t) \cong \frac{|V_{D,A}|^2}{\hbar^2} \mathrm{Re}\int_{-\infty}^\infty \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E - E_\lambda)} e^{\frac{-E_\lambda k_B T \tau^2}{\hbar^2}} d\tau$$

$$= \frac{|V_{D,A}|^2}{\hbar^2} \sqrt{\frac{\pi\hbar^2}{k_B T E_\lambda}} e^{\frac{-(E_\lambda - 2\Delta_E)^2}{4KTE_\lambda}}$$

$$= |V_{D,A}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} e^{\frac{-(E_\lambda - 2\Delta_E)^2}{4KTE_\lambda}} \ .$$

Exercise 18.2.12 *(a) Show that the maximal state-to-state coupling matrix element between the donor an acceptor eigenstates is* $|V_{DA}|$*, and use Eqs. (18.2.28, 18.2.42) to obtain the validity condition, Eq. (18.2.45). (b) Show that this condition also assures that* $t_d << \frac{1}{k_{D\to A}}$ *(the wide band limit, Eq. (17.2.8)).*

Solution 18.2.12

(a)

The eigenstates of the zero order Hamiltonian (Eq. (18.2.17)) read: $\hat{H}_0 |D\rangle \otimes |\chi_{D,\mathbf{n}}\rangle = \varepsilon_{D,\mathbf{n}} |D\rangle \otimes |\chi_{D,\mathbf{n}}\rangle$*, or* $\hat{H}_0 |A\rangle \otimes |\chi_{A,\mathbf{m}}\rangle = \varepsilon_{A,\mathbf{m}} |A\rangle \otimes |\chi_{A,\mathbf{m}}\rangle$*, and the interaction operator reads (Eq. (18.2.16)),* $\hat{V} = V_{D,A}\left(|D\rangle\langle A| + |A\rangle\langle D|\right)$*. Consequently, the coupling matrix elements obtain the form,* $V_{D,A}\langle \chi_{D,\mathbf{n}} | \chi_{A,\mathbf{m}}\rangle$*. Since the (multi-dimensional) overlap integrals between the displaces Harmonic oscillators eigenstates are bounded,* $0 \le \langle \chi_{D,\mathbf{n}} | \chi_{A,\mathbf{m}}\rangle \le 1$*, the maximal absolute value of the state-to-state coupling matrix element between the donor an acceptor is* $|V_{DA}|$*. Consequently, the validity of the perturbative expression for the rate (Eq. (18.2.28)) is limited by,* $t << \hbar / |V_{D,A}|$*. A necessary condition for the validity of Eq. (18.2.43) is that the integral decay time is much shorter than this limiting time, namely,* $t >> t_d$*, where* $t_d \equiv \frac{\hbar}{\sqrt{2E_\lambda k_B T}}$ *(Eq. (18.2.42)). This implies that a necessary condition for the validity of Eq. (18.2.43) reads* $\frac{\hbar}{\sqrt{2E_\lambda k_B T}} << \hbar / |V_{D,A}|$*, and therefore,* $\frac{|V_{D,A}|^2}{2k_B T E_\lambda} << 1$ *(Eq. (18.2.45)).*

(b)

To show that this condition also assures that $t_d << \frac{1}{k_{D\to A}}$ *we require the latter to hold for* $t_d \equiv \frac{\hbar}{\sqrt{2E_\lambda k_B T}}$ *and* $k_{D\to A} = |V_{D,A}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} e^{\frac{-(E_\lambda - 2\Delta_E)^2}{4k_B T E_\lambda}}$*, namely we require,*

$\frac{\hbar}{\sqrt{2E_\lambda k_B T}} << 1 / \left(|V_{D,A}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} e^{\frac{-(E_\lambda - 2\Delta_E)^2}{4k_B T E_\lambda}} \right)$. *A sufficient condition for this to hold is,* $\sqrt{2E_\lambda k_B T} >> |V_{D,A}|^2 \sqrt{\frac{\pi}{k_B T E_\lambda}} e^{\frac{-(E_\lambda - 2\Delta_E)^2}{4k_B T E_\lambda}}$, *where an even stronger condition reads* $\sqrt{2E_\lambda k_B T} >> |V_{D,A}|^2 \sqrt{\frac{\pi}{k_B T E_\lambda}}$, *namely* $|V_{D,A}|^2 << \sqrt{\frac{2}{\pi}} E_\lambda k_B T$. *As we can see, this is guaranteed to hold if the condition (a) is satisfied.*

Exercise 18.2.13 *According to Eq. (18.2.43), the thermal rates,* $k_{D\to A}$ *and* $k_{A\to D}$, *differ only by the sign of the driving force. Use this to derive their ratio, Eq. (18.2.46).*

Solution 18.2.13

Using: $k_{D\to A} = |V_{D,A}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} e^{\frac{-(E_\lambda - 2\Delta_E)^2}{4k_B T E_\lambda}}$ *and* $k_{A\to D} = |V_{D,A}|^2 \sqrt{\frac{\pi}{\hbar^2 k_+ T E_\lambda}} e^{\frac{-(E_\lambda + 2\Delta_E)^2}{4k_B T E_\lambda}}$, *we readily obtain Eq. (18.2.46),* $\frac{k_{A\to D}}{k_{D\to A}} = e^{\frac{-(E_\lambda + 2\Delta_E)^2 + (E_\lambda - 2\Delta_E)^2}{4k_B T E_\lambda}} = e^{\frac{-8E_\lambda \Delta_E}{4k_B T E_\lambda}} = e^{\frac{-2\Delta_E}{k_B T}}$.

Exercise 18.3.1 *According to first-order perturbation theory, the rate of population transfer between an initial thermal ensemble and a final ensemble due to an explicitly time-dependent interaction is given by Eq. (17.3.15). Replace the generic projection operators as defined in Eqs. (17.3.1-17.3.4), by the relevant projection operators into the ground and excited electronic states in a chromophore (Eq. (18.3.27)) to obtain the absorption and emission rates in Eq. (18.3.26).*

Solution 18.3.1

The general first-order approximations for the thermal rate constant reads (Eq. (17.3.15))

$k^{(1)}_{\{i\}\to\{f\}} = \lim_{t\to\infty} \frac{2}{\hbar^2} \mathrm{Re} \int_0^t tr\{\hat{\rho}_{\{i\}}(0) \left[\hat{V}^\dagger_{\{i\},\{f\}}(t')\right]_I \left[\hat{V}_{\{i\},\{f\}}(t)\right]_I\} dt'$, *where,*

$\left[\hat{V}_{\{i\},\{f\}}(t)\right]_I = e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{V}_{\{i\},\{f\}}(t) e^{\frac{-i\hat{H}_0 t}{\hbar}} = e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{P}_{\{f\}} \hat{V}(t) \hat{P}_{\{i\}} e^{\frac{-i\hat{H}_0 t}{\hbar}}$.

Introducing the projection operators to the ground and excited states, $\hat{P}_{gr}$ *and* $\hat{P}_{ex}$ *(Eq. (18.3.27)) and using their properties (Eqs. (17.3.1-17.3.3)), we obtain the following results:*

For absorption, $\hat{P}_{\{i\}} = \hat{P}_{gr}$, $\hat{P}_{\{f\}} = \hat{P}_{ex}$, *and* $\hat{\rho}_{\{i\}}(0) = \hat{\rho}_{gr}(0)$, *hence,*

$$k^{(1)}_{gr\to ex} = \lim_{t\to\infty} \frac{2}{\hbar^2} \mathrm{Re}\int_0^t tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr} e^{\frac{i\hat{H}_0 t'}{\hbar}} \hat{V}(t') e^{\frac{-i\hat{H}_0 t'}{\hbar}} \hat{P}_{ex} e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{V}(t) e^{\frac{-i\hat{H}_0 t}{\hbar}}\} dt' .$$

For emission, $\hat{P}_{\{i\}} = \hat{P}_{ex}$, $\hat{P}_{\{f\}} = \hat{P}_{gr}$, *and* $\hat{\rho}_{\{i\}}(0) = \hat{\rho}_{ex}(0)$, *hence,*

$$k^{(1)}_{ex\to gr} = \lim_{t\to\infty} \frac{2}{\hbar^2} \mathrm{Re}\int_0^t tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex} e^{\frac{i\hat{H}_0 t'}{\hbar}} \hat{V}(t') e^{\frac{-i\hat{H}_0 t'}{\hbar}} \hat{P}_{gr} e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{V}(t) e^{\frac{-i\hat{H}_0 t}{\hbar}}\} dt' .$$

Exercise 18.3.2 *The absorption and emission rates of a field-driven chromophore are given in Eq. (18.3.26). Use the explicit form of the interaction, Eqs. (18.3.15-18.3.18), the projection operators to the ground and excited states, Eq. (18.3.27), and the decomposition of the field amplitude into rotating waves,* $\sin(\Omega t) = (e^{i\Omega t} - e^{-i\Omega t})/(2i)$, *to express the rates in terms of the dipole correlation functions (Eqs. (18.3.29-18.3.31)).*

Solution 18.3.2

Substituting the interaction, $\hat{V}(t) = \sin(\Omega t)\hat{\mu}$, *in Eq. (18.3.26) and using the properties of the projection operators (Eqs. (17.3.1-17.3.3)), we obtain*

$$k^{(1)}_{gr\to ex}(t) \cong \frac{2}{\hbar^2} \mathrm{Re}\int_0^t \sin(\Omega t')\sin(\Omega t) tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr} e^{\frac{i\hat{H}_0 t'}{\hbar}} \hat{\mu} e^{\frac{-i\hat{H}_0 t'}{\hbar}} \hat{P}_{ex} e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{\mu} e^{\frac{-i\hat{H}_0 t}{\hbar}}\} dt'$$

$$= \frac{2}{\hbar^2} \mathrm{Re}\int_0^t \sin(\Omega t')\sin(\Omega t) tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex} e^{\frac{i\hat{H}_0 (t-t')}{\hbar}} \hat{P}_{ex}\hat{\mu}\hat{P}_{gr} e^{\frac{-i\hat{H}_0 (t-t')}{\hbar}}\} dt' ,$$

and

$$k^{(1)}_{ex\to gr}(t) \cong \frac{2}{\hbar^2} \mathrm{Re}\int_0^t \sin(\Omega t')\sin(\Omega t) tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex} e^{\frac{i\hat{H}_0 t'}{\hbar}} \hat{\mu} e^{\frac{-i\hat{H}_0 t'}{\hbar}} \hat{P}_{gr} e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{\mu} e^{\frac{-i\hat{H}_0 t}{\hbar}}\} dt'$$

$$= \frac{2}{\hbar^2} \mathrm{Re}\int_0^t \sin(\Omega t')\sin(\Omega t) tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr} e^{\frac{i\hat{H}_0 (t-t')}{\hbar}} \hat{P}_{gr}\hat{\mu}\hat{P}_{ex} e^{\frac{-i\hat{H}_0 (t-t')}{\hbar}}\} dt' .$$

Using the of the sine functions decomposition into "rotating waves",

$$\sin(\Omega t')\sin(\Omega t)=\frac{1}{4}\left(e^{i\Omega t'}-e^{-i\Omega t'}\right)\left(e^{-i\Omega t}-e^{i\Omega t}\right)=\frac{1}{4}\left(e^{i\Omega(t-t')}+e^{-i\Omega(t-t')}-e^{i\Omega(t+t')}-e^{-i\Omega(t+t')}\right)$$

$$=\frac{1}{4}\left(e^{i\Omega(t-t')}+e^{-i\Omega(t-t')}-e^{2i\Omega t}e^{-i\Omega(t-t')}-e^{-2i\Omega t}e^{i\Omega(t-t')}\right) ,$$

we obtain

$$k^{(1)}_{gr\to ex}(t)\cong\frac{2}{\hbar^2}\mathrm{Re}\int_0^t \sin(\Omega t')\sin(\Omega t) tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0(t-t')}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0(t-t')}{\hbar}}\}dt'$$

$$=\frac{2}{\hbar^2}\mathrm{Re}\int_0^t \frac{1}{4}\left(e^{i\Omega(t-t')}(1-e^{-2i\Omega t})+(1-e^{2i\Omega t})e^{-i\Omega(t-t')}\right) tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0(t-t')}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0(t-t')}{\hbar}}\}dt'$$

$$=\frac{1}{2\hbar^2}\mathrm{Re}[(1-e^{-2i\Omega t})\int_0^t e^{i\Omega(t-t')}tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{iH_0(t-t')}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-iH_0(t-t')}{\hbar}}\}dt'$$

$$+(1-e^{2i\Omega t})\int_0^t e^{-i\Omega(t-t')}tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{iH_0(t-t')}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-iH_0(t-t')}{\hbar}}\}dt']$$

and

$$k^{(1)}_{ex\to gr}(t)\cong\frac{2}{\hbar^2}\mathrm{Re}\int_0^t \sin(\Omega t')\sin(\Omega t) tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0(t-t')}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0(t-t')}{\hbar}}\}dt'$$

$$=\frac{2}{\hbar^2}\mathrm{Re}\int_0^t \frac{1}{4}\left(e^{i\Omega(t-t')}(1-e^{-2i\Omega t})+(1-e^{2i\Omega t})e^{-i\Omega(t-t')}\right) tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0(t-t')}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0(t-t')}{\hbar}}\}dt'$$

$$=\frac{1}{2\hbar^2}\mathrm{Re}[(1-e^{-2i\Omega t})\int_0^t e^{i\Omega\tau}tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$+(1-e^{2i\Omega t})\int_0^t e^{-i\Omega\tau}tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau] .$$

Defining: $\hat{\mu}_{ex,gr}(\tau)=e^{\frac{iH_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-iH_0\tau}{\hbar}}$ *, we have* $\hat{\mu}^{\dagger}_{ex,gr}(\tau)=e^{\frac{iH_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-iH_0\tau}{\hbar}}$ *, and hence,*

$$k^{(1)}_{gr\to ex}(t)\cong\frac{1}{2\hbar^2}\mathrm{Re}[(1-e^{-2i\Omega t})\int_0^t e^{i\Omega\tau}tr\{\hat{\rho}_{gr}(0)\hat{\mu}^{\dagger}_{ex,gr}(0)\hat{\mu}_{ex,gr}(\tau)\}d\tau$$

$$+(1-e^{2i\Omega t})\int_0^t e^{-i\Omega\tau}tr\{\hat{\rho}_{gr}(0)\hat{\mu}^{\dagger}_{ex,gr}(0)\hat{\mu}_{ex,gr}(\tau)\}d\tau],$$

and

$$k^{(1)}_{ex\to gr}(t) \cong \frac{1}{2\hbar^2}\mathrm{Re}[(1-e^{-2i\Omega t})\int_0^t e^{i\Omega\tau} tr\{\hat{\rho}_{ex}(0)\hat{\mu}_{ex,gr}(0)\hat{\mu}^{\dagger}_{ex,gr}(\tau)\}d\tau$$

$$+(1-e^{2i\Omega t})\int_0^t e^{-i\Omega\tau} tr\{\hat{\rho}_{ex}(0)\hat{\mu}_{ex,gr}(0)\hat{\mu}^{\dagger}_{ex,gr}(\tau)\}d\tau].$$

Defining, $c_{gr}(\tau) \equiv \frac{1}{4\hbar^2} tr\{\hat{\rho}_{gr}(0)\hat{\mu}^{\dagger}_{ex,gr}(0)\hat{\mu}_{ex,gr}(\tau)\}$ *and* $c_{ex}(\tau) \equiv \frac{1}{4\hbar^2} tr\{\hat{\rho}_{ex}(0)\hat{\mu}_{ex,gr}(0)\hat{\mu}^{\dagger}_{ex,gr}(\tau)\}$, *we obtain Eq. (18.3.29),*

$$k^{(1)}_{gr\to ex}(t) \cong 2\,\mathrm{Re}\left[(1-e^{-2i\Omega t})\int_0^t e^{i\Omega\tau} c_{gr}(\tau)d\tau + (1-e^{2i\Omega t})\int_0^t e^{-i\Omega\tau} c_{gr}(\tau)d\tau\right]$$

$$k^{(1)}_{ex\to gr}(t) \cong 2\,\mathrm{Re}\left[(1-e^{-2i\Omega t})\int_0^t e^{i\Omega\tau} c_{ex}(\tau)d\tau + (1-e^{2i\Omega t})\int_0^t e^{-i\Omega\tau} c_{ex}(\tau)d\tau\right].$$

Exercise 18.3.3 *(a) Given the explicit form of the zero-order Hamiltonian, Eq. (18.3.14), show that*

$$\langle ex|e^{\frac{\pm i\hat{H}_0\tau}{\hbar}}|ex\rangle = e^{\frac{\pm i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}} \quad ; \quad \langle gr|e^{\frac{\pm i\hat{H}_0\tau}{\hbar}}|gr\rangle = e^{\frac{\pm i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}$$

$$\langle gr|\mathrm{e}^{-\hat{H}_0/(k_BT)}|gr\rangle = \mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_BT)} \quad ; \quad \langle ex|\mathrm{e}^{-\hat{H}_0/(k_BT)}|ex\rangle = \mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_BT)}.$$

*(b) Use the definition of the projection operators to the ground and excited electronic states (Eq. (18.3.27)), the result (a), and Eqs. (18.3.18, 18.3.20, 18.3.21) for the interaction matrix elements, to derive Eq. (18.3.32) from Eqs. (*18.3.28, *18.3.30, 18.3.31). Recall that the trace over the full electronic and nuclear space can be expressed as* $tr\{\hat{O}\} = tr_{\mathbf{Q}}\{\langle gr|\hat{O}|gr\rangle + \langle ex|\hat{O}|ex\rangle\}$.

Solution 18.3.3

(a)

Given $\hat{H}_0 = \hat{H}_{gr,\mathbf{Q}}|gr\rangle\langle gr| + \hat{H}_{ex,\mathbf{Q}}|ex\rangle\langle ex|$ *(Eq. (18.3.14)), and using a perfect analogy to Ex 18.2.3, for any analytic function,* $f(\hat{H}_0)$ *,we obtain* $f(\hat{H}_0)|gr\rangle = f(\hat{H}_{gr,\mathbf{Q}})|gr\rangle$ *and* $f(\hat{H}_0)|ex\rangle = f(\hat{H}_{ex,\mathbf{Q}})|ex\rangle$. *Therefore, the following identities readily hold*

$$\langle ex|e^{\frac{\pm i\hat{H}_0\tau}{\hbar}}|ex\rangle = e^{\frac{\pm i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}} \quad ; \quad \langle gr|e^{\frac{\pm i\hat{H}_0\tau}{\hbar}}|gr\rangle = e^{\frac{\pm i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}$$

$$\langle gr|\mathrm{e}^{-\hat{H}_0/(k_BT)}|gr\rangle = \mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_BT)} \quad ; \quad \langle ex|\mathrm{e}^{-\hat{H}_0/(k_BT)}|ex\rangle = \mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_BT)} .$$

(b)

Starting from Eqs. (18.3.28, 18.3.30, 18.3.31) we have

$$c_{gr}(\tau) = \frac{1}{4\hbar^2} tr\{\hat{\rho}_{gr}(0)\hat{\mu}^\dagger_{ex,gr}(0)\hat{\mu}_{ex,gr}(\tau)\} = \frac{1}{4\hbar^2} tr\{\frac{1}{Z_{gr}}\mathrm{e}^{-\hat{H}_0/(k_BT)}\,\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\},$$

$$c_{ex}(\tau) \equiv \frac{1}{4\hbar^2} tr\{\hat{\rho}_{ex}(0)\hat{\mu}_{ex,gr}(0)\hat{\mu}^\dagger_{ex,gr}(\tau)\} = \frac{1}{4\hbar^2} tr\{\frac{1}{Z_{ex}}\mathrm{e}^{-\hat{H}_0/(k_BT)}\,\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}.$$

Using the projection operators, $\hat{P}_{ex} = |ex\rangle\langle ex|$ *and* $\hat{P}_{gr} = |gr\rangle\langle gr|$, *the identity,* $tr\{\hat{O}\} = tr_{\mathbf{Q}}\{\langle gr|\hat{O}|gr\rangle + \langle ex|\hat{O}|ex\rangle\}$, *and the result (a), we obtain*

$$\begin{aligned} c_{gr}(\tau) &= \frac{1}{4\hbar^2} tr\{\frac{1}{Z_{gr}}\mathrm{e}^{-\hat{H}_0/(k_BT)}\,\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\} \\ &= \frac{1}{4\hbar^2}\frac{1}{Z_{gr}} tr_{\mathbf{Q}}\{\langle gr|\mathrm{e}^{-\hat{H}_0/(k_BT)}|gr\rangle\langle gr|\hat{\mu}|ex\rangle\langle ex|e^{\frac{i\hat{H}_0\tau}{\hbar}}|ex\rangle\langle ex|\hat{\mu}|gr\rangle\langle gr|e^{\frac{-i\hat{H}_0\tau}{\hbar}}|gr\rangle\} \\ &= \frac{1}{4\hbar^2}\frac{1}{Z_{gr}} tr_{\mathbf{Q}}\{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_BT)}\langle gr|\hat{\mu}|ex\rangle e^{\frac{i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}\langle ex|\hat{\mu}|gr\rangle e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}\} , \end{aligned}$$

$$\begin{aligned} c_{ex}(\tau) &= \frac{1}{4\hbar^2} tr\{\frac{1}{Z_{ex}}\mathrm{e}^{-\hat{H}_0/(k_BT)}\,\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\} \\ &= \frac{1}{4\hbar^2}\frac{1}{Z_{ex}} tr_{\mathbf{Q}}\{\langle ex|\mathrm{e}^{-\hat{H}_0/(k_BT)}|ex\rangle\langle ex|\hat{\mu}|gr\rangle\langle gr|e^{\frac{i\hat{H}_0\tau}{\hbar}}|gr\rangle\langle gr|\hat{\mu}|ex\rangle\langle ex|e^{\frac{-i\hat{H}_0\tau}{\hbar}}|ex\rangle\} \\ &= \frac{1}{4\hbar^2}\frac{1}{Z_{ex}} tr_{\mathbf{Q}}\{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_BT)}\langle ex|\hat{\mu}|gr\rangle e^{\frac{i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}\langle gr|\hat{\mu}|ex\rangle e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}\}. \end{aligned}$$

Using, $\langle gr|\hat{\mu}|ex\rangle = \mu_{gr,ex}$, *we obtain Eq. (18.3.32)*

$$c_{gr}(\tau) = \frac{|\mu_{gr,ex}|^2}{4\hbar^2 Z_{gr}} tr_{\mathbf{Q}}\{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_BT)}\,e^{\frac{i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}\}\; c_{ex}(\tau) = \frac{|\mu_{gr,ex}|^2}{4\hbar^2 Z_{ex}} tr_{\mathbf{Q}}\{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_BT)}\,e^{\frac{i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}\}.$$

Exercise 18.3.4 *Derive Eq. (18.3.33) from Eq. (18.3.32) by evaluating the trace over the nuclear space using a complete set of eigenstates of the multidimensional Hamiltonian,* $\hat{H}_{gr,\mathbf{Q}}$ *, and an identity operator, expressed in terms of* $\hat{H}_{ex,\mathbf{Q}}$ *-eigenstates (as defined in Eqs. (18.3.23, 18.3.24)).*

Solution 18.3.4

Using complete orthonormal sets of eigenstates of $\hat{H}_{gr,\mathbf{Q}}$ *and* $\hat{H}_{ex,\mathbf{Q}}$ *for evaluating the trace in Eq. (18.3.32), we obtain*

$$c_{gr}(\tau) = \frac{|\mu_{gr,ex}|^2}{4\hbar^2} tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_B T)}}{Z_{gr}} e^{\frac{i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}} e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}\}$$

$$= \frac{|\mu_{gr,ex}|^2}{4\hbar^2} \sum_{\mathbf{n},\mathbf{m}} \langle \chi_{gr,\mathbf{n}} | \frac{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_B T)}}{Z_{gr}} e^{\frac{i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}} | \chi_{ex,\mathbf{m}} \rangle \langle \chi_{ex,\mathbf{m}} | e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}} | \chi_{gr,\mathbf{n}} \rangle$$

$$= \frac{|\mu_{gr,ex}|^2}{4\hbar^2} \sum_{\mathbf{n},\mathbf{m}} |\langle \chi_{gr,\mathbf{n}} | \chi_{ex,\mathbf{m}} \rangle|^2 \frac{\mathrm{e}^{-\varepsilon_{gr,\mathbf{n}}/(k_B T)}}{Z_{gr}} e^{\frac{i\varepsilon_{ex,\mathbf{m}}\tau}{\hbar}} e^{\frac{-i\varepsilon_{gr,\mathbf{n}}\tau}{\hbar}}$$

$$= \frac{|\mu_{gr,ex}|^2}{4\hbar^2} \sum_{\mathbf{n},\mathbf{m}} |\langle \chi_{gr,\mathbf{n}} | \chi_{ex,\mathbf{m}} \rangle|^2 \frac{\mathrm{e}^{-\varepsilon_{gr,\mathbf{n}}/(k_B T)}}{Z_{gr}} e^{\frac{-i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}})\tau}{\hbar}} ,$$

and

$$c_{ex}(\tau) = \frac{|\mu_{gr,ex}|^2}{4\hbar^2} tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_B T)}}{Z_{ex}} e^{\frac{i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}} e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}\} = \frac{|\mu_{gr,ex}|^2}{4\hbar^2} tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_B T)}}{Z_{ex}} e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}} e^{\frac{i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}\}$$

$$= \frac{|\mu_{gr,ex}|^2}{4\hbar^2} \sum_{\mathbf{n},\mathbf{m}} \langle \chi_{gr,\mathbf{n}} | \frac{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_B T)}}{Z_{ex}} e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}} | \chi_{ex,\mathbf{m}} \rangle \langle \chi_{ex,\mathbf{m}} | e^{\frac{i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}} | \chi_{gr,\mathbf{n}} \rangle$$

$$= \frac{|\mu_{gr,ex}|^2}{4\hbar^2} \sum_{\mathbf{n},\mathbf{m}} |\langle \chi_{gr,\mathbf{n}} | \chi_{ex,\mathbf{m}} \rangle|^2 \frac{\mathrm{e}^{-\varepsilon_{ex,\mathbf{m}}/(k_B T)}}{Z_{gr}} e^{\frac{-i\varepsilon_{ex,\mathbf{m}}\tau}{\hbar}} e^{\frac{i\varepsilon_{gr,\mathbf{n}}\tau}{\hbar}}$$

$$= \frac{|\mu_{gr,ex}|^2}{4\hbar^2} \sum_{\mathbf{n},\mathbf{m}} |\langle \chi_{gr,\mathbf{n}} | \chi_{ex,\mathbf{m}} \rangle|^2 \frac{\mathrm{e}^{-\varepsilon_{ex,\mathbf{m}}/(k_B T)}}{Z_{gr}} e^{\frac{i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}})\tau}{\hbar}} .$$

Exercise 18.3.5 *Within the rotating wave approximation, the interaction term in the Hamiltonian (Eq. (18.3.19)) can be replaced by* $\hat{V}(t) = \frac{e^{i\Omega t}}{2}\mu_{gr,ex}|gr\rangle\langle ex| + \frac{e^{-i\Omega t}}{2}\mu_{ex,gr}|ex\rangle\langle gr|$. *Use this interaction term in the rate expressions (Eq. (18.3.26)) to derive Eq. (18.3.35) directly.*

Solution 18.3.5

Starting from Eq. (18.3.26), using $\hat{V}(t)=\frac{e^{i\Omega t}}{2}\mu_{gr,ex}|gr\rangle\langle ex|+\frac{e^{-i\Omega t}}{2}\mu_{ex,gr}|ex\rangle\langle gr|$, $\hat{P}_{gr}|gr\rangle=|gr\rangle$, $\hat{P}_{ex}|ex\rangle=|ex\rangle$, $\hat{P}_{ex}|gr\rangle=0$, $\hat{P}_{gr}|ex\rangle=0$ *(see Eq. (18.3.27)), and the results of Ex. 18.3.3 (a), we obtain*

$$
\begin{aligned}
k^{(1)}_{gr\to ex}(t) &\cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}e^{\frac{i\hat{H}_0 t'}{\hbar}}\hat{V}(t')e^{\frac{-i\hat{H}_0 t'}{\hbar}}\hat{P}_{ex}e^{\frac{i\hat{H}_0 t}{\hbar}}\hat{V}(t)e^{\frac{-i\hat{H}_0 t}{\hbar}}\}dt' \\
&= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}e^{\frac{i\hat{H}_0 t'}{\hbar}}\frac{e^{i\Omega t'}}{2}\mu_{gr,ex}|gr\rangle\langle ex|e^{\frac{-i\hat{H}_0 t'}{\hbar}}\hat{P}_{ex}e^{\frac{i\hat{H}_0 t}{\hbar}}\frac{e^{-i\Omega t}}{2}\mu_{ex,gr}|ex\rangle\langle gr|e^{\frac{-i\hat{H}_0 t}{\hbar}}\}dt' \\
&= \frac{|\mu_{gr,ex}|^2}{2\hbar^2}\mathrm{Re}\int_0^t e^{-i\Omega(t-t')}tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_B T)}}{Z_{gr}}e^{\frac{i\hat{H}_{gr,\mathbf{Q}}t'}{\hbar}}e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}t'}{\hbar}}e^{\frac{i\hat{H}_{ex,\mathbf{Q}}t}{\hbar}}e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}t}{\hbar}}\}dt' \\
&= \frac{|\mu_{gr,ex}|^2}{2\hbar^2}\mathrm{Re}\int_0^t e^{-i\Omega(t-t')}tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_B T)}}{Z_{gr}}e^{\frac{i\hat{H}_{ex,\mathbf{Q}}(t-t')}{\hbar}}e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}(t-t')}{\hbar}}\}dt' \\
&= 2\,\mathrm{Re}\frac{|\mu_{gr,ex}|^2}{4\hbar^2}\int_0^t e^{-i\Omega\tau}tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{gr,\mathbf{Q}}/(k_B T)}}{Z_{gr}}e^{\frac{i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}\}d\tau
\end{aligned}
$$

$$
\begin{aligned}
k^{(1)}_{ex\to gr}(t) &\cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}e^{\frac{i\hat{H}_0 t'}{\hbar}}\hat{V}(t')e^{\frac{-i\hat{H}_0 t'}{\hbar}}\hat{P}_{gr}e^{\frac{i\hat{H}_0 t}{\hbar}}\hat{V}(t)e^{\frac{-i\hat{H}_0 t}{\hbar}}\}dt' \\
&= \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}e^{\frac{i\hat{H}_0 t'}{\hbar}}\frac{e^{-i\Omega t'}}{2}\mu_{ex,gr}|ex\rangle\langle gr|e^{\frac{-i\hat{H}_0 t'}{\hbar}}\hat{P}_{gr}e^{\frac{i\hat{H}_0 t}{\hbar}}\frac{e^{i\Omega t}}{2}\mu_{gr,ex}|gr\rangle\langle ex|e^{\frac{-i\hat{H}_0 t}{\hbar}}\}dt' \\
&= \frac{|\mu_{ex,gr}|^2}{2\hbar^2}\mathrm{Re}\int_0^t e^{i\Omega(t-t')}tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_B T)}}{Z_{ex}}e^{\frac{i\hat{H}_{ex,\mathbf{Q}}t'}{\hbar}}e^{\frac{-i\hat{H}_{gr,\mathbf{Q}}t'}{\hbar}}e^{\frac{i\hat{H}_{gr,\mathbf{Q}}t}{\hbar}}e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}t}{\hbar}}\}dt' \\
&= \frac{|\mu_{ex,gr}|^2}{2\hbar^2}\mathrm{Re}\int_0^t e^{i\Omega(t-t')}tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_B T)}}{Z_{ex}}e^{\frac{i\hat{H}_{gr,\mathbf{Q}}(t-t')}{\hbar}}e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}(t-t')}{\hbar}}\}dt' \\
&= 2\,\mathrm{Re}\frac{|\mu_{ex,gr}|^2}{4\hbar^2}\int_0^t e^{i\Omega\tau}tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{ex,\mathbf{Q}}/(k_B T)}}{Z_{ex}}e^{\frac{i\hat{H}_{gr,\mathbf{Q}}\tau}{\hbar}}e^{\frac{-i\hat{H}_{ex,\mathbf{Q}}\tau}{\hbar}}\}d\tau\ .
\end{aligned}
$$

Using the definition of the correlation functions in Eq. (18.3.32), we obtain Eq. (18.3.35),

$$k^{(1)}_{gr\to ex}(t)\cong 2\,\mathrm{Re}\int_0^t e^{-i\Omega\tau}c_{gr}(\tau)d\tau$$

$$k^{(1)}_{ex\to gr}(t)\cong 2\,\mathrm{Re}\int_0^t e^{i\Omega\tau}c_{ex}(\tau)d\tau\ .$$

Exercise 18.3.6 *Derive Eq. (18.3.36) by taking the upper limit of the time integral in Eqs. (18.3.33, 18.3.35) to infinity and by using a suitable definition of Dirac's delta. Use the fact that the real part of the integrand is an even function of time.*

Solution 18.3.6

Using Eqs. (18.3.33, 18.3.35) we obtain

$$k^{(1)}_{gr\to ex}(t) \cong \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n},\mathbf{m}} \frac{\mathrm{e}^{-\varepsilon_{gr,\mathbf{n}}/(k_BT)}}{Z_{gr}}\left|\langle \chi_{gr,\mathbf{n}}|\chi_{ex,\mathbf{m}}\rangle\right|^2 e^{\frac{-i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)\tau}{\hbar}} d\tau$$

$$k^{(1)}_{ex\to gr}(t) \cong \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n},\mathbf{m}} \frac{\mathrm{e}^{-\varepsilon_{ex,\mathbf{m}}/(k_BT)}}{Z_{ex}}\left|\langle \chi_{gr,\mathbf{n}}|\chi_{ex,\mathbf{m}}\rangle\right|^2 e^{\frac{i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)\tau}{\hbar}} d\tau \ .$$

Taking the upper limit in the integral to infinity and noticing that the real part of the integrand is an even function of time, we obtain

$$k_{gr\to ex}(\Omega) = \lim_{t\to\infty} k^{(1)}_{gr\to ex}(t) = \frac{\left|\mu_{gr,ex}\right|^2}{\hbar^2}\mathrm{Re}\int_{-\infty}^{\infty} \sum_{\mathbf{n},\mathbf{m}} \frac{\mathrm{e}^{-\varepsilon_{gr,\mathbf{n}}/(k_BT)}}{Z_{gr}}\left|\langle \chi_{gr,\mathbf{n}}|\chi_{ex,\mathbf{m}}\rangle\right|^2 e^{\frac{-i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)\tau}{\hbar}} d\tau$$

$$k_{ex\to gr}(\Omega) = \lim_{t\to\infty} k^{(1)}_{gr\to ex}(t) = \frac{\left|\mu_{gr,ex}\right|^2}{\hbar^2}\mathrm{Re}\int_{-\infty}^{\infty} \sum_{\mathbf{n},\mathbf{m}} \frac{\mathrm{e}^{-\varepsilon_{ex,\mathbf{m}}/(k_BT)}}{Z_{ex}}\left|\langle \chi_{gr,\mathbf{n}}|\chi_{ex,\mathbf{m}}\rangle\right|^2 e^{\frac{i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)\tau}{\hbar}} d\tau \ .$$

Using the definition of Dirac's delta, $\int_{-\infty}^{\infty} d\tau e^{\frac{-i(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)\tau}{\hbar}} = 2\pi\hbar\delta(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)$, *we obtain Eq. (18.3.36),*

$$k_{gr\to ex}(\Omega) = \lim_{t\to\infty} k^{(1)}_{gr\to ex}(t) = \frac{2\pi\left|\mu_{gr,ex}\right|^2}{\hbar}\sum_{\mathbf{n},\mathbf{m}} \frac{\mathrm{e}^{-\varepsilon_{gr,\mathbf{n}}/(k_BT)}}{Z_{gr}}\left|\langle \chi_{gr,\mathbf{n}}|\chi_{ex,\mathbf{m}}\rangle\right|^2 \delta(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega)$$

$$k_{ex\to gr}(\Omega) = \lim_{t\to\infty} k^{(1)}_{gr\to ex}(t) = \frac{2\pi\left|\mu_{gr,ex}\right|^2}{\hbar}\sum_{\mathbf{n},\mathbf{m}} \frac{\mathrm{e}^{-\varepsilon_{ex,\mathbf{m}}/(k_BT)}}{Z_{ex}}\left|\langle \chi_{gr,\mathbf{n}}|\chi_{ex,\mathbf{m}}\rangle\right|^2 \delta(\varepsilon_{gr,\mathbf{n}}-\varepsilon_{ex,\mathbf{m}}+\hbar\Omega) \ .$$

Exercise 18.3.7 *The dipole correlation functions are defined in Eq. (18.3.30). (a) Show that* $c^*_{gr}(\tau)=c_{gr}(-\tau)$ *and* $c^*_{ex}(\tau)=c_{ex}(-\tau)$. *(b) Use the result (a) to show that* $\mathrm{Re}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]$ *and* $\mathrm{Re}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]$ *are even functions of time, and that* $\mathrm{Im}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]$ *and* $\mathrm{Im}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]$ *are odd functions of time. Use this result to derive Eq. (18.3.37) from Eq. (18.3.35), in the limit* $t\to\infty$.

Solution 18.3.7

(a)

Using the definition of the correlation functions (Eqs. (18.3.30, 18.3.31)),

$$c_{gr}(\tau)=\frac{1}{4\hbar^2}tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}\ c_{ex}(\tau)=\frac{1}{4\hbar^2}tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\},$$

we obtain

$$\left[c_{gr}(\tau)\right]^*=\frac{1}{4\hbar^2}tr\{\left[\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\right]^\dagger\}$$
$$=\frac{1}{4\hbar^2}tr\{e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}\hat{\rho}_{gr}(0)\}$$
$$=\frac{1}{4\hbar^2}tr\{\hat{\rho}_{gr}(0)\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\}$$
$$=c_{gr}(-\tau)\ .$$

$$\left[c_{ex}(\tau)\right]^*=\frac{1}{4\hbar^2}tr\{\left[\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\right]^\dagger\}$$
$$=\frac{1}{4\hbar^2}tr\{e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}\hat{\rho}_{ex}(0)\}$$
$$=\frac{1}{4\hbar^2}tr\{\hat{\rho}_{ex}(0)\hat{P}_{ex}\hat{\mu}\hat{P}_{gr}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\hat{P}_{gr}\hat{\mu}\hat{P}_{ex}e^{\frac{i\hat{H}_0\tau}{\hbar}}\}$$
$$=c_{ex}(-\tau).$$

(b)

Using the result (a), we readily obtain

$$\mathrm{Re}[c_{gr}(\tau)]=\frac{c_{gr}(\tau)+\left[c_{gr}(\tau)\right]^*}{2}=\frac{c_{gr}(\tau)+c_{gr}(-\tau)}{2}$$
$$\mathrm{Re}[c_{ex}(\tau)]=\frac{c_{ex}(\tau)+\left[c_{ex}(\tau)\right]^*}{2}=\frac{c_{ex}(\tau)+c_{ex}(-\tau)}{2}\quad \mathrm{Im}[c_{ex}(\tau)]=\frac{c_{ex}(\tau)-\left[c_{ex}(\tau)\right]^*}{2i}=\frac{c_{ex}(\tau)-c_{ex}(-\tau)}{2i}\ .$$
$$\mathrm{Im}[c_{gr}(\tau)]=\frac{c_{gr}(\tau)-\left[c_{gr}(\tau)\right]^*}{2i}=\frac{c_{gr}(\tau)-c_{gr}(-\tau)}{2i}$$

Hence, $\mathrm{Re}[c_{gr}(\tau)]$ *and* $\mathrm{Re}[c_{ex}(\tau)]$ *are even functions of time, whereas* $\mathrm{Im}[c_{gr}(\tau)]$ *and* $\mathrm{Im}[c_{ex}(\tau)]$ *are odd functions of time. Consequently,*

$$\mathrm{Re}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]=\cos(\Omega\tau)\,\mathrm{Re}\left[c_{gr}(\tau)\right]+\sin(\Omega\tau)\,\mathrm{Im}\left[c_{gr}(\tau)\right]$$
$$\mathrm{Re}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]=\cos(\Omega\tau)\,\mathrm{Re}\left[c_{ex}(\tau)\right]-\sin(\Omega\tau)\,\mathrm{Im}\left[c_{ex}(\tau)\right]$$
$$\mathrm{Im}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]=\cos(\Omega\tau)\,\mathrm{Im}\left[c_{gr}(\tau)\right]-\sin(\Omega\tau)\,\mathrm{Re}\left[c_{gr}(\tau)\right]$$
$$\mathrm{Im}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]=\cos(\Omega\tau)\,\mathrm{Im}\left[c_{ex}(\tau)\right]+\sin(\Omega\tau)\,\mathrm{Re}\left[c_{ex}(\tau)\right],$$

where $\mathrm{Re}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]$ *and* $\mathrm{Re}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]$ *are shown to be even functions of time, whereas* $\mathrm{Im}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]$ *and* $\mathrm{Im}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]$ *are odd functions of time.*

In the limit $t\rightarrow\infty$*, Eq. (18.3.35) reads*

$$k_{gr\rightarrow ex}(\Omega)=2\,\mathrm{Re}\int_0^\infty e^{-i\Omega\tau}c_{gr}(\tau)d\tau$$

$$k_{ex\rightarrow gr}(\Omega)=2\,\mathrm{Re}\int_0^\infty e^{i\Omega\tau}c_{ex}(\tau)d\tau\,.$$

Since $\mathrm{Re}\left[e^{-i\Omega\tau}c_{gr}(\tau)\right]$ *and* $\mathrm{Re}\left[e^{i\Omega\tau}c_{ex}(\tau)\right]$ *are even functions of time, we can change the integration limits to obtain Eq. (18.3.37),*

$$k_{gr\rightarrow ex}(\Omega)=\mathrm{Re}\int_{-\infty}^\infty e^{-i\Omega\tau}c_{gr}(\tau)d\tau$$

$$k_{ex\rightarrow gr}(\Omega)=\mathrm{Re}\int_{-\infty}^\infty e^{i\Omega\tau}c_{ex}(\tau)d\tau\,.$$

Exercise 18.3.8 *One of the representations of Dirac's delta is* $\delta(x)=\lim_{\varepsilon\rightarrow+0}\sqrt{\frac{1}{4\pi\varepsilon}}e^{\frac{-x^2}{4\varepsilon}}$*. Use it to show that in the limit of vanishing coupling to the nuclear modes, both the absorption and the emission rates are peaked at the "adiabatic" energy gap,* $-2\Delta_E$*, namely*

$$\lim_{E_\lambda\rightarrow0}k_{gr\rightarrow ex}(\Omega)=\frac{2\pi}{\hbar}\frac{\left|\mu_{gr,ex}\right|^2}{4}\delta(-2\Delta_E-\hbar\Omega)\,,\ \lim_{E_\lambda\rightarrow0}k_{ex\rightarrow gr}(\Omega)=\frac{2\pi}{\hbar}\frac{\left|\mu_{gr,ex}\right|^2}{4}\delta(2\Delta_E+\hbar\Omega)\,.$$

Compare the result with the direct calculation of transition rate between pure states, in Eq. (15.6.29).

Solution 18.3.8

Starting from the semiclassical rate expressions (Eq. (18.3.40)),

$$k_{gr\to ex}(\Omega)=\frac{\left|\mu_{gr,ex}\right|^2}{4}\sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}}e^{\frac{-(E_\lambda-2\Delta_E-\hbar\Omega)^2}{4k_BTE_\lambda}}$$

$$k_{ex\to gr}(\Omega)=\frac{\left|\mu_{gr,ex}\right|^2}{4}\sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}}e^{\frac{-(E_\lambda+2\Delta_E+\hbar\Omega)^2}{4k_BTE_\lambda}} \quad ,$$

by taking the limit of vanishing coupling to the nuclear modes, using $\lim_{\varepsilon\to+0}\sqrt{\frac{1}{4\pi\varepsilon}}e^{\frac{-x^2}{4\varepsilon}}=\delta(x)$, *we obtain*

$$\lim_{E_\lambda\to 0}k_{gr\to ex}(\Omega)=\frac{2\pi}{\hbar}\frac{\left|\mu_{gr,ex}\right|^2}{4}\lim_{E_\lambda\to 0}\sqrt{\frac{1}{4\pi k_B T E_\lambda}}e^{\frac{-(E_\lambda-2\Delta_E-\hbar\Omega)^2}{4k_BTE_\lambda}}=\frac{2\pi}{\hbar}\frac{\left|\mu_{gr,ex}\right|^2}{4}\delta(2\Delta_E+\hbar\Omega)$$

$$\lim_{E_\lambda\to 0}k_{ex\to gr}(\Omega)=\frac{2\pi}{\hbar}\frac{\left|\mu_{gr,ex}\right|^2}{4}\lim_{E_\lambda\to 0}\sqrt{\frac{1}{4k_B T E_\lambda}}e^{\frac{-(E_\lambda+2\Delta_E+\hbar\Omega)^2}{4k_BTE_\lambda}}=\frac{2\pi}{\hbar}\frac{\left|\mu_{gr,ex}\right|^2}{4}\delta(2\Delta_E+\hbar\Omega).$$

As we can see, for vanishing coupling to the nuclear modes the rates are peaked at

$\hbar\Omega=-2\Delta_E$*, which is the adiabatic electronic transition energy.*

Exercise 18.3.9 *(a) Show that the time integrals in Eq. (18.3.38) can be rewritten as* $\int_0^t \mathrm{e}^{\frac{\pm i\tau}{\hbar}(2\Delta_E+\hbar\Omega)}c_0(\tau)\prod_{j=1}^{N}c_j(\tau)d\tau$, *where the single-mode correlation functions are defined as* $c_j(\tau)$ $=e^{2i\Delta_j{}^2\sin(\omega_j\tau)}e^{-2\Delta_j{}^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))}$. *(b) Show that* $c_0(\tau)$ *can be rewritten as* $c_0(\tau)=e^{-2\Delta_0^2(2n(\omega_0)+1)}e^{2\Delta_0^2[(n(\omega_0)+1)e^{i\omega_0\tau}+n(\omega_0)e^{-i\omega_0\tau}]}$. *(c) Follow the low frequency approximation, Eqs. (18.2.35 – 18.2.39), to show that* $\prod_{j=1}^{N}c_j(\tau)=\mathrm{e}^{\frac{i\tau}{\hbar}E_\lambda}e^{\frac{-E_\lambda k_B T\tau^2}{\hbar^2}}$*, and derive Eq. (18.3.41).*

Solution 18.3.9

(a)

Assigning indexes to the different modes, $j=0,1,2...,N$ *, in Eq. (18.3.38), and rewriting the exponent of a sum as a product of exponents, we obtain*

$$\int_0^t \mathrm{e}^{\frac{\pm i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} e^{2i\sum_{j=0}^N \Delta_j^2 \sin(\omega_j\tau)} e^{-2\sum_{j=0}^N \Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))} d\tau$$

$$= \int_0^t \mathrm{e}^{\frac{\pm i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} \left[e^{2i\Delta_0^2 \sin(\omega_0\tau)} e^{-2\Delta_0^2(1-\cos(\omega_0\tau))(1+2n(\omega_0))} \right] \cdot \left[e^{2i\Delta_1^2 \sin(\omega_1\tau)} e^{-2\Delta_1^2(1-\cos(\omega_1\tau))(1+2n(\omega_1))} \right]$$

$$\cdot \left[e^{2i\Delta_2^2 \sin(\omega_2\tau)} e^{-2\Delta_2^2(1-\cos(\omega_2\tau))(1+2n(\omega_2))} \right] \cdots \left[e^{2i\Delta_N^2 \sin(\omega_N\tau)} e^{-2\Delta_N^2(1-\cos(\omega_N\tau))(1+2n(\omega_N))} \right] d\tau$$

$$= \int_0^t \mathrm{e}^{\frac{\pm i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} c_0(\tau) \prod_{j=1}^N c_j(\tau) d\tau \ ,$$

where, $c_j(\tau) \equiv e^{2i\Delta_j^2 \sin(\omega_j\tau)} e^{-2\Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))}$.

(b)

Starting from the definition, $c_0(\tau) \equiv e^{2i\Delta_0^2 \sin(\omega_N\tau)} e^{-2\Delta_0^2(1-\cos(\omega_0\tau))(1+2n(\omega_0))}$ *, we readily obtain*

$$c_0(\tau) = e^{2i\Delta_0^2 \sin(\omega_0\tau)} e^{-2\Delta_0^2(1-\cos(\omega_0\tau))(1+2n(\omega_0))}$$
$$= e^{-2\Delta_0^2(2n(\omega_0)+1)} e^{\Delta_0^2(e^{i\omega_0\tau}-e^{-i\omega_0\tau})} e^{\Delta_0^2(1+2n(\omega_0))(e^{i\omega_0\tau}+e^{-i\omega_0\tau})}$$
$$= e^{-2\Delta_0^2(2n(\omega_0)+1)} e^{\Delta_0^2(e^{i\omega_0\tau}-e^{-i\omega_0\tau})} e^{\Delta_0^2(e^{i\omega_0\tau}+e^{-i\omega_0\tau})} e^{\Delta_0^2 2n(\omega_0)(e^{i\omega_0\tau}+e^{-i\omega_0\tau})} = e^{-2\Delta_0^2(2n(\omega_0)+1)} e^{2\Delta_0^2[(n(\omega_0)+1)e^{i\omega_0\tau}+n(\omega_0)e^{-i\omega_0\tau}]}$$
$$= e^{-2\Delta_0^2(2n(\omega_0)+1)} e^{2\Delta_0^2 e^{i\omega_0\tau}} e^{2\Delta_0^2 n(\omega_0)(e^{i\omega_0\tau}+e^{-i\omega_0\tau})}$$

.

(c)

Invoking the "low frequency" approximation for the modes associated with $j>0$, *namely* $n(\omega_j) \approx \dfrac{k_B T}{\hbar\omega_j} >> 1$, $\sin(\omega_j\tau) \approx \omega_j\tau$ *and* $\cos(\omega_j\tau) \approx 1-\omega_j^2\tau^2/2$, *we obtain*

$$c_j(\tau) = e^{2i\Delta_j^2 \sin(\omega_j\tau)} e^{-2\Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))} \cong e^{2i\Delta_j^2\omega_j\tau} e^{-\Delta_j^2\omega_j{}^2\tau^2 2k_BT/(\hbar\omega_j)}.$$

Hence,

$$\prod_{j=1}^N c_j(\tau) \cong e^{2i\sum_{j=1}^N \Delta_j^2\omega_j\tau} e^{-\sum_{j=1}^N \Delta_j^2\omega_j{}^2\tau^2 2k_BT/(\hbar\omega_j)} = e^{2i\sum_{j=1}^N \Delta_j^2\omega_j\hbar\tau/\hbar} e^{-\sum_{j=1}^N 2\Delta_j^2\omega_j\hbar k_BT\tau^2/\hbar^2} = e^{iE_\lambda\tau/\hbar} e^{-E_\lambda k_BT\tau^2/\hbar^2}$$

,

where in the last step we used the definition of the reorganization energy attributed to these modes, $E_\lambda \equiv \sum_{j=1}^N 2\Delta_j^2\hbar\omega_j$ *. Using this result and the result of (a) in Eq. (18.3.38), we obtain Eq. (18.3.41),*

$$k^{(1)}_{gr\to ex}(t) \cong \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} e^{2i\sum_j \Delta_j^2\sin(\omega_j\tau)} e^{-2\sum_j \Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))} d\tau$$

$$= \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} c_0(\tau)\prod_{j=1}^N c_j(\tau)d\tau$$

$$\approx \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} e^{iE_\lambda\tau/\hbar} e^{-E_\lambda k_B T\tau^2/\hbar^2} e^{-2\Delta_0^2(2n(\omega_0)+1)} e^{2\Delta_0^2[(n(\omega_0)+1)e^{i\omega_0\tau}+n(\omega_0)e^{-i\omega_0\tau}]} d\tau$$

and

$$k^{(1)}_{ex\to gr}(t) \cong \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} e^{2i\sum_j \Delta_j^2\sin(\omega_j\tau)} e^{-2\sum_j \Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))} d\tau$$

$$= \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} c_0(\tau)\prod_{j=1}^N c_j(\tau)d\tau$$

$$\approx \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{i\tau}{\hbar}(2\Delta_E+\hbar\Omega)} e^{iE_\lambda\tau/\hbar} e^{-E_\lambda k_B T\tau^2/\hbar^2} e^{-2\Delta_0^2(2n(\omega_0)+1)} e^{2\Delta_0^2[(n(\omega_0)+1)e^{i\omega_0\tau}+n(\omega_0)e^{-i\omega_0\tau}]} d\tau \ .$$

Exercise 18.3.10 *Introduce the Taylor expansion of* $e^{2\Delta_0^2 e^{i\omega_0\tau}}$ *into Eq. (18.3.42) and then carry out the time-integration to infinity. Notice that the time integrand is an even function of time, and use the identity,* $\int_{-\infty}^{\infty} dk e^{-zk^2}e^{ikx} = \sqrt{\frac{\pi}{z}}e^{\frac{-x^2}{4z}}$ *, to obtain Eq. (18.3.43).*

Solution 18.3.10

Expanding in a Taylor series, $e^{2\Delta_0^2 e^{i\omega_0\tau}} = \sum_{n=0}^{\infty}\frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!}e^{in\omega_0\tau}$ *, under the integral in Eq. (18.3.42), we obtain*

$$k^{(1)}_{gr\to ex}(t) \cong \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\sum_{n=0}^{\infty}\frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!}e^{-2\Delta_0^2}\,\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E+\hbar\Omega-E_\lambda-\hbar\omega_0 n)} e^{\frac{-E_\lambda k_B T\tau^2}{\hbar^2}} d\tau$$

$$k^{(1)}_{ex\to gr}(t) \cong \frac{\left|\mu_{gr,ex}\right|^2}{2\hbar^2}\sum_{n=0}^{\infty}\frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!}e^{-2\Delta_0^2}\,\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(-2\Delta_E-\hbar\Omega-E_\lambda-\hbar\omega_0 n)} e^{\frac{-E_\lambda k_B T\tau^2}{\hbar^2}} d\tau \ .$$

Replacing the upper integration limit by infinity, and using the fact that the time integrand is an even function of time, and the identity, $\int_{-\infty}^{\infty} dk e^{-zk^2} e^{ikx} = \sqrt{\frac{\pi}{z}} e^{\frac{-x^2}{4z}}$ *, we obtain Eq. (18.3.43),*

$$k_{gr\to ex}(\Omega) \cong \frac{\left|\mu_{gr,ex}\right|^2}{4\hbar^2} \sum_{n=0}^{\infty} \frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!} e^{-2\Delta_0^2} \,\mathrm{Re} \int_{-\infty}^{\infty} \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E + \hbar\Omega - E_\lambda - \hbar\omega_0 n)} e^{\frac{-E_\lambda k_B T \tau^2}{\hbar^2}} d\tau$$

$$= \sum_{n=0}^{\infty} \frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!} e^{-2\Delta_0^2} \frac{\left|\mu_{gr,ex}\right|^2}{4} \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} e^{\frac{-(\hbar\omega_0 n + E_\lambda - 2\Delta_E - \hbar\Omega)^2}{4 k_B T E_\lambda}}$$

$$k_{ex\to gr}(\Omega) \cong \frac{\left|\mu_{gr,ex}\right|^2}{4\hbar^2} \sum_{n=0}^{\infty} \frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!} e^{-2\Delta_0^2} \,\mathrm{Re} \int_{-\infty}^{\infty} \mathrm{e}^{\frac{-i\tau}{\hbar}(-2\Delta_E - \hbar\Omega - E_\lambda - \hbar\omega_0 n)} e^{\frac{-E_\lambda k_B T \tau^2}{\hbar^2}} d\tau$$

$$= \sum_{n=0}^{\infty} \frac{\left(\sqrt{2}\Delta_0\right)^{2n}}{n!} e^{-2\Delta_0^2} \frac{\left|\mu_{gr,ex}\right|^2}{4} \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} e^{\frac{-(\hbar\omega_0 n + E_\lambda + 2\Delta_E + \hbar\Omega)^2}{4 k_B T E_\lambda}} .$$

Exercise 18.3.11 *Using dimensionless position and momentum variables,* $\hat{Q}$ *and* $\hat{P}$*, a coherent state of a one-dimensional harmonic oscillator,* $|\alpha\rangle$*, is defined as* $\langle Q|\alpha\rangle = \left(\frac{1}{\pi}\right)^{1/4} e^{\frac{-(Q-\sqrt{2}\,\mathrm{Re}(\alpha))^2}{2}} e^{i\sqrt{2}\,\mathrm{Im}(\alpha) Q}$*, where* $\alpha \equiv \sqrt{\frac{1}{2}}\left(Q_0 + iP_0\right)$ *(see Eqs. (15.4.11, 15.4.36)). The projections of the coherent state on the eigenstates of the harmonic oscillator Hamiltonian,* $\frac{\hbar\omega}{2}(\hat{Q}^2 + \hat{P}^2)|\varphi_n\rangle = \hbar\omega(n+1/2)|\varphi_n\rangle$*, read* $\left|\langle\varphi_n|\alpha\rangle\right|^2 = e^{-|\alpha^2|} \frac{|\alpha|^{2n}}{n!}$ *(see Eq. (15.4.37)). Use this to show that the pre-factors multiplying the Gaussians in Eq. (18.3.43) are related to Franck-Condon overlap integrals, namely, given the harmonic oscillator ground state function,* $\varphi_0(Q) = \left(\frac{1}{\pi}\right)^{1/4} e^{\frac{-Q^2}{2}}$*, show that* $\left|\int_{-\infty}^{\infty} \varphi_n(Q+\Delta_0)\varphi_0(Q-\Delta_0) dQ\right|^2 = e^{-2\Delta_0^2} \frac{(\sqrt{2}\Delta_0)^{2n}}{n!}$.

Solution 18.3.11

Changing variable in the overlap integral, and recalling the definition of the ground state function for a displaced harmonic oscillator, we obtain

$$\int_{-\infty}^{\infty} \varphi_n(Q+\Delta_0)\varphi_0(Q-\Delta_0) dQ = \int_{-\infty}^{\infty} \varphi_n(Q)\varphi_0(Q-2\Delta_0) dQ = \int_{-\infty}^{\infty} \varphi_n(Q)\left(\frac{1}{\pi}\right)^{1/4} e^{\frac{-(Q-2\Delta_0)^2}{2}} dQ .$$

Identifying the function $\left(\frac{1}{\pi}\right)^{1/4} e^{\frac{-(Q-2\Delta_0)^2}{2}}$ *as a coherent state associated with* $\mathrm{Re}(\alpha) = \sqrt{2}\Delta_0$ *and* $\mathrm{Im}(\alpha) = 0$, *the overlap integral is the projection of the coherent state on the eigenstates of the (un-displaced) harmonic oscillator Hamiltonian,*

$$\int_{-\infty}^{\infty} \varphi_n(Q)\left(\frac{1}{\pi}\right)^{1/4} e^{\frac{-(Q-2\Delta_0)^2}{2}} dQ = \int_{-\infty}^{\infty} \varphi_n(Q)\left\langle Q \middle| \sqrt{2}\Delta_0 \right\rangle dQ = \left\langle \varphi_n \middle| \sqrt{2}\Delta_0 \right\rangle .$$

Consequently,

$$\left| \int_{-\infty}^{\infty} \varphi_n(Q+\Delta_0)\varphi_0(Q-\Delta_0)dQ \right|^2 = \left| \left\langle \varphi_n \middle| \sqrt{2}\Delta_0 \right\rangle \right|^2 = e^{-(2\Delta_0^2)} \frac{(\sqrt{2}\Delta_0)^{2n}}{n!} .$$

Exercise 18.4.1 *The Hamiltonian of the bichromophoric system in the absence of inter-chromophore interaction (*$\hat{H}_0$*) is given by Eq. (18.4.1), where the single-chromophore Hamiltonians are given by Eq. (18.4.3). Calculate the matrix elements of* $\hat{H}_0$ *in the basis of the bi-chromophore states,* $\left|D^*\right\rangle = \left|ex^{(D)}\right\rangle \otimes \left|gr^{(A)}\right\rangle$ *and* $\left|A^*\right\rangle = \left|gr^{(D)}\right\rangle \otimes \left|ex^{(A)}\right\rangle$, *and derive Eq. (18.4.7).*

Solution 18.4.1

Using the definition of the zero-order Hamiltonian (Eqs. (18.4.1, 18.4.3)) and the orthonormality conditions in each chromophore, $\left\langle ex^{(D)} \middle| gr^{(D)} \right\rangle = 0$, $\left\langle ex^{(A)} \middle| gr^{(A)} \right\rangle = 0$, $\left\langle ex^{(D)} \middle| ex^{(D)} \right\rangle = \left\langle gr^{(D)} \middle| gr^{(D)} \right\rangle = 1$, $\left\langle ex^{(A)} \middle| ex^{(A)} \right\rangle = \left\langle gr^{(A)} \middle| gr^{(A)} \right\rangle = 1$, *we obtain the matrix elements corresponding to Eqs. (18.4.7, 18.4.8),*

$$\begin{aligned}
&\left\langle D^* \middle| \hat{H}_0^{(D)} \otimes \hat{I}_0^{(D)} + \hat{I}_0^{(D)} \otimes \hat{H}_0^{(A)} \middle| D^* \right\rangle \\
&= \left\langle ex^{(D)} \right| \otimes \left\langle gr^{(A)} \right| \hat{H}_0^{(D)} \otimes \hat{I}_0^{(A)} + \hat{I}_0^{(D)} \otimes \hat{H}_0^{(A)} \left| ex^{(D)} \right\rangle \otimes \left| gr^{(A)} \right\rangle \\
&= \left\langle ex^{(D)} \right| \otimes \left\langle gr^{(A)} \right| \left[\ \hat{H}_{gr,\mathbf{Q}_D}^{(D)} \left| gr^{(D)} \right\rangle \left\langle gr^{(D)} \right| \otimes \hat{I}_0^{(A)} + \hat{H}_{ex,\mathbf{Q}_D}^{(D)} \left| ex^{(D)} \right\rangle \left\langle ex^{(D)} \right| \otimes \hat{I}_0^{(A)} \right. \\
&\left. + \hat{I}_0^{(D)} \otimes \hat{H}_{gr,\mathbf{Q}_A}^{(A)} \left| gr^{(A)} \right\rangle \left\langle gr^{(A)} \right| + \hat{I}_0^{(D)} \otimes \hat{H}_{ex,\mathbf{Q}_A}^{(A)} \left| ex^{(A)} \right\rangle \left\langle ex^{(A)} \right| \ \right] \left| ex^{(D)} \right\rangle \otimes \left| gr^{(A)} \right\rangle \\
&= \hat{H}_{ex,\mathbf{Q}_D}^{(D)} + \hat{H}_{gr,\mathbf{Q}_A}^{(A)}
\end{aligned}$$

$$\left\langle A^*\right|\hat{H}_0^{(D)}\otimes\hat{I}_0^{(D)}+\hat{I}_0^{(D)}\otimes\hat{H}_0^{(A)}\left|A^*\right\rangle$$
$$=\left\langle gr^{(D)}\right|\otimes\left\langle ex^{(A)}\right|\left[\hat{H}_0^{(D)}\otimes\hat{I}_0^{(A)}+\hat{I}_0^{(D)}\otimes\hat{H}_0^{(A)}\right]\left|gr^{(D)}\right\rangle\otimes\left|ex^{(A)}\right\rangle$$
$$=\left\langle gr^{(D)}\right|\otimes\left\langle ex^{(A)}\right|\left[\ \hat{H}_{gr,\mathbf{Q}_D}^{(D)}\left|gr^{(D)}\right\rangle\left\langle gr^{(D)}\right|\otimes\hat{I}_0^{(A)}+\hat{H}_{ex,\mathbf{Q}_D}^{(D)}\left|ex^{(D)}\right\rangle\left\langle ex^{(D)}\right|\otimes\hat{I}_0^{(A)}\right.$$
$$\left.+\hat{I}_0^{(D)}\otimes\hat{H}_{gr,\mathbf{Q}_A}^{(A)}\left|gr^{(A)}\right\rangle\left\langle gr^{(A)}\right|+\hat{I}_0^{(D)}\otimes\hat{H}_{ex,\mathbf{Q}_A}^{(A)}\left|ex^{(A)}\right\rangle\left\langle ex^{(A)}\right|\ \right]\left|gr^{(D)}\right\rangle\otimes\left|ex^{(A)}\right\rangle$$
$$=\hat{H}_{gr,\mathbf{Q}_D}^{(D)}+\hat{H}_{ex,\mathbf{Q}_A}^{(A)}$$

$$\left\langle D^*\right|\hat{H}_0^{(D)}\otimes\hat{I}_0^{(D)}+\hat{I}_0^{(D)}\otimes\hat{H}_0^{(A)}\left|A^*\right\rangle$$
$$=\left\langle ex^{(D)}\right|\otimes\left\langle gr^{(A)}\right|\left[\hat{H}_0^{(D)}\otimes\hat{I}_0^{(A)}+\hat{I}_0^{(D)}\otimes\hat{H}_0^{(A)}\right]\left|gr^{(D)}\right\rangle\otimes\left|ex^{(A)}\right\rangle$$
$$=\left\langle ex^{(D)}\right|\otimes\left\langle gr^{(A)}\right|\left[\ \hat{H}_{gr,\mathbf{Q}_D}^{(D)}\left|gr^{(D)}\right\rangle\left\langle gr^{(D)}\right|\otimes\hat{I}_0^{(A)}+\hat{H}_{ex,\mathbf{Q}_D}^{(D)}\left|ex^{(D)}\right\rangle\left\langle ex^{(D)}\right|\otimes\hat{I}_0^{(A)}\right.$$
$$\left.+\hat{I}_0^{(D)}\otimes\hat{H}_{gr,\mathbf{Q}_A}^{(A)}\left|gr^{(A)}\right\rangle\left\langle gr^{(A)}\right|+\hat{I}_0^{(D)}\otimes\hat{H}_{ex,\mathbf{Q}_A}^{(A)}\left|ex^{(A)}\right\rangle\left\langle ex^{(A)}\right|\ \right]\left|gr^{(D)}\right\rangle\otimes\left|ex^{(A)}\right\rangle$$

$$=0\ .$$

Exercise 18.4.2 *(This exercise is completely analogous to Ex. 18.2.3 for charge transfer): (a) Use the explicit expressions for the zero-order Hamiltonian (Eq. (18.4.7)) and show that* $f(\hat{H}_0)\left|D^*\right\rangle=f(\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A})\left|D^*\right\rangle$ *and* $f(\hat{H}_0)\left|A^*\right\rangle=f(\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A})\left|A^*\right\rangle$*, where* $f(\hat{H}_0)$ *is an analytic function of the respective operators. (b) Use the results of (a), the interaction operator (Eq. (18.4.10)), and the definitions of the initial and final ensembles (Eqs. (18.4.15, 18.4.16)) to derive Eq. (18.4.18) from Eq. (18.4.17). Recall that the trace over the full electronic and nuclear space can be expressed as* $tr\{\hat{O}\}=tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\left\langle D^*\right|\hat{O}\left|D^*\right\rangle+\left\langle A^*\right|\hat{O}\left|A^*\right\rangle\}$.

Solution 18.4.2

The solution follows the solution of Ex. 18.2.3, with the following replacements,

$$\left|D\right\rangle\leftrightarrow\left|D^*\right\rangle$$

$$\left|A\right\rangle\leftrightarrow\left|A^*\right\rangle$$

$$\hat{P}_D=\left|D\right\rangle\left\langle D\right|\leftrightarrow\hat{P}_{D^*}=\left|D^*\right\rangle\left\langle D^*\right|$$

$$\hat{P}_A=\left|A\right\rangle\left\langle A\right|\leftrightarrow\hat{P}_{A^*}=\left|A^*\right\rangle\left\langle A^*\right|$$

$$\hat{H}_{D,\mathbf{Q}}\leftrightarrow\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}$$

$$\hat{H}_{A,\mathbf{Q}} \leftrightarrow \hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}$$

$$\hat{H}_0 = \hat{H}_{D,\mathbf{Q}}|D\rangle\langle D| + \hat{H}_{A,\mathbf{Q}}|A\rangle\langle A| \;\leftrightarrow\; \hat{H}_0 = \hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\left|D^*\right\rangle\left\langle D^*\right| + \hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\left|A^*\right\rangle\left\langle A^*\right|$$

$$\hat{V} = V_{D,A}\left(|D\rangle\langle A| + |A\rangle\langle D|\right) \;\leftrightarrow$$

$$\hat{V} = J_{D^*}(\mathbf{Q}_D,\mathbf{Q}_A)\left|D^*\right\rangle\left\langle D^*\right| + J_{A^*}(\mathbf{Q}_D,\mathbf{Q}_A)\left|A^*\right\rangle\left\langle A^*\right| + J_{D^*,A^*}\left|D^*\right\rangle\left\langle A^*\right| + J_{D^*,A^*}\left|A^*\right\rangle\left\langle D^*\right| .$$

(notice that the diagonal interaction terms in $\hat{V}$*, namely,* $J_{D^*}(\mathbf{Q}_D,\mathbf{Q}_A)\left|D^*\right\rangle\left\langle D^*\right| + J_{A^*}(\mathbf{Q}_D,\mathbf{Q}_A)\left|A^*\right\rangle\left\langle A^*\right|$*, vanish in* $\hat{P}_{D^*}\hat{V}\hat{P}_{A^*}$ *and* $\hat{P}_{A^*}\hat{V}\hat{P}_{D^*}$*.)*

Hence, the result for the energy transfer rate,

$$k^{(1)}_{D^*\to A^*}(t) \cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{D^*}(0)\hat{P}_{D^*}\hat{V}\hat{P}_{A^*}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$= 2\,\mathrm{Re}\int_0^t \frac{|J_{D^*,A^*}|^2}{\hbar^2} tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}} e^{\frac{-i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}} e^{\frac{i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\}d\tau ,$$

is obtained in perfect analogy to the result for charge transfer rate in Ex. 18.2.3,

$$k^{(1)}_{D\to A}(t) \cong \frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_D(0)\hat{P}_D\hat{V}\hat{P}_A e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$

$$= 2\,\mathrm{Re}\int_0^t \frac{|V_{D,A}|^2}{\hbar^2} tr_{\mathbf{Q}}\{\frac{\mathrm{e}^{-\hat{H}_{D,\mathbf{Q}}/(k_BT)}}{Z_D} e^{\frac{-i\hat{H}_{D,\mathbf{Q}}\tau}{\hbar}} e^{\frac{i\hat{H}_{A,\mathbf{Q}}\tau}{\hbar}}\}d\tau .$$

Exercise 18.4.3 *(This exercise is completely analogous to Ex. 18.2.4 for charge transfer) Derive Eq. (18.4.19) from Eq. (18.4.18) by evaluating the trace over the nuclear space using a complete set of eigenstates of the multidimensional Hamiltonian,* $\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}$*, and an identity operator, expressed in terms of* $\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}$*-eigenstates (Eq. (18.4.11,18.4.12)).*

Solution 18.4.3

Starting from Eq. (18.4.18) and introducing complete orthonormal sets of $\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}$ *and* $\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}$ *eigenstates,* $\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\left|\chi_{D^*,\mathbf{n}}\right\rangle = \varepsilon_{D^*,\mathbf{n}}\left|\chi_{D^*,\mathbf{n}}\right\rangle$ *and* $\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\left|\chi_{A^*,\mathbf{m}}\right\rangle = \varepsilon_{A^*,\mathbf{m}}\left|\chi_{A^*,\mathbf{m}}\right\rangle$ *(see Eqs. (18.4.7, 18.4.8, 18.4.11)), we obtain Eq. (18.4.19),*

$$k^{(1)}_{D^*\to A^*}(t)=\frac{2|J_{D^*,A^*}|^2}{\hbar^2}\mathrm{Re}\int_0^t tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\}d\tau$$

$$=\frac{2|J_{D^*,A^*}|^2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n}}\left\langle\chi_{D^*,\mathbf{n}}\right|\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\sum_{\mathbf{m}}\left|\chi_{A^*,\mathbf{m}}\right\rangle\left\langle\chi_{A^*,\mathbf{m}}\right|e^{\frac{i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\left|\chi_{D^*,\mathbf{n}}\right\rangle d\tau$$

$$=\frac{2|J_{D^*,A^*}|^2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n}}\left\langle\chi_{D^*,\mathbf{n}}\right|\frac{\mathrm{e}^{-\varepsilon_{D^*,\mathbf{n}}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\varepsilon_{D^*,\mathbf{n}}\tau}{\hbar}}\sum_{\mathbf{m}}\left|\chi_{A^*,\mathbf{m}}\right\rangle\left\langle\chi_{A^*,\mathbf{m}}\right|e^{\frac{i\varepsilon_{A^*,\mathbf{m}}}{\hbar}}\left|\chi_{D^*,\mathbf{n}}\right\rangle d\tau$$

$$=\frac{2|J_{D^*,A^*}|^2}{\hbar^2}\mathrm{Re}\int_0^t \sum_{\mathbf{n},\mathbf{m}}\frac{\mathrm{e}^{-\varepsilon_{D^*,\mathbf{n}}/(k_BT)}}{Z_{D^*}}e^{\frac{-i(\varepsilon_{D^*,\mathbf{n}}-\varepsilon_{A^*,\mathbf{m}})\tau}{\hbar}}\left|\left\langle\chi_{D^*,\mathbf{n}}\middle|\chi_{A^*,\mathbf{m}}\right\rangle\right|^2 d\tau\ .$$

Exercise 18.4.4 *The dipole-dipole correlation function is defined in Eq. (18.4.18). Show that* $c^*_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)=c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(-\tau)$. *Use this result to derive Eq. (18.4.21) from Eq. (18.4.18), in the limit* $t\to\infty$.

Solution 18.4.4

Using the dipole-dipole correlation function in Eq. (18.4.18),

$$c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)=\frac{|J_{D^*,A^*}|^2}{\hbar^2}tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\},$$

we obtain

$$\left[c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)\right]^*=\frac{|J_{D^*,A^*}|^2}{\hbar^2}tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\left[\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\right]^\dagger\}$$

$$=\frac{|J_{D^*,A^*}|^2}{\hbar^2}tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\left[e^{\frac{-i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}\right]\}$$

$$=\frac{|J_{D^*,A^*}|^2}{\hbar^2}tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{i\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{-i\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\}=c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(-\tau)\ .$$

Consequently, the real part of the integrand in Eq. (18.4.18) is an even function of τ, $k^{(1)}_{D^*\to A^*}(t)=2\,\mathrm{Re}\int_0^t c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)d\tau=\int_0^t\left[c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)+c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(-\tau)\right]d\tau$.

Therefore, $k^{(1)}_{D^*\to A^*}(t)=\frac{1}{2}\int_{-t}^t\left[c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)+c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(-\tau)\right]d\tau=\mathrm{Re}\int_{-t}^t c_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)d\tau$.

Similarly, the imaginary part of the integrand is an odd function of time, hence the imaginary part of the integral from $-t$ *to* t *vanishes,* $\mathrm{Im}\int_{-t}^{t} c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)d\tau = \frac{1}{2i}\int_{-t}^{t}\left[c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau) - c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(-\tau)\right]d\tau = 0$

.

Consequently, $k^{(1)}_{D^*\to A^*}(t) = \int_{-t}^{t} c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)d\tau$. *Taking* $t\to\infty$, *we obtain Eq. (18.4.21).*

Exercise 18.4.5 *The dipole-dipole correlation function,* $c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)$, *is defined in Eq. (18.4.18). Use the decomposition of* $\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}$ *and* $\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}$ *in terms of "local" donor and acceptor modes (Eq. (18.4.8)), and the commutativity of donor-space and acceptor space operators, namely,*

$$[\hat{H}^{(D)}_{gr,\mathbf{Q}_D},\hat{H}^{(A)}_{gr,\mathbf{Q}_A}] = [\hat{H}^{(D)}_{gr,\mathbf{Q}_D},\hat{H}^{(A)}_{ex,\mathbf{Q}_A}] = [\hat{H}^{(D)}_{ex,\mathbf{Q}_D},\hat{H}^{(A)}_{gr,\mathbf{Q}_A}] = [\hat{H}^{(D)}_{ex,\mathbf{Q}_D},\hat{H}^{(A)}_{ex,\mathbf{Q}_A}] = 0\,,$$

to express $c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)$ *in terms of the local dipole correlation functions, as defined in Eqs. (18.3.30-18.3.32).*

Solution 18.4.5

Using the decomposition of $\hat{H}_{D^*,\mathbf{Q}_D,\mathbf{Q}_A}$ *and* $\hat{H}_{A^*,\mathbf{Q}_D,\mathbf{Q}_A}$ *in terms of "local" donor and acceptor modes (Eq. (18.4.8)), and the commutativity of donor-space and acceptor space operators, the exponents in Eq. (18.4.18) factorize into products of donor and acceptor space operators, and consequently the trace factorizes to the product of traces,*

$$tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}_{D*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\hat{H}_{D*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}_{A*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\}$$

$$= tr_{\mathbf{Q}_D}\{\frac{\mathrm{e}^{-\hat{H}^{(D)}_{ex,\mathbf{Q}_D}/(k_BT)}}{Z^{(D)}_{ex}}e^{\frac{-i\hat{H}^{(D)}_{ex,\mathbf{Q}_D}\tau}{\hbar}}e^{\frac{i\hat{H}^{(D)}_{gr,\mathbf{Q}_D}\tau}{\hbar}}\}\cdot tr_{\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}^{(A)}_{gr,\mathbf{Q}_A}/(k_BT)}}{Z^{(A)}_{gr}}e^{\frac{-i\hat{H}^{(A)}_{gr,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}^{(A)}_{ex,\mathbf{Q}_A}\tau}{\hbar}}\}\,.$$

Using this result and the expressions for the local ground and excited state correlations in each chromophore (Eq. (18.3.32)), $c^{(A)}_{gr}(\tau) \equiv \frac{\left|\mu^{(A)}_{gr,ex}\right|^2}{4\hbar^2}tr_{\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}^{(A)}_{gr,\mathbf{Q}_A}/(k_BT)}}{Z^{(A)}_{gr}}e^{\frac{i\hat{H}^{(A)}_{ex,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{-i\hat{H}^{(A)}_{gr,\mathbf{Q}_A}\tau}{\hbar}}\}$ *and* $c^{(D)}_{ex}(\tau) \equiv \frac{\left|\mu^{(D)}_{gr,ex}\right|^2}{4\hbar^2}tr_{\mathbf{Q}_D}\{\frac{\mathrm{e}^{-\hat{H}^{(D)}_{ex,\mathbf{Q}_D}/(k_BT)}}{Z^{(D)}_{ex}}e^{\frac{i\hat{H}^{(D)}_{gr,\mathbf{Q}_D}\tau}{\hbar}}e^{\frac{-i\hat{H}^{(D)}_{ex,\mathbf{Q}_D}\tau}{\hbar}}\}$, *the nuclear correlation function in Eq. (18.4.18) can be expressed as (Eq. (18.4.22)),*

$$c_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(\tau)=\frac{|J_{D^*,A^*}|^2}{\hbar^2}tr_{\mathbf{Q}_D,\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}_{D*,\mathbf{Q}_D,\mathbf{Q}_A}/(k_BT)}}{Z_{D^*}}e^{\frac{-i\hat{H}_{D*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}_{A*,\mathbf{Q}_D,\mathbf{Q}_A}\tau}{\hbar}}\}$$

$$=\frac{|J_{D^*,A^*}|^2}{\hbar^2}tr_{\mathbf{Q}_D}\{\frac{\mathrm{e}^{-\hat{H}^{(D)}_{ex,\mathbf{Q}_D}/(k_BT)}}{Z^{(D)}_{ex}}e^{\frac{-i\hat{H}^{(D)}_{ex,\mathbf{Q}_D}\tau}{\hbar}}e^{\frac{i\hat{H}^{(D)}_{gr,\mathbf{Q}_D}\tau}{\hbar}}\}\cdot tr_{\mathbf{Q}_A}\{\frac{\mathrm{e}^{-\hat{H}^{(A)}_{gr,\mathbf{Q}_A}/(k_BT)}}{Z^{(A)}_{gr}}e^{\frac{-i\hat{H}^{(A)}_{gr,\mathbf{Q}_A}\tau}{\hbar}}e^{\frac{i\hat{H}^{(A)}_{ex,\mathbf{Q}_A}\tau}{\hbar}}\}$$

$$=\frac{16|J_{D^*,A^*}|^2\hbar^2}{\left|\mu^{(D)}_{gr,ex}\right|^2\left|\mu^{(A)}_{gr,ex}\right|^2}c^{(D)}_{ex}(\tau)\cdot c^{(A)}_{gr}(\tau)\ .$$

Exercise 18.4.6 *(a) Use the identity*

$$\int_{-\infty}^{\infty}dt\,f(t)g(t)=\int_{-\infty}^{\infty}d\Omega\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dte^{i\Omega t}f(t)\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dt'e^{-i\Omega t'}g(t')$$

to express the time-integral over the nuclear correlation function in Eq. (18.4.22) as an integral over Ω*. (b) Derive Eq. (18.4.23) by substitution of the result (a) in Eq. (18.4.21) and identifying the donor emission rate and the acceptor absorption rate, as defined in Eq. (18.3.37).*

Solution 18.4.6

(a)

Using the identity,

$$\int_{-\infty}^{\infty}dt\,f(t)g(t)=\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt\,f(t)g(t')\delta(t-t')=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\Omega\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt\,f(t)g(t')e^{i\Omega(t-t')}$$

$$=\int_{-\infty}^{\infty}d\Omega\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dte^{i\Omega t}f(t)\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dt'e^{-i\Omega t'}g(t'),$$

we obtain

$$\int_{-\infty}^{\infty}dtc_{D*,\mathbf{Q}_D,\mathbf{Q}_A}(t)=\frac{16|J_{D^*,A^*}|^2\hbar^2}{\left|\mu^{(D)}_{gr,ex}\right|^2\left|\mu^{(A)}_{gr,ex}\right|^2}\int_{-\infty}^{\infty}dtc^{(D)}_{ex}(t)\cdot c^{(A)}_{gr}(t)$$

$$=\frac{16|J_{D^*,A^*}|^2\hbar^2}{\left|\mu^{(D)}_{gr,ex}\right|^2\left|\mu^{(A)}_{gr,ex}\right|^2}\int_{-\infty}^{\infty}d\Omega\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dte^{i\Omega t}c^{(D)}_{ex}(t)\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dt'e^{-i\Omega t'}c^{(A)}_{gr}(t').$$

(b)

Using the result of (a) in Eq. (18.4.21) for the energy transfer rate, and recalling the relations between integrals over the local donor and acceptor correlation functions and the respective absorption and emission rates (Eq. (18.3.37)), we obtain Eq. (18.4.23),

$$k_{D^*\to A^*}=\frac{16|J_{D^*,A^*}|^2\hbar^2}{\left|\mu_{gr,ex}^{(D)}\right|^2\left|\mu_{gr,ex}^{(A)}\right|^2}\int_{-\infty}^{\infty}d\Omega\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dte^{i\Omega t}c_{ex}^{(D)}(t)\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dt'e^{-i\Omega t'}c_{gr}^{(A)}(t')$$

$$=\frac{16|J_{D^*,A^*}|^2\hbar^2}{\left|\mu_{gr,ex}^{(D)}\right|^2\left|\mu_{gr,ex}^{(A)}\right|^2}\int_{-\infty}^{\infty}d\Omega\frac{1}{\sqrt{2\pi}}k_{ex\to gr}^{(D)}(\Omega)\frac{1}{\sqrt{2\pi}}k_{gr\to ex}^{(A)}(\Omega)$$

$$=\frac{8|J_{D^*,A^*}|^2\hbar^2}{\pi\left|\mu_{gr,ex}^{(D)}\right|^2\left|\mu_{gr,ex}^{(A)}\right|^2}\int_{-\infty}^{\infty}d\Omega k_{ex\to gr}^{(D)}(\Omega)k_{gr\to ex}^{(A)}(\Omega)\ .$$

Exercise 18.4.7 *The golden rule expression for the time-dependent charge transfer rate within the spin boson model is given by Eq. (18.2.33). Invoking additional approximations, one obtains the semi-classical golden rule rate (Marcus formula), Eq. (18.2.43). Use the analogy between Eq. (18.2.33) and Eq. (18.4.24) to derive Eq. (18.4.25) for the electronic energy transfer rate, within the same set of approximations.*

Solution 18.4.7

The expressions for the charge and energy transfer rates, Eq. (18.2.33), and Eq. (18.4.24), respectively,

$$k_{D\to A}^{(1)}(t)=\frac{2|V_{D,A}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}2\Delta_E}e^{2i\sum_j\Delta_j^2\sin(\omega_j\tau)}e^{-2\sum_j\Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))}d\tau$$

and

$$k_{D^*\to A^*}^{(1)}(t)=\frac{2|J_{D^*,A^*}|^2}{\hbar^2}\mathrm{Re}\int_0^t \mathrm{e}^{\frac{-i\tau}{\hbar}(2\Delta_E^{(A)}-2\Delta_E^{(D)})}e^{2i\sum_{j\in\{j_D,j_A\}}\Delta_j^2\sin(\omega_j\tau)}e^{-2\sum_{j\in\{j_D,j_A\}}\Delta_j^2(1-\cos(\omega_j\tau))(1+2n(\omega_j))}d\tau,$$ *are perfectly analogous, where,* $2\Delta_E\leftrightarrow 2\Delta_E^{(A)}-2\Delta_E^{(D)}$, $V_{D,A}\leftrightarrow J_{D^*,A^*}$, *and in the case of energy-transfer the sum over nuclear modes includes the two chromophores. Invoking the same set of approximations with respect to the nuclear degrees of freedom (Eqs. (18.2.35-18.2.38, 18.2.44, 18.2.45)), the semiclassical approximation for the energy transfer rate (Eq. (18.4.25)) can be readily obtained, based on the parallel expression for charge transfer rate (Eq. (18.2.43)),*

$$k_{D\to A}=|V_{D,A}|^2\sqrt{\frac{\pi}{\hbar^2k_BTE_\lambda}}e^{\frac{-(E_\lambda-2\Delta_E)^2}{4k_BTE_\lambda}}\quad\leftrightarrow\quad k_{D^*\to A^*}=|J_{D^*,A^*}|^2\sqrt{\frac{\pi}{\hbar^2k_BTE_\lambda}}e^{\frac{-(E_\lambda-(2\Delta_E^{(A)}-2\Delta_E^{(D)}))^2}{4k_BTE_\lambda}}\ .$$

Exercise 18.4.8 *Use the semi-classical golden rule expressions for the absorption and emission spectral lines (Eq. (18.3.40)), with the local chromophore reorganization energies,* $E_\lambda^{(D)} \equiv \sum_{j_D} 2\Delta_{j_D}^2 \omega_{j_D} \hbar$ *and* $E_\lambda^{(A)} \equiv \sum_{j_A} 2\Delta_{j_A}^2 \omega_{j_A} \hbar$*, to derive the Marcus-like formula for the electronic energy transfer rate (Eq. (18.4.25)) as the spectral overlap integral, Eq. (18.4.23). Notice that the total reorganization energy includes all the modes of the donor and the acceptor chromophores,* $E_\lambda = E_\lambda^{(D)} + E_\lambda^{(A)}$.

Solution 18.4.8

Starting from the spectral overlap integral (Eq. (18.4.23)),

$$k_{D^*\to A^*} = \frac{8|J_{D^*,A^*}|^2 \hbar^2}{\pi \left|\mu_{gr,ex}^{(D)}\right|^2 \left|\mu_{gr,ex}^{(A)}\right|^2} \int_{-\infty}^{\infty} d\Omega k_{ex\to gr}^{(D)}(\Omega) k_{gr\to ex}^{(A)}(\Omega),$$

and invoking the semi-classical approximations for the donor emission and the acceptor absorption rates (Eq. (18.3.40)),

$$k_{gr\to ex}^{(A)}(\Omega) = \frac{\left|\mu_{gr,ex}^{(A)}\right|^2}{4} \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda^{(A)}}} e^{\frac{-(E_\lambda^{(A)} - 2\Delta_E^{(A)} - \hbar\Omega)^2}{4k_B T E_\lambda^{(A)}}}$$

$$k_{ex\to gr}^{(D)}(\Omega) = \frac{\left|\mu_{gr,ex}^{(D)}\right|^2}{4} \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda^{(D)}}} e^{\frac{-(E_\lambda^{(D)} + 2\Delta_E^{(D)} + \hbar\Omega)^2}{4k_B T E_\lambda^{(D)}}},$$

we obtain

$$k_{D^*\to A^*} = \frac{8|J_{D^*,A^*}|^2 \hbar^2}{\pi \left|\mu_{gr,ex}^{(D)}\right|^2 \left|\mu_{gr,ex}^{(A)}\right|^2} \int_{-\infty}^{\infty} d\Omega k_{ex\to gr}^{(D)}(\Omega) k_{gr\to ex}^{(A)}(\Omega) k_{D^*\to A^*}$$

$$= \frac{|J_{D^*,A^*}|^2 \hbar^2}{2\pi} \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda^{(D)}}} \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda^{(A)}}} \int_{-\infty}^{\infty} d\Omega e^{\frac{-(E_\lambda^{(D)} + 2\Delta_E^{(D)} + \hbar\Omega)^2}{4k_B T E_\lambda^{(D)}}} e^{\frac{-(E_\lambda^{(A)} - 2\Delta_E^{(A)} - \hbar\Omega)^2}{4k_B T E_\lambda^{(A)}}}.$$

Defining,

$$x_1 \equiv -\frac{E_\lambda^{(D)} + 2\Delta_E^{(D)}}{\hbar} \quad ; \quad x_2 \equiv \frac{E_\lambda^{(A)} - 2\Delta_E^{(A)}}{\hbar} \quad ; \quad \alpha_1 \equiv \frac{\hbar^2}{4k_B T E_\lambda^{(D)}} \quad ; \quad \alpha_2 \equiv \frac{\hbar^2}{4k_B T E_\lambda^{(A)}},$$

$$F_D(\Omega) = e^{\frac{-(E_\lambda^{(D)} + 2\Delta_E^{(D)} + \hbar\Omega)^2}{4k_B T E_\lambda^{(D)}}} = e^{-\alpha_1(\Omega - x_1)^2} \quad ; \quad F_A(\Omega) = e^{\frac{-(E_\lambda^{(A)} - 2\Delta_E^{(A)} - \hbar\Omega)^2}{4k_B T E_\lambda^{(A)}}} = e^{-\alpha_2(\Omega - x_2)^2},$$

and using the identity,

$$e^{-\alpha_1(\Omega-x_1)^2}e^{-\alpha_2(\Omega-x_2)^2}=e^{-(\alpha_1+\alpha_2)(\Omega-\frac{(x_1\alpha_1+x_2\alpha_2)}{(\alpha_1+\alpha_2)})^2+\frac{(x_1\alpha_1+x_2\alpha_2)^2}{(\alpha_1+\alpha_2)}-\alpha_1x_1{}^2-\alpha_2x_2{}^2},$$

we obtain

$$\int_{-\infty}^{\infty}d\Omega e^{-(\alpha_1+\alpha_2)(\Omega-\frac{(x_1\alpha_1+x_2\alpha_2)}{(\alpha_1+\alpha_2)})^2+\frac{(x_1\alpha_1+x_2\alpha_2)^2}{(\alpha_1+\alpha_2)}-\alpha_1x_1{}^2-\alpha_2x_2{}^2}=\sqrt{\frac{\pi}{\alpha_1+\alpha_2}}e^{\frac{(x_1\alpha_1+x_2\alpha_2)^2}{(\alpha_1+\alpha_2)}-\alpha_1x_1{}^2-\alpha_2x_2{}^2}$$

$$=\sqrt{\frac{\pi}{\alpha_1+\alpha_2}}e^{\frac{(x_1\alpha_1+x_2\alpha_2)^2-(\alpha_1+\alpha_2)\alpha_1x_1{}^2-(\alpha_1+\alpha_2)\alpha_2x_2{}^2}{(\alpha_1+\alpha_2)}}=\sqrt{\frac{\pi}{\alpha_1+\alpha_2}}e^{\frac{x_1{}^2\alpha_1{}^2+x_2{}^2\alpha_2{}^2+2x_2\alpha_2x_1\alpha_1-(\alpha_1+\alpha_2)\alpha_1x_1{}^2-(\alpha_1+\alpha_2)\alpha_2x_2{}^2}{(\alpha_1+\alpha_2)}}$$

$$=\sqrt{\frac{\pi}{\alpha_1+\alpha_2}}e^{\frac{2x_2\alpha_2x_1\alpha_1-\alpha_2\alpha_1x_1{}^2-\alpha_1\alpha_2x_2{}^2}{(\alpha_1+\alpha_2)}}=\sqrt{\frac{\pi}{\alpha_1+\alpha_2}}e^{\frac{-\alpha_1\alpha_2}{(\alpha_1+\alpha_2)}(x_1-x_2)^2}.$$

Consequently,

$$k_{D^*\to A^*}=\frac{|J_{D^*,A^*}|^2\,\hbar^2}{2\pi}\sqrt{\frac{\pi}{\hbar^2k_BTE_\lambda^{(D)}}}\sqrt{\frac{\pi}{\hbar^2k_BTE_\lambda^{(A)}}}\sqrt{\frac{\pi}{\alpha_1+\alpha_2}}e^{\frac{-\alpha_1\alpha_2}{(\alpha_1+\alpha_2)}(x_1-x_2)^2}$$

$$=\frac{|J_{D^*,A^*}|^2}{2\pi\hbar}\sqrt{\frac{\pi}{k_BTE_\lambda^{(D)}}}\sqrt{\frac{\pi}{k_BTE_\lambda^{(A)}}}$$

$$\cdot\sqrt{\frac{\pi}{\frac{1}{4k_BTE_\lambda^{(D)}}+\frac{1}{4k_BTE_\lambda^{(A)}}}}e^{\frac{-1}{4k_BTE_\lambda^{(D)}4k_BTE_\lambda^{(A)}(\frac{1}{4k_BTE_\lambda^{(D)}}+\frac{1}{4k_BTE_\lambda^{(A)}})}(-E_\lambda^{(D)}-2\Delta_E^{(D)}-E_\lambda^{(A)}+2\Delta_E^{(A)})^2}$$

$$=\frac{|J_{D^*,A^*}|^2}{2\hbar}\sqrt{\frac{4\pi}{k_BTE_\lambda^{(A)}+k_BTE_\lambda^{(D)}}}e^{\frac{-1}{4k_BTE_\lambda^{(D)}+4k_BTE_\lambda^{(A)}}(E_\lambda^{(D)}+2\Delta_E^{(D)}+E_\lambda^{(A)}-2\Delta_E^{(A)})^2}$$

$$=|J_{D^*,A^*}|^2\sqrt{\frac{\pi}{\hbar^2k_BT(E_\lambda^{(D)}+E_\lambda^{(A)})}}e^{\frac{-1}{4k_BT(E_\lambda^{(D)}+E_\lambda^{(A)})}(E_\lambda^{(D)}+E_\lambda^{(A)}-(2\Delta_E^{(A)}-2\Delta_E^{(D)}))^2}.$$

The result is identical to Eq. (18.4.25), where the total reorganization energy is the sum of the local donor and acceptor reorganization energies.

19 Open Quantum Systems

Exercise 19.1.1 *Use the identity* $\frac{\partial}{\partial t}\int_0^t f(t,t')dt' = \int_0^t \frac{\partial}{\partial t} f(t,t')dt' + f(t,t)$ *to show that the expression in Eq. (19.1.4) for the Q-space projection,* $\left|\hat{Q}\psi(t)\right\rangle$*, is indeed a solution to its defining equation, Eq. (19.1.3).*

Solution 19.1.1

Starting from the proposed expression, $\left|\hat{Q}\psi(t)\right\rangle = \hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t d\tau \hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle$,

where $\hat{U}_Q(t,\tau)$ *is defined as the solution to* $\frac{\partial}{\partial t}\hat{U}_Q(t,\tau) = -\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\hat{U}_Q(t,\tau)$*, with* $\hat{U}_Q(t,t) \equiv \hat{Q}$*,*

we obtain $\frac{\partial}{\partial t}\left|\hat{Q}\psi(t)\right\rangle = \frac{\partial}{\partial t}\hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\frac{\partial}{\partial t}\int_0^t d\tau \hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle$.

Using the identity, $\frac{\partial}{\partial t}\int_0^t f(t,t')dt' = \int_0^t \frac{\partial}{\partial t} f(t,t')dt' + f(t,t)$*, we obtain*

$$\frac{\partial}{\partial t}\left|\hat{Q}\psi(t)\right\rangle = \frac{\partial}{\partial t}\hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\frac{\partial}{\partial t}\int_0^t d\tau \hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle$$

$$= \frac{\partial}{\partial t}\hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t d\tau \frac{\partial}{\partial t}\hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle - \frac{i}{\hbar}\hat{U}_Q(t,t)\hat{H}(t)\left|\hat{P}\psi(t)\right\rangle .$$

Using the Schrödinger equation, $\frac{\partial}{\partial t}\hat{U}_Q(t,\tau) = -\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\hat{U}_Q(t,\tau)$*, and* $\hat{U}_Q(t,t) = \hat{Q}$*, we obtain*

$$\frac{\partial}{\partial t}\left|\hat{Q}\psi(t)\right\rangle$$

$$= -\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t d\tau\left(-\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\hat{U}_Q(t,\tau)\right)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle - \frac{i}{\hbar}\hat{Q}\hat{H}(t)\left|\hat{P}\psi(t)\right\rangle$$

$$= -\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\left[\hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t d\tau \hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle\right] - \frac{i}{\hbar}\hat{Q}\hat{H}(t)\left|\hat{P}\psi(t)\right\rangle$$

$$= -\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\left[\left|\hat{Q}\psi(t)\right\rangle\right] - \frac{i}{\hbar}\hat{Q}\hat{H}(t)\left|\hat{P}\psi(t)\right\rangle .$$

As we can see, the proposed expression, $\left|\hat{Q}\psi(t)\right\rangle = \hat{U}_Q(t,0)\left|\psi(0)\right\rangle - \frac{i}{\hbar}\int_0^t d\tau \hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle$,

satisfies Eq. (19.1.3), $\frac{\partial}{\partial t}\left|\hat{Q}\psi(t)\right\rangle = -\frac{i}{\hbar}\hat{Q}\hat{H}(t)\hat{Q}\left[\left|\hat{Q}\psi(t)\right\rangle\right] - \frac{i}{\hbar}\hat{Q}\hat{H}(t)\left|\hat{P}\psi(t)\right\rangle$.

Exercise 19.1.2 *Show that in the general case, where* $\left|\hat{Q}\psi(0)\right\rangle \neq 0$, *substitution of Eq. (19.1.4) in Eq. (19.1.3) results in an additional inhomogeneous term in the equation for the P-space projection. Show that for a time-independent Hamiltonian, the corresponding inhomogeneous equation in the interaction picture is Eq. (19.1.10).*

Solution 19.1.2

Substitution of Eq. (19.1.4) in Eq. (19.1.3) results in,

$$\frac{\partial}{\partial t}\left|\hat{P}\psi(t)\right\rangle = -\frac{i}{\hbar}\hat{P}\hat{H}(t)\left|\hat{P}\psi(t)\right\rangle - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}\hat{H}(t)\hat{U}_Q(t,\tau)\hat{H}(\tau)\left|\hat{P}\psi(\tau)\right\rangle - \frac{i}{\hbar}\hat{P}\hat{H}(t)\hat{U}_Q(t,0)\left|\psi(0)\right\rangle.$$

For a time-independent Hamiltonian we have, $\hat{U}_Q(t,\tau) = \hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}$, *and therefore this result reads*

$$\frac{\partial}{\partial t}\left|\hat{P}\psi(t)\right\rangle = -\frac{i}{\hbar}\hat{P}\hat{H}\hat{P}\left|\hat{P}\psi(t)\right\rangle - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}\left|\hat{P}\psi(\tau)\right\rangle - \frac{i}{\hbar}\hat{P}\hat{H}\hat{Q}e^{\frac{-it}{\hbar}\hat{Q}\hat{H}\hat{Q}}\left|\hat{Q}\psi(0)\right\rangle.$$

Transforming to the interaction picture, $\left|\hat{P}\psi_I(t)\right\rangle \equiv e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\left|\hat{P}\psi(t)\right\rangle$, *we obtain*

$$\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle = \frac{i}{\hbar}\hat{P}\hat{H}\hat{P}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\left|\hat{P}\psi(t)\right\rangle - \frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{P}\left|\hat{P}\psi(t)\right\rangle$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}e^{\frac{-it}{\hbar}\hat{P}\hat{H}\hat{P}}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\left|\hat{P}\psi(\tau)\right\rangle - \frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-it}{\hbar}\hat{Q}\hat{H}\hat{Q}}\left|\hat{Q}\psi(0)\right\rangle.$$

Hence, we obtain Eq. (19.1.10),

$$\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle + \frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}e^{\frac{-i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}\left|\hat{P}\psi_I(\tau)\right\rangle = -\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-it}{\hbar}\hat{Q}\hat{H}\hat{Q}}\left|\hat{Q}\psi(0)\right\rangle.$$

Exercise 19.1.3 *(a) Start from the defining equations for the projected density operator,*

$$\frac{\partial}{\partial t}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{P}_L\hat{\rho}(t) - \frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{Q}_L\hat{\rho}(t) \quad ;$$

$$\frac{\partial}{\partial t}\hat{Q}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{Q}_L\hat{L}(t)\hat{Q}_L\hat{\rho}(t) - \frac{i}{\hbar}\hat{Q}_L\hat{L}(t)\hat{P}_L\hat{\rho}(t),$$

and use the analogy to the derivation of Eq. (19.1.7), to derive Eq. (19.1.13) for time-independent Hamiltonians, when $\hat{Q}_L\hat{\rho}(0) = 0$. *(b) Use Eq. (19.1.14) to derive Eq. (19.1.15) from Eq. (19.1.13). (c) Show that in the general case, where* $\hat{Q}_L\hat{\rho}(0) \neq 0$, *the inhomogeneous equation for the P-space projected density operator in the interaction picture is Eq. (19.1.16) (follow the analogy to Ex. (19.1.2)).*

Solution 19.1.3

(a)

Given the two coupled equations for $\hat{P}_L\hat{\rho}(t)$ *and* $\hat{Q}_L\hat{\rho}(t)$,

$$\frac{\partial}{\partial t}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{P}_L\hat{\rho}(t) - \frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{Q}_L\hat{\rho}(t) \quad ; \quad \frac{\partial}{\partial t}\hat{Q}\hat{\rho}(t) = -\frac{i}{\hbar}\hat{Q}\hat{L}(t)\hat{Q}\hat{\rho}(t) - \frac{i}{\hbar}\hat{Q}\hat{L}(t)\hat{P}\hat{\rho}(t)$$

, we can use the perfect analogy to the equations for $\left|\hat{P}\psi(t)\right\rangle$ *and* $\left|\hat{Q}\psi(t)\right\rangle$ *(Eq. (19.1.3)), and follow the steps in Ex. 19.1.1 to show that the exact solution for* $\hat{Q}_L\hat{\rho}(t)$ *reads*

$\hat{Q}\hat{\rho}(t) = \hat{U}_Q(t,0)\hat{\rho}(0) - \frac{i}{\hbar}\int_0^t d\tau \hat{U}_Q(t,\tau)\hat{L}(\tau)\hat{P}_L\hat{\rho}(\tau)$, *where a Q-space propagator,* $\hat{U}_Q(t,\tau)$, *is defined by the differential equation,* $\frac{\partial}{\partial t}\hat{U}_Q(t,\tau) = -\frac{i}{\hbar}\hat{Q}_L\hat{L}(t)\hat{Q}_L\hat{U}_Q(t,\tau)$, *with* $\hat{U}_Q(t,t) \equiv \hat{Q}_L$.

Substitution in the equation for $\hat{P}_L\hat{\rho}(t)$ *yields in the most general case,*

$$\frac{\partial}{\partial t}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{P}_L\hat{\rho}(t) - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L\hat{L}(t)\hat{U}_Q(t,\tau)\hat{L}(\tau)\hat{P}_L\hat{\rho}(\tau) - \frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{U}_Q(t,0)\hat{\rho}(0).$$

For time-independent Hamiltonian (and hence time-independent Liouville operator), we have

$\hat{U}_Q(t,\tau) = \hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}$, *and therefore,*

$$\frac{d}{dt}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t) - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i\tau}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(t-\tau) - \frac{i}{\hbar}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{\rho}(0),$$

which, for $\hat{Q}_L\hat{\rho}(0) = 0$ *, leads to Eq. (19.1.13),*

$$\frac{\partial}{\partial t}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t) - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i\tau}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(t-\tau).$$

(b)

Using $\hat{\rho}_P^{(I)}(t) \equiv e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t)$ *(Eq. (19.1.14)) and the result of (a), we obtain Eq. (19.1.15),*

$$\begin{aligned}
\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t) &= \frac{\partial}{\partial t}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t) \\
&= \frac{i}{\hbar}\hat{P}_L\hat{L}\hat{P}_L e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t) - \frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t) - \frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i\tau}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(t-\tau) \\
&= -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i\tau}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(t-\tau) \\
&= -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i\tau}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\left[e^{\frac{i(t-\tau)}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{\rho}(t-\tau)\right] \\
&= -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\left[e^{\frac{i\tau}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{\rho}(\tau)\right] \\
&= -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{\rho}_P^{(I)}(\tau) .
\end{aligned}$$

(c)

Using the most general result (see (a)),

$$\frac{\partial}{\partial t}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{P}_L\hat{\rho}(t) - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L\hat{L}(t)\hat{U}_Q(t,\tau)\hat{L}(\tau)\hat{P}_L\hat{\rho}(\tau) - \frac{i}{\hbar}\hat{P}_L\hat{L}(t)\hat{U}_Q(t,0)\hat{\rho}(0),$$ *for a*

time-independent Liouville operator, $\hat{U}_Q(t,\tau) = \hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}$ *, we obtain*

$$\frac{\partial}{\partial t}\hat{P}_L\hat{\rho}(t) = -\frac{i}{\hbar}\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t) - \frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(\tau) - \frac{i}{\hbar}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{\rho}(0).$$

Transforming to the interaction representation, $\hat{\rho}_P^{(I)}(t) \equiv e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t)$ *, we obtain Eq. (19.1.16),*

$$\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t)=\frac{\partial}{\partial t}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t)$$
$$=\frac{i}{\hbar}\hat{P}_L\hat{L}\hat{P}_L e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t)-\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(\tau)-\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{\rho}(0)$$
$$=-\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{\rho}_P^{(I)}(\tau)-\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{\rho}(0)\ .$$

Exercise 19.2.1 *(a) Given the definition of the Kernel $\hat{K}(t,\tau)$ in Eq. (19.2.2), show that the exact equation for the projected state $\left|\hat{P}\psi_I(t)\right\rangle$, Eq. (19.1.9), reads $\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle=-\int_0^t d\tau\hat{K}(t,\tau)\left|\hat{P}\psi_I(\tau)\right\rangle$. (b) Derive the infinite series expansion in Eq. (19.2.2) by recursive application of the formal relation, $\hat{P}\psi_I(\tau)=\hat{P}\psi_I(t)-\int_\tau^t dt'\frac{\partial}{\partial t'}\hat{P}\psi_I(t')$.*

Solution 19.2.1

(a)

The exact equation for $\left|\hat{P}\psi_I(t)\right\rangle$ reads (Eq. (19.1.9)), $\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle=-\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}e^{\frac{-i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}\left|\hat{P}\psi_I(\tau)\right\rangle$. Using the definition of the kernel (Eq. (19.2.2)), $\hat{K}(t,\tau)\equiv\frac{1}{\hbar^2}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}e^{\frac{-i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}$, we readily obtain $\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle=-\int_0^t d\tau\hat{K}(t,\tau)\left|\hat{P}\psi_I(\tau)\right\rangle$.

(b)

Using recursively the exact relations, $\frac{\partial}{\partial t}\left|\hat{P}\psi_I(\tau)\right\rangle=-\int_0^\tau d\tau\hat{K}(\tau,\tau')\left|\hat{P}\psi_I(\tau')\right\rangle$, and $\left|\hat{P}\psi_I(\tau)\right\rangle=\left|\hat{P}\psi_I(t)\right\rangle-\int_\tau^t d\tau'\frac{\partial}{\partial\tau'}\left|\hat{P}\psi_I(\tau')\right\rangle$, in the exact expression for $\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle$, we obtain

$$\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle = -\int_0^t d\tau \hat{K}(t,\tau)\left|\hat{P}\psi_I(\tau)\right\rangle$$
$$= -\int_0^t d\tau \hat{K}(t,\tau)\left[\left|\hat{P}\psi_I(t)\right\rangle - \int_\tau^t d\tau' \frac{\partial}{\partial \tau'}\left|\hat{P}\psi_I(\tau')\right\rangle\right]$$
$$= -\int_0^t d\tau \hat{K}(t,\tau)\left[\left|\hat{P}\psi_I(t)\right\rangle - \int_\tau^t d\tau'\left(-\int_0^{\tau'} d\tau \hat{K}(\tau',\tau'')\left|\hat{P}\psi_I(\tau'')\right\rangle\right)\right]$$
$$= -\int_0^t d\tau \hat{K}(t,\tau)\left[\left|\hat{P}\psi_I(t)\right\rangle - \int_\tau^t d\tau'\left(-\int_0^{\tau'} d\tau'' \hat{K}(\tau',\tau'')\left[\left|\hat{P}\psi_I(t)\right\rangle - \int_{\tau''}^t d\tau''' \frac{\partial}{\partial \tau'''}\left|\hat{P}\psi_I(\tau''')\right\rangle\right]\right)\right]$$
$$= -\int_0^t d\tau \hat{K}(t,\tau)\left[\left|\hat{P}\psi_I(t)\right\rangle - \int_\tau^t d\tau'\left(-\int_0^{\tau'} d\tau'' \hat{K}(\tau',\tau'')\left[\left|\hat{P}\psi_I(t)\right\rangle - \int_{\tau''}^t d\tau'''\left(-\int_0^{\tau'''} d\tau \hat{K}(\tau''',\tau'''')\left|\hat{P}\psi_I(\tau'''')\right\rangle\right)\right]\right)\right].$$

This recursion can be continued repeatedly to any order, as expressed in Eq. (19.2.2),

$$\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle$$
$$= -\left[\int_0^t d\tau \hat{K}(t,\tau)\left[\hat{I} + \int_\tau^t d\tau' \int_0^{\tau'} d\tau'' \hat{K}(\tau',\tau'')\left[\hat{I} + \int_{\tau''}^t d\tau''' \int_0^{\tau'''} d\tau'''' \hat{K}(\tau''',\tau'''')\left[\hat{I} + \cdots\right]\right]\right]\right]\left|\hat{P}\psi_I(t)\right\rangle .$$

For example, collecting the terms up to third order in the kernel, we obtain

$$\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle = [-\int_0^t d\tau \hat{K}(t,\tau) - \int_0^t d\tau \hat{K}(t,\tau)\int_\tau^t d\tau' \int_0^{\tau'} d\tau'' \hat{K}(\tau',\tau'')$$
$$-\int_0^t d\tau \hat{K}(t,\tau)\int_\tau^t d\tau' \int_0^{\tau'} d\tau'' \hat{K}(\tau',\tau'')\int_{\tau''}^t d\tau''' \int_0^{\tau'''} d\tau \hat{K}(\tau''',\tau'''')]\left|\hat{P}\psi_I(t)\right\rangle + o(\hat{K}^4) .$$

Exercise 19.2.2 *Use the decomposition of the Hamiltonian in Eq. (19.2.3) in terms of the projection operators,* $\hat{H} = \hat{P}\hat{H}\hat{P} + \hat{Q}\hat{H}\hat{Q} + \hat{P}\hat{H}\hat{Q} + \hat{Q}\hat{H}\hat{P}$, *where* $\hat{P} = |\varphi_0\rangle\langle\varphi_0|$, *and* $\hat{Q} = \hat{I} - \hat{P} = \sum_{j=1}^{N} |\varphi_j\rangle\langle\varphi_j|$. *Denote the eigenstates of* $\hat{P}\hat{H}\hat{P}$ *and* $\hat{Q}\hat{H}\hat{Q}$ *as* $|\chi_0\rangle$ *and* $\{|\chi_f\rangle\}$, *respectively, to derive Eq. (19.2.4).*

Solution 19.2.2

Given the model Hamiltonian,

$$\hat{H} \equiv \sum_{j=0}^{N} H_{j,j} \left|\varphi_j\right\rangle\left\langle\varphi_j\right| + \sum_{j>j'=0}^{N} \left\{H_{j,j'}\left|\varphi_j\right\rangle\left\langle\varphi_{j'}\right| + h.c.\right\} \equiv \sum_{j,j'=0}^{N} H_{j,j'}\left|\varphi_j\right\rangle\left\langle\varphi_{j'}\right|, \text{ where } \left\langle\varphi_j\middle|\varphi_{j'}\right\rangle = \delta_{j,j'}$$

, and given the projection operators, $\hat{P} = |\varphi_0\rangle\langle\varphi_0|$ *and* $\hat{Q} = \sum_{j=1}^{N}\left|\varphi_j\right\rangle\left\langle\varphi_j\right|$*, where* $\hat{P}+\hat{Q}=\hat{I}$*, we obtain*

$\hat{H} = \hat{P}\hat{H}\hat{P} + \hat{Q}\hat{H}\hat{Q} + \hat{P}\hat{H}\hat{Q} + \hat{Q}\hat{H}\hat{P}$*, where,*

$$\hat{P}\hat{H}\hat{P} = H_{0,0}\,|\varphi_0\rangle\langle\varphi_0|,$$

$$\hat{Q}\hat{H}\hat{Q} = \sum_{j''=1}^{N}\left|\varphi_{j''}\right\rangle\left\langle\varphi_{j''}\right|\sum_{j,j'=0}^{N} H_{j,j'}\left|\varphi_j\right\rangle\left\langle\varphi_{j'}\right|\sum_{j'''=1}^{N}\left|\varphi_{j'''}\right\rangle\left\langle\varphi_{j'''}\right|$$

$$= \sum_{j'''=1}^{N}\ \sum_{j,j'=0}^{N}\ \sum_{j''=1}^{N}\left|\varphi_{j''}\right\rangle\left\langle\varphi_{j''}\middle|\varphi_j\right\rangle H_{j,j'}\left\langle\varphi_{j'}\middle|\varphi_{j'''}\right\rangle\left\langle\varphi_{j'''}\right| = \sum_{j,j'=1}^{N} H_{j,j'}\left|\varphi_j\right\rangle\left\langle\varphi_{j'}\right|,$$

$$\hat{Q}\hat{H}\hat{P} = \sum_{j''=1}^{N}\left|\varphi_{j''}\right\rangle\left\langle\varphi_{j''}\right|\sum_{j,j'=0}^{N} H_{j,j'}\left|\varphi_j\right\rangle\left\langle\varphi_{j'}\middle|\varphi_0\right\rangle\left\langle\varphi_0\right|$$

$$= \sum_{j''=1}^{N}\left|\varphi_{j''}\right\rangle\sum_{j=0}^{N}\left\langle\varphi_{j''}\middle|\varphi_j\right\rangle H_{j,0}\,\langle\varphi_0| = \sum_{j''=1}^{N} H_{j'',0}\left|\varphi_{j''}\right\rangle\left\langle\varphi_0\right|,$$

$$\hat{P}\hat{H}\hat{Q} = \sum_{j''=1}^{N} H_{0,j''}\,|\varphi_0\rangle\left\langle\varphi_{j''}\right|.$$

The eigenstates of $\hat{P}\hat{H}\hat{P}$ *and* $\hat{Q}\hat{H}\hat{Q}$ *are identified as,* $\hat{P}\hat{H}\hat{P}\,|\chi_0\rangle = \varepsilon_0\,|\chi_0\rangle$*, where* $|\varphi_0\rangle = |\chi_0\rangle$*,*

and $\hat{Q}\hat{H}\hat{Q}\left|\chi_f\right\rangle = \varepsilon_f\left|\chi_f\right\rangle$ *for* $f = 1,2,...,N$*, where* $\left|\varphi_j\right\rangle = \sum_{f=1}^{N}\left|\chi_f\right\rangle\left\langle\chi_f\middle|\varphi_j\right\rangle$.

In the eigenstate basis, we obtain

$$\hat{Q}\hat{H}\hat{Q} = \sum_{f=1}^{N}\varepsilon_f\left|\chi_f\right\rangle\left\langle\chi_f\right|,$$

$$\hat{P}\hat{H}\hat{P} = \varepsilon_0\,|\chi_0\rangle\langle\chi_0|,$$

$$\hat{Q}\hat{H}\hat{P} = \sum_{j=1}^{N} H_{j,0}\left|\varphi_j\right\rangle\langle\varphi_0| = \sum_{j=1}^{N} H_{j,0}\sum_{f=1}^{N}\left|\chi_f\right\rangle\left\langle\chi_f\middle|\varphi_j\right\rangle\langle\chi_0| = \sum_{f=1}^{N}\left[\sum_{j=1}^{N} H_{j,0}\left\langle\chi_f\middle|\varphi_j\right\rangle\right]\left|\chi_f\right\rangle\langle\chi_0|,$$

$$\hat{P}\hat{H}\hat{Q} = \sum_{f=1}^{N}\left[\sum_{j=1}^{N} H_{0,j}\left\langle\varphi_j\middle|\chi_f\right\rangle\right]|\chi_0\rangle\left\langle\chi_f\right|.$$

Defining, $V_{0,f}=\sum_{j=1}^{N}H_{0,j}\left\langle\varphi_j\middle|\chi_f\right\rangle$*, we obtain Eq. (19.2.4),*

$$\hat{H}=\hat{P}\hat{H}\hat{P}+\hat{Q}\hat{H}\hat{Q}+\hat{P}\hat{H}\hat{Q}+\hat{Q}\hat{H}\hat{P}$$

$$=\varepsilon_0|\chi_0\rangle\langle\chi_0|+\sum_{f=1}^{N}\ \varepsilon_f|\chi_f\rangle\langle\chi_f|+\sum_{f=1}^{N}V_{0,f}|\chi_0\rangle\langle\chi_f|+\sum_{f=1}^{N}V_{0,f}^{*}|\chi_f\rangle\langle\chi_0|\ .$$

Exercise 19.2.3 *Derive Eq. (19.2.9) by implementing Eq. (19.1.9) for the* $\hat{P}$*-space projection,* $\hat{P}\psi_I(t)$ *, with the Hamiltonian in Eq. (19.2.4), and the projection operators,* $\hat{P}=|\chi_0\rangle\langle\chi_0|$ *and* $\hat{Q}=\sum_{f=1}^{N}\ |\chi_f\rangle\langle\chi_f|$.

Solution 19.2.3

For the given model Hamiltonian (Eq. (19.2.4)), and the projection operators, $\hat{P}=|\chi_0\rangle\langle\chi_0|$*, and* $\hat{Q}=\sum_{f=1}^{N}\ |\chi_f\rangle\langle\chi_f|$*, we have (see also Ex. 19.2.2)* $\hat{Q}\hat{H}\hat{Q}=\sum_{f=1}^{N}\varepsilon_f|\chi_f\rangle\langle\chi_f|$, $\hat{P}\hat{H}\hat{P}=\varepsilon_0|\chi_0\rangle\langle\chi_0|$, $\hat{Q}\hat{H}\hat{P}=\sum_{f=1}^{N}V_{0,f}^{*}|\chi_f\rangle\langle\chi_0|$ *and* $\hat{P}\hat{H}\hat{Q}=\sum_{f=1}^{N}V_{0,f}|\chi_0\rangle\langle\chi_f|$*. Using these expressions in Eq. (19.1.9), we obtain*

$$\frac{\partial}{\partial t}\left|\hat{P}\psi_I(t)\right\rangle=-\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}e^{\frac{-i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}\left|\hat{P}\psi_I(\tau)\right\rangle$$

$$=-\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\varepsilon_0|\chi_0\rangle\langle\chi_0|}\sum_{f'=1}^{N}V_{0,f'}|\chi_0\rangle\langle\chi_{f'}|e^{\frac{-i(t-\tau)}{\hbar}\sum_{f=1}^{N}\varepsilon_f|\chi_f\rangle\langle\chi_f|}\sum_{f''=1}^{N}V_{0,f''}^{*}|\chi_{f''}\rangle\langle\chi_0|e^{\frac{-i\tau}{\hbar}\varepsilon_0|\chi_0\rangle\langle\chi_0|}\left|\hat{P}\psi_I(\tau)\right\rangle$$

$$=-\frac{1}{\hbar^2}\int_0^t d\tau\sum_{f=1}^{N}\ |\chi_0\rangle e^{\frac{it}{\hbar}\varepsilon_0}V_{0,f}e^{\frac{-i(t-\tau)}{\hbar}\varepsilon_f}V_{0,f}^{*}e^{\frac{-i\tau}{\hbar}\varepsilon_0}\left\langle\chi_0\middle|\hat{P}\psi_I(\tau)\right\rangle\ .$$

Projecting the equation on $\langle\chi_0|$*, and denoting,* $c_0(\tau)\equiv\left\langle\chi_0\middle|\hat{P}\psi_I(\tau)\right\rangle$ *(see Eq. (19.2.7)), we obtain Eq. (19.2.9),* $\frac{\partial}{\partial t}c_0(\tau)=-\frac{1}{\hbar^2}\int_0^t d\tau\sum_{f=1}^{N}|V_{0,f}|^2e^{\frac{-i(t-\tau)}{\hbar}(\varepsilon_f-\varepsilon_0)}c_0(\tau)$.

Exercise 19.2.4 *(a) Substitute the expansion of* $|\psi_I(t)\rangle$ *(Eq. (19.2.7)) in the Schrödinger equation (Eq. (19.2.6)), and project on the eigenstates of* $\hat{H}_0$*, to obtain the coupled equations for the expansion coefficients, Eq. (19.2.8). (b) Integrate Eq. (19.2.8) over time for the initial condition,* $c_0(0)=1$ *and* $\{c_f(0)=0\}$*, to obtain Eq. (19.2.9).*

Solution 19.2.4

(a)

Substituting Eq. (19.2.7) in Eq. (19.2.6) we obtain on the left-hand side,

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = i\hbar\dot{c}_0(t)|\chi_0\rangle + \sum_{f=1}^{N} i\hbar\dot{c}_f(t)|\chi_f\rangle ,$$

where the right-hand side (for the model Hamiltonian, Eq. (19.2.4)) reads

$$\begin{aligned}
&e^{\frac{i\hat{H}_0 t}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0 t}{\hbar}}|\psi_I(t)\rangle \\
&=\left(\sum_{f=1}^{N} e^{\frac{i\hat{H}_0 t}{\hbar}}\left(V_{0,f}|\chi_0\rangle\langle\chi_f| + V_{0,f}^*|\chi_f\rangle\langle\chi_0|\right)e^{\frac{-i\hat{H}_0 t}{\hbar}}\right)\left(c_0(t)|\chi_0\rangle + \sum_{f'=1}^{N} c_{f'}(t)|\chi_{f'}\rangle\right) \\
&=\sum_{f=1}^{N}\left(V_{0,f}e^{\frac{i\varepsilon_0 t}{\hbar}}|\chi_0\rangle e^{\frac{-i\varepsilon_f t}{\hbar}}\langle\chi_f|\psi_I(t)\rangle + V_{0,f}^* e^{\frac{i\varepsilon_f t}{\hbar}}|\chi_f\rangle e^{\frac{-i\varepsilon_0 t}{\hbar}}\langle\chi_0|\psi_I(t)\rangle\right) \\
&=\sum_{f=1}^{N}\left(V_{0,f}e^{\frac{-i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_f(t)|\chi_0\rangle + V_{0,f}^* e^{\frac{i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_0(t)|\chi_f\rangle\right) .
\end{aligned}$$

To satisfy the Schrodinger equation we require the equality,

$$i\hbar\dot{c}_0(t)|\chi_0\rangle + \sum_{f=1}^{N} i\hbar\dot{c}_f(t)|\chi_f\rangle = \sum_{f=1}^{N}\left(V_{0,f}e^{\frac{-i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_f(t)|\chi_0\rangle + V_{0,f}^* e^{\frac{i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_0(t)|\chi_f\rangle\right) .$$

Projecting on $\langle\chi_0|$ *we obtain* $i\hbar\dot{c}_0(t) = \sum_{f=1}^{N} V_{0,f}e^{\frac{-i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_f(t)$*, namely*

$$\frac{\partial}{\partial t}c_0(t) = \frac{1}{i\hbar}\sum_{f=1}^{N} V_{0,f}e^{\frac{-i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_f(t) .$$

Projecting on $\langle\chi_f|$ *we obtain* $i\hbar\dot{c}_f(t) = V_{0,f}^* e^{\frac{i(\varepsilon_f-\varepsilon_0)t}{\hbar}}c_0(t)$*, namely*

$$\frac{\partial}{\partial t}c_f(t) = \frac{1}{i\hbar}V_{0,f}^* e^{\frac{i(\varepsilon_f - \varepsilon_0)t}{\hbar}} c_0(t).$$

(b)

Integrating Eq. (19.2.8) with $c_0(0) = 1$ *and* $\{c_f(0) = 0\}$, *we obtain*

$$\frac{\partial}{\partial t}c_f(t) = \frac{1}{i\hbar}V_{0,f}^* e^{\frac{i(\varepsilon_f - \varepsilon_0)t}{\hbar}} c_0(t)$$

$$\Rightarrow c_f(t) = c_f(0) + \frac{V_{0,f}^*}{i\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f - \varepsilon_i)t'}{\hbar}} c_0(t')$$

$$\Rightarrow c_f(t) = \frac{V_{0,f}^*}{i\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f - \varepsilon_i)t'}{\hbar}} c_0(t') \quad .$$

Substitution $c_f(t)$ *in the equation,* $\frac{\partial}{\partial t}c_0(t) = \frac{1}{i\hbar}\sum_{f=1}^{N} V_{0,f} e^{\frac{-i(\varepsilon_f - \varepsilon_0)t}{\hbar}} c_f(t)$, *we obtain Eq. (19.2.9),*

$$\frac{\partial}{\partial t}c_0(t) = \frac{1}{i\hbar}\sum_{f=1}^{N} V_{0,f} e^{\frac{-i(\varepsilon_f - \varepsilon_0)t}{\hbar}} \frac{V_{0,f}^*}{i\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f - \varepsilon_i)t'}{\hbar}} c_0(t') = -\sum_{f=1}^{N}\frac{|V_{0,f}|^2}{\hbar^2}\int_0^t dt' e^{\frac{-i(\varepsilon_f - \varepsilon_0)(t-t')}{\hbar}} c_0(t').$$

Exercise 19.2.5 *Use the definition of the operators* $\hat{H}_0$ *and* $\hat{V}$ *in Eq. (19.2.4), and the projection operators,* $\hat{P} = |\chi_0\rangle\langle\chi_0|$, $\hat{Q} = \sum_{f=1}^{N} |\chi_f\rangle\langle\chi_f|$, *to show that the kernel,* $\eta(t,\tau)$, *as defined in Eq. (19.2.14) can be written as* $tr\{e^{\frac{i\hat{H}_0(t-\tau)}{\hbar}}\hat{P}\hat{V}\hat{Q}e^{\frac{-i\hat{H}_0(t-\tau)}{\hbar}}\hat{Q}\hat{V}\hat{P}\}$.

Solution 19.2.5

Starting from the kernel, $\eta(t,\tau) \equiv \sum_{f=1}^{N}|V_{0,f}|^2 e^{\frac{-i(\varepsilon_f - \varepsilon_0)(t-\tau)}{\hbar}}$, *we obtain*

$$\eta(t,\tau) \equiv \sum_{f=1}^{N}|V_{0,f}|^2 e^{\frac{-i(\varepsilon_f - \varepsilon_0)(t-\tau)}{\hbar}} = \sum_{f=1}^{N} e^{\frac{-i\varepsilon_f(t-\tau)}{\hbar}} e^{\frac{i\varepsilon_0(t-\tau)}{\hbar}} \langle\chi_0|\hat{V}|\chi_f\rangle\langle\chi_f|\hat{V}|\chi_0\rangle$$

$$= \sum_{f=1}^{N} \langle\chi_0|e^{\frac{i\hat{H}_0(t-\tau)}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0(t-\tau)}{\hbar}}|\chi_f\rangle\langle\chi_f|\hat{V}|\chi_0\rangle \ .$$

Identifying the projection operators, $\hat{P} = |\chi_0\rangle\langle\chi_0|$, *and* $\hat{Q} = \sum_{f=1}^{N} |\chi_f\rangle\langle\chi_f|$, *we obtain*

$$\eta(t,\tau)=\sum_{f=1}^{N}\ \langle\chi_0|e^{\frac{i\hat{H}_0(t-\tau)}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0(t-\tau)}{\hbar}}|\chi_f\rangle\langle\chi_f|\hat{V}|\chi_0\rangle$$

$$=tr\{\hat{P}e^{\frac{i\hat{H}_0(t-\tau)}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0(t-\tau)}{\hbar}}\hat{Q}\hat{V}\}=tr\{e^{\frac{i\hat{H}_0(t-\tau)}{\hbar}}\hat{P}\hat{V}\hat{Q}e^{\frac{-i\hat{H}_0(t-\tau)}{\hbar}}\hat{Q}\hat{V}\hat{P}\}.$$

Exercise 19.2.6 *Derive Eq. (19.2.18) by implementing the general kernel formula (Eq. (19.2.2)) for the model Hamiltonian defined by Eq. (19.2.4), with the projectors,* $\hat{P}=|\chi_0\rangle\langle\chi_0|$ *and* $\hat{Q}=\sum_{f=1}^{N}\ |\chi_f\rangle\langle\chi_f|$.

Solution 19.2.6

Starting from the general expression for the kernel in Eq. (19.2.2), $\hat{K}(t,\tau)\equiv\frac{1}{\hbar^2}e^{\frac{it}{\hbar}\hat{P}\hat{H}\hat{P}}\hat{P}\hat{H}\hat{Q}e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\hat{Q}\hat{H}\hat{P}e^{\frac{-i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}$*, and introducing* $\hat{P}=|\chi_0\rangle\langle\chi_0|$, $\hat{Q}=\sum_{f=1}^{N}\ |\chi_f\rangle\langle\chi_f|$ *and* $\hat{P}\hat{H}\hat{Q}=\sum_{f=1}^{N}V_{0,f}|\chi_0\rangle\langle\chi_f|$ *(see Ex. 19.2.2), we obtain*

$$\hat{K}(t,\tau)=\frac{1}{\hbar^2}e^{\frac{i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}\sum_{f=1}^{N}V_{0,f}|\chi_0\rangle\langle\chi_f|e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}\hat{H}\hat{Q}}\sum_{f'=1}^{N}V_{0,f'}^{*}|\chi_{f'}\rangle\langle\chi_0|e^{\frac{-i\tau}{\hbar}\hat{P}\hat{H}\hat{P}}$$

$$=\frac{1}{\hbar^2}\sum_f\ |V_{0,f}|^2\ e^{\frac{-i(t-\tau)}{\hbar}(\varepsilon_f-\varepsilon_0)}|\chi_0\rangle\langle\chi_0|\ .$$

Using the definition, $\eta(t,\tau)\equiv\sum_{f=1}^{N}|V_{0,f}|^2e^{\frac{-i(\varepsilon_f-\varepsilon_0)(t-\tau)}{\hbar}}$ *(see Eq. (19.2.14)), we obtain*

$\hat{K}(t,\tau)=\eta(t,\tau)|\chi_0\rangle\langle\chi_0|$*. Substitution of the result in the general expression (Eq. (19.2.2)), recalling that* $\left(|\chi_0\rangle\langle\chi_0|\right)^2=|\chi_0\rangle\langle\chi_0|$*, we obtain*

$$\frac{\partial}{\partial t}|\chi_0\rangle\langle\chi_0|\psi_I(t)\rangle=$$

$$-\left[\int_0^t d\tau\eta(t,\tau)\left[\hat{I}+\int_\tau^t d\tau'\int_0^{\tau'}d\tau''\eta(\tau',\tau'')\left[\hat{I}+\int_{\tau''}^t d\tau'''\int_0^{\tau'''}d\tau''''\eta(\tau''',\tau'''')\left[\hat{I}+\cdots\right]\right]\right]\right]|\chi_0\rangle\langle\chi_0|\psi_I(t)\rangle\ .$$

Projecting on $\langle\chi_0|$ *and using* $c_0(t)=\langle\chi_0|\psi_I(t)\rangle$ *(Eq. (19.2.7)), we obtain Eq. (19.2.18).*

Exercise 19.2.7 *(a) In the continuous band limit, we have* $\sum_{f=1}^{N}|V_{0,f}|^2 e^{\frac{-i(\varepsilon_f-\varepsilon_0)(t-\tau)}{\hbar}} \to$ $\frac{1}{2\pi}\int d\varepsilon J_{0,f}(\varepsilon) e^{\frac{-i(\varepsilon-\varepsilon_0)(t-\tau)}{\hbar}}$ *. Show that for* $J_{0,f}(\varepsilon)\equiv J_b$ *in the range* $|\varepsilon|\le\varepsilon_b$, *and* $J_{0,f}(\varepsilon)\equiv 0$ *otherwise, the exact equation for the survival probability, Eq. (19.2.12), yields Eq. (19.2.20). (b) Show that in the limit* $\varepsilon_b\to\infty$, *the decay of the survival probability becomes exponential (Eq. (19.2.21)).*

Solution 19.2.7

(a)

For the given spectral density, we have

$$\sum_{f=1}^{N}|V_{0,f}|^2 e^{\frac{-i(\varepsilon_f-\varepsilon_0)(t-\tau)}{\hbar}} \to \frac{1}{2\pi}\int d\varepsilon J_{0,f}(\varepsilon) e^{\frac{-i(\varepsilon-\varepsilon_0)(t-\tau)}{\hbar}} = \frac{J_b}{2\pi}\int_{-\varepsilon_b}^{\varepsilon_b} d\varepsilon e^{\frac{-i(\varepsilon-\varepsilon_0)(t-\tau)}{\hbar}} .$$

Substitution in Eq. (19.2.12) yields

$$\frac{\partial}{\partial t}P_0(t) = -\frac{2}{\hbar^2}\mathrm{Re}[\int_0^t d\tau \sum_{f=1}^{N}|V_{0,f}|^2 e^{\frac{-i(\varepsilon_f-\varepsilon_0)(t-\tau)}{\hbar}} c_0^*(t)c_0(\tau)]$$

$$= -\frac{J_b}{\pi\hbar^2}\mathrm{Re}[\int_0^t d\tau \int_{-\varepsilon_b}^{\varepsilon_b} d\varepsilon e^{\frac{-i(\varepsilon-\varepsilon_0)(t-\tau)}{\hbar}} c_0^*(t)c_0(\tau)]$$

$$= \frac{-J_b}{\pi\hbar^2}\mathrm{Re}\int_0^t d\tau \int_{-\varepsilon_b}^{\varepsilon_b} d\varepsilon e^{\frac{-i(\varepsilon-\varepsilon_0)\tau}{\hbar}} c_0^*(t)c_0(t-\tau)$$

$$= \frac{-J_b}{\pi\hbar}\mathrm{Re}\int_0^t d\tau e^{\frac{i\varepsilon_0\tau}{\hbar}} \frac{e^{\frac{i\varepsilon_b\tau}{\hbar}} - e^{\frac{-i\varepsilon_b\tau}{\hbar}}}{i\tau} c_0^*(t)c_0(t-\tau)$$

$$= \frac{-2J_b}{\pi\hbar}\mathrm{Re}\int_0^t d\tau e^{\frac{i\varepsilon_0\tau}{\hbar}} \frac{\sin(\varepsilon_b\tau/\hbar)}{\tau} c_0^*(t)c_0(t-\tau)$$

$$= \frac{-2J_b\varepsilon_b}{\pi\hbar^2}\mathrm{Re}\int_0^t d\tau e^{\frac{i\varepsilon_0\tau}{\hbar}} \frac{\sin(\varepsilon_b\tau/\hbar)}{\varepsilon_b\tau/\hbar} c_0^*(t)c_0(t-\tau) .$$

(b)

Starting from the result for a finite band, $\frac{\partial}{\partial t}P_0(t) = -\frac{J_b}{\pi\hbar^2}\mathrm{Re}[\int_0^t d\tau \int_{-\varepsilon_b}^{\varepsilon_b} d\varepsilon e^{\frac{-i(\varepsilon-\varepsilon_0)(t-\tau)}{\hbar}} c_0^*(t)c_0(\tau)]$, *we can change integration variables,* $\frac{\partial}{\partial t}P_0(t)=\frac{-J_b}{\pi\hbar^2}\mathrm{Re}\int_0^t d\tau\int_{-\varepsilon_b-\varepsilon_0}^{\varepsilon_b-\varepsilon_0} d\varepsilon e^{\frac{-i\varepsilon\tau}{\hbar}} c_0^*(t)c_0(t-\tau)$.

First, we notice that in the limit $\varepsilon_b\to\infty$*, we have for any finite* ε_0*,*

$$\frac{\partial}{\partial t}P_0(t)\xrightarrow[\varepsilon_b\to\infty]{}\frac{-J_b}{\pi\hbar^2}\mathrm{Re}\int_0^t d\tau\int_{-\varepsilon_b}^{\varepsilon_b} d\varepsilon e^{\frac{-i\varepsilon'\tau}{\hbar}} c_0^*(t)c_0(t-\tau)$$

$$=\frac{-J_b}{\pi\hbar}\mathrm{Re}\int_0^t d\tau\frac{e^{\frac{i\varepsilon_b\tau}{\hbar}}-e^{\frac{-i\varepsilon_b\tau}{\hbar}}}{i\tau}c_0^*(t)c_0(t-\tau)=\frac{-2J_b}{\pi\hbar}\mathrm{Re}\int_0^t d\tau\frac{\sin(\varepsilon_b\tau/\hbar)}{\tau}c_0^*(t)c_0(t-\tau)$$

$$\xrightarrow[\varepsilon_b\to\infty]{}=\frac{-2J_b}{\hbar}\mathrm{Re}\int_0^t d\tau\delta(\tau)c_0^*(t)c_0(t-\tau)\ ,$$

where in the last step we used a standard representation of Dirac's delta, $\frac{1}{\pi}\frac{\sin(a\tau)}{\tau}\xrightarrow[a\to\infty]{}\delta(\tau)$.

Noticing that $\delta(\tau)$ *restricts the non-zero contribution to the integral to the limit* $\tau\to 0$*, the slowly varying part of the integrand can be replaced by its* $\tau\to 0$ *limit, namely*

$$\frac{\partial}{\partial t}P_0(t)\xrightarrow[\varepsilon_b\to\infty]{}\frac{-2J_b}{\hbar}\mathrm{Re}\int_0^t d\tau\delta(\tau)c_0^*(t)c_0(t-\tau)$$

$$\xrightarrow[\varepsilon_b\to\infty]{}\frac{-2J_b}{\hbar}\mathrm{Re}\int_0^t d\tau\delta(\tau)c_0^*(t)c_0(t)=\frac{-2J_b}{\hbar}|c_0(t)|^2\int_0^t d\tau\delta(\tau)\ .$$

Finally, evaluating the integral for any finite t *using the fact that Dirac's delta is an (infinitely narrow) even function of* τ*, we obtain*

$$\frac{\partial}{\partial t}P_0(t)\xrightarrow[\varepsilon_b\to\infty]{}\frac{-2J_b}{\hbar}|c_0(t)|^2\int_0^t d\tau\delta(\tau)\xrightarrow[\varepsilon_b\to\infty]{}\frac{-J_b}{\hbar}|c_0(t)|^2\int_{-\infty}^{\infty} d\tau\delta(\tau)=\frac{-J_b}{\hbar}|c_0(t)|^2.$$

Exercise 19.2.8 *Use Eqs. (19.2.22, 19.2.24) to show that*

$$\left|c_f(t)\right|^2\cong\frac{|V_{0,f}|^2}{\left(\varepsilon_f-(\varepsilon_0+\Delta)\right)^2+\left(\hbar k_{0\to\{f\}}\right)^2/4}\left(1-2e^{-k_{0\to\{f\}}t/2}\cos\left[(\varepsilon_f-(\varepsilon_0+\Delta))t/\hbar\right]+e^{-k_{0\to\{f\}}t}\right).$$

Solution 19.2.8

Using the approximation, $c_0(t)\cong e^{\frac{-k_{0\to\{f\}}t}{2}}e^{-i\frac{\Delta t}{\hbar}}$*, in Eq. (19.2.22), we obtain*

$$c_f(t) = \frac{V_{0,f}^*}{i\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f-\varepsilon_0)t'}{\hbar}} c_0(t') \cong \frac{V_{0,f}^*}{i\hbar}\int_0^t dt' e^{\frac{i(\varepsilon_f-(\varepsilon_0+\Delta))t'}{\hbar}} e^{\frac{-k_{0\to\{f\}}}{2}t'}$$

$$= \frac{V_{0,f}^*}{i\hbar}\frac{\hbar}{i(\varepsilon_f-(\varepsilon_0+\Delta)+i\hbar k_{0\to\{f\}}/2)}\left(e^{\frac{i(\varepsilon_f-(\varepsilon_0+\Delta))t}{\hbar}} e^{\frac{-k_{0\to\{f\}}}{2}t} - 1\right)$$

$$= \frac{V_{0,f}^*}{\varepsilon_f-(\varepsilon_0+\Delta)+i\hbar k_{0\to\{f\}}/2}\left(1 - e^{\frac{i(\varepsilon_f-(\varepsilon_0+\Delta))t}{\hbar}} e^{\frac{-k_{0\to\{f\}}}{2}t}\right).$$

Consequently, we obtain

$$\left|c_f(t)\right|^2 = \frac{|V_{0,f}|^2}{\left(\varepsilon_f-(\varepsilon_0+\Delta)\right)^2+\left(\hbar k_{0\to\{f\}}\right)^2/4}\left(1 - e^{\frac{i(\varepsilon_f-(\varepsilon_0+\Delta))t}{\hbar}} e^{\frac{-k_{0\to\{f\}}}{2}t}\right)\left(1 - e^{\frac{-i(\varepsilon_f-(\varepsilon_0+\Delta))t}{\hbar}} e^{\frac{-k_{0\to\{f\}}}{2}t}\right)$$

$$= \frac{|V_{0,f}|^2}{\left(\varepsilon_f-(\varepsilon_0+\Delta)\right)^2+\left(\hbar k_{0\to\{f\}}\right)^2/4}\left(1-2e^{-k_{0\to\{f\}}t/2}\cos\left[(\varepsilon_f-(\varepsilon_0+\Delta))t/\hbar\right]+e^{-k_{0\to\{f\}}t}\right).$$

Exercise 19.3.1 *Let $\hat{A}$ be an operator in a Hilbert space which is a tensor product of two Hilbert subspaces, spanned by the orthonormal vector sets, {$|s\rangle$} and {$|b\rangle$} (without loss of generality, $|s\rangle$ and $|b\rangle$ can correspond to states of "a system" and "a bath", respectively). Expanding the operator in the product basis, {$|s\rangle\otimes|b\rangle$}, we have (see also Eq. (11.6.14)), $\hat{A} = \sum_{s,b,s',b'} A_{s,b,s',b'}|s\rangle\langle s'|\otimes|b\rangle\langle b'|$, where the elements, $A_{s,b,s',b'}$, are the matrix representation of $\hat{A}$. The partial traces of $\hat{A}$ with respect to each of the subspaces are defined as $tr_B\left\{\hat{A}\right\} \equiv \sum_{b''}\langle b''|\hat{A}|b''\rangle$ and $tr_S\left\{\hat{A}\right\} \equiv \sum_{s''}\langle s''|\hat{A}|s''\rangle$ (see Eq. (15.5.3) and Ex. 15.5.1 for the definition of a trace). (a) Show that the partial trace of $\hat{A}$ with respect to one of the subspaces is an operator in the other subspace, for example, $tr_B\left\{\hat{A}\right\} = \sum_{s,s'}\alpha_{s,s'}|s\rangle\langle s'|$, where, $\alpha_{s,s'} = \sum_{b''}A_{s,b'',s',b''}$. (b) Let $\hat{S}$ and $\hat{B}$ be operators in the subspaces spanned by {$|s\rangle$} and {$|b\rangle$}, respectively. Show that $tr_B\left\{\hat{S}\otimes\hat{B}\right\} = tr_B\left\{\hat{B}\otimes\hat{S}\right\} = tr_B\left\{\hat{B}\right\}\hat{S}$. (c) Let $\hat{S}$ be an operator in the subspace spanned by {$|s\rangle$}, and let $\hat{A}$ be an operator in the full (product) space. Show that, $tr\left\{\hat{S}\hat{A}\right\} = tr_S\left\{\hat{S}tr_B\left\{\hat{A}\right\}\right\}$. (d) Let $\hat{B}$ be an operator in the subspace spanned by {$|b\rangle$}, and let $\hat{A}$ be an operator in the full (product) space. Show that, $tr_B\left\{\hat{B}\hat{A}\right\} = tr_B\left\{\hat{A}\hat{B}\right\}$.*

Solution 19.3.1

(a)

Using the general definition of an operator in the full space, $\hat{A} = \sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'| \otimes |b\rangle\langle b'|$, *and the definition of the partial trace of* $\hat{A}$, *we obtain*

$$tr_B\left\{\hat{A}\right\} \equiv \sum_{b''} \langle b''|\hat{A}|b''\rangle = \sum_{b''} \langle b''|\left[\sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'| \otimes |b\rangle\langle b'|\right]|b''\rangle$$

$$= \sum_{b''} \left[\sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'|\langle b''|b\rangle\langle b'|b''\rangle\right]$$

$$= \sum_{s,s'} \left[\sum_{b''} A_{s,b'',s',b''}\right]|s\rangle\langle s'| = \sum_{s,s'} \alpha_{s,s'} |s\rangle\langle s'| \ .$$

(b)

For $\hat{S} = \sum_{s,s'} S_{s,s'} |s\rangle\langle s'|$ *and* $\hat{B} = \sum_{b,b'} B_{b,b'} |b\rangle\langle b'|$, *we obtain*

$$tr_B\left\{\hat{S}\otimes\hat{B}\right\} = \sum_{b''} \langle b''|\hat{S}\otimes\hat{B}|b''\rangle = \hat{S}\sum_{b''} \langle b''|\hat{B}|b''\rangle = tr_B\left\{\hat{B}\right\}\hat{S} \, .$$

(c)

For $\hat{S} = \sum_{s,s'} S_{s,s'} |s\rangle\langle s'|$ *and* $\hat{A} = \sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'| \otimes |b\rangle\langle b'|$, *we obtain*

$$tr\left\{\hat{S}\hat{A}\right\} = \sum_{s,b} \langle s| \otimes \langle b|\hat{S}\hat{A}|s\rangle \otimes |b\rangle$$

$$= \sum_{s,b} \langle s| \otimes \langle b|\hat{S}\left[\sum_{s'',b'',s',b'} A_{s'',b'',s',b'} |s''\rangle\langle s'| \otimes |b''\rangle\langle b'|\right]|s\rangle \otimes |b\rangle$$

$$= \sum_{s} \langle s|\hat{S}\left[\sum_{s'',s'}\sum_{b} A_{s'',b,s',b} |s''\rangle\langle s'|\right]|s\rangle \ .$$

Using (a), we have $\sum_{s'',s'}\sum_{b} A_{s'',b,s',b} |s''\rangle\langle s'| = tr_B\left\{\hat{A}\right\}$, *and therefore,*

$$tr\left\{\hat{S}\hat{A}\right\} = \sum_{s} \langle s|\hat{S}\left[\sum_{s'',s'}\sum_{b} A_{s'',b,s',b} |s''\rangle\langle s'|\right]|s\rangle = \sum_{s} \langle s|\hat{S} tr_B\left\{\hat{A}\right\}|s\rangle = tr_S\left\{\hat{S} tr_B\left\{\hat{A}\right\}\right\}.$$

(d)

For $\sum_{b,b'} B_{b,b'} |b\rangle\langle b'|$ *and* $\hat{A} = \sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'| \otimes |b\rangle\langle b'|$, *we obtain*

$$tr_B\left\{\hat{B}\hat{A}\right\} = \sum_{b''''} \langle b''''|\left[\sum_{b'',b'''} B_{b'',b'''} |b''\rangle\langle b'''|\right]\left[\sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'||b\rangle\langle b'|\right]|b''''\rangle$$

$$= \sum_{b''''} \langle b''''|b''\rangle \sum_{s,b,s',b'} \sum_{b'',b'''} B_{b'',b'''} \langle b'''|b\rangle A_{s,b,s',b'} |s\rangle\langle s'|\langle b'|b''''\rangle$$

$$= \sum_{s,b,s',b'} B_{b',b} A_{s,b,s',b'} |s\rangle\langle s'| \ ,$$

$$tr_B\left\{\hat{A}\hat{B}\right\} = \sum_{b''''} \langle b''''|\left[\sum_{s,b,s',b'} A_{s,b,s',b'} |s\rangle\langle s'||b\rangle\langle b'|\right]\left[\sum_{b'',b'''} B_{b'',b'''} |b''\rangle\langle b'''|\right]|b''''\rangle$$

$$= \sum_{b''''} \langle b''''|b\rangle \sum_{s,b,s',b'} \sum_{b'',b'''} A_{s,b,s',b'} |s\rangle\langle s'|\langle b'|b''\rangle B_{b'',b'''} \langle b'''|b''''\rangle$$

$$= \sum_{s,b,s',b'} A_{s,b,s',b'} B_{b',b} |s\rangle\langle s'| \ .$$

Hence, $tr_B\left\{\hat{B}\hat{A}\right\} = tr_B\left\{\hat{A}\hat{B}\right\}$.

Exercise 19.3.2 *(a) Show that* $\hat{P}_L$ *and* $\hat{Q}_L$, *as defined in Eqs. (19.3.7, 19.3.8), satisfy the relations* $\hat{Q}_L^2 = \hat{Q}_L$, $\hat{P}_L^2 = \hat{P}_L$, *and* $\hat{Q}_L\hat{P}_L = \hat{P}_L\hat{Q}_L = 0$. *(b) Show that* $[\hat{P}_L, \hat{L}_S] = 0$ *and* $[\hat{P}_L, \hat{L}_B] = 0$.

Solution 19.3.2

(a)

Using the definitions: $\hat{P}_L\hat{\rho}(t) \equiv \hat{\rho}_B tr_B\{\hat{\rho}(t)\} \equiv \hat{\rho}_B\hat{\rho}_S(t)$ *and* $\hat{Q}_L\hat{\rho}(t) \equiv \hat{\rho}(t) - \hat{P}_L\hat{\rho}(t)$, *and using* $tr_B\{\hat{\rho}_B\} = 1$ *(Eq. (19.3.6)), we obtain*

$$\hat{P}_L\hat{P}_L\hat{\rho}(t) = \hat{\rho}_B tr_B\{\hat{\rho}_B tr_B\{\hat{\rho}(t)\}\} = \hat{\rho}_B tr_B\{\hat{\rho}_B\} tr_B\{\hat{\rho}(t)\} = \hat{\rho}_B tr_B\{\hat{\rho}(t)\} = \hat{P}_L\hat{\rho}(t)$$

$$\hat{Q}_L\hat{P}_L\hat{\rho}(t) = (\hat{I} - \hat{P}_L)\hat{P}_L\hat{\rho}(t) = \hat{P}_L\hat{\rho}(t) - \hat{P}_L\hat{P}_L\hat{\rho}(t) = 0$$

$$\hat{P}_L\hat{Q}_L\hat{\rho}(t) = \hat{P}_L(\hat{I} - \hat{P}_L)\hat{\rho}(t) = \hat{P}_L\hat{\rho}(t) - \hat{P}_L\hat{P}_L\hat{\rho}(t) = 0$$

$$\hat{Q}_L\hat{Q}_L\hat{\rho}(t) = (I - \hat{P}_L)\hat{Q}_L\hat{\rho}(t) = \hat{Q}_L\hat{\rho}(t) - \hat{P}_L\hat{Q}_L\hat{\rho}(t) = \hat{Q}_L\hat{\rho}(t) \ .$$

(b)

Using the definitions $\hat{L}_S\hat{O} \equiv [\hat{H}_S, \hat{O}]$ *and* $\hat{L}_B\hat{O} \equiv [\hat{H}_B, \hat{O}]$ *(Eq. (19.3.5)), we obtain*

$$\left[\hat{P}_L, \hat{L}_S\right]\hat{\rho}(t) = \hat{P}_L\hat{L}_S\hat{\rho}(t) - \hat{L}_S\hat{P}_L\hat{\rho}(t)$$
$$= \hat{\rho}_B tr_B\{\hat{H}_S\hat{\rho} - \hat{\rho}\hat{H}_S\} - \hat{H}_S\hat{\rho}_B tr_B\{\hat{\rho}\} + \hat{\rho}_B tr_B\{\hat{\rho}\}\hat{H}_S$$
$$= \hat{H}_S\hat{\rho}_B tr_B\{\hat{\rho}\} - \hat{\rho}_B tr_B\{\hat{\rho}\}\hat{H}_S - \hat{H}_S\hat{\rho}_B tr_B\{\hat{\rho}\} + \hat{\rho}_B tr_B\{\hat{\rho}\}\hat{H}_S = 0$$

and

$$\left[\hat{P}_L, \hat{L}_B\right]\hat{\rho}(t) = \hat{P}_L\hat{L}_B\hat{\rho}(t) - \hat{L}_B\hat{P}_L\hat{\rho}(t)$$
$$= \hat{\rho}_B tr_B\{\hat{H}_B\hat{\rho} - \hat{\rho}\hat{H}_B\} - \hat{H}_B\hat{\rho}_B tr_B\{\hat{\rho}\} + \hat{\rho}_B tr_B\{\hat{\rho}\}\hat{H}_B \ .$$

Using Ex. 19.3.1 (d) we have, $tr_B\{\hat{H}_B\hat{\rho} - \hat{\rho}\hat{H}_B\} = 0$. *Recalling that* $tr_B\{\hat{\rho}\}$ *is a system space operator, and that* $[\hat{\rho}_B, \hat{H}_B] = 0$ *(Eq. (19.3.6)), we obtain*

$$\left[\hat{P}_L, \hat{L}_B\right]\hat{\rho}(t)$$
$$= 0 - \hat{H}_B\hat{\rho}_B tr_B\{\hat{\rho}\} + \hat{\rho}_B tr_B\{\hat{\rho}\}\hat{H}_B$$
$$= -tr_B\{\hat{\rho}\}[\hat{\rho}_B, \hat{H}_B] = 0 \ .$$

Exercise 19.3.3 *For the system-bath operators as defined in Eqs. (19.3.3-19.3.6, 19.3.12-19.3.13), show that the projection operators* $\hat{P}_L$ *and* $\hat{Q}_L$, *as defined in Eqs. (19.3.7, 19.3.8), satisfy the relations in Eq. (19.3.14).*

Solution 19.3.3

Using the notation, $\hat{P}_L\hat{\rho}(t) \equiv \hat{\rho}_B tr_B\{\hat{\rho}(t)\} \equiv \hat{\rho}_B\hat{\rho}_S(t)$, *and the definition of the full Liouville operator (Eqs. (19.3.4, 19.3.5)), we obtain*

$$\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t) = \hat{\rho}_B tr_B\left\{[\hat{H}_S + \hat{H}_B + \hat{H}_{SB}]\hat{\rho}_B\hat{\rho}_S(t)\right\} - \hat{\rho}_B tr_B\left\{\hat{\rho}_B\hat{\rho}_S(t)[\hat{H}_S + \hat{H}_B + \hat{H}_{SB}]\right\}$$
$$= \hat{\rho}_B tr_B\left\{\hat{H}_S\hat{\rho}_B\hat{\rho}_S(t)\right\} + \hat{\rho}_B tr_B\left\{\hat{H}_B\hat{\rho}_B\hat{\rho}_S(t)\right\} + \hat{\rho}_B tr_B\left\{\hat{H}_{SB}\hat{\rho}_B\hat{\rho}_S(t)\right\}$$
$$-\hat{\rho}_B tr_B\left\{\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S\right\} - \hat{\rho}_B tr_B\left\{\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_B\right\} - \hat{\rho}_B tr_B\left\{\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_{SB}\right\}$$
$$= \hat{\rho}_B\hat{H}_S\hat{\rho}_S(t) + \hat{\rho}_B tr_B\left\{\hat{H}_B\hat{\rho}_B\right\}\hat{\rho}_S(t) + \hat{\rho}_B tr_B\left\{\hat{H}_{SB}\hat{\rho}_B\right\}\hat{\rho}_S(t)$$
$$-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S - \hat{\rho}_B tr_B\left\{\hat{\rho}_B\hat{H}_B\right\}\hat{\rho}_S(t) - \hat{\rho}_B\hat{\rho}_S(t) tr_B\left\{\hat{\rho}_B\hat{H}_{SB}\right\} \ .$$

Since $tr_B\left\{\hat{\rho}_B\hat{H}_{SB}\right\} = 0$ *(Eqs. (19.3.12, 19.3.13)), we obtain*

$$\hat{\rho}_B\hat{H}_S\hat{\rho}_S(t)+\hat{\rho}_B tr_B\left\{\hat{H}_B\hat{\rho}_B\right\}\hat{\rho}_S(t)+\hat{\rho}_B tr_B\left\{\hat{H}_{SB}\hat{\rho}_B\right\}\hat{\rho}_S(t)$$
$$-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S-\hat{\rho}_B tr_B\left\{\hat{\rho}_B\hat{H}_B\right\}\hat{\rho}_S(t)-\hat{\rho}_B\hat{\rho}_S(t)tr_B\left\{\hat{\rho}_B\hat{H}_{SB}\right\}$$
$$=\hat{\rho}_B\hat{H}_S\hat{\rho}_S(t)-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S$$
$$=[\hat{H}_S,\hat{\rho}_B\hat{\rho}_S(t)]=[\hat{H}_S,\hat{P}_L\hat{\rho}(t)]=\hat{P}_L\hat{L}_S\hat{P}_L\hat{\rho}(t)\ ,$$

and hence, $\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)=\hat{P}_L\hat{L}_S\hat{P}_L\hat{\rho}(t)$.

To derive the reduced expression for $\hat{P}_L\hat{L}\hat{Q}_L\hat{\rho}(t)=\hat{P}_L\hat{L}\hat{\rho}(t)-\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)$, *let us first notice that*

$$\hat{P}_L\hat{L}\hat{\rho}(t)$$
$$=\hat{\rho}_B tr_B\left\{[\hat{H}_S+\hat{H}_B+\hat{H}_{SB}]\hat{\rho}(t)\right\}-\hat{\rho}_B tr_B\{\hat{\rho}(t)[\hat{H}_S+\hat{H}_B+\hat{H}_{SB}]\}$$
$$=\hat{\rho}_B tr_B\left\{\hat{H}_S\hat{\rho}(t)\right\}+\hat{\rho}_B tr_B\left\{\hat{H}_B\hat{\rho}(t)\right\}+\hat{\rho}_B tr_B\left\{\hat{H}_{SB}\hat{\rho}(t)\right\}$$
$$-\hat{\rho}_B tr_B\left\{\hat{\rho}(t)\hat{H}_S\right\}-\hat{\rho}_B tr_B\left\{\hat{\rho}(t)\hat{H}_B\right\}-\hat{\rho}_B tr_B\left\{\hat{\rho}(t)\hat{H}_{SB}\right\}$$
$$=\hat{\rho}_B[\hat{H}_S,\hat{\rho}_S(t)]+\hat{\rho}_B tr_B\{\hat{L}_{SB}\hat{\rho}(t)\}$$
$$=\hat{P}_L\hat{L}_S\hat{P}_L\hat{\rho}(t)+\hat{P}_L\hat{L}_{SB}\hat{\rho}(t)\ .$$

As we have shown, $\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)=\hat{P}_L\hat{L}_S\hat{P}_L\hat{\rho}(t)$, *and therefore we obtain*

$$\hat{P}_L\hat{L}\hat{Q}_L\hat{\rho}(t)=\hat{P}_L\hat{L}\hat{\rho}(t)-\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)=\hat{P}_L\hat{L}_{SB}\hat{\rho}(t).$$

Similarly, to derive the reduced expression for $\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(t)=\hat{L}\hat{P}_L\hat{\rho}(t)-\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)$, *we notice that*

$$\hat{L}\hat{P}_L\hat{\rho}(t)$$
$$=[\hat{H}_S+\hat{H}_B+\hat{H}_{SB}]\hat{\rho}_B\hat{\rho}_S(t)-\hat{\rho}_B\hat{\rho}_S(t)[\hat{H}_S+\hat{H}_B+\hat{H}_{SB}]$$
$$=\hat{H}_S\hat{\rho}_B\hat{\rho}_S(t)+\hat{H}_B\hat{\rho}_B\hat{\rho}_S(t)+\hat{H}_{SB}\hat{\rho}_B\hat{\rho}_S(t)$$
$$-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_B-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_{SB}$$
$$=\hat{\rho}_B\hat{H}_S\hat{\rho}_S(t)+\hat{H}_B\hat{\rho}_B\hat{\rho}_S(t)+\hat{H}_{SB}\hat{\rho}_B\hat{\rho}_S(t)$$
$$-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S-\hat{\rho}_B\hat{H}_B\hat{\rho}_S(t)-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_{SB}\quad .$$

Using $[\hat{H}_B,\hat{\rho}_B]=0$, *we obtain*

$$\hat{L}\hat{P}_L\hat{\rho}(t)$$
$$=\hat{\rho}_B\hat{H}_S\hat{\rho}_S(t)-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_S+\hat{H}_{SB}\hat{\rho}_B\hat{\rho}_S(t)-\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_{SB}$$
$$=\hat{P}_L\hat{L}_S\hat{\rho}_S(t)+\hat{L}_{SB}\hat{\rho}_B\hat{\rho}_S(t)=\hat{P}_L\hat{L}_S\hat{P}_L\hat{\rho}(t)+\hat{L}_{SB}\hat{P}_L\hat{\rho}(t)\quad ,$$

and therefore,

$$\hat{Q}_L\hat{L}\hat{P}_L\hat{\rho}(t)=\hat{L}\hat{P}_L\hat{\rho}(t)-\hat{P}_L\hat{L}\hat{P}_L\hat{\rho}(t)=\hat{L}_{SB}\hat{P}_L\hat{\rho}(t).$$

Exercise 19.3.4 *(a) Use Eqs. (19.1.12, 19.3.9, 19.3.14, 19.3.15) in Eq. (19.3.1) to show that* $\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t) \cong -\frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L e^{\frac{it}{\hbar}\hat{L}_S}\hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{L}_S}\hat{\rho}_P^{(I)}(t)$. *(b) Show that according to the definition of* $\hat{P}_L$ *(Eq. (19.3.7)), for any scalar* α *one has,* $\hat{P}_L e^{\alpha\hat{L}_B} = \hat{P}_L$. *Use this identity and the definition,* $\hat{\rho}_P^{(I)}(t) \equiv e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t)$ *(Eq. (19.1.14)), to derive Eq. (19.3.16).*

Solution 19.3.4

(a)

Starting from Eq. (19.3.1), $\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t) \cong -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{\rho}_P^{(I)}(t)$,

we first introduce the identities in Eq. (19.3.14), to obtain

$$\frac{d}{dt}\hat{\rho}_P^{(I)}(t) \cong -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}_S\hat{P}_L}\hat{P}_L\hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{L}_{SB}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}_S\hat{P}_L}\hat{\rho}_P^{(I)}(t).$$

Then, introducing the approximation $e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L} \approx e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L(\hat{L}_S+\hat{L}_B)\hat{Q}_L}$ *(Eq. (19.3.15)), we obtain*

$$\frac{d}{dt}\hat{\rho}_P^{(I)}(t) \cong -\frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}_S\hat{P}_L}\hat{P}_L\hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L(\hat{L}_S+\hat{L}_B)\hat{Q}_L}\hat{L}_{SB}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}_S\hat{P}_L}\hat{\rho}_P^{(I)}(t).$$

Using again the properties of the projection operators (Eqs. (19.1.12, 19.3.9, 19.3.14)) and $[\hat{L}_S,\hat{L}_B]=0$ *(Eq. (19.3.4)), the result can be rewritten as,*

$$\frac{d}{dt}\hat{\rho}_P^{(I)}(t) \cong -\frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L e^{\frac{it}{\hbar}\hat{L}_S}\hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{L}_S}\hat{\rho}_P^{(I)}(t).$$

(b)

First, we notice that the operators, $e^{\alpha\hat{L}_B}\hat{\rho}$ *and* $e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B}$ *are identical for* $\alpha=0$, *and have identical derivative with respect to* α,

$$\frac{d}{d\alpha}e^{\alpha\hat{L}_B}\hat{\rho} = \hat{L}_B e^{\alpha\hat{L}_B}\hat{\rho} = \hat{H}_B e^{\alpha\hat{L}_B}\hat{\rho} - e^{\alpha\hat{L}_B}\hat{\rho}\hat{H}_B = [\hat{H}_B, e^{\alpha\hat{L}_B}\hat{\rho}]$$

$$\frac{d}{d\alpha}e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B} = \hat{H}_B e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B} - e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B}\hat{H}_B = [\hat{H}_B, e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B}]\ .$$

We can therefore conclude that, $e^{\alpha\hat{L}_B}\hat{\rho}=e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B}$ *, for any* α *. Consequently,*

$tr_B\{e^{\alpha\hat{L}_B}\hat{\rho}(t)\}=tr_B\{e^{\alpha\hat{H}_B}\hat{\rho}(t)e^{-\alpha\hat{H}_B}\}=tr_B\{\hat{\rho}(t)e^{-\alpha\hat{H}_B}e^{\alpha\hat{H}_B}\}=tr_B\{\hat{\rho}(t)\}$ *, where we used the invariance to permutation under the partial trace (Ex. 19.3.1 (d)).*

Hence, $\hat{P}_L e^{\alpha\hat{L}_B}\hat{\rho}=\hat{\rho}_B tr_B\{e^{\alpha\hat{L}_B}\hat{\rho}\}=\hat{\rho}_B tr_B\{\hat{\rho}\}=\hat{P}_L\hat{\rho}$ *. Using the equivalence,* $\hat{P}_L e^{\alpha\hat{L}_B}=\hat{P}_L$ *, in the result of (a) (and recalling that* $\hat{\rho}_P^{(I)}(t)\equiv e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{\rho}(t)$ *, Eq. (19.1.14)), we obtain Eq. (19.3.16),*

$$\frac{d}{dt}\hat{\rho}_P^{(I)}(t)\cong-\frac{1}{\hbar^2}\int_0^t d\tau\hat{P}_L e^{\frac{it}{\hbar}\hat{L}_S}\hat{L}_{SB}e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{L}_S}\hat{\rho}_P^{(I)}(t)$$
$$=-\frac{1}{\hbar^2}\int_0^t d\tau\hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{\rho}_P^{(I)}(t)\ .$$

Exercise 19.3.5 *(a) Use the identities for any scalar* α*,* $e^{\alpha\hat{L}_S}\hat{\rho}\equiv e^{\alpha\hat{H}_S}\hat{\rho}e^{-\alpha\hat{H}_S}$ *, and* $e^{\alpha\hat{L}_B}\hat{\rho}\equiv e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B}$ *, to derive Eq. (19.3.17) from Eq. (19.3.16).*

Solution 19.3.5

Using the identities, $e^{\alpha\hat{L}_S}\hat{\rho}\equiv e^{\alpha\hat{H}_S}\hat{\rho}e^{-\alpha\hat{H}_S}$ *and* $e^{\alpha\hat{L}_B}\hat{\rho}\equiv e^{\alpha\hat{H}_B}\hat{\rho}e^{-\alpha\hat{H}_B}$ *(see Ex. 19.3.4) in Eq. (19.3.16), we obtain*

$$\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t)\cong-\frac{1}{\hbar^2}\int_0^t d\tau\hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{\rho}_P^{(I)}(t)$$
$$=-\frac{1}{\hbar^2}\int_0^t d\tau\hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}$$
$$[e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}_P^{(I)}(t)e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$-e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)}e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}_P^{(I)}(t)e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)}]$$

$$= -\frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}[$$
$$\hat{H}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$-\hat{H}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$-e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB}$$
$$+e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB}]$$

$$= -\frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L [$$
$$e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$-e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$-e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$+e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_P^{(I)}(t) e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i(t-\tau)}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}].$$

Using the interaction picture representation, $\hat{H}_{SB}^{(I)}(t) \equiv e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$*, we obtain Eq. (19.3.17),*

$$\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t) \cong -\frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L [\hat{H}_{SB}^{(I)}(t)\hat{H}_{SB}^{(I)}(\tau)\hat{\rho}_P^{(I)}(t) - \hat{H}_{SB}^{(I)}(t)\hat{\rho}_P^{(I)}(t)\hat{H}_{SB}^{(I)}(\tau)$$
$$-\hat{H}_{SB}^{(I)}(\tau)\hat{\rho}_P^{(I)}(t)\hat{H}_{SB}^{(I)}(t) + \hat{\rho}_P^{(I)}(t)\hat{H}_{SB}^{(I)}(\tau)\hat{H}_{SB}^{(I)}(t)]$$
$$= -\frac{1}{\hbar^2}\int_0^t d\tau \hat{P}_L [\hat{H}_{SB}^{(I)}(t),[\hat{H}_{SB}^{(I)}(\tau),\hat{\rho}_P^{(I)}(t)]$$
$$= -\frac{1}{\hbar^2}\hat{\rho}_B\int_0^t d\tau tr_B\{[\hat{H}_{SB}^{(I)}(t),[\hat{H}_{SB}^{(I)}(\tau),\hat{\rho}_P^{(I)}(t)]\} \ .$$

Exercise 19.3.6 *Use the identities,* $\hat{\rho}_P^{(I)}(t) = e^{\frac{it}{\hbar}\hat{L}_S}\hat{P}_L\hat{\rho}(t) = \hat{\rho}_B e^{\frac{it}{\hbar}\hat{L}_S}\hat{\rho}_S(t)$*, and Eq. (19.3.16) to derive Eq. (19.3.18).*

Solution 19.3.6

Using $\hat{\rho}_P^{(I)}(t) = e^{\frac{it}{\hbar}\hat{L}_S}\hat{P}_L\hat{\rho}(t) = \hat{\rho}_B e^{\frac{it}{\hbar}\hat{L}_S}\hat{\rho}_S(t)$ *in Eq. (19.3.16), we obtain Eq. (19.3.18),*

$$\hat{\rho}_B \frac{\partial}{\partial t} e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_S(t) \cong -\frac{1}{\hbar^2} \hat{\rho}_B \int_0^t d\tau tr_B \{ e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_B \hat{\rho}_S(t) \}$$
$$\Rightarrow \frac{\partial}{\partial t} e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_S(t) \cong -\frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{\rho}_B e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_S(t) \}$$
$$\Rightarrow \frac{i}{\hbar} \hat{L}_S e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_S(t) + e^{\frac{it}{\hbar}\hat{L}_S} [\frac{\partial}{\partial t} \hat{\rho}_S(t)] \cong -\frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{\rho}_B e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_S(t) \}$$
$$\Rightarrow \frac{\partial}{\partial t} \hat{\rho}_S(t) \cong -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ e^{\frac{it}{\hbar}\hat{L}_B} \hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{\rho}_B e^{\frac{it}{\hbar}\hat{L}_S} \hat{\rho}_S(t) \}$$
$$= -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ \hat{L}_{SB} e^{\frac{-i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{i(t-\tau)}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{\rho}_B \} \hat{\rho}_S(t)$$
$$= -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{\rho}_B \} \hat{\rho}_S(t) \ .$$

Exercise 19.3.7 *Use the identity,* $e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{A} = e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{A} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$ *to derive Eq. (19.3.19) from Eq. (19.3.18).*

Solution 19.3.7

Starting from Eq. (19.3.18), using $e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{A} = e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{A} e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$*, we obtain Eq. (19.3.19),*

$$\frac{\partial}{\partial t} \hat{\rho}_S(t) \cong -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{\rho}_B \hat{\rho}_S(t) \}$$
$$= -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)} \hat{L}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_B \hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \}$$
$$= -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ \hat{L}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{L}_S+\hat{L}_B)}$$
$$[\hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_B \hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} - e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_B \hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB}] \}$$
$$= -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{$$
$$\hat{H}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_B \hat{\rho}_S(t) - \hat{H}_{SB} \hat{\rho}_B \hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$- e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{\rho}_B \hat{\rho}_S(t) \hat{H}_{SB} + \hat{\rho}_B \hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} \}$$
$$= -\frac{i}{\hbar} \hat{L}_S \hat{\rho}_S(t) - \frac{1}{\hbar^2} \int_0^t d\tau tr_B \{ [\hat{H}_{SB}, [e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}, \hat{\rho}_B \hat{\rho}_S(t)]] \} \ .$$

Exercise 19.3.8 *Follow the alternative derivation given here to obtain the Redfield equation directly: (a) Transform the full Liouville equation,* $\frac{\partial}{\partial t}\hat{\rho}(t)=\frac{-i}{\hbar}[\hat{\mathrm{H}},\hat{\rho}(t)]$, *with* $\hat{H}=\hat{H}_S+\hat{H}_B+\hat{H}_{SB}$ *, into the interaction picture representation,* $\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)=\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(t)]$, *where,* $\hat{O}^{(I)}(t)\equiv e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\hat{O}(t)e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}$. *(b) Integrate the equation over time and show that it can be rearranged exactly as* $\frac{\partial}{\partial t}\hat{\rho}^{I}(t)=$

$$\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]-\frac{1}{\hbar^2}\int_0^t dt'[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t)]]-\frac{i}{\hbar^3}\int_0^t dt'\int_{t'}^t dt''[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),[\hat{\mathrm{H}}_{SB}^{(I)}(t''),\hat{\rho}^{(I)}(t'')]$$

. (c) Neglect the terms of third order and higher in the system-bath coupling, and obtain an approximate Markovian equation for $\hat{\rho}^{(I)}(t)$, $\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)\cong\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]$ $-\frac{1}{\hbar^2}\int_0^t dt'[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t)]]$. *(d) Defining the reduced system density operator as* $\hat{\rho}_S^{(I)}(t)\equiv tr_B[\hat{\rho}^{(I)}(t)]$, *and assuming an initial product density:* $\hat{\rho}^{(I)}(0)=\hat{\rho}(0)=\hat{\rho}_B\hat{\rho}_S(0)$, *show that for* $tr_B\{\hat{\rho}_B\,\hat{\mathrm{H}}_{SB}\}=0$ *(Eqs. (19.3.12, 19.3.13)), we obtain,* $\frac{\partial}{\partial t}\hat{\rho}_S^{(I)}(t)=-\frac{1}{\hbar^2}\int_0^t dt' tr_B[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t)]]$. *(e) Without loss of accuracy to second order in the system-bath coupling, replace* $\hat{\rho}^{(I)}(t)\cong\hat{\rho}_B\otimes\hat{\rho}_S^{(I)}(t)$ *under the latter time-integral and show that this leads to Eq. (19.3.17), and hence to the Redfield equation, Eq. (19.3.19).*

Solution 19.3.8

(a)

To follow the time evolution of the full density operator, the Liouville-von Neumann equation of motion, $\frac{\partial}{\partial t}\hat{\rho}(t)=\frac{-i}{\hbar}[\hat{\mathrm{H}},\hat{\rho}(t)]$, *needs to be solved. Transforming the operators into the interaction picture representation,* $\hat{O}^{(I)}(t)\equiv e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\hat{O}(t)e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}$, *and taking the time-derivative of* $\hat{\rho}^{(I)}(t)$, *we obtain*

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)=\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B,\hat{\rho}^{(I)}(t)]+\frac{-i}{\hbar}e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B+\hat{\mathrm{H}}_{SB},\hat{\rho}(t)]e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}$$

$$=\frac{-i}{\hbar}e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}[\hat{\mathrm{H}}_{SB},\hat{\rho}(t)]e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}=\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(t)] \quad .$$

(b)

Integrating the differential equation, $\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)=\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(t)]$, *we obtain* $\hat{\rho}^{(I)}(t)=\hat{\rho}^{(I)}(0)+\frac{-i}{\hbar}\int_0^t dt'[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t')]$. *Using this result, we can rewrite the time-derivative as*

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)=\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]-\frac{1}{\hbar^2}\int_0^t dt'[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t')]].$$

Using a similar integral form for $\hat{\rho}^{(I)}(t')$ *under the time integral, namely* $\hat{\rho}^{(I)}(t')=\hat{\rho}^{(I)}(t)+\frac{i}{\hbar}\int_{t'}^t dt''[\hat{\mathrm{H}}_{SB}^{(I)}(t''),\hat{\rho}^{(I)}(t'')]$, *we obtain*

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)=\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]-\frac{1}{\hbar^2}\int_0^t dt'[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t)]]$$

$$-\frac{i}{\hbar^3}\int_0^t dt'\int_{t'}^t dt''[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),[\hat{\mathrm{H}}_{SB}^{(I)}(t''),\hat{\rho}^{(I)}(t'')]]] \quad .$$

(c)

Neglecting terms which are third-order and higher in the system-bath coupling operator, we obtain an approximated Markovian equation for $\hat{\rho}^{(I)}(t)$,

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)\cong\frac{-i}{\hbar}[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]-\frac{1}{\hbar^2}\int_0^t dt'[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t)]].$$

(d)

For $\hat{\rho}^{(I)}(0)=\hat{\rho}(0)=\hat{\rho}_B\hat{\rho}_S(0)$ *we obtain*

$$tr_B\{[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]\}=tr_B\{[e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t},\hat{\rho}_B\hat{\rho}_S(0)]\}$$
$$=tr_B\{e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\hat{\rho}_B\hat{\rho}_S(0)\}-tr_B\{\hat{\rho}_B\hat{\rho}_S(0)e^{\frac{i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}[\hat{\mathrm{H}}_S+\hat{\mathrm{H}}_B]t}\}$$
$$=e^{\frac{i}{\hbar}\hat{\mathrm{H}}_S t}tr_B\{e^{\frac{i}{\hbar}\hat{\mathrm{H}}_B t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_B t}\hat{\rho}_B\}e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_S t}\hat{\rho}_S(0)-\hat{\rho}_S(0)e^{\frac{i}{\hbar}\hat{\mathrm{H}}_S t}tr_B\{\hat{\rho}_B e^{\frac{i}{\hbar}\hat{\mathrm{H}}_B t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_B t}\}e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_S t}.$$

Using: $[\hat{\rho}_B,\hat{H}_B]=0$*, we obtain*

$$tr_B\{[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]\}$$
$$=e^{\frac{i}{\hbar}\hat{\mathrm{H}}_S t}tr_B\{e^{\frac{i}{\hbar}\hat{\mathrm{H}}_B t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_B t}\hat{\rho}_B\}e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_S t}\hat{\rho}_S(0)-\hat{\rho}_S(0)e^{\frac{i}{\hbar}\hat{\mathrm{H}}_S t}tr_B\{\hat{\rho}_B e^{\frac{i}{\hbar}\hat{\mathrm{H}}_B t}\,\hat{\mathrm{H}}_{SB}\,e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_B t}\}e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_S t}$$
$$=e^{\frac{i}{\hbar}\hat{\mathrm{H}}_S t}tr_B\{\hat{\mathrm{H}}_{SB}\,\hat{\rho}_B\}e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_S t}\hat{\rho}_S(0)-\hat{\rho}_S(0)e^{\frac{i}{\hbar}\hat{\mathrm{H}}_S t}tr_B\{\hat{\rho}_B\,\hat{\mathrm{H}}_{SB}\}e^{\frac{-i}{\hbar}\hat{\mathrm{H}}_S t},$$

and using, $tr_B\{\hat{\rho}_B\,\hat{\mathrm{H}}_{SB}\}=0$*, we obtain,* $tr_B\{[\hat{\mathrm{H}}_{SB}^{(I)}(t),\hat{\rho}^{(I)}(0)]\}=0$.

Consequently, using the definition, $\hat{\rho}_S^{(I)}(t)\equiv tr_B\{\hat{\rho}^{(I)}(t)\}$*, and taking the trace over the bath in the result of (c), we obtain*

$$\frac{\partial}{\partial t}\hat{\rho}_S^{(I)}(t)\equiv tr_B\{\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t)\}\cong-\frac{1}{\hbar^2}\int_0^t dt' tr_B\{[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}^{(I)}(t)]]\}.$$

(e)

Replacing $\hat{\rho}^{(I)}(t)\cong\hat{\rho}_B\otimes\hat{\rho}_S^{(I)}(t)$ *under the time-integral in the result of (d), we obtain Eq. (19.3.17), which yields the Redfield equation (Eq. (19.3.19), using Ex. 19.3.6 and Ex. 19.3.7),*

$$\frac{\partial}{\partial t}\hat{\rho}_S^{(I)}(t)\cong-\frac{1}{\hbar^2}\int_0^t dt' tr_B\{[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}_B\hat{\rho}_S^{(I)}(t)]]\}$$
$$=-\frac{1}{\hbar^2}\int_0^t dt' tr_B\{[\hat{\mathrm{H}}_{SB}^{(I)}(t),[\hat{\mathrm{H}}_{SB}^{(I)}(t'),\hat{\rho}_B tr_B\{\hat{\rho}^{(I)}(t)\}]]\}.$$

Exercise 19.3.9 *When the system and bath are initially correlated,* $\hat{Q}_L\hat{\rho}(0)\neq 0$*, the exact equation for the* $\hat{P}_L$*-space density operator obtains an inhomogeneous term (Eq. (19.1.16)). Expanding this term up to first-order in the system-bath coupling, show that Eq. (19.3.19) is generalized to,*

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)] - \frac{1}{\hbar^2}\int_0^t d\tau tr_B\{[\hat{H}_{SB},[e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)},\hat{\rho}_B\hat{\rho}_S(t)]]\}$$

$$-\frac{i}{\hbar}\hat{\rho}_B tr_B\{[e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)},\hat{\rho}(0)]\} \ .$$

Solution 19.3.9

Let us recall Eq. (19.1.16),

$$\frac{\partial}{\partial t}\hat{\rho}_P^{(I)}(t) + \frac{1}{\hbar^2}\int_0^t d\tau e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{L}\hat{P}_L e^{\frac{-i\tau}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{\rho}_P^{(I)}(\tau)$$

$$= -\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{\rho}(0) \ .$$

Focusing on the inhomogeneous term, using $\hat{P}_L\hat{L}\hat{P}_L = \hat{P}_L\hat{L}_S\hat{P}_L$, $\hat{P}_L\hat{L}\hat{Q}_L = \hat{P}_L\hat{L}_{SB}$ *(Eq. (19.3.14)), and* $\hat{P}_L e^{\frac{it}{\hbar}\hat{L}_B} = \hat{P}_L$ *(Ex. 19.3.4 (b)), we obtain*

$$-\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{\rho}(0) = -\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}_S\hat{P}_L}\hat{P}_L\hat{L}_{SB}e^{\frac{-it}{\hbar}\hat{Q}_L(\hat{L}_S+\hat{L}_B+\hat{L}_{SB})\hat{Q}_L}\hat{Q}_L\hat{\rho}(0)$$

$$= -\frac{i}{\hbar}\hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-it}{\hbar}\hat{Q}_L(\hat{L}_S+\hat{L}_B+\hat{L}_{SB})\hat{Q}_L}\hat{Q}_L\hat{\rho}(0) \ .$$

Restricting to first order in the system-bath coupling, we approximate, $e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L} \approx e^{\frac{-i(t-\tau)}{\hbar}\hat{Q}_L(\hat{L}_S+\hat{L}_B)\hat{Q}_L}$ *(Eq. (19.3.15)), to obtain*

$$-\frac{i}{\hbar}e^{\frac{it}{\hbar}\hat{P}_L\hat{L}\hat{P}_L}\hat{P}_L\hat{L}\hat{Q}_L e^{\frac{-it}{\hbar}\hat{Q}_L\hat{L}\hat{Q}_L}\hat{Q}_L\hat{\rho}(0) \cong -\frac{i}{\hbar}\hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-it}{\hbar}\hat{Q}_L(\hat{L}_S+\hat{L}_B)\hat{Q}_L}\hat{Q}_L\hat{\rho}(0)$$

$$= -\frac{i}{\hbar}\hat{P}_L e^{\frac{it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{L}_{SB}e^{\frac{-it}{\hbar}(\hat{L}_S+\hat{L}_B)}\hat{\rho}(0)$$

$$= -\frac{i}{\hbar}\hat{P}_L e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\left[\hat{H}_{SB}e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}(0)e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)} - e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}(0)e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}\right]e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}$$

$$= -\frac{i}{\hbar}\hat{P}_L\left[e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}(0) - \hat{\rho}(0)e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)}\right]$$

$$= -\frac{i}{\hbar}\hat{\rho}_B tr_B\{\left[e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)},\hat{\rho}(0)\right]\} \ .$$

Consequently,

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)]$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau tr_B\{[\hat{H}_{SB},[e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)},\hat{\rho}_B\hat{\rho}_S(t)]]\}$$
$$-\frac{i}{\hbar}\hat{\rho}_B tr_B\{[e^{\frac{it}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{-it}{\hbar}(\hat{H}_S+\hat{H}_B)},\hat{\rho}(0)]\}\ .$$

Exercise 19.3.10 *Using the expansion of the system-bath coupling operator,* $\hat{H}_{SB} \equiv \sum_\alpha \hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}$ *(Eq. (19.3.12)), we obtain* $e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)} \equiv \sum_\alpha \hat{V}_\alpha^{(S)}(\tau)\hat{U}_\alpha^{(B)}(\tau)$, *where* $\hat{V}_\alpha^{(S)}(\tau) \equiv e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_\alpha^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}$ *and* $\hat{U}_\alpha^{(B)}(\tau) \equiv e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_\alpha^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}$. *Using these expressions, show that* $\hat{D}\hat{\rho}_S(t)$, *as defined in Eq. (19.3.20), can be expressed in terms of the bath coupling correlation functions* $c_{\alpha,\alpha'}(\tau)$ *and* $\bar{c}_{\alpha,\alpha'}(\tau)$ *(Eqs. (19.3.21, 19.3.22)).*

Solution 19.3.10

Starting from Eq. (19.3.20), using $\hat{V}_\alpha^{(S)}(\tau) \equiv e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_\alpha^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}$ *and* $\hat{U}_\alpha^{(B)}(\tau) \equiv e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_\alpha^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}$, *we obtain*

$$\hat{D}\hat{\rho}_S(t) \equiv -\frac{1}{\hbar^2}\int_0^t d\tau tr_B\{[\hat{H}_{SB},[e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)},\hat{\rho}_B\hat{\rho}_S(t)]]\}$$
$$= -\frac{1}{\hbar^2}\int_0^t d\tau tr_B\{[\hat{H}_{SB}e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}_B\hat{\rho}_S(t) - \hat{H}_{SB}\hat{\rho}_B\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}$$
$$-e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{\rho}_B\hat{\rho}_S(t)\hat{H}_{SB} + \hat{\rho}_B\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_S+\hat{H}_B)}\hat{H}_{SB}]\}$$
$$= -\sum_{\alpha,\alpha'}\frac{1}{\hbar^2}\int_0^t d\tau tr_B\{\hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}\hat{V}_{\alpha'}^{(S)}(\tau)\hat{U}_{\alpha'}^{(B)}(\tau)\hat{\rho}_B\hat{\rho}_S(t) - \hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}\hat{\rho}_B\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}(\tau)\hat{U}_{\alpha'}^{(B)}(\tau)$$
$$-\hat{V}_\alpha^{(S)}(\tau)\hat{U}_\alpha^{(B)}(\tau)\hat{\rho}_B\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}\hat{U}_{\alpha'}^{(B)} + \hat{\rho}_B\hat{\rho}_S(t)\hat{V}_\alpha^{(S)}(\tau)\hat{U}_\alpha^{(B)}(\tau)\hat{V}_{\alpha'}^{(S)}\hat{U}_{\alpha'}^{(B)}\}$$
$$= -\sum_{\alpha,\alpha'}\frac{1}{\hbar^2}\int_0^t d\tau[tr_B\{\hat{U}_\alpha^{(B)}\hat{U}_{\alpha'}^{(B)}(\tau)\hat{\rho}_B\}\hat{V}_\alpha^{(S)}\hat{V}_{\alpha'}^{(S)}(\tau)\hat{\rho}_S(t) - tr_B\{\hat{U}_\alpha^{(B)}\hat{\rho}_B\hat{U}_{\alpha'}^{(B)}(\tau)\}\hat{V}_\alpha^{(S)}\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}(\tau)$$
$$-tr_B\{\hat{U}_\alpha^{(B)}(\tau)\hat{\rho}_B\hat{U}_{\alpha'}^{(B)}\}\hat{V}_\alpha^{(S)}(\tau)\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)} + tr_B\{\hat{\rho}_B\hat{U}_\alpha^{(B)}(\tau)\hat{U}_{\alpha'}^{(B)}\}\hat{\rho}_S(t)\hat{V}_\alpha^{(S)}(\tau)\hat{V}_{\alpha'}^{(S)}]\ .$$

Using the definitions in Eq. (19.3.21),

$c_{\alpha,\alpha'}(\tau) \equiv tr_B\{\hat{U}_\alpha^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_{\alpha'}^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$ *and* $\bar{c}_{\alpha,\alpha'}(\tau) \equiv tr_B\{e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_\alpha^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{U}_{\alpha'}^{(B)} \hat{\rho}_B\} = c_{\alpha,\alpha'}(-\tau)$,

we obtain

$$\hat{D}\hat{\rho}_S(t) = -\sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^t d\tau [c_{\alpha,\alpha'}(\tau)\hat{V}_\alpha^{(S)}\hat{V}_{\alpha'}^{(S)}(\tau)\hat{\rho}_S(t) - \bar{c}_{\alpha',\alpha}(\tau)\hat{V}_\alpha^{(S)}\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}(\tau)$$
$$-c_{\alpha',\alpha}(\tau)\hat{V}_\alpha^{(S)}(\tau)\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)} + \bar{c}_{\alpha,\alpha'}(\tau)\hat{\rho}_S(t)\hat{V}_\alpha^{(S)}(\tau)\hat{V}_{\alpha'}^{(S)}] \ .$$

Exchanging summation indexes and gathering similar terms, we finally obtain Eq. (19.3.22),

$$\hat{D}\hat{\rho}_S(t)$$
$$= -\sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^t d\tau [c_{\alpha,\alpha'}(\tau)\hat{V}_\alpha^{(S)}\hat{V}_{\alpha'}^{(S)}(\tau)\hat{\rho}_S(t) - \bar{c}_{\alpha',\alpha}(\tau)\hat{V}_\alpha^{(S)}\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}(\tau)$$
$$-c_{\alpha,\alpha'}(\tau)\hat{V}_{\alpha'}^{(S)}(\tau)\hat{\rho}_S(t)\hat{V}_\alpha^{(S)} + \bar{c}_{\alpha',\alpha}(\tau)\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}(\tau)\hat{V}_\alpha^{(S)}]$$
$$= -\sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^t d\tau (c_{\alpha,\alpha'}(\tau)[\hat{V}_\alpha^{(S)}, \hat{V}_{\alpha'}^{(S)}(\tau)\hat{\rho}_S(t)] + \bar{c}_{\alpha',\alpha}(\tau)[\hat{\rho}_S(t)\hat{V}_{\alpha'}^{(S)}(\tau), \hat{V}_\alpha^{(S)}]) \ .$$

Exercise 19.3.11 *The Redfield equation for the reduced density operator (Eq. (19.3.19)) can be written as* $\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(t)] + \hat{D}\hat{\rho}_S(t)$, *with* $\hat{D}\hat{\rho}_S(t)$ *defined according to Eq. (19.3.22). Defining* $\rho_{n',n}(t) \equiv \langle \varphi_{n'}|\hat{\rho}_S(t)|\varphi_n\rangle$ *and* $V_{n',n}^{(\alpha)} \equiv \langle \varphi_{n'}|\hat{V}_\alpha^{(S)}|\varphi_n\rangle$, *where* $\{|\varphi_n\rangle\}$ *are a complete orthonormal system of* $\hat{H}_S$ *eigenstates with the corresponding energies,* $\{E_n\}$, *derive Eq. (19.3.23), using the definitions in Eqs. (19.3.24, 19.3.25).*

Solution 19.3.11

Starting from Eq. (19.3.22) for the dissipator,

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\sum_{\alpha,\alpha'} \int_0^t d\tau c_{\alpha,\alpha'}(\tau)[\hat{V}_\alpha^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \bar{c}_{\alpha',\alpha}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_\alpha^{(S)}]$$
$$= -\frac{1}{\hbar^2}\sum_{\alpha,\alpha'} \{\int_0^t d\tau c_{\alpha,\alpha'}(\tau)\hat{V}_\alpha^{(S)}e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t) - \int_0^t d\tau c_{\alpha,\alpha'}(\tau)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_\alpha^{(S)}$$
$$+\int_0^t d\tau \bar{c}_{\alpha',\alpha}(\tau)\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{V}_\alpha^{(S)} - \int_0^t d\tau \bar{c}_{\alpha',\alpha}(\tau)\hat{V}_\alpha^{(S)}\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\} ,$$

we introduce a complete orthonormal set of $\hat{H}_S$ *-eigenstates,* $\hat{H}_S\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle$. *The corresponding equation for the matrix elements of* $\hat{D}\hat{\rho}_S(t)$ *in terms of the matrix representations of the system operators,* $\rho_{n',n}(t) \equiv \left\langle\varphi_{n'}\right|\hat{\rho}_S(t)\left|\varphi_n\right\rangle$ *and* $V^{(\alpha)}_{n',n} \equiv \left\langle\varphi_{n'}\right|\hat{V}^{(S)}_\alpha\left|\varphi_n\right\rangle$, *reads*

$$\left[\hat{D}\hat{\rho}_S(t)\right]_{n',n} = -\frac{1}{\hbar^2}\sum_{\alpha,\alpha'}\sum_{m,m'}$$

$$\{\int_0^t d\tau c_{\alpha,\alpha'}(\tau)V^{(\alpha)}_{n',m}e^{\frac{-i\tau}{\hbar}E_m}V^{(\alpha')}_{m,m'}e^{\frac{i\tau}{\hbar}E_{m'}}\rho_{m',n}(t)$$

$$-\int_0^t d\tau c_{\alpha,\alpha'}(\tau)e^{\frac{-i\tau}{\hbar}E_{n'}}V^{(\alpha')}_{n',m}e^{\frac{i\tau}{\hbar}E_m}\rho_{m,m'}(t)V^{(\alpha)}_{m',n}$$

$$+\int_0^t d\tau \bar{c}_{\alpha',\alpha}(\tau)\rho_{n',m}(t)e^{\frac{-i\tau}{\hbar}E_m}V^{(\alpha')}_{m,m'}e^{\frac{i\tau}{\hbar}E_{m'}}V^{(\alpha)}_{m',n}$$

$$-\int_0^t d\tau \bar{c}_{\alpha',\alpha}(\tau)V^{(\alpha)}_{n',m}\rho_{m,m'}(t)e^{\frac{-i\tau}{\hbar}E_{m'}}V^{(\alpha')}_{m',n}e^{\frac{i\tau}{\hbar}E_n}\}.$$

Defining, $g^{(\alpha,\alpha')}_{n,n'}(t) \equiv \frac{1}{\hbar^2}\int_0^t c_{\alpha,\alpha'}(\tau)e^{\frac{-i\tau}{\hbar}(E_n - E_{n'})}d\tau$ *and* $\bar{g}^{(\alpha,\alpha')}_{n,n'}(t) \equiv \frac{1}{\hbar^2}\int_0^t \bar{c}_{\alpha,\alpha'}(\tau)e^{\frac{-i\tau}{\hbar}(E_n - E_{n'})}d\tau$ *(Eq. (19.3.25)), we obtain*

$$\left[\hat{D}\hat{\rho}_S(t)\right]_{n',n} = -\sum_{\alpha,\alpha'}\sum_{m,m'}\{g^{(\alpha,\alpha')}_{m,m'}(t)V^{(\alpha)}_{n',m}V^{(\alpha')}_{m,m'}\rho_{m',n}(t) - g^{(\alpha,\alpha')}_{n',m}V^{(\alpha')}_{n',m}\rho_{m,m'}(t)V^{(\alpha)}_{m',n}$$

$$+\bar{g}^{(\alpha',\alpha)}_{m,m'}(t)\rho_{n',m}(t)V^{(\alpha')}_{m,m'}V^{(\alpha)}_{m',n} - \bar{g}^{(\alpha',\alpha)}_{m',n}(t)V^{(\alpha)}_{n',m}\rho_{m,m'}(t)V^{(\alpha')}_{m',n}\}.$$

Changing summation indexes, we obtain

$$\left[\hat{D}\hat{\rho}_S(t)\right]_{n',n} = -\sum_{\alpha,\alpha'}\{\sum_{l,m'}\sum_{m} g^{(\alpha,\alpha')}_{l,m'}(t)V^{(\alpha)}_{n',l}V^{(\alpha')}_{l,m'}\delta_{m,n}\rho_{m',m}(t) - \sum_{m,m'} g^{(\alpha,\alpha')}_{n',m'}V^{(\alpha')}_{n',m'}V^{(\alpha)}_{m,n}\rho_{m',m}(t)$$

$$+\sum_{m,l}\sum_{m'}\bar{g}^{(\alpha',\alpha)}_{m,l}(t)V^{(\alpha')}_{m,l}V^{(\alpha)}_{l,n}\delta_{m',n'}\rho_{m',m}(t) - \sum_{m,m'}\bar{g}^{(\alpha',\alpha)}_{m,n}(t)V^{(\alpha)}_{n',m'}V^{(\alpha')}_{m,n}\rho_{m',m}(t)\}$$

$$= -\sum_{m,m'}\sum_{\alpha,\alpha'}\{\left(\sum_{l} g^{(\alpha,\alpha')}_{l,m'}(t)V^{(\alpha)}_{n',l}V^{(\alpha')}_{l,m'}\delta_{m,n}\right) - g^{(\alpha,\alpha')}_{n',m'}(t)V^{(\alpha')}_{n',m'}V^{(\alpha)}_{m,n}$$

$$+\left(\sum_{l}\bar{g}^{(\alpha',\alpha)}_{m,l}(t)V^{(\alpha')}_{m,l}V^{(\alpha)}_{l,n}\delta_{m',n'}\right) - \bar{g}^{(\alpha',\alpha)}_{m,n}(t)V^{(\alpha)}_{n',m'}V^{(\alpha')}_{m,n}\}\rho_{m',m}(t)$$

$$\equiv -\sum_{m,m'} R_{n',n,m',m}(t)\rho_{m',m}(t),$$

where in the last step we identified the elements of the Redfield tensor (Eq. (19.3.24)),

$$R_{n',n,m',m}(t) = \sum_{\alpha,\alpha'} \{\sum_{l} [g_{l,m'}^{(\alpha,\alpha')}(t)V_{n',l}^{(\alpha)}V_{l,m'}^{(\alpha')}\delta_{m,n} + \bar{g}_{m,l}^{(\alpha',\alpha)}(t)V_{m,l}^{(\alpha')}V_{l,n}^{(\alpha)}\delta_{m',n'}]$$

$$-[g_{n',m'}^{(\alpha,\alpha')}(t)V_{n',m'}^{(\alpha')}V_{m,n}^{(\alpha)} + \bar{g}_{m,n}^{(\alpha',\alpha)}(t)V_{n',m'}^{(\alpha)}V_{m,n}^{(\alpha')}]\} \ .$$

Representing the additional terms in the Redfield equation, $\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(t)] + \hat{D}\hat{\rho}_S(t)$ *(Eqs. (19.3.19, 19.3.20)), in the same matrix representation we obtain Eq. (19.3.23),*

$$\frac{\partial}{\partial t}\rho_{n',n}(t) \cong -\frac{i}{\hbar}(E_{n'} - E_n)\rho_{n',n}(t) - \sum_{m',m} R_{n',n,m',m}(t)\rho_{m',m}(t) .$$

Exercise 19.4.1 *Given Eq. (19.4.3) for the dynamics of the reduced system density matrix elements,* $\frac{\partial}{\partial t}\rho_{n',n}(t) = -\frac{i}{\hbar}(E_{n'} - E_n)\rho_{n',n}(t) - \sum_{m',m} R_{n',n,m',m}^{(St)}\rho_{m',m}(t)$, *and the transformation,* $\rho_{n',n}^{(I)}(t) = e^{i\omega_{n',n}t}\rho_{n',n}(t)$ *(Eq. (19.4.5)), derive Eq. (19.4.6) with the time-dependent tensor,* $R_{n',n,m',m}^{(I)}(t)$, *as defined in Eq. (19.4.7).*

Solution 19.4.1

Taking the time-derivative of the density matrix elements in the interaction representation (Eq. (19.4.5)), we obtain $\frac{\partial}{\partial t}\rho_{n',n}^{(I)}(t) = \frac{\partial}{\partial t}e^{i\omega_{n',n}t}\rho_{n',n}(t) = e^{i\omega_{n',n}t}\frac{\partial}{\partial t}\rho_{n',n}(t) + i\omega_{n',n}\rho_{n',n}^{(I)}(t)$. *Using Eq. (19.4.3), we obtain*

$$\frac{\partial}{\partial t}\rho_{n',n}^{(I)}(t) = e^{i\omega_{n',n}t}\frac{\partial}{\partial t}\rho_{n',n}(t) + i\omega_{n',n}\rho_{n',n}^{(I)}(t)$$
$$= -\frac{i}{\hbar}(E_{n'} - E_n)e^{i\omega_{n',n}t}\rho_{n',n}(t) - \sum_{m',m} e^{i\omega_{n',n}t}R_{n',n,m',m}^{(St)}\rho_{m',m}(t) + i\omega_{n',n}\rho_{n',n}^{(I)}(t)$$
$$= -\sum_{m',m} e^{i\omega_{n',n}t}R_{n',n,m',m}^{(St)}\rho_{m',m}(t)$$
$$= -\sum_{m',m} e^{i\omega_{n',n}t}R_{n',n,m',m}^{(St)}e^{-i\omega_{m',m}t}e^{i\omega_{m',m}t}\rho_{m',m}(t)$$
$$= -\sum_{m',m} R_{n',n,m',m}^{(St)}e^{i(\omega_{n',n}-\omega_{m',m})t}\rho_{m',m}^{(I)}(t) \ .$$

Identifying, $R_{n',n,m',m}^{(I)}(t) \equiv R_{n',n,m',m}^{(St)}e^{i(\omega_{n',n}-\omega_{m',m})t}$ *(Eq. (19.4.7)), we obtain Eq. (19.4.6),*

$$\frac{\partial}{\partial t}\rho_{n',n}^{(I)}(t) = -\sum_{m',m} R_{n',n,m',m}^{(I)}(t)\rho_{m',m}^{(I)}(t) .$$

Exercise 19.4.2 *Show that time averaging of Eq. (19.4.6) over the short oscillation period, T_c, leads to Eqs. (19.4.8, 19.4.9).*

Solution 19.4.2

Approximating the time-derivative of $\rho^I_{n',n}(t)$ by its average over a short period, T_c, in which $\rho^I_{n',n}(t)$ is nearly constant, and using Eq. (19.4.6), we obtain

$$\frac{\partial}{\partial t}\rho^I_{n',n}(t) \approx \frac{1}{T_c}\int_{t-T_c/2}^{t+T_c/2} dt' \frac{\partial}{\partial t'}\rho^I_{n',n}(t') \approx -\sum_{m',m} \frac{1}{T_c}\int_{t-T_c/2}^{t+T_c/2} dt' R^I_{n',n,m',m}(t')\rho^I_{m',m}(t).$$

Using the explicit time-dependence of $R^I_{n',n,m',m}(t')$ (Eq. (19.4.7)), we obtain

$$\frac{\partial}{\partial t}\rho^I_{n',n}(t) \approx -\sum_{m',m} \frac{1}{T_c}\int_{t-T_c/2}^{t+T_c/2} dt' \left[R^{(St)}_{n',n,m',m}\right] e^{i(\omega_{n',n}-\omega_{m',m})t'} \rho^I_{m',m}(t).$$

Using our discrete model, $\omega_{n',n} = \frac{2\pi}{T_c} l_{n',n}$, $\omega_{m',m} = \frac{2\pi}{T_c} l_{m',m}$, we obtain Eqs. (19.4.8, 19.4.9),

$$\frac{\partial}{\partial t}\rho^I_{n',n}(t) \approx -\sum_{m',m}\left[R^{(St)}_{n',n,m',m}\right]\frac{1}{T_c}\int_{t-T_c/2}^{t+T_c/2} dt' e^{i\frac{2\pi}{T_c}(l_{n',n}-l_{m',m})t'} \rho^I_{m',m}(t) = -\sum_{m',m}\left[R^{(St)}_{n',n,m',m}\right]\delta_{l_{n',n},l_{m',m}}\rho^I_{m',m}(t).$$

Exercise 19.4.3 *Substitute Eq. (19.4.12) in Eq. (19.4.11) to derive the Pauli master equation (Eq. (19.4.13), with the population transition rates given in Eq. (19.4.14).*

Solution 19.4.3

Using Eq. (19.4.12) in Eq. (19.4.11) we obtain

$$\begin{aligned}
\frac{\partial}{\partial t}P_n(t) &\cong -\sum_m R^{(St)}_{n,n,m,m}P_m(t) \\
&= -\sum_m\sum_{\alpha,\alpha'}\{\left(\sum_l [G^{(\alpha,\alpha')}_{l,m}V^{(\alpha)}_{n,l}V^{(\alpha')}_{l,m}\delta_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,l}V^{(\alpha')}_{m,l}V^{(\alpha)}_{l,n}\delta_{m,n}]\right) - [G^{(\alpha,\alpha')}_{n,m}V^{(\alpha')}_{n,m}V^{(\alpha)}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,n}V^{(\alpha)}_{n,m}V^{(\alpha')}_{m,n}]\}P_m(t) \\
&= -\sum_{\alpha,\alpha'}\sum_l [G^{(\alpha,\alpha')}_{l,n}V^{(\alpha)}_{n,l}V^{(\alpha')}_{l,n} + \bar{G}^{(\alpha',\alpha)}_{n,l}V^{(\alpha')}_{n,l}V^{(\alpha)}_{l,n}]P_n(t) + \sum_{\alpha,\alpha'}\sum_m [G^{(\alpha,\alpha')}_{n,m}V^{(\alpha')}_{n,m}V^{(\alpha)}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,n}V^{(\alpha)}_{n,m}V^{(\alpha')}_{m,n}]P_m(t) \\
&= -\sum_m\sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{m,n}V^{(\alpha)}_{n,m}V^{(\alpha')}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{n,m}V^{(\alpha')}_{n,m}V^{(\alpha)}_{m,n}]P_n(t) + \sum_m\sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{n,m}V^{(\alpha')}_{n,m}V^{(\alpha)}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,n}V^{(\alpha)}_{n,m}V^{(\alpha')}_{m,n}]P_m(t)
\end{aligned}$$

.

Defining, $k_{m,n} = k_{m\to n} = \sum_{\alpha,\alpha'} \{G^{(\alpha,\alpha')}_{n,m} V^{(\alpha')}_{n,m} V^{(\alpha)}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,n} V^{(\alpha)}_{n,m} V^{(\alpha')}_{m,n}\}$ *(Eq. (19.4.14)), we obtain Eq. (19.4.13),*

$$\frac{\partial}{\partial t} P_n(t) \cong -\sum_m \sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{m,n} V^{(\alpha)}_{n,m} V^{(\alpha')}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{n,m} V^{(\alpha')}_{n,m} V^{(\alpha)}_{m,n}] P_n(t)$$

$$+\sum_m \sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{n,m} V^{(\alpha')}_{n,m} V^{(\alpha)}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,n} V^{(\alpha)}_{n,m} V^{(\alpha')}_{m,n}] P_m(t) = -\sum_m k_{n\to m} P_n(t) + \sum_m k_{m\to n} P_m(t) \ .$$

Exercise 19.4.4 *Use the Pauli master equation (Eq. (19.4.13)) for* $\frac{\partial}{\partial t} P_n(t)$*, to show that* $\frac{\partial}{\partial t} \sum_n P_n(t) = 0$. *(Recall that each summation is over the entire spectrum of* $\hat{H}_S$ *-eigenstates.)*

Solution 19.4.4

Using Eq. (19.4.13), $\frac{\partial}{\partial t} P_n(t) = \sum_m k_{m\to n} P_m(t) - \sum_m k_{n\to m} P_n(t)$, *we obtain*

$$\frac{\partial}{\partial t} \sum_n P_n(t) = \sum_{m,n} k_{m\to n} P_m(t) - \sum_{m,n} k_{n\to m} P_n(t) = \sum_{m,n} k_{m\to n} P_m(t) - \sum_{n,m} k_{m\to n} P_m(t) = 0 \ .$$

Exercise 19.4.5 *Use the structure of the matrix* $\mathbf{K}$*, as expressed in Eq. (19.4.17), to show that its rows are linearly dependent, and hence there exist a non-trivial solution,* $\mathbf{P}$*, to the homogeneous equation,* $\mathbf{KP} = \mathbf{0}$.

Solution 19.4.5

Given the matrix $\mathbf{K}$ *as defined in Eq. (19.4.17),* $[\mathbf{K}]_{n,m} = (1-\delta_{m,n}) k_{m\to n} - \delta_{m,n} \sum_{n'\neq n} k_{n\to n'}$, *we can readily verify that the sum of entries in each column vanishes,*

$$\sum_{n=1}^{N} [\mathbf{K}]_{n,m} = \sum_{n=1}^{N} (1-\delta_{m,n}) k_{m\to n} - \sum_{n=1}^{N} \delta_{m,n} \sum_{n'\neq n}^{N} k_{n\to n'} = \left(\sum_{n\neq m}^{N} k_{m\to n} \right) - \left(\sum_{n'\neq m}^{N} k_{m\to n'} \right) = 0 \,.$$

Denoting the n^{th} *row vector of the matrix* $\mathbf{K}$ *as,* $\mathbf{R}_n = \left([\mathbf{K}]_{n,1}, [\mathbf{K}]_{n,2}, ..., [\mathbf{K}]_{n,N}\right)$, *we therefore obtain* $\sum_{n=1}^{N} \mathbf{R}_n = \mathbf{0}$, *namely* $\mathbf{R}_n = -\sum_{m=1,m\neq n}^{N} \mathbf{R}_m$, *which means that the rows of* $\mathbf{K}$ *are linearly-dependent. Hence, the homogeneous system of equations,* $\mathbf{KP} = 0$, *has a non-trivial solution.*

Exercise 19.4.6 *Show that for a Hermitian operator,* $\hat{H}_{SB} \equiv \sum_{\alpha=1}^{N} \hat{V}_\alpha^{(S)} \hat{U}_\alpha^{(B)}$, *and using the definitions of* $G_{n,n'}^{(\alpha,\alpha')}$, $\bar{G}_{n,n'}^{(\alpha,\alpha')}$ *(Eq. (19.4.2)) and* $V_{n',n}^{(\alpha)} = \langle \varphi_{n'} | \hat{V}_\alpha^{(S)} | \varphi_n \rangle$, *we have* $\sum_{\alpha,\alpha'} \bar{G}_{m,n}^{(\alpha',\alpha)} V_{n,m}^{(\alpha)} V_{m,n}^{(\alpha')} = \left[\sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)} \right]^*$, *and therefore the population transition rates defined in Eq. (19.4.14) are real-valued (Eq. (19.4.19)).*

Solution 19.4.6

Using the definition, $V_{n',n}^{(\alpha)} = \langle \varphi_{n'} | \hat{V}_\alpha^{(S)} | \varphi_n \rangle$, *and Eqs. (19.4.2, 19.4.4) for* $G_{n,n'}^{(\alpha,\alpha')}$ *and* $\bar{G}s_{n,n'}^{(\alpha,\alpha')}$ *in terms of the bath coupling operators,*

$$G_{n,n'}^{(\alpha,\alpha')} \equiv \frac{1}{\hbar^2} \int_0^\infty c_{\alpha,\alpha'}(\tau) e^{\frac{-i\tau}{\hbar}(E_n - E_{n'})} d\tau \quad ; \quad \bar{G}_{n,n'}^{(\alpha,\alpha')} \equiv \frac{1}{\hbar^2} \int_0^\infty \bar{c}_{\alpha,\alpha'}(\tau) e^{\frac{-i\tau}{\hbar}(E_n - E_{n'})} d\tau ,$$

$$c_{\alpha,\alpha'}(\tau) = \sum_{b,b'} \langle b | \hat{U}_\alpha^{(B)} | b' \rangle \langle b' | \hat{U}_{\alpha'}^{(B)} | b \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'} - E_b)},$$

$$\bar{c}_{\alpha,\alpha'}(\tau) = \sum_{b,b'} \langle b | \hat{U}_\alpha^{(B)} | b' \rangle \langle b' | \hat{U}_{\alpha'}^{(B)} | b \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_b - E_{b'})} ,$$

we obtain

$$\sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)} = \sum_{\alpha,\alpha'} \frac{1}{\hbar^2} \int_0^\infty d\tau \sum_{b,b'} \langle b | \hat{U}_\alpha^{(B)} | b' \rangle \langle b' | \hat{U}_{\alpha'}^{(B)} | b \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'} - E_b)} e^{\frac{-i\tau}{\hbar}(E_n - E_m)} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)}$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2} \int_0^\infty d\tau \sum_{b,b'} \langle b | \otimes \langle \varphi_m | \hat{U}_\alpha^{(B)} \hat{V}_\alpha^{(S)} | b' \rangle \otimes | \varphi_n \rangle \langle b' | \otimes \langle \varphi_n | \hat{U}_{\alpha'}^{(B)} \hat{V}_{\alpha'}^{(S)} | b \rangle \otimes | \varphi_m \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'} - E_b)} e^{\frac{-i\tau}{\hbar}(E_n - E_m)} .$$

Identifying the full coupling operator, $\hat{H}_{SB} \equiv \sum_{\alpha=1}^{N} \hat{V}_\alpha^{(S)} \hat{U}_\alpha^{(B)}$, *we obtain*

$$\sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)}$$

$$= \frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{b,b'} \langle b| \otimes \langle \varphi_m | \hat{H}_{SB} | b' \rangle \otimes | \varphi_n \rangle \langle b' | \otimes \langle \varphi_n | \hat{H}_{SB} | b \rangle \otimes | \varphi_m \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{-i\tau}{\hbar}(E_n-E_m)} \; .$$

Therefore, using the Hermiticity of $\hat{H}_{SB}$*, we obtain*

$$\left(\sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)}\right)^*$$

$$= \frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{b,b'} \langle b'| \otimes \langle \varphi_n | \hat{H}_{SB} | b \rangle \otimes | \varphi_m \rangle \langle b | \otimes \langle \varphi_m | \hat{H}_{SB} | b' \rangle \otimes | \varphi_n \rangle \rho_b e^{\frac{i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{i\tau}{\hbar}(E_n-E_m)} \; .$$

Using again the product expansion of the coupling, $\hat{H}_{SB} \equiv \sum_{\alpha=1}^{N} \hat{V}_\alpha^{(S)} \hat{U}_\alpha^{(B)}$*, we obtain*

$$\left(\sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)}\right)^*$$

$$= \frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{b,b'} \langle b'| \otimes \langle \varphi_n | \hat{H}_{SB} | b \rangle \otimes | \varphi_m \rangle \langle b | \otimes \langle \varphi_m | \hat{H}_{SB} | b' \rangle \otimes | \varphi_n \rangle \rho_b e^{\frac{i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{i\tau}{\hbar}(E_n-E_m)}$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{b,b'} \langle b'| \otimes \langle \varphi_n | \hat{U}_\alpha^{(B)} \hat{V}_\alpha^{(S)} | b \rangle \otimes | \varphi_m \rangle \langle b | \otimes \langle \varphi_m | \hat{U}_{\alpha'}^{(B)} \hat{V}_{\alpha'}^{(S)} | b' \rangle \otimes | \varphi_n \rangle \rho_b e^{\frac{i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{i\tau}{\hbar}(E_n-E_m)}$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{b,b'} \langle b | \hat{U}_{\alpha'}^{(B)} | b' \rangle \langle b' | \hat{U}_\alpha^{(B)} | b \rangle \rho_b e^{\frac{i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{-i\tau}{\hbar}(E_m-E_n)} \hat{V}_{n,m}^{(\alpha)} \hat{V}_{m,n}^{(\alpha')} \; ,$$

and using again Eqs. (19.4.2, 19.4.4), we obtain

$$\left(\sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)}\right)^* = \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{b,b'} \langle b | \hat{U}_{\alpha'}^{(B)} | b' \rangle \langle b' | \hat{U}_\alpha^{(B)} | b \rangle \rho_b e^{\frac{i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{-i\tau}{\hbar}(E_m-E_n)} \hat{V}_{n,m}^{(\alpha)} \hat{V}_{m,n}^{(\alpha')}$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty d\tau \bar{c}_{\alpha',\alpha}(\tau) e^{\frac{-i\tau}{\hbar}(E_m-E_n)} \hat{V}_{n,m}^{(\alpha)} \hat{V}_{m,n}^{(\alpha')} = \sum_{\alpha,\alpha'} \bar{G}_{m,n}^{(\alpha',\alpha)} \hat{V}_{n,m}^{(\alpha)} \hat{V}_{m,n}^{(\alpha')} \; .$$

Hence, the rate as defined in Eq. (19.4.14) is real-valued (Eq. (19.4.19)):

$$k_{m,n} = \sum_{\alpha,\alpha'} \{ G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)} + \bar{G}_{m,n}^{(\alpha',\alpha)} V_{n,m}^{(\alpha)} V_{m,n}^{(\alpha')} \} = \sum_{\alpha,\alpha'} \{ G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)} + (G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)})^* \}$$

$$= 2\,\mathrm{Re} \sum_{\alpha,\alpha'} G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)} \; .$$

Exercise 19.4.7 *Use Eqs. (19.4.2, 19.4.4) in Eq. (19.4.19) to derive Eq. (19.4.20).*

Solution 19.4.7

Using Eqs. (19.4.2, 19.4.4) and the definition, $V_{n',n}^{(\alpha)} = \langle \varphi_{n'} | \hat{V}_{\alpha}^{(S)} | \varphi_n \rangle$, *in Eq. (19.4.19), we obtain*

$$k_{m\to n} = \sum_{\alpha,\alpha'} 2\,\mathrm{Re}\{G_{n,m}^{(\alpha,\alpha')} V_{n,m}^{(\alpha')} V_{m,n}^{(\alpha)}\}$$

$$= \sum_{\alpha,\alpha'} 2\,\mathrm{Re}\{\frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b | \hat{U}_{\alpha}^{(B)} | b' \rangle \langle b' | \hat{U}_{\alpha'}^{(B)} | b \rangle \langle \varphi_n | \hat{V}_{\alpha'}^{(S)} | \varphi_m \rangle \langle \varphi_m | \hat{V}_{\alpha}^{(S)} | \varphi_n \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{-i\tau}{\hbar}(E_n-E_m)} d\tau\}$$

$$= \sum_{\alpha,\alpha'} 2\,\mathrm{Re}\{\frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b | \otimes \langle \varphi_m | \hat{U}_{\alpha}^{(B)} \hat{V}_{\alpha}^{(S)} | b' \rangle \otimes | \varphi_n \rangle \langle b' | \otimes \langle \varphi_n | \hat{U}_{\alpha'}^{(B)} \hat{V}_{\alpha'}^{(S)} | b \rangle \otimes | \varphi_m \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{-i\tau}{\hbar}(E_n-E_m)} d\tau\}.$$

Identifying $\sum_{\alpha} \hat{U}_{\alpha}^{(B)} \hat{V}_{\alpha}^{(S)} = \hat{H}_{SB}$, *we obtain*

$$k_{m\to n} = 2\,\mathrm{Re}\{\frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b | \otimes \langle \varphi_m | \hat{H}_{SB} | b' \rangle \otimes | \varphi_n \rangle \langle b' | \otimes \langle \varphi_n | \hat{H}_{SB} | b \rangle \otimes | \varphi_m \rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'}-E_b)} e^{\frac{-i\tau}{\hbar}(E_n-E_m)} d\tau\}$$

$$= 2\,\mathrm{Re}\{\frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b | \otimes \langle \varphi_m | \hat{\rho}_B \hat{H}_{SB} | b' \rangle \otimes | \varphi_n \rangle \langle b' | \otimes \langle \varphi_n | e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} | b \rangle \otimes | \varphi_m \rangle d\tau\} \ .$$

Recalling that $\sum_{b'} |b'\rangle\langle b'|$ *is the identity operator in the bath, and that*

$$\sum_b \langle b | \otimes \langle \varphi_m | \hat{O} | b \rangle \otimes | \varphi_m \rangle = \sum_{b,n} \langle b | \otimes \langle \varphi_n | \Big[| \varphi_m \rangle \langle \varphi_m | \hat{O} \Big] | b \rangle \otimes | \varphi_n \rangle = tr\{ | \varphi_m \rangle \langle \varphi_m | \hat{O} \},$$

we obtain Eq. (19.4.20),

$$k_{m\to n} = 2\,\mathrm{Re}\{\frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b | \otimes \langle \varphi_m | \hat{\rho}_B \hat{H}_{SB} | b' \rangle \otimes | \varphi_n \rangle \langle b' | \otimes \langle \varphi_n | e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} | b \rangle \otimes | \varphi_m \rangle d\tau\}$$

$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{ | \varphi_m \rangle \langle \varphi_m | \hat{\rho}_B \hat{H}_{SB} | \varphi_n \rangle \langle \varphi_n | e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} \hat{H}_{SB} e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} \} d\tau$$

$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{ | \varphi_m \rangle \langle \varphi_m | \hat{\rho}_B \hat{H}_{SB} | \varphi_n \rangle \langle \varphi_n | e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} \hat{H}_{SB} e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)} \} d\tau \ .$$

In the last step we used the invariance of time-integral to the sign of τ. *This can be verified by taking the complex conjugate of the trace, recalling that* $tr\{\hat{O}\}^* = tr\{\hat{O}^\dagger\}$, *and then using the commutators,* $[| \varphi_{m/n} \rangle \langle \varphi_{m/n} |, \hat{H}_S] = 0$ *and* $[\hat{\rho}_B, \hat{H}_B] = 0$,

$$k_{m\to n} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{|\varphi_m\rangle\langle\varphi_m|\hat{\rho}_B\hat{H}_{SB}|\varphi_n\rangle\langle\varphi_n|e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\}d\tau$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{|\varphi_m\rangle\langle\varphi_m|\hat{\rho}_B\hat{H}_{SB}|\varphi_n\rangle\langle\varphi_n|e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\}^* d\tau$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\hat{H}_{SB}e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}|\varphi_n\rangle\langle\varphi_n|\hat{H}_{SB}\hat{\rho}_B|\varphi_m\rangle\langle\varphi_m|\}$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{\hat{\rho}_B|\varphi_m\rangle\langle\varphi_m|\hat{H}_{SB}|\varphi_n\rangle\langle\varphi_n|e^{\frac{i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\hat{H}_{SB}e^{\frac{-i\tau}{\hbar}(\hat{H}_B+\hat{H}_S)}\}.$$

Exercise 19.4.8 *Use the definitions:* $\hat{H}_0 = \hat{H}_B + \hat{H}_S$, $\hat{H}_B|b\rangle = E_b|b\rangle$, $\hat{\rho}_B|b\rangle = \rho_b|b\rangle$, $\hat{H}_S|\varphi_m\rangle = E_m|\varphi_m\rangle$, $\hat{P}_{\{i\}} = |\varphi_m\rangle\langle\varphi_m|\otimes\sum_b|b\rangle\langle b|$, $\hat{P}_{\{f\}} = |\varphi_n\rangle\langle\varphi_n|\otimes\sum_b|b\rangle\langle b|$ *and* $\hat{\rho}_{\{i\}} = |\varphi_m\rangle\langle\varphi_m|\otimes\hat{\rho}_B$ *to derive Eq. (19.4.22) from Eq. (19.4.21).*

Solution 19.4.8

Starting from Eq. (19.4.21), using, $\hat{H}_0 = \hat{H}_B + \hat{H}_S$, $\hat{H}_B|b\rangle = E_b|b\rangle$, $\hat{\rho}_B|b\rangle = \rho_b|b\rangle$, $\hat{H}_S|\varphi_{n/m}\rangle = E_{n/m}|\varphi_{n/m}\rangle$, $\hat{P}_{\{i\}} = |\varphi_m\rangle\langle\varphi_m|\otimes\sum_b|b\rangle\langle b|$, $\hat{P}_{\{f\}} = |\varphi_n\rangle\langle\varphi_n|\otimes\sum_b|b\rangle\langle b|$ *and* $\hat{\rho}_{\{i\}} = |\varphi_m\rangle\langle\varphi_m|\otimes\hat{\rho}_B$, *we obtain Eq. (19.4.22),*

$$k_{m\to n} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{\hat{\rho}_{\{i\}}\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}e^{\frac{i\tau}{\hbar}\hat{H}_0}\hat{V}e^{\frac{-i\tau}{\hbar}\hat{H}_0}\}d\tau$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr\{\hat{\rho}_B|\varphi_m\rangle\langle\varphi_m|\hat{V}|\varphi_n\rangle\langle\varphi_n|e^{\frac{i\tau}{\hbar}\hat{H}_0}\hat{V}e^{\frac{-i\tau}{\hbar}\hat{H}_0}\}d\tau$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_m|\hat{V}|\varphi_n\rangle\langle\varphi_n|e^{\frac{i\tau}{\hbar}\hat{H}_0}\hat{V}e^{\frac{-i\tau}{\hbar}\hat{H}_0}|\varphi_m\rangle\}d\tau$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\sum_{b,b'}\int_0^\infty\langle b|\langle\varphi_m|\hat{\rho}_B\hat{V}|\varphi_n\rangle|b'\rangle\langle b'|\langle\varphi_n|e^{\frac{i\tau}{\hbar}\hat{H}_0}\hat{V}e^{\frac{-i\tau}{\hbar}\hat{H}_0}|\varphi_m\rangle|b\rangle d\tau$$
$$= 2\,\mathrm{Re}\frac{1}{\hbar^2}\sum_{b,b'}\int_0^\infty\langle b|\langle\varphi_m|\rho_b\hat{V}|\varphi_n\rangle|b'\rangle\langle b'|\langle\varphi_n|e^{\frac{i\tau}{\hbar}(E_n+E_{b'})}\hat{V}e^{\frac{-i\tau}{\hbar}(E_m+E_b)}|\varphi_m\rangle|b\rangle d\tau$$

$$= \mathrm{Re}\frac{1}{\hbar^2}\sum_{b,b'}\int_{-\infty}^{\infty}\rho_b e^{\frac{i\tau}{\hbar}(E_n+E_{b'}-E_m-E_b)}\,|\langle b'|\langle\varphi_n|\hat{V}|\varphi_m\rangle|b\rangle|^2\,d\tau$$

$$= \frac{2\pi}{\hbar}\sum_{b,b'}\rho_b\,|\langle b'|\langle\varphi_n|\hat{V}|\varphi_m\rangle|b\rangle|^2\,\delta(E_n-E_m-[E_b-E_{b'}])\ .$$

Exercise 19.4.9 *Let us denote the probability of populating the* n *th eigenstate of* $\hat{H}_S$ *as* $P_n(t)$ *. (a) Given* $P_n(t)\geq 0$ *for any* n*, and recalling that population transfer rates are non-negative (* $k_{m\to n}\geq 0$*), use Eq. (19.4.13) to show that when a certain probability vanishes,* $P_n(t)=0$*, it means that* $\frac{\partial}{\partial t}P_n(t)\geq 0$*. (b) Use the result of (a) to show that if all the probabilities are non-negative at* $t=0$ *(namely,* $P_n(0)\geq 0$ *for any* n*), they remain so at any later times, namely,* $P_n(t)\geq 0$ *for* $t>0$*.*

Solution 19.4.9

(a)

We consider a solution to the master equation (Eq. (19.4.13)), $\frac{\partial}{\partial t}P_n(t)=\sum_m k_{m\to n}P_m(t)-\sum_m k_{n\to m}P_n(t)$*. Setting a specific probability to zero,* $P_n(t)=0$*, the respective time-derivative reads* $\frac{\partial}{\partial t}P_n(t)=\sum_m k_{m\to n}P_m(t)$*. Since* $\{k_{m\to n}\geq 0\}$ *(Eq. (19.4.22)), if all the probabilities are non-negatives,* $P_m(t)\geq 0$*, the time derivative is also non-negative,* $\frac{\partial}{\partial t}P_n(t)\geq 0$*.*

(b)

In (a) we saw that if all the probabilities are non-negative at a certain time, the time-derivative of any zero probability cannot be negative. Hence, the value of any probability cannot drop below zero. Therefore, we conclude that that if all the probabilities are non-negative at $t=0$ *(namely,* $P_n(0)\geq 0$ *for any* n*), they remain so at any later times, namely,* $P_n(t)\geq 0$ *for* $t>0$*.*

Exercise 19.4.10 *(a) For a canonical density operator,* $\hat{\rho}_B=\frac{e^{-\hat{H}_B/(k_BT)}}{Z_B}$*, use Eq. (19.4.22) to show that* $k_{m\to n}=\frac{2\pi}{\hbar}\sum_{b,b'}\frac{e^{-E_b/(k_BT)}}{Z_B}|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2\,\delta(E_m-E_n-[E_{b'}-E_b])$*, and* $k_{n\to m}=\frac{2\pi}{\hbar}\sum_{b,b'}\frac{e^{-E_{b'}/(k_BT)}}{Z_B}|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2\,\delta(E_m-E_n-[E_{b'}-E_b])$*.*

(b) Replacing the discrete summations over the bath Hamiltonian eigenstates by energy integrals, where, $|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2 \rightarrow \lambda(E_{b'},E_b)$ *, and introducing the bath density of states,* $\rho(E_b)$ *, show that*

$$k_{m\rightarrow n} = \frac{2\pi}{\hbar}\int dE_b \int dE_{b'} \rho(E_{b'})\rho(E_b)\frac{e^{-E_b/(k_BT)}}{Z_B}\lambda(E_{b'},E_b)\delta(E_m - E_n - E_{b'} + E_b)$$

and

$$k_{n\rightarrow m} = \frac{2\pi}{\hbar}\int dE_b \int dE_{b'} \rho(E_{b'})\rho(E_b)\frac{e^{-E_{b'}/(k_BT)}}{Z_B}\lambda(E_{b'},E_b)\delta(E_m - E_n - E_{b'} + E_b).$$

(c) Changing integration variables and defining the transition frequency, $\hbar\omega_{n,m} = E_n - E_m$ *, show that*

$$k_{m\rightarrow n} = \frac{e^{\frac{-\hbar\omega_{n,m}}{2}/(k_BT)}}{Z_B}\frac{2\pi}{\hbar}\int dE \rho(E - \frac{\hbar\omega_{n,m}}{2})\rho(E + \frac{\hbar\omega_{n,m}}{2})\frac{e^{-E/(k_BT)}}{Z_B}\lambda(E - \frac{\hbar\omega_{n,m}}{2}, E + \frac{\hbar\omega_{n,m}}{2})$$

and

$$k_{n\rightarrow m} = \frac{e^{\frac{\hbar\omega_{n,m}}{2}/(k_BT)}}{Z_B}\frac{2\pi}{\hbar}\int dE \rho(E - \frac{\hbar\omega_{n,m}}{2})\rho(E + \frac{\hbar\omega_{n,m}}{2})\frac{e^{-E/(k_BT)}}{Z_B}\lambda(E - \frac{\hbar\omega_{n,m}}{2}, E + \frac{\hbar\omega_{n,m}}{2}),$$

where $k_{m\rightarrow n} = k_{n\rightarrow m} e^{-(E_n - E_m)/(k_BT)}$.

Solution 19.4.10

(a)

Using Eq. (19.4.22) with $\hat{\rho}_B = \frac{e^{-\hat{H}_B/(k_BT)}}{Z_B}$ *, and hence,* $\hat{\rho}_B|b\rangle = \frac{e^{-\hat{H}_B/(k_BT)}}{Z_B}|b\rangle = \frac{e^{-E_b/(k_BT)}}{Z_B}|b\rangle \equiv \rho_b|b\rangle$ *,*

we readily obtain

$$k_{m\rightarrow n} = \frac{2\pi}{\hbar}\sum_{b,b'}\rho_b |\langle b'|\langle\varphi_n|\hat{V}|\varphi_m\rangle|b\rangle|^2 \ \delta(E_n - E_m - [E_b - E_{b'}])$$
$$= \frac{2\pi}{\hbar}\sum_{b,b'}\frac{e^{-E_b/(k_BT)}}{Z_B}|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2 \ \delta(E_m - E_n - [E_{b'} - E_b])$$

and

$$k_{n\rightarrow m} = \frac{2\pi}{\hbar}\sum_{b,b'}\rho_b |\langle b'|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b\rangle|^2 \ \delta(E_m - E_n - [E_b - E_{b'}])$$
$$= \frac{2\pi}{\hbar}\sum_{b,b'}\frac{e^{-E_{b'}/(k_BT)}}{Z_B}|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2 \ \delta(E_m - E_n - [E_{b'} - E_b]).$$

(b)

Replacing the discrete summations over the bath Hamiltonian eigenstates by energy integrals with $|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2 \rightarrow \lambda(E_{b'},E_b)$ *, we obtain*

$$k_{m\to n} = \frac{2\pi}{\hbar}\sum_{b,b'}\frac{e^{-E_b/(k_BT)}}{Z_B}|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2\ \delta(E_m - E_n - [E_{b'} - E_b])$$

$$= \frac{2\pi}{\hbar}\int dE_b\int dE_{b'}\rho(E_{b'})\rho(E_b)\frac{e^{-E_b/(k_BT)}}{Z_B}\lambda(E_{b'},E_b)\delta(E_m - E_n - E_{b'} + E_b)$$

$$k_{n\to m} = \frac{2\pi}{\hbar}\sum_{b,b'}\frac{e^{-E_{b'}/(k_BT)}}{Z_B}|\langle b|\langle\varphi_m|\hat{V}|\varphi_n\rangle|b'\rangle|^2\ \delta(E_m - E_n - [E_{b'} - E_b])$$

$$= \frac{2\pi}{\hbar}\int dE_b\int dE_{b'}\rho(E_{b'})\rho(E_b)\frac{e^{-E_{b'}/(k_BT)}}{Z_B}\lambda(E_{b'},E_b)\delta(E_m - E_n - E_{b'} + E_b)\ .$$

(c)

Integrating over E_b *we obtain for* $k_{m\to n}$,

$$k_{m\to n} = \frac{2\pi}{\hbar}\int dE_b\int dE_{b'}\rho(E_{b'})\rho(E_b)\frac{e^{-E_b/(k_BT)}}{Z_B}\lambda(E_{b'},E_b)\delta(E_m - E_n - E_{b'} + E_b)$$

$$= \frac{2\pi}{\hbar}\int dE_{b'}\rho(E_{b'})\rho(-E_m + E_n + E_{b'})\frac{e^{-(-E_m+E_n+E_{b'})/(k_BT)}}{Z_B}\lambda(E_{b'},-E_m + E_n + E_{b'}).$$

Changing integration variable, $E_{b'} = E + \frac{E_m - E_n}{2} = E - \frac{\hbar\omega_{n,m}}{2}$, *we obtain*

$$k_{m\to n} = \frac{2\pi}{\hbar}\int dE\rho(E + \frac{E_m - E_n}{2})\rho(E - \frac{E_m - E_n}{2})\frac{e^{-(E-\frac{E_m-E_n}{2})/(k_BT)}}{Z_B}\lambda(E + \frac{E_m - E_n}{2}, E - \frac{E_m - E_n}{2})$$

$$= \frac{e^{\frac{E_m-E_n}{2}/(k_BT)}}{Z_B}\frac{2\pi}{\hbar}\int dE\rho(E + \frac{E_m - E_n}{2})\rho(E - \frac{E_m - E_n}{2})\frac{e^{-E/(k_BT)}}{Z_B}\lambda(E + \frac{E_m - E_n}{2}, E - \frac{E_m - E_n}{2}).$$

Similarly, integrating over $E_{b'}$ *we obtain for* $k_{n\to m}$,

$$k_{n\to m} = \frac{2\pi}{\hbar}\int dE_b\int dE_{b'}\rho(E_{b'})\rho(E_b)\frac{e^{-E_{b'}/(k_BT)}}{Z_B}\lambda(E_{b'},E_b)\delta(E_m - E_n - E_{b'} + E_b)$$

$$= \frac{2\pi}{\hbar}\int dE_b\rho(E_m - E_n + E_b)\rho(E_b)\frac{e^{-(E_m-E_n+E_b)/(k_BT)}}{Z_B}\lambda(E_m - E_n + E_b, E_b)\ .$$

Changing integration variable, $E_b = E - \frac{E_m - E_n}{2} = E + \frac{\hbar\omega_{n,m}}{2}$, *we obtain*

$$k_{n\to m} = \frac{2\pi}{\hbar}\int dE\rho(E + \frac{E_m - E_n}{2})\rho(E - \frac{E_m - E_n}{2})\frac{e^{-(E+\frac{E_m-E_n}{2})/(k_BT)}}{Z_B}\lambda(E + \frac{E_m - E_n}{2}, E - \frac{E_m - E_n}{2})$$

$$= \frac{e^{\frac{E_n-E_m}{2}/(k_BT)}}{Z_B}\frac{2\pi}{\hbar}\int dE\rho(E + \frac{E_m - E_n}{2})\rho(E - \frac{E_m - E_n}{2})\frac{e^{-E/(k_BT)}}{Z_B}\lambda(E + \frac{E_m - E_n}{2}, E - \frac{E_m - E_n}{2})\ .$$

Consequently, we obtain

$$\frac{k_{m\to n}}{k_{n\to m}} = \frac{e^{\frac{E_m-E_n}{2}/(k_BT)}}{e^{\frac{E_n-E_m}{2}/(k_BT)}} = e^{(E_m-E_n)/(k_BT)} .$$

Exercise 19.4.11 *Use the detailed balance condition, Eq. (19.4.24), to show that the Boltzmann probability distribution, $P_n(t) = const \cdot e^{-E_n/(k_BT)}$, is a stationary solution of the Pauli master equation (Eq. (19.4.13)).*

Solution 19.4.11

Using, $k_{m\to n} = k_{n\to m} e^{-(E_n-E_m)/(k_BT)}$ (Eq. (19.4.24)), the master equation (Eq. (19.4.13)) reads

$$\frac{\partial}{\partial t}P_n(t) = \sum_m k_{m\to n}P_m(t) - \sum_m k_{n\to m}P_n(t) = \sum_m e^{-(E_n-E_m)/(k_BT)}k_{n\to m}P_m(t) - \sum_m k_{n\to m}P_n(t) .$$

Setting $P_n(t) = c\cdot e^{-E_n/(k_BT)}$, we readily obtain

$$\frac{\partial}{\partial t}P_n(t) = \sum_m e^{-(E_n-E_m)/(k_BT)}k_{n\to m}\cdot c\cdot e^{-E_m/(k_BT)} - \sum_m k_{n\to m}\cdot c\cdot e^{-E_n/(k_BT)}$$

$$= \sum_m e^{-E_n/(k_BT)}k_{n\to m}\cdot c - \sum_m k_{n\to m}\cdot c\cdot e^{-E_n/(k_BT)} = 0 .$$

Exercise 19.4.12 *(a) Show that under the constraint of "diagonal coupling" (Eq. (19.4.26)) the stationary Redfield tensor (Eq. (19.4.1)) obtains the form $R^{(St)}_{n',n,m',m} = k_{n',n}\delta_{m,n}\delta_{m',n'}$, where $k_{n',n} = \sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{n',n'}V^{(\alpha')}_{n',n'} - \bar{G}^{(\alpha',\alpha)}_{n,n}V^{(\alpha')}_{n,n}](V^{(\alpha)}_{n',n'} - V^{(\alpha)}_{n,n})$ (Eq. (19.4.28)). (b) Use this result and Eqs. (19.4.8, 19.4.9) to derive Eq. (19.4.27). (c) Use Eq. (19.4.5) to derive Eq. (19.4.29).*

Solution 19.4.12

(a)

Using, $\{V^{(\alpha)}_{n,m}\} = \{V^{(\alpha)}_{n,n}\delta_{n,m}\}$, we obtain

$$R^{(St)}_{n',n,m',m} = \sum_{\alpha,\alpha'} \{-[G^{(\alpha,\alpha')}_{n',m'} V^{(\alpha')}_{n',m'} V^{(\alpha)}_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,n} V^{(\alpha)}_{n',m'} V^{(\alpha')}_{m,n}]$$
$$+\sum_{l} [G^{(\alpha,\alpha')}_{l,m'} V^{(\alpha)}_{n',l} V^{(\alpha')}_{l,m'} \delta_{m,n} + \bar{G}^{(\alpha',\alpha)}_{m,l} V^{(\alpha')}_{m,l} V^{(\alpha)}_{l,n} \delta_{m',n'}]\}$$
$$= \sum_{\alpha,\alpha'} \{-[G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha')}_{n',n'} V^{(\alpha)}_{n,n} \delta_{m,n}\delta_{m',n'} + \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha)}_{n',n'} V^{(\alpha')}_{n,n} \delta_{m,n}\delta_{m',n'}]$$
$$+[G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha)}_{n',n'} V^{(\alpha')}_{n',n'} \delta_{m,n}\delta_{m',n'} + \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{n,n} \delta_{m',n'}\delta_{m,n}]\}$$
$$= \delta_{m,n}\delta_{m',n'} \sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha)}_{n',n'} V^{(\alpha')}_{n',n'} + \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{n,n} - G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha')}_{n',n'} V^{(\alpha)}_{n,n} - \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha)}_{n',n'} V^{(\alpha')}_{n,n}]$$
$$= \delta_{m,n}\delta_{m',n'} \sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha')}_{n',n'} (V^{(\alpha)}_{n',n'} - V^{(\alpha)}_{n,n}) + \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n} (V^{(\alpha)}_{n,n} - V^{(\alpha)}_{n',n'})] .$$

Defining, $k_{n',n} = \sum_{\alpha,\alpha'} [G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha')}_{n',n'} - \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n}](V^{(\alpha)}_{n',n'} - V^{(\alpha)}_{n,n})$, *we obtain* $R^{(St)}_{n',n,m',m} = \delta_{m,n}\delta_{m',n'} k_{n',n}$.

(b)

Using the result of (a) in Eqs. (19.4.8, 19.4.9), we obtain Eq. (19.4.27),

$$\frac{\partial}{\partial t}\rho^{(I)}_{n',n}(t) \cong -\sum_{m',m} \bar{R}_{n',n,m',m}\rho^{(I)}_{m',m}(t) \approx -\sum_{m',m} \delta_{l_{n',n},l_{m',m}} R^{(St)}_{n',n,m',m}\rho^{(I)}_{m',m}(t)$$
$$= -\sum_{m',m} \delta_{l_{n',n},l_{m',m}} \delta_{m,n}\delta_{m',n'} k_{n',n}\rho^{(I)}_{m',m}(t) = -k_{n',n}\rho^{(I)}_{n',n}(t) \ .$$

(c)

Using the result of (b), and the definition of the interaction picture representation, $\rho^{(I)}_{n',n}(t) = e^{i\omega_{n',n}t}\rho_{n',n}(t)$ *(Eq. (19.4.5)), we obtain Eq. (19.4.29),*

$$\frac{\partial}{\partial t}\rho_{n',n}(t) = \frac{\partial}{\partial t} e^{-i\omega_{n',n}t}\rho^{(I)}_{n',n}(t) = -i\omega_{n',n}\rho_{n',n}(t) + e^{-i\omega_{n',n}t}\frac{\partial}{\partial t}\rho^{(I)}_{n',n}(t)$$
$$= -i\omega_{n',n}\rho_{n',n}(t) - k_{n',n}e^{-i\omega_{n',n}t}\rho^{(I)}_{n',n}(t)$$
$$= \left(-i\omega_{n',n} - k_{n',n}\right)\rho_{n',n}(t)$$
$$= -\{\mathrm{Re}(k_{n',n}) + i[\omega_{n',n} + \mathrm{Im}(k_{n',n})]\}\rho_{n',n}(t) \ .$$

Exercise 19.4.13 *Use Eqs. (19.4.2, 19.4.4) and the definition of* $k_{n',n}$ *(Eq. (19.4.28)) to show that*

$$\mathrm{Re}[k_{n',n}] = \frac{1}{\hbar^2}\sum_{b,b'} \int_0^\infty \rho_b \cos[(E_{b'} - E_b)\tau/\hbar] \, |\langle b|\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle|b'\rangle - \langle b|\langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle|b'\rangle|^2 \, d\tau \quad \textit{and}$$

to derive Eq. (19.4.31).

Solution 19.4.13

By its definition (Eq. (19.4.28)), the decoherence rate reads

$$k_{n',n} = \sum_{\alpha,\alpha'} G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha')}_{n',n'} V^{(\alpha)}_{n',n'} - \sum_{\alpha,\alpha'} G^{(\alpha,\alpha')}_{n',n'} V^{(\alpha')}_{n',n'} V^{(\alpha)}_{n,n} + \sum_{\alpha,\alpha'} \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{n,n} - \sum_{\alpha,\alpha'} \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{n',n'} .$$

To evaluate the different contributions, we use Eqs. (19.4.2, 19.4.4),

$$\sum_{\alpha,\alpha'} G^{(\alpha,\alpha')}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{m,m} = \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\hat{U}^{(B)}_{\alpha}|b'\rangle\langle b'|\hat{U}^{(B)}_{\alpha'}|b\rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_{b'}-E_b)} V^{(\alpha')}_{n,n} V^{(\alpha)}_{m,m} d\tau$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{U}^{(B)}_{\alpha} e^{\frac{-i\tau}{\hbar}\hat{H}_B}|b'\rangle\langle b'|\hat{U}^{(B)}_{\alpha'}|b\rangle \langle\varphi_n|\hat{V}^{(S)}_{\alpha'}|\varphi_n\rangle\langle\varphi_m|\hat{V}^{(S)}_{\alpha}|\varphi_m\rangle d\tau$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\otimes\langle\varphi_m|\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{V}^{(S)}_{\alpha}\hat{U}^{(B)}_{\alpha} e^{\frac{-i\tau}{\hbar}\hat{H}_B}|b'\rangle\otimes|\varphi_m\rangle\langle b'|\otimes\langle\varphi_n|\hat{V}^{(S)}_{\alpha'}\hat{U}^{(B)}_{\alpha'}|b\rangle\otimes|\varphi_n\rangle d\tau$$

$$= \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\otimes\langle\varphi_m|\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{H}_{SB} e^{\frac{-i\tau}{\hbar}\hat{H}_B}|b'\rangle\otimes|\varphi_m\rangle\langle b'|\otimes\langle\varphi_n|\hat{H}_{SB}|b\rangle\otimes|\varphi_n\rangle d\tau$$

$$= \frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B \langle\varphi_m|\hat{H}_{SB}|\varphi_m\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B} \langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\} d\tau ,$$

and therefore,

$$\sum_{\alpha,\alpha'} G^{(\alpha,\alpha')}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{n,n} = \frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B \langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B} \langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\} d\tau .$$

Similarly,

$$\sum_{\alpha,\alpha'} \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha')}_{n,n} V^{(\alpha)}_{m,m} = \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\hat{U}^{(B)}_{\alpha'}|b'\rangle\langle b'|\hat{U}^{(B)}_{\alpha}|b\rangle \rho_b e^{\frac{-i\tau}{\hbar}(E_b-E_{b'})} V^{(\alpha')}_{n,n} V^{(\alpha)}_{m,m} d\tau$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\hat{\rho}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}^{(B)}_{\alpha'} e^{\frac{i\tau}{\hbar}\hat{H}_B}|b'\rangle\langle b'|\hat{U}^{(B)}_{\alpha}|b\rangle \langle\varphi_m|\hat{V}^{(S)}_{\alpha}|\varphi_m\rangle\langle\varphi_n|\hat{V}^{(S)}_{\alpha'}|\varphi_n\rangle d\tau$$

$$= \sum_{\alpha,\alpha'} \frac{1}{\hbar^2}\int_0^\infty \sum_{b,b'} \langle b|\otimes\langle\varphi_n|\hat{\rho}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}^{(B)}_{\alpha'}\hat{V}^{(S)}_{\alpha'} e^{\frac{i\tau}{\hbar}\hat{H}_B}|b'\rangle\otimes|\varphi_n\rangle\langle b'|\otimes\langle\varphi_m|\hat{U}^{(B)}_{\alpha}\hat{V}^{(S)}_{\alpha}|b\rangle\otimes|\varphi_m\rangle d\tau$$

$$= \frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B \langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B} \langle\varphi_m|\hat{H}_{SB}|\varphi_m\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\} d\tau ,$$

and therefore,

$$\sum_{\alpha,\alpha'} \bar{G}^{(\alpha',\alpha)}_{n,n} V^{(\alpha)}_{n,n} V^{(\alpha')}_{n,n} = \frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B \langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B} \langle\varphi_n|\hat{H}_{SB}|\varphi_n\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\} d\tau .$$

Consequently,

$$k_{n',n}=\sum_{\alpha,\alpha'} G^{(\alpha,\alpha')}_{n',n'}V^{(\alpha')}_{n',n'}V^{(\alpha)}_{n',n'}-\sum_{\alpha,\alpha'} G^{(\alpha,\alpha')}_{n',n'}V^{(\alpha')}_{n',n'}V^{(\alpha)}_{n,n}+\sum_{\alpha,\alpha'} \bar{G}^{(\alpha',\alpha)}_{n,n}V^{(\alpha')}_{n,n}V^{(\alpha)}_{n,n}-\sum_{\alpha,\alpha'} \bar{G}^{(\alpha',\alpha)}_{n,n}V^{(\alpha')}_{n,n}V^{(\alpha)}_{n',n'}$$

$$=\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau$$

$$+\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\}d\tau$$

$$-\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau$$

$$-\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\}d\tau\ .$$

The expression for the real part of $k_{n',n}$ *simplifies using,* $tr\{\hat{O}\}=tr\{\hat{O}^\dagger\}^*$,

$$\mathrm{Re}[k_{n',n}]=\mathrm{Re}\Big[\ \frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau$$

$$+\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau$$

$$-\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau$$

$$-\frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle e^{\frac{-i\tau}{\hbar}\hat{H}_B}\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau\ \Big]$$

$$=\mathrm{Re}\Big[\ \frac{1}{\hbar^2}\int_0^\infty tr_B\{\hat{\rho}_B\Big[\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle-\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle\Big]$$

$$\cdot e^{\frac{-i\tau}{\hbar}\hat{H}_B}\Big[\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle-\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle\Big]e^{\frac{i\tau}{\hbar}\hat{H}_B}\}d\tau\ \Big]\ .$$

Introducing a complete orthonormal system of the bath Hamiltonian eigenstates, we obtain

$$\mathrm{Re}[k_{n',n}]=\mathrm{Re}\Big[\ \frac{1}{\hbar^2}\int_0^\infty\sum_{b,b'}\rho_b\langle b|\Big[\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle-\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle\Big]|b'\rangle$$

$$\langle b'|e^{\frac{-i\tau}{\hbar}E_{b'}}\Big[\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle-\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle\Big]e^{\frac{i\tau}{\hbar}E_b}|b\rangle d\tau\ \Big]$$

$$=\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau\sum_{b,b'}\rho_b e^{\frac{-i\tau}{\hbar}(E_{b'}-E_b)}|\langle b|\Big[\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle-\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle\Big]|b'\rangle|^2$$

$$=\frac{1}{\hbar^2}\int_0^\infty d\tau\sum_{b,b'}\rho_b\cos((E_{b'}-E_b)\tau/\hbar)|\langle b|\Big[\langle\varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle-\langle\varphi_{n}|\hat{H}_{SB}|\varphi_{n}\rangle\Big]|b'\rangle|^2\ .$$

Since the time integrand is an even function of time, we obtain Eq. (19.4.31),

$$\mathrm{Re}[k_{n',n}] = \frac{1}{2\hbar^2}\mathrm{Re}\int_{-\infty}^{\infty} d\tau \sum_{b,b'} \rho_b e^{i(E_{b'}-E_b)\tau/\hbar} \,|\langle b|\Big[\langle \varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle - \langle \varphi_n|\hat{H}_{SB}|\varphi_n\rangle\Big]|b'\rangle|^2$$

$$= \frac{\pi}{\hbar}\sum_{b,b'} \rho_b \,|\langle b|\Big[\langle \varphi_{n'}|\hat{H}_{SB}|\varphi_{n'}\rangle - \langle \varphi_n|\hat{H}_{SB}|\varphi_n\rangle\Big]|b'\rangle|^2 \;\delta(E_{b'}-E_b)\,.$$

Exercise 19.5.1 *(a) Use the commutation relation between the bosonic annihilation and creation operators, (Eqs. (8.5.5-8.5.7)),* $[\hat{b}_{j'},\hat{b}_j^\dagger] = \delta_{j,j'}$, *to show that the traces over the single mode subspace,* $tr_j\{\hat{b}_j f(\hat{b}_j^\dagger \hat{b}_j)\}$ *and* $tr_j\{\hat{b}_j^\dagger f(\hat{b}_j^\dagger \hat{b}_j)\}$, *vanish for any analytic function (* $f(\hat{A}) = \sum_{n=0}^{\infty} f_n \hat{A}^n$ *). (b) Given the definition of the bosonic bath Hamiltonian and coupling operators (Eq. (19.5.1) with* $\hat{U}_B = \sum_{j=1}^{N_\omega} \lambda_j \hat{b}_j$ *), and the bath density operator (Eq. (19.5.3)),* $\hat{\rho}_B = e^{-\hat{H}_B/(k_BT)} / tr_B\{e^{-\hat{H}_B/(k_BT)}\}$, *use the result of (a) to show that,* $tr_B\{\hat{U}_B\hat{\rho}_B\} = tr_B\{\hat{U}_B^\dagger\hat{\rho}_B\} = 0$.

Solution 19.5.1

(a)

For an analytic function we can expand, $f(\hat{b}_j^\dagger \hat{b}_j) = \sum_{n=0}^{\infty} f_n \left[\hat{b}_j^\dagger \hat{b}_j\right]^n$. *Hence, it is sufficient to show that* $tr_j\{\hat{b}_j(\hat{b}_j^\dagger \hat{b}_j)^n\} = tr_j\{\hat{b}_j^\dagger(\hat{b}_j^\dagger \hat{b}_j)^n\} = 0$ *for any* n. *Using* $[\hat{b}_{j'},\hat{b}_j^\dagger] = \delta_{j,j'} \Rightarrow \hat{b}_j\hat{b}_j^\dagger = 1 + \hat{b}_j^\dagger\hat{b}_j$, *and the invariance of the trace to cyclic permutations, we obtain*

$$\begin{aligned}
&tr_j\{b_j(b_j^\dagger b_j)^{n+1}\} = tr_j\{b_j b_j^\dagger b_j (b_j^\dagger b_j)^n\}\\
&= tr_j\{b_j(b_j^\dagger b_j)^n\} + tr_j\{b_j^\dagger b_j b_j (b_j^\dagger b_j)^n\}\\
&= tr_j\{b_j(b_j^\dagger b_j)^n\} + tr_j\{b_j(b_j^\dagger b_j)^{n+1}\}\\
&\Rightarrow tr_j\{b_j(b_j^\dagger b_j)^n\} = 0
\end{aligned}$$

and

$$\begin{aligned}
&tr_j\{(b_j^\dagger b_j)^{n+1} b_j^\dagger\} = tr_j\{(b_j^\dagger b_j)^n b_j^\dagger b_j b_j^\dagger\}\\
&= tr_j\{(b_j^\dagger b_j)^n b_j^\dagger\} + tr_j\{(b_j^\dagger b_j)^n b_j^\dagger b_j^\dagger b_j\}\\
&= tr_j\{(b_j^\dagger b_j)^n b_j^\dagger\} + tr_j\{b_j^\dagger b_j (b_j^\dagger b_j)^n b_j^\dagger\}\\
&= tr_j\{(b_j^\dagger b_j)^n b_j^\dagger\} + tr_j\{(b_j^\dagger b_j)^{n+1} b_j^\dagger\}
\end{aligned}$$

$$\Rightarrow tr_j\{(b_j^\dagger b_j)^n b_j^\dagger\} = 0 \quad .$$

(b)

Using Eq. (19.5.1) for the bath Hamiltonian, $\hat{H}_B = \sum_{j=1}^{N_\omega} \hbar\omega_j (\hat{b}_j^\dagger \hat{b}_j + \frac{1}{2})$*, and the coupling operator,* $\hat{U}_B = \sum_{j=1}^{N_\omega} \lambda_j \hat{b}_j$ *, using Eq. (19.5.3) for the bath density,* $\hat{\rho}_B = \frac{e^{-\hat{H}_B/(k_B T)}}{Z}$*, recalling that* $tr\,\{\hat{O}_j \otimes \hat{O}_{j'}\} = tr_j\{\hat{O}_j\} \cdot tr_{j'}\{\hat{O}_{j'}\}$*, and using the results of (a), we obtain*

$$tr_B\{\hat{U}_B \hat{\rho}_B\} = tr_B\{\sum_{j=1}^{N_\omega} \lambda_j \hat{b}_j e^{\frac{-1}{k_B T}\sum_{j'=1}^{N_\omega} \hbar\omega_{j'}(\hat{b}_{j'}^\dagger \hat{b}_{j'} + \frac{1}{2})}\} / Z = \frac{1}{Z} tr_B\{\sum_{j=1}^{N_\omega} \lambda_j \hat{b}_j \prod_{j'=1}^{N_\omega} e^{\frac{-\hbar\omega_{j'}}{k_B T}(\hat{b}_{j'}^\dagger \hat{b}_{j'} + \frac{1}{2})}\}$$

$$= \frac{1}{Z}\sum_{j=1}^{N_\omega} \lambda_j tr_1\{e^{\frac{-\hbar\omega_1}{k_B T}(\hat{b}_1^\dagger \hat{b}_1)}\} \cdot tr_2\{e^{\frac{-\hbar\omega_2}{k_B T}(\hat{b}_2^\dagger \hat{b}_2)}\} \cdots tr_j\{\hat{b}_j e^{\frac{-\hbar\omega_j}{k_B T}(\hat{b}_j^\dagger \hat{b}_j)}\} \cdots = 0$$

$$tr_B\{\hat{U}_\alpha^{(B)\dagger} \hat{\rho}_B\} = tr_B\{\sum_{j=1}^{N_\omega} \lambda_j^* \hat{b}_j^\dagger e^{\frac{-1}{k_B T}\sum_{j'=1}^{N_\omega} \hbar\omega_{j'}(\hat{b}_{j'}^\dagger \hat{b}_{j'} + \frac{1}{2})}\} / Z = \frac{1}{Z} tr_B\{\sum_{j=1}^{N_\omega} \lambda_j^* \hat{b}_j^\dagger \prod_{j'=1}^{N_\omega} e^{\frac{-\hbar\omega_{j'}}{k_B T}(\hat{b}_{j'}^\dagger \hat{b}_{j'} + \frac{1}{2})}\}$$

$$= \frac{1}{Z}\sum_{j=1}^{N_\omega} \lambda_j^* tr_1\{e^{\frac{-\hbar\omega_1}{k_B T}(\hat{b}_1^\dagger \hat{b}_1)}\} \cdot tr_2\{e^{\frac{-\hbar\omega_2}{k_B T}(\hat{b}_2^\dagger \hat{b}_2)}\} \cdots tr_j\{\hat{b}_j^\dagger e^{\frac{-\hbar\omega_j}{k_B T}(\hat{b}_j^\dagger \hat{b}_j)}\} \cdots = 0 \ .$$

Exercise 19.5.2 *(a) Use the explicit expressions (Eqs. (19.5.1, 19.5.3)),* $\hat{U}_B = \sum_{j=1}^{N_\omega} \lambda_j \hat{b}_j$ *,* $\hat{H}_B = \sum_{j=1}^{N_\omega} \hbar\omega_j (\hat{b}_j^\dagger \hat{b}_j + \frac{1}{2})$*,* $\hat{\rho}_B = \frac{e^{-\hat{H}_B/(k_B T)}}{tr_B\{e^{-\hat{H}_B/(k_B T)}\}}$*, to show that the bath correlation functions,* $c_e(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$ *and* $c_a(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$*, read* $c_e(\tau) = \sum_{j=1}^{N_\omega} |\lambda_j|^2 e^{-i\tau\omega_j}[1 + n(\omega_j)]$ *and* $c_a(\tau) = \sum_{j=1}^{N_\omega} |\lambda_j|^2 e^{i\tau\omega_j} n(\omega_j)$*.*

(b) For a general system-bath coupling operator, $\hat{H}_{SB} \equiv \sum_\alpha \hat{V}_\alpha^{(S)} \hat{U}_\alpha^{(B)}$ *(Eq. (19.3.12)), the Redfield (Born-Markov) dissipator obtains the form of Eqs. (19.3.21, 19.3.22),* $\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\sum_{\alpha,\alpha'} \int_0^t d\tau \{c_{\alpha,\alpha'}(\tau)[\hat{V}_\alpha^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_{\alpha'}^{(S)} e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] + \bar{c}_{\alpha',\alpha}(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_{\alpha'}^{(S)} e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_\alpha^{(S)}]\}$*, where* $c_{\alpha,\alpha'}(\tau) \equiv tr_B\{\hat{U}_\alpha^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_{\alpha'}^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$ *and* $\bar{c}_{\alpha,\alpha'}(\tau) = c_{\alpha,\alpha'}(-\tau)$*. Map the coupling operator defined*

in Eq. (19.5.1), $\hat{H}_{SB} \equiv \hat{V}_S \hat{U}_B + \hat{V}_S^\dagger \hat{U}_B^\dagger$, *on this general form by identifying,* $\hat{V}_S \equiv \hat{V}_1^{(S)}$, $\hat{U}_B \equiv \hat{U}_1^{(B)}$, $\hat{V}_S^\dagger \equiv \hat{V}_2^{(S)}$, $\hat{U}_B^\dagger \equiv \hat{U}_2^{(B)}$, *to show that*

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_{2,1}^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_{1,2}^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} .$$

(c) Use the identities $c_{1,2}(\tau) = c_e(\tau)$ *and* $c_{2,1}(\tau) = c_a(\tau)$ *to derive Eq. (19.5.5).*

Solution 19.5.2

(a)

Using, $\hat{U}_B = \sum_{j=1}^{N_\omega}\lambda_j\hat{b}_j$, $\hat{U}_B^\dagger = \sum_{j=1}^{N_\omega}\lambda_j^*\hat{b}_j^\dagger$ *and* $\hat{H}_B = \sum_{j=1}^{N_\omega}\hbar\omega_j(\hat{b}_j^\dagger\hat{b}_j + \frac{1}{2})$, *we first obtain*

$$c_a(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{N_\omega}\lambda_j^*\lambda_{j'} tr_B\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} ,$$

$$c_e(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{N_\omega}\lambda_{j'}^*\lambda_j tr_B\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} .$$

Focusing on $tr_B\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$, *we notice that* $e^{\frac{-i\tau}{\hbar}\hat{H}_B} = \prod_{j=1}^{N_\omega} e^{\frac{-i\tau}{\hbar}\hat{h}_j}$ *and* $e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B = \prod_{j=1}^{N_\omega} e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}$, *where,* $\hat{h}_j \equiv \hbar\omega_j(\hat{b}_j^\dagger\hat{b}_j + \frac{1}{2})$ *and* $Z_j = tr_j\{e^{\frac{-1}{k_BT}\hat{h}_j}\}$. *Therefore,*

$$tr_B\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$= \begin{cases} j = j' \;\; ; \;\; tr_1\{\frac{e^{\frac{-1}{k_BT}\hat{h}_1}}{Z_1}\}\cdot tr_2\{\frac{e^{\frac{-1}{k_BT}\hat{h}_2}}{Z_2}\}\cdots tr_j\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}\cdots \\ j \neq j' \;\; ; \;\; tr_1\{\frac{e^{\frac{-1}{k_BT}\hat{h}_1}}{Z_1}\}\cdot tr_2\{\frac{e^{\frac{-1}{k_BT}\hat{h}_2}}{Z_2}\}\cdots tr_j\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j} e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}\cdots tr_{j'}\{e^{\frac{-i\tau}{\hbar}\hat{h}_{j'}}\hat{b}_{j'} e^{\frac{i\tau}{\hbar}\hat{h}_{j'}}\frac{e^{\frac{-1}{k_BT}\hat{h}_{j'}}}{Z_{j'}}\}\cdots \end{cases} .$$

Since $tr_j\{\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}=1$, *whereas,* $tr_j\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}=tr_{j'}\{e^{\frac{-i\tau}{\hbar}\hat{h}_{j'}}\hat{b}_{j'}e^{\frac{i\tau}{\hbar}\hat{h}_{j'}}\frac{e^{\frac{-1}{k_BT}\hat{h}_{j'}}}{Z_{j'}}\}=0$ *(see Ex. 19.5.1 (a)), we obtain* $tr_B\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}=\delta_{j,j'}tr_j\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}$,

and similarly, $tr_B\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}=\delta_{j,j'}tr_j\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}$.

Consequently,

$$c_a(\tau)=tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}=\sum_{j,j'=1}^{N_\omega}\lambda_j^*\lambda_{j'}tr_B\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2 tr_j\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}$$

and

$$c_e(\tau)=tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}=\sum_{j,j'=1}^{N_\omega}\lambda_{j'}^*\lambda_j tr_B\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2 tr_j\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\}\ .$$

To evaluate the single mode traces, we use a complete orthonormal set of $\hat{h}_j$ *eigenstates,* $\hat{h}_j|n_j\rangle=\hbar\omega_j(n_j+\frac{1}{2})|n_j\rangle$. *Recalling that (see Eqs. (8.5.3, 8.5.4))* $\hat{b}_j|n\rangle=\sqrt{n}|n-1\rangle$, *and* $\hat{b}_j^\dagger|n\rangle=\sqrt{n+1}|n+1\rangle$, *we obtain*

$$c_a(\tau)=\sum_{j=1}^{N_\omega}|\lambda_j|^2\sum_{n_j}\left\langle n_j\left|\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\right|n_j\right\rangle$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2\sum_{n_j}\left\langle n_j\left|\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j\right|n_j\right\rangle e^{\frac{i\tau}{\hbar}\hbar\omega_j(n_j+\frac{1}{2})}\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{Z_j}$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2\sum_{n_j}\left\langle n_j\left|\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hbar\omega_j(n_j-\frac{1}{2})}\sqrt{n_j}\right|n_j-1\right\rangle e^{\frac{i\tau}{\hbar}\hbar\omega_j(n_j+\frac{1}{2})}\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{Z_j}$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2\, e^{i\omega_j\tau}\sum_{n_j} n_j\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{Z_j}=\sum_{j=1}^{N_\omega}|\lambda_j|^2\, e^{i\omega_j\tau}n(\omega_j)\ ,$$

$$c_e(\tau)=\sum_{j=1}^{N_\omega}|\lambda_j|^2\sum_{n_j}\left\langle n_j\left|\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\right|n_j\right\rangle$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2\sum_{n_j}\left\langle n_j\left|\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j^\dagger\right|n_j\right\rangle e^{\frac{i\tau}{\hbar}\hbar\omega_j(n_j+\frac{1}{2})}\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{Z_j}$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2\sum_{n_j}\left\langle n_j\left|\hat{b}_j e^{\frac{-i\tau}{\hbar}\hbar\omega_j(n_j+1+\frac{1}{2})}\sqrt{n_j+1}\right|n_j+1\right\rangle e^{\frac{i\tau}{\hbar}\hbar\omega_j(n_j+\frac{1}{2})}\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{Z_j}$$

$$=\sum_{j=1}^{N_\omega}|\lambda_j|^2\, e^{-i\omega_j\tau}\sum_{n_j}(n_j+1)\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{Z_j}=\sum_{j=1}^{N_\omega}|\lambda_j|^2\, e^{-i\omega_j\tau}[n(\omega_j)+1]\ ,$$

where in the last steps we identified the thermal occupation number of a harmonic mode (see Ex. 18.2.7), $n(\omega_j)\equiv\sum_{n_j}n_j\frac{e^{\frac{-\hbar\omega_j}{k_BT}(n_j+\frac{1}{2})}}{\sum_{n_j'}e^{\frac{-\hbar\omega_j}{k_BT}(n_j'+\frac{1}{2})}}$.

(b)

For a general system-bath coupling operator, $\hat{H}_{SB}\equiv\sum_\alpha\hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}$ *(Eq. (19.3.12)), the Redfield (Born-Markov) dissipator obtains the form of Eqs. (19.3.21, 19.3.22),* $\hat{D}\hat{\rho}_S(t)=$

$$-\frac{1}{\hbar^2}\sum_{\alpha,\alpha'}\int_0^t d\tau\{c_{\alpha,\alpha'}(\tau)[\hat{V}_\alpha^{(S)},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+\bar{c}_{\alpha',\alpha}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_\alpha^{(S)}]\}\quad \textit{where,}$$

$c_{\alpha,\alpha'}(\tau)\equiv tr_B\{\hat{U}_\alpha^{(B)}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_{\alpha'}^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$ *, and* $\bar{c}_{\alpha,\alpha'}(\tau)=c_{\alpha,\alpha'}(-\tau)$.

Defining, $\hat{V}_S \equiv \hat{V}_1^{(S)}$, $\hat{U}_B \equiv \hat{U}_1^{(B)}$, $\hat{V}_S^\dagger \equiv \hat{V}_2^{(S)}$, $\hat{U}_B^\dagger \equiv \hat{U}_2^{(B)}$, *we can rewrite the system bath coupling operator in Eq. (19.5.1) as,* $\hat{H}_{SB} \equiv \hat{V}_S \hat{U}_B + \hat{V}_S^\dagger \hat{U}_B^\dagger = \hat{V}_1^{(S)}\hat{U}_1^{(B)} + \hat{V}_2^{(S)}\hat{U}_2^{(B)}$. *Using the general Redfield dissipator for* $\hat{H}_{SB} \equiv \sum_{\alpha=1}^{2} \hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}$ *(Eqs. (19.3.21, 19.3.22)), we obtain*

$$\hat{D}\hat{\rho}_S(t) =$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,1}(\tau)[\hat{V}_1^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + \overline{c}_{1,1}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_1^{(S)}]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_1^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + \overline{c}_{2,1}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_1^{(S)}]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_2^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + \overline{c}_{1,2}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_2^{(S)}]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,2}(\tau)[\hat{V}_2^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + \overline{c}_{2,2}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_2^{(S)}]\} ,$$

where,

$$c_{1,1}(\tau) \equiv tr_B\{\hat{U}_1^{(B)}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_1^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_{1,2}(\tau) \equiv tr_B\{\hat{U}_1^{(B)}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_2^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_{2,1}(\tau) \equiv tr_B\{\hat{U}_2^{(B)}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_1^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_{2,2}(\tau) \equiv tr_B\{\hat{U}_1^{(B)}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_1^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} .$$

Using the mapping $\hat{V}_S \equiv \hat{V}_1^{(S)}$, $\hat{U}_B \equiv \hat{U}_1^{(B)}$, $\hat{V}_S^\dagger \equiv \hat{V}_2^{(S)}$, $\hat{U}_B^\dagger \equiv \hat{U}_2^{(B)}$ *, we obtain*

$$\hat{D}\hat{\rho}_S(t) =$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,1}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{1,1}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{2,1}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{1,2}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,2}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{2,2}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} ,$$

where,

$$c_{1,1}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_{1,2}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_{2,1}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_{2,2}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} .$$

Using the definitions in (a) we recognize, $c_{1,2}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = c_e(\tau)$ *and* $c_{2,1}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = c_a(\tau)$, *where, using considerations like those applied in (a), the other correlation functions vanish,*

$$c_{1,1}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{N_\omega}\lambda_j\lambda_{j'}tr_B\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$
$$= \sum_{j=1}^{N_\omega}\lambda_j^2 tr_j\{\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\} = \sum_{j=1}^{N_\omega}\lambda_j^2\sum_{n_j}\left\langle n_j\right|\hat{b}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\left|n_j\right\rangle = 0$$
$$c_{2,2}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{N_\omega}\lambda_j^*\lambda_{j'}^* tr_B\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{b}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$= \sum_{j=1}^{N_\omega}(\lambda_j^*)^2 tr_j\{\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\} = \sum_{j=1}^{N_\omega}(\lambda_j^*)^2\sum_{n_j}\left\langle n_j\right|\hat{b}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{b}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}\hat{h}_j}}{Z_j}\left|n_j\right\rangle = 0 .$$

Hence,

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{2,1}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{1,2}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \ .$$

Using Eq. (19.3.21) we have $\overline{c}_{2,1}(\tau) = c_{2,1}(-\tau)$ *and* $\overline{c}_{1,2}(\tau) = c_{1,2}(-\tau)$. *Using* $tr\{\hat{O}\} = tr_B\{\hat{O}^\dagger\}^*$ *and cyclic permutations under the trace, we obtain*

$$c_{1,2}(-\tau) = tr_B\{\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = tr_B\{\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger\}^* = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}^* = c_{1,2}^*(\tau)$$

$$c_{2,1}(-\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = tr_B\{\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B\}^* = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}^* = c_{2.1}^*(\tau) \ .$$

Hence,

$$\hat{D}\hat{\rho}_S(t) =$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_{2.1}^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_{1,2}^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \ .$$

(c)

Using the identities, $c_{1,2}(\tau) = c_e(\tau)$, $c_{2,1}(\tau) = c_a(\tau)$ *(see (b)), we can rewrite the result of (b) as*

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\int_0^t d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a^*(\tau)(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_e^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \ .$$

Identifying

$$[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]^\dagger = [\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]$$

$$[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]^\dagger = [\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S] \ ,$$

we finally obtain Eq. (19.5.5),

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\int_0^t d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\}\,.$$

Exercise 19.5.3 *(a) Given Eqs. (19.5.4, 19.5.8), and defining the TLS eigenstate populations,* $\rho_{g,g}(t) = \langle\varphi_g|\hat{\rho}_S(t)|\varphi_g\rangle$, *and* $\rho_{e,e}(t) = \langle\varphi_e|\hat{\rho}_S(t)|\varphi_e\rangle$, *show that* $\frac{\partial}{\partial t}\rho_{g,g}(t) \cong -\frac{1}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau\{c_e(\tau)\langle g|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|g\rangle + c_a(\tau)\langle g|[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|g\rangle\}$.

(b) Introduce the identity operator in the space of the TLS, $\hat{I} = |\varphi_g\rangle\langle\varphi_g| + |\varphi_e\rangle\langle\varphi_e|$, *to show that for off-diagonal TLS coupling operators,* $\hat{V}_S \equiv \mu|\varphi_e\rangle\langle\varphi_g|$ *and* $\hat{V}_S^\dagger = \mu^*|\varphi_g\rangle\langle\varphi_e|$, *this result reads* $\frac{\partial}{\partial t}\rho_{g,g}(t) = k^{em}_{e\to g}\rho_{e,e}(t) - k^{ab}_{g\to e}\rho_{g,g}(t)$, *where* $k^{em}_{e\to g} = 2|\mu|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}$ *and* $k^{ab}_{g\to e} = 2|\mu|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}$. *(c) Show similarly that* $\frac{\partial}{\partial t}\rho_{e,e}(t) = k^{ab}_{g\to e}\rho_{g,g}(t) - k^{em}_{e\to g}\rho_{e,e}(t)$. *(d) Use the explicit expressions for the correlation functions (Eq. (19.5.6)) to derive Eq. (19.5.14). (e) Use the expressions for the correlation functions for a continuous bath (Eq. (19.5.7)) to derive Eq. (19.5.15).*

Solution 19.5.3

(a)

Given the reduced equation:

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(t)]$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\}\,,$$

and the complete orthonormal set of eigenstates, $\hat{H}_S|\varphi_g\rangle = E_g|\varphi_g\rangle$, *and* $\hat{H}_S|\varphi_e\rangle = E_e|\varphi_e\rangle$, *we obtain*

$$\frac{\partial}{\partial t}\rho_{g,g}(t)=\frac{\partial}{\partial t}\langle\varphi_g|\hat{\rho}_S(t)|\varphi_g\rangle\cong-\frac{i}{\hbar}\langle\varphi_g|[\hat{H}_S,\hat{\rho}_S(t)]|\varphi_g\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{\langle\varphi_g|\left(c_e(\tau)[\hat{V}_S,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+c_a(\tau)[\hat{V}_S^\dagger,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right)|\varphi_g\rangle+\langle\varphi_g|(h.c.)|\varphi_g\rangle\}$$
$$=-\frac{i}{\hbar}\langle\varphi_g|\hat{H}_S\hat{\rho}_S(t)-\hat{\rho}_S(t)\hat{H}_S|\varphi_g\rangle$$
$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau\langle\varphi_g|\left(c_e(\tau)[\hat{V}_S,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+c_a(\tau)[\hat{V}_S^\dagger,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right)|\varphi_g\rangle$$
$$=-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau\left(c_e(\tau)\langle\varphi_g|[\hat{V}_S,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|\varphi_g\rangle+c_a(\tau)\langle\varphi_g|[\hat{V}_S^\dagger,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|\varphi_g\rangle\right).$$

(b)

Expressing in detail the result of (a), we obtain

$$\frac{\partial}{\partial t}\rho_{g,g}(t)=$$
$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)\langle\varphi_g|\hat{V}_S e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|\varphi_g\rangle$$
$$+2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)\langle\varphi_g|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S|\varphi_g\rangle$$
$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\langle\varphi_g|\hat{V}_S^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|\varphi_g\rangle$$
$$+2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\langle\varphi_g|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S^\dagger|\varphi_g\rangle\ .$$

Introducing the identity, $\hat{I}=|\varphi_g\rangle\langle\varphi_g|+|\varphi_e\rangle\langle\varphi_e|$, *and recalling that* $\hat{V}_S\equiv\mu|\varphi_e\rangle\langle\varphi_g|$, *and* $\hat{V}_S^\dagger=\mu^*|\varphi_g\rangle\langle\varphi_e|$, *we obtain*

$$\frac{\partial}{\partial t}\rho_{g,g}(t)=$$

$$+2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)\left\langle\varphi_g\right|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\left|\varphi_e\right\rangle\left\langle\varphi_e\right|\hat{\rho}_S(t)\left|\varphi_e\right\rangle\left\langle\varphi_e\right|\hat{V}_S\left|\varphi_g\right\rangle$$

$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\left\langle\varphi_g\right|\hat{V}_S^\dagger\left|\varphi_e\right\rangle\left\langle\varphi_e\right|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S\,e^{\frac{i\tau}{\hbar}\hat{H}_S}\left|\varphi_g\right\rangle\left\langle\varphi_g\right|\hat{\rho}_S(t)\left|\varphi_g\right\rangle$$

$$=2\,\mathrm{Re}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{-i\tau}{\hbar}(E_g-E_e)}\left\langle\varphi_e\right|\hat{\rho}_S(t)\left|\varphi_e\right\rangle$$

$$-2\,\mathrm{Re}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}(E_e-E_g)}\left\langle\varphi_g\right|\hat{\rho}_S(t)\left|\varphi_g\right\rangle\ .$$

Hence, $\frac{\partial}{\partial t}\rho_{g,g}(t)=k_{e\to g}^{em}\rho_{e,e}(t)-k_{g\to e}^{ab}\rho_{g,g}(t)$, *where the transition rates read (denoting,* $E_e-E_g=2\Delta_E$*),*

$$k_{e\to g}^{em}=2\,\mathrm{Re}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}(E_e-E_g)}=2|\mu|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}$$

$$k_{g\to e}^{ab}=2\,\mathrm{Re}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}(E_e-E_g)}=2|\mu|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}\ .$$

(c)

Following (b) we obtain

$$\frac{\partial}{\partial t}\rho_{e,e}(t)=$$

$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)\left\langle\varphi_e\right|\hat{V}_S\,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\left|\varphi_e\right\rangle$$

$$+2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)\left\langle\varphi_e\right|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S\left|\varphi_e\right\rangle$$

$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\left\langle\varphi_e\right|\hat{V}_S^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S\,e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\left|\varphi_e\right\rangle$$

$$+2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\left\langle\varphi_e\right|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S\,e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S^\dagger\left|\varphi_e\right\rangle\ .$$

Introducing the identity, $\hat{I}=\left|\varphi_g\right\rangle\left\langle\varphi_g\right|+\left|\varphi_e\right\rangle\left\langle\varphi_e\right|$, *and recalling that* $\hat{V}_S\equiv\mu\left|\varphi_e\right\rangle\left\langle\varphi_g\right|$ *and* $\hat{V}_S^\dagger=\mu^*\left|\varphi_g\right\rangle\left\langle\varphi_e\right|$, *we obtain*

$$
\begin{aligned}
&\frac{\partial}{\partial t}\rho_{e,e}(t)= \\
&-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)\langle\varphi_e|\hat{V}_S|\varphi_g\rangle\langle\varphi_g|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}|\varphi_e\rangle\langle\varphi_e|\hat{\rho}_S(t)|\varphi_e\rangle \\
&+2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\langle\varphi_e|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}|\varphi_g\rangle\langle\varphi_g|\hat{\rho}_S(t)|\varphi_g\rangle\langle\varphi_g|\hat{V}_S^\dagger|\varphi_e\rangle \\
&=-2\,\mathrm{Re}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}(E_e-E_g)}\rho_{e,e}(t) \\
&+2\,\mathrm{Re}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}(E_e-E_g)}\rho_{g,g}(t) \\
&=-k_{e\to g}^{em}\rho_{e,e}(t)+k_{g\to e}^{ab}\rho_{g,g}(t)\ .
\end{aligned}
$$

(d)

Using Eq. (19.5.6), $c_a(\tau)=\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{i\tau\omega_j}n(\omega_j)$ *and* $c_e(\tau)=\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{-i\tau\omega_j}[1+n(\omega_j)]$, *in the expressions for the transition rates, we obtain Eq. (19.5.14),*

$$
\begin{aligned}
k_{e\to g}^{em}&=2|\mu|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E} \\
&=\frac{2|\mu|^2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{-i\tau\omega_j}[1+n(\omega_j)]e^{\frac{i\tau}{\hbar}2\Delta_E} \\
&=\frac{|\mu|^2}{\hbar^2}\mathrm{Re}\int_{-\infty}^\infty d\tau\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{-i\tau(\hbar\omega_j-2\Delta_E)/\hbar}[1+n(\omega_j)]=\frac{2\pi|\mu|^2}{\hbar}\sum_{j=1}^{N_\omega}|\lambda_j|^2\,[1+n(\omega_j)]\delta(\hbar\omega_j-2\Delta_E)\ ,
\end{aligned}
$$

$$
\begin{aligned}
k_{g\to e}^{ab}&=2|\mu|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E} \\
&=\frac{2|\mu|^2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{i\tau\omega_j}n(\omega_j)e^{\frac{-i\tau}{\hbar}2\Delta_E} \\
&=\frac{|\mu|^2}{\hbar^2}\mathrm{Re}\int_{-\infty}^\infty d\tau\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{i\tau(\hbar\omega_j-2\Delta_E)/\hbar}n(\omega_j)=\frac{2\pi|\mu|^2}{\hbar}\sum_{j=1}^{N_\omega}|\lambda_j|^2\,n(\omega_j)\delta(\hbar\omega_j-2\Delta_E)\ .
\end{aligned}
$$

(e)

Using the expressions for the correlation functions for a continuous bath (Eq. (19.5.7)) in the expressions for the transition rates, we obtain Eq. (19.5.15),

$$k^{em}_{e\to g} = 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}$$
$$= 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau \frac{\hbar}{2\pi}\int d\omega e^{-i\tau\omega}J(\hbar\omega)(n(\omega)+1)e^{\frac{i\tau}{\hbar}2\Delta_E}$$
$$= \frac{1}{2\pi}|\mu|^2 \operatorname{Re}\frac{1}{\hbar}\int_{-\infty}^\infty d\tau\int d\omega J(\hbar\omega)(n(\omega)+1)e^{\frac{i\tau}{\hbar}(2\Delta_E-\hbar\omega)}$$
$$= |\mu|^2 \int d\omega J(\hbar\omega)(n(\omega)+1)\delta(2\Delta_E-\hbar\omega)$$

$$= \frac{|\mu|^2}{\hbar}J(2\Delta_E)(n(\frac{2\Delta_E}{\hbar})+1) \ ,$$

$$k^{ab}_{g\to e} = 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}$$
$$= 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau \frac{\hbar}{2\pi}\int d\omega e^{i\tau\omega}J(\hbar\omega)n(\omega)e^{\frac{-i\tau}{\hbar}2\Delta_E}$$
$$= \frac{1}{2\pi}|\mu|^2 \operatorname{Re}\frac{1}{\hbar}\int_{-\infty}^\infty d\tau\int d\omega J(\hbar\omega)n(\omega)e^{\frac{-i\tau}{\hbar}(2\Delta_E-\hbar\omega)}$$
$$= |\mu|^2 \int d\omega J(\hbar\omega)n(\omega)\delta(2\Delta_E-\hbar\omega)$$

$$= \frac{|\mu|^2}{\hbar}J(2\Delta_E)n(\frac{2\Delta_E}{\hbar}) \ .$$

Exercise 19.5.4 *(a) The coherences between the TLS eigenstates are defined as* $\rho_{g,e}(t) = \langle\varphi_g|\hat\rho_S(t)|\varphi_e\rangle$ *and* $\rho_{e,g}(t) = \langle\varphi_e|\hat\rho_S(t)|\varphi_g\rangle$. *Introduce the identity operator in the space of the TLS,* $\hat I = |\varphi_g\rangle\langle\varphi_g| + |\varphi_e\rangle\langle\varphi_e|$, *into the stationary Redfield Equation (Eqs. (19.5.4, 19.5.8)), and show that for off-diagonal TLS coupling operators,* $\hat V_S \equiv \mu|\varphi_e\rangle\langle\varphi_g|$ *and* $\hat V_S^\dagger = \mu^*|\varphi_g\rangle\langle\varphi_e|$, *the coherences follow the equations* $\frac{\partial\rho_{g,e}(t)}{\partial t} \cong \frac{i}{\hbar}2\Delta_E\rho_{g,e}(t) - \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau\{[c_a(\tau)+c_e^*(\tau)]e^{\frac{-i\tau}{\hbar}2\Delta_E}\}\rho_{g,e}(t)$, *and* $\frac{\partial\rho_{e,g}(t)}{\partial t} \cong -\frac{i}{\hbar}2\Delta_E\rho_{e,g}(t) - \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau[c_e(\tau)+c^*_a(\tau)]e^{\frac{i\tau}{\hbar}2\Delta_E}\rho_{e,g}(t)$. *(b) Use the definition of the absorption and emission rates (Eq. (19.5.14)) and the definitions,* $\delta \equiv \operatorname{Im}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau\{[c_a(\tau)+c_e^*(\tau)]e^{\frac{-i\tau}{\hbar}2\Delta_E}\}$ *and,* $k^{dec} \equiv \frac{1}{2}\left(k^{ab}_{g\to e}+k^{em}_{e\to g}\right)$, *to derive Eq. (19.5.20). (c)*

Use the explicit expressions for the correlation functions for a continuous bath (Eq. (19.5.7)) to derive Eq. (19.5.21).

Solution 19.5.4

(a)

Given the stationary Redfield Equation (Eqs. (19.5.4, 19.5.8)),

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)]$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\},$$

and the complete orthonormal set of eigenstates, $\hat{H}_S|\varphi_g\rangle = E_g|\varphi_g\rangle$, *and* $\hat{H}_S|\varphi_e\rangle = E_e|\varphi_e\rangle$, *we obtain*

$$\frac{\partial}{\partial t}\rho_{g,e}(t) \equiv \frac{\partial}{\partial t}\langle\varphi_g|\hat{\rho}_S(t)|\varphi_e\rangle \cong -\frac{i}{\hbar}\langle\varphi_g|[\hat{H}_S,\hat{\rho}_S(t)]|\varphi_e\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\langle\varphi_g|\left(c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right)|\varphi_e\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\langle\varphi_g|\left(c_e^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger] + c_a^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\right)|\varphi_e\rangle$$
$$= -\frac{i}{\hbar}\langle\varphi_g|\hat{H}_S\hat{\rho}_S(t) - \hat{\rho}_S(t)\hat{H}_S|\varphi_e\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\left(c_e(\tau)[\langle\varphi_g|\hat{V}_S e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|\varphi_e\rangle - \langle\varphi_g|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S|\varphi_e\rangle]\right)$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\left(c_a(\tau)[\langle\varphi_g|\hat{V}_S^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|\varphi_e\rangle - \langle\varphi_g|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S^\dagger|\varphi_e\rangle]\right)$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\left(c_e^*(\tau)[\langle\varphi_g|\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger|\varphi_e\rangle - \langle\varphi_g|\hat{V}_S^\dagger\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}|\varphi_e\rangle]\right)$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\left(c_a^*(\tau)[\langle\varphi_g|\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{V}_S|\varphi_e\rangle - \langle\varphi_g|\hat{V}_S\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}|\varphi_e\rangle]\right).$$

Introducing, $\hat{I} = |\varphi_g\rangle\langle\varphi_g| + |\varphi_e\rangle\langle\varphi_e|$, $\hat{V}_S \equiv \mu|\varphi_e\rangle\langle\varphi_g|$, *and* $\hat{V}_S^\dagger = \mu^*|\varphi_g\rangle\langle\varphi_e|$, *we obtain*

$$\frac{\partial}{\partial t}\rho_{g,e}(t) \cong -\frac{i}{\hbar}(E_g - E_e)\rho_{g,e}(t)$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)\left\langle \varphi_g \left| \hat{V}_S^\dagger \right| \varphi_e \right\rangle \left\langle \varphi_e \left| e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S \right| \varphi_g \right\rangle \left\langle \varphi_g \left| e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t) \right| \varphi_e \right\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau c_e^*(\tau)\left\langle \varphi_g \left| \hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S} \right| \varphi_e \right\rangle \left\langle \varphi_e \left| \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S} \right| \varphi_g \right\rangle \left\langle \varphi_g \left| \hat{V}_S^\dagger \right| \varphi_e \right\rangle$$
$$= -\frac{i}{\hbar}(E_g - E_e)\rho_{g,e}(t) - \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau [c_a(\tau) + c_e^*(\tau)] e^{\frac{-i\tau}{\hbar}(E_e - E_g)}\rho_{g,e}(t) \ .$$

Denoting, $E_e - E_g = 2\Delta_E$ *, we obtain*

$$\frac{\partial \rho_{g,e}(t)}{\partial t} \cong \frac{i}{\hbar}2\Delta_E \rho_{g,e}(t) - \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau \{[c_a(\tau) + c_e^*(\tau)] e^{\frac{-i\tau}{\hbar}2\Delta_E}\}\rho_{g,e}(t) .$$

To derive the complementary equation for $\rho_{e,g}(t)$ *, we van follow the same steps. Alternatively, we can use the Hermiticity of* $\hat{\rho}_S(t)$ *, which means that* $\frac{\partial}{\partial t}\left\langle \varphi_e \left| \hat{\rho}_S(t) \right| \varphi_g \right\rangle = \frac{\partial}{\partial t}\left\langle \varphi_g \left| \hat{\rho}_S(t) \right| \varphi_e \right\rangle^*$ *, namely*

$$\frac{\partial \rho_{e,g}(t)}{\partial t} \cong \frac{-i}{\hbar}2\Delta_E \rho_{e,g}(t) - \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau \{[c_a^*(\tau) + c_e(\tau)] e^{\frac{i\tau}{\hbar}2\Delta_E}\}\rho_{e,g}(t) .$$

(b)

The expressions for the absorption and emission rates (Eq. (19.5.14)) read $k_{e\to g}^{em} = 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau) e^{\frac{i\tau}{\hbar}2\Delta_E}$ *and* $k_{g\to e}^{ab} = 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau) e^{\frac{-i\tau}{\hbar}2\Delta_E}$*. Defining additionally,* $\delta \equiv \operatorname{Im}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau \{[c_a(\tau) + c_e^*(\tau)] e^{\frac{-i\tau}{\hbar}2\Delta_E}\}$*, and* $k^{dec} \equiv \frac{1}{2}\left(k_{g\to e}^{ab} + k_{e\to g}^{em}\right)$*, the result of (a) leads to Eq. (19.5.20),*

$$\frac{\partial \rho_{g,e}(t)}{\partial t} \cong \frac{i}{\hbar}2\Delta_E \rho_{g,e}(t) - \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau \{[c_a(\tau) + c_e^*(\tau)] e^{\frac{-i\tau}{\hbar}2\Delta_E}\}\rho_{g,e}(t)$$
$$= \left[\frac{i}{\hbar}2\Delta_E - i\operatorname{Im}\frac{|\mu|^2}{\hbar^2}\left(\int_0^\infty d\tau [c_a(\tau) + c_e^*(\tau)] e^{\frac{-i\tau}{\hbar}2\Delta_E}\right) - \operatorname{Re}\frac{|\mu|^2}{\hbar^2}\left(\int_0^\infty d\tau [c_a(\tau) + c_e^*(\tau)] e^{\frac{-i\tau}{\hbar}2\Delta_E}\right)\right]\rho_{g,e}(t)$$
$$= \left[\frac{i}{\hbar}2\Delta_E - i\delta - k^{dec}\right]\rho_{g,e}(t) .$$

(c)

Using the explicit expressions for the correlation functions for a continuous bath (Eq. (19.5.7)) and the definition of δ *, we obtain Eq. (19.5.21),*

$$\hbar\delta \equiv \mathrm{Im}\frac{|\mu|^2}{\hbar}\int_0^\infty d\tau\{[c_a(\tau)+c_e^*(\tau)]e^{\frac{-i\tau}{\hbar}2\Delta_E}\}$$

$$= \mathrm{Im}\frac{|\mu|^2}{\hbar}\int_0^\infty d\tau\{[\frac{\hbar}{2\pi}\int_0^\infty d\omega e^{i\tau\omega}J(\hbar\omega)n(\omega)+\frac{\hbar}{2\pi}\int_0^\infty d\omega e^{i\tau\omega}J(\hbar\omega)(n(\omega)+1)]e^{\frac{-i\tau}{\hbar}2\Delta_E}\}$$

$$= \mathrm{Im}\frac{|\mu|^2}{2\pi}\int_0^\infty d\tau\{\int_0^\infty d\omega e^{i\tau\omega}J(\hbar\omega)(2n(\omega)+1)e^{\frac{-i\tau}{\hbar}2\Delta_E}\} \ .$$

Exercise 19.5.5 *(a) Use Eq. (19.5.23), the Pauli spin matrices* $\boldsymbol{\sigma}_x=\begin{bmatrix}0&1\\1&0\end{bmatrix}$, $\boldsymbol{\sigma}_y=\begin{bmatrix}0&-i\\i&0\end{bmatrix}$, $\boldsymbol{\sigma}_z=\begin{bmatrix}1&0\\0&-1\end{bmatrix}$ *and the TLS density matrix* $\boldsymbol{\rho}(t)=\begin{bmatrix}\rho_{e,e}(t)&\rho_{e,g}(t)\\\rho_{g,e}(t)&\rho_{g,g}(t)\end{bmatrix}$ *to show that,* $\langle\sigma_z(t)\rangle=\rho_{e,e}(t)-\rho_{g,g}(t)$, $\langle\sigma_x(t)\rangle=\rho_{g,e}(t)+\rho_{e,g}(t)$, $\langle\sigma_y(t)\rangle=-i\rho_{g,e}(t)+i\rho_{e,g}(t)$. *(b) Use Eqs. (19.5.13, 19.5.20) for the time evolution of the density matrix elements to derive Eq. (19.5.24).*

Solution 19.5.5

(a)

Using the matrix representations of the TLS operators, $\boldsymbol{\sigma}_x=\begin{bmatrix}0&1\\1&0\end{bmatrix}$, $\boldsymbol{\sigma}_y=\begin{bmatrix}0&-i\\i&0\end{bmatrix}$, $\boldsymbol{\sigma}_z=\begin{bmatrix}1&0\\0&-1\end{bmatrix}$,

and the density matrix , $\boldsymbol{\rho}(t)=\begin{bmatrix}\rho_{e,e}(t)&\rho_{e,g}(t)\\\rho_{g,e}(t)&\rho_{g,g}(t)\end{bmatrix}$, *the expectation values (Eq. (19.5.23)) read*

$$tr\{\boldsymbol{\sigma}_z\boldsymbol{\rho}\}=tr\{\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}\rho_{e,e}(t)&\rho_{e,g}(t)\\\rho_{g,e}(t)&\rho_{g,g}(t)\end{bmatrix}\}=tr\{\begin{bmatrix}\rho_{e,e}(t)&\rho_{e,g}(t)\\-\rho_{g,e}(t)&-\rho_{g,g}(t)\end{bmatrix}\}=\rho_{e,e}(t)-\rho_{g,g}(t)$$

$$tr\{\boldsymbol{\sigma}_x\boldsymbol{\rho}\}=tr\{\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}\rho_{e,e}(t)&\rho_{e,g}(t)\\\rho_{g,e}(t)&\rho_{g,g}(t)\end{bmatrix}\}=tr\{\begin{bmatrix}\rho_{g,e}(t)&\rho_{g,g}(t)\\\rho_{e,e}(t)&\rho_{e,g}(t)\end{bmatrix}\}=\rho_{g,e}(t)+\rho_{e,g}(t)$$

$$tr\{\boldsymbol{\sigma}_y\boldsymbol{\rho}\}=tr\{\begin{bmatrix}0&-i\\i&0\end{bmatrix}\begin{bmatrix}\rho_{e,e}(t)&\rho_{e,g}(t)\\\rho_{g,e}(t)&\rho_{g,g}(t)\end{bmatrix}\}=tr\{\begin{bmatrix}-i\rho_{g,e}(t)&-i\rho_{g,g}(t)\\i\rho_{e,e}(t)&i\rho_{e,g}(t)\end{bmatrix}\}=-i(\rho_{g,e}(t)-\rho_{e,g}(t)) \ .$$

(b)

Using the results of (a),

$$\langle \sigma_z(t) \rangle = \rho_{e,e}(t) - \rho_{g,g}(t) \ ; \ \langle \sigma_x(t) \rangle = \rho_{g,e}(t) + \rho_{e,g}(t) \ ; \ \langle \sigma_y(t) \rangle = -i(\rho_{g,e}(t) - \rho_{e,g}(t)) ,$$

we obtain

$$\frac{\partial}{\partial t}\langle \sigma_z(t) \rangle = \frac{\partial}{\partial t}\rho_{e,e}(t) - \frac{\partial}{\partial t}\rho_{g,g}(t)$$
$$\frac{\partial}{\partial t}\langle \sigma_x(t) \rangle = \frac{\partial}{\partial t}\rho_{g,e}(t) + \frac{\partial}{\partial t}\rho_{e,g}(t)$$

$$\frac{\partial}{\partial t}\langle \sigma_y(t) \rangle = -i\frac{\partial}{\partial t}\rho_{g,e}(t) + i\frac{\partial}{\partial t}\rho_{e,g}(t) \ .$$

To obtain closed equations for the observables, we make use of Eqs. (19.5.3, 19.20) for the explicit time-derivatives of the density matrix elements,

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = k^{em}_{e\to g}\rho_{e,e}(t) - k^{ab}_{g\to e}\rho_{g,g}(t) \quad ; \quad \frac{\partial}{\partial t}\rho_{e,e}(t) = k^{ab}_{g\to e}\rho_{g,g}(t) - k^{em}_{e\to g}\rho_{e,e}(t)$$
$$\frac{\partial}{\partial t}\rho_{e,g}(t) = \frac{-i}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{e,g}(t) - k^{dec}\rho_{e,g}(t) \quad ; \quad \frac{\partial}{\partial t}\rho_{g,e}(t) = \frac{i}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{g,e}(t) - k^{dec}\rho_{g,e}(t) ,$$

where we notice that these equations impose probability conservation on the TLS population, namely, $\rho_{g,g}(t) + \rho_{e,e}(t) = 1$. *We also recall the relation between absorption and emission rates,* $k^{em}_{e\to g} = k^{ab}_{g\to e} + k^{se}_{e\to g}$ *(Eqs. (19.5.16, 19.5.17)), and we obtain Eq. (19.5.24),*

$$\frac{\partial}{\partial t}\langle \sigma_z(t) \rangle = k^{ab}_{g\to e}\rho_{g,g}(t) - k^{em}_{e\to g}\rho_{e,e}(t) - k^{em}_{e\to g}\rho_{e,e}(t) + k^{ab}_{g\to e}\rho_{g,g}(t)$$
$$= 2k^{ab}_{g\to e}\rho_{g,g}(t) - 2k^{em}_{e\to g}\rho_{e,e}(t)$$
$$= (k^{ab}_{g\to e} + k^{em}_{e\to g} - k^{se}_{e\to g})\rho_{g,g}(t) - (k^{ab}_{g\to e} + k^{em}_{e\to g} + k^{se}_{e\to g})\rho_{e,e}(t)$$
$$= (k^{ab}_{g\to e} + k^{em}_{e\to g})(\rho_{g,g}(t) - \rho_{e,e}(t)) - k^{se}_{e\to g}$$
$$= -(k^{ab}_{g\to e} + k^{em}_{e\to g})\langle \sigma_z(t) \rangle - k^{se}_{e\to g}$$

$$\frac{\partial}{\partial t}\langle \sigma_x(t) \rangle = \frac{-i}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{e,g}(t) - k^{dec}\rho_{e,g}(t) + \frac{i}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{g,e}(t) - k^{dec}\rho_{g,e}(t)$$
$$= \frac{i}{\hbar}\left(2\Delta_E - \hbar\delta\right)(\rho_{g,e}(t) - \rho_{e,g}(t)) - k^{dec}(\rho_{e,g}(t) + \rho_{g,e}(t))$$
$$= -k^{dec}\langle \sigma_x(t) \rangle - \frac{1}{\hbar}\left(2\Delta_E - \hbar\delta\right)\langle \sigma_y(t) \rangle$$

$$\frac{\partial}{\partial t}\langle\sigma_y(t)\rangle = \frac{1}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{g,e}(t) + ik^{dec}\rho_{g,e}(t) + \frac{1}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{e,g}(t) - ik^{dec}\rho_{e,g}(t)$$
$$= \frac{1}{\hbar}\left(2\Delta_E - \hbar\delta\right)(\rho_{e,g}(t) + \rho_{g,e}(t)) - ik^{dec}(\rho_{e,g}(t) - \rho_{g,e}(t))$$
$$= -k^{dec}\langle\sigma_y(t)\rangle + \frac{1}{\hbar}\left(2\Delta_E - \hbar\delta\right)\langle\sigma_x(t)\rangle \ .$$

Exercise 19.5.6 *The reduced dynamics of the TLS density operator (Eqs. (19.5.13, 19.5.20)), under the system-bath coupling,* $\hat{H}_{SB} = \mu\hat{U}_B\hat{\sigma}_+ + \mu^*\hat{U}_B^\dagger\hat{\sigma}_-$, *was derived from the stationary Redfield equation (Eqs. (19.5.4, 19.5.8)), allegedly with no farther approximations. This simplicity is attributed to the fact that the excitation (*$\hat{\sigma}_+$*) and de-excitation (*$\hat{\sigma}_-$*) TLS operators are coupled independently to* $\hat{U}_B$ *and to* $\hat{U}_B^\dagger$*, respectively. In a more general case, however, both* $\hat{\sigma}_+$ *and* $\hat{\sigma}_-$ *may couple to the same system-bath operators. As shown in what follows, the time-evolution of the reduced density matrix is different in this case. Nevertheless, within the secular and rotating wave approximations, this difference is neglected and Eqs. (19.5.13, 19.5.20) are regained. Let us consider a system-bath coupling operator,* $\hat{H}_{SB} = \mu\left(\hat{\sigma}_+ + \hat{\sigma}_-\right)(\hat{U}_B + \hat{U}_B^\dagger) \equiv \hat{V}_S(\hat{U}_B + \hat{U}_B^\dagger)$, *where* $\hat{V}_S = \mu\left(\hat{\sigma}_+ + \hat{\sigma}_-\right)$ *is Hermitian and* $\hat{U}_B = \sum_{j=1}^{N_\omega}\lambda_j\hat{b}_j$.

(a) Show that in this case the Redfield dissipator (Eqs. (19.5.4, 19.5.8)) reads $\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\int_0^\infty d\tau\{c(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\}$, *where* $c(\tau) = c_e(\tau) + c_a(\tau)$.

(b) Defining, $C \equiv \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}$ *and* $\bar{C} \equiv \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}$ *, show that the corresponding time evolution of the reduced TLS density matrix is given by*

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = -\left[C + C^*\right]\rho_{g,g}(t) + \left[\bar{C} + \bar{C}^*\right]\rho_{e,e}(t)$$
$$\frac{\partial}{\partial t}\rho_{e,e}(t) = -\left[\bar{C} + \bar{C}^*\right]\rho_{e,e}(t) + \left[C + C^*\right]\rho_{g,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{g,e}(t) = \frac{i}{\hbar}2\Delta_E\rho_{g,e}(t) - \left[C + \bar{C}^*\right]\rho_{g,e}(t) + \left[C^* + \bar{C}\right]\rho_{e,g}(t)$$
$$\frac{\partial}{\partial t}\rho_{e,g}(t) = \frac{-i}{\hbar}2\Delta_E\rho_{e,g}(t) - \left[C^* + \bar{C}\right]\rho_{e,g}(t) + \left[C + \bar{C}^*\right]\rho_{g,e}(t) \ .$$

(c) Recalling the explicit form of the bosonic bath correlation functions (Eq. (19.5.6)), we obtain

$$C = \frac{|\mu|^2}{\hbar^2}\sum_{j=1}^{N_\omega}|\lambda_j|^2\int_0^\infty d\tau\left[e^{i\tau\omega_j}e^{\frac{-i\tau}{\hbar}2\Delta_E}n(\omega_j)+e^{-i\tau\omega_j}e^{\frac{-i\tau}{\hbar}2\Delta_E}[1+n(\omega_j)]\right]$$

$$\bar{C} = \frac{|\mu|^2}{\hbar^2}\sum_{j=1}^{N_\omega}|\lambda_j|^2\int_0^\infty d\tau\left[e^{i\tau\omega_j}e^{\frac{i\tau}{\hbar}2\Delta_E}n(\omega_j)+e^{-i\tau\omega_j}e^{\frac{i\tau}{\hbar}2\Delta_E}[1+n(\omega_j)]\right] .$$

The rotating wave approximation implies that rapidly oscillating terms can be neglected next to slowly oscillating terms under the time-integrals. Considering that both Δ_E and the bath frequencies are positive, show that this approximation means that $C \cong \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}2\Delta_E}c_a(\tau)$ and, $\bar{C} \cong \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau e^{\frac{i\tau}{\hbar}2\Delta_E}c_e(\tau)$.

(d) Recalling the definitions of the absorption and emission rates (Eq. (19.5.14)) and of $\delta \equiv \mathrm{Im}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau[c_a(\tau)+c_e^*(\tau)]e^{\frac{-i\tau}{\hbar}2\Delta_E}$, show that $\mathrm{Re}[\bar{C}] \cong k^{em}_{e\to g}/2$, $\mathrm{Re}[C] \cong k^{ab}_{g\to e}/2$, and $\mathrm{Im}[C+\bar{C}^*] \cong \delta$, and therefore

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = -k^{ab}_{g\to e}\rho_{g,g}(t)+k^{em}_{e\to g}\rho_{e,e}(t)$$
$$\frac{\partial}{\partial t}\rho_{e,e}(t) = -k^{em}_{e\to g}\rho_{e,e}(t)+k^{ab}_{g\to e}\rho_{g,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{g,e}(t) = \frac{i}{\hbar}2\Delta_E\rho_{g,e}(t)-\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}+i\delta\right]\rho_{g,e}(t)+\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}-i\delta\right]\rho_{e,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{e,g}(t) = \frac{-i}{\hbar}2\Delta_E\rho_{e,g}(t)-\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}-i\delta\right]\rho_{e,g}(t)+\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}+i\delta\right]\rho_{g,e}(t) .$$

(e) Transforming to the interaction picture representation, $\rho^I_{g,e}(t) = e^{-i2\Delta_E t/\hbar}\rho_{g,e}(t)$, $\rho^I_{e,g}(t) = e^{i2\Delta_E t/\hbar}\rho_{e,g}(t)$, the equations for the coherences obtain the form,

$$\frac{\partial}{\partial t}\rho^{I}_{g,e}(t) = -\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}+i\delta\right]\rho^{I}_{g,e}(t)+\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}-i\delta\right]e^{-i4\Delta_E t/\hbar}\rho^{I}_{e,g}(t)$$

$$\frac{\partial}{\partial t}\rho^{I}_{e,g}(t) = -\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}-i\delta\right]\rho^{I}_{e,g}(t)+\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2}+i\delta\right]e^{i4\Delta_E t/\hbar}\rho^{I}_{g,e}(t)$$

The secular approximation (see Eqs. (19.4.8, 19.4.9)) implies that the rapidly coefficients are negligible with respect to the stationary coefficients. Invoke this approximation and transform back the equations to the Schrodinger picture to regain the equations of motion for $\hat{H}_{SB}=\mu\hat{U}_B\hat{\sigma}_+ + \mu^*\hat{U}_B^\dagger\hat{\sigma}_-$ *(Eqs. (19.5.13, 19.5.20)).*

Solution 19.5.6

(a)

For a TLS coupled to a harmonic bath by the operator, $\hat{H}_{SB}=\hat{V}_S\hat{U}_B+\hat{V}_S^\dagger\hat{U}_B^\dagger$*, with* $\hat{U}_B=\sum_{j=1}^{N_\omega}\lambda_j\hat{b}_j$ *(Eq. (19.5.1)), the Redfield equation (Eqs. (19.5.4, 19.5.8)) reads*

$$\frac{\partial}{\partial t}\hat{\rho}_S(t)\cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)]$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+h.c.\} ,$$

where (Eq. (19.5.6)),

$$c_a(\tau)=tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}=\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{i\tau\omega_j}n(\omega_j)$$

$$c_e(\tau)=tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}=\sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{-i\tau\omega_j}[1+n(\omega_j)].$$

When the TLS coupling to the bath is different, namely $\hat{H}_{SB}=\hat{V}_S\hat{U}_B+\hat{V}_S\hat{U}_B^\dagger$ *where* $\hat{V}_S=\mu(\hat{\sigma}_+ + \hat{\sigma}_-)$ *is Hermitian, the expression for the dissipator simplifies. Setting* $\hat{V}_S=\hat{V}_S^\dagger$*, we readily obtain*

$$\frac{\partial}{\partial t}\hat{\rho}_S(t)\cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)]-\frac{1}{\hbar^2}\int_0^\infty d\tau\{[c_e(\tau)+c_a(\tau)][\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+h.c.\}$$

$$=-\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)]-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+h.c.\} .$$

(b)

Introducing the complete orthonormal set of TLS Hamiltonian eigenstates, $\hat{H}_S \left|\varphi_g\right\rangle = E_g \left|\varphi_g\right\rangle$, *and* $\hat{H}_S \left|\varphi_e\right\rangle = E_e \left|\varphi_e\right\rangle$, *using,* $\left\langle\varphi_g\right|\hat{V}_S\left|\varphi_g\right\rangle = \left\langle\varphi_e\right|\hat{V}_S\left|\varphi_e\right\rangle = 0$, $\left\langle\varphi_g\right|\hat{V}_S\left|\varphi_e\right\rangle = \left\langle\varphi_e\right|\hat{V}_S\left|\varphi_g\right\rangle = \mu$, *and defining* $\left\langle\varphi_{g/e}\right|\hat{\rho}_S(t)\left|\varphi_{g/e}\right\rangle \equiv \rho_{g/e,g/e}(t)$, *and* $2\Delta_E \equiv E_e - E_g$, *we obtain after some algebra,*

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = -\frac{i}{\hbar}\left\langle\varphi_g\left|[\hat{H}_S,\hat{\rho}_S(t)]\right|\varphi_g\right\rangle - \frac{1}{\hbar^2}\int_0^\infty d\tau\{c(\tau)\left\langle\varphi_g\left|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right|\varphi_g\right\rangle + c.c.\}$$
$$= -\frac{|\mu|^2}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau c(\tau)[e^{\frac{-i\tau}{\hbar}2\Delta_E}\rho_{g,g}(t) - e^{\frac{i\tau}{\hbar}2\Delta_E}\rho_{e,e}(t)]$$
$$= -\left(\frac{|\mu|^2}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau c(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}\right)\rho_{g,g}(t) + \left(\frac{|\mu|^2}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau c(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}\right)\rho_{e,e}(t)$$

$$\frac{\partial}{\partial t}\rho_{e,e}(t) = -\frac{i}{\hbar}\left\langle\varphi_e\left|[\hat{H}_S,\hat{\rho}_S(t)]\right|\varphi_e\right\rangle - \frac{1}{\hbar^2}\int_0^\infty d\tau\{c(\tau)\left\langle\varphi_e\left|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right|\varphi_e\right\rangle + c.c.\}$$
$$= -\frac{|\mu|^2}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau c(\tau)[e^{\frac{i\tau}{\hbar}2\Delta_E}\rho_{e,e}(t) - e^{\frac{-i\tau}{\hbar}2\Delta_E}\rho_{g,g}(t)]$$
$$= -\left(\frac{|\mu|^2}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau c(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}\right)\rho_{e,e}(t) + \left(\frac{|\mu|^2}{\hbar^2}2\,\mathrm{Re}\int_0^\infty d\tau c(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}\right)\rho_{g,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{g,e}(t) = -\frac{i}{\hbar}\left\langle\varphi_g\left|[\hat{H}_S,\hat{\rho}_S(t)]\right|\varphi_e\right\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c(\tau)\left\langle\varphi_g\left|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right|\varphi_e\right\rangle + c^*(\tau)\left\langle\varphi_e\left|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right|\varphi_g\right\rangle^*\}$$
$$= \frac{i}{\hbar}2\Delta_E\rho_{g,e}(t) - \left(\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau(c(\tau)+c^*(\tau))e^{\frac{-i\tau}{\hbar}2\Delta_E}\right)\rho_{g,e}(t) + \left(\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau(c(\tau)+c^*(\tau))e^{\frac{i\tau}{\hbar}2\Delta_E}\right)\rho_{e,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{e,g}(t) = -\frac{i}{\hbar}\left\langle\varphi_e\left|[\hat{H}_S,\hat{\rho}_S(t)]\right|\varphi_g\right\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c(\tau)\left\langle\varphi_e\left|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right|\varphi_g\right\rangle + c^*(\tau)\left\langle\varphi_g\left|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]\right|\varphi_e\right\rangle^*\}$$
$$= \frac{-i}{\hbar}2\Delta_E\rho_{e,g}(t) - \left(\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau(c(\tau)+c^*(\tau))e^{\frac{i\tau}{\hbar}2\Delta_E}\right)\rho_{e,g}(t) + \left(\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau(c(\tau)+c^*(\tau))e^{\frac{-i\tau}{\hbar}2\Delta_E}\right)\rho_{g,e}(t).$$

Defining, $C \equiv \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}$ *and* $\bar{C} \equiv \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau c(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}$, *these four equations read*

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = -\left[C + C^*\right]\rho_{g,g}(t) + \left[\bar{C} + \bar{C}^*\right]\rho_{e,e}(t)$$

$$\frac{\partial}{\partial t}\rho_{e,e}(t) = -\left[\bar{C} + \bar{C}^*\right]\rho_{e,e}(t) + \left[C + C^*\right]\rho_{g,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{g,e}(t) = \frac{i}{\hbar}2\Delta_E\rho_{g,e}(t) - \left[C + \bar{C}^*\right]\rho_{g,e}(t) + \left[C^* + \bar{C}\right]\rho_{e,g}(t)$$

$$\frac{\partial}{\partial t}\rho_{e,g}(t) = \frac{-i}{\hbar}2\Delta_E\rho_{e,g}(t) - \left[C^* + \bar{C}\right]\rho_{e,g}(t) + \left[C + \bar{C}^*\right]\rho_{g,e}(t) \ .$$

(c)

Recalling that $c(\tau) = c_e(\tau) + c_a(\tau)$*, and using the the explicit form of the bosonic bath correlation functions,* $c_e(\tau) = \sum_{j=1}^{N_\omega} |\lambda_j|^2 e^{-i\tau\omega_j}[1 + n(\omega_j)]$ *and* $c_a(\tau) = \sum_{j=1}^{N_\omega} |\lambda_j|^2 e^{i\tau\omega_j} n(\omega_j)$ *(Eq. (19.5.6)), we obtain*

$$C = \frac{|\mu|^2}{\hbar^2}\sum_{j=1}^{N_\omega}|\lambda_j|^2\int_0^\infty d\tau\left[e^{i\tau\omega_j}e^{\frac{-i\tau}{\hbar}2\Delta_E}n(\omega_j) + e^{-i\tau\omega_j}e^{\frac{-i\tau}{\hbar}2\Delta_E}[1 + n(\omega_j)]\right],$$

$$\bar{C} = \frac{|\mu|^2}{\hbar^2}\sum_{j=1}^{N_\omega}|\lambda_j|^2\int_0^\infty d\tau\left[e^{i\tau\omega_j}e^{\frac{i\tau}{\hbar}2\Delta_E}n(\omega_j) + e^{-i\tau\omega_j}e^{\frac{i\tau}{\hbar}2\Delta_E}[1 + n(\omega_j)]\right].$$

Noticing that the important contributions to the time integrals come from the slower oscillating terms, we can invoke the rotating wave approximation and neglect the terms associated with the higher frequencies ($\omega_j + 2\Delta_E/\hbar$*) next to terms associated with lower frequencies (*$|\omega_j - 2\Delta_E/\hbar|$*), namely,*

$$C \cong \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}2\Delta_E}c_a(\tau) \quad ; \quad \bar{C} \cong \frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau e^{\frac{i\tau}{\hbar}2\Delta_E}c_e(\tau).$$

(d)

Recalling the definitions of the absorption and emission rates (Eq. (19.5.14)), $k_{e\to g}^{em} = 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}2\Delta_E}$ *and* $k_{g\to e}^{ab} = 2|\mu|^2 \operatorname{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}2\Delta_E}$*, and using the result of (c), we obtain* $\operatorname{Re}[\bar{C}] \cong k_{e\to g}^{em}/2$*, and* $\operatorname{Re}[C] \cong k_{g\to e}^{ab}/2$*. Recalling the definition* $\delta \equiv \operatorname{Im}\frac{|\mu|^2}{\hbar^2}\int_0^\infty d\tau[c_a(\tau) + c_e^*(\tau)]e^{\frac{-i\tau}{\hbar}2\Delta_E}$ *(Eq. (19.5.21)), we obtain* $\operatorname{Im}[C + \bar{C}^*] \cong \delta$*. Using these relations in the equations derived in (b), we readily obtain*

$$\frac{\partial}{\partial t}\rho_{g,g}(t) \cong -k^{ab}_{g\to e}\rho_{g,g}(t) + k^{em}_{e\to g}\rho_{e,e}(t)$$
$$\frac{\partial}{\partial t}\rho_{e,e}(t) \cong -k^{em}_{e\to g}\rho_{e,e}(t) + k^{ab}_{g\to e}\rho_{g,g}(t)$$
$$\frac{\partial}{\partial t}\rho_{g,e}(t) = \frac{i}{\hbar}2\Delta_E\rho_{g,e}(t) - \left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} + i\delta\right]\rho_{g,e}(t) + \left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} - i\delta\right]\rho_{e,g}(t)$$
$$\frac{\partial}{\partial t}\rho_{e,g}(t) = \frac{-i}{\hbar}2\Delta_E\rho_{e,g}(t) - \left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} - i\delta\right]\rho_{e,g}(t) + \left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} + i\delta\right]\rho_{g,e}(t) \ .$$

(e)

Transforming to the interaction picture representation, $\rho^I_{g,e}(t) = e^{-i2\Delta_E t/\hbar}\rho_{g,e}(t)$, $\rho^I_{e,g}(t) = e^{i2\Delta_E t/\hbar}\rho_{e,g}(t)$, *the equations for the coherences obtain the form,*

$$\frac{\partial}{\partial t}\rho^I_{g,e}(t) = -\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} + i\delta\right]\rho^I_{g,e}(t) + \left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} - i\delta\right]e^{-i4\Delta_E t/\hbar}\rho^I_{e,g}(t)$$
$$\frac{\partial}{\partial t}\rho^I_{e,g}(t) = -\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} - i\delta\right]\rho^I_{e,g}(t) + \left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} + i\delta\right]e^{i4\Delta_E t/\hbar}\rho^I_{g,e}(t) \ .$$

Neglecting the rapidly oscillating coefficients in this representation (in consistency with the rotating wave approximation), transforming back from the interaction picture representation, and recalling the definition of the decoherence rate (Eq. (19.5.22)), we reproduce Eq. (19.5.20),

$$\frac{\partial}{\partial t}\rho^I_{g,e}(t) \cong -\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} + i\delta\right]\rho^I_{g,e}(t) \Rightarrow \frac{\partial}{\partial t}\rho_{g,e}(t) = \frac{i}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{g,e}(t) - k^{dec}\rho_{g,e}(t)$$
$$\frac{\partial}{\partial t}\rho^I_{e,g}(t) \cong -\left[\frac{k^{ab}_{g\to e}+k^{em}_{e\to g}}{2} - i\delta\right]\rho^I_{e,g}(t) \Rightarrow \frac{\partial}{\partial t}\rho_{e,g}(t) = \frac{-i}{\hbar}\left(2\Delta_E - \hbar\delta\right)\rho_{e,g}(t) - k^{dec}\rho_{e,g}(t) \ .$$

Together with the equations for the populations, derived in (d), we showed that the set of four equation derived within the rotating wave approximation for the coupling model $\hat{H}_{SB} = \mu(\hat{\sigma}_+ + \hat{\sigma}_-)\left(\hat{U}_B + \hat{U}^\dagger_B\right)$ *, reproduce the result obtained directly for the coupling model,* $\hat{H}_{SB} = \mu\hat{U}_B\hat{\sigma}_+ + \mu^*\hat{U}^\dagger_B\hat{\sigma}_-$ *(Eqs. (19.5.13, 19.5.20)).*

Exercise 19.5.7 *Use Eqs. (19.5.26-19.5.28) and the definition,* $k = \frac{\eta^2}{\hbar^2}\int_0^\infty d\tau[c_e(\tau)+c_a(\tau)]$, *to derive Eq. (19.5.29) for the reduced density matrix elements.*

Solution 19.5.7

For a TLS coupled to a harmonic bath by an operator, $\hat{H}_{SB} = \hat{V}_S(\hat{U}_B + \hat{U}_B^\dagger)$, *with* $\hat{V}_S \equiv \eta|\varphi_e\rangle\langle\varphi_e| = \eta\hat{\sigma}_+\hat{\sigma}_-$ *and* $\hat{U}_B = \sum_{j=1}^{N_\omega}\lambda_j\hat{b}_j$ *, the Redfield dissipator is given by Eq. (19.5.28), with (see Ex. 19.5.6 (a))* $c_a(\tau) = \sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{i\tau\omega_j}n(\omega_j)$ *and* $c_e(\tau) = \sum_{j=1}^{N_\omega}|\lambda_j|^2 e^{-i\tau\omega_j}[1+n(\omega_j)]$. *Consequently, the stationary Redfield equation for the TLS (Eq. (19.5.4)) reads in this case*

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)] - \frac{1}{\hbar^2}\int_0^\infty d\tau\{[c_e(\tau)+c_a(\tau)][\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\}.$$

Introducing the complete orthonormal set of the TLS Hamiltonian eigenstates, $\hat{H}_S|\varphi_g\rangle = E_g|\varphi_g\rangle$ *and* $\hat{H}_S|\varphi_e\rangle = E_e|\varphi_e\rangle$, *using,* $\langle\varphi_g|\hat{V}_S|\varphi_g\rangle = \langle\varphi_e|\hat{V}_S|\varphi_g\rangle = \langle\varphi_g|\hat{V}_S|\varphi_e\rangle = 0$ *and* $\langle\varphi_e|\hat{V}_S|\varphi_e\rangle = \eta$, *and defining* $\langle\varphi_{g/e}|\hat{\rho}_S(t)|\varphi_{g/e}\rangle \equiv \rho_{g/e,g/e}(t)$ *and* $2\Delta_E = E_e - E_g$, *we obtain after some algebra,*

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = -\frac{i}{\hbar}\langle\varphi_g|[\hat{H}_S,\hat{\rho}_S(t)]|\varphi_g\rangle$$
$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau[c_e(\tau)+c_a(\tau)]\langle\varphi_g|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|\varphi_g\rangle = 0$$

$$\frac{\partial}{\partial t}\rho_{e,e}(t) = -\frac{i}{\hbar}\langle\varphi_e|[\hat{H}_S,\hat{\rho}_S(t)]|\varphi_e\rangle$$
$$-2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau[c_e(\tau)+c_a(\tau)]\langle\varphi_e|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|\varphi_e\rangle = 0$$

$$\frac{\partial}{\partial t}\rho_{g,e}(t) = -\frac{i}{\hbar}\left\langle \varphi_g \left| [\hat{H}_S, \hat{\rho}_S(t)] \right| \varphi_e \right\rangle - \frac{1}{\hbar^2}\int_0^\infty d\tau [c_e(\tau)+c_a(\tau)] \left\langle \varphi_g \left| [\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] \right| \varphi_e \right\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau [c_e^*(\tau)+c_a^*(\tau)] \left[\left\langle \varphi_e \left| [\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] \right| \varphi_g \right\rangle \right]^*$$
$$= \frac{i}{\hbar} 2\Delta_E \rho_{g,e}(t) - \frac{|\eta|^2}{\hbar^2}\int_0^\infty d\tau [c_e^*(\tau)+c_a^*(\tau)] \left[\rho_{e,g}(t) \right]^*$$
$$= \left(\frac{i}{\hbar} 2\Delta_E - \frac{|\eta|^2}{\hbar^2}\int_0^\infty d\tau [c_e^*(\tau)+c_a^*(\tau) \right) \rho_{g,e}(t)$$

$$\frac{\partial}{\partial t}\rho_{e,g}(t) = -\frac{i}{\hbar}\left\langle \varphi_e \left| [\hat{H}_S, \hat{\rho}_S(t)] \right| \varphi_g \right\rangle - \frac{1}{\hbar^2}\int_0^\infty d\tau [c_e(\tau)+c_a(\tau)] \left\langle \varphi_e \left| [\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] \right| \varphi_g \right\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau [c_e^*(\tau)+c_a^*(\tau)] \left[\left\langle \varphi_g \left| [\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] \right| \varphi_e \right\rangle \right]^*$$
$$= \frac{-i}{\hbar} 2\Delta_E \rho_{e,g}(t) - \frac{|\eta|^2}{\hbar^2}\int_0^\infty d\tau [c_e(\tau)+c_a(\tau)] \rho_{e,g}(t)$$
$$= \left(\frac{-i}{\hbar} 2\Delta_E - \frac{|\eta|^2}{\hbar^2}\int_0^\infty d\tau [c_e(\tau)+c_a(\tau) \right) \rho_{e,g}(t) \ .$$

Introducing, $k \equiv \frac{\eta^2}{\hbar^2}\int_0^\infty d\tau [c_e(\tau)+c_a(\tau)]$, *we obtain Eq.(19.5.29),*

$$\frac{\partial}{\partial t}\rho_{g,g}(t) = 0$$
$$\frac{\partial}{\partial t}\rho_{e,e}(t) = 0$$
$$\frac{\partial}{\partial t}\rho_{e,g}(t) = -[\mathrm{Re}\{k\} + \frac{i}{\hbar}(2\Delta_E + \hbar\,\mathrm{Im}\{k\})]\rho_{e,g}(t)$$
$$\frac{\partial}{\partial t}\rho_{g,e}(t) = -[\mathrm{Re}\{k\} - \frac{i}{\hbar}(2\Delta_E + \hbar\,\mathrm{Im}\{k\})]\rho_{g,e}(t) \ .$$

Exercise 19.5.8 *(a) Use the explicit expressions for the correlation functions in the case of a continuous boson bath (Eq. (19.5.7)) to show that* $k = \frac{\eta^2}{\hbar^2}\int_0^\infty d\tau [c_e(\tau)+c_a(\tau)]$ $= \frac{\eta^2}{2\pi\hbar}\int_0^\infty d\tau \int_0^\infty d\omega J(\hbar\omega)[\cos(\tau\omega) 2n(\omega) + e^{-i\tau\omega}]$. *(b) The bath-induced decay of the coherences is* *associated with the rate,* $k^{pd} = \mathrm{Re}\{k\} \geq 0$ *(Eq. (19.5.31)). Show that* $k^{pd} = \lim_{\omega\to 0} \frac{\eta^2}{4\hbar} J(\hbar\omega)[2n(\omega)+1]$*, where for a finite temperature,* $k^{pd} \approx \lim_{\omega\to 0} \frac{k_B T\eta^2}{2\hbar} \frac{J(\hbar\omega)}{\hbar\omega}$.

Solution 19.5.8

(a)

For $k \equiv \frac{\eta^2}{\hbar^2}\int_0^\infty d\tau[c_e(\tau)+c_a(\tau)]$*, with* $c_a(\tau) = \frac{\hbar}{2\pi}\int_0^\infty d\omega e^{i\tau\omega} J(\hbar\omega)n(\omega)$ *and*

$c_e(\tau) = \frac{\hbar}{2\pi}\int_0^\infty d\omega e^{-i\tau\omega} J(\hbar\omega)(n(\omega)+1)$ *(Eq. (19.5.7)), we readily obtain*

$$k = \frac{\eta^2}{\hbar^2}\int_0^\infty d\tau[c_e(\tau)+c_a(\tau)] = \frac{\eta^2}{\pi\hbar}\int_0^\infty d\tau\int_0^\infty d\omega \cos(\tau\omega) J(\hbar\omega)n(\omega) + \frac{\eta^2}{2\pi\hbar}\int_0^\infty d\tau\int_0^\infty d\omega e^{-i\tau\omega} J(\hbar\omega)$$

$$= \frac{\eta^2}{2\pi\hbar}\int_0^\infty d\tau\int_0^\infty d\omega J(\hbar\omega)[\cos(\tau\omega) 2n(\omega) + e^{-i\tau\omega}] \ .$$

(b)

Using the result in (a), the real part of k *reads*

$$k^{pd} = \mathrm{Re}(k) = \mathrm{Re}\frac{\eta^2}{2\pi\hbar}\int_0^\infty d\tau\int_0^\infty d\omega e^{-i\tau\omega} J(\hbar\omega)[2n(\omega)+1].$$

Consequently, and using the fact that the time-integrand is an even function of time,

$$k^{pd} = \frac{\eta^2}{2\pi\hbar}\int_0^\infty d\tau\int_0^\infty d\omega J(\hbar\omega)\cos(\tau\omega)[2n(\omega)+1] = \mathrm{Re}\frac{\eta^2}{4\pi\hbar}\int_{-\infty}^\infty d\tau\int_0^\infty d\omega e^{-i\tau\omega} J(\hbar\omega)[2n(\omega)+1]$$

$$= \frac{\eta^2}{2\hbar}\int_0^\infty d(\hbar\omega) J(\hbar\omega)[2n(\omega)+1]\delta(\hbar\omega) \ .$$

Notice that $\delta(\hbar\omega)$ *restricts the important contributions to the integral to the low frequency regime. The slowly varying part of the integrand can hence be replaced by its* $\omega \to 0$ *limit, namely*

$$k^{pd} \approx \frac{\eta^2}{2\hbar} J(0)[2n(0)+1]\int_0^\infty d(\hbar\omega)\delta(\hbar\omega) = \frac{\eta^2}{4\hbar} J(0)[2n(0)+1]\int_{-\infty}^\infty d(\hbar\omega)\delta(\hbar\omega) ,$$

where in the last step we associated Dirac's delta with an (infinitely narrow) even function of $\hbar\omega$.

Consequently, we obtain $k^{pd} = \lim_{\omega\to 0} \frac{\eta^2}{4\hbar} J(\hbar\omega)[2n(\omega)+1]$, *where for any finite temperature,*

$\lim_{\omega\to 0} n(\omega) = \lim_{\omega\to 0} \frac{k_B T}{\hbar\omega}$, *and therefore,* $k^{pd} = \lim_{\omega\to 0} \frac{\eta^2 k_B T}{2\hbar^2\omega} J(\hbar\omega)$.

20 Open Many-Fermion Systems

Exercise 20.1.1 *Write the binary strings for the 16 basis vectors defined by four single particle states,* $\{|\Phi_1\rangle, |\Phi_2\rangle, |\Phi_3\rangle, |\Phi_4\rangle\}$.

Solution 20.1.1

Using the notation of Eq. (20.1.7), the set of different binary strings representing the 16 basis vectors corresponding to $M = 4$ reads

$$|\Psi^{(0)}\rangle = |0,0,0,0\rangle$$

$$\{|\Psi^{(1)}\rangle\} = \begin{Bmatrix} |\Psi^{(1)}_{\{1\}}\rangle = |1,0,0,0\rangle \\ |\Psi^{(1)}_{\{2\}}\rangle = |0,1,0,0\rangle \\ |\Psi^{(1)}_{\{3\}}\rangle = |0,0,1,0\rangle \\ |\Psi^{(1)}_{\{4\}}\rangle = |0,0,0,1\rangle \end{Bmatrix}$$

$$\{|\Psi^{(2)}\rangle\} = \begin{Bmatrix} |\Psi^{(2)}_{\{1,2\}}\rangle = |1,1,0,0\rangle \\ |\Psi^{(2)}_{\{1,3\}}\rangle = |1,0,1,0\rangle \\ |\Psi^{(2)}_{\{1,4\}}\rangle = |1,0,0,1\rangle \\ |\Psi^{(2)}_{\{2,3\}}\rangle = |0,1,1,0\rangle \\ |\Psi^{(2)}_{\{2,4\}}\rangle = |0,1,0,1\rangle \\ |\Psi^{(2)}_{\{3,4\}}\rangle = |0,0,1,1\rangle \end{Bmatrix}$$

$$\{|\Psi^{(3)}\rangle\} = \begin{Bmatrix} |\Psi^{(3)}_{\{1,2,3\}}\rangle = |1,1,1,0\rangle \\ |\Psi^{(3)}_{\{1,2,4\}}\rangle = |1,1,0,1\rangle \\ |\Psi^{(3)}_{\{1,3,4\}}\rangle = |1,0,1,1\rangle \\ |\Psi^{(3)}_{\{2,3,4\}}\rangle = |0,1,1,1\rangle \end{Bmatrix}$$

$$|\Psi^{(4)}_{1,2,3,4}\rangle = |1,1,1,1\rangle \ .$$

Exercise 20.1.2 *Use the normalization conditions (Eq. (20.1.6)),* $\langle\Psi^{(1)}_{\{l\}}|\Psi^{(1)}_{\{l\}}\rangle = 1$, *and* $\langle\Psi^{(0)}|\Psi^{(0)}\rangle = 1$, *and the definition of the creation operator (Eq. (20.1.8)) to derive Eq. (20.1.9).*

Solution 20.1.2

Using the definition of the creation operator, Eq. (20.1.8), and taking the Hermitian conjugate we obtain $\hat{a}_l^\dagger \left|\Psi^{(0)}\right\rangle \equiv \left|\Psi_{\{l\}}^{(1)}\right\rangle \Rightarrow \left\langle\Psi^{(0)}\right|\hat{a}_l = \left\langle\Psi_{\{l\}}^{(1)}\right|$. *Using this result in the normalization condition for* $\left|\Psi_{\{l\}}^{(1)}\right\rangle$, *we obtain* $1 = \left\langle\Psi_{\{l\}}^{(1)}\middle|\Psi_{\{l\}}^{(1)}\right\rangle = \left\langle\Psi^{(0)}\right|\hat{a}_l\left|\Psi_{\{l\}}^{(1)}\right\rangle$, *and using the normalization condition* $\left\langle\Psi^{(0)}\middle|\Psi^{(0)}\right\rangle = 1$, *we identify Eq. (20.1.9),* $\hat{a}_l\left|\Psi_{\{l\}}^{(1)}\right\rangle = \left|\Psi^{(0)}\right\rangle$.

Exercise 20.1.3 *Recalling the definition of a Hermitian operator (Eq. (11.2.20)), use the matrix elements of the operators,* $\hat{a}_l^\dagger$ *and* $\hat{a}_l$, *between the states,* $\left|\Psi^{(0)}\right\rangle$ *and* $\left|\Psi_{\{l\}}^{(1)}\right\rangle$, *to show that these operators are non-Hermitian.*

Solution 20.1.3

Using Eqs. (20.1.8, 20.1.9, 20.1.10), we obtain

$$\left\langle\Psi^{(0)}\right|\hat{a}_l^\dagger\left|\Psi_{\{l\}}^{(1)}\right\rangle = \left\langle\Psi^{(0)}\right|\left(\hat{a}_l^\dagger\right)^2\left|\Psi^{(0)}\right\rangle = 0 \quad ; \quad \left\langle\Psi_{\{l\}}^{(1)}\right|\hat{a}_l^\dagger\left|\Psi^{(0)}\right\rangle = 1$$

$$\left\langle\Psi^{(0)}\right|\hat{a}_l\left|\Psi_{\{l\}}^{(1)}\right\rangle = 1 \quad ; \quad \left\langle\Psi_{\{l\}}^{(1)}\right|\hat{a}_l\left|\Psi^{(0)}\right\rangle = \left\langle\Psi_{\{l\}}^{(1)}\right|\left(\hat{a}_l\right)^2\left|\Psi_{\{l\}}^{(1)}\right\rangle = 0 \ .$$

Since $\left\langle\Psi^{(0)}\right|\hat{a}_l^\dagger\left|\Psi_{\{l\}}^{(1)}\right\rangle \neq \left\langle\Psi_{\{l\}}^{(1)}\right|\hat{a}_l^\dagger\left|\Psi^{(0)}\right\rangle^*$ *and* $\left\langle\Psi^{(0)}\right|\hat{a}_l\left|\Psi_{\{l\}}^{(1)}\right\rangle \neq \left\langle\Psi_{\{l\}}^{(1)}\right|\hat{a}_l\left|\Psi^{(0)}\right\rangle^*$, *the operators* $\hat{a}_l^\dagger$ *and* $\hat{a}_l$ *are non-Hermitian.*

Exercise 20.1.4 *Use the normalization conditions (Eq. (20.1.6)),* $\left\langle\Psi^{(0)}\middle|\Psi^{(0)}\right\rangle = 1$, $\left\langle\Psi_{\{l\}}^{(1)}\middle|\Psi_{\{l\}}^{(1)}\right\rangle = 1$, $\left\langle\Psi_{\{l,l'\}}^{(2)}\middle|\Psi_{\{l,l'\}}^{(2)}\right\rangle = 1$, *and Eq. (20.1.16), to derive Eq. (20.1.17).*

Solution 20.1.4

Given the definition, $\left|\Psi_{\{l,l'\}}^{(2)}\right\rangle \equiv \hat{a}_l^\dagger\left|\Psi_{\{l'\}}^{(1)}\right\rangle = \hat{a}_l^\dagger\hat{a}_{l'}^\dagger\left|\Psi^{(0)}\right\rangle$, *and taking the Hermitian conjugate, we obtain* $\left\langle\Psi_{\{l,l'\}}^{(2)}\right| = \left\langle\Psi_{\{l'\}}^{(1)}\right|\hat{a}_l = \left\langle\Psi^{(0)}\right|\hat{a}_{l'}\hat{a}_l$.

Using the normalization of $\left|\Psi_{\{l,l'\}}^{(2)}\right\rangle$ *and* $\left|\Psi_{\{l'\}}^{(1)}\right\rangle$, *we obtain*

$$\left\langle\Psi_{\{l,l'\}}^{(2)}\middle|\Psi_{\{l,l'\}}^{(2)}\right\rangle = 1 \Rightarrow \left\langle\Psi_{\{l'\}}^{(1)}\right|\hat{a}_l\left|\Psi_{\{l,l'\}}^{(2)}\right\rangle = 1 \Rightarrow \hat{a}_l\left|\Psi_{\{l,l'\}}^{(2)}\right\rangle = \left|\Psi_{\{l'\}}^{(1)}\right\rangle.$$

Using the normalization of $\left|\Psi^{(2)}_{\{l,l'\}}\right\rangle$ *and* $\left|\Psi^{(0)}\right\rangle$ *, we obtain*

$\left\langle\Psi^{(2)}_{\{l,l'\}}\middle|\Psi^{(2)}_{\{l,l'\}}\right\rangle = 1 \Rightarrow \left\langle\Psi^{(0)}\middle|\hat{a}_{l'}\hat{a}_{l}\middle|\Psi^{(2)}_{\{l,l'\}}\right\rangle = 1 \Rightarrow \hat{a}_{l'}\hat{a}_{l}\left|\Psi^{(2)}_{\{l,l'\}}\right\rangle = \left|\Psi^{(0)}\right\rangle$.

In summary, we obtained Eq. (20.1.17), $\left|\Psi^{(0)}\right\rangle = \hat{a}_{l'}\hat{a}_{l}\left|\Psi^{(2)}_{\{l,l'\}}\right\rangle = \hat{a}_{l'}\left|\Psi^{(1)}_{\{l'\}}\right\rangle$.

Exercise 20.1.5 *Use Eqs. (20.1.16, 20.1.18) to derive Eq. (20.1.19).*

Solution 20.1.5

Using Eq. (20.1.16), $\left|\Psi^{(2)}_{\{l,l'\}}\right\rangle = \hat{a}^{\dagger}_{l}\hat{a}^{\dagger}_{l'}\left|\Psi^{(0)}\right\rangle$*, we obtain* $\left|\Psi^{(2)}_{\{l',l\}}\right\rangle = \hat{a}^{\dagger}_{l'}\hat{a}^{\dagger}_{l}\left|\Psi^{(0)}\right\rangle$*. Using Eq. (20.1.18), we obtain* $\left|\Psi^{(2)}_{\{l',l\}}\right\rangle = -\left|\Psi^{(2)}_{\{l,l'\}}\right\rangle = -\hat{a}^{\dagger}_{l}\hat{a}^{\dagger}_{l'}\left|\Psi^{(0)}\right\rangle$*. Comparing the two results we conclude that* $-\hat{a}^{\dagger}_{l}\hat{a}^{\dagger}_{l'} = \hat{a}^{\dagger}_{l'}\hat{a}^{\dagger}_{l}$ *, and taking the Hermitian conjugate we obtain* $-\hat{a}_{l'}\hat{a}_{l} = \hat{a}_{l}\,\hat{a}_{l'}$*. Consequently, we obtain Eq. (20.1.19):* $\{\hat{a}^{\dagger}_{l},\hat{a}^{\dagger}_{l'}\} = 0$ *and* $\{\hat{a}_{l}\,,\hat{a}_{l'}\} = 0$.

Exercise 20.1.6 *Use the anticommutation relations for the fermion operators (Eqs. (20.1.19, 20.1.20)), and Eqs. (20.2.21, 20.2.22) to derive Eqs. (20.1.23, 20.1.24).*

Solution 20.1.6

Using Eqs. (20.1.21, 20.1.22) we have $\left|n_1,n_2,n_3,...,n_M\right\rangle \equiv (\hat{a}^{\dagger}_1)^{n_1}(\hat{a}^{\dagger}_2)^{n_2}\cdots(\hat{a}^{\dagger}_M)^{n_M}\left|\Psi^{(0)}\right\rangle$*, where* n_l *equals one for the occupied orbitals, and zero otherwise. To obtain the expression for* $\hat{a}^{\dagger}_k\left|n_1,n_2,n_3,...,n_M\right\rangle$*, we first let* $\hat{a}^{\dagger}_k$ *"jump over" the series of creation operators associated with* $l<k$ *.* $\hat{a}^{\dagger}_k$ *trivially commutes with any* $(\hat{a}^{\dagger}_l)^0$ *(unity), whereas jumping over* $(\hat{a}^{\dagger}_l)^1$ *introduces a sign flip, since* $\hat{a}^{\dagger}_k\hat{a}^{\dagger}_l = -\hat{a}^{\dagger}_l\hat{a}^{\dagger}_k$ *(Eq. (20.1.19)). The total number of sign flips is therefore equal to the sum over the occupation numbers (zero or one) of the orbitals associated with* $l<k$ *, namely*

$$\begin{aligned}
&\hat{a}^{\dagger}_k\left|n_1,n_2,n_3,...,n_M\right\rangle = \hat{a}^{\dagger}_k(\hat{a}^{\dagger}_1)^{n_1}(\hat{a}^{\dagger}_2)^{n_2}\cdots(\hat{a}^{\dagger}_M)^{n_M}\left|\Psi^{(0)}\right\rangle\\
&=(-1)^{n_1}(\hat{a}^{\dagger}_1)^{n_1}\hat{a}^{\dagger}_k(\hat{a}^{\dagger}_2)^{n_2}\cdots(\hat{a}^{\dagger}_M)^{n_N}\left|\Psi^{(0)}\right\rangle\\
&=(-1)^{n_1}(-1)^{n_2}(\hat{a}^{\dagger}_1)^{n_1}(\hat{a}^{\dagger}_2)^{n_2}\hat{a}^{\dagger}_k\cdots(\hat{a}^{\dagger}_M)^{n_N}\left|\Psi^{(0)}\right\rangle\\
&\cdots\\
&=(-1)^{\sum_{j=1}^{k-1}n_j}(\hat{a}^{\dagger}_1)^{n_1}(\hat{a}^{\dagger}_2)^{n_2}\cdots(\hat{a}^{\dagger}_{k-1})^{n_{k-1}}\hat{a}^{\dagger}_k(\hat{a}^{\dagger}_k)^{n_k}(\hat{a}^{\dagger}_{k+1})^{n_k+1}\cdots(\hat{a}^{\dagger}_M)^{n_M}\left|\Psi^{(0)}\right\rangle \quad .
\end{aligned}$$

We now distinguish between two cases:

If $n_k = 0$, *then* $\hat{a}_k^\dagger (\hat{a}_k^\dagger)^{n_k} = \hat{a}_k^\dagger$. *Therefore,*

$$\hat{a}_k^\dagger \left| n_1, n_2, n_3, ..., n_M \right\rangle = (-1)^{\sum_{j=1}^{k-1} n_j} (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_{k-1}^\dagger)^{n_{k-1}} (\hat{a}_k^\dagger)^1 (\hat{a}_{k+1}^\dagger)^{n_k+1} \cdots (\hat{a}_M^\dagger)^{n_M} \left| \Psi^{(0)} \right\rangle$$

$$= (-1)^{\sum_{j=1}^{k-1} n_j} \left| n_1, n_2, ..., n_{k-1}, 1, n_{k+1}, ..., n_M \right\rangle .$$

If $n_k = 1$, *then* $\hat{a}_k^\dagger (\hat{a}_k^\dagger)^{n_k} = 0$ *(Eq. (20.1.20)). Therefore,* $\hat{a}_k^\dagger \left| n_1, n_2, n_3, ..., n_M \right\rangle = 0$.

Thus, we obtained Eq. (20.1.23). Eq. (20.2.24) is obtained similarly.

Exercise 20.1.7 *Use the definitions* $\hat{a}^\dagger \left|0\right\rangle = \left|1\right\rangle$, $\hat{a}^\dagger \left|1\right\rangle = 0$, $\hat{a}\left|1\right\rangle = \left|0\right\rangle$, *and* $\hat{a}^\dagger \left|1\right\rangle = 0$ *to derive the (two by two) matrix representations of the operators,* $\hat{a}^\dagger$, $\hat{a}$, $\hat{a}^\dagger \hat{a}$ *and* $\hat{a}\hat{a}^\dagger$ *in the complete orthonormal basis* $\{\left|0\right\rangle, \left|1\right\rangle\}$. *Show that these matrices satisfy the anti-commutation relation, Eq. (20.1.31).*

Solution 20.1.7

Using the definitions: $\hat{a}^\dagger \left|0\right\rangle = \left|1\right\rangle$, $\hat{a}^\dagger \left|1\right\rangle = 0$, $\hat{a}\left|1\right\rangle = \left|0\right\rangle$, $\hat{a}^\dagger \left|1\right\rangle = 0$, *and the orthonormality relations,* $\left\langle 0 | 0 \right\rangle = \left\langle 1 | 1 \right\rangle = 1$ *and* $\left\langle 0 | 1 \right\rangle = \left\langle 1 | 0 \right\rangle = 0$, *we obtain*

$$\begin{matrix} \left\langle 0 \right| \hat{a}^\dagger \left| 0 \right\rangle = 0 \\ \left\langle 1 \right| \hat{a}^\dagger \left| 0 \right\rangle = 1 \\ \left\langle 0 \right| \hat{a}^\dagger \left| 1 \right\rangle = 0 \\ \left\langle 1 \right| \hat{a}^\dagger \left| 1 \right\rangle = 0 \end{matrix} \quad \Leftrightarrow \quad \mathbf{a}^\dagger = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \quad ; \quad \begin{matrix} \left\langle 0 \right| \hat{a} \left| 0 \right\rangle = 0 \\ \left\langle 1 \right| \hat{a} \left| 0 \right\rangle = 0 \\ \left\langle 0 \right| \hat{a} \left| 1 \right\rangle = 1 \\ \left\langle 1 \right| \hat{a} \left| 1 \right\rangle = 0 \end{matrix} \quad \Leftrightarrow \quad \mathbf{a} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}.$$

$$\begin{matrix} \left\langle 0 \right| \hat{a}^\dagger \hat{a} \left| 0 \right\rangle = 0 \\ \left\langle 1 \right| \hat{a}^\dagger \hat{a} \left| 0 \right\rangle = 0 \\ \left\langle 0 \right| \hat{a}^\dagger \hat{a} \left| 1 \right\rangle = 0 \\ \left\langle 1 \right| \hat{a}^\dagger \hat{a} \left| 1 \right\rangle = 1 \end{matrix} \quad ; \quad \mathbf{a}^\dagger \mathbf{a} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \quad ; \quad \begin{matrix} \left\langle 0 \right| \hat{a} \hat{a}^\dagger \left| 0 \right\rangle = 1 \\ \left\langle 1 \right| \hat{a} \hat{a}^\dagger \left| 0 \right\rangle = 0 \\ \left\langle 0 \right| \hat{a} \hat{a}^\dagger \left| 1 \right\rangle = 0 \\ \left\langle 1 \right| \hat{a} \hat{a}^\dagger \left| 1 \right\rangle = 0 \end{matrix} \quad ; \quad \mathbf{a}\mathbf{a}^\dagger = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}.$$

These matrices are shown to satisfy the anti-commutation relations (Eq. (20.1.31)),

$$\mathbf{a}^\dagger\mathbf{a}^\dagger = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} ,$$

$$\mathbf{a}\mathbf{a} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} ,$$

$$\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

Exercise 20.1.8 *Show that the matrix representations of the creation and annihilation operators (Eqs. (20.1.36, 20.1.37)) satisfy the canonical anticommutation relations for fermions, Eqs. (20.1.19, 20.1.20). (You can use the rules of tensor products multiplication, Eq. (11.6.21).)*

Solution 20.1.8

For convenience, let us introduce the following 2 by 2 matrices,

$$\boldsymbol{\sigma}_\mathbf{I} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix},\ \boldsymbol{\sigma}_\mathbf{P} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix},\ \boldsymbol{\sigma}_- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\quad \boldsymbol{\sigma}_+ = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix},$$

where,

$$\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_\mathbf{P} = \boldsymbol{\sigma}_\mathbf{I},\ \ \boldsymbol{\sigma}_+\boldsymbol{\sigma}_- = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix},\ \boldsymbol{\sigma}_-\boldsymbol{\sigma}_+ = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix},\ \textit{and}\ \boldsymbol{\sigma}_+\boldsymbol{\sigma}_+ = \boldsymbol{\sigma}_-\boldsymbol{\sigma}_- = \mathbf{0}.$$

Using these matrices, the operators in Eq. (20.1.36, 20.1.37) are expressed as

$$\mathbf{a}_k^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{\cdots}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}\ .$$

$$\mathbf{a}_k = \overset{1}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{\cdots}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_-} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}\ .$$

Using $(\mathbf{A}\otimes\mathbf{B})\cdot(\mathbf{C}\otimes\mathbf{D}) = \mathbf{AC}\otimes\mathbf{BD}$, *we obtain*

$$\mathbf{a}_k^\dagger\mathbf{a}_k^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{k}{\boldsymbol{\sigma}_+\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} = \mathbf{0}$$

$$\mathbf{a}_k\mathbf{a}_k = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{k}{\boldsymbol{\sigma}_-\boldsymbol{\sigma}_-} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} = \mathbf{0}$$

$$\mathbf{a}_k^\dagger\mathbf{a}_k = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{k}{\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_k\mathbf{a}_k^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{k}{\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} .$$

Consequently, $\{\mathbf{a}_k^\dagger, \mathbf{a}_k^\dagger\} = \{\mathbf{a}_k, \mathbf{a}_k\} = \mathbf{0}$*, and,*

$$\{\mathbf{a}_k, \mathbf{a}_k^\dagger\} = \boldsymbol{\sigma}_\mathbf{I} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \boldsymbol{\sigma}_\mathbf{I} = \mathbf{I} .$$

Similarly, for $k' \neq k$ *(demonstrating for* $k' < k$*, without loss of generality) we have*

$$\mathbf{a}_{k'}^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{\cdots}{\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k'}{\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_{k'} = \overset{1}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{P}} \otimes \overset{\cdots}{\cdots\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k'}{\boldsymbol{\sigma}_-} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} ,$$

and therefore,

$$\mathbf{a}_k^\dagger\mathbf{a}_{k'}^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \cdots\cdots \overset{\cdots}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_{k'}^\dagger\mathbf{a}_k^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \cdots\cdots \overset{\cdots}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\boldsymbol{\sigma}_+\boldsymbol{\sigma}_\mathbf{P}} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_k^\dagger\mathbf{a}_{k'}^\dagger + \mathbf{a}_{k'}^\dagger\mathbf{a}_k^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \cdots\cdots \overset{\cdots}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\left[\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_+ + \boldsymbol{\sigma}_+\boldsymbol{\sigma}_\mathbf{P}\right]} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_+} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} .$$

Since, $\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_+ + \boldsymbol{\sigma}_+\boldsymbol{\sigma}_\mathbf{P} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} = \mathbf{0}$*, we obtain* $\{\mathbf{a}_k^\dagger, \mathbf{a}_{k'}^\dagger\} = \mathbf{0}$.

Similarly,

$$\mathbf{a}_k\mathbf{a}_{k'} = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \cdots\cdots \overset{\cdots}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_-} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_-} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_{k'}\mathbf{a}_k = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots \boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\boldsymbol{\sigma}_{-}\boldsymbol{\sigma}_\mathbf{P}} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_{-}} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_k\mathbf{a}_{k'} + \mathbf{a}_{k'}\mathbf{a}_k = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots \boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\left[\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_{-} + \boldsymbol{\sigma}_{-}\boldsymbol{\sigma}_\mathbf{P}\right]} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_{-}} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} \quad .$$

Since, $\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_{-} + \boldsymbol{\sigma}_{-}\boldsymbol{\sigma}_\mathbf{P} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} = \mathbf{0}$, *we obtain* $\{\mathbf{a}_k, \mathbf{a}_{k'}\} = \mathbf{0}$.

Finally, using,

$$\mathbf{a}_k^\dagger\mathbf{a}_{k'} = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots \boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\boldsymbol{\sigma}_\mathbf{P}\boldsymbol{\sigma}_{-}} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_{+}} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}}$$

$$\mathbf{a}_{k'}\mathbf{a}_k^\dagger = \overset{1}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{2}{\boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{\cdots}{\cdots\cdots \boldsymbol{\sigma}_\mathbf{I}} \otimes \overset{k'}{\boldsymbol{\sigma}_{-}\boldsymbol{\sigma}_\mathbf{P}} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{\cdots}{\cdots} \otimes \boldsymbol{\sigma}_\mathbf{P} \otimes \overset{k}{\boldsymbol{\sigma}_{+}} \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \cdots\cdots \otimes \boldsymbol{\sigma}_\mathbf{I} \otimes \overset{M}{\boldsymbol{\sigma}_\mathbf{I}} \,,$$

we also obtain $\{\mathbf{a}_k^\dagger, \mathbf{a}_{k'}\} = \mathbf{0}$.

Hence, we showed that Eqs. (20.1.19, 20.1.20) are satisfied:

$$\{\mathbf{a}_k^\dagger, \mathbf{a}_{k'}^\dagger\} = \mathbf{0} \quad ; \quad \{\mathbf{a}_k, \mathbf{a}_{k'}\} = \mathbf{0} \quad ; \quad \{\mathbf{a}_k^\dagger, \mathbf{a}_{k'}\} = \mathbf{I}\delta_{k,k'} \,.$$

Exercise 20.1.9 *Let us consider the Fock space corresponding to the two single particle states,* $\{|\Phi_1\rangle, |\Phi_2\rangle\}$, *with the basis vectors,* $|1,1\rangle$, $|1,0\rangle$, $|0,1\rangle$, $|0,0\rangle$. *(a) Use Eqs. (20.1.23, 20.1.24) to show that*

$\hat{a}_1^\dagger |0,0\rangle = |1,0\rangle$; $\hat{a}_1^\dagger |0,1\rangle = |1,1\rangle$; $\hat{a}_1^\dagger |1,0\rangle = \hat{a}_1^\dagger |1,1\rangle = 0$

$\hat{a}_1 |1,0\rangle = |0,0\rangle$; $\hat{a}_1 |1,1\rangle = |0,1\rangle$; $\hat{a}_1 |0,0\rangle = \hat{a}_1 |0,1\rangle = 0$

$\hat{a}_2^\dagger |0,0\rangle = |0,1\rangle$; $\hat{a}_2^\dagger |1,0\rangle = -|1,1\rangle$; $\hat{a}_2^\dagger |0,1\rangle = \hat{a}_2^\dagger |1,1\rangle = 0$

$\hat{a}_2 |1,1\rangle = -|1,0\rangle$; $\hat{a}_2 |0,1\rangle = |0,0\rangle$; $\hat{a}_2 |1,0\rangle = \hat{a}_2 |0,0\rangle = 0$.

(b) Obtain the matrix representations of the creation and annihilation operators in the basis {$|1,1\rangle$, $|1,0\rangle$, $|0,1\rangle$, $|0,0\rangle$*}, and compare the results to Eq. (20.1.39). (c) Check that the four matrices satisfy the anti-commutation relations for fermions, Eqs. (20.1.19, 20.1.20).*

Solution 20.1.9

(a)

Eqs. (20.1.23, 20.1.24) read

$$\hat{a}_k^\dagger |n_1, n_2, ..., n_M\rangle = \begin{cases} 0 & ; \quad n_k = 1 \\ (-1)^{\sum_{j=1}^{k-1} n_j} |n_1, ..., n_k + 1, ..., n_M\rangle & ; \quad n_k = 0 \end{cases},$$

$$\hat{a}_k |n_1, n_2, ..., n_M\rangle = \begin{cases} 0 & ; \quad n_k = 0 \\ (-1)^{\sum_{j=1}^{k-1} n_j} |n_1, ..., n_k - 1, ..., n_M\rangle & ; \quad n_k = 1 \end{cases}.$$

Implementing the general expressions for the space of two orbitals ($M = 2$*), we obtain*

$\hat{a}_1^\dagger |0,0\rangle = |1,0\rangle$; $\hat{a}_1^\dagger |0,1\rangle = |1,1\rangle$; $\hat{a}_1^\dagger |1,0\rangle = \hat{a}_1^\dagger |1,1\rangle = 0$

$\hat{a}_1 |1,0\rangle = |0,0\rangle$; $\hat{a}_1 |1,1\rangle = |0,1\rangle$; $\hat{a}_1 |0,0\rangle = \hat{a}_1 |0,1\rangle = 0$

$\hat{a}_2^\dagger |0,0\rangle = |0,1\rangle$; $\hat{a}_2^\dagger |1,0\rangle = -|1,1\rangle$; $\hat{a}_2^\dagger |0,1\rangle = \hat{a}_2^\dagger |1,1\rangle = 0$

$\hat{a}_2 |1,1\rangle = -|1,0\rangle$; $\hat{a}_2 |0,1\rangle = |0,0\rangle$; $\hat{a}_2 |1,0\rangle = \hat{a}_2 |0,0\rangle = 0$.

(b)

Using the relations in (a) and the orthonormality of the basis states {$|1,1\rangle$, $|1,0\rangle$, $|0,1\rangle$, $|0,0\rangle$*}, we readily reproduce the results in Eq. (20.1.39),*

$$\mathbf{a}_1 = \begin{pmatrix} \langle 1,1|\hat{a}_1|1,1\rangle & \langle 1,1|\hat{a}_1|1,0\rangle & \langle 1,1|\hat{a}_1|0,1\rangle & \langle 1,1|\hat{a}_1|0,0\rangle \\ \langle 1,0|\hat{a}_1|1,1\rangle & \langle 1,0|\hat{a}_1|1,0\rangle & \langle 1,0|\hat{a}_1|0,1\rangle & \langle 1,0|\hat{a}_1|0,0\rangle \\ \langle 0,1|\hat{a}_1|1,1\rangle & \langle 0,1|\hat{a}_1|1,0\rangle & \langle 0,1|\hat{a}_1|0,1\rangle & \langle 0,1|\hat{a}_1|0,0\rangle \\ \langle 0,0|\hat{a}_1|1,1\rangle & \langle 0,0|\hat{a}_1|1,0\rangle & \langle 0,0|\hat{a}_1|0,1\rangle & \langle 0,0|\hat{a}_1|0,0\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

$$\mathbf{a}_2 = \begin{pmatrix} \langle 1,1|\hat{a}_2|1,1\rangle & \langle 1,1|\hat{a}_2|1,0\rangle & \langle 1,1|\hat{a}_2|0,1\rangle & \langle 1,1|\hat{a}_2|0,0\rangle \\ \langle 1,0|\hat{a}_2|1,1\rangle & \langle 1,0|\hat{a}_2|1,0\rangle & \langle 1,0|\hat{a}_2|0,1\rangle & \langle 1,0|\hat{a}_2|0,0\rangle \\ \langle 0,1|\hat{a}_2|1,1\rangle & \langle 0,1|\hat{a}_2|1,0\rangle & \langle 0,1|\hat{a}_2|0,1\rangle & \langle 0,1|\hat{a}_2|0,0\rangle \\ \langle 0,0|\hat{a}_2|1,1\rangle & \langle 0,0|\hat{a}_2|1,0\rangle & \langle 0,0|\hat{a}_2|0,1\rangle & \langle 0,0|\hat{a}_2|0,0\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\mathbf{a}_1^\dagger = \begin{pmatrix} \langle 1,1|\hat{a}_1^\dagger|1,1\rangle & \langle 1,1|\hat{a}_1^\dagger|1,0\rangle & \langle 1,1|\hat{a}_1^\dagger|0,1\rangle & \langle 1,1|\hat{a}_1^\dagger|0,0\rangle \\ \langle 1,0|\hat{a}_1^\dagger|1,1\rangle & \langle 1,0|\hat{a}_1^\dagger|1,0\rangle & \langle 1,0|\hat{a}_1^\dagger|0,1\rangle & \langle 1,0|\hat{a}_1^\dagger|0,0\rangle \\ \langle 0,1|\hat{a}_1^\dagger|1,1\rangle & \langle 0,1|\hat{a}_1^\dagger|1,0\rangle & \langle 0,1|\hat{a}_1^\dagger|0,1\rangle & \langle 0,1|\hat{a}_1^\dagger|0,0\rangle \\ \langle 0,0|\hat{a}_1^\dagger|1,1\rangle & \langle 0,0|\hat{a}_1^\dagger|1,0\rangle & \langle 0,0|\hat{a}_1^\dagger|0,1\rangle & \langle 0,0|\hat{a}_1^\dagger|0,0\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{a}_2^\dagger = \begin{pmatrix} \langle 1,1|\hat{a}_2^\dagger|1,1\rangle & \langle 1,1|\hat{a}_2^\dagger|1,0\rangle & \langle 1,1|\hat{a}_2^\dagger|0,1\rangle & \langle 1,1|\hat{a}_2^\dagger|0,0\rangle \\ \langle 1,0|\hat{a}_2^\dagger|1,1\rangle & \langle 1,0|\hat{a}_2^\dagger|1,0\rangle & \langle 1,0|\hat{a}_2^\dagger|0,1\rangle & \langle 1,0|\hat{a}_2^\dagger|0,0\rangle \\ \langle 0,1|\hat{a}_2^\dagger|1,1\rangle & \langle 0,1|\hat{a}_2^\dagger|1,0\rangle & \langle 0,1|\hat{a}_2^\dagger|0,1\rangle & \langle 0,1|\hat{a}_2^\dagger|0,0\rangle \\ \langle 0,0|\hat{a}_2^\dagger|1,1\rangle & \langle 0,0|\hat{a}_2^\dagger|1,0\rangle & \langle 0,0|\hat{a}_2^\dagger|0,1\rangle & \langle 0,0|\hat{a}_2^\dagger|0,0\rangle \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

(c)

We can readily see that the anticommutation relations for fermions, Eqs. (20.1.19, 20.1.20), are satisfied by these matrices,

$$(\mathbf{a}_1)^2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow \{\mathbf{a}_1, \mathbf{a}_1\} = \mathbf{0}$$

$$(\mathbf{a}_2)^2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow \{\mathbf{a}_2, \mathbf{a}_2\} = \mathbf{0}$$

$$(\mathbf{a}_1^\dagger)^2 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow \{\mathbf{a}_1^\dagger, \mathbf{a}_1^\dagger\} = \mathbf{0}$$

$$(\mathbf{a}_2^\dagger)^2 = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow \{\mathbf{a}_2^\dagger, \mathbf{a}_2^\dagger\} = \mathbf{0}$$

$$\{\mathbf{a}_1,\mathbf{a}_2\}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{pmatrix}\begin{pmatrix}0&0&0&0\\-1&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}+\begin{pmatrix}0&0&0&0\\-1&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{pmatrix}$$

$$=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\-1&0&0&0\end{pmatrix}+\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\1&0&0&0\end{pmatrix}=\mathbf{0}$$

$$\{\mathbf{a}_1^\dagger,\mathbf{a}_2^\dagger\}=\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}\begin{pmatrix}0&-1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&-1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}$$

$$=\begin{pmatrix}0&0&0&1\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&0&0&-1\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}=\mathbf{0}$$

$$\{\mathbf{a}_1^\dagger,\mathbf{a}_2\}=\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}\begin{pmatrix}0&0&0&0\\-1&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}+\begin{pmatrix}0&0&0&0\\-1&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}$$

$$=\begin{pmatrix}0&0&0&0\\0&0&1&0\\0&0&0&0\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&0&0&0\\0&0&-1&0\\0&0&0&0\\0&0&0&0\end{pmatrix}=\mathbf{0}$$

$$\{\mathbf{a}_1,\mathbf{a}_2^\dagger\}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{pmatrix}\begin{pmatrix}0&-1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&-1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{pmatrix}$$

$$=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&-1&0&0\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&1&0&0\\0&0&0&0\end{pmatrix}=\mathbf{0}$$

$$\{\mathbf{a}_1,\mathbf{a}_1^\dagger\}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{pmatrix}\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{pmatrix}$$

$$=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}+\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}=\mathbf{I}$$

$$\{\mathbf{a}_2,\mathbf{a}_2^\dagger\}=\begin{pmatrix}0&0&0&0\\-1&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}\begin{pmatrix}0&-1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}+\begin{pmatrix}0&-1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}\begin{pmatrix}0&0&0&0\\-1&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}$$

$$=\begin{pmatrix}0&0&0&0\\0&1&0&0\\0&0&0&0\\0&0&0&1\end{pmatrix}+\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&1&0\\0&0&0&0\end{pmatrix}=\mathbf{I}\ .$$

Exercise 20.2.1 *(a) Using the binary string representation of a single determinant state (Eq. (20.1.7)), show that the expectation value of the second quantization Hamiltonian, Eqs. (20.2.3, 20.2.4), is given by Eq. (20.2.5). Compare the result to Ex. 13.3.6 for the energy expectation value of a single* N *-electron determinant. (b) Generalize the result of Ex. 13.3.6 for off-diagonal Hamiltonian matrix elements between different determinants,* $\left\langle \Psi^{(N)}_{\{l_1',l_2',l_3',...,l_N'\}} \middle| \hat{H}^{(N)} \middle| \Psi^{(N)}_{\{l_1,l_2,l_3,...,l_N\}} \right\rangle$*, and show that the result coincides with the second quantization Hamiltonian matrix elements,* $\left\langle \Psi^{(N)}_{\{l_1',l_2',l_3',...,l_N'\}} \middle| \hat{H} \middle| \Psi^{(N)}_{\{l_1,l_2,l_3,...,l_N\}} \right\rangle$

.

Solution 20.2.1

(a)

The second quantization Hamiltonian in a space of M *single particle states (Eqs. (20.2.3, 20.2.4)) reads* $\hat{H}=\sum_{i,j=1}^{M} h_{i,j}\hat{a}_i^\dagger\hat{a}_j+\frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\,\hat{a}_k$. *Using Eq. (20.1.7) to represent a single determinant of* N *electrons,* $\left|\Psi^{(N)}_{\{l_1,l_2,l_3,...,l_N\}}\right\rangle=\left|n_1,n_2,n_3,...,n_M\right\rangle$*, where* $n_l=1$ *for* $l\in\{l_1,l_2,...,l_N\}$ *and* $n_l=0$ *otherwise, the diagonal matrix elements of* $\hat{H}$ *read*

$$\langle n_1, n_2, ..., n_M | \hat{H} | n_1, n_2, ..., n_M \rangle = \sum_{i,j=1}^{M} h_{i,j} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle$$

$$+\frac{1}{2} \sum_{i,j,k,l=1}^{M} w_{i,j,k,l} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | n_1, n_2, ..., n_M \rangle \quad .$$

Using the orthogonality condition, $\left\langle \Psi^{(N)}_{\{l_1,l_2,...,l_N\}} \middle| \Psi^{(N)}_{\{l_1',l_2',...,l_N'\}} \right\rangle = \delta_{\{l_1,l_2,...,l_N\},\{l_1',l_2',...,l_N'\}}$ *(Eq. (20.1.6)), we conclude that the terms* $\langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle$ *and* $\langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | n_1, n_2, ..., n_M \rangle$ *vanish unless the determinants* $\hat{a}_i^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle$ *or* $\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | n_1, n_2, ..., n_M \rangle$ *have the same set of occupation numbers as the determinant* $| n_1, n_2, ..., n_M \rangle$. *This is the case only if successive annihilation and creation operations are associated with the same single particle states, namely,*

$$\langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle = \delta_{i,j} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_i | n_1, n_2, ..., n_M \rangle ,$$

and

$$\langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | n_1, n_2, ..., n_M \rangle = \delta_{i,l} \delta_{j,k} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_j | n_1, n_2, ..., n_M \rangle$$
$$+\delta_{i,k} \delta_{j,l} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i | n_1, n_2, ..., n_M \rangle \ .$$

Recalling the definition of the number operator (Eq. (20.1.25)), $\hat{a}_k^\dagger \hat{a}_k | n_1, n_2, ..., n_M \rangle = \hat{N}_k | n_1, n_2, ..., n_M \rangle = n_k | n_1, n_2, ..., n_M \rangle$, *and using the fermionic commutation relations, we obtain*

$$\langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle = \delta_{i,j} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_i | n_1, n_2, ..., n_M \rangle$$
$$= \delta_{i,j} \langle n_1, n_2, ..., n_M | \hat{N}_i | n_1, n_2, ..., n_M \rangle = \delta_{i,j} n_i \ ,$$

$$\begin{aligned}
&\langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | n_1, n_2, ..., n_M \rangle \\
&= \delta_{i,l} \delta_{j,k} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_j | n_1, n_2, ..., n_M \rangle + \delta_{i,k} \delta_{j,l} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i | n_1, n_2, ..., n_M \rangle \\
&= -\delta_{i,l} \delta_{j,k} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_i \hat{a}_j^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle + \delta_{i,k} \delta_{j,l} \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_i \hat{a}_j^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle \\
&= (\delta_{i,k} \delta_{j,l} - \delta_{i,l} \delta_{j,k}) \langle n_1, n_2, ..., n_M | \hat{a}_i^\dagger \hat{a}_i \hat{a}_j^\dagger \hat{a}_j | n_1, n_2, ..., n_M \rangle \\
&= (\delta_{i,k} \delta_{j,l} - \delta_{i,l} \delta_{j,k}) \langle n_1, n_2, ..., n_M | \hat{N}_i \hat{N}_j | n_1, n_2, ..., n_M \rangle \\
&= n_i n_j (\delta_{i,k} \delta_{j,l} - \delta_{i,l} \delta_{j,k}) \ .
\end{aligned}$$

Substitution in the expression for the Hamiltonian matrix element, we obtain

$$\begin{aligned}
&\langle n_1,n_2,...,n_M|\hat{H}|n_1,n_2,...,n_M\rangle \\
&=\sum_{i,j=1}^{M} h_{i,j}\langle n_1,n_2,...,n_M|\hat{a}_i^\dagger\hat{a}_j|n_1,n_2,...,n_M\rangle+\frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}\langle n_1,n_2,...,n_M|\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\,\hat{a}_k|n_1,n_2,...,n_M\rangle \\
&=\sum_{i,j=1}^{M} h_{i,j}\delta_{i,j}n_i+\frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}n_in_j\left(\delta_{i,k}\delta_{j,l}-\delta_{i,l}\delta_{j,k}\right) \\
&=\sum_{i=1}^{M} h_{i,i}n_i+\frac{1}{2}\sum_{i,j=1}^{M}\left(w_{i,j,i,j}-w_{i,j,j,i}\right)n_in_j \ .
\end{aligned}$$

Since $n_i=1$ or 0, depending on whether the single-particle state is occupied or not, respectively, the summations can be restricted to the (N) occupied single particle states, hence,

$$\begin{aligned}
&\langle n_1,n_2,...,n_M|\hat{H}|n_1,n_2,...,n_M\rangle=\sum_{i=1}^{M} h_{i,i}n_i+\frac{1}{2}\sum_{i,j=1}^{M}\left(w_{i,j,i,j}-w_{i,j,j,i}\right)n_in_j \\
&=\sum_{i\in\{l_1,l_2,...,l_N\}=1}^{N} h_{i,i}+\frac{1}{2}\sum_{i,j\in\{l_1,l_2,...,l_N\}=1}^{N}\left(w_{i,j,i,j}-w_{i,j,j,i}\right) \ .
\end{aligned}$$

Considering the definitions of $h_{i,j}$ and $w_{i,j,k,l}$ (Eq. (20.2.4)), we obtain

$$\begin{aligned}
&\langle n_1,n_2,...,n_M|\hat{H}|n_1,n_2,...,n_M\rangle=\sum_{i\in\{l_1,l_2,...,l_N\}=1}^{N}\int d\mathbf{r}\varphi_i^*(\mathbf{r})\left[\frac{-\hbar^2}{2m_e}\Delta_{\mathbf{r}}+V(\hat{\mathbf{r}})\right]\varphi_i(\mathbf{r}) \\
&+\frac{Ke^2}{2}\sum_{i,j\in\{l_1,l_2,...,l_N\}=1}^{N}\left(\int d\mathbf{r}\int d\mathbf{r}'\frac{\varphi_i^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\delta_{m_{s,i},m_{s,j}}\int d\mathbf{r}\int d\mathbf{r}'\frac{\varphi_i^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r})\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right).
\end{aligned}$$

As we can see, this result perfectly matches the result obtained in chapter 13 for the expectation value of the N -electron Hamiltonian, for a single determinant state (Eqs. (13.3.26-13.6.28)),

$$\begin{aligned}
&\varepsilon=\langle\Psi|\hat{H}|\Psi\rangle \\
&=\sum_{k=1}^{N}\langle\varphi_k|\hat{h}_k|\varphi_k\rangle+\frac{1}{2}\sum_{k=1}^{N}\sum_{j=1}^{N}\langle\varphi_k|\otimes\langle\varphi_j|\hat{w}_{k,j}[|\varphi_k\rangle\otimes|\varphi_j\rangle-\delta_{m_{s,j},m_{s,k}}|\varphi_j\rangle\otimes|\varphi_k\rangle] .
\end{aligned}$$

(b) The solution of this exercise is left for self-practice.

Exercise 20.2.2 *(a) Use the anti-commutation relations for fermion creation and annihilation operators (Eqs. (20.1.19, 20.1.20)) and the definition of the electron number operator (Eq. (20.1.26)) to show that, $[\hat{a}_j^\dagger,\hat{N}]=-\hat{a}_j^\dagger$ and $[\hat{a}_j,\hat{N}]=\hat{a}_j$. (b) Use the general operator identity,*

$[\hat{A}\hat{B},\hat{C}]=\hat{A}[\hat{B},\hat{C}]+[\hat{A},\hat{C}]\hat{B}$, *and the result of (a) to show that* $[\hat{a}_i^\dagger\hat{a}_j,\hat{N}]=0$. *(c) Use the results of (a) and (b) to show that the second quantization Hamiltonian (Eq. (20.2.3)) commutes with the total electron number operator.*

Solution 20.2.2

(a)

The total number operator (Eq. (20.1.26)) reads $\hat{N}\equiv\sum_{k=1}^{M}\hat{N}_k=\sum_{k=1}^{M}\hat{a}_k^\dagger\hat{a}_k$. *Therefore,*

$$[\hat{a}_j^\dagger,\hat{N}]=[\hat{a}_j^\dagger,\sum_{k=1}^{M}\hat{a}_k^\dagger\hat{a}_k]=\sum_{k=1}^{M}[\hat{a}_j^\dagger,\hat{a}_k^\dagger\hat{a}_k]$$

$$[\hat{a}_j,\hat{N}]=[\hat{a}_j,\sum_{k=1}^{M}\hat{a}_k^\dagger\hat{a}_k]=\sum_{k=1}^{M}[\hat{a}_j,\hat{a}_k^\dagger\hat{a}_k] \quad .$$

Using the anticommutation relations for fermion creation and annihilation operators (Eqs. (20.1.19, 20.1.20)), we obtain

$$[\hat{a}_j^\dagger,\hat{a}_k^\dagger\hat{a}_k]=\begin{cases} j=k \quad ; \quad \hat{a}_j^\dagger\hat{a}_j^\dagger\hat{a}_j-\hat{a}_j^\dagger\hat{a}_j\hat{a}_j^\dagger=-\hat{a}_j^\dagger \\ j\neq k \quad ; \quad \hat{a}_j^\dagger\hat{a}_k^\dagger\hat{a}_k-\hat{a}_k^\dagger\hat{a}_k\hat{a}_j^\dagger=\hat{a}_j^\dagger\hat{a}_k^\dagger\hat{a}_k-\hat{a}_j^\dagger\hat{a}_k^\dagger\hat{a}_k=0 \end{cases}$$

$$\Rightarrow[\hat{a}_j^\dagger,\hat{N}]=\sum_{k=1}^{M}[\hat{a}_j^\dagger,\hat{a}_k^\dagger\hat{a}_k]=-\hat{a}_j^\dagger$$

$$[\hat{a}_j,\hat{a}_k^\dagger\hat{a}_k]=\begin{cases} j=k \quad ; \quad \hat{a}_j\hat{a}_j^\dagger\hat{a}_j-\hat{a}_j^\dagger\hat{a}_j\hat{a}_j=\hat{a}_j \\ j\neq k \quad ; \quad \hat{a}_j\hat{a}_k^\dagger\hat{a}_k-\hat{a}_k^\dagger\hat{a}_k\hat{a}_j=\hat{a}_j\hat{a}_k^\dagger\hat{a}_k-\hat{a}_j\hat{a}_k^\dagger\hat{a}_k=0 \end{cases}$$

$$\Rightarrow[\hat{a}_j,\hat{N}]=\sum_{k=1}^{M}[\hat{a}_j,\hat{a}_k^\dagger\hat{a}_k]=\hat{a}_j \quad .$$

(b)

Using, $[\hat{A}\hat{B},\hat{C}]=\hat{A}[\hat{B},\hat{C}]+[\hat{A},\hat{C}]\hat{B}$, *we obtain* $[\hat{a}_i^\dagger\hat{a}_j,\hat{N}]=\hat{a}_i^\dagger[\hat{a}_j,\hat{N}]+[\hat{a}_i^\dagger,\hat{N}]\hat{a}_j$. *Using the results of (a), we obtain* $[\hat{a}_i^\dagger\hat{a}_j,\hat{N}]=\hat{a}_i^\dagger\hat{a}_j-\hat{a}_i^\dagger\hat{a}_j=0$.

(c)

Given the second quantization Hamiltonian (Eq. (20.2.3)),

$$\hat{H}=\sum_{i,j=1}^{M}h_{i,j}\hat{a}_i^\dagger\hat{a}_j+\frac{1}{2}\sum_{i,j,k,l=1}^{M}w_{i,j,k,l}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k \, ,$$

and the results of (b), $[\hat{a}_i^\dagger \hat{a}_j, \hat{N}]$, *we obtain*

$$[\hat{H},\hat{N}] = \sum_{i,j=1}^{M} h_{i,j}[\hat{a}_i^\dagger \hat{a}_j,\hat{N}] + \frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}[\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l\,\hat{a}_k,\hat{N}]$$

$$= -\frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}[\hat{a}_i^\dagger \hat{a}_l\,\hat{a}_j^\dagger \hat{a}_k,\hat{N}]$$

$$= -\frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}\left(\hat{a}_i^\dagger \hat{a}_l\,[\hat{a}_j^\dagger \hat{a}_k,\hat{N}] + [\hat{a}_i^\dagger \hat{a}_l\,,\hat{N}]\hat{a}_j^\dagger \hat{a}_k\right) = 0 \quad .$$

Exercise 20.2.3 *Show that the second quantization Hamiltonian (Eq. (20.2.3)) for a system of two orthonormal single particle states (*$|\Phi_1\rangle$ *and* $|\Phi_2\rangle$, *selected as the eigenstates of the single particle Hamiltonian,* $h_{i,j} = \varepsilon_i \delta_{i,j}$*) reads* $\hat{H} = \varepsilon_1 \hat{a}_1^\dagger \hat{a}_1 + \varepsilon_2 \hat{a}_2^\dagger \hat{a}_2 + U\hat{a}_1^\dagger \hat{a}_1\,\hat{a}_2^\dagger \hat{a}_2$, *where,* $U = (w_{1,2,1,2} - w_{1,2,2,1})$.

Solution 20.2.3

Given the second quantization Hamiltonian (Eq. (20.2.3)),

$\hat{H} = \sum_{i,j=1}^{M} h_{i,j}\hat{a}_i^\dagger \hat{a}_j + \frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l\,\hat{a}_k$, *for* $M = 2$, *we have*

$\sum_{i,j=1}^{M} h_{i,j}\hat{a}_i^\dagger \hat{a}_j = h_{1,1}\hat{a}_1^\dagger \hat{a}_1 + h_{1,2}\hat{a}_1^\dagger \hat{a}_2 + h_{2,1}\hat{a}_2^\dagger \hat{a}_1 + h_{2,2}\hat{a}_2^\dagger \hat{a}_2$, *and given* $h_{i,j} = \varepsilon_i \delta_{i,j}$, *we obtain*

$\sum_{i,j=1}^{M} h_{i,j}\hat{a}_i^\dagger \hat{a}_j = \varepsilon_1 \hat{a}_1^\dagger \hat{a}_1 + \varepsilon_2 \hat{a}_2^\dagger \hat{a}_2$.

Recalling the anticommutation relations for fermion creation and annihilation operators, the terms $\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l\,\hat{a}_k$ *vanish, unless* $i \neq j$ *and* $k \neq l$. *Hence, for* $M = 2$ *we have*

$$\frac{1}{2}\sum_{\substack{i,j,k,l=1\\ i\neq j,k\neq l}}^{2} w_{i,j,k,l}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l\,\hat{a}_k = \frac{1}{2}\left(w_{1,2,2,1}\hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_1\,\hat{a}_2 + w_{1,2,1,2}\hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_1 + w_{2,1,2,1}\hat{a}_2^\dagger \hat{a}_1^\dagger \hat{a}_1\,\hat{a}_2 + w_{2,1,1,2}\hat{a}_2^\dagger \hat{a}_1^\dagger \hat{a}_2 \hat{a}_1\right).$$

Using $\hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_1 = \hat{a}_2^\dagger \hat{a}_1^\dagger \hat{a}_1\,\hat{a}_2 = \hat{a}_1^\dagger \hat{a}_1\,\hat{a}_2^\dagger \hat{a}_2$ *and* $\hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_1\,\hat{a}_2 = \hat{a}_2^\dagger \hat{a}_1^\dagger \hat{a}_2 \hat{a}_1 = -\hat{a}_1^\dagger \hat{a}_1\,\hat{a}_2^\dagger \hat{a}_2$, *we obtain*

$$\frac{1}{2}\sum_{\substack{i,j,k,l=1\\ i\neq j,k\neq l}}^{2} w_{i,j,k,l}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l\,\hat{a}_k = \frac{1}{2}\Big((w_{1,2,1,2} + w_{2,1,2,1}) - (w_{1,2,2,1} + w_{2,1,1,2})\Big)\hat{a}_1^\dagger \hat{a}_1\,\hat{a}_2^\dagger \hat{a}_2\,.$$

Recalling the definition of $w_{i,j,k,l}$ *(Eq. (20.2.4)) and using the invariance of the results to exchange of the two particle coordinates under the integrals, we obtain*

$$w_{1,2,1,2} = Ke^2 \int d\mathbf{r} \int d\mathbf{r}' \frac{\varphi_1^*(\mathbf{r})\varphi_2^*(\mathbf{r}')\varphi_1(\mathbf{r})\varphi_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = w_{2,1,2,1}$$

$$w_{1,2,2,1} = \delta_{m_{s,1},m_{s,2}} Ke^2 \int d\mathbf{r} \int d\mathbf{r}' \frac{\varphi_1^*(\mathbf{r})\varphi_2^*(\mathbf{r}')\varphi_2(\mathbf{r})\varphi_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = w_{2,1,1,2} \ .$$

Consequently, $\frac{1}{2}\sum_{\substack{i,j,k,l=1 \\ i\neq j,k\neq l}}^{2} w_{i,j,k,l}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k = (w_{1,2,1,2} - w_{1,2,2,1})\hat{a}_1^\dagger \hat{a}_1 \hat{a}_2^\dagger \hat{a}_2$,

and finally,

$$\hat{H} = \sum_{i,j=1}^{M} h_{i,j}\hat{a}_i^\dagger \hat{a}_j + \frac{1}{2}\sum_{i,j,k,l=1}^{M} w_{i,j,k,l}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k = \varepsilon_1 \hat{a}_1^\dagger \hat{a}_1 + \varepsilon_2 \hat{a}_2^\dagger \hat{a}_2 + (w_{1,2,1,2} - w_{1,2,2,1})\hat{a}_1^\dagger \hat{a}_1 \hat{a}_2^\dagger \hat{a}_2 .$$

Exercise 20.2.4 *Use the anti-commutation relations for fermion creation and annihilation operators (Eqs. (20.1.19, 20.1.20)), and the definition of the field operators (Eqs. (20.2.8, 20.2.9)) to derive Eq. (20.2.10). Recall the formal definition of Dirac's delta in terms of a complete orthonormal set, Eq. (11.3.12).*

Solution 20.2.4

Given the definitions of the field operators (Eqs. (20.2.8, 20.2.9)), $\hat{\psi}_{\mathbf{r},\sigma}^\dagger = \sum_{k=1}^{\infty} \delta_{\sigma_k,\sigma}\varphi_k^*(\mathbf{r})\hat{a}_k^\dagger$ *and* $\hat{\psi}_{\mathbf{r},\sigma} = \sum_{k=1}^{\infty} \delta_{\sigma_k,\sigma}\varphi_k(\mathbf{r})\hat{a}_k$, *the anticommutation relations for fermion creation and annihilation operators (Eqs. (20.1.19, 20.1.20)), and the representation of Dirac's delta in terms of a complete orthonormal set,* $\delta(\mathbf{r}-\mathbf{r}') = \sum_{k=1}^{\infty} \varphi_k^*(\mathbf{r})\varphi_{k'}(\mathbf{r}')$, *we obtain*

$$\{\hat{\psi}^{\dagger}_{\mathbf{r},\sigma},\hat{\psi}_{\mathbf{r}',\sigma'}\} = \{\sum_{k=1}^{\infty}\delta_{\sigma_k,\sigma}\varphi_k^*(\mathbf{r})\hat{a}_k^{\dagger},\sum_{k'=1}^{\infty}\delta_{\sigma_{k'},\sigma'}\varphi_{k'}(\mathbf{r}')\hat{a}_{k'}\}$$
$$= \sum_{k,k',=1}^{\infty}\{\delta_{\sigma_k,\sigma}\varphi_k^*(\mathbf{r})\hat{a}_k^{\dagger},\delta_{\sigma_{k'},\sigma'}\varphi_{k'}(\mathbf{r}')\hat{a}_{k'}\} = \sum_{k,k',=1}^{\infty}\delta_{\sigma_k,\sigma}\delta_{\sigma_{k'},\sigma'}\varphi_k^*(\mathbf{r})\varphi_{k'}(\mathbf{r}')\{\hat{a}_k^{\dagger},\hat{a}_{k'}\}$$
$$= \sum_{k,k',=1}^{\infty}\delta_{\sigma_k,\sigma}\delta_{\sigma_{k'},\sigma'}\varphi_k^*(\mathbf{r})\varphi_{k'}(\mathbf{r}')\delta_{k,k'} = \sum_{k=1}^{\infty}\delta_{\sigma_k,\sigma}\delta_{\sigma_k,\sigma'}\varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r}')$$
$$= \delta_{\sigma',\sigma}\sum_{k=1}\varphi_k^*(\mathbf{r})\varphi_{k'}(\mathbf{r}') = \delta_{\sigma',\sigma}\delta(\mathbf{r}-\mathbf{r}')$$

$$\{\hat{\psi}^{\dagger}_{\mathbf{r},\sigma},\hat{\psi}^{\dagger}_{\mathbf{r}',\sigma'}\} = \{\sum_{k=1}^{\infty}\delta_{\sigma_k,\sigma}\varphi_k^*(\mathbf{r})\hat{a}_k^{\dagger},\sum_{k'=1}^{\infty}\delta_{\sigma_{k'},\sigma'}\varphi_{k'}^*(\mathbf{r}')\hat{a}_{k'}^{\dagger}\}$$
$$= \sum_{k,k',=1}^{\infty}\{\delta_{\sigma_k,\sigma}\varphi_k^*(\mathbf{r})\hat{a}_k^{\dagger},\delta_{\sigma_{k'},\sigma'}\varphi_{k'}^*(\mathbf{r}')\hat{a}_{k'}^{\dagger}\}$$
$$= \sum_{k,k',=1}^{\infty}\delta_{\sigma_k,\sigma}\delta_{\sigma_{k'},\sigma'}\varphi_k^*(\mathbf{r})\varphi_{k'}^*(\mathbf{r}')\{\hat{a}_k^{\dagger},\hat{a}_{k'}^{\dagger}\} = 0$$

$$\{\hat{\psi}_{\mathbf{r},\sigma},\hat{\psi}_{\mathbf{r}',\sigma'}\} = \{\sum_{k=1}^{\infty}\delta_{\sigma_k,\sigma}\varphi_k(\mathbf{r})\hat{a}_k,\sum_{k'=1}^{\infty}\delta_{\sigma_{k'},\sigma'}\varphi_{k'}(\mathbf{r}')\hat{a}_{k'}\}$$
$$= \sum_{k,k',=1}^{\infty}\{\delta_{\sigma_k,\sigma}\varphi_k(\mathbf{r})\hat{a}_k,\delta_{\sigma_{k'},\sigma'}\varphi_{k'}(\mathbf{r}')\hat{a}_{k'}\}$$

$$= \sum_{k,k',=1}^{\infty}\delta_{\sigma_k,\sigma}\delta_{\sigma_{k'},\sigma'}\varphi_k(\mathbf{r})\varphi_{k'}(\mathbf{r}')\{\hat{a}_k,\hat{a}_{k'}\} = 0 \quad .$$

In summary, we obtained Eq. (20.2.10), $\{\hat{\psi}^{\dagger}_{\mathbf{r},\sigma},\hat{\psi}_{\mathbf{r}',\sigma'}\} = \delta_{\sigma,\sigma'}\delta(\mathbf{r}-\mathbf{r}')$*, and* $\{\hat{\psi}^{\dagger}_{\mathbf{r},\sigma},\hat{\psi}^{\dagger}_{\mathbf{r}',\sigma'}\} = \{\hat{\psi}_{\mathbf{r},\sigma},\hat{\psi}_{\mathbf{r}',\sigma'}\} = 0$.

Exercise 20.2.5 *Accounting explicitly for the spin,* σ_k*, associated with each* k *th singe particle state, the second quantization Hamiltonian (Eq. (20.2.3)) reads* $\hat{H} = \sum_{k,k'=1}^{\infty}\delta_{\sigma_{k'},\sigma_k}h_{k,k'}\hat{a}_k^{\dagger}\hat{a}_{k'} + \frac{1}{2}\sum_{i,j,k,l=1}^{\infty}\delta_{\sigma_l,\sigma_i}\delta_{\sigma_k,\sigma_j}w_{i,j,k,l}\hat{a}_i^{\dagger}\hat{a}_j^{\dagger}\hat{a}_l\,\hat{a}_k$. *Use the definitions of the field operators to derive this result from Eq. (20.2.11).*

Solution 20.2.5

Using the definition of the field operators (Eqs. (20.2.8, 20.2.9)), and of the second quantization Hamiltonian (Eqs. (20.2.3, 20.2.4)), we obtain

$$\int d\mathbf{r}\hat{\psi}^{\dagger}_{\mathbf{r},\sigma}\hat{h}\hat{\psi}_{\mathbf{r},\sigma} = \sum_{\sigma} \int d\mathbf{r}\sum_{k=1}^{\infty}\delta_{\sigma_k,\sigma}\varphi_k^*(\mathbf{r})\hat{a}_k^{\dagger}\hat{h}\sum_{k'=1}^{\infty}\delta_{\sigma_{k'},\sigma}\varphi_{k'}(\mathbf{r})\hat{a}_{k'}$$

$$= \sum_{\sigma} \sum_{k,k'=1}^{\infty}\delta_{\sigma_k,\sigma}\delta_{\sigma_{k'},\sigma}\left(\int d\mathbf{r}\varphi_k^*(\mathbf{r})\hat{h}\varphi_{k'}(\mathbf{r})\right)\hat{a}_k^{\dagger}\hat{a}_{k'}$$

$$= \sum_{k,k'=1}^{\infty} \delta_{\sigma_{k'},\sigma_k} h_{k,k'}\hat{a}_k^{\dagger}\hat{a}_{k'}$$

$$\frac{1}{2}\sum_{\sigma,\sigma'} \int d\mathbf{r}\int d\mathbf{r}'\hat{\psi}^{\dagger}_{\mathbf{r},\sigma}\hat{\psi}^{\dagger}_{\mathbf{r}',\sigma'}\hat{w}\hat{\psi}_{\mathbf{r}',\sigma'}\hat{\psi}_{\mathbf{r},\sigma}$$

$$= \frac{1}{2}\sum_{\sigma,\sigma'} \int d\mathbf{r}\int d\mathbf{r}'\sum_{i=1}^{\infty}\delta_{\sigma_i,\sigma}\varphi_i^*(\mathbf{r})\hat{a}_i^{\dagger}\sum_{j=1}^{\infty}\delta_{\sigma_j,\sigma'}\varphi_j^*(\mathbf{r}')\hat{a}_j^{\dagger}\hat{w}\sum_{k=1}^{\infty}\delta_{\sigma_k,\sigma'}\varphi_k(\mathbf{r}')\hat{a}_k\sum_{l=1}^{\infty}\delta_{\sigma_l,\sigma}\varphi_l(\mathbf{r})\hat{a}_l$$

$$= \frac{1}{2}\sum_{i,j,k,l=1}^{\infty} \sum_{\sigma,\sigma'}\delta_{\sigma_i,\sigma}\delta_{\sigma_j,\sigma'}\delta_{\sigma_k,\sigma'}\delta_{\sigma_l,\sigma}\left(\int d\mathbf{r}\int d\mathbf{r}'\varphi_i^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\hat{w}\varphi_l(\mathbf{r})\varphi_k(\mathbf{r}')\right)\hat{a}_i^{\dagger}\hat{a}_j^{\dagger}\hat{a}_k\hat{a}_l$$

$$= \frac{1}{2}\sum_{i,j,k,l=1}^{\infty} \delta_{\sigma_l,\sigma_i}\delta_{\sigma_k,\sigma_j} w_{i,j,l,k}\hat{a}_i^{\dagger}\hat{a}_j^{\dagger}\hat{a}_k\hat{a}_l \quad .$$

Hence, we obtain Eq. (20.2.11),

$$\sum_{\sigma} \int d\mathbf{r}\hat{\psi}^{\dagger}_{\mathbf{r},\sigma}\hat{h}\hat{\psi}_{\mathbf{r},\sigma} + \frac{1}{2}\sum_{\sigma,\sigma'} \int d\mathbf{r}\int d\mathbf{r}'\hat{\psi}^{\dagger}_{\mathbf{r},\sigma}\hat{\psi}^{\dagger}_{\mathbf{r}',\sigma'}\hat{w}\hat{\psi}_{\mathbf{r}',\sigma'}\hat{\psi}_{\mathbf{r},\sigma}$$

$$= \sum_{k,k'=1}^{\infty} \delta_{\sigma_{k'},\sigma_k} h_{k,k'}\hat{a}_k^{\dagger}\hat{a}_{k'} + \frac{1}{2}\sum_{i,j,k,l=1}^{\infty} \delta_{\sigma_l,\sigma_i}\delta_{\sigma_k,\sigma_j} w_{i,j,l,k}\hat{a}_i^{\dagger}\hat{a}_j^{\dagger}\hat{a}_k\hat{a}_l \quad .$$

Exercise 20.3.1 *(a) Recalling that the trace of a tensor product of operators is a product of their traces,* $tr\left\{\hat{A}_1 \otimes \hat{A}_2 \otimes \cdots \otimes \hat{A}_N\right\} = tr\left\{\hat{A}_1\right\}\cdot tr\left\{\hat{A}_2\right\}\cdots tr\left\{\hat{A}_N\right\}$ *(Ex. 15.5.1), use the commutativity of the number operators associated with the single particle states to show that* $tr\{\hat{N}_l\hat{\rho}^{(eq)}\} = tr_l\{\hat{a}_l^{\dagger}\hat{a}_l\, e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^{\dagger}\hat{a}_l}\} / tr_l\{e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^{\dagger}\hat{a}_l}\}$. *(b) Evaluate explicitly the trace in the subspace of* l *th single particle state to derive Eq. (20.3.5).*

Solution 20.3.1

(a)

Using Eq. (20.3.4) for $\hat{\rho}^{(eq)}$*, we obtain* $N_l \equiv tr\{\hat{N}_l \hat{\rho}^{(eq)}\} = tr\{\hat{a}_l^\dagger \hat{a}_l \dfrac{e^{\frac{-1}{k_BT}\sum_k (\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k}}{tr\{e^{\frac{-1}{k_BT}\sum_k (\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k}\}}\}$.

Since $[\hat{a}_k^\dagger \hat{a}_k, \hat{a}_{k'}^\dagger \hat{a}_{k'}] = 0$ *(see Ex. 20.2.2), the exponent of the sum can be rewritten as a product of exponents,* $e^{\frac{-1}{k_BT}\sum_k (\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k} = e^{\frac{-1}{k_BT}(\varepsilon_1-\mu)\hat{a}_1^\dagger \hat{a}_1} \otimes e^{\frac{-1}{k_BT}(\varepsilon_2-\mu)\hat{a}_2^\dagger \hat{a}_2} \otimes \cdots$*. Hence,*

$$tr\{e^{\frac{-1}{k_BT}\sum_k (\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k}\} = tr_1\{e^{\frac{-1}{k_BT}(\varepsilon_1-\mu)\hat{a}_1^\dagger \hat{a}_1}\} \cdot tr_2\{e^{\frac{-1}{k_BT}(\varepsilon_2-\mu)\hat{a}_2^\dagger \hat{a}_2}\} \cdots = \prod_k tr_k\{e^{\frac{-1}{k_BT}(\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k}\},$$

and

$$N_l = tr\{\hat{a}_l^\dagger \hat{a}_l \frac{e^{\frac{-1}{k_BT}\sum_k (\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k}}{tr\{e^{\frac{-1}{k_BT}\sum_k (\varepsilon_k-\mu)\hat{a}_k^\dagger \hat{a}_k}\}}\}$$

$$= tr_1\{\frac{e^{\frac{-1}{k_BT}(\varepsilon_1-\mu)\hat{a}_1^\dagger \hat{a}_1}}{tr_1\{e^{\frac{-1}{k_BT}(\varepsilon_1-\mu)\hat{a}_1^\dagger \hat{a}_1}\}}\} \cdot tr_2\{\frac{e^{\frac{-1}{k_BT}(\varepsilon_2-\mu)\hat{a}_2^\dagger \hat{a}_2}}{tr_2\{e^{\frac{-1}{k_BT}(\varepsilon_2-\mu)\hat{a}_2^\dagger \hat{a}_2}\}}\} \cdots tr_l\{\frac{\hat{a}_l^\dagger \hat{a}_l\, e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}}{tr_l\{e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}\}}\} \cdots = tr_l\{\frac{\hat{a}_l^\dagger \hat{a}_l\, e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}}{tr_l\{e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}\}}\}.$$

As we can see, the evaluation of the multidimensional trace reduces to the calculation of the trace in the subspace of l^{th} *single particle state.*

(b)

To evaluate explicitly the trace in the subspace of l^{th} *single particle state, we use the complete basis for this subspace, namely the occupation states* $|0\rangle$ *and* $|1\rangle$*, which correspond to* $n_l = 0$ *and* $n_l = 1$*, respectively. Hence, we obtain Eq. (20.3.5),*

$$N_l = \langle 0| \frac{\hat{a}_l^\dagger \hat{a}_l\, e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}}{\langle 0|e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}|0\rangle + \langle 1|e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}|1\rangle} |0\rangle + \langle 1| \frac{\hat{a}_l^\dagger \hat{a}_l\, e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}}{\langle 0|e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}|0\rangle + \langle 1|e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)\hat{a}_l^\dagger \hat{a}_l}|1\rangle} |1\rangle$$

$$= \frac{0}{1+e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)}} + \frac{e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)}}{1+e^{\frac{-1}{k_BT}(\varepsilon_l-\mu)}} = \frac{1}{1+e^{\frac{1}{k_BT}(\varepsilon_l-\mu)}} \quad .$$

Exercise 20.4.1 *The "electrode" part in the model depicted in Eq. (20.4.1) consists of a uniform linear tight-binding chain of M_E sites at the on-site energy, μ, with the nearest-neighbor coupling matrix elements, $\beta = -|\beta|$. The eigenvalues and eigenvectors of the corresponding model Hamiltonian were first introduced in Eqs. (14.4.25, 14.4.26) and are quoted in Eq. (20.4.4). Let us consider a "half-filling model" where the system is populated by non-interacting electrons whose number equals the number of electrode sites, M_E. (a) Considering the Pauli exclusion and the Aufbau principles (chapter 13), show that for an even M_E, the energy of the highest occupied and lowest unoccupied eigenvectors of the chain Hamiltonian at zero temperature are, respectively, $\varepsilon = \mu + 2\beta\cos[\frac{\pi}{2}(1-\frac{1}{M_E+1})]$ and $\varepsilon = \mu + 2\beta\cos[\frac{\pi}{2}(1+\frac{1}{M_E+1})]$. (b) Show that for an infinite chain length, $M_E \to \infty$, these two energies coincide to the same value (the chemical potential of the many-electron system), which is equal to the on-site energy, μ. (c) Show that the energy of the highest occupied and lowest unoccupied eigenvectors of the chain Hamiltonian have the same value also for an odd M_E.*

Solution 20.4.1

(a)

The model of a uniform linear tight-binding chain of M_E sites is associated with the eigenvalues and eigenstates as given in Eq. (20.4.4),

$$\varepsilon_n = \mu + 2\beta\cos(\frac{n\pi}{M_E+1}) \quad ; \quad |\chi_n\rangle = \sum_{j=1}^{M_E} \sqrt{\frac{2}{M_E+1}}\sin(\frac{n\pi j}{M_E+1})|\varphi_j\rangle.$$

Given that the number of electrons is equal to the number of sites (M_E), and given that at zero temperature the electrons populate the eigenvectors with the lowest possible eigenvalues, subject to the Pauli exclusion (namely, up to two electrons per spatial state), and recalling that for negative β, the energy ε_n is an increasing function of n, the index of the highest occupied eigenvector must be $M_E/2$ (for an even M_E). Consequently, the highest occupied state is associated with the energy,

$$\varepsilon_{M_E/2} = \mu + 2\beta\cos[\frac{M_E\pi}{2(M_E+1)}] = \mu + 2\beta\cos[\frac{\pi}{2}(1-\frac{1}{M_E+1})],$$

and the lowest unoccupied state is associated with the energy,

$$\varepsilon_{M_E/2+1} = \mu + 2\beta\cos[\frac{(M_E/2+1)\pi}{M_E+1}] = \mu + 2\beta\cos[\frac{\pi}{2}(1+\frac{1}{M_E+1})].$$

(b)

For an infinite chain length, $M_E \to \infty$, *these two energies coincide to the same value,*

$$\varepsilon_{M_E/2} = \mu + 2\beta \cos[\frac{\pi}{2}(1 - \frac{1}{M_E+1})] \xrightarrow[M_E \to \infty]{} \mu + 2\beta\cos[\frac{\pi}{2}] = \mu$$

$$\varepsilon_{M_E/2+1} = \mu + 2\beta \cos[\frac{\pi}{2}(1 + \frac{1}{M_E+1})] \xrightarrow[M_E \to \infty]{} \mu + 2\beta\cos[\frac{\pi}{2}] = \mu \quad .$$

Hence, the chemical potential of this half-filled chain model coincides with the on-site energy, μ.

(c)

For an odd M_E*, the highest occupied eigenvector is also the lowest unoccupied, since it is occupied by a single "unpaired" electron.*

Exercise 20.4.2 *Using the explicit form of the single particle Hamiltonian, Eqs. (20.4.2, 20.4.3), in Eq. (20.4.5) and restricting the electron-electron interaction to the adsorbate space (Eq. (20.4.6)), derive Eq. (20.4.7).*

Solution 20.4.2

Adopting the single particle Hamiltonian as given by Eqs. (20.4.2, 20.4.3) we obtain

$$\hat{h} = \sum_{n=0}^{M_E} \varepsilon_n |\chi_n\rangle\langle\chi_n| + \sum_{n=1}^{M_E} \left(\gamma_n |\chi_0\rangle\langle\chi_n| + \gamma_n^* |\chi_n\rangle\langle\chi_0|\right).$$

Using $\{|\chi_n\rangle\}$, $n = 0,1,2,...,M_E$ *as an orthonormal set of spatial single particle states to represent the single-particle Hamiltonian, we obtain* $h_{i,j} = \langle\chi_i|\hat{h}|\chi_j\rangle = \varepsilon_i\delta_{i,j} + \gamma_j\delta_{i,0}(1-\delta_{j,0}) + \gamma_i^*\delta_{j,0}(1-\delta_{i,0})$.

Rrestricting the electron-electron interaction to the adsorbate space (Eq. (20.4.6)), we obtain

$$w_{i,j,k,l} = \delta_{i,0}\delta_{j,0}\delta_{k,0}\delta_{l,0}U .$$

Substitution these specific results in the formal expression for the many-electron Hamiltonian (Eq. (20.4.5)), and using the anti-commutation relation between the fermionic annihilation and creation operators, we obtain Eq. (20.4.7),

$$
\begin{aligned}
\hat{H} &= \sum_{\sigma=-1/2}^{1/2}\sum_{i,j=0}^{M_E} h_{i,j}\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{j,\sigma} + \frac{1}{2}\sum_{\sigma,\sigma'=-1/2}^{1/2}\sum_{i,j,k,l=0}^{M_E} w_{i,j,k,l}\hat{a}^{\dagger}_{i,\sigma}\hat{a}^{\dagger}_{j,\sigma'}\hat{a}_{l,\sigma'}\hat{a}_{k,\sigma} \\
&= \sum_{\sigma=-1/2}^{1/2}\sum_{i,j=0}^{M_E}\left(\varepsilon_i\delta_{i,j} + \gamma_j\delta_{i,0}(1-\delta_{j,0}) + \gamma_i^*\delta_{j,0}(1-\delta_{i,0})\right)\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{j,\sigma} \\
&+ \frac{1}{2}\sum_{\sigma,\sigma'=-1/2}^{1/2}\sum_{i,j,k,l=0}^{M_E}\delta_{i,0}\delta_{j,0}\delta_{k,0}\delta_{l,0}U\hat{a}^{\dagger}_{i,\sigma}\hat{a}^{\dagger}_{j,\sigma'}\hat{a}_{l,\sigma'}\hat{a}_{k,\sigma} \\
&= \sum_{\sigma=-1/2}^{1/2}\left(\sum_{i=0}^{M_E}\varepsilon_i\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{i,\sigma} + \sum_{i=1}^{M_E}\gamma_i\hat{a}^{\dagger}_{0,\sigma}\hat{a}_{i,\sigma} + \gamma_i^*\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{0,\sigma}\right) \\
&+ \frac{1}{2}\sum_{\sigma,\sigma'=-1/2}^{1/2} U\hat{a}^{\dagger}_{0,\sigma}\hat{a}^{\dagger}_{0,\sigma'}\hat{a}_{0,\sigma'}\hat{a}_{0,\sigma} \\
&= \varepsilon_0\hat{a}^{\dagger}_{0,1/2}\hat{a}_{0,1/2} + \varepsilon_0\hat{a}^{\dagger}_{0,-1/2}\hat{a}_{0,-1/2} + \sum_{\sigma=-1/2}^{1/2}\sum_{i=1}^{M_E}\left(\varepsilon_i\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{i,\sigma} + \gamma_i\hat{a}^{\dagger}_{0,\sigma}\hat{a}_{i,\sigma} + \gamma_i^*\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{0,\sigma}\right) \\
&+ \frac{U}{2}\left(\hat{a}^{\dagger}_{0,1/2}\hat{a}^{\dagger}_{0,1/2}\hat{a}_{0,1/2}\hat{a}_{0,1/2} + \hat{a}^{\dagger}_{0,1/2}\hat{a}^{\dagger}_{0,-1/2}\hat{a}_{0,-1/2}\hat{a}_{0,1/2} + \hat{a}^{\dagger}_{0,-1/2}\hat{a}^{\dagger}_{0,1/2}\hat{a}_{0,1/2}\hat{a}_{0,-1/2} + \hat{a}^{\dagger}_{0,-1/2}\hat{a}^{\dagger}_{0,-1/2}\hat{a}_{0,-1/2}\hat{a}_{0,-1/2}\right) \\
&= \varepsilon_0\hat{a}^{\dagger}_{0,1/2}\hat{a}_{0,1/2} + \varepsilon_0\hat{a}^{\dagger}_{0,-1/2}\hat{a}_{0,-1/2} + U\hat{a}^{\dagger}_{0,1/2}\hat{a}_{0,1/2}\hat{a}^{\dagger}_{0,-1/2}\hat{a}_{0,-1/2} + \sum_{\sigma=-1/2}^{1/2}\sum_{i=1}^{M_E}\left(\varepsilon_i\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{i,\sigma} + \gamma_i\hat{a}^{\dagger}_{0,\sigma}\hat{a}_{i,\sigma} + \gamma_i^*\hat{a}^{\dagger}_{i,\sigma}\hat{a}_{0,\sigma}\right).
\end{aligned}
$$

Exercise 20.5.1 *(a) Use the anti-commutation relation between the fermionic annihilation and creation operators,* $\{\hat{a}^{\dagger}_l, \hat{a}^{\dagger}_{l'}\} = 0$, $\{\hat{a}_l, \hat{a}_{l'}\} = 0$, $\{\hat{a}_l, \hat{a}^{\dagger}_{l'}\} = \delta_{l,l'}$ (Eqs. (20.1.19, 20.1.20)), *to show that the traces over a single orbital Fock space,* $tr_k\{\hat{a}_k f(\hat{a}^{\dagger}_k\hat{a}_k)\}$ *and* $tr_k\{\hat{a}^{\dagger}_k f(\hat{a}^{\dagger}_k\hat{a}_k)\}$, *vanish for any analytic function,* $f(\hat{A}) = \sum_{n=0}^{\infty} f_n\hat{A}^n$. *(b) Given the definition of the fermion bath Hamiltonian and coupling operators (Eq. (20.5.1) with* $\hat{U}_B \equiv \sum_{k=1}^{M_E}\gamma_k\hat{a}_k$ *), and the bath density operator (Eq. (20.5.2)), use the result of (a) to show that* $tr_B\{\hat{U}_B\hat{\rho}_B\} = tr_B\{\hat{U}^{\dagger}_B\hat{\rho}_B\} = 0$.

Solution 20.5.1

(a)

For an analytic function we can expand, $f(\hat{a}^{\dagger}_k\hat{a}_k) = \sum_{n=0}^{\infty} f_n\cdot\left[\hat{a}^{\dagger}_k\hat{a}_k\right]^n$. *Hence, it is sufficient to show that,* $tr_k\{\hat{a}_k(\hat{a}^{\dagger}_k\hat{a}_k)^n\} = tr_k\{\hat{a}^{\dagger}_k(\hat{a}^{\dagger}_k\hat{a}_k)^n\} = 0$ *for any* n. *Using* $\{\hat{a}^{\dagger}_l, \hat{a}^{\dagger}_{l'}\} = 0$, $\{\hat{a}_l, \hat{a}_{l'}\} = 0$, $\{\hat{a}_l, \hat{a}^{\dagger}_{l'}\} = \delta_{l,l'}$, *we can readily see that:*

For $n=0$, $tr_k\{\hat{a}_k\}=\langle 0|\hat{a}_k|0\rangle+\langle 1|\hat{a}_k|1\rangle=0$ *and* $tr_k\{\hat{a}_k^\dagger\}=\langle 0|\hat{a}_k^\dagger|0\rangle+\langle 1|\hat{a}_k^\dagger|1\rangle=0$.

For $n=1$, $tr\{\hat{a}_k a_k^\dagger \hat{a}_k\}=tr\{\hat{a}_k\left[1-\hat{a}_k a_k^\dagger\right]\}=tr\{\hat{a}_k\}-tr\{\hat{a}_k\hat{a}_k a_k^\dagger\}=0$ *and* $tr\{\hat{a}_k^\dagger a_k^\dagger \hat{a}_k\}=0$.

For any $n\geq 1$, *we have* $(\hat{a}_k^\dagger\hat{a}_k)^{n+1}=\hat{a}_k^\dagger\hat{a}_k(\hat{a}_k^\dagger\hat{a}_k)^n=[1-\hat{a}_k\hat{a}_k^\dagger](\hat{a}_k^\dagger\hat{a}_k)^n=(\hat{a}_k^\dagger\hat{a}_k)^n$ *and therefore,*

$tr_k\{\hat{a}_k(\hat{a}_k^\dagger\hat{a}_k)^{n+1}\}=tr_k\{\hat{a}_k(\hat{a}_k^\dagger\hat{a}_k)^1\}=0$ *and* $tr_k\{\hat{a}_k^\dagger(\hat{a}_k^\dagger\hat{a}_k)^{n+1}\}=tr_k\{\hat{a}_k^\dagger(\hat{a}_k^\dagger\hat{a}_k)^1\}=0$.

Consequently, $tr_k\{\hat{a}_k f(\hat{a}_k^\dagger\hat{a}_k)\}$ *and* $tr_k\{\hat{a}_k^\dagger f(\hat{a}_k^\dagger\hat{a}_k)\}$ *vanish for any analytic function,* $f(\hat{a}_k^\dagger\hat{a}_k)=\sum_{n=0}^{\infty} f_n\left(\hat{a}_k^\dagger\hat{a}_k\right)^n$.

(b)

Using Eq. (20.5.1) for the bath Hamiltonian, $\hat{H}_B=\sum_{k=1}^{M_E}\varepsilon_k\hat{a}_k^\dagger\hat{a}_k$, *and for the coupling operator,* $\hat{U}_B\equiv\sum_{k=1}^{M_E}\gamma_k\hat{a}_k$, *using Eq. (20.5.2) for the bath density,* $\hat{\rho}_B=\dfrac{e^{\frac{-1}{k_BT}\sum_k(\varepsilon_k-\mu)\hat{a}_k^\dagger\hat{a}_k}}{tr\{e^{\frac{-1}{k_BT}\sum_k(\varepsilon_k-\mu)\hat{a}_k^\dagger\hat{a}_k}\}}=\dfrac{1}{Z}e^{\frac{-1}{k_BT}\sum_k(\varepsilon_k-\mu)\hat{a}_k^\dagger\hat{a}_k}$,

and recalling that $tr_1\{\hat{O}_j\otimes\hat{O}_{j'}\}=tr_j\{\hat{O}_j\}\cdot tr_{j'}\{\hat{O}_{j'}\}$, *we obtain*

$$tr_B\{\hat{U}_B\hat{\rho}_B\}=\frac{1}{Z}tr_B\{\sum_{j=1}^{M_E}\gamma_j\hat{a}_j e^{\frac{-1}{k_BT}\sum_{j'=1}^{M_E}(\varepsilon_{j'}-\mu)\hat{a}_{j'}^\dagger\hat{a}_{j'}}\}=\frac{1}{Z}\sum_{j=1}^{N_\omega}\gamma_j\hat{a}_j tr_B\{\prod_{j'=1}^{M_E}e^{\frac{-1}{k_BT}(\varepsilon_{j'}-\mu)\hat{a}_{j'}^\dagger\hat{a}_{j'}}\}$$
$$=\frac{1}{Z}\sum_{j=1}^{N_\omega}\gamma_j tr_1\{e^{\frac{-1}{k_BT}(\varepsilon_1-\mu)\hat{a}_1^\dagger\hat{a}_1}\}\cdot tr_2\{e^{\frac{-1}{k_BT}(\varepsilon_2-\mu)\hat{a}_2^\dagger\hat{a}_2}\}\cdots tr_j\{\hat{a}_j e^{\frac{-1}{k_BT}(\varepsilon_j-\mu)\hat{a}_j^\dagger\hat{a}_j}\}\cdots$$

$$tr_B\{\hat{U}_B^\dagger\hat{\rho}_B\}=\frac{1}{Z}tr_B\{\sum_{j=1}^{M_E}\gamma_j^*\hat{a}_j^\dagger e^{\frac{-1}{k_BT}\sum_{j'=1}^{M_E}(\varepsilon_{j'}-\mu)\hat{a}_{j'}^\dagger\hat{a}_{j'}}\}=\frac{1}{Z}\sum_{j=1}^{N_\omega}\gamma_j^*\hat{a}_j^\dagger tr_B\{\prod_{j'=1}^{M_E}e^{\frac{-1}{k_BT}(\varepsilon_{j'}-\mu)\hat{a}_{j'}^\dagger\hat{a}_{j'}}\}$$
$$=\frac{1}{Z}\sum_{j=1}^{N_\omega}\gamma_j^* tr_1\{e^{\frac{-1}{k_BT}(\varepsilon_1-\mu)\hat{a}_1^\dagger\hat{a}_1}\}\cdot tr_2\{e^{\frac{-1}{k_BT}(\varepsilon_2-\mu)\hat{a}_2^\dagger\hat{a}_2}\}\cdots tr_j\{\hat{a}_j^\dagger e^{\frac{-1}{k_BT}(\varepsilon_j-\mu)\hat{a}_j^\dagger\hat{a}_j}\}\cdots\ .$$

Using (a) we have $tr_j\{\hat{a}_j^\dagger e^{\frac{-1}{k_BT}(\varepsilon_j-\mu)\hat{a}_j^\dagger\hat{a}_j}\}=tr_j\{\hat{a}_j e^{\frac{-1}{k_BT}(\varepsilon_j-\mu)\hat{a}_j^\dagger\hat{a}_j}\}=0$, *and therefore,* $tr_B\{\hat{U}_B\hat{\rho}_B\}=\{\hat{U}_B^\dagger\hat{\rho}_B\}=0$.

Exercise 20.5.2 *(a) Use the explicit expressions,* $\hat{U}_B \equiv \sum_{k=1}^{M_E} \gamma_k \hat{a}_k$, $\hat{H}_B = \sum_{k=1}^{M_E} \varepsilon_k \hat{a}_k^\dagger \hat{a}_k$, $\hat{\rho}_B = e^{\frac{-1}{k_B T}\sum_k (\varepsilon_k - \mu)\hat{a}_k^\dagger \hat{a}_k} / tr\{e^{\frac{-1}{k_B T}\sum_k (\varepsilon_k - \mu)\hat{a}_k^\dagger \hat{a}_k}\}$*, and the fermionic anti-commutation relations to show that the bath correlation functions,* $c_e(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$ *and* $c_a(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$*, read* $c_e(\tau) = \sum_{k=1}^{M_E} |\gamma_k|^2 e^{\frac{-i\tau}{\hbar}\varepsilon_k}[1 - \frac{1}{1+e^{\frac{1}{k_B T}(\varepsilon_k - \mu)}}]$ *and*

$$c_a(\tau) = \sum_{k=1}^{M_E} |\gamma_k|^2 e^{\frac{i\tau}{\hbar}\varepsilon_k} \frac{1}{1+e^{\frac{1}{k_B T}(\varepsilon_k - \mu)}} .$$

(b) For a general system-bath coupling operator, $\hat{H}_{SB} \equiv \sum_\alpha \hat{V}_\alpha^{(S)} \hat{U}_\alpha^{(B)}$ *(Eq. (19.3.12)), the Redfield (Born-Markov) dissipator obtains the form of Eqs. (19.3.21, 19.3.22),* $\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\sum_{\alpha,\alpha'} \int_0^t d\tau \{c_{\alpha,\alpha'}(\tau)[\hat{V}_\alpha^{(S)}, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_{\alpha'}^{(S)} e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] + \bar{c}_{\alpha',\alpha}(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_{\alpha'}^{(S)} e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_\alpha^{(S)}]\}$ *where,* $c_{\alpha,\alpha'}(\tau) \equiv tr_B\{\hat{U}_\alpha^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_{\alpha'}^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$ *and* $\bar{c}_{\alpha,\alpha'}(\tau) = c_{\alpha,\alpha'}(-\tau)$*. Map the coupling operator defined in Eq. (20.5.1),* $\hat{H}_{SB} \equiv \hat{V}_S \hat{U}_B + \hat{V}_S^\dagger \hat{U}_B^\dagger$*, on this general form by identifying:* $\hat{V}_S \equiv \hat{V}_1^{(S)}$, $\hat{U}_B \equiv \hat{U}_1^{(B)}$, $\hat{V}_S^\dagger \equiv \hat{V}_2^{(S)}$, $\hat{U}_B^\dagger \equiv \hat{U}_2^{(B)}$ *to show that,*

$$\hat{D}\hat{\rho}_S(t) =$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau \{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] + c_{2,1}^*(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau \{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S} \hat{\rho}_S(t)] + c_{1,2}^*(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S} \hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} .$$

(c) Use the identities, $c_{1,2}(\tau) = c_e(\tau)$, $c_{2,1}(\tau) = c_a(\tau)$*, to derive Eq. (20.5.3).*

Solution 20.5.2

(a)

Using: $\hat{H}_B = \sum_{k=1}^{M_E} \varepsilon_k \hat{a}_k^\dagger \hat{a}_k$, $\hat{U}_B \equiv \sum_{k=1}^{M_E} \gamma_k \hat{a}_k$, $\hat{U}_B^\dagger \equiv \sum_{k=1}^{M_E} \gamma_k^* \hat{a}_k^\dagger$ *and* $\hat{\rho}_B = \frac{1}{Z} e^{\frac{-1}{k_B T}\sum_k (\varepsilon_k - \mu)\hat{a}_k^\dagger \hat{a}_k}\}$*, we obtain*

$$c_a(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{M_E}\gamma_j^*\gamma_{j'} tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$c_e(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{M_E}\gamma_{j'}^*\gamma_j tr_B\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}.$$

Focusing on $tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$, *we notice that* $e^{\frac{-i\tau}{\hbar}\hat{H}_B} = \prod_{j=1}^{M_E} e^{\frac{-i\tau}{\hbar}\hat{h}_j}$ *and*

$e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B = \prod_{j=1}^{M_E} e^{\frac{i\tau}{\hbar}\hat{h}_j}\dfrac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}$, *where,* $\hat{h}_j \equiv \varepsilon_j\hat{a}_j^\dagger\hat{a}_j$, $\hat{N}_j \equiv \hat{a}_j^\dagger\hat{a}_j$ *and* $Z_j = tr_j\{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}\}$.

Therefore, for $j = j'$,

$$tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = tr_1\{\frac{e^{\frac{-1}{k_BT}(\hat{h}_1-\mu\hat{N}_1)}}{Z_1}\}\cdot tr_2\{\frac{e^{\frac{-1}{k_BT}(\hat{h}_2-\mu\hat{N}_2)}}{Z_2}\}\cdots tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\}\cdots,$$

and for $j \neq j'$,

$$tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = tr_1\{\frac{e^{\frac{-1}{k_BT}(\hat{h}_1-\mu\hat{N}_1)}}{Z_1}\}\cdot tr_2\{\frac{e^{\frac{-1}{k_BT}(\hat{h}_2-\mu\hat{N}_2)}}{Z_2}\}$$

$$\cdots tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j} e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\}\cdots tr_{j'}\{e^{\frac{-i\tau}{\hbar}\hat{h}_{j'}}\hat{a}_{j'} e^{\frac{i\tau}{\hbar}\hat{h}_{j'}}\frac{e^{\frac{-1}{k_BT}(\hat{h}_{j'}-\mu\hat{N}_{j'})}}{Z_{j'}}\}\cdots.$$

Since $tr_j\{\dfrac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = 1$, *and* $tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j} e^{\frac{i\tau}{\hbar}\hat{h}_j}\dfrac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = tr_{j'}\{e^{\frac{-i\tau}{\hbar}\hat{h}_{j'}}\hat{a}_{j'} e^{\frac{i\tau}{\hbar}\hat{h}_{j'}}\dfrac{e^{\frac{-1}{k_BT}(\hat{h}_{j'}-\mu\hat{N}_{j'})}}{Z_{j'}}\} = 0$

(see Ex. 20.5.1 (a)), we obtain $tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'} e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \delta_{j,j'} tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\dfrac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\}$,

and similarly, $tr_B\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \delta_{j,j'} tr_j\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\dfrac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\}$.

Consequently:

$$c_a(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{M_E}\gamma_j^*\gamma_{j'}tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$= \sum_{j,j'=1}^{M_E}\gamma_j^*\gamma_{j'}\delta_{j,j'}tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = \sum_{j=1}^{M_E}|\gamma_j|^2 tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} \ ,$$

$$c_e(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{M_E}\gamma_{j'}^*\gamma_j tr_B\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$= \sum_{j,j'=1}^{M_E}\gamma_{j'}^*\gamma_j\delta_{j,j'}tr_j\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = \sum_{j=1}^{M_E}|\gamma_j|^2 tr_j\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} .$$

Using the fermionic anticommutation relations, we obtain

$$\hat{a}_j^\dagger e^{\frac{\pm i\tau}{\hbar}\hat{h}_j} = \hat{a}_j^\dagger e^{\frac{\pm i\tau}{\hbar}\varepsilon_j\hat{a}_j^\dagger\hat{a}_j} = \hat{a}_j^\dagger\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{\pm i\tau}{\hbar}\varepsilon_j\right)^n(\hat{a}_j^\dagger\hat{a}_j)^n = \hat{a}_j^\dagger$$

and

$$\hat{a}_j e^{\frac{\pm i\tau}{\hbar}\hat{h}_j} = \hat{a}_j e^{\frac{\pm i\tau}{\hbar}\varepsilon_j\hat{a}_j^\dagger\hat{a}_j} = \hat{a}_j\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{\pm i\tau}{\hbar}\varepsilon_j\right)^n(\hat{a}_j^\dagger\hat{a}_j)^n = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{\pm i\tau}{\hbar}\varepsilon_j\right)^n\hat{a}_j(\hat{a}_j^\dagger\hat{a}_j)^n$$

$$= \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{\pm i\tau}{\hbar}\varepsilon_j\right)^n\hat{a}_j = \hat{a}_j e^{\frac{\pm i\tau}{\hbar}\varepsilon_j} .$$

Therefore,

$$c_a(\tau) = \sum_{j=1}^{M_E}|\gamma_j|^2 e^{\frac{i\tau}{\hbar}\varepsilon_j}tr_j\{\hat{a}_j^\dagger\hat{a}_j\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\}$$

and

$$c_e(\tau) = \sum_{j=1}^{M_E}|\gamma_j|^2\ e^{\frac{-i\tau}{\hbar}\varepsilon_j}tr_j\{\hat{a}_j\hat{a}_j^\dagger\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} .$$

For the explicit calculation of the traces, we recall the result of Ex. 20.3.1 (b) for the average thermal occupation numbers of electrons,

$$tr_j\{\hat{a}_j^\dagger\hat{a}_j\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = tr_j\{\hat{a}_j^\dagger\hat{a}_j\frac{e^{\frac{-1}{k_BT}(\varepsilon_j-\mu)\hat{a}_j^\dagger\hat{a}_j}}{Z_j}\} = \frac{1}{1+e^{\frac{1}{k_BT}(\varepsilon_j-\mu)}} \ ,$$

and consequently, for holes,

$$tr_j\{\hat{a}_j\hat{a}_j^\dagger \frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = tr_j\{\left(1-\hat{a}_j^\dagger\hat{a}_j\right)\frac{e^{\frac{-1}{k_BT}(\varepsilon_j-\mu)\hat{a}_j^\dagger\hat{a}_j}}{Z_j}\} = 1-\frac{1}{1+e^{\frac{1}{k_BT}(\varepsilon_j-\mu)}}.$$

Hence, the correlation functions read

$$c_a(\tau)=\sum_{j=1}^{M_E}|\gamma_j|^2\frac{e^{\frac{i\tau}{\hbar}\varepsilon_j}}{1+e^{\frac{1}{k_BT}(\varepsilon_j-\mu)}} \quad ; \quad c_e(\tau)=\sum_{j=1}^{M_E}|\gamma_j|^2\, e^{\frac{-i\tau}{\hbar}\varepsilon_j}\frac{e^{\frac{1}{k_BT}(\varepsilon_j-\mu)}}{1+e^{\frac{1}{k_BT}(\varepsilon_j-\mu)}}.$$

(b)

For a general system-bath coupling operator, $\hat{H}_{SB}\equiv\sum_\alpha \hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}$ *(Eq. (19.3.12)), the Redfield (Born-Markov) dissipator obtains the form of Eqs. (19.3.21, 19.3.22),* $\hat{D}\hat{\rho}_S(t)=$ $-\frac{1}{\hbar^2}\sum_{\alpha,\alpha'}\int_0^t d\tau\{c_{\alpha,\alpha'}(\tau)[\hat{V}_\alpha^{(S)},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+\bar{c}_{\alpha',\alpha}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{\alpha'}^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_\alpha^{(S)}]\}$ *where,* $c_{\alpha,\alpha'}(\tau)\equiv tr_B\{\hat{U}_\alpha^{(B)}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_{\alpha'}^{(B)}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$*, and* $\bar{c}_{\alpha,\alpha'}(\tau)=c_{\alpha,\alpha'}(-\tau)$.

Defining: $\hat{V}_S\equiv\hat{V}_1^{(S)}$, $\hat{U}_B\equiv\hat{U}_1^{(B)}$, $\hat{V}_S^\dagger\equiv\hat{V}_2^{(S)}$, $\hat{U}_B^\dagger\equiv\hat{U}_2^{(B)}$*, the system-bath coupling operator in Eq. (20.5.1) can be written as,* $\hat{H}_{SB}\equiv\hat{V}_S\hat{U}_B+\hat{V}_S^\dagger\hat{U}_B^\dagger=\hat{V}_1^{(S)}\hat{U}_1^{(B)}+\hat{V}_2^{(S)}\hat{U}_2^{(B)}$*. Using the general Redfield dissipator for* $\hat{H}_{SB}\equiv\sum_{\alpha=1}^{2}\hat{V}_\alpha^{(S)}\hat{U}_\alpha^{(B)}$ *(Eqs. (19.3.21, 19.3.22)), we obtain*

$$\begin{aligned}
&\hat{D}\hat{\rho}_S(t)=\\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,1}(\tau)[\hat{V}_1^{(S)},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+\bar{c}_{1,1}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_1^{(S)}]\}\\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_1^{(S)},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+\bar{c}_{2,1}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_1^{(S)}]\}\\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_2^{(S)},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+\bar{c}_{1,2}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_1^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_2^{(S)}]\}\\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,2}(\tau)[\hat{V}_2^{(S)},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+\bar{c}_{2,2}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_2^{(S)}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_2^{(S)}]\},
\end{aligned}$$

where,

$$c_{1,1}(\tau) \equiv tr_B\{\hat{U}_1^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_1^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$$

$$c_{1,2}(\tau) \equiv tr_B\{\hat{U}_1^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_2^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$$

$$c_{2,1}(\tau) \equiv tr_B\{\hat{U}_2^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_1^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$$

$$c_{2,2}(\tau) \equiv tr_B\{\hat{U}_1^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_1^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\} \ .$$

Using the mapping, $\hat{V}_S \equiv \hat{V}_1^{(S)}$, $\hat{U}_B \equiv \hat{U}_1^{(B)}$, $\hat{V}_S^\dagger \equiv \hat{V}_2^{(S)}$, $\hat{U}_B^\dagger \equiv \hat{U}_2^{(B)}$ *, we obtain*

$$\begin{aligned}
&\hat{D}\hat{\rho}_S(t) = \\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,1}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{1,1}(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\} \\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{2,1}(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\} \\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{1,2}(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \\
&-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,2}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{2,2}(\tau)[\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \ ,
\end{aligned}$$

where,

$$c_{1,1}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$$

$$c_{1,2}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$$

$$c_{2,1}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$$

$$c_{2,2}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\} .$$

Using the definitions in (a), we identify,

$$c_{1,2}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\} = c_e(\tau) \ \text{ and } \ c_{2,1}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\} = c_a(\tau) \, ,$$

where, using considerations like those applied in (a), the other correlation functions vanish,

$$c_{1,1}(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{M_E}\gamma_j\gamma_{j'}tr_B\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$= \sum_{j=1}^{M_E}\gamma_j^2 tr_j\{\hat{a}_j e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = \sum_{j=1}^{M_E}\gamma_j^2 tr_j\{e^{\frac{-i\tau}{\hbar}\varepsilon_j}\hat{a}_j\hat{a}_j e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = 0$$

$$c_{2,2}(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = \sum_{j,j'=1}^{M_E}\gamma_j^*\gamma_{j'}^* tr_B\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{a}_{j'}^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$$

$$= \sum_{j=1}^{M_E}(\gamma_j^*)^2 tr_j\{\hat{a}_j^\dagger e^{\frac{-i\tau}{\hbar}\hat{h}_j}\hat{a}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = \sum_{j=1}^{M_E}(\gamma_j^*)^2 tr_j\{\hat{a}_j^\dagger\hat{a}_j^\dagger e^{\frac{i\tau}{\hbar}\hat{h}_j}\frac{e^{\frac{-1}{k_BT}(\hat{h}_j-\mu\hat{N}_j)}}{Z_j}\} = 0 \ .$$

Hence,

$$\hat{D}\hat{\rho}_S(t) =$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{2,1}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + \overline{c}_{1,2}(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \ .$$

Using Eq. (19.3.21), we have $\overline{c}_{2,1}(\tau) = c_{2,1}(-\tau)$ *and* $\overline{c}_{1,2}(\tau) = c_{1,2}(-\tau)$. *Using* $tr\{\hat{O}\} = tr_B\{\hat{O}^\dagger\}^*$ *and cyclic permutations under the trace, we obtain*

$$c_{1,2}(-\tau) = tr_B\{\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = tr_B\{\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger\}^* = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}^* = c_{1,2}^*(\tau)$$
$$c_{2,1}(-\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\} = tr_B\{\hat{\rho}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B\}^* = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}^* = c_{2.1}^*(\tau) \ .$$

Hence,

$$\hat{D}\hat{\rho}_S(t) =$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{1,2}(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_{2.1}^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S]\}$$
$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_{2,1}(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_{1,2}^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_S^\dagger]\} \ .$$

(c)

Using the identities, $c_{1,2}(\tau)=c_e(\tau)$, $c_{2,1}(\tau)=c_a(\tau)$ *(see (b)), we can rewrite the result of (b) as,*

$$\hat{D}\hat{\rho}_S(t)=$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_e(\tau)[\hat{V}_S,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+c_a^*(\tau)(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_S]\}$$

$$-\frac{1}{\hbar^2}\int_0^t d\tau\{c_a(\tau)[\hat{V}_S^\dagger,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+c_e^*(\tau)[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_S^\dagger]\} \quad .$$

Identifying

$$[\hat{V}_S,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]^\dagger=[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_S^\dagger]$$

and

$$[\hat{V}_S^\dagger,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]^\dagger=[\hat{\rho}_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}_S],$$

we obtain the dissipator in Eq. (20.5.3),

$$\hat{D}\hat{\rho}_S(t)=-\frac{1}{\hbar^2}\int_0^t d\tau\{c_e(\tau)[\hat{V}_S,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+c_a(\tau)[\hat{V}_S^\dagger,e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]+h.c.\}.$$

Exercise 20.5.3 *Consider the adsorbate-electrode model, characterized by the single particle Hamiltonian in Eqs. (20.4.2, 20.4.3). The eigenvalues and eigenvectors of the single particle electrode Hamiltonian (corresponding to a linear uniform chain) are given by Eq. (20.4.4) (see also Eqs. (14.4.25, 14.4.26)) where the adsorbate-electrode coupling is restricted to the terminal electrode site and depends on the projections of the chain eigenvectors* ($\{|\chi_k\rangle\}$) *on the first electrode site, namely* $\gamma_k=\gamma\langle\varphi_1|\chi_k\rangle$ *(see Eq. (20.4.3)). Show that: (a)* $|\gamma_k|^2=2|\gamma|^2[1-\frac{(\varepsilon_k-\mu)^2}{4\beta^2}]/(M_E+1)$. *(b) The density of states for the linear chain model reads* $\rho(\varepsilon_k)\equiv\left.\frac{\partial n(\varepsilon)}{\partial\varepsilon}\right|_{\varepsilon=\varepsilon_k}\approx(M_E+1)/(\pi\sqrt{4\beta^2-(\varepsilon_k-\mu)^2})$. *(c) The respective spectral density of the adsorbate-electrode interaction (Eq. (20.5.5)) is given by Eq. (20.5.7).*

Solution 20.5.3

(a)

Using the explicit expression for the linear chain eigenvectors (Eq. (20.4.4)), $|\chi_n\rangle = \sum_{j=1}^{M_E} \sqrt{\frac{2}{M_E+1}} \sin(\frac{n\pi j}{M_E+1})|\varphi_j\rangle$, *the coupling matrix elements read* $\gamma_k = \gamma\langle\varphi_1|\chi_k\rangle = \gamma\sqrt{\frac{2}{M_E+1}}\sin(\frac{\pi k}{M_E+1})$.

Consequently, $|\gamma_k|^2 = |\gamma\langle\varphi_1|\chi_k\rangle|^2 = \frac{2|\gamma|^2}{M_E+1}\sin^2(\frac{k\pi}{M_E+1}) = \frac{2|\gamma|^2}{M_E+1}[1-\cos^2(\frac{k\pi}{M_E+1})]$.

Using the explicit expression for the linear chain eigenvalues (Eq. (20.4.4)), $\varepsilon_n = \mu + 2\beta\cos(\frac{n\pi}{M_E+1})$, *we obtain* $|\gamma_k|^2 = \frac{2|\gamma|^2}{M_E+1}[1-\cos^2(\frac{k\pi}{M_E+1})] = \frac{2|\gamma|^2}{M_E+1}[1-\frac{(\varepsilon_k-\mu)^2}{4\beta^2}]$.

(b)

For the linear chain model with $\varepsilon_n = \mu + 2\beta\cos(\frac{n\pi}{M_E+1})$ *and* $\beta < 0$, *the number of states up to an energy,* ε, *in an interval* $\varepsilon_n < \varepsilon < \varepsilon_{n+1}$ *is* n, *namely* $n(\varepsilon) = \frac{M_E+1}{\pi} arc\cos[\frac{\varepsilon-\mu}{2\beta}]$. *For sufficiently large* M_E *we can regard the energy as a continuous variable to obtain*

$$\rho(\varepsilon) = \frac{d}{d\varepsilon}n(\varepsilon) = \frac{M_E+1}{\pi}\frac{d}{d\varepsilon}arc\cos(\frac{\varepsilon-\mu}{2\beta}) = \frac{M_E+1}{\pi}\frac{-1}{\sqrt{1-(\frac{\varepsilon-\mu}{2\beta})^2}}\frac{1}{2\beta}$$

$$= \frac{M_E+1}{\pi}\frac{1}{\sqrt{1-(\frac{\varepsilon-\mu}{2\beta})^2}}\frac{1}{2|\beta|} = \frac{M_E+1}{\pi}\frac{1}{\sqrt{4\beta^2-(\varepsilon-\mu)^2}} \quad .$$

(c)

Using the definition of the spectral density, $J(\varepsilon) \equiv 2\pi\gamma^2(\varepsilon)\rho(\varepsilon)$, *with (see (a) and (b)),* $\gamma^2(\varepsilon_k) = |\gamma_k|^2 = \frac{2|\gamma|^2}{M_E+1}[1-\frac{(\varepsilon_k-\mu)^2}{4\beta^2}]$, *and* $\rho(\varepsilon_k) = \frac{M_E+1}{\pi}\frac{1}{\sqrt{4\beta^2-(\varepsilon-\mu)^2}}$, *we obtain Eq. (20.5.7),*

$$J(\varepsilon_k) \equiv 2\pi\frac{2|\gamma|^2}{M_E+1}[1-\frac{(\varepsilon_k-\mu)^2}{4\beta^2}]\frac{M_E+1}{\pi}\frac{1}{\sqrt{4\beta^2-(\varepsilon-\mu)^2}} = \frac{|\gamma|^2}{\beta^2}\sqrt{4\beta^2-(\varepsilon_k-\mu)^2} .$$

Exercise 20.5.4 *Show that the matrix representation of Eq. (20.5.8) in the basis of the system Hamiltonian eigenstates (Eq. (20.5.9)) is given by Eqs. (20.5.11, 20.5.12).*

Solution 20.5.4

Starting from the reduced equation, Eq. (20.5.8),

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}_S(t)]$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\} ,$$

we introduce a complete orthonormal set of $\hat{H}_S$ *-eigenstates,* $\hat{H}_S|\Psi_m\rangle = E_m|\Psi_m\rangle$ *(Eq. (20.5.9)). The corresponding equation for the matrix elements,* $[\hat{\rho}_S(t)]_{n',n} = \langle\Psi_{n'}|\hat{\rho}_S(t)|\Psi_n\rangle$*, in terms of the matrix representations of the system operators,* $[\hat{V}_S]_{n',n} = \langle\Psi_{n'}|\hat{V}_S|\Psi_n\rangle$ *reads*

$$\frac{\partial}{\partial t}[\hat{\rho}_S(t)]_{n',n} \cong -\frac{i}{\hbar}[E_{n'}-E_n][\hat{\rho}_S(t)]_{n',n}$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)\Bigg(\sum_{k,m'}[\hat{V}_S]_{n',k}e^{\frac{-i\tau}{\hbar}E_k}[\hat{V}_S^\dagger]_{k,m'}e^{\frac{i\tau}{\hbar}E_{m'}}[\hat{\rho}_S(t)]_{m',n}$$
$$-\sum_{m,m'}e^{\frac{-i\tau}{\hbar}E_{n'}}[\hat{V}_S^\dagger]_{n',m'}e^{\frac{i\tau}{\hbar}E_{m'}}[\hat{\rho}_S(t)]_{m',m}[\hat{V}_S]_{m,n}\Bigg)$$
$$+c_a(\tau)\Bigg(\sum_{k,m'}[\hat{V}_S^\dagger]_{n',k}e^{\frac{-i\tau}{\hbar}E_k}[\hat{V}_S]_{k,m'}e^{\frac{i\tau}{\hbar}E_{m'}}[\hat{\rho}_S(t)]_{m',n}$$
$$-\sum_{m,m'}e^{\frac{-i\tau}{\hbar}E_{n'}}[\hat{V}_S]_{n'm'}e^{\frac{i\tau}{\hbar}E_{m'}}[\hat{\rho}_S(t)]_{m',m}[\hat{V}_S^\dagger]_{m,n}\Bigg)+[h.c.]_{n',n}\}$$
$$\equiv -\frac{i}{\hbar}[E_{n'}-E_n][\hat{\rho}_S(t)]_{n',n} + B_{n',n} + B^*_{n,n'} ,$$

where,

$$B_{n',n} = -\frac{1}{\hbar^2}\int_0^\infty d\tau$$
$$\{c_e(\tau)\left(\sum_{k,m'} \left[\hat{V}_S\right]_{n',k} e^{\frac{-i\tau}{\hbar}E_k} \left[\hat{V}_S^\dagger\right]_{k,m'} e^{\frac{i\tau}{\hbar}E_{m'}} \left[\hat{\rho}_S(t)\right]_{m',n}\right.$$
$$\left.-\sum_{m,m'} e^{\frac{-i\tau}{\hbar}E_{n'}} \left[\hat{V}_S^\dagger\right]_{n',m'} e^{\frac{i\tau}{\hbar}E_{m'}} \left[\hat{\rho}_S(t)\right]_{m',m} \left[\hat{V}_S\right]_{m,n}\right)$$
$$+c_a(\tau)\left(\sum_{k,m'} \left[\hat{V}_S^\dagger\right]_{n',k} e^{\frac{-i\tau}{\hbar}E_k} \left[\hat{V}_S\right]_{k,m'} e^{\frac{i\tau}{\hbar}E_{m'}} \left[\hat{\rho}_S(t)\right]_{m',n}\right.$$
$$\left.-\sum_{m,m'} e^{\frac{-i\tau}{\hbar}E_{n'}} \left[\hat{V}_S\right]_{n'm'} e^{\frac{i\tau}{\hbar}E_{m'}} \left[\hat{\rho}_S(t)\right]_{m',m} \left[\hat{V}_S^\dagger\right]_{m,n}\right)\}$$

$$= -\frac{1}{\hbar^2}\int_0^\infty d\tau$$
$$\{c_e(\tau)\left(\sum_{k,m,m'} e^{\frac{-i\tau}{\hbar}(E_k - E_{m'})} \left[\hat{V}_S\right]_{n',k} \left[\hat{V}_S^\dagger\right]_{k,m'} \delta_{m,n} \left[\hat{\rho}_S(t)\right]_{m',m}\right.$$
$$\left.-\sum_{m,m'} e^{\frac{-i\tau}{\hbar}(E_{n'} - E_{m'})} \left[\hat{V}_S^\dagger\right]_{n',m'} \left[\hat{\rho}_S(t)\right]_{m',m} \left[\hat{V}_S\right]_{m,n}\right)$$
$$+c_a(\tau)\left(\sum_{k,m,m'} e^{\frac{-i\tau}{\hbar}(E_k - E_{m'})} \left[\hat{V}_S^\dagger\right]_{n',k} \left[\hat{V}_S\right]_{k,m'} \delta_{m,n} \left[\hat{\rho}_S(t)\right]_{m',m}\right.$$
$$\left.-\sum_{m,m'} e^{\frac{-i\tau}{\hbar}(E_{n'} - E_{m'})} \left[\hat{V}_S\right]_{n'm'} \left[\hat{\rho}_S(t)\right]_{m',m} \left[\hat{V}_S^\dagger\right]_{m,n}\right)\}$$

$$= \sum_{m,m'} \left(-\frac{\delta_{m,n}}{\hbar^2}\sum_k \int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_k - E_{m'})} \left(c_e(\tau)\left[\hat{V}_S\right]_{n',k}\left[\hat{V}_S^\dagger\right]_{k,m'} + c_a(\tau)\left[\hat{V}_S^\dagger\right]_{n',k}\left[\hat{V}_S\right]_{k,m'}\right)\right.$$
$$\left.+\frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_{n'} - E_{m'})} \left(c_e(\tau)\left[\hat{V}_S^\dagger\right]_{n',m'}\left[\hat{V}_S\right]_{m,n} + c_a(\tau)\left[\hat{V}_S\right]_{n'm'}\left[\hat{V}_S^\dagger\right]_{m,n}\right)\right)\left[\hat{\rho}_S(t)\right]_{m',m} \quad .$$

Defining,

$$A_{n',n,m',m} \equiv \delta_{m,n}\sum_k \frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_k - E_{m'})} \left(c_e(\tau)\left[\hat{V}_S\right]_{n',k}\left[\hat{V}_S^\dagger\right]_{k,m'} + c_a(\tau)\left[\hat{V}_S^\dagger\right]_{n',k}\left[\hat{V}_S\right]_{k,m'}\right)$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_{n'} - E_{m'})} \left(c_e(\tau)\left[\hat{V}_S^\dagger\right]_{n',m'}\left[\hat{V}_S\right]_{m,n} + c_a(\tau)\left[\hat{V}_S\right]_{n',m'}\left[\hat{V}_S^\dagger\right]_{m,n}\right),$$

we obtain, $B_{n',n} = -\sum_{m,m'} A_{n',n,m',m}\left[\hat{\rho}_S(t)\right]_{m',m}$, *and therefore,*

$$\frac{\partial}{\partial t}\left[\hat{\rho}_S(t)\right]_{n',n} \cong -\frac{i}{\hbar}[E_{n'}-E_n]\left[\hat{\rho}_S(t)\right]_{n',n} - \sum_{m,m'} A_{n',n,m',m}\left[\hat{\rho}_S(t)\right]_{m',m} - \sum_{m,m'} A^*_{n,n',m',m}\left[\hat{\rho}_S(t)\right]_{m,m'}$$

$$= -\frac{i}{\hbar}[E_{n'}-E_n]\left[\hat{\rho}_S(t)\right]_{n',n} - \sum_{m,m'} A_{n',n,m',m}\left[\hat{\rho}_S(t)\right]_{m',m} - \sum_{m',m} A^*_{n,n',m,m'}\left[\hat{\rho}_S(t)\right]_{m',m}$$

$$= -\frac{i}{\hbar}[E_{n'}-E_n]\left[\hat{\rho}_S(t)\right]_{n',n} - \sum_{m,m'} \left(A_{n',n,m',m} + A^*_{n,n',m,m'}\right)\left[\hat{\rho}_S(t)\right]_{m',m} \quad .$$

Exercise 20.5.5 *Show that setting the coherences of the reduced density matrix to zero in Eqs. (20.5.11, 20.5.12) leads to Eq. (20.5.13).*

Solution 20.5.5

Starting from Eqs. (20.5.11),

$$\frac{\partial}{\partial t}\left[\hat{\rho}_S(t)\right]_{n',n} \cong -\frac{i}{\hbar}(E_{n'}-E_n)\left[\hat{\rho}_S(t)\right]_{n',n} - \sum_{m',m}\left(A_{n',n,m',m} + A^*_{n,n',m,m'}\right)\left[\hat{\rho}_S(t)\right]_{m',m},$$

and setting the coherences to zero, $\left[\hat{\rho}_S(t)\right]_{m',m} \cong \left[\hat{\rho}_S(t)\right]_{m,m}\delta_{m,m'}$*, we obtain*

$$\frac{\partial}{\partial t}\left[\hat{\rho}_S(t)\right]_{n,n} \cong -\sum_m\left(A_{n,n,m,m} + A^*_{n,n,m,m}\right)\left[\hat{\rho}_S(t)\right]_{m,m} = -\sum_m 2\,\mathrm{Re}\left(A_{n,n,m,m}\right)\left[\hat{\rho}_S(t)\right]_{m,m}.$$

Using Eq. (20.5.12) for $A_{n',n,m',m}$*, we obtain*

$$A_{n,n,m,m} = \delta_{m,n}\sum_k \frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_k-E_m)}\{c_e(\tau)\left[\hat{V}_S\right]_{n,k}\left[\hat{V}_S^\dagger\right]_{k,m} + c_a(\tau)\left[\hat{V}_S^\dagger\right]_{n,k}\left[\hat{V}_S\right]_{k,m}\}$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_n-E_m)}\{c_e(\tau)\left[\hat{V}_S^\dagger\right]_{n,m}\left[\hat{V}_S\right]_{m,n} + c_a(\tau)\left[\hat{V}_S\right]_{n,m}\left[\hat{V}_S^\dagger\right]_{m,n}\}$$

$$= \delta_{m,n}\frac{1}{\hbar^2}\sum_k\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_k-E_n)}\{c_e(\tau)\left|\left[\hat{V}_S\right]_{n,k}\right|^2 + c_a(\tau)\left|\left[\hat{V}_S^\dagger\right]_{n,k}\right|^2\}$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_n-E_m)}\{c_e(\tau)\left|\left[\hat{V}_S\right]_{m,n}\right|^2 + c_a(\tau)\left|\left[\hat{V}_S^\dagger\right]_{m,n}\right|^2\},$$

and therefore,

$$\frac{\partial}{\partial t}[\hat{\rho}_S(t)]_{n,n} \cong$$

$$-\sum_k \left(\left|\left[\hat{V}_S\right]_{n,k}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_k-E_n)} c_e(\tau) + \left|\left[\hat{V}_S^\dagger\right]_{n,k}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_k-E_n)} c_a(\tau)\right)[\hat{\rho}_S(t)]_{n,n}$$

$$+\sum_m \left(\left|\left[\hat{V}_S\right]_{m,n}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_n-E_m)} c_e(\tau) + \left|\left[\hat{V}_S^\dagger\right]_{m,n}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_n-E_m)} c_a(\tau)\right)[\hat{\rho}_S(t)]_{m,m}$$

$$=-\sum_{n'} \left(\left|\left[\hat{V}_S\right]_{n,n'}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_{n'}-E_n)} c_e(\tau) + \left|\left[\hat{V}_S^\dagger\right]_{n,n'}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_{n'}-E_n)} c_a(\tau)\right)[\hat{\rho}_S(t)]_{n,n}$$

$$+\sum_{n'} \left(\left|\left[\hat{V}_S\right]_{n',n}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_n-E_{n'})} c_e(\tau) + \left|\left[\hat{V}_S^\dagger\right]_{n',n}\right|^2 \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_n-E_{n'})} c_a(\tau)\right)[\hat{\rho}_S(t)]_{n',n'} \ .$$

Recalling the expressions for the correlation functions in terms of the continuous reservoir spectral density (Eq. (20.5.6)), $c_a(\tau)=\frac{1}{2\pi}\int d\varepsilon e^{i\tau\varepsilon/\hbar}J(\varepsilon)f_e(\varepsilon)$; $c_e(\tau)=\frac{1}{2\pi}\int d\varepsilon e^{-i\tau\varepsilon/\hbar}J(\varepsilon)f_h(\varepsilon)$, *we obtain*

$$\frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_{n'}-E_n)} c_e(\tau) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau \frac{1}{2\pi}\int d\varepsilon e^{\frac{-i\tau}{\hbar}(E_{n'}-E_n)} e^{-i\tau\varepsilon/\hbar}J(\varepsilon)f_h(\varepsilon)$$

$$=\frac{1}{\hbar^2}\mathrm{Re}\int d\varepsilon\int_{-\infty}^\infty d\tau\frac{1}{2\pi}e^{\frac{-i\tau}{\hbar}(\varepsilon+E_{n'}-E_n)}J(\varepsilon)f_h(\varepsilon)=\frac{1}{\hbar}\int d\varepsilon\delta(\varepsilon+E_{n'}-E_n)J(\varepsilon)f_h(\varepsilon)$$

$$=\frac{1}{\hbar}J(E_n-E_{n'})f_h(E_n-E_{n'})$$

and

$$\frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(E_{n'}-E_n)} c_a(\tau) = \frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty d\tau \frac{1}{2\pi}\int d\varepsilon e^{\frac{-i\tau}{\hbar}(E_{n'}-E_n)} e^{i\tau\varepsilon/\hbar}J(\varepsilon)f_e(\varepsilon)$$

$$=\frac{1}{\hbar^2}\mathrm{Re}\int d\varepsilon\int_{-\infty}^\infty d\tau\frac{1}{2\pi}e^{\frac{-i\tau}{\hbar}(-\varepsilon+E_{n'}-E_n)}J(\varepsilon)f_e(\varepsilon)=\frac{1}{\hbar}\int d\varepsilon\delta(-\varepsilon+E_{n'}-E_n)J(\varepsilon)f_e(\varepsilon)$$

$$=\frac{1}{\hbar}J(E_{n'}-E_n)f_e(E_{n'}-E_n)\,.$$

Consequently,

$$\frac{\partial}{\partial t}[\hat{\rho}_S(t)]_{n,n} \cong$$

$$-\sum_{n'}\left(\left|\left[\hat{V}_S\right]_{n,n'}\right|^2 \frac{1}{\hbar}J(E_n-E_{n'})f_h(E_n-E_{n'}) + \left|\left[\hat{V}_S^\dagger\right]_{n,n'}\right|^2 \frac{1}{\hbar}J(E_{n'}-E_n)f_e(E_{n'}-E_n)\right)[\hat{\rho}_S(t)]_{n,n}$$

$$+\sum_{n'}\left(\left|\left[\hat{V}_S\right]_{n',n}\right|^2\frac{1}{\hbar}J(E_{n'}-E_n)f_h(E_{n'}-E_n)+\left|\left[\hat{V}_S^{\dagger}\right]_{n',n}\right|^2\frac{1}{\hbar}J(E_n-E_{n'})f_e(E_n-E_{n'})\right)\left[\hat{\rho}_S(t)\right]_{n',n'}.$$

Defining, $P_n(t)\equiv\left[\hat{\rho}_S(t)\right]_{n,n}$ *and*

$$k_{n\to n'}\equiv\left|\left[\hat{V}_S\right]_{n,n'}\right|^2\frac{1}{\hbar}J(E_n-E_{n'})f_h(E_n-E_{n'})+\left|\left[\hat{V}_S^{\dagger}\right]_{n,n'}\right|^2\frac{1}{\hbar}J(E_{n'}-E_n)f_e(E_{n'}-E_n),$$

we obtain the master equation for the system eigenstate populations (Eq. (20.5.13)),

$$\frac{\partial}{\partial t}P_n(t)\cong-\sum_{n'}k_{n\to n'}P_n(t)+\sum_{n'}k_{n'\to n}P_{n'}(t).$$

Exercise 20.5.6 *The adsorbate-electrode Hamiltonian can be conveniently split into zero order and perturbation Hamiltonians,* $\hat{H}=\hat{H}_0+\hat{V}$, *where,* $\hat{H}_0=\hat{H}_S+\hat{H}_B$, *and* $\hat{V}=\hat{H}_{SB}$ *(see Eq. (20.5.1)). Using Eq. (20.5.9), the eigenvectors of* $\hat{H}_0$ *are defined by the equation,* $\hat{H}_0\left|\Psi_n\right\rangle\otimes\left|n_1,n_2,....,n_{M_E}\right\rangle=(E_n+\sum_{k=1}^{M_E}n_k\varepsilon_k)\left|\Psi_n\right\rangle\otimes\left|n_1,n_2,....,n_{M_E}\right\rangle$. *A charge transfer event between the electrode and the adsorbate can be formulated as a transition between incoherent ensembles of (orthogonal)* $\hat{H}_0$ *eigenstates, where the initial and final states are defined, respectively, by projection operators to the initial and final system Hamiltonian eigenstates,* $\hat{P}_{\{i\}}=\left|\Psi_n\right\rangle\left\langle\Psi_n\right|$, *and* $\hat{P}_{\{f\}}=\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|$. *In the weak molecule-electrode coupling limit, the charge transfer rate can be evaluated by Fermi's golden rule (see chapter 17), where the electrode is initially in a thermal state,* $\hat{\rho}_{\{i\}}(0)=\left|\Psi_n\right\rangle\left\langle\Psi_n\right|\otimes\hat{\rho}_B$. *Starting from the generic perturbative rate expression (Eq. (17.3.12)),* $k^{(1)}_{\{i\}\to\{f\}}(t)\cong\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$, *and using Eq. (20.5.4) for the bath correlation functions, show that the transition rates appearing in the master equation are reproduced at the infinite time limit (under fast bath relaxation assumption), namely* $k_{n\to n'}=\lim_{t\to\infty}k^{(1)}_{\{i\}\to\{f\}}(t)$.

Solution 20.5.6

Identifying the uncoupled system and bath as a zero-order Hamiltonian, $\hat{H}_0\equiv\hat{H}_S+\hat{H}_B$ *with* $\hat{H}_S=\sum_{m=1}^{M_A}\varepsilon_m\hat{a}_m^{\dagger}\hat{a}_m+\sum_{i,j,k,l\in\{m\}}w_{i,j,k,l}\hat{a}_i^{\dagger}\hat{a}_j^{\dagger}\hat{a}_l\hat{a}_k$, *and* $\hat{H}_B=\sum_{k=1}^{M_E}\varepsilon_k\hat{a}_k^{\dagger}\hat{a}_k$, *where,*

$\hat{H}_0\left|\Psi_n\right\rangle\otimes\left|n_1,n_2,....,n_{M_E}\right\rangle=(E_n+\sum_{k=1}^{M_E}n_k\varepsilon_k)\left|\Psi_n\right\rangle\otimes\left|n_1,n_2,....,n_{M_E}\right\rangle$, *we introduce projection operators into ensembles of* $\hat{H}_0$*-eigenstates, characterized by specific system eigenstates,* $\hat{P}_{\{i\}}\equiv\left|\Psi_n\right\rangle\left\langle\Psi_n\right|$ *and* $\hat{P}_{\{f\}}\equiv\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|$.

The initial and final ensembles are coupled by the system-bath interaction, which reads $\hat{V}\equiv\hat{H}_{SB}=\hat{V}_S\otimes\hat{U}_B+\hat{V}_S^\dagger\otimes\hat{U}_B^\dagger$, *with* $\hat{V}_S\equiv\sum_{m=1}^{M_A}\nu_m\hat{a}_m^\dagger$ *and* $\hat{U}_B\equiv\sum_{k=1}^{M_E}\gamma_k\hat{a}_k$.

Assuming an initial thermal state of the bath, the initial density reads

$$\hat{\rho}_{\{i\}}(0)\equiv\hat{P}_{\{i\}}\otimes\hat{\rho}_B=\left|\Psi_n\right\rangle\left\langle\Psi_n\right|\otimes\hat{\rho}_B=\left|\Psi_n\right\rangle\left\langle\Psi_n\right|\otimes\frac{1}{Z}e^{\frac{-1}{k_BT}\sum_{k=1}^{M_E}(\varepsilon_k-\mu)\hat{a}_k^\dagger\hat{a}_k} .$$

The transition rate to the final system eigenstate in the weak coupling limit is given by the approximation (Eq. (17.3.12)), $k_{n\to n'}^{(1)}(t)\cong\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$.

Substituting the relevant operators, we obtain in this case

$$k_{\{i\}\to\{f\}}^{(1)}(t)\cong\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\hat{\rho}_{\{i\}}(0)\hat{P}_{\{i\}}\hat{V}\hat{P}_{\{f\}}e^{\frac{i\hat{H}_0\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_0\tau}{\hbar}}\}d\tau$$
$$=\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr\{\left|\Psi_n\right\rangle\left\langle\Psi_n\right|\otimes\hat{\rho}_B\left|\Psi_n\right\rangle\left\langle\Psi_n\right|\hat{V}\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|e^{\frac{i\hat{H}_S\tau}{\hbar}}e^{\frac{i\hat{H}_B\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_S\tau}{\hbar}}e^{\frac{-i\hat{H}_B\tau}{\hbar}}\}d\tau$$
$$=\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr_B\{\hat{\rho}_B\left\langle\Psi_n\right|\hat{V}\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|e^{\frac{i\hat{H}_S\tau}{\hbar}}e^{\frac{i\hat{H}_B\tau}{\hbar}}\hat{V}e^{\frac{-i\hat{H}_S\tau}{\hbar}}e^{\frac{-i\hat{H}_B\tau}{\hbar}}\left|\Psi_n\right\rangle\}d\tau$$
$$=\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr_B\{\hat{\rho}_B\left\langle\Psi_n\right|\hat{V}_S\otimes\hat{U}_B\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|e^{\frac{i\hat{H}_S\tau}{\hbar}}e^{\frac{i\hat{H}_B\tau}{\hbar}}\hat{V}_S\otimes\hat{U}_Be^{\frac{-i\hat{H}_S\tau}{\hbar}}e^{\frac{-i\hat{H}_B\tau}{\hbar}}\left|\Psi_n\right\rangle\}d\tau$$
$$+\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr_B\{\hat{\rho}_B\left\langle\Psi_n\right|\hat{V}_S\otimes\hat{U}_B\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|e^{\frac{i\hat{H}_S\tau}{\hbar}}e^{\frac{i\hat{H}_B\tau}{\hbar}}\hat{V}_S^\dagger\otimes\hat{U}_B^\dagger e^{\frac{-i\hat{H}_S\tau}{\hbar}}e^{\frac{-i\hat{H}_B\tau}{\hbar}}\left|\Psi_n\right\rangle\}d\tau$$
$$+\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr_B\{\hat{\rho}_B\left\langle\Psi_n\right|\hat{V}_S^\dagger\otimes\hat{U}_B^\dagger\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|e^{\frac{i\hat{H}_S\tau}{\hbar}}e^{\frac{i\hat{H}_B\tau}{\hbar}}\hat{V}_S\otimes\hat{U}_Be^{\frac{-i\hat{H}_S\tau}{\hbar}}e^{\frac{-i\hat{H}_B\tau}{\hbar}}\left|\Psi_n\right\rangle\}d\tau$$
$$+\frac{2}{\hbar^2}\mathrm{Re}\int_0^t tr_B\{\hat{\rho}_B\left\langle\Psi_n\right|\hat{V}_S^\dagger\otimes\hat{U}_B^\dagger\left|\Psi_{n'}\right\rangle\left\langle\Psi_{n'}\right|e^{\frac{i\hat{H}_S\tau}{\hbar}}e^{\frac{i\hat{H}_B\tau}{\hbar}}\hat{V}_S^\dagger\otimes\hat{U}_B^\dagger e^{\frac{-i\hat{H}_S\tau}{\hbar}}e^{\frac{-i\hat{H}_B\tau}{\hbar}}\left|\Psi_n\right\rangle\}d\tau$$

$$= \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \; tr_B \{ \hat{\rho}_B \hat{U}_B e^{\frac{i\hat{H}_B \tau}{\hbar}} \hat{U}_B e^{\frac{-i\hat{H}_B \tau}{\hbar}} \} \langle \Psi_n | \hat{V}_S \, | \Psi_{n'} \rangle \langle \Psi_{n'} | e^{\frac{i\hat{H}_S \tau}{\hbar}} \hat{V}_S \, e^{\frac{-i\hat{H}_S \tau}{\hbar}} | \Psi_n \rangle d\tau$$
$$+ \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \; tr_B \{ \hat{\rho}_B \hat{U}_B e^{\frac{i\hat{H}_B \tau}{\hbar}} \hat{U}_B^\dagger e^{\frac{-i\hat{H}_B \tau}{\hbar}} \} \langle \Psi_n | \hat{V}_S \, | \Psi_{n'} \rangle \langle \Psi_{n'} | e^{\frac{i\hat{H}_S \tau}{\hbar}} \hat{V}_S^\dagger e^{\frac{-i\hat{H}_S \tau}{\hbar}} | \Psi_n \rangle d\tau$$
$$+ \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \; tr_B \{ \hat{\rho}_B \hat{U}_B^\dagger e^{\frac{i\hat{H}_B \tau}{\hbar}} \hat{U}_B e^{\frac{-i\hat{H}_B \tau}{\hbar}} \} \langle \Psi_n | \hat{V}_S^\dagger | \Psi_{n'} \rangle \langle \Psi_{n'} | e^{\frac{i\hat{H}_S \tau}{\hbar}} \hat{V}_S \, e^{\frac{-i\hat{H}_S \tau}{\hbar}} | \Psi_n \rangle d\tau$$
$$+ \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \; tr_B \{ \hat{\rho}_B \hat{U}_B^\dagger e^{\frac{i\hat{H}_B \tau}{\hbar}} \hat{U}_B^\dagger e^{\frac{-i\hat{H}_B \tau}{\hbar}} \} \langle \Psi_n | \hat{V}_S^\dagger | \Psi_{n'} \rangle \langle \Psi_{n'} | e^{\frac{i\hat{H}_S \tau}{\hbar}} \hat{V}_S^\dagger e^{\frac{-i\hat{H}_S \tau}{\hbar}} | \Psi_n \rangle d\tau \quad .$$

Identifying the correlation functions for the fermion reservoir (Eqs. (20.5.4, 20.5.6) and Ex. 20.5.2), we have

$$tr_B \{ \hat{\rho}_B \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \} = c_a(-\tau) = \frac{1}{2\pi} \int d\varepsilon e^{-i\tau\varepsilon/\hbar} J(\varepsilon) f_e(\varepsilon)$$
$$tr_B \{ \hat{\rho}_B \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \} = c_e(-\tau) = \frac{1}{2\pi} \int d\varepsilon e^{i\tau\varepsilon/\hbar} J(\varepsilon) f_h(\varepsilon)$$
$$tr_B \{ \hat{\rho}_B \hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B} \} = tr_B \{ \hat{\rho}_B \hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B} \} = 0 \quad .$$

Therefore,

$$k^{(1)}_{\{i\}\to\{f\}}(t)$$
$$= \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \; \frac{1}{2\pi} \int d\varepsilon e^{i\tau\varepsilon/\hbar} J(\varepsilon) f_h(\varepsilon) \langle \Psi_n | \hat{V}_S \, | \Psi_{n'} \rangle \langle \Psi_{n'} | e^{\frac{i\hat{H}_S \tau}{\hbar}} \hat{V}_S^\dagger e^{\frac{-i\hat{H}_S \tau}{\hbar}} | \Psi_n \rangle d\tau$$
$$+ \frac{2}{\hbar^2} \mathrm{Re} \int_0^t \; \frac{1}{2\pi} \int d\varepsilon e^{-i\tau\varepsilon/\hbar} J(\varepsilon) f_e(\varepsilon) \langle \Psi_n | \hat{V}_S^\dagger | \Psi_{n'} \rangle \langle \Psi_{n'} | e^{\frac{i\hat{H}_S \tau}{\hbar}} \hat{V}_S \, e^{\frac{-i\hat{H}_S \tau}{\hbar}} | \Psi_n \rangle d\tau$$
$$= \frac{2}{\hbar^2} \int_0^t \mathrm{Re} \frac{1}{2\pi} \int d\varepsilon e^{\frac{i(E_{n'} - E_n + \varepsilon)\tau}{\hbar}} J(\varepsilon) f_h(\varepsilon) \, | \langle \Psi_n | \hat{V}_S \, | \Psi_{n'} \rangle |^2 \, d\tau$$
$$+ \frac{2}{\hbar^2} \int_0^t \mathrm{Re} \frac{1}{2\pi} \int d\varepsilon e^{\frac{i(E_{n'} - E_n - \varepsilon)\tau}{\hbar}} J(\varepsilon) f_e(\varepsilon) \, | \langle \Psi_{n'} | \hat{V}_S \, | \Psi_n \rangle |^2 \, d\tau \quad .$$

Under fast bath relaxation assumption, we associate the rate with the infinite time limit, $k_{n\to n'} = \lim_{t\to\infty} k^{(1)}_{\{i\}\to\{f\}}(t)$. *Noticing that the time integrand is an even function of time, we obtain*

$$
\begin{aligned}
k_{n\to n'} &= \lim_{t\to\infty} k^{(1)}_{\{i\}\to\{f\}}(t) \\
&= \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{Re}\frac{1}{2\pi}\int d\varepsilon e^{\frac{i(E_{n'}-E_n+\varepsilon)\tau}{\hbar}} J(\varepsilon) f_h(\varepsilon) |\langle \Psi_n | \hat{V}_S | \Psi_{n'}\rangle|^2 \, d\tau \\
&+ \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{Re}\frac{1}{2\pi}\int d\varepsilon e^{\frac{i(E_{n'}-E_n-\varepsilon)\tau}{\hbar}} J(\varepsilon) f_e(\varepsilon) |\langle \Psi_{n'} | \hat{V}_S | \Psi_{n}\rangle|^2 \, d\tau \\
&= \frac{1}{\hbar}\int d\varepsilon \delta(E_{n'}-E_n+\varepsilon) J(\varepsilon) f_h(\varepsilon) |\langle \Psi_n | \hat{V}_S | \Psi_{n'}\rangle|^2 \\
&+ \frac{1}{\hbar}\int d\varepsilon \delta(E_{n'}-E_n-\varepsilon) J(\varepsilon) f_e(\varepsilon) |\langle \Psi_{n'} | \hat{V}_S | \Psi_{n}\rangle|^2 \ .
\end{aligned}
$$

Hence,

$$
k_{n\to n'} = |\langle \Psi_n | \hat{V}_S | \Psi_{n'}\rangle|^2 \frac{1}{\hbar} J(E_n - E_{n'}) f_h(E_n - E_{n'}) + |\langle \Psi_{n'} | \hat{V}_S | \Psi_{n}\rangle|^2 \frac{1}{\hbar} J(E_{n'} - E_n) f_e(E_{n'} - E_n) .
$$

The Fermi golden rule result is therefore shown to coincide precisely with the rates appearing in the master equation as obtained within the stationary Born-Markov and secular approximations (Eq. (20.5.13)).

Exercise 20.5.7 *In the absence of electron-electron interaction, the system Hamiltonian in Eq. (20.5.1) reads* $\hat{H}_S = \sum_{m=1}^{M_A} \varepsilon_m \hat{a}_m^\dagger \hat{a}_m$*. (a) Show that the eigenvectors of* $\hat{H}_S$ *in this case are the* M_A*-particle determinants,* $\{ |n_1, n_2, n_3, ..., n_{M_A}\rangle \}$ *(defined in Eqs. (20.1.3, 20.1.7)), with the corresponding eigenvalues,* $\{\sum_{m=1}^{M_A} \varepsilon_m n_m\}$*, where* $\{\varepsilon_m\}$ *are the single particle Hamiltonian eigenstates. (b) Denoting each eigenstate by the vector of occupation numbers,* $|n_1, n_2, n_3, ..., n_{M_A}\rangle \Leftrightarrow \mathbf{n}$ *and using the system-bath coupling (*$\hat{V}_S$*) in Eq. (20.5.1), show that the transition rate between nondegenerate* $\hat{H}_S$ *eigenvectors (Eq. (20.5.13)) reads in this case* $k_{\mathbf{n}\to\mathbf{n}'} = \sum_{m=1}^{M_A} [\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{a,m}]$*, where* $\mathbf{e}_m$ *is a unit vector of length* M_A *with elements* $[\mathbf{e}_m]_{m'} = \delta_{m,m'}$*. Here* $k_{e,m} \equiv |\nu_m|^2 \frac{J(\varepsilon_m)}{\hbar} f_h(\varepsilon_m)$ *and* $k_{a,m} \equiv |\nu_m|^2 \frac{J(\varepsilon_m)}{\hbar} f_e(\varepsilon_m)$ *are rates of single-electron emission to the reservoir, or absorption from the reservoir. Notice that the rate vanishes unless the two occupation vectors are identical except of a* *flip between zero and one at the m th entry, which corresponds to either absorption or emission of a single electron at m th single particle state.*

Solution 20.5.7

(a)

Using Eqs. (20.1.23, 20.1.24) we obtain

$$\sum_{m=1}^{M_A} \varepsilon_m \hat{a}_m^\dagger \hat{a}_m \left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle = \left[\sum_{m=1}^{M_A} \varepsilon_m n_m \right] \left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle$$

$$\sum_{m=1}^{M_A} \hat{a}_m^\dagger \hat{a}_m \left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle = \left[\sum_{m=1}^{M_A} n_m \right] \left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle \quad .$$

Hence, the state $\left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle$ is an eigenstate of $\hat{H}_S = \sum_{m=1}^{M_A} \varepsilon_m \hat{a}_m^\dagger \hat{a}_m$ and $\hat{N}_S = \sum_{m=1}^{M_A} \hat{a}_m^\dagger \hat{a}_m$ with the eigenvalues $\sum_{m=1}^{M_A} \varepsilon_m n_m$, and $\sum_{m=1}^{M_A} n_m$, respectively.

(b)

Denoting each eigenstate by the vector of occupation numbers, $\left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle \Leftrightarrow \mathbf{n}$, and introducing the system-bath coupling, $\hat{V}_S \equiv \sum_{m=1}^{M_A} v_m \hat{a}_m^\dagger$ (Eq. (20.5.1)), the respective coupling matrix elements read

$$|\langle \mathbf{n}' | \hat{V}_S | \mathbf{n} \rangle|^2 \equiv$$

$$\left| \left\langle n_1', n_2', n_3', ..., n_{M_A}' \right| \sum_{m=1}^{M_A} v_m \hat{a}_m^\dagger \left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle \right|^2$$

$$= \left| \sum_{m=1}^{M_A} v_m \left\langle n_1', n_2', n_3', ..., n_{M_A}' \right| \hat{a}_m^\dagger \left| n_1, n_2, n_3, ..., n_{M_A} \right\rangle \right|^2$$

$$= \left| \sum_{m=1}^{M_A} v_m \delta_{n_m',1} \delta_{n_m,0} \prod_{\substack{k=1 \\ k \neq m}}^{M_A} \delta_{n_k, n_k'} \right|^2 = \sum_{m=1}^{M_A} |v_m|^2 \delta_{n_m',1} \delta_{n_m,0} \prod_{\substack{k=1 \\ k \neq m}}^{M_A} \delta_{n_k, n_k'} \quad ,$$

where we have used Eqs. (20.1.23, 20.1.24) and the orthonormality of the eigenstates. The product of Kronecker deltas ($\delta_{n_m',1}\delta_{n_m,0}\prod_{\substack{k=1\\k\neq m}}^{M_A}\delta_{n_k,n_k'}$ *) vanishes unless the vector* $\mathbf{n}'$ *is identical to the vector* $\mathbf{n}$*, except for a single entry at the* m *th position, where* n_m *must equal one in* $\mathbf{n}'$ *and zero in* $\mathbf{n}$*. Given this constraint on* $\mathbf{n}'$ *and* $\mathbf{n}$*, the energy difference between the two states must be the respective orbital energy,* $E_{\mathbf{n}'} - E_{\mathbf{n}} = \varepsilon_m$*. Notice that the product of Kronecker deltas can be compactly presented by introducing a unit vector* $\mathbf{e}_m$ *of length* M_A*, with elements* $[\mathbf{e}_m]_{m'} = \delta_{m,m'}$*, where,*

$$\delta_{n_m',1}\delta_{n_m,0}\prod_{\substack{k=1\\k\neq m}}^{M_A}\delta_{n_k,n_k'} \equiv \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}\ . \ \textit{Hence,}\ \ |\langle\mathbf{n}'|\hat{V}_S|\mathbf{n}\rangle|^2 = \sum_{m=1}^{M_A}|v_m|^2\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}\ .$$

Using this result in the rate expression for transition between nondegenerate eigenstates (Eq. (20.5.13)), we obtain

$$k_{\mathbf{n}\to\mathbf{n}'} \equiv \left|\left[\hat{V}_S\right]_{\mathbf{n},\mathbf{n}'}\right|^2 \frac{J(E_{\mathbf{n}}-E_{\mathbf{n}'})}{\hbar} f_h(E_{\mathbf{n}}-E_{\mathbf{n}'}) + \left|\left[\hat{V}_S\right]_{\mathbf{n}',\mathbf{n}}\right|^2 \frac{J(E_{\mathbf{n}'}-E_{\mathbf{n}})}{\hbar} f_e(E_{\mathbf{n}'}-E_{\mathbf{n}})$$
$$= \sum_{m=1}^{M_A}|v_m|^2\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}\frac{J(\varepsilon_m)}{\hbar}f_h(\varepsilon_m) + \sum_{m=1}^{M_A}|v_m|^2\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}\frac{J(\varepsilon_m)}{\hbar}f_e(\varepsilon_m)$$
$$= \sum_{m=1}^{M_A}\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}k_{e,m} + \sum_{m=1}^{M_A}\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}k_{a,m}\ ,$$

where we defined rates for single electron emission ($k_{e,m} \equiv |v_m|^2\frac{J(\varepsilon_m)}{\hbar}f_h(\varepsilon_m)$ *) or absorption (* $k_{a,m} \equiv |v_m|^2\frac{J(\varepsilon_m)}{\hbar}f_e(\varepsilon_m)$*), associated with the* m *th single particle state.*

Exercise 20.5.8 *Use the explicit rate expressions (Eq. (20.5.15)) to derive the ratio in Eq. (20.5.16).*

Solution 20.5.8

Using the explicit expressions for electron absorption and emission rates (Eq. (20.5.15)), and the Fermi distribution functions (Eq. (20.3.6)), we obtain Eq. (20.5.16),

$$\frac{k_{em}}{k_{ab}} = \frac{k_{n\to n'}}{k_{n'\to n}} = \frac{\left|\left[\hat{V}_S\right]_{n,n'}\right|^2 \frac{J(E_n - E_{n'})}{\hbar} f_h(E_n - E_{n'})}{\left|\left[\hat{V}_S\right]_{n,n'}\right|^2 \frac{J(E_n - E_{n'})}{\hbar} f_e(E_n - E_{n'})} = \frac{f_h(E_n - E_{n'})}{f_e(E_n - E_{n'})} = \frac{1 - f_e(E_n - E_{n'})}{f_e(E_n - E_{n'})}$$

$$= \frac{1}{f_e(E_n - E_{n'})} - 1 = e^{\frac{E_n - E_{n'} - \mu}{k_B T}}.$$

Exercise 20.5.9 *Recalling that each system eigenstate is associated with a well-defined number of electrons (see Eqs. (20.5.9, 20.5.10)) and restricting to* $N_{n'} = N_n - 1$, *Eq. (20.5.16) can be written as* $\frac{k_{n\to n'}}{k_{n'\to n}} = e^{\frac{(E_n - \mu N_n) - (E_{n'} - \mu N_{n'})}{k_B T}}$. *Use this to show that the probability distribution in Eq. (20.5.17) is a stationary solution to the master equation, Eq. (20.5.13).*

Solution 20.5.9

Let us considering two system Hamiltonian eigenstates, $|n\rangle$ *and* $|n'\rangle$, *associated with the occupation numbers,* N_n *and* $N_{n'} = N_n - 1$, *respectively. Eq. (20.5.16) therefore yields*

$$\frac{k_{n\to n'}}{k_{n'\to n}} = e^{\frac{(E_n - \mu N_n) - (E_{n'} - \mu N_{n'})}{k_B T}} \Rightarrow k_{n\to n'} = k_{n'\to n} e^{\frac{(E_n - \mu N_n) - (E_{n'} - \mu N_{n'})}{k_B T}}.$$

Using this result in the master equation (Eq. (20.5.13)), we obtain

$$\frac{\partial}{\partial t} P_n(t) \cong \sum_{n'} k_{n'\to n} P_{n'}(t) - \sum_{n'} k_{n\to n'} P_n(t) = \sum_{n'} k_{n'\to n} P_{n'}(t) - \sum_{n'} k_{n'\to n} e^{\frac{(E_n - \mu N_n) - (E_{n'} - \mu N_{n'})}{k_B T}} P_n(t).$$

Setting the probability distribution according to Eq. (20.5.17), $P_n = \frac{1}{Z} e^{\frac{-(E_n - \mu N_n)}{k_B T}}$, *we readily see that the stationarity condition is satisfied,*

$$\frac{\partial}{\partial t} P_n \cong \sum_{n'} k_{n'\to n} \frac{1}{Z} e^{\frac{-(E_{n'} - \mu N_{n'})}{k_B T}} - \sum_{n'} k_{n'\to n} e^{\frac{(E_n - \mu N_n) - (E_{n'} - \mu N_{n'})}{k_B T}} \frac{1}{Z} e^{\frac{-(E_n - \mu N_n)}{k_B T}}$$

$$= \sum_{n'} k_{n'\to n} \frac{1}{Z} e^{\frac{-(E_{n'} - \mu N_{n'})}{k_B T}} - \sum_{n'} k_{n'\to n} \frac{1}{Z} e^{\frac{-(E_{n'} - \mu N_{n'})}{k_B T}} = 0.$$

Exercise 20.5.10 *(a) Given Eq. (20.5.8), and defining the TLS eigenstate populations,* $\rho_{0,0}(t) = \langle 0|\hat{\rho}_S(t)|0\rangle$, *and* $\rho_{1,1}(t) = \langle 1|\hat{\rho}_S(t)|1\rangle$, *show that* $\frac{\partial}{\partial t}\rho_{0,0}(t) \cong -\frac{1}{\hbar^2} 2\,\mathrm{Re}\int_0^\infty d\tau$ $\{c_e(\tau)\langle 0|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|0\rangle + c_a(\tau)\langle 0|[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|0\rangle\}$.

(b) Introduce the identity operator in the Fock space of the adsorbate, $\hat{I} = |0\rangle\langle 0| + |1\rangle\langle 1|$, *to show that for the off-diagonal TLS coupling operators (Eq. (20.5.20)),* $\hat{V}_S = |1\rangle\langle 0|$, *and* $\hat{V}_S^\dagger = |0\rangle\langle 1|$, *this result reads* $\frac{\partial}{\partial t}\rho_{0,0}(t) = k_{1\to 0}^{em}\rho_{1,1}(t) - k_{0\to 1}^{ab}\rho_{0,0}(t)$, *where* $k_{1\to 0}^{em} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau) e^{\frac{i\tau}{\hbar}\varepsilon_0}$ *and* $k_{0\to 1}^{ab} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau) e^{\frac{-i\tau}{\hbar}\varepsilon_0}$. *(c) Show similarly that* $\frac{\partial}{\partial t}\rho_{1,1}(t) = k_{0\to 1}^{ab}\rho_{0,0}(t) - k_{1\to 0}^{em}\rho_{1,1}(t)$. *(d) Use the explicit expressions for the correlation functions (Eq. (20.5.4)) to derive Eq. (20.5.23). (e) Use the expressions for the correlation functions for a continuous bath (Eq. (20.5.6)) to derive Eq. (20.5.24).*

Solution 20.5.10

(a)

Starting from Eq. (20.5.8),

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) \cong -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(t)]$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + c_a(\tau)[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)] + h.c.\},$$

and recalling that $\langle 0|\hat{A}^\dagger|0\rangle = \langle 0|\hat{A}|0\rangle^*$, *we obtain*

$$\frac{\partial}{\partial t}\langle 0|\hat{\rho}_S(t)|0\rangle \cong -\frac{i}{\hbar}\langle 0|[\hat{H}_S, \hat{\rho}_S(t)]|0\rangle$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau\{c_e(\tau)\langle 0|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|0\rangle + c_a(\tau)\langle 0|[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|0\rangle + c.c.\}$$
$$= -\frac{1}{\hbar^2}\int_0^\infty d\tau\, 2\,\mathrm{Re}\{c_e(\tau)\langle 0|[\hat{V}_S, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|0\rangle + c_a(\tau)\langle 0|[\hat{V}_S^\dagger, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]|0\rangle\} \ .$$

(b)

Introducing the identity operator in the Fock space of the adsorbate, $\hat{I} = |0\rangle\langle 0| + |1\rangle\langle 1|$, *and using Eqs. (20.5.19, 20.5.20), namely,* $\hat{V}_S = |1\rangle\langle 0|$, $\hat{V}_S^\dagger = |0\rangle\langle 1|$, $\hat{H}_S|0\rangle = 0|0\rangle$ *and* $\hat{H}_S|1\rangle = \varepsilon_0|1\rangle$, *the result of (a) reads*

$$\frac{\partial}{\partial t}\langle 0|\hat{\rho}_S(t)|0\rangle \cong$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)\langle 0|\hat{V}_S e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|0\rangle\} + \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)\langle 0|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S|0\rangle\}$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)\langle 0|\hat{V}_S^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|0\rangle\} + \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)\langle 0|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S^\dagger|0\rangle\}$$

$$= \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)\langle 0|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)\hat{V}_S|0\rangle\} - \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)\langle 0|\hat{V}_S^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)|0\rangle\}$$

$$= \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)e^{\frac{i\tau}{\hbar}\varepsilon_0}\langle 1|\hat{\rho}_S(t)|1\rangle\} - \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)e^{\frac{-i\tau}{\hbar}\varepsilon_0}\langle 0|\hat{\rho}_S(t)|0\rangle\}\ .$$

Consequently,

$$\frac{\partial}{\partial t}\rho_{0,0}(t) \cong \frac{2}{\hbar^2}\mathrm{Re}\{\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}\varepsilon_0}\}\rho_{1,1}(t) - \frac{2}{\hbar^2}\mathrm{Re}\{\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}\varepsilon_0}\}\rho_{0,0}(t)$$

$$= k_{1\to 0}^{em}\rho_{1,1}(t) - k_{0\to 1}^{ab}\rho_{0,0}(t)\,,$$

where,

$$k_{1\to 0}^{em} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}\varepsilon_0} \quad and \quad k_{0\to 1}^{ab} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}\varepsilon_0}\ .$$

(c)

Similarly,

$$\frac{\partial}{\partial t}\langle 1|\hat{\rho}_S(t)|1\rangle \cong$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)\langle 1|\hat{V}_S\, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\,\hat{\rho}_S(t)|1\rangle\} + \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)\langle 1|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\,\hat{\rho}_S(t)\hat{V}_S\,|1\rangle\}$$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)\langle 1|\hat{V}_S^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S\, e^{\frac{i\tau}{\hbar}\hat{H}_S}\,\hat{\rho}_S(t)|1\rangle\} + \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)\langle 1|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S\, e^{\frac{i\tau}{\hbar}\hat{H}_S}\,\hat{\rho}_S(t)\hat{V}_S^\dagger\,|1\rangle\}$$

$$= -\frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)\langle 1|\hat{V}_S\, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_S}\,\hat{\rho}_S(t)|1\rangle\} + \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)\langle 1|e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_S\, e^{\frac{i\tau}{\hbar}\hat{H}_S}\,\hat{\rho}_S(t)\hat{V}_S^\dagger\,|1\rangle\}$$

$$= -\frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_e(\tau)e^{\frac{i\tau}{\hbar}\varepsilon_0}\,\langle 1|\hat{\rho}_S(t)|1\rangle\} + \frac{1}{\hbar^2}\int_0^\infty d\tau 2\,\mathrm{Re}\{c_a(\tau)e^{\frac{-i\tau}{\hbar}\varepsilon_0}\,\langle 0|\hat{\rho}_S(t)|0\rangle\}\ .$$

Hence, $\frac{\partial}{\partial t}\rho_{1,1}(t) \cong -k^{em}_{1\to 0}\rho_{1,1}(t) + k^{ab}_{0\to 1}\rho_{0,0}(t)$.

(d)

Using the explicit expressions for the correlation functions (Eq. (20.5.4)),

$$c_a(\tau) = tr_B\{\hat{U}_B^\dagger e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B e^{\frac{i\tau}{\hbar}\hat{H}_B}\,\hat{\rho}_B\} = \sum_{k=1}^{M_E}|\gamma_k|^2 e^{\frac{i\tau}{\hbar}\varepsilon_k}\, f_e(\varepsilon_k)$$

$$c_e(\tau) = tr_B\{\hat{U}_B e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}_B^\dagger e^{\frac{i\tau}{\hbar}\hat{H}_B}\,\hat{\rho}_B\} = \sum_{k=1}^{M_E}|\gamma_k|^2 e^{\frac{-i\tau}{\hbar}\varepsilon_k}\, f_h(\varepsilon_k)\,,$$

we obtain Eq. (20.5.23),

$$k^{em}_{1\to 0} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau)e^{\frac{i\tau}{\hbar}\varepsilon_0} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{k=1}^{M_E}|\gamma_k|^2 e^{\frac{-i\tau}{\hbar}\varepsilon_k}\, f_h(\varepsilon_k)e^{\frac{i\tau}{\hbar}\varepsilon_0}$$

$$= \sum_{k=1}^{M_E}|\gamma_k|^2 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(\varepsilon_k-\varepsilon_0)}\, f_h(\varepsilon_k) = \sum_{k=1}^{M_E}|\gamma_k|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_{-\infty}^\infty d\tau e^{\frac{-i\tau}{\hbar}(\varepsilon_k-\varepsilon_0)}\, f_h(\varepsilon_k)$$

$$= \frac{2\pi}{\hbar}\sum_{k=1}^{M_E}|\gamma_k|^2\delta(\varepsilon_k-\varepsilon_0)\, f_h(\varepsilon_k)$$

$$k^{ab}_{0\to 1} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau)e^{\frac{-i\tau}{\hbar}\varepsilon_0} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{k=1}^{M_E}|\gamma_k|^2 e^{\frac{i\tau}{\hbar}\varepsilon_k}\, f_e(\varepsilon_k)e^{\frac{-i\tau}{\hbar}\varepsilon_0}$$

$$= \sum_{k=1}^{M_E}|\gamma_k|^2 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau e^{\frac{i\tau}{\hbar}(\varepsilon_k-\varepsilon_0)}\, f_e(\varepsilon_k) = \sum_{k=1}^{M_E}|\gamma_k|^2\,\mathrm{Re}\frac{1}{\hbar^2}\int_{-\infty}^\infty d\tau e^{\frac{i\tau}{\hbar}(\varepsilon_k-\varepsilon_0)}\, f_e(\varepsilon_k)$$

$$= \frac{2\pi}{\hbar}\sum_{k=1}^{M_E}|\gamma_k|^2\delta(\varepsilon_k-\varepsilon_0)\, f_e(\varepsilon_k)\ .$$

(e)

Using the expressions for the correlation functions for a continuous bath (Eq. (20.5.6)),

$$c_a(\tau) = \frac{1}{2\pi}\int d\varepsilon e^{i\tau\varepsilon/\hbar} J(\varepsilon) f_e(\varepsilon) \quad ; \quad c_e(\tau) = \frac{1}{2\pi}\int d\varepsilon e^{-i\tau\varepsilon/\hbar} J(\varepsilon) f_h(\varepsilon),$$

we obtain Eq. (20.5.24),

$$k_{1\to 0}^{em} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_e(\tau) e^{\frac{i\tau}{\hbar}\varepsilon_0} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau \frac{1}{2\pi}\int d\varepsilon e^{-i\tau\varepsilon/\hbar} J(\varepsilon) f_h(\varepsilon) e^{\frac{i\tau}{\hbar}\varepsilon_0}$$
$$= \frac{1}{2\pi\hbar^2}\int d\varepsilon J(\varepsilon) f_h(\varepsilon) 2\,\mathrm{Re}\int_0^\infty d\tau e^{\frac{-i\tau}{\hbar}(\varepsilon-\varepsilon_0)} = \frac{1}{2\pi\hbar^2}\int d\varepsilon J(\varepsilon) f_h(\varepsilon)\,\mathrm{Re}\int_{-\infty}^\infty d\tau e^{\frac{-i\tau}{\hbar}(\varepsilon-\varepsilon_0)}$$
$$= \frac{1}{\hbar}\int d\varepsilon J(\varepsilon) f_h(\varepsilon)\delta(\varepsilon-\varepsilon_0) = \frac{1}{\hbar} J(\varepsilon_0) f_h(\varepsilon_0)$$

$$k_{0\to 1}^{ab} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau c_a(\tau) e^{\frac{-i\tau}{\hbar}\varepsilon_0} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_0^\infty d\tau \frac{1}{2\pi}\int d\varepsilon e^{i\tau\varepsilon/\hbar} J(\varepsilon) f_e(\varepsilon) e^{\frac{-i\tau}{\hbar}\varepsilon_0}$$
$$= \frac{1}{2\pi\hbar^2}\int d\varepsilon J(\varepsilon) f_e(\varepsilon) 2\,\mathrm{Re}\int_0^\infty d\tau e^{\frac{i\tau}{\hbar}(\varepsilon-\varepsilon_0)} = \frac{1}{2\pi\hbar^2}\int d\varepsilon J(\varepsilon) f_e(\varepsilon)\,\mathrm{Re}\int_{-\infty}^\infty d\tau e^{\frac{i\tau}{\hbar}(\varepsilon-\varepsilon_0)}$$

$$= \frac{1}{\hbar}\int d\varepsilon J(\varepsilon) f_e(\varepsilon)\delta(\varepsilon-\varepsilon_0) = \frac{1}{\hbar} J(\varepsilon_0) f_e(\varepsilon_0)\ .$$

Exercise 20.5.11 *Use Eq. (20.5.24) and the definition of the Fermi-Dirac distribution function (Eq. (20.3.6)) to derive Eq. (20.5.25).*

Solution 20.5.11

The equations for the adsorbate space populations read (Eq. (20.5.22))

$$\frac{\partial}{\partial t}\rho_{0,0}(t) = k_{1\to 0}^{em}\rho_{1,1}(t) - k_{0\to 1}^{ab}\rho_{0,0}(t) \ \ \textit{and}\ \ \frac{\partial}{\partial t}\rho_{1,1}(t) = k_{0\to 1}^{ab}\rho_{0,0}(t) - k_{1\to 0}^{em}\rho_{1,1}(t)\,.$$

One can readily verify that the solution to these equations is (see Ex. 17.3.7),

$$\rho_{0,0}(t) = \rho_{0,0}(0)\,\mathrm{e}^{-(k_{0\to 1}^{ab}+k_{1\to 0}^{em})t} + \frac{k_{1\to 0}^{em}}{k_{0\to 1}^{ab}+k_{1\to 0}^{em}}(1-\mathrm{e}^{-(k_{0\to 1}^{ab}+k_{1\to 0}^{em})t}) \quad ; \quad \rho_{1,1}(t) = 1-\rho_{0,0}(t)\,.$$

Consequently, $\lim_{t\to\infty}\rho_{0,0}(t)=\dfrac{k^{em}_{1\to 0}}{k^{ab}_{0\to 1}+k^{em}_{1\to 0}}$ *, and* $\lim_{t\to\infty}\rho_{1,1}(t)=\dfrac{k^{ab}_{0\to 1}}{k^{ab}_{0\to 1}+k^{em}_{1\to 0}}$ *, which means that the asymptotic population ratio reads* $\dfrac{\rho_{1,1}(\infty)}{\rho_{0,0}(\infty)}=\dfrac{k^{ab}_{0\to 1}}{k^{em}_{1\to 0}}$.

Using $k^{em}_{1\to 0}=\dfrac{1}{\hbar}J(\varepsilon_0)f_h(\varepsilon_0)$, $k^{ab}_{0\to 1}=\dfrac{1}{\hbar}J(\varepsilon_0)f_e(\varepsilon_0)$, $f_e(\varepsilon)=\dfrac{1}{1+e^{(\varepsilon-\mu)/(k_BT)}}$ *and* $f_h(\varepsilon)=1-f_e(\varepsilon)$ *(Eqs. (20.3.6, 20.5.4)), we obtain Eq. (20.5.25),*

$$\frac{\rho_{1,1}(\infty)}{\rho_{0,0}(\infty)}=\frac{k^{ab}_{0\to 1}}{k^{em}_{1\to 0}}=\frac{f_e(\varepsilon_0)}{f_h(\varepsilon_0)}=\frac{f_e(\varepsilon_0)}{1-f_e(\varepsilon_0)}=\frac{1}{(1+e^{(\varepsilon_0-\mu)/(k_BT)})(1-\frac{1}{1+e^{(\varepsilon_0-\mu)/(k_BT)}})}=e^{-(\varepsilon_0-\mu)/(k_BT)}.$$

Exercise 20.6.1 *For a generic system-bath coupling term,* $\hat{H}_{SB}\equiv\sum_\alpha \hat{V}^{(S)}_\alpha\hat{U}^{(B)}_\alpha$ *, the dissipator in the Born Markov approximation obtains the form shown in (Eqs. (19.3.21, 19.3.22)). To bring to this form the coupling operator,* $\hat{H}_{SB}=\sum_K\left(\hat{V}_{S,K}\otimes\hat{U}_{B,K}+\hat{V}^\dagger_{S,K}\otimes\hat{U}^\dagger_{B,K}\right)$*, let us define* $\hat{H}_{SB}\equiv\sum_{\alpha\in K,n}\hat{V}^{(S)}_\alpha\hat{U}^{(B)}_\alpha=\sum_K\sum_{n=1}^{2}\hat{V}^{(S)}_{K,n}\hat{U}^{(B)}_{K,n}$*, where* $\hat{V}^{(S)}_{K,1}=\hat{V}_{S,K}$, $\hat{V}^{(S)}_{K,2}=\hat{V}^\dagger_{S,K}$, $\hat{U}^{(B)}_{K,1}=\hat{U}_{B,K}=\sum_{k_K}\gamma_{k_K}\hat{a}_{k_K}$, $\hat{U}^{(B)}_{K,2}=\hat{U}^\dagger_{B,K}=\sum_{k_K}\gamma^*_{k_K}\hat{a}^\dagger_{k_K}$ *, such that the dissipator (Eq. (19.3.22)) obtains the form*

$$\hat{D}\hat{\rho}_S(t)=$$
$$-\frac{1}{\hbar^2}\sum_{K,K'}\sum_{n,n'\in 1,2}\int_0^t d\tau\{c_{K,n,K',n'}(\tau)[\hat{V}^{(S)}_{K,n},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}_{K',n',K,n}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,n}]\}$$

, with the bath correlation functions, $c_{K,n,K',n'}(\tau)=tr_B\{\hat{U}^{(B)}_{K,n}e^{\frac{-i\tau}{\hbar}\hat{H}_B}\hat{U}^{(B)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_B}\hat{\rho}_B\}$, $\bar{c}_{K,n,K',n'}(\tau)=c_{K,n,K',n'}(-\tau)$*, where* $\hat{H}_B=\sum_K\hat{H}_K$, $\hat{\rho}_B=\prod_K\hat{\rho}_K$ *. (a) Use the results of Ex. 20.5.1. to show that the correlation functions involving different reservoirs vanish, namely* $c_{K,n,K',n'}(\tau)=\delta_{K,K'}c^{(K)}_{n,n'}(\tau)$*, where* $c^{(K)}_{n,n'}(\tau)=tr_K\{\hat{U}^{(B)}_{K,n}e^{\frac{-i\tau}{\hbar}\hat{H}_K}\hat{U}^{(B)}_{K,n'}e^{\frac{i\tau}{\hbar}\hat{H}_K}\hat{\rho}_K\}$*. (b) Using this result, show that the dissipator reads*

$$\hat{D}\hat{\rho}_S(t)=-\frac{1}{\hbar^2}\sum_K\sum_{n,n'\in 1,2}\int_0^t d\tau\{c^{(K)}_{n,n'}(\tau)[\hat{V}^{(S)}_{K,n},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,n'}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}^{(K)}_{n',n}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,n'}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,n}]\}$$

(c) Apply the treatment in Ex. (20.5.2) to the dissipator in (b) to derive Eq. (20.6.4), where the absorption and emission correlation functions are defined in Eq. (20.6.5).

Solution 20.6.1

(a)

Starting from the definition of the coupling correlation function for multiple reservoirs, $c_{K,n,K',n'}(\tau) = tr_B\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}^{(B)}_{K',n'} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\}$*, and using the decomposition of the bath Hamiltonian,* $\hat{H}_B = \sum_K \hat{H}_K$ *, and hence,* $\hat{\rho}_B = \prod_K \hat{\rho}_K$ *, we obtain*

$$c_{K,n,K',n'}(\tau) = tr_B\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_B} \hat{U}^{(B)}_{K',n'} e^{\frac{i\tau}{\hbar}\hat{H}_B} \hat{\rho}_B\} = tr_B\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\sum_{K'}\hat{H}_{K'}} \hat{U}^{(B)}_{K',n'} e^{\frac{i\tau}{\hbar}\sum_{K'}\hat{H}_{K'}} \hat{\rho}_B\}$$
$$= tr_B\{\hat{U}^{(B)}_{K,n} \left(e^{\frac{-i\tau}{\hbar}\hat{H}_1} e^{\frac{-i\tau}{\hbar}\hat{H}_2} \cdots \right) \hat{U}^{(B)}_{K',n'} \left(e^{\frac{i\tau}{\hbar}\hat{H}_1} e^{\frac{i\tau}{\hbar}\hat{H}_2} \cdots \right) \left(\hat{\rho}_1 \hat{\rho}_2 \cdots \right)\} \ .$$

Noticing that the operator under the trace is a tensor product of operators associated with the single reservoir spaces, and recalling that $tr\{\hat{A} \otimes \hat{B}\} = tr\{\hat{A}\} tr\{\hat{B}\}$ *, we obtain for* $K = K'$*,*

$$c_{K,n,K,n'}(\tau) = tr_1\{e^{\frac{-i\tau}{\hbar}\hat{H}_1} e^{\frac{i\tau}{\hbar}\hat{H}_1} \hat{\rho}_1\} tr_2\{e^{\frac{-i\tau}{\hbar}\hat{H}_2} e^{\frac{i\tau}{\hbar}\hat{H}_2} \hat{\rho}_2\} \cdots tr_K\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}^{(B)}_{K,n'} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} \cdots$$
$$= tr_1\{\hat{\rho}_1\} tr_2\{\hat{\rho}_2\} \cdots tr_K\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}^{(B)}_{K,n'} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} \cdots$$
$$= tr_K\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}^{(B)}_{K,n'} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} ,$$

and similarly, for $K \neq K'$*,*

$$c_{K,n,K',n'}(\tau) = tr_1\{\hat{\rho}_1\} tr_2\{\hat{\rho}_2\} \cdots tr_K\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_K} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} \cdots tr_{K'}\{e^{\frac{-i\tau}{\hbar}\hat{H}_{K'}} \hat{U}^{(B)}_{K',n'} e^{\frac{i\tau}{\hbar}\hat{H}_{K'}} \hat{\rho}_{K'}\} \cdots$$
$$= tr_1\{\hat{\rho}_1\} tr_2\{\hat{\rho}_2\} \cdots tr_K\{\hat{U}^{(B)}_{K,n} \hat{\rho}_K\} \cdots tr_{K'}\{\hat{U}^{(B)}_{K',n'} \hat{\rho}_{K'}\} \cdots$$
$$= tr_K\{\hat{U}^{(B)}_{K,n} \hat{\rho}_K\} \cdot tr_{K'}\{\hat{U}^{(B)}_{K',n'} \hat{\rho}_{K'}\} \ .$$

Recalling that $\hat{U}^{(B)}_{K,n}$ *is either* $\hat{U}^{(B)}_{K,1} = \sum_{k_K=1} \gamma_{k_K} \hat{a}_{k_K}$ *, or* $\hat{U}^{(B)}_{K,2} = \sum_{k_K=1} \gamma^*_{k_K} \hat{a}^\dagger_{k_K}$ *, and using the result of Ex.20.5.1, we have*

$$tr_{k_K}\{\hat{a}_{k_K} f(\hat{a}^\dagger_{k_K} \hat{a}_{k_K})\} = tr_{k_K}\{\hat{a}^\dagger_{k_K} f(\hat{a}^\dagger_{k_K} \hat{a}_{k_K})\} = 0 \Rightarrow tr_K\{\hat{U}^{(B)}_{K,1} \hat{\rho}_K\} = tr_K\{\hat{U}^{(B)}_{K,2} \hat{\rho}_K\} = 0 \ .$$

Consequently,

$$c_{K,n,K',n'}(\tau) = \delta_{K,K'} tr_K\{\hat{U}^{(B)}_{K,n} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}^{(B)}_{K,n'} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} \equiv \delta_{K,K'} c^{(K)}_{n,n'}(\tau) \ .$$

(b)

Using the result of (a) in the dissipator for multiple reservoirs,

$$\hat{D}\hat{\rho}_S(t)=$$

$$-\frac{1}{\hbar^2}\sum_{K,K'}\sum_{n,n'\in 1,2}\int_0^t d\tau\{c_{K,n,K',n'}(\tau)[\hat{V}^{(S)}_{K,n},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}_{K',n',K,n}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,n}]\},$$

where, $\bar{c}_{K,n,K',n'}(\tau)=c_{K,n,K',n'}(-\tau)$, *we obtain,*

$$\hat{D}\hat{\rho}_S(t)$$

$$=-\frac{1}{\hbar^2}\sum_{K,K'}\sum_{n,n'\in 1,2}$$

$$\int_0^t d\tau\{\delta_{K,K'}c^{(K)}_{n,n'}(\tau)[\hat{V}^{(S)}_{K,n},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\delta_{K,K'}\bar{c}^{(K)}_{n',n}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K',n'}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,n}]\}$$

$$=-\frac{1}{\hbar^2}\sum_{K}\sum_{n,n'\in 1,2}$$

$$\int_0^t d\tau\{c^{(K)}_{n,n'}(\tau)[\hat{V}^{(S)}_{K,n},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,n'}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}^{(K)}_{n',n}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,n'}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,n}]\} \quad .$$

(c)

Starting from the dissipator in (b) we obtain

$$\hat{D}\hat{\rho}_S(t)=-\frac{1}{\hbar^2}\sum_{K}$$

$$\int_0^t d\tau\{c^{(K)}_{1,1}(\tau)[\hat{V}^{(S)}_{K,1},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,1}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}^{(K)}_{1,1}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,1}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,1}]\}$$

$$\int_0^t d\tau\{c^{(K)}_{1,2}(\tau)[\hat{V}^{(S)}_{K,1},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,2}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}^{(K)}_{2,1}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,2}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,1}]\}$$

$$\int_0^t d\tau\{c^{(K)}_{2,1}(\tau)[\hat{V}^{(S)}_{K,2},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,1}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}^{(K)}_{1,2}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,1}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,2}]\}$$

$$\int_0^t d\tau\{c^{(K)}_{2,2}(\tau)[\hat{V}^{(S)}_{K,2},e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,2}e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)]+\bar{c}^{(K)}_{2,2}(\tau)[\rho_S(t)e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}^{(S)}_{K,2}e^{\frac{i\tau}{\hbar}\hat{H}_S},\hat{V}^{(S)}_{K,2}]\} \quad .$$

Using $\hat{V}^{(S)}_{K,1}=\hat{V}_{S,K}$, $\hat{V}^{(S)}_{K,2}=\hat{V}^{\dagger}_{S,K}$, $\hat{U}^{(B)}_{K,1}=\hat{U}_{B,K}=\sum_{k_K=1}\gamma_{k_K}\hat{a}_{k_K}$, $\hat{U}^{(B)}_{K,2}=\hat{U}^{\dagger}_{B,K}=\sum_{k_K=1}\gamma^{*}_{k_K}\hat{a}^{\dagger}_{k_K}$,

we can identify the single reservoir correlation functions (see Ex. 20.5.2 and Eqs. (20.5.4, 20.5.6)),

$$c^{(K)}_{1,1}(\tau)=tr_K\{\hat{U}^{(B)}_{K,1}e^{\frac{-i\tau}{\hbar}\hat{H}_K}\hat{U}^{(B)}_{K,1}e^{\frac{i\tau}{\hbar}\hat{H}_K}\hat{\rho}_K\}=tr_K\{\hat{U}_{B,K}e^{\frac{-i\tau}{\hbar}\hat{H}_K}\hat{U}_{B,K}e^{\frac{i\tau}{\hbar}\hat{H}_K}\hat{\rho}_K\}=0$$

$$c^{(K)}_{2,2}(\tau)=tr_K\{\hat{U}^{(B)}_{K,2}e^{\frac{-i\tau}{\hbar}\hat{H}_K}\hat{U}^{(B)}_{K,2}e^{\frac{i\tau}{\hbar}\hat{H}_K}\hat{\rho}_K\}=tr_K\{\hat{U}^{\dagger}_{B,K}e^{\frac{-i\tau}{\hbar}\hat{H}_K}\hat{U}^{\dagger}_{B,K}e^{\frac{i\tau}{\hbar}\hat{H}_K}\hat{\rho}_K\}=0$$

$$c_{1,2}^{(K)}(\tau) = tr_K\{\hat{U}_{K,1}^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}_{K,2}^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} = tr_K\{\hat{U}_{B,K} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}_{B,K}^{\dagger} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\}$$

$$= \sum_{k_K=1} |\gamma_{k_K}|^2 \, e^{\frac{-i\tau}{\hbar}\varepsilon_{k_K}} \, \frac{e^{\frac{1}{k_B T}(\varepsilon_{k_K}-\mu_K)}}{1+e^{\frac{1}{k_B T}(\varepsilon_{k_K}-\mu_K)}} \equiv c_{e,K}(\tau)$$

$$c_{2,1}^{(K)}(\tau) = tr_K\{\hat{U}_{K,2}^{(B)} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}_{K,1}^{(B)} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\} = tr_K\{\hat{U}_{B,K}^{\dagger} e^{\frac{-i\tau}{\hbar}\hat{H}_K} \hat{U}_{B,K} e^{\frac{i\tau}{\hbar}\hat{H}_K} \hat{\rho}_K\}$$

$$= \sum_{k_K=1} |\gamma_{k_K}|^2 \frac{e^{\frac{i\tau}{\hbar}\varepsilon_{k_K}}}{1+e^{\frac{1}{k_B T}(\varepsilon_{k_K}-\mu_K)}} \equiv c_{a,K}(\tau) \ .$$

Consequently, and using $c_{e,K}(-\tau) = c_{e,K}^{*}(\tau)$, $c_{a,K}(-\tau) = c_{a,K}^{*}(\tau)$ *we obtain*

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\sum_K$$

$$\int_0^t d\tau\{c_{e,K}(\tau)[\hat{V}_{S,K}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K}^{\dagger} e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + c_{a,K}^{*}(\tau)[\rho_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K}^{\dagger} e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_{S,K}]\}$$

$$\int_0^t d\tau\{c_{a,K}(\tau)[\hat{V}_{S,K}^{\dagger}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K} e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + c_{e,K}^{*}(\tau)[\rho_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K} e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_{S,K}^{\dagger}]\} \ .$$

Using the identities,

$$[\hat{V}_{S,K}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K}^{\dagger} e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]^{\dagger} = [\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K} e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_{S,K}^{\dagger}]$$

and

$$[\hat{V}_{S,K}^{\dagger}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K} e^{\frac{i\tau}{\hbar}\hat{H}_S}\hat{\rho}_S(t)]^{\dagger} = [\hat{\rho}_S(t) e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K}^{\dagger} e^{\frac{i\tau}{\hbar}\hat{H}_S}, \hat{V}_{S,K}],$$

we obtain the dissipator appearing in Eq. (20.6.4),

$$\hat{D}\hat{\rho}_S(t) = -\frac{1}{\hbar^2}\sum_K$$

$$\int_0^t d\tau\{c_{e,K}(\tau)[\hat{V}_{S,K}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K}^{\dagger} e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + c_{a,K}(\tau)[\hat{V}_{S,K}^{\dagger}, e^{\frac{-i\tau}{\hbar}\hat{H}_S}\hat{V}_{S,K} e^{\frac{i\tau}{\hbar}\hat{H}_S}\rho_S(t)] + h.c.\} \ .$$

Exercise 20.6.2 *Use Eq. (20.6.22) for calculating the system eigenstate populations at steady state,* $P_0^{(st)}$ *and* $P_1^{(st)}$, *and show that the normalized populations (*$P_0^{(st)} + P_1^{(st)} = 1$*) are given by Eq. (20.6.24).*

Solution 20.6.2

At steady state, Eq. (20.6.22) reads

$$\frac{\partial}{\partial t}P_0^{(st)} = (k_{1\to0}^{(R)} + k_{1\to0}^{(L)})P_1^{(st)} - (k_{0\to1}^{(R)} + k_{0\to1}^{(L)})P_0^{(st)} = 0$$

$$\frac{\partial}{\partial t}P_1^{(st)} = (k_{0\to1}^{(R)} + k_{0\to1}^{(L)})P_0^{(st)} - (k_{1\to0}^{(R)} + k_{1\to0}^{(L)})P_1^{(st)} = 0 \ .$$

Consequently,

$$(k_{1\to0}^{(R)} + k_{1\to0}^{(L)})P_1^{(st)} = (k_{0\to1}^{(R)} + k_{0\to1}^{(L)})P_0^{(st)}$$
$$\Rightarrow \frac{P_1^{(st)}}{P_0^{(st)}} = \frac{k_{0\to1}^{(R)} + k_{0\to1}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}$$

$$\Rightarrow P_1^{(st)} = \frac{k_{0\to1}^{(R)} + k_{0\to1}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}P_0^{(st)}.$$

Requiring normalization, we obtain Eq. (20.6.24),

$$1 = P_1^{(st)} + P_0^{(st)} = \frac{k_{0\to1}^{(R)} + k_{0\to1}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}P_0^{(st)} + \frac{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}P_0^{(st)} = \frac{k_{0\to1}^{(R)} + k_{0\to1}^{(L)} + k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}P_0^{(st)}$$
$$\Rightarrow P_0^{(st)} = \frac{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}{k_{0\to1}^{(R)} + k_{0\to1}^{(L)} + k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}$$

$$\Rightarrow P_1^{(st)} = \frac{k_{0\to1}^{(R)} + k_{0\to1}^{(L)}}{k_{0\to1}^{(R)} + k_{0\to1}^{(L)} + k_{1\to0}^{(R)} + k_{1\to0}^{(L)}} \ .$$

Exercise 20.6.3 *Use Eqs. (20.6.24, 20.6.26) to derive Eq. (20.6.27).*

Solution 20.6.3

Starting from Eq. (20.6.24) for the steady state probabilities,

$$P_0^{(st)} = \frac{k_{1\to0}^{(R)} + k_{1\to0}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)} + k_{0\to1}^{(R)} + k_{0\to1}^{(L)}} \quad ; \quad P_1^{(st)} = \frac{k_{0\to1}^{(R)} + k_{0\to1}^{(L)}}{k_{1\to0}^{(R)} + k_{1\to0}^{(L)} + k_{0\to1}^{(R)} + k_{0\to1}^{(L)}},$$

we can use Eq. (20.6.26) for the transition rates, $k_{1\to0}^{(K)} = \frac{1}{\hbar}J_K(\varepsilon_0)f_{h,K}(\varepsilon_0)$, $k_{0\to1}^{(K)} = \frac{1}{\hbar}J_K(\varepsilon_0)f_{e,K}(\varepsilon_0)$

. *Recalling that* $f_{e,R}(\varepsilon_0) + f_{h,R}(\varepsilon_0) = f_{e,L}(\varepsilon_0) + f_{h,L}(\varepsilon_0) = 1$, *we obtain Eq. (20.6.27),*

$$P_1^{(st)} = \frac{J_R(\varepsilon_0)f_{e,R}(\varepsilon_0) + J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)}{J_R(\varepsilon_0)f_{h,R}(\varepsilon_0) + J_L(\varepsilon_0)f_{h,L}(\varepsilon_0) + J_R(\varepsilon_0)f_{e,R}(\varepsilon_0) + J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)}$$

$$= \frac{J_R(\varepsilon_0)f_{e,R}(\varepsilon_0) + J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)}{J_R(\varepsilon_0) + J_L(\varepsilon_0)} = \frac{J_R(\varepsilon_0)}{J_R(\varepsilon_0) + J_L(\varepsilon_0)}f_{e,R}(\varepsilon_0) + \frac{J_L(\varepsilon_0)}{J_R(\varepsilon_0) + J_L(\varepsilon_0)}f_{e,L}(\varepsilon_0) \ .$$

Exercise 20.6.4 *Use Eqs. (20.6.26, 20.6.27) in Eq. (20.6.25) to derive Eq. (20.6.28).*

Solution 20.6.4

Substitution of the rate expressions (Eq. (20.2.26)) in Eq. (20.6.25) for the steady state current, we obtain

$$I_{L\to R}^{(st)} = ek_{0\to 1}^{(L)}P_0^{(st)} - ek_{1\to 0}^{(L)}P_1^{(st)} = \frac{e}{\hbar}J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)P_0^{(st)} - \frac{e}{\hbar}J_L(\varepsilon_0)f_{h,L}(\varepsilon_0)P_1^{(st)}$$

$$= \frac{e}{\hbar}J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)[1-P_1^{(st)}] - \frac{e}{\hbar}J_L(\varepsilon_0)f_{h,L}(\varepsilon_0)P_1^{(st)} = \frac{e}{\hbar}J_L(\varepsilon_0)[f_{e,L}(\varepsilon_0) - P_1^{(st)}].$$

Using Eq. (20.6.27) for the steady state probability, we obtain Eq. (20.6.28),

$$I_{L\to R}^{(st)} = \frac{e}{\hbar}J_L(\varepsilon_0)[f_{e,L}(\varepsilon_0) - P_1^{(st)}]$$

$$= \frac{e}{\hbar}J_L(\varepsilon_0)[f_{e,L}(\varepsilon_0) - \frac{J_R(\varepsilon_0)f_{e,R}(\varepsilon_0)}{J_R(\varepsilon_0)+J_L(\varepsilon_0)} - \frac{J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)}{J_R(\varepsilon_0)+J_L(\varepsilon_0)}]$$

$$= \frac{e}{\hbar}J_L(\varepsilon_0)[\frac{J_R(\varepsilon_0)f_{e,L}(\varepsilon_0) + f_{e,L}(\varepsilon_0)J_L(\varepsilon_0) - J_R(\varepsilon_0)f_{e,R}(\varepsilon_0) - J_L(\varepsilon_0)f_{e,L}(\varepsilon_0)}{J_R(\varepsilon_0)+J_L(\varepsilon_0)}]$$

$$= \frac{e}{\hbar}J_L(\varepsilon_0)[\frac{J_R(\varepsilon_0)f_{e,L}(\varepsilon_0) - J_R(\varepsilon_0)f_{e,R}(\varepsilon_0)}{J_R(\varepsilon_0)+J_L(\varepsilon_0)}] = \frac{e}{\hbar}\frac{J_L(\varepsilon_0)J_R(\varepsilon_0}{J_R(\varepsilon_0)+J_L(\varepsilon_0)})[f_{e,L}(\varepsilon_0) - f_{e,R}(\varepsilon_0)] \ .$$

Exercise 20.6.5 *(a) Use the results of Ex. 20.5.7 to show that for a system of noninteracting fermions, the equation for the steady state population of the* $\mathbf{n}$ *th many-particle state (*$P_{\mathbf{n}}^{(st)}$*, Eq. (20.6.16)) reads* $\sum_{m=1}^{M_A}[\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e_m}}k_{e,m} + \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e_m}}k_{a,m}]P_{\mathbf{n}'}^{(st)} - [\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e_m}}k_{e,m} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e_m}}k_{a,m}]P_{\mathbf{n}}^{(st)} = 0$*, where* $k_{e,m} = \frac{1}{\hbar}J_{R,m}(\varepsilon_m)f_{h,R}(\varepsilon_m) + \frac{1}{\hbar}J_{L,m}(\varepsilon_m)f_{h,L}(\varepsilon_m)$, $k_{a,m} = \frac{1}{\hbar}J_{R,m}(\varepsilon_m)f_{e,R}(\varepsilon_m) + \frac{1}{\hbar}J_{L,m}(\varepsilon_m)f_{e,L}(\varepsilon_m)$ *, and* $J_{K,m}(\varepsilon) = |v_{m,K}|^2 J_K(\varepsilon)$. *(b) Show that* $P_{\mathbf{n}}^{(st)} = \prod_{m=1}^{M_A}\left(P_{m,[\mathbf{n}]_m}^{(st)}\right)$*, with* $P_{m,[\mathbf{n}]_m}^{(st)} = \frac{k_{a,m}}{k_{e,m}+k_{a,m}}\delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m}+k_{a,m}}\delta_{[\mathbf{n}]_m,0}$*, satisfies the equation for the steady state population of the* $\mathbf{n}^{th}$ *many particle-state in (a). (c) Show that* $P_{m,1}^{(st)} + P_{m,0}^{(st)} = 1$*, and therefore the sum over all the eigenstate populations reads* $\sum_{\mathbf{n}} P_{\mathbf{n}}^{(st)} = 1$*. (d) Use the explicit expressions for the absorption and emission rates in (a) to derive Eq. (20.6.31) for the occupation probabilities of the single particle states, at steady state.*

Solution 20.6.5

(a)

We recall that for a system of non-interacting electrons, the system Hamiltonian eigenstates are associated with determinants, each denoted by a vector of occupation numbers, $\mathbf{n}$*, of the single particle states. The transition rates between the system Hamiltonian eigenstates, induced by the* K *th* *reservoir, read (Ex. 20.5.7)*

$$k^{(K)}_{\mathbf{n}\to\mathbf{n}'} = \sum_{m=1}^{M_A} \left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} |v_{m,K}|^2 \frac{J_K(\varepsilon_m)}{\hbar} f_{h,K}(\varepsilon_m) + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} |v_{m,K}|^2 \frac{J_K(\varepsilon_m)}{\hbar} f_{e,K}(\varepsilon_m) \right).$$

Hence,

$$k^{(R)}_{\mathbf{n}\to\mathbf{n}'} + k^{(L)}_{\mathbf{n}\to\mathbf{n}'}$$
$$= \sum_{m=1}^{M_A} (\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} \left[|v_{m,R}|^2 \frac{J_R(\varepsilon_m)}{\hbar} f_{h,R}(\varepsilon_m) + |v_{m,L}|^2 \frac{J_L(\varepsilon_m)}{\hbar} f_{h,L}(\varepsilon_m) \right]$$
$$+ \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e_m}} \left[|v_{m,R}|^2 \frac{J_R(\varepsilon_m)}{\hbar} f_{e,R}(\varepsilon_m) + |v_{m,L}|^2 \frac{J_L(\varepsilon_m)}{\hbar} f_{e,L}(\varepsilon_m) \right])$$
$$= \sum_{m=1}^{M_A} \left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{a,m} \right)$$

where we define,

$$k_{e,m} = |v_{m,R}|^2 \frac{J_R(\varepsilon_m)}{\hbar} f_{h,R}(\varepsilon_m) + |v_{m,L}|^2 \frac{J_L(\varepsilon_m)}{\hbar} f_{h,L}(\varepsilon_m)$$

$$k_{a,m} = |v_{m,R}|^2 \frac{J_R(\varepsilon_m)}{\hbar} f_{e,R}(\varepsilon_m) + |v_{m,L}|^2 \frac{J_L(\varepsilon_m)}{\hbar} f_{e,L}(\varepsilon_m).$$

Using this expression in the general condition for steady state (Eq. (20.6.16)) according to the master equation, we obtain for any $\mathbf{n}$,

$$\sum_{\mathbf{n}'} \left(k^{(R)}_{\mathbf{n}'\to\mathbf{n}} + k^{(L)}_{\mathbf{n}'\to\mathbf{n}} \right) P^{(st)}_{\mathbf{n}'} - \sum_{\mathbf{n}'} \left(k^{(R)}_{\mathbf{n}\to\mathbf{n}'} + k^{(L)}_{\mathbf{n}\to\mathbf{n}'} \right) P^{(st)}_{\mathbf{n}} = 0$$
$$\Rightarrow \sum_{\mathbf{n}'} \left(\sum_{m=1}^{M_A} \left(\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{a,m} \right) \right) P^{(st)}_{\mathbf{n}'} - \sum_{\mathbf{n}'} \left(\sum_{m=1}^{M_A} \left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{a,m} \right) \right) P^{(st)}_{\mathbf{n}} = 0$$
$$\Rightarrow \sum_{m=1}^{M_A} \left[\left(\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{a,m} \right) P^{(st)}_{\mathbf{n}'} - \left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{a,m} \right) P^{(st)}_{\mathbf{n}} \right] = 0,$$

where in the last step we used the fact that the double summation over $\mathbf{n}'$ *and* m *is redundant due to the Kronecker deltas.*

(b)

To show that the probabilities of occupying the many-electron eigenstates at steady state are given as products, $P^{(st)}_{\mathbf{n}} \equiv \prod_{m=1}^{M_A} \left(P^{(st)}_{m,[\mathbf{n}]_m} \right)$, *with* $P^{(st)}_{m,[\mathbf{n}]_m} = \frac{k_{a,m}}{k_{e,m}+k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m}+k_{a,m}} \delta_{[\mathbf{n}]_m,0}$, *we check for consistency with the stationarity condition derived from the master equation in (a), which we rewrite as,* $\sum_{m=1}^{M_A} \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} \left(k_{e,m} P^{(st)}_{\mathbf{n}'} - k_{a,m} P^{(st)}_{\mathbf{n}} \right) + \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} \left(k_{a,m} P^{(st)}_{\mathbf{n}'} - k_{e,m} P^{(st)}_{\mathbf{n}} \right) = 0$.

First, let us notice that the term, $\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e_m}} \left(k_{e,m} P^{(st)}_{\mathbf{n}'} - k_{a,m} P^{(st)}_{\mathbf{n}} \right)$, *vanishes identically unless the vectors* $\mathbf{n}'$ *and* $\mathbf{n}$ *are the same except for a single entry at the* m *th position, where* n_m *must equal one in*

$\mathbf{n}'$ *and zero in* $\mathbf{n}$. *In this case, assigning*

$$P_{\mathbf{n}}^{(st)} = \prod_{m=1}^{M_A} \left(P_{m,[\mathbf{n}]_m}^{(st)} \right) = \prod_{m=1}^{M_A} \left(\frac{k_{a,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,0} \right),$$

means that

$$\frac{P_{\mathbf{n}}^{(st)}}{P_{\mathbf{n}'}^{(st)}} = \frac{P_{1,[\mathbf{n}]_1}^{(st)} P_{2,[\mathbf{n}]_2}^{(st)} \cdots P_{m,0}^{(st)} \cdots P_{M_A,[\mathbf{n}]_{M_A}}^{(st)}}{P_{1,[\mathbf{n}]_1}^{(st)} P_{2,[\mathbf{n}]_2}^{(st)} \cdots P_{m,1}^{(st)} \cdots P_{M_A,[\mathbf{n}]_{M_A}}^{(st)}} = \frac{P_{m,0}^{(st)}}{P_{m,1}^{(st)}} = \frac{k_{e,m}}{k_{a,m}} \Rightarrow P_{\mathbf{n}}^{(st)} k_{a,m} = P_{\mathbf{n}'}^{(st)} k_{e,m}.$$

Consequently, we obtain in this case, $k_{e,m} P_{\mathbf{n}'}^{(st)} - k_{a,m} P_{\mathbf{n}}^{(st)} = 0$, *and therefore, for any* $\mathbf{n}'$ *and* $\mathbf{n}$,

$$P_{\mathbf{n}}^{(st)} \equiv \prod_{m=1}^{M_A} \left(\frac{k_{a,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,0} \right) \Rightarrow \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} \left(k_{e,m} P_{\mathbf{n}'}^{(st)} - k_{a,m} P_{\mathbf{n}}^{(st)} \right) = 0.$$

Similarly, we can see that,

$$P_{\mathbf{n}}^{(st)} \equiv \prod_{m=1}^{M_A} \left(\frac{k_{a,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,0} \right) \Rightarrow \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} \left(k_{a,m} P_{\mathbf{n}'}^{(st)} - k_{e,m} P_{\mathbf{n}}^{(st)} \right) = 0 \ .$$

We therefore conclude that the assignment, $P_{\mathbf{n}}^{(st)} \equiv \prod_{m=1}^{M_A} \left(\frac{k_{a,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,0} \right)$,

leads to, $\sum_{m=1}^{M_A} \left(\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{a,m} \right) P_{\mathbf{n}'}^{(st)} - \left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m} k_{e,m} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m} k_{a,m} \right) P_{\mathbf{n}}^{(st)} = 0$, *for any* $\mathbf{n}'$ *and* $\mathbf{n}$, *which is the condition for a steady state solution of the master equation (Eq. (20.6.16)),*

$$\sum_{\mathbf{n}'} \left(k_{\mathbf{n}'\to\mathbf{n}}^{(R)} + k_{\mathbf{n}'\to\mathbf{n}}^{(L)} \right) P_{\mathbf{n}'}^{(st)} - \sum_{\mathbf{n}'} \left(k_{\mathbf{n}\to\mathbf{n}'}^{(R)} + k_{\mathbf{n}\to\mathbf{n}'}^{(L)} \right) P_{\mathbf{n}}^{(st)} = 0.$$

(c)

Using, $P_{\mathbf{n}}^{(st)} \equiv \prod_{m=1}^{M_A} \left(P_{m,[\mathbf{n}]_m}^{(st)} \right)$, *and the identity,* $P_{m,1}^{(st)} + P_{m,0}^{(st)} = \frac{k_{a,m}}{k_{e,m} + k_{a,m}} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} = 1$, *we can see that the sum of* $P_{\mathbf{n}}^{(st)}$ *over the system eigenstates equals unity,*

$$\sum_{\mathbf{n}} P_{\mathbf{n}}^{(st)} = \sum_{n_1} \sum_{n_2} \sum_{n_3} \cdots P_{n_1,n_2,n_3,....}^{(st)}$$

$$= \sum_{n_1} \sum_{n_2} \sum_{n_3} P_{1,n_1}^{(st)} P_{2,n_2}^{(st)} P_{3,n_3}^{(st)} \cdots$$

$$= \left(\sum_{n_1} P_{1,n_1}^{(st)} \right) \sum_{n_2} \sum_{n_3} P_{2,n_2}^{(st)} P_{3,n_3}^{(st)} \cdots$$

$$= \left(P_{1,0}^{(st)} + P_{1,1}^{(st)} \right) \sum_{n_2} \sum_{n_3} P_{2,n_2}^{(st)} P_{3,n_3}^{(st)} \cdots$$

$$= \left(\sum_{n_2} P_{2,n_2}^{(st)} \right) \sum_{n_3} P_{3,n_3}^{(st)} \cdots$$

$$= \left(P_{2,0}^{(st)} + P_{2,1}^{(st)} \right) \sum_{n_3} P_{3,n_3}^{(st)} \cdots$$

$$= \sum_{n_3} P_{3,n_3}^{(st)} \cdots = 1 \ .$$

(d)

Using, $P_{m,[\mathbf{n}]_m}^{(st)} = \frac{k_{a,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,0}$*, and the explicit expressions for the absorption and emission rates,* $k_{e,m} = \frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m)$ *and* $k_{a,m} = \frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m)$ *we obtain Eq. (20.6.31) for the occupation probabilities of the single particle states at steady state,*

$$P_{m,[\mathbf{n}]_m}^{(st)} = \frac{k_{a,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m} + k_{a,m}} \delta_{[\mathbf{n}]_m,0} \Rightarrow$$

$$P_{m,1}^{(st)} = \frac{\frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m)}{\frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m) + \frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m)}$$

$$= \frac{J_{R,m}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} f_{e,R}(\varepsilon_m) + \frac{J_{L,m}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} f_{e,L}(\varepsilon_m)$$

$$P_{m,0}^{(st)} = \frac{\frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m)}{\frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m) + \frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m)}$$

$$= \frac{J_{R,m}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} f_{h,R}(\varepsilon_m) + \frac{J_{L,m}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} f_{h,L}(\varepsilon_m) \ .$$

Exercise 20.6.6 *For a system of noninteracting fermions, the equation for the steady-state current (Eq. (20.6.20)) can be written as* $I_{L\to R}^{(st)} = e\sum_{\mathbf{n},\mathbf{n}'} k_{\mathbf{n}'\to\mathbf{n}}^{(L)} P_{\mathbf{n}'}^{(st)}[N_{\mathbf{n}} - N_{\mathbf{n}'}]$*, where* $\mathbf{n}$ *is an occupation vector,* $\mathbf{n} = (n_1, n_2, n_3, ..., n_{M_A})$*. (a) Using Eq. (20.6.29) for the state-to-state transition rates, and the results of Ex. 20.6.5 for the corresponding steady state populations in this case,* $P_{\mathbf{n}}^{(st)} = \prod_{m=1}^{M_A}\left(P_{m,[\mathbf{n}]_m}^{(st)}\right)$*, with* $P_{m,[\mathbf{n}]_m}^{(st)} = \frac{k_{a,m}}{k_{e,m}+k_{a,m}}\delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m}+k_{a,m}}\delta_{[\mathbf{n}]_m,0}$*, show that* $I_{L\to R}^{(st)} = e\sum_{m=1}^{M_A}[-P_{m,1}^{(st)}k_{e,m}^{(L)} + P_{m,0}^{(st)}k_{a,m}^{(L)}]$*.*

(b) Use the explicit expressions for the emission and absorption rates (see Ex. 20.6.5), $k_{e,m} = \frac{1}{\hbar}J_{R,m}(\varepsilon_m)f_{h,R}(\varepsilon_m) + \frac{1}{\hbar}J_{L,m}(\varepsilon_m)f_{h,L}(\varepsilon_m)$, $k_{a,m} = \frac{1}{\hbar}J_{R,m}(\varepsilon_m)f_{e,R}(\varepsilon_m) + \frac{1}{\hbar}J_{L,m}(\varepsilon_m)f_{e,L}(\varepsilon_m)$ *, to derive Eq. (20.6.33) for the steady-state current.*

Solution 20.6.6

(a)

The transition rates induced by coupling to the left electrode read (see Eq. (20.6.29) and Ex. 20.6.5),

$$k_{\mathbf{n}\to\mathbf{n}'}^{(L)} = \sum_{m=1}^{M_A}\left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}\left|v_{m,L}\right|^2\frac{J_L(\varepsilon_m)}{\hbar}f_{h,L}(\varepsilon_m) + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}\left|v_{m,L}\right|^2\frac{J_L(\varepsilon_m)}{\hbar}f_{e,L}(\varepsilon_m)\right)$$

$$= \sum_{m=1}^{M_A}\left(\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}k_{e,m}^{(L)} + \delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}k_{a,m}^{(L)}\right) .$$

Using this expression in Eq. (20.6.20) for the current, we obtain

$$I_{L\to R}^{(st)} = e\sum_{\mathbf{n},\mathbf{n}'} k_{\mathbf{n}'\to\mathbf{n}}^{(L)} P_{\mathbf{n}'}^{(st)}[N_{\mathbf{n}} - N_{\mathbf{n}'}]$$

$$= e\sum_{\mathbf{n},\mathbf{n}'}\sum_{m=1}^{M_A}\left(\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}k_{e,m}^{(L)} + \delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}k_{a,m}^{(L)}\right)P_{\mathbf{n}'}^{(st)}[N_{\mathbf{n}} - N_{\mathbf{n}'}]$$

$$= e\sum_{\mathbf{n},\mathbf{n}'}\sum_{m=1}^{M_A}\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}k_{a,m}^{(L)}P_{\mathbf{n}'}^{(st)} - e\sum_{\mathbf{n},\mathbf{n}'}\sum_{m=1}^{M_A}\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}k_{e,m}^{(L)}P_{\mathbf{n}'}^{(st)} \quad ,$$

where in the last step we noticed that $\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e_m}} = 1 \Rightarrow N_{\mathbf{n}} - N_{\mathbf{n}'} = -1$ *and* $\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e_m}} = 1 \Rightarrow N_{\mathbf{n}} - N_{\mathbf{n}'} = 1$.

We now notice that $\mathbf{n}'$ *and* m *define uniquely a single vector* $\mathbf{n}$ *with non-zero contribution to the summations. Therefore, the sum over* $\mathbf{n}$ *can be omitted, while adjusting the respective Kronecker deltas,*

$$I_{L\to R}^{(st)} = e\sum_{\mathbf{n},\mathbf{n}'}\sum_{m=1}^{M_A}\delta_{\mathbf{n}-\mathbf{n}',\mathbf{e}_m}k_{a,m}^{(L)}P_{\mathbf{n}'}^{(st)} - e\sum_{\mathbf{n},\mathbf{n}'}\sum_{m=1}^{M_A}\delta_{\mathbf{n}'-\mathbf{n},\mathbf{e}_m}k_{e,m}^{(L)}P_{\mathbf{n}'}^{(st)}$$

$$= e\sum_{m=1}^{M_A}k_{a,m}^{(L)}\sum_{\mathbf{n}'}\delta_{[\mathbf{n}']_m,0}P_{\mathbf{n}'}^{(st)} - e\sum_{m=1}^{M_A}k_{e,m}^{(L)}\sum_{\mathbf{n}'}\delta_{[\mathbf{n}']_m,1}P_{\mathbf{n}'}^{(st)} .$$

Recalling that the full summation is normalized, $\sum_{\mathbf{n}'} P_{\mathbf{n}'}^{(st)} = 1$ *(see Ex. 20.6.5 (c)), we obtain* $\sum_{\mathbf{n}'} \delta_{[\mathbf{n}']_m,1} P_{\mathbf{n}'}^{(st)} = P_{m,1}^{(st)}$, *and* $\sum_{\mathbf{n}'} \delta_{[\mathbf{n}']_m,0} P_{\mathbf{n}'}^{(st)} = P_{m,0}^{(st)}$. *Consequently, the steady state current reads*

$$I_{L\to R}^{(st)} = e\sum_{m=1}^{M_A} k_{a,m}^{(L)} \sum_{\mathbf{n}'} \delta_{[\mathbf{n}']_m,0} P_{\mathbf{n}'}^{(st)} - e\sum_{m=1}^{M_A} k_{e,m}^{(L)} \sum_{\mathbf{n}'} \delta_{[\mathbf{n}']_m,1} P_{\mathbf{n}'}^{(st)}$$
$$= e\sum_{m=1}^{M_A} k_{a,m}^{(L)} P_{m,1}^{(st)} - e\sum_{m=1}^{M_A} k_{e,m}^{(L)} P_{m,1}^{(st)}$$
$$= e\sum_{m=1}^{M_A} \left(k_{a,m}^{(L)} P_{m,0}^{(st)} - k_{e,m}^{(L)} P_{m,1}^{(st)} \right) .$$

(b)

Using the explicit expression for $P_{m,1}^{(st)}$ *and* $P_{m,0}^{(st)}$, *namely* $P_{m,[\mathbf{n}]_m}^{(st)} = \frac{k_{a,m}}{k_{e,m}+k_{a,m}} \delta_{[\mathbf{n}]_m,1} + \frac{k_{e,m}}{k_{e,m}+k_{a,m}} \delta_{[\mathbf{n}]_m,0}$

, we obtain

$$I_{L\to R}^{(st)} = e\sum_{m=1}^{M_A} \left(k_{a,m}^{(L)} P_{m,0}^{(st)} - k_{e,m}^{(L)} P_{m,1}^{(st)} \right)$$
$$= e\sum_{m=1}^{M_A} \left(k_{a,m}^{(L)} \frac{k_{e,m}}{k_{e,m}+k_{a,m}} - k_{e,m}^{(L)} \frac{k_{a,m}}{k_{e,m}+k_{a,m}} \right)$$
$$= e\sum_{m=1}^{M_A} \left(\frac{k_{e,m}^{(L)} k_{a,m}^{(L)} + k_{e,m}^{(R)} k_{a,m}^{(L)}}{k_{e,m}+k_{a,m}} - \frac{k_{a,m}^{(R)} k_{e,m}^{(L)} + k_{a,m}^{(L)} k_{e,m}^{(L)}}{k_{e,m}+k_{a,m}} \right)$$
$$= e\sum_{m=1}^{M_A} \left(\frac{k_{e,m}^{(R)} k_{a,m}^{(L)} - k_{a,m}^{(R)} k_{e,m}^{(L)}}{k_{e,m}+k_{a,m}} \right) .$$

Using the explicit expressions for the rates,

$$k_{e,m} = \frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m)$$

and

$$k_{a,m} = \frac{1}{\hbar} J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) + \frac{1}{\hbar} J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m) ,$$

we obtain Eq. (20.6.33),

$$I_{L\to R}^{(st)} = e\sum_{m=1}^{M_A} \left(\frac{k_{e,m}^{(R)}k_{a,m}^{(L)} - k_{a,m}^{(R)}k_{e,m}^{(L)}}{k_{e,m} + k_{a,m}} \right)$$

$$= e\sum_{m=1}^{M_A} \left(\frac{\frac{1}{\hbar}J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m)\frac{1}{\hbar}J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m) - \frac{1}{\hbar}J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m)\frac{1}{\hbar}J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m)}{\frac{1}{\hbar}J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) + \frac{1}{\hbar}J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m) + \frac{1}{\hbar}J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) + \frac{1}{\hbar}J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m)} \right)$$

$$= \frac{e}{\hbar}\sum_{m=1}^{M_A} \left(\frac{J_{R,m}(\varepsilon_m) f_{h,R}(\varepsilon_m) J_{L,m}(\varepsilon_m) f_{e,L}(\varepsilon_m) - J_{R,m}(\varepsilon_m) f_{e,R}(\varepsilon_m) J_{L,m}(\varepsilon_m) f_{h,L}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} \right)$$

$$= \frac{e}{\hbar}\sum_{m=1}^{M_A} \frac{J_{R,m}(\varepsilon_m) J_{L,m}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} \left(f_{h,R}(\varepsilon_m) f_{e,L}(\varepsilon_m) - f_{e,R}(\varepsilon_m) f_{h,L}(\varepsilon_m) \right)$$

$$= \frac{e}{\hbar}\sum_{m=1}^{M_A} \frac{J_{R,m}(\varepsilon_m) J_{L,m}(\varepsilon_m)}{J_{R,m}(\varepsilon_m) + J_{L,m}(\varepsilon_m)} \left(f_{e,L}(\varepsilon_m) - f_{e,R}(\varepsilon_m) \right) .$$