Electronic Structure

Basic Theory and Practical Methods

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Solutions for Exercises

Appendix S

Solutions to exercises

Compiled as an Appendix so it refers properly to the main text. But it is not included in published book

Solutions for Exercises in
Electronic Structure: Basic Theory and methods
First Ed. 2004 and Second Ed. 2020
by
Richard M. Martin

These solutions are meant to apply for both the first and second editions. The exercises are mainly the same in the two editions; however, there are some differences and the exercise numbers have changed in many cases. To avoid confusion, the exercise statements are given along with the solutions so it is clear which problem the solution is for. The references are numbered as in the second edition, but I have included enough information to find a reference even one does not have the second edition.

In addition, I have tried to indicate the differences between the exercises in the two editions. The statement of the exercise may be slightly different from the final published version since there were some typos and grammatical corrections in the published version.

Many of the solutions below are expressed in words rather than equations. In the view of the author the exercises are an extension of the text. The main purpose is to not to solve mathematical problems but to increase understanding. In some cases this means working out mathematical expressions in more depth than is desirable in the text; it is better not to load the text with details but rather to describe the physical effects with only essential mathematics and have exercises that go into more depth. In many cases it is appropriate to go to references rather than for me to write out solutions; if the reader goes to the references he/she learns more than just the solution to the particular problem!

Many solutions or part of the solutions were provided by Benchen Huang. I have tried to indicate in every case the parts provided by him by giving credit to ”Benchen” or ”Benchen Huang”.

At the end are two separate appendices:
One is copies of pages from Pines’ book with detailed solution for a problem in Chapter 5. The other is the detailed solution of the two site Hubbard model by Luke Shulenberger.

NOTES:

Solutions not done for Chapters 16 and 17 as of September 16, 2021.

These solutions have NOT been checked carefully and in some cases the notation may be different from the text. I hope the readers will let me know of errors and corrections!

Many places have notes: NOT FINISHED or ADD MORE or similar comments.

There are two sets of solutions for chapter 5. The first is by RMM and it refers to the extensive derivation by Pines copied in Appendix T. The second set is due to Benchen Huang. It is very detailed but has fewer comments.

SOLUTIONS

There are no exercises in Chapters 1 and 2.

Solutions for Chapter 3

Exercise 3.1. Show that the many-body Schrödinger equation (3.13) also results from explicit variation of the energy in (3.9) without use of Lagrange multipliers.

Solution:

In (3.9) the wavefunction does not need to be normalized. If we vary the wavefunction in (3.9), then we must consider the variation in both numerator and denominator. The simplest form is to vary the bra and the ket independently which leads to the variational equation

$$\frac{\delta E}{\delta\langle\Psi}| = \frac{1}{\langle\Psi|\Psi\rangle}\left[\hat{H}|\Psi\rangle - \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}|\Psi\rangle\right] = 0, \tag{S.1}$$

which immediately gives the desired result

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \tag{S.2}$$

If we insist that that the bra and ket are not independent, then we arrive at equations that are the sum of a term like the one above plus the complex conjugate equal to zero. This is equivalent since the value for the energy must be real, we also have the equivalent expression

$$\langle\Psi|\hat{H} = E\langle\Psi|. \tag{S.3}$$

We can also write out explicitly the expressions in the form of a functional variation like in Appendix A.

Eq due to Benchen Huang

$$\begin{aligned}
\delta E &= \frac{\langle\Psi|\Psi\rangle\left(\langle\delta\Psi|H|\Psi\rangle + \langle\Psi|H|\delta\Psi\rangle\right) - \langle\Psi|H|\Psi\rangle(\langle\delta\Psi||\Psi\rangle + \langle\Psi||\delta\Psi\rangle)}{\langle\Psi||\Psi\rangle^2} \\
&= \frac{\langle\delta\Psi|H|\Psi\rangle + \langle\Psi|H|\delta\Psi\rangle}{\langle\Psi||\Psi\rangle} - E\frac{\langle\delta\Psi||\Psi\rangle + \langle\Psi||\delta\Psi\rangle}{\langle\Psi||\Psi\rangle} \\
&= \frac{\langle\delta\Psi|H - E|\Psi\rangle}{\langle\Psi||\Psi\rangle} + c.c. = 0
\end{aligned} \tag{S.4}$$

Exercise 3.2 Show that the independent-particle Schrödinger equation (3.36) is a special case of the many-body solution. First show this for one particle; then for many non-interacting particles.

Solution:

For one particle the result is simply that the sum in the many-body equation is just one particle and there is no interaction.

For many electrons the essential point is that the particles are fermions and there no interaction terms. At this point we are ignoring spin–orbit interaction, so the problem reduces to independent problems for the two spin states. Thus this problem is the same as Hartree-Fock with no interactions. In that case the essential point is that the orbitals in the many-body wavefunction Eq. (3.43) are given by which leads to the Hartree-Fock equations in

Eq. (3.45) or 3.46. This is the desired result since there are no interactions.
A key step in the logic is in Exercise 3.6 that the solutions of the independent-particle Schrödinger equation (3.36) are functions that are orthogonal, which is a general property of second order differential equations. For orthogonal orbitals the determinate simplifies and the proper expression for the antisymmetric wavefunctions for many fermions is given by the independent-particle function that are orthogonal which the requirement that they are also normalized and N orbitals are filled for N electrons of a given spin, i.e., one it obeys the exclusion principle that there is particle per orbital. This applies to both ground state with only the N lowest energy states occupied or excited states with some of higher states occupied.

Exercise 3.3 As part of his undergraduate thesis, Feynman showed that the force theorem applied to a nucleus leads to the force being exactly the electric field at the given nucleus due to the charge density of the rest of the system (electrons and other nuclei) times the charge of the given nucleus. Derive this result from (3.18).
(NOTE: it would be better to refer to the following equation (3.19).)

Solution:
As shown by (3.19), the force is the field of the nucleus acting on the charge of the rest of the crystal. Partial integration yields the desired result that the force is the electric field at the given nucleus due to the charge density of the rest of the system (electrons and other nuclei) times the charge of the given nucleus. This can be written out explicitly using the fact that in a system of ion and nuclei viewed as fixed positive charges Z_I, in units where $|e| = 1$ the external potential acting on the electrons is:
$V_{ext}(\vec{r} = -\sum_I \frac{Z_I}{|\vec{R}_I - \vec{r}|}$. And then we can do the differentiation:

$$\frac{\partial E_{II}}{\partial \vec{R}_I} = -\sum_J \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|^2} \frac{\vec{R}_I - \vec{R}_J}{|\vec{R}_I - \vec{R}_J|} \tag{S.5}$$

$$\frac{\partial E_{elec-ion}}{\partial \vec{R}_I} = \int d^3 r n(\vec{r}) \frac{\partial V_{ext}(\vec{r})}{\partial \vec{R}_I} = \int d^3 r n(\vec{r}) \frac{Z_I}{|\vec{R}_I - \vec{r}|^2} \frac{\vec{R}_I - \vec{r}}{|\vec{R}_I - \vec{r}|}, \tag{S.6}$$

So that we have for the force:

$$\vec{F}_I = -\frac{\partial E_{elec-ion}}{\partial \vec{R}_I} = -\int d^3 r n(\vec{r}) \frac{Z_I}{|\vec{R}_I - \vec{r}|^2} \frac{\vec{R}_I - \vec{r}}{|\vec{R}_I - \vec{r}|} + \sum_J \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|^2} \frac{\vec{R}_I - \vec{R}_J}{|\vec{R}_I - \vec{R}_J|}, \tag{S.7}$$

which has the interpretation as Coulomb force on nucleus I.

Exercise 3.4 Derive the additional terms that must be included so that the expression for the force given by the force theorem is identical to the explicit derivative of the energy, if the basis depends explicitly on the positions for the nuclei. Show that the contribution of these terms vanishes if the basis is complete.

Solution:
The key step in deriving the theorem is that the terms involving the derivative of Ψ in (3.18) vanish. This follows from the general requirement that the energy is minimized for

the exact ground state Ψ. But what does minimized mean? If there is a complete basis set it is minimized with respect to all possible variations and there is no linear term in the energy as a function of any possible variation of Ψ. However, if the basis set is not complete and it depends on the nuclear positions (e.g., , a finite set of orbitals centered on the nuclei) the ground state is minimized only with respect to all possible variations within that set of orbitals. In that case there can be a linear variation of the energy as a function of Ψ with the nuclear positions that does not vanish. These are called Pulay corrections.
It is useful to note that if the functions do not depend on the nuclear positions, the terms vanish even if the basis set is not complete. One of the great advantages of plane waves is that the functions are not tied to the nuclei. This also applies to real-space grids so long as the positions of grid points are not constrained and are independent of the nuclear positions.

Exercise 3.5 Derive the stress theorem (3.23). Show that this equation reduces to the well-known virial theorem (3.24) in the case of isotropic pressure and Coulomb interactions.

Solution:
The expression is simply a scaling of space as described in the text. The details require careful formulation and they can be found in the 1985 paper by Nielsen and Martin [162]. The virial theorem follows if one uses the relation to pressure given below (3.23). Often the theorem is quoted only for the special case of $P = 0$.

Exercise 3.6 Show that the relations for non-interacting particles given in the equations following Eq. (3.36) remain valid, if a fully antisymmetric determinant wavefunction like Eq. (3.43) is created from the orbitals. Note that this holds *only if the particles are non-interacting*.

Solution:
The key step is explained in the solution of Exercise 3.2 and repeated here in slightly different words. Note that the particles are non-interacting, which is stronger requirement than that they are independent; the latter can occur in a Hartree-Fock-type approximation even though interactions are included approximately. The solutions of the independent-particle Schrödinger equation (3.36) are functions that are orthogonal, which is a general property of second order differential equations. For orthogonal orbitals the determinate simplifies and the proper expression for the antisymmetric wavefunctions for many fermions is given by the independent-particle function that are orthogonal. It is not stated explicitly in the statement of this exercise, but it is implicitly assumed that the orbitals are normalized and N orbitals are filled for N electrons of a given spin, i.e., it obeys the exclusion principle that there is particle per orbital. This applies to both ground state with only the N lowest energy states occupied or excited states with some of higher states occupied.

Exercise 3.7. Derive the Fermi–Dirac distribution (3.38) for non-interacting particles from the general definition of the density matrix (3.32) using the fact that the sum over many-body states in (3.32) can be reduced to a sum over all possible occupation numbers $\{n_i^\sigma\}$ for each of the independent particle states, subject to the conditions that each n_i^σ can be either 0 or 1, and $\sum_i n_i^\sigma = N^\sigma$.

Solution:

If one treats a fixed number of fermions, the probability is difficult to calculate due to the number constraint. However, if the number of fermions is not conserved, then the occupation of each state is zero or one weighted by the Boltzmann factor, independent of the occupation of all other states. The partition function for the entire system is the product of partition functions for each state i. It follows immediately that the probability of occupation of each state given by

$$f_i^\sigma = \frac{0 + 1e^{-\beta\epsilon_i^\sigma}}{1 + e^{-\beta\epsilon_i^\sigma}} = \frac{1}{e^{\beta\epsilon_i^\sigma} + 1}. \tag{S.8}$$

The final expression follows using the fact that the chemical potential μ represents the energy of particles in a reservoir that can supply arbitrary numbers of particles. Then the above formula holds except that the Boltzmann factor depends upon the *difference* of the energy for a fermion in state i and the energy of the reservoir which can supply or absorb any number of fermions at energy μ. This leads to the expression (3.38),

$$f_i^\sigma = \frac{1}{e^{\beta(\varepsilon_i^\sigma - \mu)} + 1}. \tag{S.9}$$

Exercise 3.8 Following Exercise 3.7, show that Eq. (3.35)) simplifies to Eq. (3.37) for any operator in the independent-particle approximation.

Solution:

The expectation value in Eq. (3.35) can be written in terms of the eigenvectors of the hamiltonian as in Eq. (3.32), so that Eq. (3.35) can be written as a sum over eigenstates with probability given by the Boltzman factor in Eq. (3.29). In an independent-particle problem the states can be classified by the set of occupations of 0 or 1 in states i with energy ε_i. In Exercise 3.7 it was shown that for independent particles in states with occupation 0 or 1, the Boltzman factor leads to the probability of occupation 1 given by f_i defined in Eq. (S.9) independently for each independent-particle state i. This is the physical reasoning that explains the form in Eq. (3.37), which can also be expressed in terms of the independent-particle density matrix $\hat{\rho} = \sum_i |\psi_i^\sigma\rangle f_i^\sigma \langle\psi_i^\sigma|$, given in Eq. (3.40).

From Benchen's notes

Since we know that $\hat{\rho} = \sum_i |\psi_i^\sigma\rangle f_i^\sigma \langle\psi_i^\sigma|$, we have:

$$\begin{aligned}
\langle\hat{O}\rangle = Tr\hat{\rho}\hat{O} &= \sum_{i,j} \langle\Psi_i||\psi_j^\sigma\rangle f_j^\sigma \langle\psi_j^\sigma|\hat{O}|\Psi_i\rangle \\
&= \sum_j f_j^\sigma \langle\psi_j^\sigma|\hat{O}(\sum_i |\Psi_i\rangle\langle\Psi_i|)|\psi_j^\sigma\rangle \\
&= \sum_i f_i^\sigma \langle\psi_i^\sigma|\hat{O}|\psi_i^\sigma\rangle
\end{aligned} \tag{S.10}$$

Exercise 3.9 Why is the independent particle density matrix (3.41) diagonal in spin? Is this always the case?

Solution:

As discussed at the beginning on this chapter, in much of this book the expressions assume spin is conserved and one can diagonalize to treat spin up and down independently.

However, the density matrix is *not* always diagonal in the spins. If the hamiltonian is spin independent, then this is sufficient for calculations of the energy, but the form with correct particle symmetry in general is a linear combination of up and down states. If there is spin-orbit interaction, then of course spin is not separately conserved.

Exercise 3.10 Show that the Hartree–Fock wavefunction Eq. (3.43) is normalized if the independent-particle orbitals are orthonormal.

Solution:

To find the norm $\langle \Phi | \Phi \rangle$ of the Hartree–Fock wavefunction in Eq. (3.43) we note that the determinant can be expanded into $N!$ terms, each a product of the N independent-particle orbitals. In the orbitals are orthogonal, for each of the $N!$ terms in $\langle \Phi |$ the overlap integral is non-zero only for one of the $N!$ functions in $| \Phi \rangle$. That term is the product of the N overlaps $\langle \psi_i | \psi_i \rangle$, which is unity if the each orbital ψ_i is normalized. Because of the factor $(1/N!)^{1/2}$ the result is $\langle \Phi | \Phi \rangle = N!/N! = 1$.

Exercise 3.11. Show that the Hartree–Fock wavefunction (3.43) leads to the exchange term in (3.44) and that the variational equation leads to the Hartree–Fock equation (3.45) if the independent-particle orbitals are orthonormal. Explain why the forms are more complicated if the independent-particle orbitals are not orthonormal.

Solution:

If the the independent-particle orbitals are orthonormal then all integrals simplify, and the needed expectation values can be written as shown in (3.44). The integrals over all the other electron coordinates simplify because $\langle \psi_i | \psi |_j \rangle = \delta_{ij}$. The two electron terms are non-zero only if the orbitals involved are in either the same order in the two determinants or are interchanged. This leads to the form in (3.44). In the general case $\langle \psi_i | \psi |_j \rangle = S_{ij}$, and the right hand side of (3.44) must involve integrals over four functions i, j, k, l. The form (3.45) follows straightforwardly from the variation of each independent-particle function.

The derivation of the equations has been written out in detail by Benchen Huang:

$$
\begin{aligned}
\langle \Phi | H | \Phi \rangle = & \frac{1}{N!}(N-1)!N \sum_{i,\sigma} \int d\vec{r} \psi_i^{\sigma *}(\vec{r}) \left[-\frac{1}{2}\nabla^2 + V_{ext} \right] \psi_i^{\sigma}(\vec{r}) \\
& + \frac{1}{N!}(N-2)!C_N^2 \sum_{i,j,\sigma_i,\sigma_j} \int d\vec{r} d\vec{r}' \psi_i^{\sigma_i *}(\vec{r}) \psi_j^{\sigma_j *}(\vec{r'}) \frac{1}{|\vec{r} - \vec{r}'|} \psi_i^{\sigma_i}(\vec{r}) \psi_j^{\sigma_j}(\vec{r}') \\
& - \frac{1}{N!}(N-2)!C_N^2 \sum_{i,j,\sigma} \int d\vec{r} d\vec{r'} \psi_i^{\sigma *}(\vec{r}) \psi_j^{\sigma *}(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_i^{\sigma}(\vec{r'}) \psi_j^{\sigma}(\vec{r}) \\
& = \sum_{i,\sigma} \int d\vec{r} \psi_i^{\sigma *}(\vec{r}) \left[-\frac{1}{2}\nabla^2 + V_{ext} \right] \psi_i^{\sigma}(\vec{r}) \\
& + \frac{1}{2} \sum_{i,j,\sigma_i,\sigma_j} \int d\vec{r} d\vec{r}' \psi_i^{\sigma_i *}(\vec{r}) \psi_j^{\sigma_j *}(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_i^{\sigma_i}(\vec{r}) \psi_j^{\sigma_j}(\vec{r}') \\
& - \frac{1}{2} \sum_{i,j,\sigma} \int d\vec{r} d\vec{r}' \psi_i^{\sigma *}(\vec{r}) \psi_j^{\sigma *}(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_i^{\sigma}(\vec{r'}) \psi_j^{\sigma}(\vec{r})
\end{aligned}
\tag{S.11}
$$

Next we derive the Hartree Fock equation. Since there are constraints on N spin orbitals, we have N Lagrange multipliers:

$$\begin{aligned}
&\delta(\langle\Phi|H|\Phi\rangle - \sum_{i,\sigma}\epsilon_i^\sigma\,\langle\psi_i^\sigma|-\rangle\,N) = \langle\delta\Phi|H|\Phi\rangle - \sum_{i,\sigma}\epsilon_i^\sigma\langle\delta\psi_i^\sigma||\psi_i^\sigma\rangle + c.c.\\
&= \sum_{i,\sigma}\int d\vec{r}\delta\psi_i^{\sigma *}[-\frac{1}{2}\nabla^2 + V_{ext}]\psi_i^\sigma\\
&+ \sum_{i,j,\sigma\sigma_j}\int d\vec{r}d\vec{r}'\,\delta\psi_i^{\sigma *}(\vec{r})\psi_j^{\sigma_j *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_i^\sigma(\vec{r})\psi_j^{\sigma_j}(\vec{r}')\\
&- \sum_{i,j,\sigma}\int d\vec{r}d\vec{r}'\,\delta\psi_i^{\sigma *}(\vec{r})\psi_j^{\sigma *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_i^\sigma(\vec{r}')\psi_j^\sigma(\vec{r}) - \sum_{i,\sigma}\epsilon_i^\sigma\langle\delta\psi_i^\sigma||\psi_i^\sigma\rangle + c.c. = 0
\end{aligned} \tag{S.12}$$

The second and third term of the second equality involves permutation of i and j indices. Since the variation is arbitrary, we would have:

$$\begin{aligned}
&\left[-\frac{1}{2}\nabla^2 + V_{ext} + \sum_{j,\sigma_j}\int d\vec{r}'\psi_j^{\sigma_j *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_j^{\sigma_j}(\vec{r}')\right]\ \psi_i^\sigma(\vec{r})\\
&-\sum_j\int d\vec{r}'\psi_j^{\sigma *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_i^\sigma(\vec{r}')\psi_j^\sigma(\vec{r}) - \epsilon_i^\sigma\psi_i^\sigma + c.c. = 0
\end{aligned} \tag{S.13}$$

$$\begin{aligned}
&\left[-\frac{1}{2}\nabla^2 + V_{ext} + \sum_{j,\sigma_j}\int d\vec{r}'\psi_j^{\sigma_j *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_j^{\sigma_j}(\vec{r}')\right]\ \psi_i^\sigma(\vec{r})\\
&-\sum_j\int d\vec{r}'\psi_j^{\sigma *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_i^\sigma(\vec{r}')\psi_j^\sigma(\vec{r}) = \epsilon_i^\sigma\psi_i^\sigma
\end{aligned} \tag{S.14}$$

which are the Hartree Fock equations.

Exercise 3.12 Show explicitly from the definition (3.54) that the exchange hole around each electron always integrates to one missing electron. Show that, as stated in the text, this is directly related to the fact that "exchange" includes a self-term that cancels the unphysical self-interaction in the Hartree energy.

Solution:

Note: There is a misprint in (3.54) - a spurious vertical bar following the summation sign. The correct expression is

$$\Delta n_{\mathrm{HFA}}(\mathbf{r},\sigma;\mathbf{r}',\sigma') = \Delta n_x(\mathbf{r},\sigma;\mathbf{r}',\sigma') = -\delta_{\sigma\sigma'}\left|\textstyle\sum_i \psi_i^{\sigma *}(\mathbf{r})\psi_i^\sigma(\mathbf{r}')\right|^2. \tag{S.15}$$

The desired result is found by integrating the expression over all $\mathbf{r}'$ for a given $\mathbf{r}$., which can be written

$$\textstyle\int d\mathbf{r}'\Delta n_{\mathrm{HFA}}(\mathbf{r},\sigma;\mathbf{r}',\sigma) = \sum_{ij}\int d\mathbf{r}'\psi_i^\sigma(\mathbf{r})\psi_i^\sigma(\mathbf{r}'*)\psi_j^{\sigma *}(\mathbf{r})\psi_j^\sigma(\mathbf{r}'). \tag{S.16}$$

From the orthonormality of the functions, it immediately follows that the only non-zero terms are for $i = j$ and the expression becomes

$$\int d\mathbf{r}' \Delta n_{\mathrm{HFA}}(\mathbf{r}, \sigma; \mathbf{r}', \sigma) = -n(\mathbf{r}, \sigma). \tag{S.17}$$

This is the desired relation since the probability of finding an electron at $\mathbf{r}$ with spin σ is $n(\mathbf{r}, \sigma)$, the integral over the exchange hole is -1.

The derivation has been worked out in detail by Benchen Huang:
We start from the definition of n and $\triangle n$, and by performing several integrations to see the physical meaning of exchange hole. We know that:

$$\begin{aligned} \triangle n(\vec{r}, \sigma; \vec{r}', \sigma') &= n(\vec{r}, \sigma; \vec{r}', \sigma') - n(\vec{r}, \sigma) n(\vec{r}', \sigma') \\ &= n_{xc}(\vec{r}, \sigma; \vec{r}', \sigma') n(\vec{r}, \sigma) \end{aligned} \tag{S.18}$$

If we integrate $\vec{r}'$ and σ', we would get:

$$\sum_{\sigma'} \int d\vec{r}' \triangle n(\vec{r}, \sigma; \vec{r}', \sigma') = (N-1) n(\vec{r}, \sigma) - N n(\vec{r}, \sigma) = -n(\vec{r}, \sigma) \tag{S.19}$$

If we integrate $\vec{r}, \vec{r}'$ and σ, σ', we would get:

$$\sum_{\sigma, \sigma'} \int d\vec{r} d\vec{r}' \triangle n(\vec{r}, \sigma; \vec{r}', \sigma') = N(N-1) - N^2 = -N \tag{S.20}$$

$$\sum_{\sigma'} \int d^3 r' n_x(\vec{r}, \sigma; \vec{r}', \sigma') = \sum_{\sigma'} \int d\vec{r}' \frac{\triangle n(\vec{r}, \sigma; \vec{r}', \sigma')}{n(\vec{r}, \sigma)} = -1 \tag{S.21}$$

So the exchange hole around each electron integrates to -1.

Exercise 3.13. Derive the formulas for the pair distribution (3.53) and the exchange hole (3.54) for non-interacting fermions by inserting the Hartree–Fock wavefunction (3.43) into the general definition (3.50).

Solution:
This is a bit tedious to write down (An explicit derivation is given below.) but it is straightforward to show that the expressions involve all pairs of orbitals since there are two arguments ($\mathbf{r}, \sigma$ and $\mathbf{r}', \sigma'$) in the expression (3.50). One always finds two terms as in the expansion of the 2×2 determinant in (3.53). This leads directly to (3.54) as sown in the following exercise.

The derivation has been worked out in detail by Benchen Huang:

$$\begin{aligned} n_{HFA}(\vec{r}, \sigma; \vec{r}', \sigma') &= N(N-1) \int d\vec{r}_3 ... d\vec{r}_N |\Psi|^2 \\ &= N(N-1) \frac{1}{N!} (N-2)! \frac{1}{2} \sum_{i,j} \begin{vmatrix} \phi_i(\vec{r}, \sigma) & \phi_j(\vec{r}, \sigma) \\ \phi_i(\vec{r}', \sigma') & \phi_j(\vec{r}', \sigma') \end{vmatrix}^2 \\ &= \frac{1}{2} \sum_{i,j} \begin{vmatrix} \phi_i(\vec{r}, \sigma) & \phi_j(\vec{r}, \sigma) \\ \phi_i(\vec{r}', \sigma') & \phi_j(\vec{r}', \sigma') \end{vmatrix}^2 \end{aligned} \tag{S.22}$$

Note that in the summation, index i and j could be the same. Now we can set one step further to calculate the $\triangle n$:

$$\begin{aligned}
\triangle n_{HFA}(\vec{r},\sigma;\vec{r}',\sigma') &= n_{HFA}(\vec{r},\sigma;\vec{r}',\sigma') - n(\vec{r},\sigma)n(\vec{r}',\sigma') \\
&= \frac{1}{2}\sum_{i,j}\begin{vmatrix}\phi_i(\vec{r},\sigma) & \phi_j(\vec{r},\sigma) \\ \phi_i(\vec{r}',\sigma') & \phi_j(\vec{r}',\sigma')\end{vmatrix}^2 - \sum_{i,j}|\phi_i(\vec{r},\sigma)|^2|\phi_j(\vec{r}',\sigma')|^2 \\
&= -\left|\sum_i \phi_i^{\sigma *}(\vec{r},\sigma)\phi_i^{\sigma'}(\vec{r}',\sigma')\right|^2 = -\delta_{\sigma\sigma'}\left|\sum_i \psi_i^{\sigma *}(\vec{r})\psi_i^{\sigma}(\vec{r}')\right|^2
\end{aligned} \tag{S.23}$$

Note from Benchen: I'm not 100 percent sure about the last equality because I don't know if $\chi_i^*(\sigma)\chi_i(\sigma') = \delta_{\sigma\sigma'}$.

CHECK

Exercise 3.14 By expanding the 2×2 determinant in Eq. (3.53): (a) show that

$$\sum_{\sigma'}\int \mathrm{d}r'\Delta n_x(\mathbf{r},\sigma;\mathbf{r}',\sigma') = (N-1)n(\mathbf{r},\sigma), \tag{S.24}$$

where $n(\mathbf{r},\sigma)$ is the density; and (b) derive the formula (3.54) for the exchange hole.

Solution:

The determinant in Eq. (3.53) has the form $D = \phi_i(\mathbf{r},\sigma)\phi_j(\mathbf{r}',\sigma') - \phi_j(\mathbf{r},\sigma)\phi_i(\mathbf{r}',\sigma')$ so that one-half the sum over all i and j of the square of the determinant is the product $n(\mathbf{r},\sigma)n(\mathbf{r}',\sigma') - crossterm$. The product is the probablity for uncorrelated particles and the cross term is the correction. The sum over i and j vanishes except for the terms with $i = j$ and the same spin, which is exactly the expression in (3.54).

The explicit equations been worked out by Benchen Huang:

$$\begin{aligned}
\sum_{\sigma'}\int d\vec{r}' n_{HFA}(\vec{r},\sigma;\vec{r}',\sigma') &= \sum_{\sigma'}\int d\vec{r}'\frac{1}{2}\sum_{i,j}\begin{vmatrix}\phi_i(\vec{r},\sigma) & \phi_j(\vec{r},\sigma) \\ \phi_i(\vec{r}',\sigma') & \phi_j(\vec{r}',\sigma')\end{vmatrix}^2 \\
&= \frac{1}{2}\sum_{\sigma'}\sum_{i,j}\int d\vec{r}'\, |\phi_i(\vec{r},\sigma)\phi_j(\vec{r}',\sigma') - \phi_j(\vec{r},\sigma)\phi_i(\vec{r}',\sigma')|^2 \\
&= \sum_i |\phi_i(\vec{r},\sigma)|^2 \sum_{\sigma'}\int d\vec{r}' \sum_j |\phi_j(\vec{r}',\sigma')|^2 \\
&\quad - \sum_{\sigma'}\sum_{i,j}\left[\int d\vec{r}'\phi_j^*(\vec{r}',\sigma')\phi_i(\vec{r}',\sigma')\right]\phi_i^*(\vec{r},\sigma)\phi_j(\vec{r},\sigma) \\
&= Nn(\vec{r},\sigma) - \sum_{\sigma'}\sum_{i=j}\left[\int d\vec{r}'\phi_j^*(\vec{r}',\sigma')\phi_i(\vec{r}',\sigma')\right]\phi_i^*(\vec{r},\sigma)\phi_j(\vec{r},\sigma) \\
&= (N-1)n(\vec{r},\sigma)
\end{aligned} \tag{S.25}$$

Exercise 3.15. The relation (3.55) is a general property of non-interacting identical particles (see, e.g., Landau and Pitaevskii, Statistical Physics: Part 1 [278]). As shown in (3.54),

$\Delta n_x(\mathbf{r}, \sigma; \mathbf{r}', \sigma')$ is always negative for fermions. Show that for bosons with a symmetric wavefunction, the corresponding exchange term is always positive.

Solution:

For the case of non-interacting bosons, the wavefunction is a "permanent" - a symmetrized wavefunction. All expressions are identical to those for fermions except that the wavefunction does not change sign when particles are interchanged. All results are the same except there are no negative signs. Writing out the expressions leads to exactly the same expression for the joint probability for fermions and bosons except for the sign. This establishes the relation (3.55) for both bosons and fermions.

Exercise 3.16 Derive the results stated after Eq. (3.57) that: (a) for a one-electron problem like hydrogen, the exchange term exactly cancels the Hartree term as it should; and (b) for the ground state of two electrons in a spin singlet state, e.g., in helium, the Hartree–Fock approximation leads to a V_{eff} sum of the external (nuclear) potential plus one-half the Hartree potential.

Solution:

(a) For any case where there is only one single-particle wavefunction, the direct (Hartree) potential and the exchange potentials are identical and cancel out leaving only the bare potential, the potential due to the proton in H.
(b) For two electrons in the ground state in the Hartree-Fock uncorrelated approximation, the two particles are in the same spatial state with up and down spins. The Hartree term involves the total density so that it is 4 times that for one electron alone. However the exchange term involves each electron separately (since it involves only electrons with the same spin) so that it is 1/2 the Hartree term.

Exercise 3.17 Following the exercise above, consider two electrons in a spin triplet state. Show that the situation is not so simple as for the singlet case, i.e., that in the Hartree–Fock approximation there must be two different functions V_{eff} for two different orbitals.

Solution:

This is really a simple problem stated in a complicated way. Two electrons of the same spin cannot be in the same state. In Hartree-Fock this is apparent because the two-particle wavefuntion is a determinant that vanishes if the two orbitals in the dedterminant are the same.

Exercise 3.18 Derive Koopmans' theorem by explicitly taking matrix elements of the hamiltonian with an orbital to show that the eigenvalue is the same as the energy difference if that orbital is removed.

Solution:

Solution due to Benchen

We know that orbitals would satisfy the HF equation as:

$$\begin{aligned}&\left[-\frac{1}{2}\nabla^2 + V_{ext} + \sum_{j,\sigma_j}\int d\vec{r}'\psi_j^{\sigma_j *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_j^{\sigma_j}(\vec{r}')\right]\ \psi_i^\sigma(\vec{r})\\ &-\sum_j\int d\vec{r}'\psi_j^{\sigma *}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_i^\sigma(\vec{r}')\psi_j^\sigma(\vec{r}) = \epsilon_i^\sigma\psi_i^\sigma\end{aligned} \tag{S.26}$$

First of all we could compute the value of ϵ_i^σ as:

$$\epsilon_i^\sigma = h_{ii} + \sum_{j\neq i,\sigma_j} J_{ij,\sigma_j} + J_{ii,\sigma=\sigma_j} + J_{ii,\sigma\neq\sigma_j} - \sum_{j\neq i} K_{ij} - K_{ii}, \tag{S.27}$$

where J stands for the Coulombic repulsion term while K stands for the exchange integral. In this formula, $J_{ii,\sigma=\sigma_j}$ is the unphysical term and it cancels with K_{ii}. If we remove a electron away from orbital i, then we lost the single electron term of that orbital, interaction between that electron with electrons in other orbitals, and interaction between that electron with the other electron in the same spatial orbital but different spin, which is exactly the expression of ϵ_i^σ. Since now we are considering a orbital not occupied, we have:

$$\epsilon_i^\sigma = h_{ii} + \sum_{j,\sigma_j} J_{ij,\sigma_j} - \sum_j K_{ij} \tag{S.28}$$

If we have one more electron occupying this orbital, we would get an additional energy exactly the same as ϵ_i^σ.

Exercise 3.19. (NOTE: There is a error in the statement of the problem in the first printing of first edition. Corrected in the second printing. This correct form is given here, with the changes indicated by the italicized parts.)

For adding electrons one must compute empty orbitals of the Hartree–Fock equation (3.45). Show that such an empty orbital does not experience *a self contribution to the exchange energy, whereas for a filled state there is an attractive self term in the exchange.* This is responsible for much of the overestimate of energy gaps in the Hartree–Fock approximation.

Solution:

This result follows immediately from the definition, since the exchange term involves only integrals over the occupied states. The gap is increased because this term lowers the filled states, but not the empty ones.

Exercise 3.20 In a finite system Hartree–Fock eigenfunctions have the (surprising) property that the form of the long-range decay of *all* bound states is the same, independent of binding energy. For example, core states have the same exponential decay as valence states, although the prefactor is smaller. Show that this follows from (3.45).

Solution:

This follows because each orbital is mixed with each other orbital by the exchange terms and because of orthogonality. To see this consider the Schrödinger equation as written in Eq. (3.46). If there were no exchange term V_x this would be a simple differential equation and each bound state would decay at large distance with a value depending on its eigenvalue. However, the non-local exchange term VI_x^i in Eq. (3.48) has a different consequence. To see its effect consider the action on state ψ_i. The factor of $1/\psi_i$ in Eq. (3.48) is canceled leaving a sum over all the other occupied functions ψ_j. Thus each orbital in general has some part of the longest range behavior of the density. For a very localized state like a core state the coefficient is very small (This can be seen in the expression in square brackets is small because the overlap with extended states is small.) nevertheless it is non-zero. Since the determinant is invariant to mixing the orbitals, it should be possible to require that only one orbital has the longest range part and all the others are shorter range, but this is not required and it is not the case for the eigenvectors in the Hartree-Fock method.

Exercise 3.21 Show that all contributions involving i and j both occupied vanish in the expectation value Eq. (D.4).

Solution:

This follows because there is a double sum over i and j. For each pair i, j there is another j, i that cancels it it since the denominator changes sign. A essential ingredient is that the expectation value for must be real in which case the numerators are real and the same for i, j and j, i.

Exercise 3.22 Show that the correlation hole always integrates to zero, i.e., it rearranges the charge correlation. This does not require complex calculations beyond Hartree–Fock theory; all that is needed is to show that conservation laws must lead to this result.

Solution:

It is instructive to realize that this follows from the definitions of exchange and correlation. *The essential point is that it is the total exchange-correlation hole that is the physical quantity.* As stated in the text the division into exchange and correlation is arbitrary (but useful) and we use the accepted convention that correlation is *defined* to be correlation beyond Hartree-Fock. This is essentially what is in the text where it is stated that correlation only affects the relative positions of other particles, with no change in the number. To see this more mathematically one can start from the definition in terms of the many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, ldots)$. If one particle is at position $\mathbf{r}_0$, the probability of finding another at point $\mathbf{r}$ is $p_0(\mathbf{r}) \int d\mathbf{r}_3 d\mathbf{r}_4 \ldots |\Psi(\mathbf{r}_0, \mathbf{r}, \mathbf{r}_3, \mathbf{r}_4, ldots)|^2$. The integral over positions $\mathbf{r}$ is $\int d\mathbf{r} p(\mathbf{r})$ which counts all particles except the one at $\mathbf{r}_0$. This is a formal way of saying the exchange-correlation hole integrates to one missing electron as stated in the text after Eq. (3.58).

The fact the the exchange hole integrates to minus one follows from the fact that this argument applies as well to the approximation that particles are uncorrelated except for the requirement of antisymmetry, as in Hartree-Fock. Since correlation is *defined* to be correlation beyond Hartree-Fock, the correlation hole integrates to zero.

Exercise 3.23 As an example of the force theorem consider a one-dimensional harmonic oscillator with hamiltonian given by $-\frac{1}{2}(\mathrm{d}^2/\mathrm{d}x^2) + \frac{1}{2}Ax^2$, where A is the spring constant and the mass is set to unity. Using the exact solution for the energy and wavefunction, calculate the generalized force $\mathrm{d}E/\mathrm{d}A$ by direct differentiation and by the force theorem.

Solution:

The exact ground state solution is an Gaussian $\psi(x) = (\frac{\omega}{\pi})^{1/4} exp(-(1/2)\omega x^2)$ with energy $E_0 = (1/2)\omega$ with $\omega = A^{1/2}$ in units where the mass is unity. The derivative of the ground state energy is $dE_0/dA = \frac{1}{2\omega} dE_0/d\omega = \frac{1}{4\omega}$. The generalized force theorem is $dE_0/dA = \langle dH/dA \rangle = \langle (1/2)x^2 \rangle$. Using a table of integrals for gaussians, the expectation value of x^2 gives $\langle (1/2)x^2 \rangle = \int dx (1/2) x^2 |\psi(x)|^2 = (\frac{\omega}{\pi})^{1/2} \frac{\pi^{1/2}}{4\omega^{3/2}} = \frac{1}{4\omega}$.

Exercises 24, 25 in first edition moved to App. D in second edition.

Solutions for Chapter 4
Same as first edition

Exercise 4.1 Derive the expression for primitive reciprocal lattice in three dimensions given in Equation (4.13).

Solution:

This can be derived using the fact that the cross product of two vectors $\mathbf{a}_2 \times \mathbf{a}_3$ is perpendicular to both, as required in the definition of $\mathbf{b}_1$, and the requirement that $\mathbf{b}_1 \cdot \mathbf{a}_1 = 2\pi$, and similarly for the other vectors.

From Benchen's notes

In terms of matrices $\mathbf{b} = 2\pi(\mathbf{a}^T)^{-1}$, we can write out the explicit form as:

$$\mathbf{b} = 2\pi \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix}^{-1} \tag{S.29}$$

$$\begin{aligned} \vec{b}_1 &= \frac{2\pi}{\Omega}[(a_{2y}b_{3z} - a_{2z}a_{3y})\hat{i} + (a_{2z}a_{3x} - a_{3z}a_{2x})\hat{j} + (a_{2x}a_{3y} - a_{2y}a_{3x})\hat{k}] \\ &= \frac{2\pi}{\Omega}\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{vmatrix} = \frac{2\pi(\vec{a}_2 \times \vec{a}_3)}{\Omega} \end{aligned} \tag{S.30}$$

And for the other two vectors the same procedures apply.

Exercise 4.2 For a two-dimensional lattice give an expression for primitive reciprocal lattice vectors that is equivalent to the one for three dimensions given in Equation (4.13).

Solution:

This can be derived from the 3 dimensional form by taking cross products of $\mathbf{a}_1$ and $\mathbf{a}_2$ with the unit vector perpendicular to the plane, which can be written:

From Benchen's notes

$$\vec{b}_1 = \frac{2\pi(\vec{a}_2 \times \hat{z})}{\Omega},\ \vec{b}_1 = \frac{2\pi(\hat{z} \times \vec{a}_1)}{\Omega} \tag{S.31}$$

Exercise 4.3 Show that for the two-dimensional triangular lattice the reciprocal lattice is also triangular and is rotated by 90°.

Solution:

Since the reciprocal lattice vectors are orthogonal to the respective real lattice vectors, explicit construction shows that the reciprocal lattice is triangular and rotated by 90°. See Fig. 4.1.

Exercise 4.4 Show that the volume of the primitive cell in any dimension is given by Equation (4.4).

Solution:

Here we consider that "any" means D = 1,2 or 3 dimensions. Then it is a matter to work out the expressions for a determinant of the square $D \times D$ matrix with columns the vector components of the D vectors:

$$\begin{vmatrix} \mathbf{a}_{11} & \mathbf{a}_{21} & \cdots \\ \mathbf{a}_{12} & \mathbf{a}_{22} & \cdots \\ \vdots & \vdots & \end{vmatrix} \tag{S.32}$$

The algebra is the same as used in the previous problems.

The general solution in any dimension, including greater than 3, can be worked out by induction using the fact that a determinant of dimension N can by expressed in terms of indeterminists of dimension $N - 1$.

Exercise 4.5 Find the Wigner–Seitz cell for the two-dimensional triangular lattice. Does it have the symmetry of a triangle or of a hexagon. Support your answer in terms of the symmetry of the triangular lattice.

Solution:
The solution is given in Fig. 4.1 for the special case where the angles are $60°$. In this case the Wigner–Seitz cell is a hexagon. This must be the case since the negative is any reciprocal lattice vector is also a reciprocal lattice vector. In 2 dimensions the lattice is called "triangular" but in 3 dimensions the similar lattice is called "hexagonal."

Exercise 4.6 Draw the Wigner–Seitz cell and the first Brillouin zone for the two-dimensional triangular lattice.
Solution:
See previous problem. Note the Brillouin zone is rotated by $90°$.

Exercise 4.7 Consider a honeycomb plane of graphite in which each atom has three nearest neighbors. Give primitive translation vectors, basis vectors for the atoms in the unit cell, and reciprocal lattice primitive vectors. Show that the BZ is hexagonal.

Solution:
See also Exercise 14.19. The lattice is illustrated in Fig. 4.5 and the primitive lattice vectors are $\mathbf{a}_1 = (1, 0)a$ and $\mathbf{a}_2 = (\frac{1}{2}, \frac{\sqrt{3}}{2})a$, where the nearest neighbor distance is $a/\sqrt{3}$. The reciprocal lattice vectors follow from the definition and are $\mathbf{b}_1 = (0, \frac{2}{\sqrt{3}})2\pi/a$ and $\mathbf{b}_2 = (-1, \frac{1}{\sqrt{3}})2\pi/a$. Thus the BZ is hexagonal and the reciprocal lattice vectors are rotated by $30°$ relative to the real space vectors.

Exercise 4.8 Covalent crystals tend to form structures in which the bonds are *not* at $180°$. Show that this means that the structures will have more than one atom per primitive cell.

Solution:
All Bravais lattices have the property that if $\mathbf{a}$ is a primitive translation vector then $n\mathbf{a}$ is a translation vector where n is any integer. It follows that the points are always in straight lines. If the bond angles are *not* at $180°$. the atoms are not in straight lines and there must be more then one atom per primitive cell.

Exercise 4.9 Show that the fcc and bcc lattices are reciprocal to one another. Do this in two ways: by drawing the vectors and taking cross products and by explicit inversion of the lattice vector matrices.

Solution:

This is a matter of drawing the vectors to reproduce the figure in the text. The explicit inversion is given in the solution to Exercise 4.1. The results are in Eq. (4.14).

Exercise 4.10 Consider a body centered cubic crystal, like Na, composed of an element with one atom at each lattice site. What is the Bravais lattice in terms of the conventional cube edge a? How many nearest neighbors does each atom have? How many second neighbors? Now suppose that the crystal is changed to a diatomic crystal like CsCl with all the nearest neighbors of a Cs atom being Cl, and vice versa. Now what is the Bravais lattice in terms of the conventional cube edge a? What is the basis?

Solution:

The real space lattice is bcc with the lattice vectors $1/2, 1/2, 1/2)$, etc., in units of the cube edge unusually called a. The Bravais lattice is conventionally given in units of $2\pi/a$, where it is fcc with vectors $(1, 1, 0)$, etc. To derive this use the basic formula

$$\vec{b}_1 = \frac{2\pi(\vec{a}_2 \times \vec{a}_3)}{\Omega}, \tag{S.33}$$

where $\vec{a}_2 \times \vec{a}_3 = |\vec{a}_2|||\vec{a}_3)| \sin\theta \mathbf{n}$ where θ is the angle between $\vec{a}_2$ and $\vec{a}_3$ and $\mathbf{n}$ is the normal unit vector, and $\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$.

There are 8 first neighbors and 6 second neighbors.

The Bravais is simple cubic with vectors $(1, 0, 0)$, etc., and the basis is two atoms that can be chosen to have positions $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$.

Exercise 4.11 Derive the value of the ideal c/a ratio for packing of hard spheres in the hcp structure.

Solution:

The ratio is twice the vertical distance between layers of close packed planes as depicted in Fig. 4.9. In units of a (the distance between spheres) the distance between layers is $[1 - (1/2)^2 - ((1/2)tan(\pi/6))^2]^{1/2} = [1 - (1/4)(1 + 1/3)]^{1/2} = (2/3)^{1/2}$. So the result is $2 \times (2/3)^{1/2} = (8/3)^{1/2}$

One can note that this is twice the height of a tetrahedron over its side length.

Exercise 4.12 Derive the formulas given in (4.12), paying careful attention to the definitions of the matrices and the places where the transpose is required.

Solution:

Explicitly the expression is

From Benchen

$$\mathbf{b}\,\mathbf{a}^T = \begin{bmatrix} b_{1x} & b_{1y} & b_{1z} \\ b_{2x} & b_{2y} & b_{2z} \\ b_{3x} & b_{3y} & b_{3z} \end{bmatrix} \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix} = 2\pi\mathbf{I}$$

Exercise 4.13 Derive the formulas given in (4.18).

From Benchen

Solution:

$$\begin{aligned}(\vec{k}+\vec{G})(\vec{\tau}+\vec{T}) &= \sum_i (k_i^L + m_i)\vec{b}_i \sum_j (\tau_j^L + n_j)\vec{a}_j \\ &= \sum_{ij} (k_i^L + m_i)(\tau_j^L + n_j)\delta_{ij} \\ &= 2\pi \sum_i (k_i^L + m_i)(\tau_i^L + n_i) \\ &= 2\pi(\vec{k}^L + \vec{m})(\vec{\tau}^L + \vec{n})\end{aligned} \tag{S.34}$$

From Benchen

Exercise 4.14 Derive the formulas given in (4.19).

Solution:

We have to write $\vec{\tau}+\vec{T}$ as:

$$(\tau^L + \mathbf{n})\mathbf{a} = (r_1 + n_1 \; r_2 + n_2 \; r_3 + n_3) \begin{bmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{bmatrix} \tag{S.35}$$

$$\begin{aligned}|\vec{\tau}+\vec{T}|^2 &= (\vec{\tau}+\vec{T})(\vec{\tau}+\vec{T})^T \\ &= \begin{bmatrix} r_1 + n_1 & r_2 + n_2 & r_3 + n_3 \end{bmatrix} \begin{bmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{bmatrix} \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix} \begin{bmatrix} r_1 + n_1 \\ r_2 + n_2 \\ r_3 + n_3 \end{bmatrix} \\ &= (\tau^L + \mathbf{n})\mathbf{a}\mathbf{a}^T(\tau^L + \mathbf{n})^T\end{aligned} \tag{S.36}$$

For example, if the three basis vectors are orthogonal, then $\mathbf{aa}^T$ actually represents a diagonal matrix with square of basis vectors, and the physical meaning of length here is more straight forward. And the length of $\vec{k}+\vec{G}$ is the same way.

Exercise 4.15 Derive the relations given in (4.20) and (4.21) for the parallelepiped that bounds a sphere in real and in reciprocal space. Explain the reason why the dimensions of the parallelepiped in reciprocal space involve the primitive vectors for the real lattice and vice versa.

Solution:

The expressions follow straightforwardly from the description in the text. The key point is the the distance in any one direction is the distance to the plane that bounds the cell in that direction. For the real space lattice the perpendicular direction is given by the reciprocal lattice vector, and vice versa.

Exercise 4.16 Determine the coordinates of the points on the boundary of the Brillouin zone for fcc(X, W, K, U) and bcc(H, N, P) lattices.

Solution:

For fcc $X = (1,0,0)2\pi/a$ (1/2 the reciprocal lattice vector $(2,0,0)2\pi/a$) and the other points can be found using Fig. 4.10 and the fact that this is a cubic lattice with orthogonal vectors the same length in the three directions. For bcc the expressions are analogous with the point $H == (1, 0, 0)2\pi/a$ (1/2 the reciprocal lattice vector $(2, 0, 0)2\pi/a$). See Eq. (4.14).

CHECK is this right

Exercise 4.17 Derive the formulas given in (4.20) and (4.21). Hint: Use the relations of real and reciprocal space given in the sentences before these equations.

This exercise was included by mistake. It is essentially the same as Ex. 4.15.

Here is a good exercise.

One of the derivations of the Bloch theorem is given in Eqs 4.23 to 4.31. Since the crystal is invariant to translations, **k** is conserved and the hamiltoniancan be defined for each **k** in the BZ and diagonalized separately for each **k**. Derive the formula for the eigenvalue of the translation operator acting on the wavefuntions given in Eq. 4.30.

Solution:

If we apply the T_m operator, we have:

due to Benchen

$$\begin{aligned}\hat{T}_m\psi_{\vec{k}}(\vec{r}) &= \psi_{\vec{k}}(\vec{r}+\vec{T}_m) = t_1^{n_1}t_2^{n_2}t_3^{n_3}\psi_{\vec{k}}(\vec{r}) \\ &= exp\left[i\vec{k}\cdot(m_1\vec{a}_1+m_2\vec{a}_2+m_3\vec{a}_3)\right]\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{T}_m}\psi_{\vec{k}}(\vec{r})\end{aligned} \tag{S.37}$$

Exercise 4.18 Show that the expressions for integrals over the Brillouin zone Eq. (4.35), applied to the case of free electrons, lead to the same relations between density of one spin state n^σ and the Fermi momentum k_F^σ that was found in the section on homogeneous gas in Eq. (5.5). (From this one relation follow the other relations given after Eq. (5.5).)

Solution:

This exercise is closely related to Exercise 5.4. The first expression Eq. (5.5) is the requirement that the volume of the occupied states in k-space is $(2\pi)^3/\Omega$ times the number of electrons per cell for each spin. In this problem you are asked to show that this is also equivalent to the expressions in Eq. (4.35), applied to the case of free electrons. In this case the bands are isotropic and filled to the Fermi energy, which is described by Eq. (4.35) if the integrand $f_i(\mathbf{k}) = 1$ for $k < k_F$ and zero otherwise. Thus if we consider the integral over filled states instead of the integral over the BZ in Eq. (4.35), the middle expression is just $\Omega_{filled}/\Omega_{filled} = 1$. Thus Eq. (4.35) becomes

$$\frac{\Omega_{\text{cell}}}{(2\pi)^d}\int_{\text{filled}} \mathrm{d}\mathbf{k}\, f_i(\mathbf{k}) = 1. \tag{S.38}$$

At this point we we have not specified what is Ω_{cell}. There is no periodic cell but in this case the equivalent is the volume per electron (of each spin). As discussed in Exercise 5.4 the density can be viewed as the number of electrons N in a large volume divided by the volume Ω, so that the volume per electron is the inverse of the density Ω/N. Then Ω_{cell} is replaced by Ω/N. Then Ω_{cell} is replaced by Ω/N. Since the integral is the volume in k space, we have

$$\int_{\text{filled}} \mathrm{d}\mathbf{k}\, f_i(\mathbf{k}) = \frac{4\pi}{3}\left(k_F^\sigma\right)^3 = (2\pi)^3\frac{N}{\Omega}. \tag{S.39}$$

Finally note that although we have used the artifice of a large volume, the final result is simple in terms of the density $\frac{N}{\Omega}$ which is a physical quantity.

Exercise 4.19 In one dimension, dispersion can have singularities only at the end points where $E(k) - E_0 = A(k - k_0)^2$, with A positive or negative. Show that the singularities in the DOS form have the form $\rho(E) \propto |E - E_0|^{-1/2}$, as illustrated in the left panel of Fig. 14.4.

Solution:

The DOS is the density of states per unit energy. For each band there is a state for each k-point, the DOS is proportional to the volume k space per unit energy.
In one dimension with $E(k) - E_0 = A(k - k_0)^2$, we have $dE/dk = 2A(k - k_0) = 2A|E - E_0|^{1/2}$. Thus the DOS is proportional to $dk/dE = |E - E_0|^{-1/2}$. A signature of one dimension is that the DOS diverges at the boundary.

Exercise 4.20 Show that singularities like those in Fig. 14.4 occur in three dimensions, using (4.46) and the fact that $E \propto Ak_x^2 + Bk_y^2 + Ck_z^2$ with A, B, C all positive (negative) at minima (maxima) or with different signs at saddle points.

Solution:

We can use the same logic as in the previous problem. To simply notation assume the band is isotropic with $A = B = C$. If it is not isotropic the same logic but more complicated expressions. Then the volume in k-space is proportional to $k^2 dk$ and the DOS is proportional to $k^2 dk/dE = |E - E_0|^{1/2}$. This the signature is the square root form shown in Fig. 14.4.

NOT FINISHED FOR SADDLE POINT. See [598] L. Mihaly and M. C. Martin, Solid State Physics : Problems and Solutions.

Exercise 4.21 The "special points" defined by Monkhorst and Pack are chosen to integrate periodic functions efficiently with rapidly decreasing magnitude of the Fourier components. This is a set of exercises to illustrate this property:

(a) Show that in one dimension the average of $f(k)$ at the k points $\frac{1}{4}\frac{\pi}{a}$ and $\frac{3}{4}\frac{\pi}{a}$ is exact if f is a sum of Fourier components $k + n\frac{2\pi}{a}$, with $n = 0, 1, 2, 3$, but that the error is maximum for $n = 4$.

(b) Derive the general form of (4.41).

(c) Why are uniform sets of points more efficient if they do it not include the Γ point?

(d) Derive the 2- and 10-point sets given for an fcc lattice, where symmetry has been used to reduce the points to the irreducible BZ.

Solution:

Parts from Benchen

(a) The statement of this problem is embarrassing. I confused the periodicity in real space with Fourier components $2n\pi/a$ and functions that are periodic in reciprocal space with Fourier components na. The problem should have said "Fourier components na, with $n = 1, 2, 3$." Because $f(k)$ is a sum of cosines, if the sum is only up to $n = 3$ the sum of values of the at the two points are the desired result (the average) plus terms $A_n[\cos((n\pi/4) + \cos(3n\pi/4)]$, where A_n is the magnitude of the Fourier component. Each of the terms sum to zero for $n = 1, 2, 3$. However, if $f(k)$ includes a Fourier component with non-zero A_4

the sum is $A_4[\cos((\pi) + \cos(3\pi)] = 2A_4$, which the maximum possible error. One has to have more k points to treat such Fourier components.

(b) The derivation of Eq. (4.41) follows the same logic for each direction in a three dimensional crystal, which is given in the paper by Monkhorst and Pack [287]. Here we consider orthogonal lattice vectors but it is generalizes readily to the general case. The directions can be treated independently. It is easiest to see by noticing that the set of points is equally spaced by $\mathbf{G}/N$ in each direction. The sum is over N k points from $-(N-1)(\pi/Na)$ to $+(N-1)(\pi/Na)$ which integrates a function exactly if it has only Fourier components up to N. The proof follows from the relations:

$$W(m) = \frac{1}{N}\sum_{n=1}^{n=N} e^{ik_n ma}, \quad k_n = \frac{2n-N-1}{2N}\frac{2\pi}{a}, \tag{S.40}$$

where k_n are the special points defined in Eq. (4.41). The sum is zero except for Fourier component m an integer multiple of N. For $m = IN$ where I is an integer, the phases add constructively so that $|W| = 1$. This is exactly what is expected for a grid that corresponds to a lattice of vectors in reciprocal space separated by $1/N$ compared to the crystal reciprocal lattice.

(c) Using the fact that $\pm k$ are equivalent for properties like the sum of eigenvalues, etc., the total number of inequivalent points is always smaller for a given spacing. In general, the Γ point and other high-symmetry points are not representative of other points in BZ; hence they are less effective in calculating the integral. Take 2D square lattice as an example, the more general points have 8-fold symmetry while M points on the BZ boundary has only 4-fold and Γ point is not degenerate at all. So excluding these points can make the sampling more efficient. This makes a large difference in three dimensions as illustrated in the text and part (d).

(d) This is left for the reader to do explicitly. The idea is that the sum is reduced to 1/48 of the BZ by symmetry and the 2 and 10 point formulas are efficient because they have fewer points on the boundaries of 1/48 of the BZ; each point not on a boundary is equivalent to 48 points in the full BZ. Points on the boundary are equivalent to fewer other points, and the zone center and zone corner are the worst because they are unique.

Exercise 4.22 The bands of any one-dimensional crystal are solutions of the Schrödinger equation (4.22) with a periodic potential $V(x+a) = V(x)$. The complete solution can be reduced to an informative analytic expression in terms of the scattering properties of a single unit cell and the Bloch theorem. This exercise follows the illuminating discussion by Ashcroft and Mermin [280], Problem 8.1, and it lays a foundation for exercises that illustrate the pseudopotential concept (Exercise 11.2, 11.6, and 11.14) and the relation to plane wave, APW, KKR, and MTO methods, respectively, in Exercise 12.6, 16.1, 16.7, and 16.13.)

An elegant approach is to consider a different problem first: an infinite line with $\tilde{V}(x) = 0$ except for a single cell in which the potential is the same as in a cell of the crystal, $\tilde{V}(x) = V(x)$ for $-a/2 < x < a/2$. At any positive energy $\varepsilon \equiv (\hbar^2/2m_e)K^2$, there are two solutions: $\psi_l(x)$ and $\psi_r(x)$ corresponding to waves incident from the left

and from the right. Outside the cell, $\psi_l(x)$ is a given by $\psi_l(x) = \mathrm{e}^{iKx} + r\mathrm{e}^{-iKx}$, $x < -\frac{a}{2}$, and $\psi_l(x) = t\mathrm{e}^{iKx}$, $x > a/2$, where t and r are transmission and reflection amplitudes. There is a corresponding expression for $\psi_r(x)$. Inside the cell, the functions can be found by integration of the equation, but we can proceed without specifying the explicit solution.
(a) The transmission coefficient can be written as $t = |t|\mathrm{e}^{i\delta}$, with δ a phase shift which is related the phase shifts defined in Appendix J as clarified in Exercise 11.2. It is well known from scattering theory that $|t|^2 + |r|^2 = 1$ and $r = \pm i|r|\mathrm{e}^{i\delta}$, which are left as an exercise to derive.
(b) A solution $\psi(x)$ in the crystal at energy ε (if it exists) can be expressed as a linear combination of $\psi_l(x)$ and $\psi_r(x)$ evaluated at the same energy. Within the central cell all functions satisfy the same equation and $\psi(x)$ can always be written as a linear combination,

$$\psi(x) = A\psi_l(x) + B\psi_r(x), \quad -\frac{a}{2} < x < \frac{a}{2}, \tag{S.41}$$

with A and B chosen so that $\psi(x)$ satisfies the Bloch theorem for *some crystal momentum* k. Since $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ must be continuous, it follows that $\psi(\frac{a}{2}) = \mathrm{e}^{ika}\psi(-\frac{a}{2})$ and $\psi'(\frac{a}{2}) = \mathrm{e}^{ika}\psi'(-\frac{a}{2})$. Using this information and the forms of $\psi_l(x)$ and $\psi_r(x)$, find the 2×2 secular equation and show that the solution is given by

$$2t\cos(ka) = \mathrm{e}^{-iKa} + (t^2 - r^2)\mathrm{e}^{iKa}. \tag{S.42}$$

Verify that this is the correct solution for free electrons, $V(x) = 0$.
(c) Show that in terms of the phase shift, the solution, (4.48), can be written

$$|t|\cos(ka) = \cos(Ka + \delta), \quad \varepsilon \equiv \frac{\hbar^2}{2m_e}K^2. \tag{S.43}$$

(d) Analyze (4.49) to illustrate properties of bands and indicate which are special features of one dimension. (i) Since since $|t|$ and δ are functions of energy ε, it is most convenient to fix ε and use (4.49) to find the wavevector k; this exemplifies the “root tracing” method used in augmented methods (Chapter 16). (ii) There are necessarily band gaps where there are no solutions, except for the free electron case. (iii) There is exactly one band of allowed states $\varepsilon(k)$ between each gap. (iv) The density of states, (4.46), has the form shown in the left panel in Fig. 14.4.
(e) Finally, discuss the problems with extending this approach to higher dimensions.

Solution for **Exercise 4.22**:
The solution follows Ashcroft and Mermin [280], problem 8.1, where many steps are left as exercises.
(a) This is a standard problem in almost every quantum mechanics book. For a single cell with $\tilde{V}(x) = 0$ except $\tilde{V}(x) = V(x)$ for $-\frac{a}{2} < x < \frac{a}{2}$. At any energy $\varepsilon > 0$ there are two solutions: a wave incident from the left given by $\psi_l(x) = \exp iKx + r\exp -iKx$, $x < -\frac{a}{2}$, $t\exp iKx$, $x > \frac{a}{2}$, and a corresponding wave $\psi_l(x)$ incident from the right, where $\varepsilon \equiv \frac{\hbar^2}{2m_e}K^2$. The transmission coefficient can always be written in terms of the phase shift η as $t = |t|\exp i\eta$.

It follows from particle conservation that $|t|^2 + |r|^2 = 1$.
One proof that $r = |r| \exp i\eta \pm \pi/2$ follows A and M Eq. 8.75.

(b) Using the definitions of ψ_l, ψ_r and $\psi(x) = A\psi_l + B\psi_r$, it is straightforward to find the matrix equation for the coefficients.

From this it follows "easily" (but see below) that

$$2t\cos(ka) = \exp -iKa + (t^2 - r^2)\exp iKa. \tag{S.44}$$

Working this out in detail does not look so easy. Here is an explicit derivation provided by Benchen to use the boundary conditions to determine relation between A and B, at $x = -\frac{a}{2}$:

$$\psi\left(-\frac{a}{2}\right) = Ae^{-iK\frac{a}{2}} + Are^{iK\frac{a}{2}} + Bte^{iK\frac{a}{2}},\ \psi'\left(-\frac{a}{2}\right) = iK\left(Ae^{-iK\frac{a}{2}} - Are^{iK\frac{a}{2}} - Bte^{iK\frac{a}{2}}\right) \tag{S.45}$$

At $x = \frac{a}{2}$, we have:

$$\psi\left(\frac{a}{2}\right) = Ate^{iK\frac{a}{2}} + Be^{-iK\frac{a}{2}} + Bre^{iK\frac{a}{2}},\ \psi'\left(\frac{a}{2}\right) = iK\left(Ate^{iK\frac{a}{2}} - Be^{-iK\frac{a}{2}} + Bre^{iK\frac{a}{2}}\right) \tag{S.46}$$

By $\psi(\frac{a}{2}) = e^{ika}\psi(-\frac{a}{2})$ and $\psi'(\frac{a}{2}) = e^{ika}\psi'(-\frac{a}{2})$, we will get two secular equations for A and B. To ensure nonzero solutions we have:

$$\begin{vmatrix} te^{iK\frac{a}{2}} - e^{ika}e^{-iK\frac{a}{2}} - re^{ika}e^{iK\frac{a}{2}} & re^{iK\frac{a}{2}} + e^{-iK\frac{a}{2}} - te^{ika}e^{iK\frac{a}{2}} \\ te^{iK\frac{a}{2}} - e^{ika}e^{-iK\frac{a}{2}} + re^{ika}e^{iK\frac{a}{2}} & re^{iK\frac{a}{2}} - e^{-iK\frac{a}{2}} + te^{ika}e^{iK\frac{a}{2}} \end{vmatrix} = 0 \tag{S.47}$$

Simplifying it we get:

$$2tcos(ka) = e^{-iKa} + (t^2 - r^2)e^{iKa} \tag{S.48}$$

For free electrons, $V(x) = 0$, $t = 1$, $r = 0$ and the solution is simply $K = k$, which the correct solution .

(c) Substituting $|t|^2 + |r|^2 = 1$ and $r = \pm i|r| \exp i\eta$ in 4.48, a little algebra leads to

$$|t|\cos(ka) = \cos Ka + \eta,\quad \varepsilon \equiv \frac{\hbar^2}{2m_e}K^2. \tag{S.49}$$

Explicit derivation provided by Benchen:
Since we have $t = |t|e^{i\delta}$ and $r = \pm i|r|e^{i\delta}$, we could plug this into the above equation to get:

$$2|t|e^{i\delta}cos(ka) = e^{-iKa} + (|t|^2 + |r|^2)e^{2i\delta}e^{iKa} = e^{-iKa} + e^{2i\delta}e^{iKa} \tag{S.50}$$

$$|t|cos(ka) = cos(Ka + \delta) \tag{S.51}$$

(d) Many properties of bands are illustrated by Eq. (4.49) including:
i) In one dimension it is straightforward to find $|t|$ and η for any energy ε. Then Eq. (4.49) is simply the solution of a transcendental equation, which is called "root tracing". On the other hand it is much more difficult to find the energy that leads to a given $|t|$ and η, which is a non-linear problem that depends upon the particular potential.

ii) As a function of $\varepsilon \equiv \frac{\hbar^2}{2m_e} K^2$, $\cos Ka + \eta$ covers the entire range from -1 to 1. There can be no solution for $\cos Ka + \eta > |t|$ since $\cos(ka)$ cannot exceed unity. Thus there are necessarily band gaps in all cases, except for the free electrons.
iii) Each period of $\cos Ka + \eta$ leads to two bands and two band gaps.
iv) Band edges occur at extrema of $\cos(ka)$; since the cosine is quadratic function of k at the extrema, it follows that $\varepsilon(k)$ is quadratic and the density of states has the form shown (see also Exercise 14.6).
(e) It is very difficult to extend this approach to higher dimensions because the there is a separate boundary condition for each direction. The requirement that *all* the boundary conditions are satisfied is a more complicated procedure than the other band methods are the subject of Chapters 12 -17. Many of the methods solve the Schrödinger equation directly in a basis; however, the present method has close connections to augmented methods that involve matching the solution of the radial equation in a sphere to the wavefunction an interstitial region that connects spheres.

Solutions for Chapter 5

Same as exercises first edition. An alternative set of solutions with much more details is given in the following section called "Alternative Set of Solutions for Chapter 5"

Exercise 5.1 For fcc and bcc crystals with Z valence electrons per primitive cells, show that r_s is given, respectively, by

$$r_s = \frac{a}{2}\left(\frac{3}{2\pi Z}\right)^{1/3} \text{and} r_s = \frac{a}{2}\left(\frac{3}{\pi Z}\right)^{1/3}.$$

If r_s is in atomic units (a_0) and the cube edge a is in Angstrons, then $r_s = 0.738 Z^{-1/3} a$ and $r_s = 0.930 Z^{-1/3} a$.

Solution:
Note that $\frac{4\pi}{3} r_s^3$ is the volume per electron and the equations can be written

$$\frac{4\pi}{3} r_s^3 = \frac{a^3}{4Z} \text{ and } \frac{4\pi}{3} r_s^3 = \frac{a^3}{2Z}.$$

The result follows from the fact that the conventional cube contains 4 and 2 atoms per cube for fcc and bcc respectively.

Exercise 5.2 For semiconductors with eight valence electrons per primitive cell in diamond- or zinc-blende-structure crystals, show that $r_s = 0.369a$.

Solution:
The result follows from the above equations with the fact that these crystals are fcc.

Exercise 5.3 Argue that the expression for Coulomb interaction in large parentheses in (5.4) is finite due to cancellation of the two divergent terms. Show that the scaled hamiltonian given in (5.4) is indeed equivalent to the original hamiltonian (5.2).

Solution:
The scaled hamiltonian results from the definitions with $r/a_0 \to r/r_s$ in the original hamiltonian in atomic units in (5.2). The cancelation of the divergence at large distance in the last two terms follows from the fact that the sum in the first term approaches a continuum o points $1/|\mathbf{r}_i - \mathbf{r}_j|$ where the volume for each point j is $4\pi r_s^3/3$ which is $4\pi/3$ in units of r_s. This is has the same form at large distance as the last term which in the integral of $1/|\mathbf{r}|$ divided by the volume per point.

Exercise 5.4 Derive the relation (5.5) between the Fermi wavevector k_F^σ and the density n^σ for a given spin. Do this by considering a large cube of side L, and requiring the wavefunctions to be periodic in length L in each direction (Born–von Karmen boundary conditions).

Solution:
This is algebraic substitution and is not given explicitly here. The first expression is the volume of the occupied states in K-space is $(2\pi)^3/\Omega$ times the number of electrons per cell for each spin. The point is essentially the same as in Exercise 4.18 The point of considering

a large cube is to go back to the definitions of the density of $\mathbf{k}$ points for a given density in real space using the simplest possible geometry.

Exercise 5.5 Show that relation (5.6), between k_F and the density parameter r_s for an unpolarized gas, follows from the basic definition (5.5) (see also previous problem.)

Solution:
This is algebraic substitution and is not given explicitly here.

Exercise 5.6 Show that Eq. (5.10) follows from Eq. (5.9) by carrying out the indicated differentiation and partial integration. Use this form to derive the $T = 0$ form, Eq. (5.11). Also show that the factor in brackets approaches unity for $y \to 0$.

Solution:
The derivation of the form is given explicitly in Goedecker, Phys. Rev. B, 58, 3501 (1998)[302]. It results from transforming the three dimension form to the one dimensional integral in Eq. (5.10) and partial integration. The result for temperature zero follows from the fact that f' approaches a delta function for $k = k_F$ scaled by $1/(\beta k_F/2)$, and carrying out the derivatives with the dimensionless parameter $y = k_F r$.

Exercise 5.7 Verify expression (5.8) for the kinetic energy of the ground state of a non-interacting electron gas. Note that in (5.8), the denominator counts the number of states and the numerator is the same integral but weighted by the kinetic energy of a state, so that this equation is independent of the number of spins. Derive the corresponding results for one and two dimensions.

Solution:
The result follows since the integral in the numerator is $k_F^5/5$ and in the denominator $k_F^3/3$. For one and two dimensions the result is $1/2$ and $2/3$. This applies to each spin separately.

Exercise 5.8 Show that plane waves are eigenstates for the Hartree–Fock theory of a homogeneous electron gas – assuming the ground state is homogeneous, which may not be the case when interactions are included. Thus the kinetic energy is the same for Hartree–Fock theory as for non-interacting particles.

Solution:
The only requirement is that the solutions are plane waves which follows from the fact that the hamiltonian is translation invariant. The kinetic energy is the same operator in Hartree-Fock and non-interacting independent particles.

Exercise 5.9
Derive expression (5.12) for eigenvalues in the Hartree–Fock approximation from the general definition in (3.48). Hint: The exchange integral for plane wave states has the form $-4\pi \sum_{\mathbf{k}'}^{k'<k_F} 1/|\mathbf{k} - \mathbf{k}'|^2$. This leads to the singular log form in three dimensions. For more details, see, e.g., Ashcroft or Pines [280, 297].

Solution:

(See also similar problem in the companion book (Martin, Reining, Ceperley), Chap. 4, Ex. 4.2.)
The eigenvalues are the kinetic energy plus the exchange energy as given in (5.12)

$$\varepsilon_k = \frac{1}{2}k^2 + \frac{k_F}{\pi} f(x), \tag{S.52}$$

where $x = k/k_F$. The object of the exercise is to show that $f(x)$ is given by the expression Eq. (5.13)

$$f(x) = -\left(1 + \frac{1-x^2}{2x} \ln |\frac{1+x}{1-x}|\right). \tag{S.53}$$

This follows from the general expression for the Hartree-Fock hamiltonian operator given in (3.45),

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{j,\sigma_j} \int \mathrm{d}\mathbf{r}' \psi_j^{\sigma_j *}(\mathbf{r}')\psi_j^{\sigma_j}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\psi_i^\sigma(\mathbf{r})$$
$$-\sum_j \int \mathrm{d}\mathbf{r}' \psi_j^{\sigma *}(\mathbf{r}')\psi_i^\sigma(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_j^\sigma(\mathbf{r}) = \varepsilon_i^\sigma \psi_i^\sigma(\mathbf{r}), \tag{S.54}$$

where the sum is over occupied states. In the homogeneous system the external potential and the the direct Coulomb term are constants that merely shifts the energy of all states and is not considered here. For a plane wave with wavevector $\mathbf{k}$, $\psi_i^\sigma(\mathbf{r}) = (1/\Omega^{1/2})e^{i\mathbf{k}\cdot\mathbf{r}}$ where Ω is the volume, the last term on the left side becomes

$$-\frac{1}{\Omega^{3/2}} \sum_{\mathbf{k}', k'<k_F} \int \mathrm{d}\mathbf{r}' e^{-i\mathbf{k}'\cdot\mathbf{r}'} e^{i\mathbf{k}\cdot\mathbf{r}'} \frac{1}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{k}'\cdot\mathbf{r}}, \tag{S.55}$$

where the sum is over states with $k' < k_F$. If we define $\mathbf{k}' = \mathbf{k} + \mathbf{q}$, this becomes

$$\left[-\frac{1}{\Omega} \sum_{\mathbf{k}', k'<k_F} \int \mathrm{d}\mathbf{r}' e^{-i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})} \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] \frac{1}{\Omega^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{S.56}$$

Transforming to an integral over $\mathbf{k}'$ and using the Fourier transform of the Coulomb potential, the term in square brackets becomes

$$-\frac{4\pi}{(2\pi)^3} \int^{k'=k_F} \mathrm{d}\mathbf{k}' \frac{1}{q^2}. \tag{S.57}$$

The only difficulty is to express q and the limits of the integral in terms of $\mathbf{k}'$ and carry out the integral. This can be done using the diagram shown in Fig. S.1 where the magnitude q is given in terms of the components of $\mathbf{k}'$. In spherical coordinates, we have Thus the integral becomes

$$-\frac{4\pi}{(2\pi)^2} \int_0^{k_F} \mathrm{d}k' k'^2 \int \mathrm{d}(-cos(\theta)) \frac{1}{k^2 - 2kk'cos(\theta) + k'^2}, \tag{S.58}$$

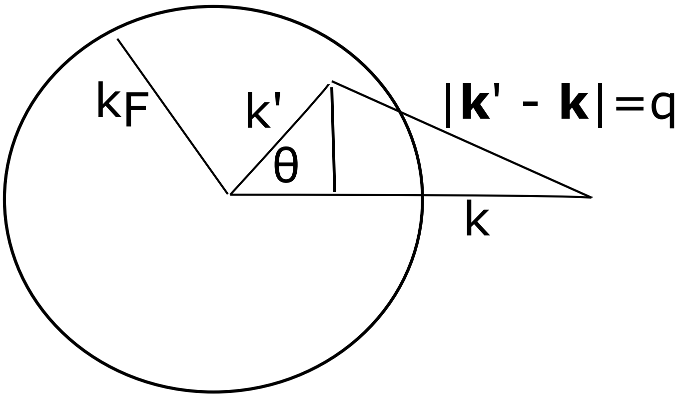


Figure S.1. Geometrical conditions that define the variables needed in the solution of Exercise 5.9.

with $q^2 = k^2 - 2kk'cos(\theta) + k'^2$. The double integral can be worked out using the geometrical conditions defined in Fig. S.1. It is most convenient to work with variables scaled by k_F in order to find the expression Eq. (S.52) in terms of $x = k/k_F$ and $x' = k'/k_F$ with the factor k_F/π, and the expression becomes

$$\frac{k_F}{\pi}\int_0^1 \mathrm{d}x' \frac{x'}{2x} \ln\left|\frac{x^2+2xx'+x'^2}{x^2-2xx'+x'^2}\right| = \frac{k_F}{\pi}\int_0^1 \mathrm{d}x' \frac{x'}{x} \ln\left|\frac{x+x'}{x-x'}\right|. \tag{S.59}$$

With the definition that this expression is $(k_F/\pi)f(x)$ and a partial integration this becomes the desired result in Eq. (S.53).

The implication of these results for the effective mass of electrons at the Fermi surface is a disaster - a mass that goes to zero since the dispersion is vertical at $k = k_F$ due to the log terms. This is totally at variance with experiment and Fermi liquid theory. The divergence is due to the long range nature of the Coulomb which goes as $1/q^2$. If the interaction is screened there is no divergence and there is an effective mass that is finite and is affected by interaction as expected.

Exercise 5.10 Derive the broadening of the bands in the Hartree–Fock approximation from the unpolarized gas $\Delta W = (9/4\pi^2)^{1/3}/r_s$ using (5.12).

Solution:

The result follows from (5.12) where one must take the limit of small x to show $f(0) = -2$, as stated after the equation, and express k_F in terms of r_s.

Exercise 5.11 Derive analytically that the electron velocity $v = \mathrm{d}\varepsilon/\mathrm{d}k$ diverges at $k = k_F$ in the Hartree–Fock approximation. Argue that: (1) this happens in *all* metals due to the Coulomb interaction and the Hartree–Fock approximation, and (2) there is no divergence for short-range interactions.

Solution:

The velocity is the derivative of the energy in Eq. (5.12) and it is straightforward to show it has the log divergence. The log comes from the $1/q^2$ interaction as derived in Exercise 5.9. The same integrals for short range interactions have renomalization of the velocity but no divergence.

Exercise 5.12 Show that the average value of the factor $f(x)$ in Eq. (5.13) is $-3/4$, as stated before (5.15). Then, for the ground state of the homogeneous gas, verify the result for the exchange energy (5.15).

Solution:

This is a matter of doing the integral. Note that in 3 dimensions the average is $\propto \int x^2 dx f(x)$ so that the integral involves only powers of x times log functions. The result is given in Slater's paper Phys. Rev. 81, 385 (1951) [453].

It is interesting to note that the factor $3/4$ is related to the difference between the Kohn–Sham formula for the exchange potential (8.16) and the local form Slater had proposed earlier [453] based on his approach of finding a local potential that is a weighted average of the non-local Hartree–Fock exchange operators (9.20). By averaging the *exchange potential* of the homogeneous gas, Slater found $V_x = 2\epsilon_x$, rather than the factor $\frac{4}{3}$ in (8.16) found by Kohn and Sham from the derivative of the exchange energy.

Exercise 5.13 Show that (5.19) follows directly from evaluating the expressions in (3.54) or (3.52) by inserting the plane wave eigenfunctions (normalized to a large volume Ω) and evaluating the resulting expression. Alternatively, $g_x(r)$ can be found from the general relation (3.56) of the pair correlation function and the density matrix for non-interacting fermions (see, e.g., the books by Landau and Pitaevskii and Jones and March [278, 260], $g_x(r) = 1 - |\rho(r)|^2/n^2$, where n is the density and the density matrix $\rho(r)$ is given by (5.11).

Solution:

The alternative method leads to the result with only a little algebra. But of course that relies upon the derivation of the other formulas.

The direct evaluation using (3.52) for the exchange hole is

$$2\pi \int \cos\theta d\theta \int_0^{k_F} k^2 dk e^{ikr\cos\theta} = 2\pi \int \cos\theta d\theta \frac{k_F^3}{y^3} \int_0^1 y^2 dy e^{iy\cos\theta} \tag{S.60}$$

Carrying out the integral leads to the described result.

Alternative detailed solution in set of solutions for Ch 5 by Benchen. See below.

Exercise 5.14

Consider a point charge in an otherwise uniform gas. Use the Thomas–Fermi (TF) approximation (Chapter 6) to derive the TF screening length (5.21). (Hint: Assume the change in the density due to the impurity is $\delta n(r) \propto \exp(-k_{TF}r)/r$ and determine the decay constant k_{TF} from the TF equations expanded to linear order in $\delta n(r)$.)

Solution:

The density of electrons in the presence of the impurity is given by $n(r) = n_0 + \delta n(r)$ and in the TF approximation the energy is given by

$$E_{\mathrm{TF}}[n] = C_1 \int \mathrm{d}^3 r\; n(\mathbf{r})^{(5/3)} + \int \mathrm{d}^3 r\; V_{\mathrm{ext}}(r) n(r) + \frac{1}{2} \int \mathrm{d}^3 r \mathrm{d}^3 r'\; \frac{n(r)n(r')}{|\mathbf{r}-\mathbf{r}'|}, \tag{S.61}$$

where the first term is the local approximation to the kinetic energy with $C_1 = \frac{3}{10}(3\pi^2)^{(2/3)} = 2.871$ in atomic units. For a point charge $V_{ext} = -Q/r$ and by charge neutrality $\int \delta n(r) = Q$.

If we assume $\delta n(r) = A\exp(-k_{TF}r)/r$, then it follows that $Q = \int \delta n(r) = 4\pi A \int drr\exp(-k_{TF}r) = 4\pi A/k_{TF}^2 \int x\exp(x) = 4\pi A/k_{TF}^2$ or $A = (k_{TF}^2/4\pi)Q$. Also if the density has this form, it is readily proven using the Poisson equation that the potential is $\phi(r) = -Q\exp(-k_{TF}r)/r$.

To evaluate the kinetic term, expand the expression $(n_0 + \delta n)^{5/3} = n_0^{5/3}[1 + \frac{5}{3}\frac{\delta n}{n_0} + \frac{5}{9}(\frac{\delta n}{n_0})^2 + \ldots]$. This leads to the kinetic term T

$$\begin{aligned} T = C_1 \int \mathrm{d}^3 r\; n(r)^{(5/3)} &= C_1 n_0^{5/3} \int \mathrm{d}^3 r\; [1 + \frac{5}{3}\frac{\delta n}{n_0} + \frac{5}{9}(\frac{\delta n}{n_0})^2 + \ldots] \\ &= T_0 + E_F Q + E_F \frac{1}{3n_0} \int \mathrm{d}^3 r\; (\delta n(r))^2 + \ldots, \end{aligned} \tag{S.62}$$

where T_0 is the total kinetic energy and we have used the relation $C_1 n_0^{2/3} = \frac{3}{5}E_F$. Inserting the form of the density $\delta n(r) = (k_{TF}^2/4\pi)Q\exp(-k_{TF}r)/r$, the integrals can be evaluated to yield

$$T = Constant + \frac{E_F}{24\pi}\frac{Q^2}{n_0}k_{TF}^3. \tag{S.63}$$

For the potential terms, the sum of the two terms is

$$V = -Q^2 k_{TF} + \frac{1}{4}Q^2 k_{TF} = -\frac{3}{4}Q^2 k_{TF}. \tag{S.64}$$

The first term is readily evaluated as a radial integral. The second term can be determined by first finding the potential due to $\delta n(r)$ which is $V_n = phi(r) + Q/r = (Q/r)(1 - \exp(-k_{TF}r))$.

Finally, we have the total energy in the TF approximation:

$$E_{TF} = Constant + Q^2[\frac{E_F}{24\pi n_0}k_{TF}^3 - \frac{3}{4}k_{TF}. \tag{S.65}$$

Minimizing the energy with respect to k_{TF} leads to

$$k_{TF} = 6\pi n_0/E_F, \tag{S.66}$$

and inserting the expressions in terms of r_s, $n_0 = \frac{3}{4\pi r_s^3}$ and $E_F = \frac{1}{2}(\frac{9}{4}\pi)^{2/3}$, leads to the final result

$$k_{TF} = (\frac{12}{\pi})^{1/3}(\frac{1}{r_s})^{1/2}, \tag{S.67}$$

which is the formula given in (5.21).

Exercise 5.15 Derive the expression for the exchange–correlation hole (5.29) in terms of the hole at larger densities (smaller r_s). Would there be an analogous form that involves an integral of λ from 1 to ∞, i.e., for larger r_s?

Solution:
This is basically three steps: identifying the steps that the equations can be written in the scaled form in Exercise 5.3, the energy is given by the coupling constant average, and the xc energy is determined by the integral over the hole. Detailed derivation left for the reader.

Exercise 5.16 Using Fig. 5.5 sketch the shape of the average hole, (5.29), for antiparallel-spin electrons Al, Na, and Cs.

Solution:
This is meant to be qualitative. Values of r_s are given in Table 5.1. We can see from Fig. 5.5 that the hole becomes much more pronounced in Cs ($r_s \approx 5$) compared to Al ($r_s \approx 2$). From the figures (and the knowledge that there is no hole at infinite density ($r_s = 0$) we can see that the average hole in Al is roughly that for $r_s = 1$ in Fig. 5.5 and for Cs is is similar to the curve for $r_s = 3$.

Exercise 5.17 Derive the expression for the equilibrium r_s given in (5.32) from the expression for total energy and using $\alpha = 1.80$. In which direction will the predicted r_s change if correlation is included? Find the explicit expression using the Wigner interpolation formula for ϵ_c.

Solution:
**Misprint in text! 0.899 should be $0.814^2 = 0.663$ I have no idea where 0.899 came from ** This problem is worked out in Ashcroft and Mermin p. 410-414, which agrees with the corrected result.

Differentiating to find the stationary point we find a quadratic equation and the result is the equation

$$\frac{r_s}{a_0} = 0.81 + \sqrt{0.66 + 3.31\left(\frac{R_c}{a_0}\right)^2}, \tag{S.68}$$

which is the same as Eq. (5.32) corrected and rounded to fewer decimal places.

Exercise 5.18 Derive the Lindhard expression for the dielectric function of a homogeneous gas (5.38). This is a tedious integral and the steps are given by Pines [297], p. 144.

Solution:
See solution in pages copied from Pines book in appendix for solutions.

Alternative Set of Solutions for Chapter 5

Provided by Benchen. Not edited by me.

5.1

For fcc lattice, each cubic cell contains 4 atoms so we have:

$$r_s = \left(\frac{3a^3}{16\pi Z}\right)^{\frac{1}{3}} = \frac{a}{2}\left(\frac{3}{2\pi Z}\right)^{\frac{1}{3}} \tag{S.69}$$

For bcc lattice, each cubic cell contains 2 atoms:

$$r_s = \left(\frac{3a^3}{8\pi Z}\right)^{\frac{1}{3}} = \frac{a}{2}\left(\frac{3}{\pi Z}\right)^{\frac{1}{3}} \tag{S.70}$$

5.2

For a diamond cell, it contains 8 atoms and each primitive cell contains 2 atoms. So $Z = 4$ and we have:

$$r_s = \left(\frac{3a^3}{8\times 4\pi \times 4}\right)^{\frac{1}{3}} = \frac{a}{4}\left(\frac{3}{2\pi Z}\right)^{\frac{1}{3}} = 0.369a \tag{S.71}$$

5.3 NOT DONE

5.4

The wavefunction of electrons have to satisfy certain boundary conditions:

$$\begin{aligned}\psi(x+L_x,y,z) &= \psi(x,y,z),\\ \psi(x,y+L_y,z) &= \psi(x,y,z),\\ \psi(x,y,z+L_z) &= \psi(x,y,z)\end{aligned}$$

And from Bloch's Theorem we know that: $\psi(x+L) = e^{ikL}\psi(x)$, so k could only take discrete values of $\frac{2\pi l}{L}$. So the number density of k values in reciprocal space is by: $\frac{\Omega}{(2\pi)^3}$. So we have:

$$N_e^\sigma = \frac{\Omega}{(2\pi)^3} \times \frac{4}{3}\pi (k_F^\sigma)^3,\ (k_F^\sigma)^3 = 6\pi^2 n^\sigma \tag{S.72}$$

5.5

$$k_F = (3\pi^2 n)^{\frac{1}{3}} = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{1}{r_s} \tag{S.73}$$

5.6

There are several notation issues in this question that may cumber the derivation. Let's start with the original definition.

$$\begin{aligned}\rho(\vec{r}-\vec{r'}) = \rho(\vec{r}) &= \frac{1}{(2\pi)^3}\int d\vec{k} f(\varepsilon)e^{i\vec{k}\cdot\vec{r}} \\ &= \frac{1}{(2\pi)^2}\int_0^{\pi} sin\theta d\theta \int_0^{\infty} k^2 dk f(\varepsilon)e^{ikrcos\theta} \\ &= \frac{1}{2\pi^2 r}\int_0^{\infty} ksin(kr)f(\varepsilon)dk \\ &= \frac{1}{(2\pi)^2 r}\int_{-\infty}^{\infty} ksin(kr)f(\varepsilon)dk\end{aligned} \tag{S.74}$$

Now let's switch back to the final expression and try to start from there and get back to the above formula:

$$\begin{aligned}\rho(r) &= -\frac{\beta}{(2\pi)^2}\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d}{dr}\int_{-\infty}^{\infty} dkcos(kr)f'\left(\beta\left(\frac{1}{2}k^2-\mu\right)\right) \\ &= -\frac{1}{(2\pi)^2}\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d}{dr}\int_{-\infty}^{\infty} \frac{cos(kr)}{k}df\left(\beta\left(\frac{1}{2}k^2-\mu\right)\right) \\ &= -\frac{1}{(2\pi)^2}\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d}{dr}\int_{-\infty}^{\infty} \frac{krsin(kr)+cos(kr)}{k^2}f(\varepsilon)dk \\ &= -\frac{1}{(2\pi)^2}\frac{1}{r}\frac{d}{dr}\int_{-\infty}^{\infty} cos(kr)f(\varepsilon)dk \\ &= \frac{1}{(2\pi)^2 r}\int_{-\infty}^{\infty} ksin(kr)f(\varepsilon)dk\end{aligned} \tag{S.75}$$

So we see that we arrive at the same expression. But several things worth mentioning are: the expression (5.10) in the book lacking a minus sign and also the following:

$$f'\left(\beta\left(\frac{1}{2}k^2-\mu\right)\right) \neq \frac{df}{dk},\ \frac{df}{dk} = f'\beta k \tag{S.76}$$

If the temperature is zero, then the Fermi function would be a step function and its derivative would be a negative delta function, so we could simplify density as:

$$\begin{aligned}\rho(r) &= -\frac{1}{(2\pi)^2}\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d}{dr}\int_{-\infty}^{\infty} dk\frac{cos(kr)}{k}\frac{d}{dk}f\left(\beta\left(\frac{1}{2}k^2-\mu\right)\right) \\ &= \frac{1}{(2\pi)^2}\frac{1}{r}\frac{d}{dr}\frac{1}{r}\frac{d}{dr}\frac{2cos(k_F r)}{k_F} \\ &= \frac{k_F^3}{6\pi^2}\left[3\frac{siny-ycosy}{y^3}\right] = n^{\sigma}\left[3\frac{siny-ycosy}{y^3}\right]\end{aligned} \tag{S.77}$$

The derived density is for **each spin**, and if the system is unpolarized, we can write the total density as:

$$\rho(r) = \frac{k_F^3}{3\pi^2}\left[3\frac{siny-ycosy}{y^3}\right] \tag{S.78}$$

5.7

For 3D cases, we have:

$$T_0^\sigma = \frac{\hbar^2}{2m_e} \frac{4\pi \int_0^{k_F} k^4 dk}{4\pi \int_0^{k_F} k^2 dk} = \frac{3}{5} E_{F0}^\sigma \tag{S.79}$$

For 2D and 1D cases,

$$T_0^\sigma = \frac{\hbar^2}{2m_e} \frac{2\pi \int_0^{k_F} k^3 dk}{2\pi \int_0^{k_F} k dk} = \frac{1}{2} E_{F0}^\sigma$$

$$T_0^\sigma = \frac{\hbar^2}{2m_e} \frac{\int_0^{k_F} k^2 dk}{\int_0^{k_F} dk} = \frac{1}{3} E_{F0}^\sigma$$

5.8

In Hartree Fock Approximation for the homogeneous electron gas, there is only two terms in the Hamiltonian, kinetic energy operator and exchange integral, and we know that plane waves are the eigenfunction of kinetic operator. So we only need to verify whether plane waves are the eigenfunction of the exchange integral operator or not:

$$\begin{aligned}
&\sum_j \int d\vec{r}' \psi_j^{\sigma *}(\vec{r}') \psi_i^\sigma(\vec{r}') \frac{1}{|\vec{r}-\vec{r}'|} \psi_j^\sigma(\vec{r}) \\
&= \sum_j \frac{1}{\Omega} \int d\vec{r}' exp\left(-i\vec{k}_j \cdot \vec{r}' + i\vec{k}_i \cdot \vec{r}'\right) \frac{1}{|\vec{r}-\vec{r}'|} \frac{1}{\sqrt{\Omega}} exp\left(i\vec{k}_j \cdot \vec{r}\right) \\
&= \sum_j \frac{1}{\Omega} \int d\vec{r}' exp\left(-i(\vec{k}_j - \vec{k}_i) \cdot (\vec{r}' - \vec{r})\right) \frac{1}{|\vec{r}-\vec{r}'|} \frac{1}{\sqrt{\Omega}} exp\left(i\vec{k}_i \cdot \vec{r}\right) \\
&= \left[\sum_j \frac{1}{\Omega} \int d\vec{r}' exp\left(-i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}'\right) \frac{1}{|\vec{r}'|}\right] \frac{1}{\sqrt{\Omega}} exp\left(i\vec{k}_i \cdot \vec{r}\right)
\end{aligned} \tag{S.80}$$

So we see that plane waves are indeed the eigenfunction of exchange integral operator. So it's also the eigenstate of Hartree Fock equations.

5.9

$$\begin{aligned}
\varepsilon &= \frac{k^2}{2} - \sum_j \frac{1}{\Omega} \int d\vec{r}' exp\left(-i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}'\right) \frac{1}{|\vec{r}'|} \\
&= \frac{k^2}{2} - \frac{1}{\Omega} \sum_{k' < k_F} \frac{4\pi}{|\vec{k}' - \vec{k}|^2} \\
&= \frac{k^2}{2} - \frac{1}{2\pi^2} \int_0^{k_F} d^3\vec{k}' \frac{1}{|\vec{k}' - \vec{k}|^2} \\
&= \frac{k^2}{2} + \frac{k_F}{\pi} f\left(\frac{k}{k_F}\right),
\end{aligned} \tag{S.81}$$

where the second equality is due to the 3D Fourier transform of $\frac{1}{r}$ (a noteworthy fact is that this transform starts from Yukawa potential and then take the parameter to be 0), and $f(x)$ is defined by:

$$f(x) = -\left(1 + \frac{1-x^2}{2x} ln\left|\frac{1+x}{1-x}\right|\right) \tag{S.82}$$

5.10

$$\triangle W = \frac{k_F}{\pi} = \left(\frac{9}{4\pi^2}\right)^{\frac{1}{3}} \frac{1}{r_s} \tag{S.83}$$

5.11

$$v = \frac{d\varepsilon}{dk} = k + \frac{1}{\pi}\frac{df}{dx} = k + \frac{1}{\pi}\left(-\frac{1}{x} + \frac{1+x^2}{2x^2} ln\left|\frac{1+x}{1-x}\right|\right) \tag{S.84}$$

So that when $k = k_F$, the log term would blow up while the rest terms are finite, so the velocity would be infinity, which is unphysical.

5.12

$$\bar{f} = \frac{\int_0^1 f(x)x^2dx}{\int_0^1 x^2dx} = -\frac{3}{2}, \quad \frac{k_F}{2\pi}\bar{f} = -\frac{3k_F}{4\pi} \tag{S.85}$$

5.13

$$\begin{aligned}
g_x^{\sigma,\sigma} &= 1 + \frac{\Delta n_{HFA}(\vec{r},\sigma;\vec{r}',\sigma')}{n(\vec{r},\sigma)n(\vec{r}',\sigma')} = 1 - \left|\frac{\sum_i \psi_i^{\sigma *}(\vec{r})\psi_i^{\sigma}(\vec{r}')}{n}\right|^2 \\
&= 1 - \left|\frac{1}{n\Omega}\sum_{k<k_F} e^{i\vec{k}\cdot\vec{r}}\right|^2 = 1 - \left|\frac{1}{n}\int_0^{k_F}\frac{d^3\vec{k}}{(2\pi)^3}e^{i\vec{k}\cdot\vec{r}}\right|^2 \\
&= 1 - \left|\frac{1}{n}\int_0^{\pi} sin\theta d\theta \int_0^{k_F}\frac{k^2dk}{(2\pi)^2} exp(ikrcos\theta)\right|^2 \\
&= 1 - \left|\frac{1}{2\pi^2 nr}\int_0^{k_F} ksin(kr)dk\right|^2 \\
&= 1 - \left[3\frac{sin(y) - ycos(y)}{y^3}\right]^2
\end{aligned} \tag{S.86}$$

where $y = k_F r$. And of course, by using $\rho(r)$ to derive this result would be even easier. (Check exercise 5.6 out!)

5.14 NOT DONE

5.17

First of all let's ignore the correlation effect. We would have:

$$\frac{E_{total}}{N} = \frac{3R_c^2}{2r_s^3} + \frac{1.105}{r_s^2} - \frac{1.358}{r_s} \tag{S.87}$$

By taking the extremum, we could find that the r_s is:

$$\frac{r_s}{a_0} = 0.813 + \sqrt{0.664 + 3.31\left(\frac{R_c}{a_0}\right)^2}, \tag{S.88}$$

which is close to the (5.32). If we include the effect of correlation, then r_s would be smaller.

Solutions for Chapter 6

The exercises in Ch 6 and 7 are mainly ”thinking” questions that do NOT require extensive calculation, but they may be hard to deal with because it is difficult to understand what is exact in principle in DFT. I wrote these questions for a class where we could discuss the issues and see that the answers are not hard if you know what to do! See comments at start of solutions for Chapter 7 for examples.

Exercises same as in first edition except 6.2 in first ed. omitted in second edition. Equation numbers shifted by 1 in second edition.

Exercise 6.1 Derive the Thomas–Fermi equation, (6.5), from the variational of the functional. Use the method of Lagrange multipliers as given in (3.10) and used in (6.3).

Solution:

This is a straightforward application of the variational method where $V_x(\mathbf{r}) = C_2(4/3)n^{1/3}(\mathbf{r})$ if we include the Dirac addition of exchange in the local approximation. All terms are local except the Hartree potential. The definition of functional derivatives is in Appendix A and Exercise A.1.

expressions due to Benchen

Solution:

$$\begin{aligned}\frac{\delta\Omega_{TF}[n]}{\delta n(\vec{r})} &= \frac{\delta E_{TF}[n]}{\delta n(\vec{r})} - \mu\int d^3r\delta n(\vec{r}) \\ &= \frac{5}{3}C_1\int d^3rn(\vec{r})^{2/3}\delta n + \int d^3rV_{ext}(\vec{r})\delta n \\ &+ \frac{4}{3}C_2\int d^3rn(\vec{r})^{1/3}\delta n + \int d^3rd^3r'\frac{n}{|\vec{r}-\vec{r}'|}\delta n - \mu\int d^3r\delta n(\vec{r}) \\ &= \int\left[\frac{5}{3}C_1n(\vec{r})^{2/3} + V(\vec{r}) - \mu\right]\delta nd^3r\end{aligned} \tag{S.89}$$

Since the variation of density is arbitrary, then the terms in the bracket has to be zero.

Omitted this Ex in Second Edition.

Omitted this Ex in Second Edition.

Omitted this Ex in Second Edition.

Ex. 6.2 in first Ed. Derive the Thomas–Fermi–Weizsacker equation which is the generalization of (6.5) when the Weizsacker gradient term is included. The gradient expression is given following (6.5). Variations of a functional of the gradient of the density are discussed in Chapter 8.

Solution:

Solution by Benchen:

Now we have included the gradient term:

$$E_{TFW}[n] = \int d^3r\left[C_1n^{5/3} + V_{ext}(\vec{r})n + C_2n^{4/3} + \int d^3r'\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{1}{4}\frac{(\nabla n)^2}{n(\vec{r})}\right] \tag{S.90}$$

So the variation is the following:

$$\begin{aligned}
\frac{\delta\Omega_{TF}[n]}{\delta n(\vec{r})} &= \frac{\delta E_{TF}[n]}{\delta n(\vec{r})} - \frac{\delta E_{TF}[n]}{\delta|\nabla n|}\frac{\nabla n(\vec{r})}{|\nabla n|} - \mu\int d^3r\delta n(\vec{r})\\
&= \frac{5}{3}C_1\int d^3rn(\vec{r})^{2/3}\delta n + \int d^3rV_{ext}(\vec{r})\delta n\\
&+ \frac{4}{3}C_2\int d^3rn(\vec{r})^{1/3}\delta n + \int d^3rd^3r'\frac{n}{|\vec{r}-\vec{r}'|}\delta n\\
&+ \frac{1}{2}\int d^3r\nabla\cdot\left(\frac{|\nabla n|}{n(\vec{r})}\frac{\nabla n(\vec{r})}{|\nabla n|}\right)\delta n - \mu\int d^3r\delta n(\vec{r})\\
&= \int d^3r\left[\frac{5}{3}C_1n(\vec{r})^{2/3} + V(\vec{r}) + \frac{1}{2}\frac{n\nabla^2n-(\nabla n)^2}{n(\vec{r})^2} - \mu\right]\delta n
\end{aligned} \tag{S.91}$$

The terms in the bracket has to be zero.

NOTE: Numbers for following exercises are different in Second Edition since Ex. 6.2 in first edition is omitted.

Ex numbers different in Second Edition.

Exercise 6.2 This is essentiall=y the same as **Exercise 5.14**. No solution given here. for a problem involving the Thomas–Fermi (TF) approximation.

Exercise 6.3 The simplest example of the Mermin theorem is the homogeneous gas. For a gas held at fixed volume, as the temperature is varied the density does not change. Describe the meaning of the Mermin functional in this case.

Solution:

The key point is that the Mermin functional is defined for a given temperature T. It is not the same as the T=0 functional. Even though the the density does not change the functional changes. The free energy is determined by the density *and* the temperature, not just the density.

Exercise 6.4 Theorem I of Hohenberg–Kohn shows that $n_0(\mathbf{r})$, *in principle*, uniquely determines all properties of the many-body system of electrons, including ground and excited states. We have argued that, for example, the electron density uniquely determines the positions and types of nuclei, which then defines the complete hamiltonian and therefore, *in principle*, determines all properties. Show explicitly that only the density and its derivatives near the nuclei are sufficient to establish the proof in this case.

Solution:

Near each nucleus the hamiltonian is dominated by the divergent nuclear potential, so that the electron density must have the same cusp condition (ratio of $\frac{dn}{dr}$ to n) as given by the non-interacting electron Schrödinger equation. Since this is known as a function of the nuclear charge, it follows that only the density near the nuclei is sufficient to determine the external potential and thus satisfy the Hohenberg–Kohn theorem.

Exercise 6.5 In one dimension it is possible to construct orthonormal independent-particle orbitals that describe *any* density that satisfies simple positivity and continuity conditions. See Exercise 7.9.

Solution:
See Exercise 7.9.

Exercise 6.6 Following the approach of Section 6.6, show that it is not possible to construct the density of the 2s state of hydrogen (one electron in the potential of a proton) as the ground state density of any smooth potential, i.e., one without delta functions.

Solution:
In this one-electron case the wave function must be proportional to $\sqrt{n}$ (with a plus or minus sign). If the wavefunction changes sign then it cannot be a ground state. Thus the only possibility is that the wavefunction is given by
$\psi(r) \propto |(r - r_1)| \exp(-\alpha r/2)$
If this is the ground state of a potential $V(r)$ the potential must satisfy $V(r) = [(\boldsymbol{\nabla}^2 + \epsilon)\psi(r)]/\psi(r)$. However, this expression diverges at $r = r_1$.

Another way to derive the conclusion is to note that the only external potential that gives this state as an eigenstate is the $1/r$ Coulomb potential (plus a constant). But the wavefunction is not the ground state of this potential. Since it is not the ground state of this potential, and it is not an eigenstate of any other potential, it follows that it cannot be the ground state of any potential.

Exercise 6.7 Consider the lowest-energy state of Li with three electrons, which may be $1\mathrm{s}^2 2\mathrm{s}$, or one of the degenerate states $(1\mathrm{s})^2 2\mathrm{p}^0$, $1\mathrm{s}^2 2\mathrm{p}^-$, or $1\mathrm{s}^2 2\mathrm{p}^+$. The densities of the last two states are identical, so that the density does not determine the state. Show that, nevertheless, the energy is the same for any combination of these states so that the energy is still a functional of the density as needed for the Hohenberg–Kohn functional.

Solution:
First, the theory is meant to describe the full many-body problem; thus we emphasize that the notation does not denote independent-particle orbitals but rather the correlated state of three electrons. The latter two states are the degenerate lowest energy states with angular momentum ± 1. Any linear combination has the same energy, for example, the real states with

Exercise 6.8 In this problem you are asked to show that in the absence of an external magnetic field the total density is, in principle, enough to determine all the properties of the system even if it is spin polarized. To do this, consider the system in a Zeeman field $\mathbf{h} \cdot \vec{\sigma}$ that distinguishes between $\vec{\sigma}$ parallel and antiparallel to $\mathbf{h}$. Show that if $\mathbf{h}$ is reversed, the new solution will have exactly the same density, but with $\vec{\sigma}$ reversed. Using this fact show that you can reach the desired conclusion.

Solution:
Note that the assumption is that it is spin polarized, i.e., no orbital comment is considered and it is implicitly assumed the is on spin–orbit interaction. Thus this is an example of the next problem, i.e., an HK functional with spin polarization in presence of spin independent external potential. For the last part of the problem, we see that the system can be polarized *only if* the functional leads to lower total energy for the polarized system since the density is the same. Thus such a solution is an effect of interactions. The comments about a Zeeman field apply to the Kohn–Sham approach in which the Kohn–Sham potential for the auxiliary

independent-particle system is spin-dependent which is equivalent to an external Zeeman field.

Exercise 6.9 Suppose particles can be divided into two types (e.g., spins) of density n_1 and n_2 with internal energy $E_{\rm int}[n_1, n_2]$. If the external potential acts on n_1 and n_2 equally, the total energy can be written $E_{\rm total} = E[n_1, n_2] + \int V_{\rm ext} n$, where $n = n_1 + n_2$. Show that $E_{\rm total}$ is a functional only of n. Do this in three ways: (a) using arguments similar to the original arguments of Hohenberg and Kohn; (b) the Levy–Lieb constrained search method; and (c) formal solution by variational equations in terms of n and $\sigma = n_1 - n_2$.

Solution:

The full solution will not be written out, but the key point given here is sufficient for all the proofs. First note that the internal energy can always be written $E_{\rm int}[n_1, n_2] = E_{\rm int}[n, \sigma]$. Then all the proofs reduce to the fact that the ground state is defined as the state in which all variables are at the values for minimum energy. The proof using the Hohenberg–Kohn argument is the same as the argument presented in the text. The last two ways of proving the result follow from the fact that $E_{\rm int}$ is minimized with respect to the function σ. Thus for any n, σ is determined by the minimization condition and it follows that σ fixed by n.

The physics is brought out bye the Levy-Lieb construction that searches for the lowest energy many-body wavefunction for a given density; a polarized solution occurs if the lowest energy wavefunction is polarized.

Exercise 6.10 Consider a many-body hamiltonian $\hat{H} = \hat{H}_{\rm int} + V_{\rm ext}$, where $\hat{H}_{\rm int}$ denotes all intrinsic internal kinetic and interaction terms and $V_{\rm ext}$ is the external potential. Show that the external potential $V_{\rm ext}(\mathbf{r})$ is determined to within a constant, given $\hat{H}_{\rm int}$ and *any* eigenfunction Ψ_i. Hint: solve for $V_{\rm ext}(\mathbf{r})$ using the Schrödinger equation. (Note a specific example of a determinant wavefunction is considered as an exercise in Chapter 7.)

Solution:

For a single particle it is clear that the Schrödinger equation can be inverted to find the potential given the wavefunction and the eigenvalue. For the ground state there are no zeros in the parafunction and it is straightforward. Exactly the same reasoning applies to the many-body case, where the ground state has no nodes. This is a general theorem used in Monte Carlo simulations that find the ground state sampling the wavefunction considered as a probability which must always be positive. (See [1].)

Exercise 6.11 Show that in a finite system the kinetic energy must be a non-analytic function of the density n with derivatives that are discontinuous at integer occupations. Hint: It is sufficient to show the result in an independent-particle example (see Exercise 7.5) with an argument that the result must also apply to many-body cases. Generalize this argument to all properties of the system and to solids with an insulating gap.

Solution:

This problem should have been in the next chapter. For a finite system the arguments in this chapter do not define the Hohenberg–Kohn functional for fractional numbers of particles. One could consider a large finite system where the variation with number approaches a derivative. In that case, for a system with a finite gap the functional must jump as the number changes around the gap. (The gap is well defined in the interacting many-body system by the jump in $E(N = 1) - E(N)$ so that $E(N + 1) + E(N - 1) - 2E(N)$ is vanishingly small for large N, except at points where there is a gap $E_{gap} = E(N + 1) + E(N - 1) - 2E(N)$. (See [1] where the gap defined in this way is crucial in the theory of interacting systems.) All parts of the functional including the kinetic energy must jump. (The kinetic energy plays a special role in the Kohn–Sham approach where it is difficult to construct a functional of the density only, and the need to have a discontinuous function is one way to see the difficulty of constructing functionals, even fopr non-interacting systems. The problem does not go away with interactions!)

Solutions for Chapter 7

As stated at the beginning of the solutions for Chapter 6, the exercises in Ch 6 and 7 are mainly "thinking" questions that do NOT require extensive calculation, but they may be hard to deal with because it is difficult to understand what is exact in principle in DFT. For example, in exercise like Exercise 6.6, part a, think about the logic: The ground state solution of the Schr. Eq. for a H atom is well-known. Can I work backward and show that the only potential that gives the wavefuntion is the Coulomb potential? (That is also the point of Ex 7.6) and several other problems that relate to possible potentials and densities. This is enough to answer the question.

Another example is Exercise 7.10, which is clear if you know the meaning of "to lowest order". That is the hint. The change in density is proportional to the potential. Then ask yourself what is the condition to work backward from the density to get the potential.

Exercises same as in first edition except in second edition. Exercises 7.11 and 7.15 are omitted and all the Exercises from Ch. 9 in first Ed. are moved here

Exercise 7.1 For any one-electron problem, one can readily determine whether or not any given density is a possible ground state density. Using the known properties of solutions of the Schrödinger equation, give a sufficient set of conditions that any function must satisfy in order to guarantee that it is the ground state density of some potential. See Exercise 7.7 for an example of an allowed density and Exercise 6.6 for a function that is not an allowed ground state density.

Solution:

Using the reasoning involved in Exercise 7.2, it follows that for a one-electron problem *any* function that integrates to unity and is everywhere positive (i.e., it has no zeros) is a ground state of a potential.

Exercise 7.2 For any density $n(\mathbf{r})$ that is allowed (see Exercise 7.1) and integrates to one electron, show that the Kohn–Sham potential $V^{\sigma}_{\rm eff}(\mathbf{r})|_{\rm min} \equiv V^{\sigma}_{\rm KS}(\mathbf{r})$ is unique, except for an arbitrary constant, and give an explicit algorithm for constructing $V^{\sigma}_{\rm KS}(\mathbf{r})$ from $n(\mathbf{r})$. See **Exercise 7.7** for an explicit example of an allowed density.

Solution:

The potential $V^{\sigma}_{KS}(\mathbf{r})$ is easily by inverting the Schrödinger equation since the wavefunction $(\psi(\mathbf{r}) = (n(\mathbf{r}))^{\frac{1}{2}}$ and eigenvalue $\varepsilon = \langle\psi|\hat{H}|\psi\rangle$ are known. Here $\hat{H}$ is the actual hamiltonian for the one-electron system, $-\frac{1}{2}\nabla^2 + V_{external}(\mathbf{r})$, it follows that $V^{\sigma}_{KS}(\mathbf{r}) = V_{external}(\mathbf{r})$ apart from an arbitrary constant with σ the spin of the one electron.

Exercise 7.3 Generalize the arguments of **Exercise 7.2** to show that $V^{\sigma}_{\rm KS}(\mathbf{r})$ is unique, except for an arbitrary constant, for a non-interacting Kohn–Sham system of any integer number of electrons.

Solution:

All the steps in the solution for Exercise 7.2 apply here also. In this case, since the system is defined to be non-interacting, $\hat{H}$ contains some effective potential. The needed proof still follows since the resulting Kohn–Sham potential is always the same apart for an arbitrary constant. In general, there are two potentials $V^{\sigma}_{KS}(\mathbf{r})$ for the two spins.

Exercise 7.4 For any non-interacting Kohn–Sham system, use the result of Exercise 7.3 to show that the kinetic energy T_s for each spin σ must be a unique functional of the density $n(\mathbf{r}, \sigma)$ for that spin. Generalize the argument to show that *all* properties of the system are uniquely determined by the density.

Solution:

Since it is shown in Exercise 7.3 that the Kohn–Sham potential for each spin $V^{\sigma}_{KS}(\mathbf{r})$ is a unique functional of the density for that spin, it follows immediately that independent-particle kinetic energy T_s for each spin σ must be a unique functional of the density for that spin. This is simply the statement that the Kohn–Sham equations are completely determined by $V^{\sigma}_{KS}(\mathbf{r})$ and their solution determines T_s. It also follows that *all* properties of the Kohn–Sham system are uniquely determined since the Kohn–Sham equation determines all the independent-particle eigenstates. Finally, one must invoke the Hohenberg–Kohn theorem to conclude that *in principle* all properties of the interacting system are determined by the unique Kohn–Sham potential.

Exercise 7.5 Based on the result of **Exercise 7.4**, show that in a finite system with discrete states the kinetic energy functional $T_s[n]$ must be a non-analytic function of the density n with derivatives that are discontinuous at integer occupations. Hint: Use the known solutions of the Schrödinger equation, ψ_i that are different for each i. Generalize this argument to all properties of the system and to filled bands in the case of a solids.

Solution:

See answer to Exercise 6.6. The general case is easily proven by considering the density that corresponds to an excited state of non-interacting particles in an external potential. There is no other potential for which the wavefunction is an eigenstate (except for a trivial addition of a constant). Since it is not the ground state of this potential, it follows that it cannot be the ground state of any potential. This is specific example where the density can be constructed from a single determinant of orbitals but *not* orbitals that are the lowest eigenstates of any potential.

Additional observation by Benchen:

We take the example of 1D infinite well of length L. First let's consider the one electron case. We know that the wavefunction is:

$$\psi_i = \sqrt{\frac{2}{L}} sin\left(\frac{i\pi x}{L}\right), \; n(x) = \frac{2}{L} sin^2\left(\frac{i\pi x}{L}\right) \tag{S.92}$$

This is a special case because kinetic energy functional could be written in an analytic form. We have:

$$T_s[n] = \int_0^L \frac{1}{2}\left(\frac{i\pi}{L}\right)^2 n(x)dx \tag{S.93}$$

So we could write the functional derivative as:

$$\frac{\delta T_s[n]}{\delta n} = \frac{i^2\pi^2}{2L}, \tag{S.94}$$

which is a constant and depends on the occupied orbital. If now there happens an excitation, this derivative would be different and depends on the new orbital. There is a discontinuity.

In the more general cases, where there are more than one electron, the coefficient coming out of the gradient calculation would be different for different orbitals so we can't write the kinetic energy functional in an analytic form. Besides, if there is an addition or subtraction of an integer of electrons, by analogy the derivative would be discontinuous as well.

Exercise 7.6 As an example of the fact that arbitrary densities *cannot* be constructed from the lowest eigenstates of a non-interacting hamiltonian, see Exercise 6.6. Use this example as the basis for constructing a general argument that it is not possible to construct any density from a determinant formed from the lowest N eigenvectors of a non-interacting particle problem.

Solution:

The essential point is that the ground state density never has nodes. (Sese solution for Exercise 6.10.) Since a determinant formed from the lowest N eigenvectors of a non-interacting particle problem is an example of a ground state, it cannot describe a density withe a surface of zeros. This assumes that the potential has no singularities. This is not specifically stated in the problem statement, but it is stated in the text that some of the conclusions apply only if the potential is required to be non-singular.

Exercise 7.7 As an example of the explicit construction of a potential determined by the density, find the one-dimensional potential $V(x)$ that gives the density $A\exp(-\alpha x^2)$, where normalization constant A is chosen so that the density corresponds to one electron. Express the answer in terms of α.

Solution:

The wavefunction is $\psi(x) \propto \exp(-\alpha x^2/2)$ and it is easiest to use atomic units. Inverting the Schrödinger equation, $[(-1/2)(d^2/dx^2 + V(x)]\psi(x) = \varepsilon\psi(x)$, where ε is the eigenvalue, leads to the equation for find V, $V(x)\psi(x) = [(1/2)(d^2/dx^2 - \varepsilon]\psi(x)$, apart from an arbitrary constant. Taking the derivatives gives $[(1/2)(\alpha x)^2 + \alpha]\psi(x)$ so that $V(x) = (1/2)\alpha^2 x^2 + constant$.

Exercise 7.8 For a one-electron radial problem it is straightforward to find the unique Kohn–Sham potential that will lead to any radial density with no nodes. (The Schrödinger equation in radial coordinates is given in Section 10.1.)

(a) Find the potential $V_{\mathrm{KS}}(r)$ that gives the hydrogen atom density.

(b) Find the potential for a gaussian density $A\exp(-\alpha r^2)$, where A is a normalization constant chosen so that the density integrates to one (See also Exercise 7.7.). Express the answer in terms of α.

Solution:

The radial equation is given in Eq. (10.4),

$$-\frac{1}{2r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\frac{\mathrm{d}}{\mathrm{d}r}\psi_{n,l}(r)\right] + \left[\frac{l(l+1)}{2r^2} + V_{\mathrm{ext}}(r) - \varepsilon_{n,l}\right]\psi_{n,l}(r) = 0, \tag{S.95}$$

and $V(r)$ can be found by the same approach as in Exercise 7.7.

(a) For H the ground state wavefunction is $\psi(r) \propto \exp(-r)$ in atomic units. Taking the derivatives, we find $V(r) = +1/r + constant$

(b) Taking derivatives similar to the previous problem, we find $V(r) = 2(\alpha r)^2 + constant$. (Verify that factor of 2 is correct.)

Exercise 7.9 This problem is an example of explicit construction of orthonormal independent-particle orbitals that describe *any* density of N particles and, furthermore, that there are many such choices for the same density. This example is for one dimension and is taken from p. 55 of Book by Parr and Yang [273]. For a density $n(x)$ and $s(x) \equiv n(x)/N$ given in the range $x_1 \leq x \leq x_2$, define the set of functions

$$\psi_k(x) = [s(x)]^{1/2} \exp{[i2\pi k q(x)]}, \tag{S.96}$$

with $q(x) \equiv \int_{x_1}^{x} s(x')\mathrm{d}x'$ and k = integers or half-integers. Show that the orbitals satisfy the desired conditions since each has the same density $s(x)$ and the orbitals are orthonormal. Show that it follows that an infinite number of such choices can be made.

Solution:

The full solution is in the reference given. As a step toward understanding, the factor $q(x) \equiv \int_{x_1}^{x} s(x')\mathrm{d}x'$ increases as x so the factor exp $[i2\pi k q(x)]$ is similar to a Bloch factor exp $[i2\pi k x]$.

due to Benchen

It's easy to verify that these orbitals are properly normalized and N orbitals would yield the desired density. We only need to show explicitly that they are also orthogonal.

$$\begin{aligned}
\langle\psi_k||\psi_l\rangle &= \int_{x_1}^{x_2} s(x) exp\left[i2\pi n q(x)\right] dx \\
&= \int_{x_1}^{x_2} \frac{dq}{dx} exp\left[i2\pi n q(x)\right] dx \\
&= \int_{0}^{1} exp\left[i2\pi n q(x)\right] dq \\
&= \frac{1}{2\pi i n}\left(e^{i2\pi n} - 1\right) = 0
\end{aligned} \tag{S.97}$$

where we write$k - l = n$ and w have assumed that $k \neq l$. So we see that these orbitals are orthonormal. Since ks are either integers or half integers, and we only N orbitals, there are infinite ways to choose N integers or half integers.

Exercise 7.10 Show that, to lowest-order, small deviations from the homogeneous density can be reproduced by non-interacting fermions. Hint: Use the fact that, to lowest order, any change in the density is linear in the potential.

Solution:

This is a case that really does not involve DFT reasoning, only that you know the meaning of "to lowest order". That is the hint. The change in density is proportional to the potential. Then ask yourself what is the condition to work backward from the density to get the potential.

To lowest order the change in density is proportional to the potential. The derivative is a susceptibility as worked out in Chapter 20 and appendix D. So long as the system is stable the susceptibility is finite and we can define the inverse, the relation defines the potential that would produce any given density (to lowest order). This dependents upon the susceptibility being general enough that any density can be created; one way to see that this is possible is to consider the Fourier transform where there are specific expressions given for independent-particle systems like the Kohn–Sham system general Fourier components.

Exercise 7.11 Consider an independent-particle hamiltonian $\hat{H} = \hat{H}_{\text{int}} + V_{\text{ext}}$ for which the wavefunction for any state i is a single determinant Φ_i and the subscript "int" denotes all internal terms. Then the total energy can be written $E_{\text{tot}} = E_{\text{int}}[\Phi] + \int \mathrm{d}^3\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r})$. Show that the external potential $V_{\text{ext}}(\mathbf{r})$ is determined to within a constant given $\hat{H}_{\text{int}}$ and any eigenfunction Φ_i, not only the ground state. (Hint: Solve for $V_{\text{ext}}(\mathbf{r})$ using the Schrödinger equation.) Explain why it is more difficult numerically to find $V_{\text{ext}}(\mathbf{r})$ from the wavefunction for an excited state than for the ground state.

Solution:
This is really the same as several previous problems. The basic ideas are in Exercise 7.7. In this problem you are asked to consider excited states. The derivations apply for any eigenstate. A difficulty for excited states is the nodes in the wavefunction. Where it goes to zero the both sides of the equations to determine $V(x)$ vanish making the numerical calculation difficult.

Ex. 7.11 in first ed. is moved to 9.1 in second ed. See solution there.

Following numbers are different in First Ed. Exercise 7.12 For a two-electron problem in a singlet state, it is straightforward to find the Kohn–Sham potential that will lead to any density with no nodes. The purpose of this exercise is to emphasize the relation to the one-electron case in **Exercise 7.8** by constructing the potential $V_{\text{KS}}(r)$ for the following cases:
(a) a density that is twice that of the H atom;
(b) a gaussian density $A\exp(-\alpha r^2)$, where A is chosen so that the density integrates to two electrons.

Solution:
The point of this exercise is to be aware of of which aspects are relevant which are part of understanding how the derivation for one electron are generalized to more than one. Independent electrons in a singlet state is the simplest case. This is NOT DFT; it is simply the inversion of an independent-particle Schrödinger equation using an eigenvector.
(a) Both this part and part (b) involve solution for up and down electron states in the same potential, which is just two equations that are identical and are the same as if there were only one electron. Thus the inversion of the Schrödinger equations leads to the Coulomb potential of a nucleus with with charge +1. The total electron density is twice that of H. The interpretation may seem tricky because it seems so unphysical. The moral of this story is that any method that attempts to be physical must have some way of taking into account electron-electron interactions even if it is approximate. For example, Kohn–Sham DFT would include an average interaction that greatly affects the binding energy. It might even be unstable. (It would be a good exercise to check stability for a chosen functional.) Hartree-Fock would have an average repulsion of one electron due to the other (no self-

term). A more realistic problem would be He with nucleus of charge 2 with two electrons each having a scaled hydrogen-like wavefunction.
(b) This case is really the same as Exercise 7.7 with the same equation for the up and down electrons. It may be more physical that part (a) since there may be real problems where interactions between particles may be small or may have little effect if the binding is very strong. It is like a textbook problem of independent non-interacting particles with no issues related to Coulomb interactions.

Exercise 7.13 Project: Using an atomic program (such as the one discussed in conjunction with Chapter 10) one can find the density of a closed-shell atom and the Kohn–Sham potential.

(a) This exercise is to invert the problem: construct a minimization program to find the potential $V(r)$ that will produce that density and show that it is the same potential. This is essential for the potential to be unique.

(b) Now modify the density by multiplying by a gaussian and normalizing. For this density find the potential.

Solution:
This is a problem that requires a computer calculation. The idea is an iterative loop to vary the potential until; one gets the desired density. This is an example of the general problem of finding the exact Kohn–Sham potential which has been done for atoms with densities determined by very accurate many-body methods. An example is the work of Umrigar - check references and where it is in this book and in [1].

THE FOLLOWING PROBLEMS WERE IN CHAPTER 9 IN THE FIRST EDITION. ALL ARE MOVED HERE IN THE SAME ORDER.

Exercise 7.14 In actual calculations one can determine the energy from either of the two functionals, Eq. (7.21) or Eq. (7.22). Describe how it can be useful to compute both. Which is expected to be closest to the actual converged result before convergence is reached? Which is a true variational bound? Can the difference be used as a measure of convergence?

Solution:
This is really just an exercise to state in your own words what is in the text - or to give your own may to thin it about different from the text. In the opinion of the author the key points are:
The Kohn–Sham function in Eq. (7.21) is variational as shown explicitly in the text. This is an essential aspect for DFT! The energy is always above the correct Kohn–Sham solution for the given functional. (Since the functional is approximate we do not know if the energy is above or below the true energy for the system!)
The functional in Eq. (7.22) is lower than the correct Kohn–Sham energy for the giben functional. This is not so obvious but it is shown in the text.
If we have two functionals below and above the correct energy, and they must be equal if we had the correction self-consistent solution, the difference is a measure of how close we are to the correct energy.

The analysis in text shows that usually the second energy is closer to the final self-consistent energy. This may be surprising but it is simply that the input density is in general closer to the correct self-consistent density than the output density! See the text.

Exercise 7.15 As posed before Eq. (7.24), derive the expressions for the linear terms and thus the form of (7.24).

Solution:

The expression for the potential before Eq. (7.24) is the definition of the effective potential for a give density. To linear order the difference in the last term in Eq. (7.23) is canceled by the previous term. This leaves the quadratic terms defined by the first line in Eq. (7.25) which equals the second line. It is a good exercise in the meaning of functionals to see that the Coulomb term is the second derivative of the Hartree energy in Eq. (7.4).

Explicit equations due to Benchen:

$$\begin{aligned} E_{KS}[V^{in}] - E_{HWF}[n^{in}] &= -\sum_{\sigma} \int d\vec{r} V^{\sigma}_{n^{in}}(\vec{r}) \left[n^{out}(\vec{r},\sigma) - n^{in}(\vec{r},\sigma) \right] \\ &+ E_{pot}[n^{out}] - E_{pot}[n^{in}] \\ &= -\sum_{\sigma} \int d\vec{r} V^{\sigma}_{n^{in}}(\vec{r}) \triangle n(\vec{r},\sigma) + \frac{\delta E_{pot}}{\delta n} \triangle n(\vec{r},\sigma) \\ &+ \frac{1}{2} \frac{\delta^2 E_{pot}}{\delta n(\vec{r},\sigma) \delta n(\vec{r}',\sigma')} \triangle n(\vec{r},\sigma) \triangle n(\vec{r}',\sigma') \\ &= \frac{1}{2} \sum_{\sigma,\sigma'} \int d\vec{r} \int d\vec{r}' K(\vec{r},\sigma;\vec{r}',\sigma') \triangle n(\vec{r},\sigma) \triangle n(\vec{r}',\sigma') \end{aligned} \tag{S.98}$$

Note in the book Eq. (7.24) ((9.11) in first Ed) lacks a minus sign in front of the first term on the right hand side. Since $\frac{\delta E_{pot}}{\delta n} = V^{\sigma}_{n^{in}}(\vec{r})$, then the linear term would cancel and only second and higher order terms survive.

Exercise 7.16 Fill in the steps to show that Eq. (7.26) defines a functional that is indeed extremal at the correct solution for independent variations of potential and density.

Solution:

The functional is extremal if the linear variations vanish for both potential and density. To prove this we must derived Eq. (7.27), which gives explicitly the linear terms; there we see that they vanish at self-consistency where output density and potential are the same as the input. This is done by straightforward expansion of the terms in Eq. (7.26). Since the potential and density are viewed as independent the middle term is linear in each and the derivatives easily lead to the terms $-V^{\sigma,\mathrm{in}}(\mathbf{r})\delta n(\mathbf{r},\sigma)$ and $-n^{\mathrm{in}}(\mathbf{r},\sigma)\delta V^{\sigma}(\mathbf{r})$ The other terms follow because the fist line only involves the variation of the density and as stated after Eq. (7.27), $V^{\sigma,\mathrm{in}}(\mathbf{r})$ is just the definition of that potential. The only thing left to do is to show the derivative of the sum of eigenvalues $E_s[V]$ with respect to V is the density. This follows from the same logic as for DFT (it is explicitly done in the Levy-Lieb derivation), but in the case the total energy for non-interacting particles is simply $E_s[V]$ and the problem is simpler. The only way the potential enters the independent-particle hamiltonian is the bilinear term Vn. At the solution all internal degree of freedom (the independent-particle wavefunctions) are st the variational minimum and the derivative is simply n. At the self-consistent solution this is the output density that is determined by the input potential, i.e., the term $n^{\mathrm{out}}_{V^{\mathrm{in}}}(\mathbf{r},\sigma)$. This completes the derivation that the expression is extremal.

It is not asked for in this problem, but we can also note that it is a saddle point. It is shown in the chapter before Eq. (7.26) that the Kohn–Sham functional in a variational minimum with energy that increases quadratically around the solution, and the HWF expression is maximum at the solution. This does not change in the generalized functional, so that the solution is an saddle point.

Exercise 7.17 On general thermodynamic grounds, show that $E(T)$ increases quadratically with T, whereas $F(T)$ decreases quadratically. Thus a linear combination of $E(T)$ and $F(T)$ can be chosen in which the quadratic terms cancel. Using the expressions for $E(T)$ and $F(T)$ that follow from the occupation numbers, find the value of α for which $\alpha E(T) + (1-\alpha)F(T) = E(T=0)$ with corrections $\propto T^4$.

Solution:

The use of the the calculation of energy and free energy is exemplified by the calculations in Gillan, J. Phys.: Condensed Matter 1,689(1989).[369], who says: “It is easily shown that for small T the free energy deviates from E_0 by a quantity quadratic in T: $F = E_0 - \gamma T^2$; and that the deviation of the energy E is equal and opposite: $E = E_0 + \gamma T^2$.”

The problem we want to consider is a metal. For an insulator the difference from T=0 for all quantitative are exponentially small. For a metal one must integrate over the density of states which leads to the Sommerfeld expansion given in many texts such as Ashcroft and Mermin, Appendix C and detailed expressions in Marder [300] page 146. The energy is given by $E = \int d\varepsilon \rho(\varepsilon)\varepsilon f(\varepsilon - \mu)$ where ρ is the density of states and f is the Fermi function. The key is an integration by parts to a form that involves $df/d\varepsilon$ which is symmetric about $\varepsilon - \mu = 0$ and decays rapidly for small T. This shows that odd powers of T vanish and the result is that the energy E increases $\propto T^2$ + higher order terms. For the lowest order term it is sufficient to consider $\rho(\varepsilon)$ to be constant ρ near the Fermi energy so that $E = -\int d\varepsilon \rho df/d\varepsilon$ at $\varepsilon = \mu$). The result is a definite integral that can be evaluated to yield $E = E_) + (\pi^2/6)\rho(k_b T)^2$. This corresponds to the linear specific heat $C = dE/dT = \gamma T$ where γ is a constant for low T. Thus $E = E_0 + (1/2)CT = E_0 + (1/2)\gamma T^2$ for small T.

In an actual calculation the free energy would be calculated by $F = E - TS$ where the entropy S is given by Eq. (7.29). However, we can use well-known general thermodynamic arguments to show the desired result that it decreases an equal and opposite amount. A change in the entropy is related to the energy by $dS = dE/T$. Thus at low T, $dS = CdT$ and $F = E - TS = E_0 + (1/2)\gamma T^2 - \gamma T^2 = E_0 - (1/2)\gamma T^2$. This is sufficient for the proofs needed here.

Exercise 7.18 Complete the arguments to show that (7.32) is extremal at the correct solution for independent variations of all the quantities: V^{in}, n^{in}, μ, T, and the form of the occupation function $f(\varepsilon)$.

Solution:

The extremal properties with respect to the potential and density are the same as shown in Exercise 7.16. The linear term involving the chemical potential μ is vanishes at the correct number. The argument for the variation with the form of $f(\varepsilon)$ may seem unusual, but it is one way to see how the Fermi function is derived, Indeed the general form derived by Mermin is using the variational condition. See also the following exercise.

ERROR! I believe there is a mistake in the statement of the e4xercise. I think that the functional is NOT extremal with respect to temperature T. If we fix V, n, and μ it is like and ordinary independent-particle problem and the free energy is is linear except at $T = 0$.

ERROR in problem

Exercise 7.19 Show that the form of the electronic entropy $\sum_i f_i \ln f_i + \sum_i (1 - f_i)\ln(1 - f_i)$ presented in (7.32) in fact follows from the general many-body from in terms of the density matrix given by Mermin in (6.20).

Solution:

Before starting the derivation, it is good to recall that the general expressions are given in Section 3.5 and the reason that a log is involved is that the entropy is the log of the number of possible states, and the sum of two terms involving f and $1 - f$ is because the number of states at fixed density is the number of electron-hole pairs. For independent particles this is just the product of electron and hole states. The general expression is in Eq. (3.28) and the expression for the density matrix for independent particles is in Eq. (3.40).

CHECK THIS!

I believe the following is correct but it is very hand waving! Unlike the energy the entropy is not an expectation value. (In many cases there are analytic expression, but in a general case derive the form using the single body density matrix for particles Eq. (3.40) and the principle that number conserving excitations are products of electrons and holes. Then Eq. (3.28) leads directly to the expression involving $\sum_i f_i \ln f_i + \sum_i (1 - f_i)\ln(1 - f_i)$.

Exercise 7.20 Show that $\tilde{\chi}$ in Equation (7.34) is given by

$$\tilde{\chi} + 1 = \frac{\delta n^{\mathrm{out}}}{\delta n^{\mathrm{in}}} = \frac{\delta n^{\mathrm{out}}}{\delta V^{\mathrm{in}}}\frac{\delta V^{\mathrm{in}}}{\delta n^{\mathrm{in}}}, \tag{S.99}$$

where $\delta n^{\mathrm{out}}/\delta V^{\mathrm{in}}$ is a response function defined to be χ^0 in Equation (D.6) and the last term $\delta V^{\mathrm{in}}/\delta n^{\mathrm{in}}$ is K defined in Equation (7.25). Thus the needed function $\tilde{\chi}$ can be calculated and is closely related to other uses of response functions.

Solution:

Really this is just the definition plus the chain rule. The expression for K follows from the definition that the potential is the derivative of the potential part of the energy here called E_{pot}. What we want is the derivative of the potential which is the second derivative of the E_{pot}. Since E_{pot} is the internal energy called H_{xc} in Equation (7.25) plus the part due to the external potential $\int V_{ext}(\mathbf{r})n(\mathbf{r})$, the expression in Equation (7.25) follows because the last term is linear in the density (V_{ext} is a fixed quality) and does not contribute to the second derivative.

Exercise 7.21 Derive the constraint on the α parameter in the simple linear mixing scheme in terms of the response function; i.e., that the iterations converge only if $\alpha < 2/\tilde{\chi}^{-1}_{\rm max} = 2\tilde{\chi}_{\rm min}$. See also Exercise 13.3.

Solution:

It is sufficient to examine the iterations close to the minimum where linear response is enough. The behavior from self-consistency depends on the problem, but it is always linear near the solution. The expression for the error at step i $(1 - \alpha\tilde{\chi}^{-1}_{\rm max})^i$ given after Eq. (7.36) shows that if $\alpha > 2\chi$ the output "overshoots" and the results diverge alternating plus and minus around the solution. (Since χ is a matrix it is not as simple as scalars, but the idea is that one has the examine the maximum or minimum eigenvalues of χ.

Exercise 7.22 Derive the two terms in the corrections to the force given in Eq. (7.40) for a self-consistent independent-particle method, starting from the general form, Eq. (3.18). The self-consistency adds the second term that is not present is the general case where the hamiltonian never changes. Hint: Derive this term from the original definition of the force as a derivative of the total energy.

Solution:

The first term is the contribution if the wavefunctions vary, where $2\times$ the real part takes into account the variation of the ket vector.

The second term can be derived using the expression for the energy in Eqs. (7.26) and 7.27. There Eqs. (7.26) was considered to define a function for arbitrary V and n. However, the equations can be used for specific variations around the solution. At the solution all quantities agree and the linear variation is zero. However, the expression for the force involves a variation in the potential. In the general many-body expression the only part of the potential that varies is the external potential and we arrive at the form given in Eq. (3.18) or Eq. (3.19). However, in the Kohn–Sham problem the potential may not be fully self-consistent so that the potential and density are not consistent. If we consider Eq. (7.26) and assign $n^{\rm in}$ to denote the correct self-consistent density, then $V^{\sigma}_{n^{\rm in}}$ is the correct Kohn–Sham self-consistent potential V_{KS}, whereas the non-self-consistent potential is V^{in}. Then the first line of Eq. (7.27) is the desired result, the second line of Eq. (7.40).

What about the other term in Eq. (7.27) that involves that δV? It also is an error but it has a different interpretation. It does not change the interpretation that the force is the density times the gradient of the potential; it is merely the fact that the density is not exactly correct.

Reader, CHECK this is really correct!

Solutions for Chapter 8

These are the Ex. in the second ed. Some of the problems in Chapter 8 the first edition are the same as the ones below, but some have been moved to Chapter 9 of the second edition (the problems involving the OEP and KLI).

Exercise 8.1 Derive the "spin-scaling relation" (8.9). From this it follows that in the homogeneous gas, one needs only the exchange in the unpolarized case.

Solution:

The relations follow from the fact that exchange involves only the same spin, so it is a sum of a term for up and for down. Since $E_x[n]$ on the right side of (8.9) is defined to be the energy for system with density $n = 2n^\uparrow = 2n^\downarrow$, it follows that $(1/2)E_x[2n^\uparrow]$ is the exchange energy for up spins and similarly for down spins and the total for a polarized (or unpolarized) system is the expression in (8.9).

Explicit Eqs. from Benchen:

Since the exchange interaction only happens within same spin electrons so we could separate the functional as:

$$E_x[n^\uparrow, n^\downarrow] = E_x[n^\uparrow, 0] + E_x[0, n^\downarrow] \tag{S.100}$$

For an unpolarized case, we have:

$$E_x[n] = E_x[\frac{n}{2}, \frac{n}{2}] = E_x[\frac{n}{2}, 0] + E_x[0, \frac{n}{2}] = 2E_x[\frac{n}{2}, 0] \tag{S.101}$$

So apply the above equation to the question we have:

$$E_x[n^\uparrow, n^\downarrow] = E_x[n^\uparrow, 0] + E_x[0, n^\downarrow] = \frac{1}{2}E_x[2n^\uparrow] + \frac{1}{2}E_x[2n^\downarrow] \tag{S.102}$$

There might be some confusion with the notation. $E_x[n^\uparrow, n^\downarrow]$ stands for the general spin case where it might be polarized or unpolarized. $E_x[n]$ means unpolarized case where the total density is n. So $E_x[2n^\uparrow]$ stands for **unpolarized** case where the total density is twice the density of $n^\uparrow$.

Exercise 8.2 (a) Show that the expression for the dimensionless gradients $s_1 = s$ in (8.10) can be written in terms of r_s as (8.11).
(b) Find the form of the second gradient s_2 in terms of r_s.

Solution:

This is a matter of inserting the definitions of k_F and r_s. Explicit Eqs. from Benchen:
(a)

$$s_1 = \frac{|\nabla n|}{2k_F n} = \frac{4\pi r_s^4}{2 \times 3(2\pi/3)^{1/3} \times 3} \times \frac{9}{4\pi r_s^4}|\nabla r_s| = \frac{|\nabla r_s|}{2(2\pi/3)^{1/3}} \tag{S.103}$$

Note that there is a typo in the book. There shouldn't be a r_s in the denominator otherwise it wouldn't be dimensionless.
(b)

$$s_2 = \frac{|\nabla^2 n|}{4(3\pi^2)^{2/3} n^{5/3}} = \frac{|4\nabla r_s - r_s \nabla^2 r_s|}{(12\pi^2)^{1/3}} \tag{S.104}$$

Exercise 8.3 Use the known form of the density near a nucleus to analyze the final term in (8.18) near the nucleus. Show that the term involves higher-order derivatives of the density that are singular at the nucleus.
(a) Argue that such a potential is unphysical using the facts that the exact form of the exchange potential is known and correlation is negligible compared to the divergent nuclear potential.
(b) Show that, nevertheless, the result for the total energy is correct since it is just a transformation of the equations.
(c) Finally, discuss how the singularity can lead to numerical difficulties in actual calculations.

Solution:
The problem is the gradient of the density ∇n. Near the nucleus the density has a cusp so that $\nabla n = (dn(r)/dr)\hat{r}$.

NOTE: NOT FINISHED

See note - not finished

Note that his is analogous to the famous cusp condition on the wavefunction for two electrons that interact with a Coulomb potential as discussed in [1].

Exercise 8.4 Show that if a three-dimensional system is compressed in one direction so that the electrons are confined to a region that approaches a two-dimensional plane, the density diverges and the LDA expression for the exchange energy approaches negative infinity. Show that this is unphysical and that the exchange energy should approach a finite value that depends on the area density. Argue that this is not necessarily the case for a GGA, but that the unphysical behavior can be avoided only by stringent conditions on the form of the GGA.

Solution:
You can answer the first parts straightforwardly. It is simple to see that the LDA diverges since it is proportional to $n^{1/3}$ and it is straightforward to prove that the actual coulomb terms for electrons in 2d does not diverge. The exchange in two dimensions for the Coulomb interaction $1/r$ (the three-dimensional form so that the potential extends into the space in the third dimension. Thus the integral is proportional to $\int (1/r) r dr$ which is finite. The last part is tricky: how can gradients be arranged to give a finite result. In fact this is one of the limits considered in the functionals such as the SCAN meta-GGA in Chapter 9. See the original papers for the reasoning.

Exercise 8.5 Problem on a diatomic molecule that demonstrates the breaking of symmetry in mean-field solutions such as LSDA.
(a) Prove that the lowest state is a singlet for two electrons in any local potential.
(b) Show this explicitly for the two-site Hubbard model with two electrons.
(c) Carry out the unrestricted HF calculation for the two-site Hubbard model with two electrons. Show that for large U the lowest-energy state has broken symmetry.
(d) Computational exercise (using available codes for DFT calculations): Carry out the same set of calculations for the hydrogen molecule in the LSDA. Show that the lowest-energy state changes from the correct symmetric singlet to a broken symmetry state as the atoms are pulled apart.

(e) Explain why the unrestricted solution has broken symmetry in parts (c) and (d), and discuss the extent to which it represents correct aspects of the physics even though the symmetry is not correct.
(f) Explain how to form a state with proper symmetry using the solutions of (c) and (d) and a sum of determinants.

Solution:
This is a problem with many parts that I think are very instructive. I have done this is class as important example that shows key aspects of many-body systems. A long very detailed solution for part b is given at the end of these solution notes.

Part a. The solution to part b can be carried over to any problem with the argument that for a more complicated problem the energy is always pushed down if one adds additional states at higher energy. The fact that it has the same symmetry as for independent particles is one of the ways of looking at the problem as evolving continuously from the non-interacting case as interactions are “turned on”, which is on the important concepts in many-body physics. A formal proof is that the ground state is always a state with no nodes (see [1]).

Part b. A long very detailed solution is given at the end of these solution notes. Since the total number of states is 4, the solution for 0 and 4 electrons is trivial. For 1 and 3 electrons the states are simply banding and antibonding. The interesting case is 2 electrons that can be departed into spin singlets and triplets. The result is that all solutions can be found with no more than 2x2 matrices. There is always a state that is spin singlet and even in space that has the same symmetry as an independent-particle bonding state, with binding energy that is reduced by the repulsive interaction but is always positive, i.e., the lowest energy state.

Part c. The HF solution is for uncorrected particles but keeping the interaction. For large enough repulsive interaction the solution is for the two electrons to be on different sites. (See the list of all states in the detailed solution to part b.) which are a triplet with spin 1, and two singlet states with up on one atom and down on the other. The unrestricted HF solution is a single determinant that is one of the two states, i.e., a broken symmetry state with that is not a proper singlet and not even or odd. The solution to part f resolves the quandary and restores the symmetry.

Part d. For az hydrogen molecule this is a computational problem, but we can understand the results without doing the calculation. A Kohn–Sham DFT calculation is for a independent-particle problem in an effective potential which is a single determinant. We consider a spin-dependent functional and the possibility of a broken symmetry, i.e., an unrestricted solution. It is intuitive clear that as the atoms are pulled apart the ratio of interaction to the interatomic independent-particle terms increase, at some point the ground state will have broken symmetry solution just like the unrestricted HF. The spin density is opposite around the two atoms and the Kohn–Sham potential is higher for one spin than the other around each atom. The solution of part f brings out something that is missing in the Kohn–Sham solution.

Part e. The reasons for the broken symmetry have been described above. The sense in which this captures real physics is that it indicates the correlated regime where there is a large correlation: If one electron is near the left atom the other is more likely to near the right atom. Of course this always happens for any degree of repulsion and the broken symmetry indicate where this become the dominant physics and bonding can be viewed as a perturbation.

Part f. Finally we come to the solution that can be stated definitive for the Hubbard model; The true ground state is a linear combination of the two degenerate broken symmetry states, i.e., the bonding combination. This is the way that one achieves a proper spin singlet which is not a state with up on one site and down on the other. It is a multiple determinant. What do we learn about real problems? For a hydrogen molecule the logic applies but the final solution depends changes in quantitative ways when one makes the linear combination. For a larger system it is MUCH more difficult! The number of determinants grows exponentially and there is no exact solution. An example is an antiferromagnet in a DFT calculation. Is this correct? It may be that indeed there is long range order with net spin on each site. This is real physics unlike the broken symmetry in in the molecule. Thus the DFT solution may be correct even if it is not quantitatively correct. But one can understand the physics better by realizing that DFT is designed to give only the (spin) density NOT the correlations; one must use a different theory to describe the correlations. The value of the net average spin always is decreased by the fact that correlated spin flips are included. At some point the DFT solution is not broken symmetry and this is also what happens in the real world. Thus it becomes a question of accuracy in the reproduction of the ground state using a practical, approximate functional, keeping in mind that theory (even the exact theory) is ONLY for the average (spin) density and energy, NOT the correlations.

Exercise 8.6 Compute the exact exchange potential as a function of radius r in an H atom using the exact wavefunction in the ground state. This can be done with the formulas in Chapter 10 and numerical integration. Compare with the LDA approximation for the exchange potential using the exact density and expression (8.16), (note the system is full-spin polarized). Show the comparison explicitly by plotting the potentials as a function of radius. Justify the different functional forms of the potentials at large radius in the two cases.

Solution:

The exact exchange potential can be found because cancels exactly the Hartree potential, which can be found by standard equations for the Coulomb potential for a spherically symmetry charge density which is given. In the LDA exchange potential can be calculated from the density at each point. To calculate the potential as a function of radius requires a calculation left for the reader to do.

Calculation not actually done!

However we the total exchange energy is given in Table 9.1! The results in Table 9.1 are computed with the density from EXX, which is essentially the same as Hartree-Fock. For H Hartree-Fock is exact. Since the results in Table 9.1 are calculated with the EXX density, the results for EXX are exact and for the LDA there are in the table. We see that the LDA is not too bad as a fraction, but because the exchange energy is so large it is finally a very bad approximation. See Table 9.1 for the great improvement using GGA and hybrid functionals.

Exercise 8.7 The hydrogen atom is also a test case for correlation functionals; of course, correlation should be zero in a one-electron problem. Calculate the correlation potential using the approximate forms given in Appendix B (or the simpler Wigner interpolation form). Is the result close to zero? Does the correlation potential tend to cancel the errors in the local exchange approximation?

Solution:

If we use the known density of the atom (exponential decay) to calculate the various terms, it is straightforward to evaluate the terms for any functional, and to integrate the terms to get the total correlation energy. This is left for the reader to do.

Calculation not actually done!

However, we can see from Table 9.1 the results for the total correlation energy. (See the previous problem.) The LDA is amazingly good considering it is based on a homogeneous gas! But till not good enough and the GGA and hybrids are much better.

Solutions for Chapter 9

THIS IS A NEW CHAPTER IN THE SECOND EDITION.

Some Some of the problems in Chapter 8 the first edition (the ones involving the OEP and KLI) and others are new exercises.

The exercises that were in chapter 9 in the first edition are all are moved to the end of exercises in chapter 7 in the same order in the second edition.

Exercise 9.1 (Ex. 7.11 in fist ed.) It is interesting to note that construction of a kinetic energy functional of the density is a "fermion problem." See Section H.1 and Exercise H.1 and H.2. For non-interacting bosons, construct explicitly a practical, exact density functional theory.

Solution:

The exact result is given by all particles in a symmetric product wavefunction $\Psi(\{\mathbf{r}_i\}) = \prod_i^N \psi(\mathbf{r}_i)$ with $\psi(\mathbf{r}) = \sqrt{n(\mathbf{r})}$. Then the kinetic energy functional is simply N times the kinetic energy for a single particle $T[n] = -\frac{N}{2}\int \sqrt{n}\nabla^2\sqrt{n} = -\frac{N}{2}(\int \nabla^2 n - \frac{1}{2}\frac{(\nabla n)^2}{n})$

Exercise 9.2 (Ex. 8.5 in first ed.) Derive the general OEP expression, (9.11), using the chain rule, and show that it leads to the compact integral expression, (9.17).

Solution:

The expression using the chain rule is in Eq. (9.13) (8.27) in first ed.). The physical picture is that the wavefunctions are determined by the potential and the last term is the dependence of the potential on the density. However, this is not trivial. If it were the LDA the dependence is not hard to work out, but in this case the potential is calculated self-consistently with the density using the functional of the wavefunctions.

Solution due to Benchen:

First of all we could multiply Eq. (9.13) (8.27) in first ed.) by $\chi_0^\sigma(\vec{r}',\vec{r})$ on both sides to get:

$$V_{xc}^{\sigma,OEP}(\vec{r}')\chi_0^\sigma(\vec{r}',\vec{r}) = \frac{\delta E_{xc}^{OEP}}{\delta n^\sigma(\vec{r}')}\chi_0^\sigma(\vec{r}',\vec{r}), \tag{S.105}$$

Then we could expand it as:

$$\begin{aligned}&\sum_{i=1}^{N^\sigma}\psi_i^{\sigma *}(\vec{r}')V_{xc}^{\sigma,OEP}(\vec{r})G_0^\sigma(\vec{r}',\vec{r})\psi_i^\sigma(\vec{r}) + c.c.\\ &\quad = \sum_{\sigma'}\sum_{i=1}^{N^{\sigma'}}\int d\vec{r}'' \int d\vec{r}_1 \left[\frac{\delta E_{xc}^{OEP}}{\delta\psi_i^{\sigma'}(\vec{r}'')}\frac{\delta\psi_i^{\sigma'}(\vec{r}'')}{\delta V^{\sigma',KS}(\vec{r}_1)} + c.c.\right]\frac{\delta V^{\sigma',KS}(\vec{r}_1)}{\delta n^\sigma(\vec{r}')}\chi_0^\sigma(\vec{r}',\vec{r})\end{aligned} \tag{S.106}$$

Then we could integrate $\vec{r}'$ on both sides to get:

$$\sum_{i=1}^{N^\sigma} \int d\vec{r}' \psi_i^{\sigma *}(\vec{r}') V_{xc}^{\sigma,OEP}(\vec{r}) G_0^\sigma(\vec{r}', \vec{r}) \psi_i^\sigma(\vec{r}) + c.c.$$
$$= \sum_{\sigma'} \sum_{i=1}^{N^{\sigma'}} \int d\vec{r}'' \int d\vec{r}_1 \left[\frac{\delta E_{xc}^{OEP}}{\delta \psi_i^{\sigma'}(\vec{r}'')} \frac{\delta \psi_i^{\sigma'}(\vec{r}'')}{\delta V^{\sigma',KS}(\vec{r}_1)} + c.c. \right] \int d\vec{r}' \chi_0^{\sigma',-1}(\vec{r}_1, \vec{r}') \chi_0^\sigma(\vec{r}', \vec{r}) \tag{S.107}$$

For the response functions we have:

$$\int d\vec{r}' \chi_0^{\sigma',-1}(\vec{r}_1, \vec{r}') \chi_0^\sigma(\vec{r}', \vec{r}) = \delta_{\sigma\sigma'} \delta(\vec{r}_1 - \vec{r}). \tag{S.108}$$

(check equation (13) and (16) in *A.Gorling and M.Levy: Phys.Rev.A 50,196(1994)*) So we plug it in to get:

$$\sum_{i=1}^{N^\sigma} \int d\vec{r}' \left[\psi_i^{\sigma *}(\vec{r}') V_{xc}^{\sigma,OEP}(\vec{r}') G_0^\sigma(\vec{r}', \vec{r}) \psi_i^\sigma(\vec{r}) - \frac{\delta E_{xc}^{OEP}}{\delta \psi_i^\sigma(\vec{r}')} \frac{\delta \psi_i^\sigma(\vec{r}')}{\delta V^{\sigma,KS}(\vec{r})} \right] + c.c. = 0, \tag{S.109}$$

where we have rename the variable $\vec{r}''$ to $\vec{r}'$. By expanding the second term we can get:

$$\sum_{i=1}^{N^\sigma} \int d\vec{r}' \psi_i^{\sigma *}(\vec{r}') \left[V_{xc}^{\sigma,OEP}(\vec{r}') - V_{i,xc}^{\sigma,NL}(\vec{r}') \right] G_0^\sigma(\vec{r}', \vec{r}) \psi_i^\sigma(\vec{r}) + c.c. = 0 \tag{S.110}$$

Note that in the book there is a typo in Eq. (9.13) (8.27) in first ed.), where on the right hand side there should be ψ^* not ψ.

Exercise 9.3 (Ex. 8.6 in First ed.) Write out explicit expressions for the inversion of the response function needed in (9.11) by expressing the response function in a basis. Consider appropriate bases for two cases: a radially symmetric atom (with the potential and density on a one-dimensional radial grid) and a periodic crystal (with all quantities represented in Fourier space).

Solution:

This is a matter of writhing out the equations to see exactly what needs to be done. The calculation of $\chi_0^{\sigma,\mathrm{KS}}(\mathbf{r}, \mathbf{r}')$ is the sum on the right side of Eq. (9.16) which involves the wavefunctions in a basis. However, χ is expressed in terms of continuous positions in real space. This is what needs to be inverted. To do this we need finite matrix expressed in a basis which may or may not be the same as the basis for the wavefunctions. For the cases mentioned one would use a set of radial functions or plane waves, but in general they are exactly the same for for the wavefunctions. For example, for a periodic system in general the density involves plane waves up to a cutoff twice as large as the wavefunctions. Once χ is expressed in a basis, it is just a matter of matrix inversion.

Exercise 9.4 (Ex. 8.7 in First ed.) An impediment in actual application of the OEP formula, (9.11) is the fact that the response function is singular. Show that this is the case since a constant shift in the potential causes no change in the density. Describe how such a response function can be inverted. Hint: One can define a non-singular function by projecting out the singular part. This may be most transparent in the case of a periodic crystal where trouble arises from a constant potential which is known to be undetermined.

Solution:

As stated in the exercise, for plane waves it is essay to omit the constant $\mathbf{k} = 0$ term. for a finite system, it is not so obvious. One way is to define a basis where each basis function has average value zero.

Exercise 9.5 (Ex. 8.8 in First ed.) Show that the approximation, (9.18), substituted into the integral equation, (9.17), leads to the KLI form, (9.19), and discuss the ways in which this is a much simpler expression than the integral equation, (9.17).

Solution:

The great implication of KLI is that is the denominator is constant the sums are just overlaps fo wavefunctions and the result is for the OEP is a vast simplification that does not even require an inversion.

Explicit solution due to Benchen:

By substituting q. (9.18) into (9.17) ((8.32) into (8.31) in First Ed.) we get:

$$\sum_{i=1}^{N^\sigma} \int d\vec{r}' \psi_i^{\sigma*}(\vec{r}') \left[V_{xc}^{\sigma,KLI}(\vec{r}') - V_{i,xc}^{\sigma,NL}(\vec{r}')\right] \left[\delta(\vec{r}-\vec{r}') - \psi_i^{\sigma}(\vec{r}')\psi_i^{\sigma*}(\vec{r})\right] \psi_i^{\sigma}(\vec{r}) + c.c. = 0 \tag{S.111}$$

Further simplification would lead to:

$$n^\sigma(\vec{r}) V_{xc}^{\sigma,KLI}(\vec{r}) - \sum_i n_i^\sigma V_{i,xc}^{\sigma,NL}(\vec{r}) = \sum_i n_i^\sigma \left(\bar{V}_{xc}^{\sigma,KLI} - \bar{V}_{i,xc}^{\sigma,NL}\right) \tag{S.112}$$

$$\begin{aligned} V_{xc}^{\sigma,KLI}(\vec{r}) &= \sum_i \frac{n_i^\sigma}{n^\sigma} \left(V_{i,xc}^{\sigma,NL}(\vec{r}) + \bar{V}_{xc}^{\sigma,KLI} - \bar{V}_{i,xc}^{\sigma,NL}\right) \\ &= V_{xc}^{\sigma,S}(\vec{r}) + \sum_i \frac{n_i^\sigma}{n^\sigma} \left(\bar{V}_{xc}^{\sigma,KLI} - \bar{V}_{i,xc}^{\sigma,NL}\right) \end{aligned} \tag{S.113}$$

Exercise 9.6 Derive the power law for the London dispersion interaction, using a model with two oscillators, each with a charged particle attached to a spring, that are coupled by the Coulomb interaction. The longest range term results for using the lowest non-zero term in a perturbation expansion. Is this sufficient to establish the result for any problem approximated by a single pole?

Solution:

Not worked out specifically. A nice derivation is in Kittel for coupled harmonic oscillators. The basic idea is second order perturbation theory where the energy is proportional to the interaction ($1/r^3$ for dipoles) squared divided by an energy denominator, leading the $1/r^6$.

Exercise 9.7 Derive the relation in Eq. (9.28) using the expression for a coefficient in Eq. (9.25) and the single-pole approximation in Eq. (9.27).

Solution:

Carrying out the integral for C_{6AB} in Eq. (9.25) using the from for α in Eq. (9.27) we find

(see Tkatchenko, PhysRevLett.102.073005)

$$C_{6AB} = \frac{3}{2}\alpha_A^0 \alpha_B^0 \frac{\omega_A^0 \omega_B^0}{\omega_A^0 + \omega_B^0}. \tag{S.114}$$

From the this point algebraic manipulations lead to Eq. (9.28).

Exercise 9.8 Show that the polarizability in Eq. (21.7) has units of volume. Show also that the polarizability of a perfectly conducting sphere is equal to its volume. This is derived in Jackson [480] and other books, but it is a good exercise to do it yourself.

Solution:

See texts on electrodynamics such as Jackson [480] and the text by Zangwill listed at the end of Appendix E. The idea is that a conducting sphere has zero field inside, i.e., the field is excluded in for the volume of the sphere. This is the basis for the idea of an effective volume in a molecule or insulating solid where the field is reduced for the volume.

Exercise 9.9 See Exercise 8.6 and 8.7 for exchange and correlation (fictitious) terms in the LDA for H. Compare with the results in Table 9.1. Discuss the extent to which the results are improved in the hybrid functionals.

Solution:

Even though Exercise 8.6 and 8.7 are not solved explicitly, we can answer this question, as is pointed out in the solutions to those problems. The results in Table 9.1 are computed with the density from EXX, which is essentially the same as Hartree-Fock. The LDA is amazingly good considering it is based on a homogeneous gas! But till not good enough and the GGA and hybrids are much better. The results for the total support the general idea that DFT can provide accurate results many systems, including H with in some ways is a worst case!

Solutions for Chapter 10
Same as exercises in first edition.

Exercise 10.1 Show explicitly that the wave equation can indeed be written in the form of Eq. (10.4).

Solution:

Equation (10.4) follows from the transformation to radial coordinates in the previous equation and the derivation of the angular momentum contribution the the energy $\ell(\ell+1)$ derived in standard texts.

Exercise 10.2 Derive the form of the radial equation, Eq. (10.8) in terms of the transformed variable $\rho \equiv \ln(r)$. Give two reasons why a uniform grid in the variable ρ is an advantageous choice for an atom.

Solution:

There is an error in the equation in the text. The factor of $\ell/2$ should be $1/2$. The equation follows by transforming the variables and using the definition $\tilde{\phi}_l(\rho) = r^{1/2}\psi(r)$. It is most convenient to use Eq. (10.5) in terms of $\phi = r\psi = r^{1/2}\tilde{\phi}$ so that $\tilde{\phi} = r^{-1/2}\phi$ and transform to an equation in term of $\rho = \ln(r)$. The derivatives transform as $d/dr = (1/r)d/d\rho = e^{-\rho}d/d\rho$. If we work in terms of e^{ρ} instead of r the derivative are easy to evaluate and

$$\frac{d^2}{dr^2}\phi = e^{-\rho}\frac{1}{d\rho}\left[e^{-\rho}\frac{1}{d\rho}e^{\rho/2}\tilde{\phi}\right] = e^{-3\rho/2}\left[-\frac{1}{4}\tilde{\phi} + \frac{d^2}{d\rho^2}\tilde{\phi}\right]. \tag{S.115}$$

From this follows Eq. (10.8) using the relation $(\ell+1/2)^2 = \ell(\ell+1) + 1/4$.

Two reasons are that near the origin the wavefunctions have a power law like hydrogen functions (see Eq. (10.9)) and in the the tails the functions have exponential decay. As an aside, for DFT the functions do not decay properly for a neutral atom since the potential do not have the proper Coulomb form. However, Hartree Fock does have the proper form of decay. The reason is that for a neutral atom the DFT potential is neutral, but the actual potential felt by an electron is that due to the nucleus and the other electrons, i.e., a net positive charge of 1.

Exercise 10.3 Show that the Hartree–Fock equations are exact for the states of H. Show that the change in energy computed by *energy differences* gives exact excitations; but the eigenvalues do not.

Solution:

The proof that the Hartree–Fock equations are exact for the states of H is the same as for any one-electron problem: the exchange term exactly cancels the spurious self-interaction term. Thus each state of H is given exactly by the HF equation for that state, and the change in energy computed by *energy differences* between two different calculation gives the exact excitation energies.

However, the eigenvalues of the unoccupied states are NOT exact. By Koopmans' theorem they are the energies required to add an electron keeping the occupied states constant. These are not true excitation energies of any system.

Exercise 10.4 Show that the OEP equations are exact for the states of H, just like Hartree–Fock. But unlike Hartree–Fock the eigenvalues give exact excitation energies.

Solution:

The OEP equations are exact for the occupied state of H, just like Hartree–Fock because the exchange term exactly cancels the spurious self-interaction term. But unlike Hartree–Fock the OEP potential is the same for all states. Thus the potential is just the Coulomb potential of the proton $-1/r$ and the eigenvalues of this potential are the exact eigenvalues for H in its ground and excited states. Thus (unlike Hartree–Fock) differences between eigenvalues are the exact excitation energies. Of course, this applies only to the case of one particle where there are no interactions and the issues are o0nly whether or not the method produces the exact results.

Exercise 10.5 Show that the general Hartree–Fock equations simplify in the closed-shell case so that the exchange potential is spherically symmetric.

Solution:

The essential point is that the closed shell system is spherically symmetric. The Hartree term in the potential is the potential due to all the electrons and is clearly spherically symmetric. The exchange term is not so obvious since the equation involves the given wavefunction itself. The essential point is that effect of the non-local operator is symmetric, which can be shown be considering the operation on a wavefunction of a given angular momentum l, m. The is most easily see in Eq. (3.45), and the conclusion also applies to Eq. (3.48) since it is just a transformation. In Eq. (3.45) The issue is the integral in the exchange term in the second line where the sum is over all occupied states j. If we multiply by $\psi_i^\sigma(\mathbf{r})$ and integrate over $\mathbf{r}$ the result is manifestly invariant. Similarly each other term in the equation is invariant. Thus the wavefunctions in Eq. (3.45) can be expanded in a basis of radial functions and solved for each l, m.

CHECK the logic in Exercise 10.5 is correct!

Exercise 10.6 Show that for the ground state of He the general Hartree–Fock equations simplify to the very simple problem of one electron moving in the average potential of the other, with both electrons required to be in the same spatial orbital.

Solution:

Since the ground state is a spin singlet, the energy is the same as for the same spatial orbital with up and down spins. Thus the self term is exactly 1/2 the Hartree term leaving the net effect of a potential that it the Coulomb potential due to the nucleus and the average of the other electron.

Exercise 10.7 There are results that emerge in relativistic quantum mechanics that may be surprising. For example, show that there is a 2p state that has non-zero expectation value at the origin, whereas it is zero in the non-relativistic theory.

Solution:

In the non-relativistic theory the wavefunctions near the origin behave as $\psi(r) \propto r^\ell$ so that $\psi(0) = 0$ for all $\ell > 0$. Often spin is added in the non-relativistic equations as just doubling the number of eigenfunctions. However, it a proper relativistic theory there is spin–orbit interaction that mixes the spatial angular momentum. For example in spherical symmetry the $\ell = 1$ p states is split into a triplet with $j = 3/2$ and a singlet with $j = 1/2$. The latter mixes with the $\ell = 0$ s states which have $j = 1/2$. Thus the p state acquires a non-zero value at the nucleus.

Exercise 10.8 The Slater transition state argument (Slater's 1974 book [489], p. 51) is based on two facts. First, an eigenvalue is the derivative of the energy with respect to the occupation of the given state (the "Janak theorem"), and, second, that the eigenvalue varies with occupation and can be represented in a power series.

(a) Using these facts derive the "half-way" rule.

(b) Argue that one can derive the "half-way" rule based purely on the fact that one wants a result that is symmetric between the two states.

(c) Derive the explicit expression (10.21) for electron removal.

Solution:

All the arguments follow from the idea that the energy is a quadratic function of occupation, if occupation is considered to be a continuous variable. This is exactly true in models that have interactions between particles, which causes a quadratic term in the energy. In a many-electron atom or other finite system, the orbitals change with occupation and the quadratic dependence should be viewed as the lowest order approximation. Assuming the energy is a quadratic function of occupation the derivative at the midpoint is the slope of the energy at interger occupations $E(N+1) - E(N) = dE/dN = \varepsilon(N + 1/2)$ where the eigenvalue ε is the derive of the energy and it is evaluated at the half-way point. The physical significance is that it is the energy at integer values that is physical for an isolated finite system and the derivative is a way of calculating the energy differences using a theory where the occupation can be continuous. A fractional occupation actually occurs if the system is not isolated; however, care must be taken to interpret the physics correctly. See [1] for more indepth discussion.

Exercise 10.9 Solve the Schrödinger equation in Section 10.1 for a particle in a spherical box of radius R. If the boundary conditions are that $\psi = 0$ at $r = R$, show that the solutions are $\psi(r) = \sin kr/r$ and derive the eigenvalues and normalization factors for the states with the three lowest energies. Show that all energies scale as $\propto 1/R^2$.

Solution:

For a spherical box, the radial equations for $\ell = 0$ and $\phi(r) = r\psi(r)$ are exactly the same as $\psi(x)$ in a one-dimensional box of length L. The solutions with boundary conditions zero at both ends are $\psi(x) \propto \sin kx$ or $\phi(r) \propto \sin kr/r$, and in each case energies scale as $\propto 1/L^2$ or $\propto 1/R^2$.

The problem was poorly stated since it asked for the lowest states. It should have said the lowest states for $\ell = 0$.

In addition there are states of the spherical box with angular momentum $\ell > 0$ where there is a "centrifugal" term that acts like a potential $\ell(\ell+1)/r^2$.

Exercise 10.10 Derive the pressure $-\mathrm{d}E/\mathrm{d}\Omega$ from the expression for the energy in the problem above. Show that this is equivalent to the expression for the pressure in a spherical geometry given in (I.8).

Solution:

Since the energy scales as $1/R^2$, the pressure $dE/d\Omega = (1/4\pi R^2) dE/dR \propto 1/R^5$. The expression in (I.8) has this scaling (For this non-interacting problem the exchange term in is not relevant.) If we take the expression in (I.8) and insert the expressions for the lowest wavefunction $\phi(r) \propto \sin kr/r$, it is straightforward to carry out the derivatives.

Exercise 10.11 The expression (10.22) provides a way to calculate interactions.

(a) Show that these are "effective" in the sense that orbital relations are included and are *exact* if the energies $E(N)$, $E(N-1)$, and $E(N-2)$ are exact.

(b) Derive expression (10.22) using the same arguments as in Exercise 10.8.

(c) Use an atomic code to calculate the first and second ionization energies of $3\mathrm{d}$ electrons in Cu. The difference is the effective d–d interaction. A better measure of the net effect in a solid is to calculate the difference $E(3\mathrm{d}^9) - E(3\mathrm{d}^8 4\mathrm{s}^1)$. Compare your results with those of Mihaly and Martin [490]. In this case, the effective d–d interaction is decreased because the added s electron "screens" the change in charge of the d state. As argued in the paper by Herbst et al. Phys. Rev. B 17, 3089 (1978) [492] this is close to the screening that occurs in a solid; hence, the screened interaction is the appropriate effective interaction in the solid.

Solution:

(a) The term "exact" applies if we define the conditions: In free space and one is filling the same orbital (strictly only for a singlet with spin degeneracy) or orbitals with the same density so the interactions are the same and the orbital does not change, the interaction is purely quadratic and the expression applies. If the orbitals relax it is not purely quadratic and it is effective

In a solid there is screening and there is another use of the term "effective" to mean the screening due to other electrons in the solid. This leads to an effective interaction since the other orbitals relax. However, as long as this screening is linear it is just a factor.

(b) This is just a matter of using the eigenvalue for half-occupation intermediate between the two integer occupations, no matter what is the value of N.

(c) This is a computational exercise to be worked out by the reader.

Exercise 10.12 Following the arguments given in conjunction with (10.23)–(10.25), derive the approximate expressions (10.24) and (10.25) for the band width. The full argument requires justifying the argument that this corresponds to the maximum band width in a solid and deriving the explicit expression using the linearized formulas for energy as a function of boundary condition.

Solution:

The key point is that the band minimum is for the case with slope equal zero at the cell boundary and maximum for value zero where the wavefunction changes sign, as illustrated in Fig. 4.11. In a 3 dimensional close packed crystal the Wigner-Seitz cell is almost spherical and the band maximum corresponds to value zero in all directions.

If we follow the prescription before (10.23), when we take the difference of the two equations the potential term $V(r)\psi^1(r)\psi^2(r)$ drops out since v is the same in the two equations. The kinetic energy integrated up the boundary is the first derivative of ψ at the boundary. This leads to (10.23). Equation (10.24) follows because only one of the terms on the left side is non-zero. Equation (10.25) follows with a factor of 4 time the expression in Equation (10.24) using the argument that the functions are approximated by even and odd combinations of the atomic states, which is illustrated in Fig. 4.11.

The relations can be worked out explicitly as in the following equations due to Benchen: After we follow the instructions by the question and do the subtraction, we get:

$$\begin{aligned} LHS &= -\frac{1}{2}\int_0^{r_0} r^2\left(\psi_2\frac{d^2\psi_1}{dr^2}-\psi_1\frac{d^2\psi_2}{dr^2}\right)dr - \int_0^{r_0} r\left(\psi_2\frac{d\psi_1}{dr}-\psi_1\frac{d\psi_2}{dr}\right)dr \\ &= -\frac{1}{2}\int_0^{r_0} r^2 d\left(\psi_2\frac{d\psi_1}{dr}-\psi_1\frac{d\psi_2}{dr}\right) - \int_0^{r_0} r\left(\psi_2\frac{d\psi_1}{dr}-\psi_1\frac{d\psi_2}{dr}\right)dr \\ &= -\frac{1}{2}\left[r^2\left(\psi_2\frac{d\psi_1}{dr}-\psi_1\frac{d\psi_2}{dr}\right)\right]\Bigg|_0^{r_0} \\ &= -\frac{1}{2}r_0^2\left(\psi_2\frac{d\psi_1}{dr}-\psi_1\frac{d\psi_2}{dr}\right)_{r=r_0} \end{aligned} \tag{S.116}$$

So we have:

$$-\frac{1}{2}r_0^2\left(\psi_2\frac{d\psi_1}{dr}-\psi_1\frac{d\psi_2}{dr}\right)_{r=r_0} = (\varepsilon_1-\varepsilon_2)\int_0^{r_0} r^2\psi_1\psi_2 dr \tag{S.117}$$

If we take $\psi_2(r_0)=0$, we would have:

$$W=\varepsilon_2-\varepsilon_1=-\frac{r_0^2\left(\psi_1\frac{d\psi_2}{dr}\right)_{r=r_0}}{2\int_0^{r_0} r^2\psi_1\psi_2 dr} \tag{S.118}$$

And if we take atomic function for further approximation, and knowing at r_0, ψ_1, ψ_2 and their slope would be twice of that of atomic functions, we get:

$$W=\varepsilon_2-\varepsilon_1=-\frac{2r_0^2\left(\psi^a\frac{d\psi^a}{dr}\right)_{r=r_0}}{\int_0^{r_0} r^2(\psi^a)^2 dr} \tag{S.119}$$

Exercise 10.13 The wavefunction for atomic hydrogen can be used to estimate hydrogen band widths at various states, using the approximate form of Eq. (10.25). Apply this approach to the H_2 molecule to calculate bonding/anti-bonding splitting and compare these with the results shown in Fig. 8.2. Use this expression to derive a general argument for the functional form of the splitting as a function of proton separation R at large R. Evaluate explicitly at the equilibrium R and compare with Fig. 8.2. Calculate the band width expected for hydrogen at high density ($r_s = 1.0$) where it is expected to be stable as a close packed crystal with 12 neighbors. (The result can be compared with the calculations in Exercises 12.13 and 13.4.)

Solution:

The wavefunction for atomic hydrogen is $\psi(r) \propto \exp(-r/a_0)$. Thus the expression given in Eq. (10.25) gives:

$$W \approx -2\frac{r_0^2\left(\psi^a \frac{\mathrm{d}\psi^a}{\mathrm{d}r}\right)_{r=r_0}}{\int_0^{r_0} \mathrm{d}r r^2 (\psi^a)^2} = 2\frac{r_0^2}{a_0}\frac{\exp(-2r_0/a_0)}{\int_0^{r_0} \mathrm{d}r r^2 \exp(-2r_0/a_0)} = 8\frac{r_0^2}{a_0^4}\frac{\exp(-2r_0/a_0)}{1-\exp(-2r_0/a_0)(1+\frac{2r_0}{a_0}+\frac{2r_0^2}{a_0^2}}.$$

In atomic units this can be written in terms of the bond length $R = 2r_0/a_0$:

$$W \approx 2R^2\frac{1}{\exp R-(1+R+\frac{1}{2}R^2)}.$$

At large distance, clearly the predicted width (the difference of even and odd states, i.e, the bonding/anti-bonding splitting) is exponential in the distance $W \approx 2R^2\exp(-R)$ in atomic units.

At the equilibrium position in H_2, $r_0 \approx 0.7a_0$ is half the bond length, or $R \approx 1.4$. This yields $W \approx 5.8$ Hart. The results shown in Fig. 8.2 show that the splitting of the even and odd states is $\approx 10eV$. We see that the formula has given a huge overestimate of the splitting. The reason is that the derivation of the equation assumed each atom is surrounded by other atoms so that it is in a spherical environment. The wavefunction or its slope is required to vanish on a sphere that is very close to nucleus in this case. This is a very poor assumption for a molecule. It is a much better assumption for a close packed solid (see the second part of the problem) where there are twelve neighbors. As a first approximation we can estimate that the effect in a molecule is reduced by a factor of 12, i.e., $\approx 5.8/12 \approx 0.5$ Hart. $\approx$ 13 eV, which is quite close to the actual value of $\approx$ 10 eV.

As explained above the estimate should be reasonable for the band width expected for hydrogen at high density in a close packed crystal with 12 neighbors. If we consider a very high density, $r_s = 1.0$, which corresponds to a bond length $R \approx 2$. The predicted width is $W \approx 3.3$ Hart. This is the full width of the band and the occupied width is roughly 1/2 this value (since there is one electron per atom) which is ≈ 1.6 Hart. This is actually a very reasonable estimate that can be compared with the free electron estimate of $E_{Fermi} = 1.84$ Hart. (See Table 5.3 for E_{Fermi} as a function of r_s. As discussed in Chapter 12 and Exercise 12.13 and 13.4, the nearly free-electron approximation is an excellent approximation for H at such high density.

Exercise 10.14 Use an atomic code (possibly modified to have different boundary conditions) to calculate the band widths for elemental solids using the approach described in Section 10.7. As an example consider 3d and 4s bands in fcc Cu. Compare these with the bands shown in Fig. 16.4.

Solution:

This is a problem the requires computation - not worked out here.

Solutions for Chapter 11
Same as first edition

Exercise 11.1 Consider s-wave ($l = 0$) scattering in the example illustrated in Fig. 11.1. Using formula Equation (J.4) for the radial wavefunction ψ, with the definition $\phi = r\psi$, and the graphical construction indicated in Fig. 11.1, show that the scattering length approaches a well-defined limit as $\kappa \to 0$, and find the relation to the phase shift $\eta_0(\varepsilon)$.

Solution:

The formulas for the Bessel and Neuman function j_0 and n_0 in App. K show that $\phi = r\psi$. Must check - since n_0 diverges, must work out what happens. Need to check refs for scattering.

NOTE: NOT FINISHED

See note - not finished

Exercise 11.2 The pseudopotential concept can be illustrated by a square well in one dimension with width s and depth $-V_0$. (See also Exercises 11.6 and 11.14; the general solution for bands in one dimension in Exercise 4.22; and relations to the plane wave, APW, KKR, and MTO methods, respectively, in Exercises 12.6, 16.1, 16.7, and 16.13.)
A plane wave with energy $\varepsilon > 0$ travelling to the right has a reflection coefficient r and transmission coefficient t (see Exercise 4.22).
(a) By matching the wavefunction at the boundary, derive r and t as a function of V_0, s, and ε. Note that the phase shift δ is the shift of phase of the transmitted wave compared to the wave in the absence of the well.
(b) Show that the same transmission coefficient t can be found with different V_0' and/or s' at a chosen energy ε_0.
(c) Combined with the analysis in Exercise 4.22, show that a band in a one-dimensional crystal is reproduced approximately by the modified potential. The bands agree exactly at energy $\varepsilon_k = \varepsilon_0$ and have errors linear in $\varepsilon_k - \varepsilon_0$ plus higher-order terms.

Solution:

This problem is more complicated than it should have been and it is incomplete in an important way. If it had asked for bound states instead of transmission of states at positive energies, it would have been more appropriate. Usually for pseudopotentials one considers bound states. Pseudopotentials work for unbound states also but it is not as instructive. See below and Exercise 11.14 for examples of bound states. It is incomplete because it only asks for transmission t; this illustrates only part of the idea of pseudopotentials. Even though this determines the magnitude of the reflection it does not determine the phase. See Exercise 11.6 where we see that both t and r must be the same at the given energy to describe the bands. In higher dimensions this is the requirement that the scattering must be the same in all directions, i.e., for the same angular momenta. Thus a pseudopotential replaces a state with a strong potential with a pseudofunction with the same angular momentum. In one dimension this means the same parity. That does not change the solution here but it does change the interpretation.

Part (a) from Benchen

(a) The transmittance is:

$$t = \frac{F}{A} = \frac{e^{iks}}{cos(k's) - i\frac{k^2+k'^2}{2kk'}sin(k's)}, \tag{S.120}$$

so that

$$|t| = \frac{4(kk')^2}{4(kk')^2 + (k'^2 - k^2)^2 sin^2(2k's)} = \frac{1}{1 + \frac{V_0}{4E(E+V_0)}sin^2(2k's)}, \tag{S.121}$$

where $\hbar^2 k^2 = 2m_e E$ and $\hbar^2 k'^2 = 2m_e(E + V_0)$, and this equation can easily be rewritten in terms of ε, V_0, s. This calculation could be found in quantum mechanics textbooks, e.g., Griffith. The idea is that matching the wavefunctions value and slope at the edges of the cell.

(b) The last equation is easiest to demonstrate the result. For given values of the well depth V_0 and width s, the fact that the sine function is periodic means that the transmission can be the same for two or more different values of V_0, s. For example, for a fixed V_0 the argument of the sin function can change by multiples of 2π by varying s. The analogy to a pseudopotential is that for a strong potential with fixed values of V_0, s, the same transmission at a given energy E can occur with a weak potential weak different V_0, s.

A physical picture can be understood by the fact that a phase shift greater than 2π occurs if there is a bound state. This illustrates a pseudopotential: the same scattering occurs for a strong potential with a bound state (analogous to a core state in an atom) and a weak potential with no bound state and a phase shift $\eta + 2\pi$.

(c) The statement of the problem is not quite correct. As discussed in Exercise 11.6 the phase of both the transmission and reflection must be correct to determine the interference between two wells; therefore the solution for a periodic set of wells requires both to be correct and the bands are the same at that chosen E. **This is an example of the fact that the scattering must be the same in all directions. That means backward and forward in 1D, and the same angular momentum in in 2D and 3D. As stated above, I believe this means having pseudofunctions with the same symmetry (even or odd) as the orginal function.**

More instructive exercise

If the Ex. had asked for negative energies, the solution would be the same except with decaying functions outside the well (complex k). A detailed solution can be found on wikipedia and I stole the following graph from there. See

`https://en.m.wikipedia.org/wiki/Finite_potential_well`

In this case an example of a solution with several bound states is shown in the figure taken from that web page. There are three bound states. It is clear that one can find a weak potential with the lowest energy state having same energy as the top state. Since it is the lowest energy state it has no nodes like a pseudofunction and it is even as required to have the same symmetry are the original function shown in the graph. However, that potential

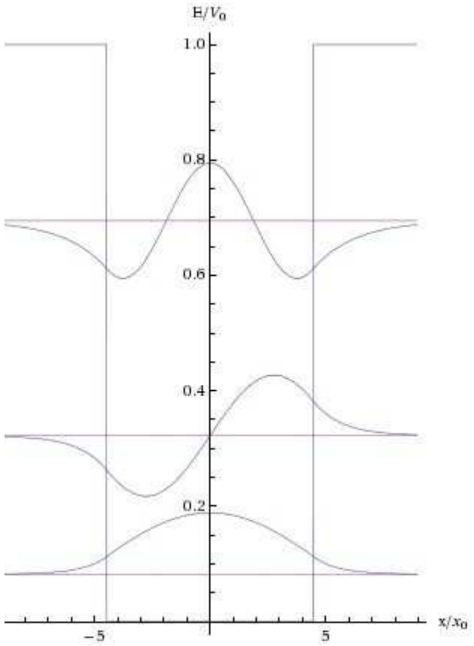


Figure S.2. Bound states in a finite square well in one dimension

will not have a state at the same energy as the middle state in the figure, i.e., the states are not reproduced correctly at that energy. This looks like a great error in 1D, but in higher dimensions it can be work because states of a local potential have angular momentum states with energy that increases with momentum. There is still error in the energy of other states and the accuracy is determined by the "hardness". The "transferability" to different situations is improved by the norm-conserving condition.

Exercise 11.3 Following Eq. (11.9) it is stated that if $u_{li} = \psi^c_{li}$ in the OPW, then the smooth function $\tilde{\psi}^v_l(\mathbf{r})$ has no radial nodes. Show that this follows from definition of the OPW.

Solution:

NOTE: NOT FINISHED

See note - not finished

Exercise 11.4 Verify expression Equation (11.10) for the norm of an OPW. Show this means that different OPWs are not orthonormal and each has norm less than unity.

Solution:

It's pretty straight forward to show that:

From Benchen

$$\begin{aligned}\langle \chi^{OPW}_{\mathbf{q}} | \chi^{OPW}_{\mathbf{q}} \rangle &= \frac{1}{\Omega}\int d\mathbf{r} - 2\sum_j |\langle u_j|\mathbf{q}\rangle|^2 + \sum_j \langle u_j|\mathbf{q}\rangle \sum_i \langle \mathbf{q}|u_i\rangle\, \delta_{ij} \\ &= 1 - \sum_j |\langle u_j|\mathbf{q}\rangle|^2\end{aligned} \tag{S.122}$$

Exercise 11.5 Derive the transformation from the OPW equation Equation (11.11) to the pseudopotential equation Equation (11.12) for the smooth part of the wavefunction.

Solution:

From Benchen

First of all, we use ψ_j^c as u_j, and we have for these wavefunctions:

$$-\frac{1}{2}\nabla^2\psi_j^c + V(\vec{r})\psi_j^c = \varepsilon_j^c\psi_j^c \tag{S.123}$$

And for the expansion coefficient, we have:

$$B_j + \left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle = 0 \tag{S.124}$$

So we can plug equation (11.4) into (11.10) to get:

$$\left[-\frac{1}{2}\nabla^2 + V(\vec{r})\right]\left(\tilde{\psi}_i^v - \sum_j \left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle \psi_j^c\right) = \varepsilon_i^v \left(\tilde{\psi}_i^v - \sum_j \left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle \psi_j^c\right) \tag{S.125}$$

Further simplification would lead to:

$$\left[-\frac{1}{2}\nabla^2 + V(\vec{r})\right]\tilde{\psi}_i^v + \sum_j (\varepsilon_i^v - \varepsilon_j^c)\left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle \psi_j^c = \varepsilon_i^v \tilde{\psi}_i^v \tag{S.126}$$

Since we have the relation:

$$V^R \tilde{\psi}_i^v = \sum_j (\varepsilon_i^v - \varepsilon_j^c)\left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle \psi_j^c \tag{S.127}$$

So we have derived equation (11.10).

Exercise 11.6 Consider the one-dimensional square well defined in Exercise 11.2. There (and in Exercise 4.22) the scattering was considered in terms of left and right propagating waves ψ_l and ψ_r. However, pseudopotentials are defined for eigenstates of the symmetry. In one dimension the only spatial symmetry is inversion, so that all states can be classified as even or odd. Here we construct a pseudopotential; the analysis is also closely related to the KKR solution in Exercise 16.7.

(a) Using linear combinations of ψ_l and ψ_r, construct even and odd functions, and show they have the form

$$\begin{aligned} \psi^+ &= \mathrm{e}^{-ik|x|} + (t+r)\mathrm{e}^{ik|x|}, \\ \psi^- &= \left[\mathrm{e}^{-ik|x|} + (t-r)\mathrm{e}^{ik|x|}\right] \mathrm{sign}(x). \end{aligned} \tag{S.128}$$

(c) From the relation of t and r given in Exercise 4.22, show that the even and odd phase shifts are given by

$$\begin{aligned} \mathrm{e}^{2i\eta^+} &\equiv t + r = \mathrm{e}^{i(\delta+\theta)}, \\ \mathrm{e}^{2i\eta^-} &\equiv t - r = \mathrm{e}^{i(\delta-\theta)}, \end{aligned} \tag{S.129}$$

where $t = |t|\mathrm{e}^{i\delta}$ and $\theta \equiv \cos^{-1}(|t|)$.

(d) Repeat the analysis of Exercise 11.2 and show that the band of a one dimensional crystal at a given energy ε is reproduced by a pseudopotential if *both* phase shifts $\eta^+(\varepsilon)$ and $\eta^-(\varepsilon)$ are correct.

Solution:

(a) The even wavefunction comes from the addition of two plane waves:

(a) and (b) from Benchen

$$\psi^+ = e^{-ik|x|} + (r+t)e^{ik|x|} \tag{S.130}$$

And the odd wavefunction comes from the subtraction of the two:

$$\psi^- = \left[e^{-ik|x|} + (r-t)e^{ik|x|}\right] sign(x) \tag{S.131}$$

(b) Since we have: $r = i|r|e^{i\delta}$ and $cos\theta = |t|$, we would derive it as:

$$e^{2i\eta^+} = t + r = \left(\frac{|t| + i|r|}{|t|^2 + |r|^2}\right) e^{i\delta} = e^{i(\delta+\theta)} \tag{S.132}$$

$$e^{2i\eta^-} = t - r = \left(\frac{|t| - i|r|}{|t|^2 + |r|^2}\right) e^{i\delta} = e^{i(\delta-\theta)} \tag{S.133}$$

(c) The interference between different wells requires the both forward and backward scattering t and r including their phases be correct. This is the reason that the pseudopotentials are for states with the same symmetry in order for the scterring the be the same in all directions for the weak and strong potentials. Here it means even and odd. In higher dimensions it means the same angular momentum. See Exercise 11.2.

Exercise 11.7 Find the analytic formulas for the Fourier transforms of a spherical square well potential $V(r) = v_0, r < R_0$, and a gaussian potential $V(r) = A_0 \exp -\alpha r^2$, using the expansion of a plane wave in spherical harmonics.

Solution:

For the first potential, we have:

From Benchen

$$\begin{aligned} V(\mathbf{k}) &= \int_0^{R_0} d\mathbf{r} v_0 e^{-i\vec{k}\cdot\vec{r}} = \frac{4\pi v_0}{k}\int_0^{R_0} r sin(kr) dr \\ &= \frac{4\pi v_0}{k}\frac{sin(kr) - kr cos(kr)}{k^2} = v_0 \frac{4\pi r_0^2}{k} j_1(kr) \end{aligned}$$

For the second potential, the same procedure applies.

Exercise 11.8 Show that the radial Schrödinger equation can be transformed to the nonlinear first-order differential equation Equation (11.24).

Solution:

The radial Schr. Eq. is:

From Benchen

$$-\frac{1}{2}\phi_l''(r) + \left[\frac{l(l+1)}{2r^2} + V_{eff}(r) - \varepsilon\right]\phi_l(r) = 0 \tag{S.134}$$

And we also have the relation:

$$x'(\varepsilon, r) + x^2(\varepsilon, r) = \frac{\phi_l''(r)}{\phi_l(r)}, \tag{S.135}$$

which leads to

$$x'(\varepsilon,r)+x^2(\varepsilon,r)=\frac{l(l+1)}{r^2}+2\left[V_{eff}(r)-\varepsilon\right] \tag{S.136}$$

Exercise 11.9 Show that Equation (11.26) indeed holds for any function f and that this relation leads to Equation (11.27) with the choice $f(r)=(\partial/\partial\varepsilon)x_l(\varepsilon,r)$. To do this use the fact that $\phi=0$ at the origin so that the final answer depends only on $f(R)$ and $\phi(R)$ at the outer radius.

Solution:

From Benchen First of all let's prove equation (11.26):

$$\frac{1}{\phi_l^2(r)}\frac{\partial}{\partial r}[\phi_l^2(r)f(r)]=f'(r)+2f(r)\frac{dln\phi_l(r)}{dr}=f'(r)+2x_l(\varepsilon,r)f(r) \tag{S.137}$$

And then combining with equation (11.25) we would have:

$$\frac{1}{\phi_l^2(r)}\frac{\partial}{\partial r}\left[\phi_l^2(r)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,r)\right]=-2 \tag{S.138}$$

Multiplying $\phi_l^2(r)$ on both sides on integrate between 0 and R we have:

$$-2\int_0^R\phi_l^2(r)dr=\int_0^R\phi_l^2(r)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,r)dr=\phi_l^2(R)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,R) \tag{S.139}$$

So as a conclusion we have:

$$\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,R)=-\frac{2}{\phi_l^2(R)}\int_0^R\phi_l^2(r)dr \tag{S.140}$$

Exercise 11.10 Show that the third condition of norm conservation (agreement of logarithmic derivatives of the wavefunction) ensures that the potential is continuous at R_c.

Solution:

From Benchen First of all let's prove equation (11.26):

$$\frac{1}{\phi_l^2(r)}\frac{\partial}{\partial r}[\phi_l^2(r)f(r)]=f'(r)+2f(r)\frac{dln\phi_l(r)}{dr}=f'(r)+2x_l(\varepsilon,r)f(r) \tag{S.141}$$

And then combining with equation (11.25) we would have:

$$\frac{1}{\phi_l^2(r)}\frac{\partial}{\partial r}\left[\phi_l^2(r)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,r)\right]=-2 \tag{S.142}$$

Multiplying $\phi_l^2(r)$ on both sides on integrate between 0 and R we have:

$$-2\int_0^R\phi_l^2(r)dr=\int_0^R\phi_l^2(r)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,r)dr=\phi_l^2(R)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,R) \tag{S.143}$$

So as a conclusion we have:

$$\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,R)=-\frac{2}{\phi_l^2(R)}\int_0^R\phi_l^2(r)dr \tag{S.144}$$

Exercise 11.11 Computational exercise (using available codes for pseudopotential calculations): Generate a "high quality" (small R_c) pseudopotential for Si in the usual atomic ground state 3s^{2}3p^2. Check that the eigenvalues are the same as the all-electron calculation.

(a) Use the same pseudopotential to calculate the eigenvalues in various ionization states $+1$, $+2$, $+3$, $+4$. How do the eigenvalues agree with the all-electron results.

(b) Repeat for a poorer quality (larger R_c) pseudopotential. Is the agreement worse? Why or why not?

(c) Carry out another set of calculations for a "compressed atom," i.e., confined to a radius $\approx\frac{1}{2}$ the nearest neighbor distance. (This may require changes in the code.) Calculate the changes in eigenvalues using the all-electron code and using the same pseudopotential, i.e., one derived from the "compressed atom." How do they agree?

(d) Non-linear core correlation corrections can also be tested. In many generation codes, the corrections can simply be turned on or off. One can also calculate explicitly the exchange–correlation energy using the pseudo and the entire density. The largest effects are for spin polarized transition metals, e.g., Mn 3d$^{5\uparrow}$ compared to 3d$^{4\uparrow}$ 3d$^{1\downarrow}$.

Solution:

Computational exercise not solved here.

Exercise 11.12 Show that unphysical "ghost states" can occur at low energies as eigenvalues of the hamiltonian with the non-local potential operator Equation (11.41) if $V_{\text{local}}(r)$ is chosen to be large and negative (attractive) so that the non-local $\delta V_l(r)$ must be large and positive. Hint: Consider the limit of a very large negative $V_{\text{local}}(r)$ acting on a state that is orthogonal to $\phi_l(r)$.

Solution:

To find out why there might be ghost states, we usually resort to spectral analysis. Let's use ϵ_0 and ϵ_1 to denote the two lowest eigenvalues. For the Hamiltonian, we can write it as: From Benchen

$$\hat{H}_l = \hat{T} + V_{local} + |\chi_l\rangle\lambda\langle\chi_l| \tag{S.145}$$

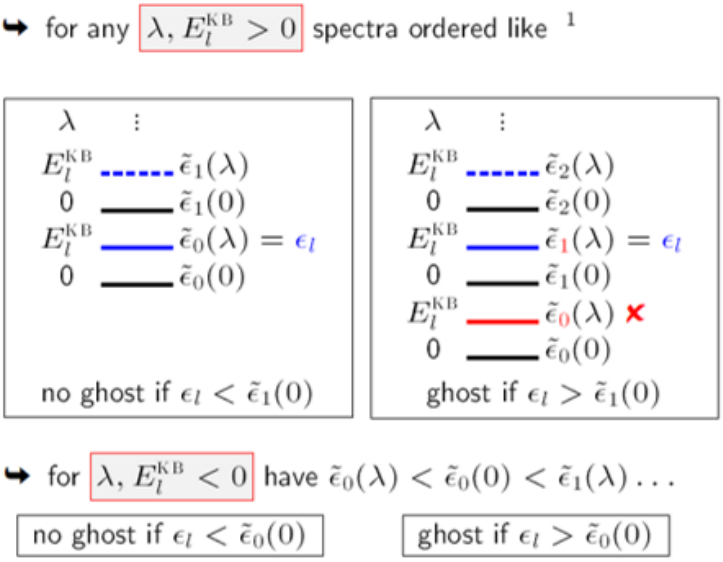
If $\lambda = 0$, then the energy we get is $\tilde{\epsilon}_i(0)$ with local potential only. And if $\lambda = E_l^{KB}$, that would give the reference valence level ϵ_l.

Take the $\lambda, E_l^{KB} > 0$ case as an example, from the Figure 2 we see that if ϵ_l, which is pre-known from atomic calculations, is larger than $\tilde{\epsilon}_1$, then there would be a ghost state below it. And that situation is likely to happen when the local potential is extremely negative, causing a really low eigenvalue $\tilde{\epsilon}_0$.

Exercise 11.13 Show that each ψ_s is a solution of $\hat{H}\psi_s = \varepsilon_s\psi_s$ if the "ultrasoft" potential is constructed using Equation (11.47).

Solution:

Here for sake of simplicity we assume that all wavefunctions, basis sets are real. So we From Benchen



↪ for any $\boxed{\lambda,\, E_l^{\mathrm{KB}} > 0}$ spectra ordered like [1]

↪ for $\boxed{\lambda,\, E_l^{\mathrm{KB}} < 0}$ have $\tilde{\epsilon}_0(\lambda) < \tilde{\epsilon}_0(0) < \tilde{\epsilon}_1(\lambda) \ldots$

$\boxed{\text{no ghost if } \epsilon_l < \tilde{\epsilon}_0(0)}$ $\boxed{\text{ghost if } \epsilon_l > \tilde{\epsilon}_0(0)}$

Figure S.3. ghost state demonstration

have:

$$
\begin{aligned}
\hat{H}|\psi_s\rangle &= \left[-\frac{1}{2}\nabla^2 + V_{local} + \sum_{l,m}\left(\sum_{p,q} B_{p,q}|\beta_p\rangle\langle\beta_q|\right)\right]|\psi_s\rangle \\
&= \left(-\frac{1}{2}\nabla^2 + V_{local} + \sum_{p,q} B_{p,q}\sum_r B^{-1}_{p,r}|\chi_r\rangle \sum_t B^{-1}_{q,t}\langle\chi_t|\right)|\psi_s\rangle \\
&= \left(-\frac{1}{2}\nabla^2 + V_{local}\right)\psi_s + \sum_{p,q,r,t}\left(B_{p,q}B^{-1}_{p,r}\right)\left(B_{s,t}B^{-1}_{q,t}\right)|\chi_r\rangle \\
&= \left(-\frac{1}{2}\nabla^2 + V_{local}\right)\psi_s + \sum_{p,q,r,t}\delta_{qr}\delta_{sq}|\chi_r\rangle \\
&= \left(-\frac{1}{2}\nabla^2 + V_{local}\right)\psi_s + |\chi_s\rangle = \varepsilon_s|\psi_s\rangle
\end{aligned}
\tag{S.146}
$$

Exercise 11.14 The square well in one dimension considered in Exercises 11.2 and 11.6 illustrates ideas of the OPW and pseudopotential methods and also shows close relations to other methods (see Exercise 11.2). In this example we consider a bound state with $\varepsilon < 0$, but similar ideas apply for $\varepsilon > 0$ (Exercise 11.2).

(a) A deep well has states analogous to core states with $\varepsilon_c \ll 0$. Consider a well with width $s = 2a_0$ and depth $-V_0 = -12Ha$. Solve for the two lowest "core" states using the approximation that they are bound states of an infinite well. Solve for the third "valence" state by matching the wavefunction.

(b) Construct a generalized OPW-like valence state using the definition $\psi^v(x) = \tilde{\psi}^v(x) + \sum_j B_j u_j(x)$, analogous to (11.4). Rather than using the expressions in Fourier space, it is easiest to use the definition $B_j = \langle u_j | \tilde{\psi}^v \rangle$. The overlap B_j is zero for one of the "core" states; give the reason and generalize the argument to apply to core states of an atom in three dimensions. Show that the "smooth state" $\tilde{\psi}^v$ is indeed smoother than the original ψ^v.
(c) Construct the PKA pseudopotential analogous to (11.13) and show that its operation on $\tilde{\psi}^v$ is effectively that of a weaker potential.
(d) Construct a model potential with the same width s but weaker potential V_0' that has the same logarithmic derivative at the "valence" energy ε. Is this potential norm-conserving?
(e) Construct a norm-conserving potential, which can be done by first finding a nodeless norm-conserving wavefunction and inverting it as in (11.32). If the form of the wavefunction is analytic, e.g., a polynomial inside the well, all steps can be done analytically.
(f) Write a computer code to integrate the one-dimensional Schrödinger equation and evaluate the logarithmic derivative as a function of energy near ε and compare the results for the original problem with the pseudopotentials from parts (d) and (e).
(g) Transform the potential to a separable form as in Section 11.8. There is only one projector since only one state is considered. Show that for a symmetric well in one dimension the general form involves only two projectors for even and odd functions.
(h) Generate an "ultrasoft" potential and the resulting generalized eigenvalue problem analogous to (11.59). Discuss the relation to the OPW method and PKA form of the potential.
(i) Generate a PAW function and show the relation to the OPW and APW methods (part (b) above and Exercise 16.1).

Solution:

Computational problem. Solution not given here.
But we note some important points. This deals with bound states like what is suggested in the solution to Exercise 11.2, where we point out that a bound state is more appropriate for actual construction of a pseudopotential and the unbound states. See also Exercise 11.6. The construction here is for the third state which is even like the example illustrated in the figure in the solution for Exercise 11.2.

Solutions for Chapter 12
Same as first edition

Exercise 12.1 See many excellent problems (and solutions) on the nearly-free-electron approximation in the book by Mihaly and Martin [598].

Solution:

No solution given here.

Exercise 12.2 Show that the Fourier transform of (12.15) leads to the expression in terms of form and structure factors given in (12.16).

Solution:

From Benchen

$$\begin{aligned}
V(\mathbf{G}) &= \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} d\mathbf{r} V(\mathbf{r}) exp(i\mathbf{G}\cdot\mathbf{r}) \\
&= \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} d\mathbf{r} \sum_{\kappa=1}^{n_{spec}} \sum_{j=1}^{n^{\kappa}} \sum_{\mathbf{T}} V^{\kappa}(\mathbf{r} - \tau_{\kappa,j} - \mathbf{T}) exp(i\mathbf{G}\cdot\mathbf{r}) \\
&= \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} d\mathbf{r} \sum_{\kappa=1}^{n_{spec}} \sum_{j=1}^{n^{\kappa}} \sum_{\mathbf{T}} V^{\kappa}(\mathbf{r}) exp(i\mathbf{G}\cdot(\mathbf{r} + \tau_{\kappa,j} + \mathbf{T})) \qquad \text{(S.147)} \\
&= \sum_{\kappa=1}^{n_{spec}} \frac{\Omega^{\kappa}}{\Omega_{cell}} \sum_{j=1}^{n^{\kappa}} exp(i\mathbf{G}\cdot\tau_{\kappa,j}) \frac{1}{\Omega^{\kappa}} \int_{all\ space} d\mathbf{r} V^{\kappa}(\mathbf{r}) exp(i\mathbf{G}\cdot\mathbf{r}) \\
&= \sum_{\kappa=1}^{n_{spec}} \frac{\Omega^{\kappa}}{\Omega_{cell}} S^{\kappa}(\mathbf{G}) V^{\kappa}(\mathbf{G})
\end{aligned}$$

Exercise 12.3 Show the equivalence of expressions (4.11) and (12.18) which express the final Fourier component in two ways, one an integral over the cell and the other as a structure factor times an integral for one unit only but over all space.

Solution:

This follows because $V^{\kappa}(\mathbf{r})$ is the potential due to one atom. The Fourier transform of a periodic array of the atoms is non-zero only for reciprocal lattice vectors and is the integral over the cell. The proof is the same as the manipulations in the previous problem.

Exercise 12.4 Plot the bands for a nearly-free-electron system in one dimension if the lattice constant is a.

(a) First plot the bands using analytic expressions for the energy in the free-electron limit.

(b) Then qualitatively sketch the changes if there is a small lattice potential.

(c) Use an empirical pseudopotential program, such as ones listed in Appendix R, or write your own to calculate the bands for a pure sine wave potential $V(x) = V_0 \sin(2\pi x/a)$. This is the Mathieu potential for which there are solutions; check your results with known results.

Solution:

Parts (a) and (b). Straightforward to plot bands in one dimension - just $|k + G|^2$ where

k varies from $-\pi/a$ to π/a and $G = n(2\pi/a)$. A small potential opens gaps at the BZ boundaries, but leaves the degeneracies at $k = 0$.
Part (c). Solution of the Mathieu potential in one, two and three dimensions - paper by J. C. Slater, Phys Rev 87, 807 (1952).

Exercise 12.5 Consider a one-dimensional crystal with potential $V(x) = V_0 \cos(2\pi x/a)$ as in Exercise 12.4. In this exercise make the simplifying approximation that a state with wavevector k is the solution of the 2×2 hamiltonian

$$\begin{vmatrix} \frac{k^2}{2} - \varepsilon(k) & V_0 \\ V_0 & \frac{(k-G)^2}{2} - \varepsilon(k) \end{vmatrix} = 0, \tag{S.148}$$

where $G = 2\pi/a$. Give the analytic expressions for the bands $\varepsilon(k)$ and the periodic part of the Bloch functions $u_k(x)$. If there are two electrons per cell, give the expression for the density $n(x)$ as an integral over k. Evaluate the density using a grid of "special" k points (Section 4.6). Note that more points are required for an accurate answer if V_0 is small. Plot the lowest two bands and the electron density for the case where $V_0 = \frac{1}{4}(\pi/a)^2$ in atomic units. (See Exercise 23.13 Wannier functions and Exercise 24.10 for polarization using a variation of this model.)

Solution:

The solution of the two by two problem is a straightforward solution of a quadratic equation for the eigenvalues and eigenvectors. The density is just 2 times the sum of squares of the eigenfunctions at the special points.

Not worked out explicitly.

Exercise 12.6 Consider a one-dimensional crystal with a square well potential which in the cell at the origin has the form $V(x) = V_0$ for $-s/2 < x < s/2$ and $V = 0$ otherwise. The potential is repeated periodically in one dimension with $V(x + Na) = V(x)$, with cell length $a > s$. (See also Exercises 11.2, 11.6, 11.14; the general solution for bands in one dimension in Exercise 4.22; and relations to the APW, KKR, and MTO methods, respectively, in Exercises 16.1, 16.7, and 16.13.)
(a) First find the Fourier transform of the potential $V(G)$.
(b) Computational exercise: Construct a computer (it is a matter of setting up the hamiltonian and diagonalizing) or use an available empirical pseudopotential code (see Appendix R) to solve for the bands. As an explicit example, choose $a = 4$, $s = 2$, and $V_0 = 0.2$ in atomic units and choose a sufficient number of plane waves so that the solution is accurate.
(c) Compare the results with the solutions in Exercise 16.1 in which the bands are found by matching the wavefunctions at the boundary, i.e., a simple example of the APW method. Of course, the result must be the same as derived by other methods: compare and contrast the plane approach with the general solution for any potential in one dimension given in Exercise 4.22.

Solution:

Computational exercise not worked out explicitly here.

Exercise 12.7 Find the bands for Al using a simple empirical pseudopotential. One source is the paper by Segall Phys. Rev. 124, 1797 (1961) [558] that shows bands similar to those in Fig. 16.6 calculated with $V(111) = 0.0115 Ha$ and $V(111) = 0.0215 Ha$ and mass $m^* = 1.03m$. (The last can be included as a scaling factor.) Use the NFEA to calculate energies at the X point analytically. Use an empirical pseudopotential program (See notes on codes in Exercise 12.12.) to generate full bands.

Solution:

Computational exercise not worked out explicitly here. The codes listed in App. R can be used. For example, the codes at nanohub include easy to use codes for empirical pseudopotentials.

Exercise 12.8 Show that the derivations in Section 12.1 also hold for non-local potentials as given in Eq. (12.24).

Solution:

One van see that the expressions apply to non-local potentials by noting that they depend only on the fact that the sum of potentials is periodic. The explict derivation is the same as given in the next problem.

Exercise 12.9 Derive the semilocal and separable forms of the pseudopotential in Eqs. (12.23) and (12.24). Hint: Use the definitions of the potential operators in real space in Chapter 11 and the expansion of a plane wave in spherical harmonics, Eq. (J.1).

Solution:

From Benchen

For the semilocal form in (12.23) we can expand $e^{i\mathbf{k}\cdot\mathbf{r}}$ as (J.1) does. Since we have assumed no explicit dependence on m, we can simplify it using (J.2) as:

$$\begin{aligned}
\delta V^{\kappa}_{NL}(\mathbf{K}_n, \mathbf{K}_{n'}) &= \sum_{lm} \langle \mathbf{K}_n | Y_{lm} \rangle \, \delta V^{\kappa}_l \, \langle Y_{lm} | \mathbf{K}_{n'} \rangle \\
&= \frac{(4\pi)^2}{\Omega^{\kappa}} \sum_{l'm'} \sum_{lm} \sum_{l''m''} (i^{l'})^* i^{l''} \, \langle j_{l'}(|\mathbf{K}_n| r) Y^*_{l'm'}(\hat{q}) Y_{l'm'}(\hat{r}) | Y_{lm}(\hat{r}) \rangle \\
&\times \delta V^{\kappa}_l(r) \, \langle Y_{lm}(\hat{r}) | j_{l''}(|\mathbf{K}_{n'}| r) Y^*_{l''m''}(\hat{q}) Y_{l''m''}(\hat{r}) \rangle \\
&= \frac{(4\pi)^2}{\Omega^{\kappa}} \sum_{l'm'} \sum_{lm} \sum_{l''m''} \delta_{ll'mm'} \delta_{ll''mm''} \langle j_{l'}(|\mathbf{K}_n| r) Y^*_{l'm'}(\hat{q}) | \\
&\times \delta V^{\kappa}_l(r) | j_{l''}(|\mathbf{K}_{n'}| r) Y^*_{l''m''}(\hat{q}) \rangle \\
&= 4\pi \sum_{l} \sum_{m} \langle Y_{lm}(\hat{q}) | Y_{lm}(\hat{q}) \rangle \, \frac{4\pi}{\Omega^{\kappa}} \langle j_l(|\mathbf{K}_n| r) | \delta V^{\kappa}_l(r) | j_l(|\mathbf{K}_{n'}| r) \rangle \\
&= \frac{4\pi}{\Omega^{\kappa}} \sum_{l} (2l+1) P_l(cos\theta) \int dr r^2 j_l(|\mathbf{K}_n| r) j_l(|\mathbf{K}_{n'}| r) \delta V^{\kappa}_l(r)
\end{aligned} \tag{S.149}$$

For the nonlocal form in 12.24 the derivation is simpler. It just the expression in 11.41 with ψ replaced by a plane wave with wavevector $\mathbf{k} + \mathbf{K}$ where $\mathbf{K}$ denotes $\mathbf{K}_m$ or $\mathbf{K}_{m'}$. Using the expansion of the plane wave in spherical waves in Eq. (J.1), we get the from in 12.24.

Exercise 12.10 Pseudopotentials are used because calculations with the full nuclear Coulomb potential are very expensive for heavy atoms of nuclear charge Z. Derive the power law with which the number of plane waves needed scales with Z. Do this by using perturbation theory for very high Fourier components, where the matrix element is given by $V(G)$ and the energy denominator is approximately given by the kinetic energy. Argue that screening is not effective for high Fourier components.

Solution:

Screening is not effective for very high Fourier components because the charge density is smoother then the nuclear potential and the Fourier components of the change decrease for high Fourier components. An example is the Thomas-Fermi approximation for screening of a charge that has a Gaussian decay.

In perturbation theory the energy varies as $V^2/(E - E_{max})$ where $E = k^2/2m$ and $V \propto 1/q^6 \approx 1/k^2$. Thus the effect scales as $1/E^3$. This is a slow cutoff as far as computations are concerned, but the perturbation theory can be used to add the effect analytically. For heavy atoms this is still much much more expensive than pseudopotentials, but it is not hard to do for a case like hydrogen with a reasonable number of plane waves. See Exercise 12.13 for this case.

Exercise 12.11 Project: Use an empirical pseudopotential program (see notes on codes in Exercise 12.12) to find the bands and charge densities of Si in the diamond structure at the lattice constant 10.26 a_0. The bands should be insulating and the bonds should be visible in the charge density.

(a) Verify that the minimum along the Δ direction (see Fig. 4.10) is qualitatively the same as in experiment, which is given in many texts, e.g., Kittel [285].

(b) Now compress the system until it is metallic (this can only be done in theory; in reality it transforms). Can you tell when the system becomes a metal just from the density? In principle, if you had the exact functional, what aspect of the density would be the signature of the insulator–metal transition?

(c) Do a similar calculation replacing the Si atoms with Al, still in the diamond structure with lattice constant 10.26 a_0. (Of course this is a theoretical structure.) There are three Al electrons/atom, i.e., six electrons per cell and it turns out to be a metal. Show that it must be metallic *without doing the calculation*. Does the density plot look a lot like Si? Can you find any feature that shows it is a metal?

Solution:

This can be done with codes in App. R.

Al is a metal because it has an odd number of electrons. But it is very hard to see this just by looking at the density; it can be be established by the fact that the density integrates to an odd number of electrons, but we knew that is advance!

Exercise 12.12 Project: Use an empirical pseudopotential program to find the bands for GaAs. (See codes listed in Appendix R. Figure 14.9 was calculated using online tools at nanohob.org which also has empirical pseudopotential codes.)

(a) Verify that it has a direct gap at Γ.

(b) Displace the atoms in the unit cell a small amount along the (111) direction. Check the

splitting of the top of the valence band at γ. Is the splitting what you expect?
(c) Repeat with the displacement in the (100) direction.

Solution:

Computational exercise.

Exercise 12.13 This exercise is to work out the form factor for the screened H potential in the Thomas–Fermi approximation and calculate the bands for fcc H at very high density, $r_s = 1.0$.
(a) Estimate the deviation of the bands from the free electron parabola by calculating the gaps at the X and L points of the BZ in lowest non-zero-order perturbation theory.
(b) Carry out calculations using an empirical pseudopotential program (see Exercise 12.12) and compare with the results from perturbation theory.
(c) Compare with the simple expression for the band width in Exercise 10.13 and with fully self-consistent band structure results as described in Exercise 13.4.

Solution:

Using the Thomas–Fermi approximation the potential is given by eq:tf-screening. The values can be worked out easily using the expressions for k_{TF} in Eq. (5.21). The bands are no worked out here.

Note that this is an example of screening no being effects at high k so that the potential is simple $\propto 1/k^2$ as discussed in Exercise 12.10.

Solutions for Chapter 13

Same as first edition except Ex. 13.1 is omitted. It was not an exercise, only a pointer to other exercises.

Exercise 13.1 There are excellent open source codes available on-line for DFT calculations using plane waves (see Appendix R). Two well-known ones are ABINIT and quantumESPRESSO which have large user groups. These codes can be used in the calculations for metallic H in Exercise 13.4 and other problems in the book. The codes often have tutorials similar to the exercises and also many examples for materials.

Solution:

No need for solution.

Exercise 13.2 Show that the Eq. (7.20) leads to the expression Eq. (13.2) written in Fourier components. In particular, show that the groupings of terms lead to two well-defined neutral groupings: the difference of the ion and the electron terms in the square bracket and the sum of eigenvalues that are the solution of a the Kohn–Sham equation with a neutral potential.

Solution:

This follows directly if one uses two facts (at least things that are usually true). Usually the largest screening (largest value of ϵ) is for lowest wavevector G_{min}. The error in the output is in the right direction but overshoots by the factor of ϵ. This is very familiar from dielectric screening where $E = \epsilon D$ where D is the internal field. It is inherent in the expressions for response functions in this book. It then follows that α must be less than $1/\epsilon$ to converge.

Exercise 13.3 Derive the result that the α parameter in the linear mixing scheme (13.5) must be less than $1/\epsilon(G_{\mathrm{min}})$ for convergence. Show that this is a specific form of the general equations in Section 7.4 and is closely related to Exercise 7.21. In this case it is assumed that ϵ_{max} occurs for $G = G_{\mathrm{min}}$. Discuss the validity of this assumption. Justify it in the difficult extreme case of a metal surface as discussed in Section 13.2.

Solution:

This is not a familiar property but it follows from the hint. The point is that the density of states (the number of states per unit energy) as a function of energy E is the sum over $\mathbf{k}$ of $\delta(\varepsilon(\mathbf{k}) - E)$. The distribution of values x of a function in real space $f(\mathbf{r})$ is the sum over points $\mathbf{r}$ of $\delta(f(\mathbf{r}) - x)$.

Exercise 13.4 This exercise is to calculate the band structure of metallic H at high density ($r_s = 1$ is a good choice) in the fcc structure and to compare with (1) the free-electron bands expected for that density and (2) bands calculated with the Thomas–Fermi approximation for the potential (**Exercise 12.13**). Use the Coulomb potential for the proton and investigate the number of plane waves required for convergence. (There is no need to use a pseudopotential at high density, since a feasible number of planes is sufficient.) Comparison with the results of Exercise 12.13 can be done either by comparing the gaps at the X and L points of the BZ in lowest non-zero-order perturbation theory, or by carrying out the full band calculation with the Thomas–Fermi potential.

Solution:

Calculational problem not solved here. Calculations with the bare potential are feasible. An example for Li in the literature (can’t remeber reference right now.)

Solutions for Chapter 14

Most are same as first edition except Eq. numbers are slightly shifted.

Tight-binding is used more in second ed. in Chapters 20 and 26-28. Exs. 14.17 and 14.24 in first edition are omitted, there are now references to Ch. 20 and 26, and Ex. 14.20 below is added in second edition. Other differences?

Exercise 14.1 See Appendix R for examples of codes are available (or can be run online) for tight-binding calculations that are both pedagogical and able to treat problems such as semiconductor devices.

Solution:

No need for solution here.

Exercise 14.2 See many excellent problems (and solutions) on tight-binding bands, densities of states, and the meaning of the bands in the book by Mihaly and Martin [598].

Solution:

See text referred to in Ex.

Exercise 14.3 Using translation invariance of the matrix elements, show that matrix elements of the hamiltonian with basis functions $\chi_{m\mathbf{k}}$ and $\chi_{m'\mathbf{k}'}$ are non-zero only for $\mathbf{k} = \mathbf{k}'$, i.e., the Bloch theorem, and derive the form given in Equation (14.4).

Solution:

The first part is simply that $\mathbf{k}$ is conserved, which is proved in many places in this book. If we want to use this is a good case to derive this property, consider Equation (14.4) with two functions at $\mathbf{k}$ and $\mathbf{k}'$. Inserting the definition in Eq. (14.3), we find the expression involves the factor $\sum_m e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{T}_m} = 0$ unless $\mathbf{k} - \mathbf{k}' = 0$. Also we find the result Equation (14.4) for $\mathbf{k} = \mathbf{k}'$.

Exercise 14.4 Derive the factor $A_{m\mathbf{k}}$ in (14.3) required for the Bloch basis states $\chi_{m\mathbf{k}}(\mathbf{r})$ to be normalized. Show that $A_{m\mathbf{k}} = 1$ if the functions $\chi_m(\mathbf{r} - (\tau_m + \mathbf{T}))$ are orthonormal and that in general $A_{m\mathbf{k}} = (S_{m,m}(\mathbf{k} = 0))^{-\frac{1}{2}}$, where $S(\mathbf{k})$ is defined in (14.5). This relation is used in Exercise 23.2 in examples of Wannier functions.

Solution:

If the functions $\chi_m(\mathbf{r} - (\tau_m + \mathbf{T}))$ are not orthonormal, then the $\int d\mathbf{r}|\chi_{m\mathbf{k}}(\mathbf{r})|^2 = A_{m\mathbf{k}} S_{m,m}(\mathbf{k} = 0)$, which leads to the desired relation.

Exercise 14.5 Show that, in general, one has the relation $K_{ll'm} = (-1)^{l+l'} K_{l'lm}$ under interchange on the indices of the K matrix. This follows from a consistent definition of the orbitals.

Solution:

The result follows because the wavefunctions have parity $(-1)^1$ and the interchange is a inversion of the directional band from one atom to the other, which leads to a change of sign of each function. It is not required but it is useful to note that m is the azimuthal quantum number around the axis between the atoms, and matrix elements are zero unless the values of m on each atom are the same.

Exercise 14.6 Show that for an s band in a line, square lattice, and simple cubic lattice with only nearest neighbor hamiltonian matrix elements, the respective densities of states (DOS) have the forms shown schematically in Fig. 14.4. First determine the form for the DOS for the one-dimensional line analytically. Then use this result along with the fact that the bands, (14.13), are simply a sum of cosines for orthogonal directions to derive the form of the DOS for the square and simple cubic lattice. Show that the bands are divided into segments of width $4t$ as stated, and show that in three dimensions the DOS is exactly symmetric and flat in the central range.

Solution:

The density of states for 1D has the form shown which can realized by the definition in Eq. (4.46) and the fact that the states are uniformly along the line $-\pi/a < k < \pi/a$. The energy near the band edge is quadratic $\varepsilon \propto k^2$ and thus the DOS is $\propto dk/dE = 1/(dE/dk)$ which diverges as $1/k \propto 1/E^{1/2}$. At the upper end of the spectrum the same arguments apply. In between there is variation that depends upon the system.

For higher dimensions, this not the most concise derivation but I think it is instructive.

In 2D the dispersion can be expressed as $\varepsilon(k_x, k_y)$. Near a band edge it has the form $\varepsilon = Ak_x^2 + Bk_y^2$. For each value of k_y the DOS has the form of a 1D DOS. The total DOS in 2D is found by summing over k_y which leads to a constant DOS so long as the energy has the quadratic form. Just as for 1D, the upper end of the spectrum where the energy is $\varepsilon = -Ck_x^2 - Dk_y^2$ the same arguments apply. In between there is variation that depends upon the system, but at some point there is a change when the dispersion along the two directions has opposite sign $\varepsilon = Ek_x^2 - Fk_y^2$. In that case there is a direction where $\varepsilon = 0$ and the DOS has a 1D type divergence, leading to the peak in the middle of the DOS.

We can repeat this for 3D with the result that it is a sum of 2D DOS. This leads to the form near the upper and lower bounds $\propto E^{1/2}$ since the 2D DOS is constant and the 2D DOS is $\propto k \propto E^{1/2}$. At intermediate energies there can be saddle points such as one where $\varepsilon = Ak_x^2 + Bk_y^2 - Ck_z^2$ where the dispersion along one direction is negative. At such a point the DOS is different above and below the saddle point energy. The arguments are analogous to those for 1D. For energy above the saddle point there is a direction where $Ak_x^2 + Bk_y^2 - Ck_z^2 = 0$; the DOS is like the 2D DOS for the other two directions. For energy below the saddle point the coefficient C decreases from positive to zero as the energy increases and the DOS is like an upside down 3D form. Similar arguments apply the next saddle point where the dispersion is negative along two directions, leading the the form of the DOS shown in the figure.

See note

NOTE: FINISH? - is the reasoning for “upside down” OK?

Exercise 14.7 Consider an s band in a square lattice with nearest neighbor matrix element t and one electron per cell. Show that the Fermi surface is a square as shown in Fig. 14.3 and there is a divergence in the density of states at the Fermi energy as shown in Fig. 14.4.

Solution:

The form for an s band in a square lattice with nearest neighbor matrix element t is given

by (see text and following problem)
$\varepsilon(\mathbf{k}) = 2t(\cos(k_x a) + \cos(k_y a))$,
where the on-site matrix element has been chosen to be zero.
The key point is that the cosine terms change sign between the zone center $\mathbf{k} = 0$ and the zone boundary. The general relation is $\cos(k_x a) = -\cos([k_x + \pi/a]a)$ and similarly for the y direction. From this result we can derive two points:
1) The bands are symmetric about $\epsilon = 0$; if $t < 0$ the bands are minimum at $\mathbf{k} = 0$ and maximum the zone corner $\mathbf{k} = (\pi/a, \pi/a)$. If the band is $1/2$ full, then the Fermi energy must be $E_F = 0$ since $1/2$ the eigenvalues have energy $\epsilon < 0$.
2) The solution for $\varepsilon(\mathbf{k}) = 0$ is the rotated square shown in Fig. 14.3. The equation for the square is $k_y = \pi/a \pm |k_x|$, and using the above relation it follows that $\varepsilon(\mathbf{k})) = 2t(\cos(k_x a) + \cos(k_y a)) = 2t(\cos(k_x a) + \cos([\pi/a \pm |k_x|]a)) = 2t(\cos(k_x a) - \cos(k_x a)) = 0$.
A full derivation of the density of states is discussed in Exercise 14.6 and in the book

"Solid State Physics: Problems and Solutions", by Mihaly and Martin, Wiley (1996). One can show that the density of states diverges at the Fermi energy simply by noting that the derivative $d\epsilon/dk_p = 0$ everywhere on the Fermi surface where k_p denotes the direction of $\mathbf{k}$ perpendicular the Fermi surface. Using the general relation Eq. (4.46) (see Ashcroft and Mermin, p. 143-4) which can be written,
$\rho(E) = \frac{\Omega_{\text{cell}}}{(2\pi)^d} \int_{\text{BZ}} \mathrm{d}\mathbf{k}\, \delta(\varepsilon_{i,\mathbf{k}} - E) \propto \int_S (E) dS \frac{1}{|d\epsilon/d\mathbf{k}|}$,
with $S(E)$ the surface with energy E it follows that the DOS diverges at $E = 0$.

Exercise 14.8 Derive the expression for the tight-binding s band $\varepsilon(\mathbf{k})$ in a simple cubic crystal. Assume the states are orthonormal and have hamiltonian matrix elements t_1, t_2, and t_3 for the first three neighbors. The bands for $t_2 = t_3 = 0$ are an approximation for the s-like conduction bands in CsCl which has simple cubic structure. Compare with a calculated band structure in the literature.

Solution:
$\varepsilon(\mathbf{k})) = E_0 + 2t_1(c_x + c_y + c_z) + 4t_2(c_x c_y + c_x c_z + c_y c_z) + 8t_3(c_x c_y c_z)$,
where E_0 is the on-site matrix element and $c_x = \cos(k_x a)$, $c_y = \cos(k_y a)$ and $c_z = \cos(k_z a)$
(from the paper by Slater and Koster [613], Table III)

Exercise 14.9 Derive the expression for an s band $\varepsilon(\mathbf{k})$ in a fcc crystal with nearest neighbor hamiltonian matrix element t assuming the states are orthonormal. This should be a qualitative approximation for the lowest conduction band in a fcc metal like Al or an ionic insulator like NaCl which has the fcc structure. Compare with the nearly-free-electron bands in Fig. 12.1, Fig. 16.6, or calculated band structures in the literature. (Note that there is a relation to the expressions derived in **Exercise 14.8** for second neighbors in a simple cubic lattice. Explain the relation in detail.)

Solution:
$\varepsilon(\mathbf{k})) = E_0 + 4t_2(c_x c_y + c_x c_z + c_y c_z)$,
where a is the fcc cube edge, E_0 is the on-site matrix element and $c_x = \cos(\frac{1}{2}k_x a)$, $c_y =$

$\cos(\frac{1}{2}k_y a)$ and $c_z = \cos(\frac{1}{2}k_z a)$.
The relation to Exercise 14.8 is that the second neighbors in a simple cubic lattice are in the fcc positions and the factor of $\frac{1}{2}$ is due to the choice of a to be the conventional cube edge for the fcc lattice which is twice the value of a in the corresponding simple cubic lattice.

Exercise 14.10 Derive the expression for an s band in a hcp crystal with nearest neighbor hamiltonian matrix element t assuming the states are orthonormal. Assume the c/a ratio is the ideal value. Explicitly evaluate the bands in the direction along the c axis perpendicular to the hexagonal planes. Show that the lower and upper bands touch at the zone boundary,i.e., there is no gap at the zone boundary. Explain why this happens even though there are two atoms per primitive cell.

Solution:
The structure is triangular places on atoms stacked in ABAB... sequence with two atoms per cell. The two atoms are equivalent since they are in the A and B planes the are only shifted as shown in the figure in the text. The hamiltonian is 2x2 with a simple form: in plane variation on the diagonal a sum of coupling to the 6 neighbors and coupling in the z direction to the 3 atoms above and s below that are equivalent. There are no angular factors for the s orbitals so the hamiltonianhas the form:

$$H(k) = \begin{bmatrix} H_{11} & 6t\ cos(k_z c/2) \\ 6t\ cos(k_z c/2) & H_{22} \end{bmatrix}, \tag{S.150}$$

where $H_{11} = H_{22} = t(2cos(k_x a) + 2cos(k_x a/2 + k_y 3^{1/2} a/2) + 2cos(k_x a/2 - k_y 3^{1/2} a/2))$.

There is no gap at any point on the zone boundary in the z direction because the A and B layers are equivalent and the AB and BA couplings are the same. For each value of k_x, k_y it is like a 1D chain viewed as 2 sites per cell and matrix elements t_1 and t_2, but with with equal coupling $t_1 = t_2$, which is equivalent to one site per cell. See Chapter 26 m (in the second edition) for the 2-site chain and the explicit derivation in Exercise 26.2.

Exercise 14.11 Derive expressions for p bands respectively in simple cubic and fcc crystals with nearest neighbor hamiltonian matrix element $t_{pp\sigma}$ and $t_{pp\pi}$. Compare with calculated bands in the literature for the Cl p state in CsCl and NaCl, respectively, to find reasonable values of $t_{pp\pi}$ and $t_{pp\sigma}$.

Solution:
See Ashcroft 10.2c for fcc

Exercise 14.12 There is a close relation of p bands to the equations for phonons as expressed in Exercises 20.3–20.5. As an example, derive the explicit relation of tight-binding equations for p bands in Exercise 14.11 and the phonon dispersion curves in Exercise 20.6 for a nearest neighbor central potential model.

Solution:
See Exercise 20.2 - 20.6 for more complete descriptions and solutions.
The problem for p states and phonons map onto one another because the 3 orthogonal degrees for freedom for p states on an atom is equivalent to the 3 degrees of freedom

for motion of the atom. However, there are crucial differences in the interpretation. The eigenvalues for the linear Schrodinger Eq. are the energies whereas they are $M\omega^2$ for the classical harmonic oscillator. The zero of energy is merely a constant shift for the Schrodinger Eq. (the onsite energies which are diagonal matrix elements), whereas the zero for phonos is dete4rmined by translation invariance that there is no energy cost to move all atoms the same. This requires a relation between the on-site and intersite matrix elements, which is called the "acoustic sum rule." (see Pick, Cohen and Martin [180]) and it is worked out in Exercise 20.4.

See Exercise 14.11 and the hamiltonian matrix for fcc

Exercise 14.13 See Exercise 26.2 for bands in the 2-site model in Fig. 26.2.

Solution:

See that Ex.

Exercise 14.14 Consider a model like that in **Exercise 26.2** except that the state on the B atom has p symmetry. For on-site energies $\varepsilon_A > \varepsilon_B$, this is a one-dimensional model for an ionic crystal like NaCl. From the symmetry of the crystal, show that two bands are formed from the s and p$_x$ states decoupled from bands formed by the orthogonal p$_y$ and p$_z$ states. Assume the states are orthonormal and there are only nearest neighbor hamiltonian matrix elements of magnitude t. In terms of $\Delta = \varepsilon_A - \varepsilon_B$ and t, give analytic expressions for s–p$_x$ bands $\varepsilon_i(k)$. Describe any simplifications in the expressions at $k = 0$ and the BZ boundary. Plot the bands in the Brillouin zone for the case $\Delta = 4t$ and show there is qualitative agreement with published bands of NaCl in the (100) direction. What values of Δ and t provide a reasonable description of NaCl bands? Suggest changes that would better describe the bands.

Solution:

The py and pz states are decoupled because there are odd in the directions perpendicular the the line whereas s and Px are even. For the s and px states, The only difference from a problem with two a states is that the s-p matrix element changes sign for the left and right neighbors so the hamiltonian matrix is

$$\left|\hat{H}(k) - \varepsilon(k)\right| = \begin{vmatrix} E_A - \varepsilon(k) & t(k) \\ t^*(k) & E_B - \varepsilon(k) \end{vmatrix} = 0, \tag{S.151}$$

with $t(k) = 2t_{sp}sin(k)$.

Thus the states are decoupled at k=0 and k = π and they repel at other k.

An example of the bands of NaCl predicted by many-body methods is in Bechstedt, et al., PRB 72, 245114 (2005). The gap is so big that there is not much dispersion. The present model is not so good because there are significant s-s and p-p matrix elements, especially for the more spread out s atates which causes larger dispersion.

Exercise 14.15 Show that the model of Cu and O states shown on the left-hand side of Fig. 14.8 leads to effective model nearest neighbor interactions between Cu states as shown on the right-hand side of the figure. Hint: Construct a 3×3 matrix and diagonalize to find the highest band that corresponds to the band that crosses the Fermi energy in Fig. 17.8.

Solution:
The 3×3 hamiltonian is defined by the Cu dxy and two O p states, px on the x axis and py on the y axis. In the nearest neighbor model there is only d-p matrix element $t_{pd} \equiv t$ and the hamiltonian can be written

$$H(k) = \begin{bmatrix} \varepsilon_d & tcos(k_x a/2) & tcos(k_y a/2) \\ tcos(k_x a/2) & \varepsilon_p & 0 \\ tcos(k_x a/2) & 0 & \varepsilon_p \end{bmatrix}, \tag{S.152}$$

This can be block diagonalized to a 2×2 and a 1×1 by defining the even and odd combination of the O states. The dxy couples only to the combination of O states that has dxy symmetry, i.e., have opposite signs for the lobes pointing to the a Cu atom; the matrix elements are then equal since the dxy state has opposite sign in the x and y directions.

The result is a flat band with energy ε_p, and the two mixed Cu-O bands given by the 2 x 2 problem in Eq. (S.151) with $t(\mathbf{k}) = \sqrt{2}t(cos(k_x) + cos(k_y)$. This leads to an antibonding band above ε_d, and the other a bonding band below ε_p. If there is one hole (5 electrons in the 6 orbitals counting spin) the Fermi energy is in the middle of the upper antibonding band.

This is the nature of the bands that actually occur in a full calculation.

Exercise 14.16 Show that the expression for bands with non-orthogonal basis orbitals, Eq. (14.15), is correct. The bands are no longer symmetric about $\varepsilon = 0$. Why is this? What is the physical interpretation? See the following problem for more general properties.

Solution:
The general form of the equations for the equations with non-orthogonal orbitals is $|H(\mathbf{k}) - \varepsilon S(\mathbf{k})| = 0$. For a single function this is a scalar equation and and $\varepsilon = H(\mathbf{k})/S(\mathbf{k})$ and for one dimension and nearest neighbor it has the form given in Eq. (14.15). This can be understood in terms of the overlap term having opposite effects at the zone center and zone boundary. It is equivalent to more distant neighbor interactions in a orthonormal basis, which makes the bands not symmetric about the band center.

Exercise 14.17 This problem is to analyze the general consequences of the overlap term in a non-orthogonal basis. Show that the effect of the overlap can be transformed to an orthogonal form, with the result that the hamiltonian matrix elements have infinite range, decaying exponentially. This is the correct result as shown by the decay of orthonormal Wannier functions in Chapter 23. Thus show that rigorously it can never be fully consistent to assume that the hamiltonian matrix elements are finite range and yet the orbitals are orthogonal. The same conclusion is found in Exercise 23.2.

Solution:
Following the previous exercise, the general form of the equations for the equations with non-orthogonal orbitals is $|H(\mathbf{k}) - \varepsilon S(\mathbf{k})| = 0$. In general this leads to a matrix equation in terms of HS^{-1}, and it can be illustrated by the scalar form in Eq. (14.15). If we expand the denominator in powers of s we see that $\varepsilon(\mathbf{k})$ has Fourier components that extend without limit. In one dimension it is easy to see that each power of s corresponds to a Fourier component increased by a lattice vector. Thus the matrix elements decrease by a

factor of s from one neighbor to the next, this is an exponential decay. This is an example of generating Wannier functions that defines a orthonormal basis.

Exercise 14.18 Give a simple argument why "cosine" appeared many times in this chapter, whereas "sine" did not appear at all.

Solution:

The reason is that in all Bravais lattices if there is an neighbor at $\mathbf{r}$ there is also one at $-\mathbf{r}$. The factors of $e^{1\mathbf{k}\cdot\mathbf{r}}$ sum to a cosine.

However, this is really only because the explicit examples were all simple case where the basis states were even parity. For matrix elements between states of opposite parity sines occur. See for example the problems with s and p states like 14.14 and 26.2. In addition, however, that if time reversal symmetry is broken as in a Chern insulator or if we consider spin-orbit interactions, the reasoning is different. See the 2D square lattice with p states in Chapter 27.

Exercise 14.19 This problem relates to the structure and bands of a plane of graphene. Show that the Brillouin zone has the shape and orientation shown in the two cases in Fig. 14.7; also show that one of the K points is given by $k_x = 4\pi/3a, k_y = 0$ and find the coordinates of all six K points. Show that the bands indeed touch at all six K points.

Solution for Exercise 14.19 and Exercise 14.20

See also Exercise 4.7 which shows that for a graphene sheet oriented as in Fig. 14.7, part a, the primitive lattice vectors are $\mathbf{a}_1 = (1,0)a$ and $\mathbf{a}_2 = (\frac{1}{2}, \frac{\sqrt{3}}{2})a$, where the nearest neighbor distance is $a/\sqrt{3}$, and the primitive reciprocal lattice vectors can be chose to be $\mathbf{b}_1 = (0, \frac{2}{\sqrt{3}})2\pi/a$ and $\mathbf{b}_2 = (-1, \frac{1}{\sqrt{3}})2\pi/a$. Thus the BZ is hexagonal and the M point is $\frac{1}{2}$ any of the 6 equivalent shortest vectors; the M point indicated is $(1, \frac{1}{\sqrt{3}})\pi/a$. The K point at the corner indicated on the figure is $(\frac{1}{3}, \frac{1}{\sqrt{3}})2\pi/a$; an equivalent corner point is $(\frac{2}{3}, 0)2\pi/a$. (Note there is an error in the first printing of the first edition. The K point given in the text and Eqs. (14.15) and (14.16) should have x and y interchanged.) The correct equations are:

CHECK: Is error only in first printing? Does this answer both problems?

$$H_{12}(\mathbf{k}) = t\left[\mathrm{e}^{\mathrm{i}k_y a/\sqrt{3}} + 2\mathrm{e}^{-\mathrm{i}k_y a/2\sqrt{3}}\cos\Big(k_x\frac{a}{2}\Big)\right], \tag{S.153}$$

where a is the lattice constant. This is readily solved to yield the bands (see Saito, Phys. Rev. B 46, 1804-1811 (1992)[233] where a different convention is used for the x and y axes)

$$\varepsilon(\mathbf{k}) = \pm|H_{12}(\mathbf{k})| = \pm t\left[1 + 4\cos\Big(k_y\tfrac{\sqrt{3}a}{2}\Big)\cos\big(k_x\tfrac{a}{2}\big) + 4\cos^2\big(k_x\tfrac{a}{2}\big)\right]^{1/2} \tag{S.154}$$

If we evaluate the terms in the square bracket in Eq. (14.19) at the K point $(\frac{2}{3}, 0)2\pi/a$, we find $\left[1 + 4(-\frac{1}{2}) + 4(-\frac{1}{2})^2\right] = 0$.

Thus the bands touch at the K points where the coupling vanishes and the solution is $\varepsilon(K) = 0$ for both the upper and the lower bands.

Exercise 14.20 Derive Eq. (14.17) for the bands in graphene.

Solution for Exercise 14.20:
See solution for previous problem.

Exercise 14.21 Show that rolling of a graphene sheet to form $(n,0)$ and (n,n) tubes leads, respectively, to the structures and Brillouin zones for the "zigzag" and "armchair" tubes that are shown in Fig. 14.7. For the armchair tubes show that the allowed states always include the states at the K point in graphene, so that simple mapping of graphene bands always leads to the prediction of metallic bands. For the zigzag tubes, give the conditions for which the allowed states include the graphene K point.

Solution:
See references given in text which give a full analysis.

Exercise 14.22 Show that the expressions for the force and stress theorems in tight-binding form, Eqs. (14.28) and Equation (14.29), follow immediately from the condition that energy is minimum w.r.t. the coefficients in the wavefunctions.

Solution:
This is really just the same as the proofs in all cases of the force theorem: Linear variations come only from the explicit dependence in the hamiltonian since the energy is minimum wr.t. the eigenfunctions. Even though the parafunction changes the energy changes only to second order.

Exercise 14.23 Consider a heteropolar diatomic molecule with a total of two electrons. The hamiltonian is approximated by a orthogonal tight-binding model with one state per atom and hamiltonian matrix elements $H_{11} = E_1$, $H_{22} = E_2$, and $H_{12} = H_{21} = t(x)$, where x is the distance between atoms. Find the analytic expression for the ground state energy E.
(a) Calculate the force on atoms 1 and 2 directly from the derivative of the analytic expression for the energy, and also from the force theorem.
(b) Do the same for a generalized force $\mathrm{d}E/\mathrm{d}\Delta$, where $\Delta = E_1 - E_2$.

Solution:
This is a problem to work out a simple example. The energy is the lowest state of a 2 x 2 problem and the force is due to the variation of $t(x)$, which depends on the distance. There must be no net force the force on each atom is equal magnitude and opposite direction and is non-zero if the molecule is not at the minimum energy length. The magnitude is $|dt/dx|$. In general there must be some other term in the energy to balance this term as described in the text. A generalized force is the derivative with respect to any quantity. The example in part (b) might be a model for a molecule in an environment that changes the relative energies of two atoms, e.g., it might describe an internal strain defined as the change in bond length with applied pressure.

Exercise 14.24 Find expressions for the valence and conduction band eigenvalues in a diamond-structure crystal at $\mathbf{k} = 0$ in terms of the matrix elements of the hamiltonian, the on-site energies E_{s} and E_{p}, and the matrix elements $H_{\mathrm{ss}\sigma}$, $H_{\mathrm{sp}\sigma}$, $H_{\mathrm{pp}\sigma}$, and $H_{\mathrm{pp}\pi}$. Do this in two steps. First, show that the eigenstates at $\mathbf{k} = 0$ are pure s or pure p. Next, use this fact to find expressions for the four eigenvalues for bonding and anti-bonding s and p states. Assuming four electrons per atom, identify the valence and conduction states and the gap between filled and empty states at $\mathbf{k} = 0$. Find numerical values for Si using Harrison's "universal" table (Harrison's books in 1989 and 1999 [354, 615])and compare with bands that can be found in many references. The valence bands should be similar but the conduction bands are quite different.

Solution:

The s and p states are decoupled at $\mathbf{k} = 0$ since they have opposite parity. The gap for the s states is easy to figure out since there are two atoms per cell, each with an s state. If the are labelled A and B, and the 4 neighbors of an A atom are B atoms and vice versa. Since the s states have the same energy E_s on the two atoms, the $\mathbf{k} = 0$ energies are $E_s \pm 4t_{ss}$, where t_{ss} is the ss matrix element. The 3 p states per atom lead to triply degenerate banding and antibonding states like the s states, but one must take into account the angular factors. The unit vector toward a neighbor is $(1, 1, 1)/\sqrt{3}$ (and the three other vectors in the tetrahedron) so that a typical matrix element is (see Table 14.1) $t_{pp} = t_{pp\sigma}/3 + 2t_{pp\pi}/3$. It is not hard to see from the structure in Fig. 4.7 that at $\mathbf{k} = 0$ the p_x, p_y and p_z are are independent and form a triplet with energies $E_p \pm 4t_{pp}$.

CHECK this is really correct!

Solutions for Chapter 15

Same as in first edition.

Exercise 15.1 There are excellent open source codes (SEE Appendix R) freely available on-line for DFT calculations using gaussian, such as CRYSTAL and numerical orbitals, such as FHI-aims and SIESTA. These codes can be used for localized systems and crystals. (Plane waves can be used for localized systems also, but that is not appropriate for examples since many plane waves are needed. Real-space grids, wavelets, etc. also require large basis sets.) he codes often have tutorials similar to the exercises and also many examples for materials.

Exercise 15.2 Show that the product of two gaussians is a gaussian as in Eq. (15.2), and derive the expressions for the coefficients in the product gaussian Eqs. (15.3)–15.5.

Solution

The proof is simply a consequence of the fact that the sum of two quadratic functions is a quadratic function. the equations are simplified if we choose the origin at one center $R_A = 0$ and and $\alpha = 1$. Then all cases can be reduced to the form $x^2 + b(x - B)^2 = (1 + b)x^2 - 2bBx + bB^2$ where B is R_B in units where $\alpha = 1$. This can be written $(1 + b)(x^2 - 2Cx + C^2) + D$. With some algebra this leads to the form given and K is determined by normalization. This is worked out in many standard texts.

Exercise 15.3 Find the analytic formula for the kinetic energy matrix element between gaussian basis functions with spreads α and β and separated by displacement $\mathbf{R}$.

(a) First consider only simple gaussians with s symmetry and not multiplied by powers of the radius.

(b) Then show that the formulas can be generalized to any l, m and power r^p by taking appropriate derivatives of expressions derived in (a). You do not need to work out all the detailed formulas, which can be found in texts.

Solution

The kinetic energy is the matrix element of $-\boldsymbol{\nabla}^2/2$ which is straughforward to work out and the Gaussian integrals are standard and not worked out here.

Exercise 15.4 Derive Eq. (15.17) using a chain rule and show that the right-hand side vanishes if the basis is complete. Hint: Use the completeness relation.

Solution

The equation follows simply from taking the derivatives. The fact that it vanishes for a complete basis is a matter of understanding that in a complete basis the density at a point is independent of the choice of and complete basis, i.e., it is the same for any positions of the centers of the orbitals and the derivative is manifestly zero.

Exercise 15.5 Construct a simple computer program for a gaussian s band in one dimension. This entails calculating the overlap and hamiltonian matrix elements that are analytic if we assume the potential is also a sum of gaussians centered on each atom. Vary the band shapes from nearly-nearest-neighbor tight-binding-like given in (14.15) to nearly-free-electron-like.

Solution

Computational problem and no solution is given here.

Exercise 15.6 Use the results for the eigenvectors from Exercise 15.5 to construct Wannier functions. Construct the atom-centered “maximally projected” form defined in Section 23.2 with the phase (sign) chosen to maximize the function on the central atom.

(a) Show that the function has positive and negative values (a plot is best) and it is longer range than the gaussian basis function.

(b) With a careful fit to the long-range behavior (the log of the absolute value) of the Wannier function, show it decays exponentially as a function of distance as claimed in Section 23.2.

Solution

Computational problem and no solution is given here.

Solutions for Chapter 16

Same as in first edition.

Sorry, but solutions are not worked out for this chapter. Many derivation for the equations in the actual methods used can be found in the references given in the text. Some good general references are given at the end of the chapter.

Exercise 16.1 The basic ideas of the APW method can be illustrated by a one-dimensional Schrödinger equation for which the solution is given in Exercise 4.22. In addition, close relations to pseudopotentials, plane wave, KKR, and MTO methods are brought out by comparison with Exercises 11.14, 12.6, 16.7, and 16.13. Consider an array of potentials $V(x)$ spaced by lattice constant a; $V(x)$ is arbitrary except that it is assumed to be like a muffin-tin composed of non-overlapping potentials with $V(x) = 0$ in the interstitial regions. For actual calculations it is useful to treat the case where $V(x)$ is a periodic array of square wells.
(a) Consider the deep well defined in Exercise 11.14 with width $s = 2a_0$ and depth $-V_0 = -12Ha$. Solve for the two lowest states (analogous to "core" states) using the approximation that they are bound states of an infinite well.
(b) Construct APW functions that are e^{ikx} outside the well; inside, the APW is a sum of solutions at energy ε (as yet unknown) that matches e^{ikx} at the boundary. Show that the expansion inside the cell analogous to (16.2), and the plane wave expansion, analogous to (16.4), are sums only over two terms, sine and cosine, and give the explicit form for the APW.
(c) Derive the explicit APW hamiltonian for this case. Include the terms from the discontinuity of the derivative. Show that the equation has the simple interpretation of plane waves in the interstitial with boundary conditions due to the well.
(d) Construct a computer code to solve for the eigenvalues and compare to the results of the general method described in **Exercise 4.22**.
(e) Use the computer code also to treat the shallow square well defined in Exercise 12.6 and compare with the results found there using the plane wave method.
(f) Compare and contrast the APW, plane wave, and the general approach in Exercise 4.22.

Exercise 16.2 Derive the form for the contribution to the hamiltonian matrix elements from the kink in the wavefunctions given in Eq. (16.8) using Green's identity to transform to a surface integral.

Exercise 16.3 Derive the identity given in (16.21)–(16.23) for the expansion of a spherical wave defined about one center in terms of spherical waves about another center. One procedure is through the use of Eq. (J.1), which is also given in (16.4).

Exercise 16.4 Evaluate values for the logarithmic derivatives of the radial wavefunctions for free electrons and compare with the curves shown in Fig. 16.3 for Cu. The expressions follow from (16.4) (also given in Eq. (J.1)) for zero potential and the functions should be evaluated at the radius $S = 2.415a_0$ appropriate for metallic Cu.

Exercise 16.5 Show that the nearly parabolic s band for Cu in Fig. 16.4 are well approximated by free-electron values given that Cu has fcc crystal structure with cube edge

$a = 6.831a_0$. Show also that the states at the zone boundary labeled would be expected to act like p states (l=1, odd) about each atom. (Quantitative comparisons are given in the book by Kubler and Eyert [157], p. 25).

Exercise 16.6 As the simplest example of the "s–d" hybridization model, derive the bands for a 2×2 hamiltonian for flat bands crossing a wide band in one dimension: $H_{11}(k) = E_1 + W \cos(2\pi k/a)$, $H_{22}(k) = E_2$, and $H_{12}(k) = H_{21}(k) = \Delta$. Find the minimum gap, and the minimum direct gap in the bands. Show that the bands have a form resembling the bands in a transition metal.

Exercise 16.7 The KKR method can be illustrated by a one-dimensional Schrödinger equation, for which the solution is given in Exercise 4.22. See the paper by Butler, Phys. Rev. B 31, 3260 (1985) [694] for an extended analysis. Close relations to pseudopotentials, plane wave, APW, and MTO methods are brought out by comparison with Exercises 11.6, 12.6, 16.1, and 16.13. As in **Exercise 16.1**, the KKR approach can be applied to any periodic potential $V(x)$. The KKR solution is then given by (16.28) with the structure constants defined in (16.26). (Here we assume $V(x)$ is symmetric in each cell for simplicity. If it is not symmetric there are also cross terms η^{+-}.)
(a) The phase shifts are found from the potential in a single cell. In **Exercise 11.6** it is shown that the scattering is described by two phase shifts η^+ and η^-.
(b) In one dimension the structure constants define a 2×2 matrix $B_{L,L'}(\varepsilon, \mathbf{k})$, with $L = +, -$ and $L' = +, -$. Each term is a sum of exponentials that oscillates and does not converge at large distance. Find physically meaning expressions for $B_{L,L'}(\varepsilon, \mathbf{k})$ by adding a damped exponential convergence factor.
(c) Using the relations from Exercise 11.6, show that the KKR equations lead to the same results as the general solution, (4.49), with $\delta = \eta^+ + \eta^-$ and $|t| = \cos(\eta^+ - \eta^-)$.

Exercise 16.8 This exercise is to show the relation of the Green's function expression, (16.31), and the Schrödinger equation. This can be done in four steps that reveal subtle features.
(a) Show that application of the free-electron hamiltonian $\hat{H}_0$ to both sides of the equation leads to a Schrödinger-like equation but without the eigenvalue. Hint: Use the fact that $\hat{H}_0\, G_0 = \delta(|\mathbf{r} - \mathbf{r}'|)$.
(b) Show that this is consistent with the Schrödinger equation using the fact that a constant shift in V has no effect on the wavefunction.
(c) Give an auxiliary equation that allows one to find the eigenvalue.
(d) Finally, give the expression for the full Green's function G analogous to (16.12) from which one can derive the full spectrum of eigenvalues.

Exercise 16.9 Show that $\chi_L^{\mathrm{MTO}}(\varepsilon, 0, \mathbf{r})$, defined in (16.37) is continuous and has continuous derivative (i.e., D is the same inside and outside) at the boundary $r = S$.

Exercise 16.10 Find the relation of the mass parameter μ to the energy derivative $dD(E)/dE$ evaluated at the band center, assuming P_l has the simple form given in (16.48).

Exercise 16.11 The diamond structure can be viewed as a dense-packed structure of touching spheres with some spheres not filled with atoms. Show this explicitly, starting with the crystal structure shown in Fig. 4.7 and insert empty spheres in the holes in the structure.

Exercise 16.12 Show that (16.37) indeed leads to a function that is continuous and has a continuous derivative at its boundary.

Exercise 16.13 The MTO method can be illustrated by a one-dimensional Schrödinger equation. The purpose of this exercise is to show that the solution in Exercises 4.22 and 16.7 can be viewed as "tail cancellation." (An extended analysis can be found in a paper by Mishra and Satpathy, Am. J. Phys. 69, 512 (2001) [708].) This re-interpretation of the equations can be cast in terms of the solutions of the single cell problem given in Exercise 4.22, ψ_l and ψ_r, which correspond to waves incident from the left and from the right; only the part outside the cell is needed. Consider the superposition of waves inside a central cell at $T = 0$ formed by the sum of waves $\psi_l(x)$ and $\psi_r(x)$ from all *other* cells at positions $T \neq 0$ with a phase factor $\mathrm{e}^{\mathrm{i}kT}$. Show that the requirement that the sum of waves from all other cells vanishes at any point x in the central cell (i.e., tail cancellation) and leads to the same equations as in Exercises 4.22 and 16.7.

Solutions for Chapter 17

Same as in first edition.

Sorry, but solutions are not worked out for this chapter. Many derivation for the equations in the actual methods used can be found in the references given in the text. Some good general references are given at the end of the chapter.

Exercise 17.1 Derive Eq. (17.4) from the definition of $\dot{\psi}$. In addition, show the more general relation

$$(\hat{H} - \varepsilon)\psi^{(n)}(\varepsilon, r) = n\psi^{(n+1)}(\varepsilon, r), \tag{S.155}$$

where n is the order of the derivative. Hint: Use the normalization condition.

Exercise 17.2 Carry out the manipulations to show that the hamiltonian and overlap matrix elements can be cast in the linearized energy-independent form of Eqs. (17.14) to (17.17). Thus the matrix elements are expressed in terms of Π and Ω, which are functions of the wavefunctions ψ and $\dot{\psi}$ calculated in the sphere at the chosen energy E_ν.

Exercise 17.3 Derive the result that $l_{\rm max} \approx 8$ in LAPW calculations. Consider a simple cubic crystal with one atom/cell with the volume of the atomic sphere $\approx 1/2$ the volume of the unit cell. The order of magnitude of ≈ 100 planes waves is reasonable since it corresponds to a resolution of $\approx 100^{1/3}$ points in each direction. If the plane waves are in a sphere of radius $G_{\rm max}$, find $G_{\rm max}$ in terms of the lattice constant a. This is sufficient to find an estimate of $l_{\rm max}$ using the arguments in the text. If the number of plane waves were increased to 1,000, what would be the corresponding $l_{\rm max}$?

Exercise 17.4 The condition (17.23) requires that the LMTO be independent of the energy to first order and is the key step that defines an LMTO orbital; this removes the rather arbitrary form of the MTO and leads to the expression in terms of $\dot{\psi}$. Show that this condition leads to the expression, (17.24), for the J function proportional to $\dot{\psi}$ inside the sphere.

Exercise 17.5 If the augmented wavefunction (LAPW or LMTO) is expanded in Y_{lm} up to $l_{\rm max}$, what is the corresponding $l_{\rm max}^{\rm density}$ needed in an exact expansion for the charge density for the given wavefunction? Give reasons why it may not be essential to have $l_{\rm max}^{\rm density}$ this large in an actual calculation.

Exercise 17.6 If the density is expanded in Y_{lm} up to $l_{\rm max}^{\rm density}$, what is $l_{\rm max}$ for the Hartree potential? For $V_{\rm xc}$?

Exercise 17.7 What is the maximum angular momentum $l_{\rm max}^{\rm pot}$ of the potential Equation (17.35) needed for exact evaluation of matrix elements $\langle L|V|L'\rangle$ if the wavefunction is expended up to $l_{\rm max}$? Just as in Exercise 17.5, give reasons why smaller values of $l_{\rm max}^{\rm pot}$ may be acceptable.

Exercise 17.8 Consider the compound $\rm YBa_2Cu_3O_7$. Determine the number of electrons that would be required to fill the oxygen states to make a closed-shell ionic compound. Show that for $\rm YBa_2Cu_3O_7$ there is one too few electrons per Cu atom. Thus, this material corresponds to one missing electron (i.e., one hole per Cu).

Solutions for Chapter 18

This was in Chapter 23 in first edition. Exs. are the same.

NOTE: The references for recursion in the text are to books. One reference online that is useful is The recursive solution of the Schrödinger equation, Roger Haydock, Computer Physics Communications 20, 11-16 (1980).

Exercise 18.1 Derive the result stated in the text that the normalization constant in (18.11) is given by $C_{n+1} = 1/\beta_n$, $n \geq 1$. Show this by directly calculating the normalization of ψ_{n+1} assuming ψ_n is normalized.

Solution:

This argument follows that given in the paper by Haydock, but it is equivalent to other derivations. The result follows using the definitions of α and β given after (18.11) that at each step the operation

$$\hat{H}\psi_n - \alpha_n\psi_n - \beta_{n-1}\psi_{n-1} = \beta_{n+1}\psi_{n+1}$$

defines the next component where the terms $-\alpha_n\psi_n - \beta_{n-1}\psi_{n-1}$ subtract the component of $\hat{H}\psi_n$ along the previous eigenvectors, so that $\beta_{n+1}\psi_{n+1}$ is the orthogonal component. By definition $\beta_{n+1} = H_{n,n+1}$ where ψ_{n+1} is normalized. Thus this is really a definition of how the next vector is constructed iteratively the operation $\hat{H}\psi_n$ projected into the orthogonal space and interpreted as a hamiltonian matrix element with an normalized vector.

Exercise 18.2 Derive the continued fraction representation of (18.12) using the Lanczos algorithm for the coefficients. It follows that the spectrum of eigenvalues is given by the poles of the continued fraction (i.e., the zeros of the denominator) in (18.12). (Thus the spectrum of eigenvalues is given either by the continued fraction form or by the zeros of the polynomial of the previous problem.)

Solution:

The Greens function is given by the inverse of the matrix $\varepsilon - H$ and the tri-diagonal matrix makes the inversion have this special form. The key point is that we want the first component of G called $G_{0,0}$ It can be derived by considering the simplest 2×2 matrix. For any symmetric matrix A let $B = A^{-1}$ so that $AB = 1$. Thus $A_{1,1}B_{1,1} + A_{1,2}B_{2,1} = 1$, and $A_{2,1}B_{1,1} + A_{2,2}B_{2,1} = 0$, so that $B_{2,1} = -A_{2,1}B_{1,1}/A_{2,2}$ and inserting in the first equation, $A_{1,1}B_{1,1} - A_{1,2}A_{2,1}B_{1,1}/A_{2,2} = 1$.
Finally we have
$B_{1,1} = [A_{1,1} - A_{1,2}A_{2,1}/A_{2,2}]^{-1}$.
Identifing A as $\varepsilon - H$ and $B_{1,1}$ as the first component of G defined to be $G_{0,0}$ leads to the desired result. This can be continued to the next step and a series of continued fractions.

Exercise 18.3 Derive the form of the terminator given in (18.13) and (18.14). Show that imaginary part is non-zero in the band range indicated, so that no poles and only continuous DOS can result in this range. In fact, there is another solution with a plus sign in the square root in (18.14); show that this is not allowed since $t(z)$ must vanish for $|z| \to \infty$.

Solution:

The form in (18.13) follows from the same logic as in the previous problem. If the series has the same form at every step, then it has the self-consistent solution of $t(z)$ in terms of

$t(z)$. Then (18.14) follows from solving for $t(z)$. This is the famous "semicircular density of states" where the square root is imaginary where the argument is negative, only in the rage where $(z-\alpha_\infty)^2 - 4\beta_\infty^2 < 0$, i.e., where $|z-\alpha_\infty| < 2|\beta_\infty|$.

Exercise 18.4 Show that the square root form for terminator (18.14) satisfies Kramers–Kronig relations, Eq. (D.18), as it must if $G(z)$ is a physically meaningful Green's function.

Solution:

This follows because it is an analytic function that vanishes at large z, which is the requirement for a physically meaningful G.

Exercise 18.5 Show that the Green's function $G(z) = 1/(\hat{H} - z)$ becomes more localized for large z for the case where $\hat{H}$ is a short-range operator in real space. This is the essence of localization in both the recursion and Fermi function expansion methods. Hint: First consider the $z \to \infty$ limit and then terms in powers of $\hat{H}/z$.

Solution:

The arguments about the range follow because of the assumption that H is localized, i.e., is connects only nearby regions. Thus each power of an operator involving H extends the range further. For large z, G can be expended in powers of H/z and it converges faster for larger z.

Exercise 18.6 Derive Eq. (18.29) by showing that the variation around $X = S^-$ is quadratic and always positive for matrices B that are negative definite.

Solution:

It is easy to see that the right hand side is zero for $X = S^{-1}$. For $X = S^{-1}(1+\Delta)$, the term in parentheses is negative since the terms linear in Δ vanish and the quadratic terms are negative since S is positive definite. The result follows if B is negative definite.

Exercise 18.7 This exercise is to derive the form of the "purification" functional, Eq. (18.24), that leads to idempotency of the density matrix.
(a) The first step is to demonstrate that the function $y = 3x^2 - 2x^3$ has the form shown in the left panel of Fig. 18.6 and that the result y is always closer to 0 or 1 than the input x.
(b) Next, generalize this to a matrix equation for any symmetric matrix leading to eigenvalues closer to 0 or 1.
(c) Finally, show that the functional (18.23) minimized using the gradients (18.24) leads to the desired result.

Error in text. Eq. numbers in part (c) should be (18.23) and (18.24).

Solution:

Part (a) is a matter of plotting the graph. Comparing to the straight line we see that the curve is always closer to 0 for input $x < 1/2$ or 1 for $x > 1/2$.
(b) This can be shown by considering the matrix diagonalized so the eigenvalues are on the diagonal and the problem reduces to separate problem for each eigenvalue.
(c) This is a matter of rewriting the scalar equations in terms of matrices and it is easiest to see in the diagonalized form.

Exercise 18.8 This exercise is designed to provide simple examples of the properties of the unconstrained functional, Eq. (18.26).

(a) Consider a diagonal 2×2 hamiltonian with $H_{11} = \epsilon_1 < 0$, $H_{22} = \epsilon_2 > 0$, and $H_{12} = H_{21} = 0$ in an orthonormal basis, ψ_1 and ψ_2. Show that minimization of the functional leads to the ground state ψ_1 properly normalized.
(b) Now consider the same basis as in part (a) but with a hamiltonian that is not diagonal: $H_{11} = H_{22} = 0$ and $H_{12} = H_{21} = \epsilon_0$. Show that in this case the functional also leads to the properly normalized ground state $\psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$.

Solution:

Part (a) works since it is two scalar equations. We know this must work in part (b) since it can be done in the diagonalized form, but it is interesting to see in the form given in part (b). This is a minimization problem not worked out here. See examples in the references given in the text.

DO MORE IN **Exercise 18.8**?

Exercise 18.9 Show that the functional, Eq. (18.27), has the property that it leads to orthonormal eigenvectors for states below the Fermi energy μ and projects to zero the amplitude of any states with eigenvalue above the Fermi energy.

Solution:

This is similar to the pervious exercises. The form of the functional shown in the figure drives the solution to occupation of states with negative eigenvalues. This is a minimization problem not worked out here. See examples in the references given in the text.

DO MORE IN **Exercise 18.9**?

Solutions for Chapter 19

This was in Ch. 18 in first edition. Exs. are the same.

Exercise 19.1 In the text it was stated that the "SHAKE" algorithm (see Ryckaert, et al., J. Comput. Phys. 33, 327 (1977) [788] and article by Car and Parrinello in in volume [789] maintains constraints in a holonomic manner, i.e., with no energy loss. An alternative might be the Gram–Schmidt procedure in which one updates the wavefunctions with $\hat{H}\psi_i$ and then orthonormalizes starting with the lowest state.

(a) Show that this will cause energy loss. Hint: one way is to consider the two-state problem in Exercise 19.2. Treat the wavefunctions explicitly and show that there is a difference from the equations given below in which the constraint is imposed analytically.

(b) Read the references for SHAKE in the articles mentioned in the problem [788, 789] and summarize how it works.

Solution:

See the two state problem in Exercise 19.2 which is equivalent to a harmonic oscillator. A Gram-Schmitt scheme would update at each step with a linearized form and orthogonalization

NOTE: NOT FINISHED

See note - not finished

Exercise 19.2 Car–Parrinello-type simulation for one electron in a two-state problem is the simplest case and is considered in the tutorial-type paper by Pastore, Smargiassi, and Buda [791]. In this case, the wavefunction can always be written as a linear combination of any two orthonormal states ϕ_1 and ϕ_2,

$$\psi = \cos\left(\frac{\theta}{2}\right)\phi_1 + \sin\left(\frac{\theta}{2}\right)\phi_2.$$

With this definition orthogonality and normalization are explicitly included and we can consider θ to be the variable in the fictitious lagrangian (written for simplicity in the case where ϕ_1 and ϕ_2 are eigenvectors):

$$L = \mu|\frac{\mathrm{d}\theta}{\mathrm{d}t}|^2 + \epsilon_1 \cos^2 + \epsilon_2 \sin^2$$

Solving the Lagrange equations gives

$$\mu\frac{\mathrm{d}^2\theta(t)}{\mathrm{d}t^2} = (\epsilon_2 - \epsilon_1)\sin\left(\theta(t) - \theta_0\right),$$

which is the equation for a pendulum. For small deviations $\theta - \theta_0$, the solution is simple harmonic oscillations of frequency $\omega_e^2 = \Delta E/\mu$. Thus so long as the oscillations are small, the electronic degrees of freedom act like simple oscillators.

Pastore et al. [791] have analyzed the two-state model and large cell calculations to identify the key features, as illustrated in the figures from their paper. If μ is chosen so that the fictitious electronic frequencies are well above all lattice frequencies and motions are small, then there is only slow energy transfer and the Car–Parrinello method works well. This can be done in an insulator. But level crossing, metals, etc., give interesting difficulties.

The exercise is to analyze the algorithm for three cases in which the system is driven by an external perturbation of frequency ω_0:

a. For the case of small amplitudes and μ chosen so that $\omega_e >> \omega_0$, show that the electrons respond almost instantaneously adiabatically following the driving field.

b. For the more difficult case with ω_e of order ω_0, show that the electrons couple strongly with large non-linear oscillations. (Note: this fictitious dynamics is *not* the correct quantum dynamics.)

c. For the case where there is a level crossing and ΔE changes sign, show that the electrons can undergo real transitions. (See note in (b).)

Solution:

See the reference is the problem for an instructive tutorial.

Exercise 19.3 Project for simulation of quantum systems with Car–Parrinello methods. The purpose of this problem set is to write programs and carry out calculations in simple cases for the Car–Parrinello method for simulation of quantum systems by molecular dynamics techniques. Ignore the spin of the electron, which only adds a factor of 2 in paramagnetic cases with even numbers of electrons per cell.

(a) For the case of an "empty lattice" where the potential energy is a constant set equal to zero, write down the Car–Parrinello equations of motion for the electrons. Work in atomic units.

(i) Set up the problem on a one-dimensional lattice, where the wavefunctions are required to be periodic with length *L*. Write a program that iterates the Verlet equation for a single wavefunction expressed in terms of Fourier coefficients up to $M \times (2\pi/L)$.

(ii) Choose $L = 10$ a.u., $\mu = 300$ a.u., and $M = 16$, which are reasonable numbers for solids. Start with a wavefunction having random coefficients, velocities zero, and iterate the equations. Choose a time step and show that the fictitious energy is conserved for your chosen time step. Show that you can carry out the exercise equivalent to the original calculation of Car and Parrinello in Fig. 19.1. Extract energy from the system by rescaling the velocities at each step. Show that the system approaches the correct ground state with energy zero. Make a graph of the energy versus time analogous to Fig. 19.1.

(iii) Now consider several states. Add the orthogonalization constraints, and find the ground state for two, three, and four filled states. Verify that you find the correct lowest states for a line with periodic boundary conditions.

Make a graph of the total energy and fictitious kinetic energy as a function of time. Show the variation in total energy on a fine scale to verify that it is well conserved.

(b) Now add a potential $V(x) = A\sin(2\pi x/L)$. Use an FFT to transform the wavefunction to real space, multiply by the potential, and the inverse FFT to transform back to Fourier space.

(i) For two electrons per cell (up and down) one has a filled band with a gap to the next band. Find the ground wavefunction and electron density for a value of $A = 1$ Hartree, a reasonable number for a solid. (All results can be verified by using the plane wave methods and diagonalization as described in Chapter 12.)

(c) Consider a system with the electrons coupled to slow classical degrees of freedom; let A be coupled to an oscillator, $A = A_0 + A_1 x$, and the energy of the oscillator $E = 0.5 M\omega_0^2 x^2$. Choose values typical for ions and phonon frequencies (Chapter 20).

(i) Choose a fictitious mass μ so that all the electronic frequencies are much greater than ω_0. See Exercise 19.2.

(ii) Start the system at $x = 0$, which is not the minimum, and let it evolve. Does the oscillator go through several periods before significant energy is transferred to the electron state? Plot the total energy of the system and the fictitious kinetic energy as a function of time. Show that the total energy is accurately conserved, and the fictitious kinetic energy is much less than the oscillator kinetic energy for several cycles.

(iii) The oscillator should oscillate around the minimum. Check, by calculating the total energy by the quenching method, for fixed *x*, for several values of *x* near the minimum. Is the minimum in energy found this way, close to the minimum found from the oscillations of the dynamic system?

Solution:

Computation problem not solve here.

Solutions for Chapter 20
This was in Ch. 19 in first edition. Exs. are the same.

Exercise 20.1 See many excellent problems (and solutions) on phonons in the book by Mihaly and Martin [598].

Exercise 20.2 Show that the Bloch theorem for phonons follows from exactly the same logic as for electrons treated in the local orbital representation (Exercise 14.3).

Solution:

See solution in Exercise 14.3 and the places where it is shown in the text.

Exercise 20.3 By comparing expressions Eq. (14.7) and (20.8), show that the equations for phonons are exactly the same as a tight-binding formulation in which there are three states of p symmetry for each atom, corresponding to the three degrees of freedom for the atomic displacements. Show explicitly the correspondence of the terms of the two problems, especially the fact that the eigenvalue in the electron problem corresponds to the *square* of the frequency in the phonon problem.

Solution:

We can see the equations for p states and vibrations are essentially the same because they are solutions of wave equations for three degrees of freedom on each atomic site. The TB equations are more general since they apply for non-orthogonal basis; the overlap matrix S is unity for phonons so the phonon case corresponds to orthogonal TB equations. (ASIDE: Why are phonons orthonormal? Would there ever be non-orthogonal basis?). Phonons have eigenvalues ω^2 because they are quantized harmonic oscillators.

Exercise 20.4 This exercise is to explain a salient difference in the tight-binding electron and the phonon problems. The force constant has the property of *translational invariance*; show that the fact that the total energy does not change if all the atoms are displaced uniformly leads to the relation $\sum_J C_{I,\alpha;J,\beta} = 0$. This condition can be used to fix the self term $C_{I,\alpha;I,\beta}$ so that, unlike the electron tight-binding problem, the on-site term is not an independent variable. In addition, show that this means that there are three zero frequency phonon modes at $\mathbf{k} = 0$. The relation between the on-site and intersite matrix elements is called the "acoustic sum rule." (see Pick, Cohen and Martin [180]).

Solution:

The difference is that the hamiltonian for electrons is for a fixed lattice. They are invariant to displacement of all electrons by a lattice constant but no invariant to general displacements of the electrons if the lattice of nuclei is held fixed. Phonons are defined differently: they are equations for the entire lattice and the energy does not change if the entire lattice is displaced uniformly.

This is illuminating for the theory of phonons starting from the total energy of the electrons. In fact the total energy is for the entire lattice including the nuclei and the forces and vibration energies are for the entire system. In this book and almost everywhere the theory is worked out in the adiabatic approximation where the electrons are in the ground state.

Exercise 20.5 The simplest model for phonons is the central force model in which the energy is a function only of the distance between the nearest neighbors. Find expressions for a force constant $C_{I,\alpha;J,\beta}$ using the definition as a second derivative of the energy expressed as a sum of pair terms $E = \sum_{I<J} E_{IJ}(|\mathbf{R}_I - \mathbf{R}_J|)$. Show that the resulting expressions are equivalent to a tight-binding problem of electron p states, Exercise 14.11, with the $t_{pp\pi}$ matrix elements equal to zero.

Solution:

As noted in Exercise 20.3, the phonon equations are the same as for p states. The central forces constant for phonons corresponds to having energy a function only of distance between the atoms. For p states this means only $t_{pp\sigma}$ matrix elements as illustrated in Fig. 14.2.

Exercise 20.6 Find expressions for phonon dispersion curves respectively in elemental simple cubic and fcc crystals using the simplest model for phonons, a nearest-neighbor central potential model with energy given by $E = \frac{1}{2}\sum_{I<J} K|\mathbf{R}_I - \mathbf{R}_J|^2$, where J is restricted to nearest neighbor. Show the relation to tight-binding equations for p bands in Exercise 14.11 as explicit examples of the relationship given in Exercises 20.3–20.5.
(a) Show that there are two dispersion curves that have zero frequency for all k in simple cubic but not in fcc crystals. Explain why this instability occurs in a simple cubic crystal in a central potential model.
(b) There is a corresponding result in the tight-binding model for p bands in a simple cubic crystal if the only non-zero matrix element is $t_{pp\sigma}$ between nearest neighbors. Show that in this case there are two bands with no dispersion.

Solution:

A simple way to derive this result is to consider the equations for a simple cubic crystal. The problem reduces to a case where the energy is a sum of terms for decoupled lines of atoms along the 3 axes. Consider $\mathbf{k}$ along a cubic axis $(k_x, 0, 0)$. For phonons the energy is a function of displacement in the x direction and independent of displacement in the y and z directions, which means two zero frequency dispersion curves. For the tight binding problem, there are two flat bands for p_y and p_z. The same happens for the other cubic directions. Consider now a general $\mathbf{k} = (k_x, k_y, k_z)$; the energy is simply a sum of terms for the three axes with no coupling between them, i.e., $E(\mathbf{k}) = E(k_x) + E(k_y) + E(k_z)$.

NOTE: NOT FINISHED

See note - not finished

Exercise 20.7 Computational exercise : Using the properties established in Exercises 20.3–20.5, construct a computer program (or use a tight-binding code that is available) to evaluate phonon frequencies in a model analogous to a tight-binding model for electrons.

Solution:

Computational ex. no solution given here.

Exercise 20.8 Why is there no term involving $\partial^2 n/(\partial\lambda_i\partial\lambda_j)$ in the expression for $\partial^2 E/(\partial\lambda_i\partial\lambda_j)$ in Eq. (20.12)?

Solution:

The lack of this term in the second equation follows directly from the first equation, i.e., the Hellman-Feynman theorem. To understand it from a physical perspective, it is because the quantity calculated is the second derivative of the energy w.r.t. an effect external to the electron system. It is *not* required that the second derivative of the energy with respect to changes in $n(\mathbf{r})$ are zero, but rather that at second order the second derivative of the energy does not depend on the second derivative $n(\mathbf{r})$.

Exercise 20.9 Show that Eq. (20.19) follows from Eq. (20.26) by taking matrix elements of the equation.

Solution:

See note - not finished

NOTE: NOT FINISHED - CHECK. MISTAKE IN EQ?

Exercise 20.10 This is an example of the variational principle in perturbation theory. Consider a system composed of three points x_0, x_1, x_2 in a line connected by two springs. The energy is $E = \frac{1}{2}k_1(x_1 - x_0)^2 + \frac{1}{2}k_2(x_2 - x_1)^2$. Suppose forces $f = f_0 = -f_2$ are applied to the two ends.

(a) Identify the functional $F[f, x_1]$ valid for all f and x_1.

(b) If the middle position x_1 is free to move, calculate the change in position $x_1 - x_0$ and total length $x_2 - x_0$ as a function of f.

(c) See Exercise D.7 for extension to non-linear springs.

Solution: (See also Exercise G.4 for a closely related exercise.)
The energy $E = \frac{1}{2}k_1(x_1 - x_0)^2 + \frac{1}{2}k_2(x_2 - x_1)^2$ is expressed in terms of three positions; since the absolute position is not relevant, the energy can be expressed in terms of two variables that can be chosen to be the length $L = x_2 - x_0$ and $x_1 - x_0 \equiv y$. A symmetric form is
$E = \frac{1}{2}k_1(x_1 - x_0 - L/2)^2 + \frac{1}{2}k_2(L/2 + x_1 - x_0)^2 = \frac{1}{2}k_1(L/2 - y)^2 + \frac{1}{2}k_2(L/2 + y)^2 = \frac{1}{2}(k_1 + k_2)(y^2 + L^2) + (k_2 - k_1)Ly.$
This is analogous to the internal energy of a solid expressed as a function of internal variables (analogous to y) and the volume (analogous to L). We can convert this to a function of the force f and y, which is analogous to the internal energy of a solid expressed as a function of internal variables (analogous to y) and the externally applied pressure (analogous to f):
$f = -dE/dL = (k_1 + k_2)L + (k_1 - k_2)y$ so that $L = f/(k_1 + k_2) - [(k_1 - k_2)/(k_1 + k_2)]y$
Substituting this in the expression for the energy gives the desired expression. It is straightforward and not written out here.

This expression gives the energy as a function of the applied force and y; if it is minimized with respect to y, itis the equilibrium energy as a function of force f This is analogous to the enthalpy which the the energy as a function of pressure in a solid. It does not appear very useful. It is much easier to calculate the energy as a function of the internal variables, just as in a solid where iot is easier to calculate energy as a function of volume.

It is interesting to note that one dimension is special. Since the force is transmitted from one atom to the next the effect of the applied force is transmitted into the body. The interpretation leads to problems identifying what is intrinsic as explained in some detail in the paper by Nielsen and Martin [162, 102]. It is the same as the issues with regard to polarization where the effects of charge at the surface does not decrease as the size of solid increases so that one must take great care to identify the intrinsic polarization and the surface effect, as described in Chapter 24.

Solutions for Chapter 21

This was in Ch. 20 in first edition. Exs. are the same except two new Exs are added.

Exercise 21.1 Derive expression Equation (21.9) for the dielectric function for non-interacting particles. Show that the first term in brackets comes from the A^2 term as stated following Eq. (21.9).

Solution:

see note in text

This is straightforward perturbation theory for the second term. The first term arises because $\mathbf{A}$ is just a multiplicative term that acts on each electron. NOTE: I have forgotten the physical reason this terms must be present!

Exercise 21.2 Derive the matrix equation Equation (21.15) for the eigenvalues Ω_n of the density response from the preceding equations. Although there are many indices, this is a straightforward problem of matrix manipulation.

Solution:

As stated this is tedious. See the reference given and many more recent papers and texts.

Exercise 21.3 The general approach for exponentials of operators is described in the text preceding Eq. (21.18); it is also used in the rotation operators in Appendix N. Show that for any operator A, $\exp(A) = \sum_i |\zeta_i\rangle \exp(A_{ii})\langle\zeta_i|$, where A_{ii} and ζ_i are eigenvalues and eigenvectors of A. Hint: Use the power series expansion of the exponential and show the equivalence of the two sides of the equation at every order.

Solution:

This can be shown by following the hint. At each order one can insert a complete set of states and show that it is equivalent to the expression in terms of eigenvalues and vectors.

Exercise 21.4 Show that Eq. (21.18) has error of order $\propto \delta t^2$. Would the error be of the same order if the potential part were not symmetric?

Solution:

See references for the Suzuki-Trotter form (often called just Trotter) for the fill reasoning. The simple way to see it is that the symmetric form has the derivation operator at the middle of a time step, whereas if it were are the start or the end of the step it would introduce an extra error.

Exercise 21.5 Derive the f sum rule for the strength function $S(\omega)$ in Eq. (21.23). The proof is analogous to Exercise E.2.

Solution:

See derivation in Exercise E.2.

Exercise 21.6 Describe qualitatively how the top and bottom parts of Fig. 21.6 lead to broad and sharp spectra, respectively.

Solution:

See note in text

The qualitative answer is given in the caption, that the rapid decay In the topo curve corresponds to a broad peak that can be described by broadened Lorentzian, just like a friction term in a harmonic oscillator.

NOTE: I am not sure why there are persistent oscillations in the top part on the figure.

Solutions for Chapter 22

This is a new Chapter not in first edition.

Exercise 22.1 The work function ϕ in Section 22.2 involves intrinsic properties of the material plus surface effects that are equivalent to the change in potential of a capacitor as described in Section F.5. An important effect is the reduction of the work function of a metal by adding a layer of atoms that donate electrons (become positively charged). The magnitude can be estimated by simple models. Consider a metal with a layer of adatoms in a square array separated by 4 a_0 positive charge $|e|$ at a height of 4 a_0 above the surface layer of atoms(the compensating negative charge is assumed to be on the surface layer of the metal). Find the change in the work function in eV.

Solution:

This is a problem that might apply to a metal coated with atoms that changes the work function, a well known phenomenon. It is the voltage of a capacitor with charge density $e/16a_0^2$ and spacing $4a_0$. One has to get the right units! Left as exercise for the reader!

Exercise 22.2 Show that there is always a surface (end) state due to the form of the density of states in a one-dimensional system shown in Fig. 14.4. This is an example of a state caused by a potential as described by Tamm. (Hint: use a Green's function formulation. Since the density of states diverges at the edge of the band any localized effect, such as the potential at the surface, always leads to a bound state either below the band for attractive potentials or above the band for repulsive potentials.)

Solution:

The solution using the Green's function $G(\omega)$ follows the hint, and it requires two basic ideas: a pole in $G(\omega)$ in an energy range where there is no bulk state (a gap) denotes a bound state, and G is determined by the Green's function for the unperturbed system G^0 (i.e., the infinite bulk) and the perturbation potential. The relation is

Such a state is guaranteed if the Green's function for the unperturbed system G^0 diverges at the band edge. This occurs in 1 dimension, and in 2 or 3 dimensions if the perturbation is periodic so that $\mathbf{k}_{surface}$ is conserved. In that case the problem reduces a one-dimensional problem for the position orthogonal z to the surface for each $\mathbf{k}_{surface}$.

NOTE: NOT FINISHED - where is the appropriate G in the book

See note - not finished

Exercise 22.3 See Exercise 26.7 for an analytic solution for a Shockley midgap surface state wavefunction as it decays into the crystal for a two-site model.

Solution:

See that Ex.

Exercise 22.4 Show that the potential has the "polar catastrophe" form shown at the top of Fig. 22.6 for the sequences of + and - charged planes. Show that if there is there is added a layer with 1/2 negative change per cell, the resulting potential does not increase indefinitely.

Solution:

Consider plane perpendicular to x and a potential defined to be zero at $x = -\infty$. A critical point is that the crystal is neutral. This is often an assumption that is hidden and not made explicit. Then there is no electric field outside the crystal and the potential is zero up to the first plane at the surface. As one crosses the first plane (which is charged, chosen to be + in Fig,22.6) the electric field jumps to a finite value exactly like a capacitor. The potential for a negative electron is shown in Fig. 22.6. Crossing the next plane of opposite charge the field is again zero as shown. The potential increases the same at each pair of planes, so that is increases indefinitely.

As shown at the bottom of Fig. 22.6 reducing the charge of the first plane by 1/2 cures the problem.

What does this have to do with neutrality? The half charge at the surface is the physical realization of neutrality in a local sense. The first example with the catastrophe is really artificial; it is neutral only id the system terminates in a plane with the opposite charge; it is not a physical situation that the potential for electrons in the left region of the crystal depends upon the right edge at a large distance. In the text is clarified that a physical situation is that changed plane come from transfer of charge between planes with naturally leads to half charge at a plane that has a neighboring plane on only one side. This is the physical realization of change neutrality and is what happen in an ionic system that results from bring together neutral atoms which transfer charge to make an ionic crystal,

Exercise 22.5 Describe qualitatively the bands shown in Fig. 22.7 in terms of the d states shown in the figure. Explain why the three bands would be independent for a layer of Ti atoms in vacuum, but they are mixed and repel one another because it is a surface layer. Explain also that spin–orbit interaction splits the states at Γ and mixes the states at other $\mathbf{k}$ points.

Solution:

For a layer in the vacuum the d_{xy} (even in reflection in the plane) states are decoupled from the d_{xz} and d_{yz} which are odd. However the up-down symmetry is broken in a surface; the states are not even and odd and the states are mixed.

Spin-orbit coupling mixes the three d states even without symmetry breaking. For example, a small SO coupling mixes the d_{xy}, d_{xz} and d_{yz} states and gives rise to a a large mixing at the points where the bands cross in the figure, i.e., where they would be degenerate except for SO coupling.

Solutions for Chapter 23

This was in Ch. 21 in first edition. Exs. are the same except addition of short Exercise 23.10 pointing to another Ch.

bf Many solutions in this chapter are only references to papers, where they are written out explicitly.

Exercise 23.1 This exercise is to construct a localized Wannier function for the s bands described in Section 14.5 and Exercises 14.6 and 14.7. The hamiltonian has only nearest-neighbor matrix elements t and the basis is assumed to be orthogonal. For all cases (line, square, and simple cubic lattices), show that one can choose the periodic part of the Bloch functions $u_{i\mathbf{k}}(\mathbf{r})$ to be real, in which case they are independent of $\mathbf{k}$. Next, show from the definition, Eq. (23.6), that this choice leads to the most localized possible Wannier function, which is identical to the basis function.

Solution:

There is an error in these Exs and they are stated in a way are much harder than they need to be. The error is that in general $u_{\mathbf{k}}(\mathbf{r})$ is NOT independent of $\mathbf{k}$.

It is useful to see how the functions are defined in terms of the u's because the theory later is in terms of the periodic u's. However, to solve these Exs, there is no need to introduce the u's which just complicates the problem. The solution can be stated in a simpler, more general way for a problem with one basis function per site and one site per cell, i.e., one band so that there are no issues of multiple bands. The basis functions are assumed to be orthonormal. No matter what is the hamiltonian, the Bloch function $\psi_{i\mathbf{k}}(\mathbf{r})$ can be expressed as $\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{n}} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{T}_{\mathbf{n}}}\chi(\mathbf{r}-\mathbf{T}_{\mathbf{n}})$, where there is a phase factor $\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{T}_{\mathbf{n}}}$ times each function centered at cell $\mathbf{n}$. At any point $\mathbf{r}$ only functions that are non-zero at $\mathbf{r}$ contribute. Then it is most straightforward to use the definition of the Wannier function in Eq. (23.4)

$$w_{i\mathbf{n}}(\mathbf{r}) = \frac{\Omega_{\mathrm{cell}}}{(2\pi)^3}\int_{\mathrm{BZ}} \mathrm{d}\mathbf{k}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{T}_{\mathbf{n}}}\psi_{i\mathbf{k}}(\mathbf{r}) = \frac{\Omega_{\mathrm{cell}}}{(2\pi)^3}\int_{\mathrm{BZ}} \mathrm{d}\mathbf{k}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{T}_{\mathbf{n}}}\sum_{\mathbf{n}'}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{T}_{\mathbf{n}'}}\chi(\mathbf{r}-\mathbf{T}_{\mathbf{n}'}). \tag{S.156}$$

For one band, the integral over $\mathbf{k}$ is non-zero only for $\mathbf{T}_{\mathbf{n}} = \mathbf{T}_{\mathbf{n}'}$ and it follows that the Wannier function centered on site 0 is $w(\mathbf{r}) = \chi(\mathbf{r})$

In terms of the periodic part of the Bloch functions u, they can always be chosen to be real if there is a center of inversion. This follows because the basis function $\chi(\mathbf{r})$ can be chosen to be symmetric. We can see from Eq. (23.6) that for a symmetric function the Wannier function (chosen to be the basis function) is a real cosine transform of the u's. *But this does not mean they are independent of* $\mathbf{k}$. Of course they can also be complex by a unitary transformation, but this is the most useful case. For example, the Berry phase is $\pm\pi$ so the the imaginary part vanishes in many of the derivations later in this book.

Exercise 23.2 This exercise is to analyze Wannier functions for s bands as described in Exercise 23.1, except that the basis is non-orthogonal with nearest-neighbor overlap s. Show that one can choose the periodic part of the Bloch functions $u_{i\mathbf{k}}(\mathbf{r})$ to be real, and find the $\mathbf{k}$ dependence of $u_{i\mathbf{k}}(\mathbf{r})$ as a function of s. (Hint: For non-orthogonal functions, the normalization coefficient given in Exercise 14.4 is $\mathbf{k}$ dependent, which is relevant for constructing the Wannier function using Eq. (23.6).) Show that the resulting Wannier function has infinite range; even though it decays rapidly, its amplitude does not vanish at any finite distance.

Solution:

I believe there is a more elegant solution but I cannot reproduce it now.

This problem can be solved by noting that the generalized eigenvalue problem can be converted to a problem with orthogonal functions withe hamiltonian $S^{1/2}HS^{1/2}$, as done in Exercise 14.17. There it is shown that the decay is exponential.

Is this a quandary? The overlap matrices led to a longer range hamiltonian in terms of orthogonal functions. Since we never said anything about the shape of the wavefunctions, why does the extent of the hamiltonian matrix elements imply anything about Wannier functions. The answer is that the Wannier functions are expressed as linear combinations of the basis functions $\chi(\mathbf{r})$. The hamiltonian matrix elements are non-zero only if the two Wannier functions involved are both non-zero. It is a different problem to find the $\mathbf{r}$ dependence of the basis functions $\chi(\mathbf{r})$.

Exercise 23.3 Derive Eq. (23.8) using definition Equation (23.6) and properties of the eigenfunctions.

Solution:

The definition of each of the the Wannier functions is an integral over $\mathbf{k}$ of the periodic Bloch function in Eq. (23.6). Thus Eq. (23.8) can be written as (ignoring prefactors)

$$\langle i\mathbf{m}|j\mathbf{m}'\rangle \propto \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{k} \int \mathrm{d}\mathbf{k}' \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{r}-\mathbf{T}_\mathbf{m})} u_{i\mathbf{k}}(\mathbf{r}) \mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot(\mathbf{r}-\mathbf{T}_{\mathbf{m}'})} u_{i\mathbf{k}'}(\mathbf{r}). \tag{S.157}$$

Since the product of the u's is a periodic function the integral over $\mathbf{r}$ is non-zero only for $\mathbf{k} = \mathbf{k}'$ and the integral over $\mathbf{k}$ is zero unless $\mathbf{T}_\mathbf{m} = \mathbf{T}_{\mathbf{m}'}$, which establishes the orthogonality given that the u's are normalized.

Exercise 23.4 Show that expression Equation (23.13) to second order in $\mathbf{q}$ follows in analogy to the expansion that leads to Eq. (23.9).

Solution:

This is just a straightforward expansion as in Eq. (23.9). The exercise is given to ask the reader to be sure he/she realizes that this is key to the later arguments.

Exercise 23.5 Show that Ω_I is always positive by noting that $\hat{Q} = \hat{Q}^2$ so that Eq. (23.19) can be written as the sum of expectation values of squares of operators.

Solution:

The reason $\hat{Q} = \hat{Q}^2$ is that applying the projection operator once projects the empty states and and there is no change by applying it again any number of times. Thus $\hat{\mathbf{r}}_\alpha \hat{Q} \hat{\mathbf{r}}_\alpha = \hat{\mathbf{r}}_\alpha \hat{Q} \hat{Q} \hat{\mathbf{r}}_\alpha$ which is an absolute value squared since we can let the operators act to the left and right in a symmetric form.

Exercise 23.6 Show that Equation (23.23) and Equation (23.24) have the same limit for $\mathbf{b} \to 0$ as Eqs. (23.20) and Equation (23.21), and that they obey the translation invariance conditions, Eq. (23.22). Show further that this means that Ω is unchanged.

Solution:
NOTE: The formulas are written following the notation of Marzari and Vanderbilt [900]; it may seem confusing unless one understands that the weight factore have magnitude $\propto 1/b^2$. This form is useful to take into account the cartesian components in 2 and 3 dimensions.
The equivalence in the small $\mathbf{b}$ limit follows if we expand the log as $ln(x) = x - 1 + \ldots$. This applies at any point $\mathbf{k}$. GHowever, the translation invariance conditions, Eq. (23.22), involves the depe4ndence as a function of $\mathbf{k}$ for all $\mathbf{k}$ in the BZ. The translation invariance involves a shift by a multiple of a lattice constant where change of phase of the function $\psi_{i\mathbf{k}}(\mathbf{r}) \rightarrow \mathrm{e}^{-\mathbf{ik}\cdot\mathbf{T}_m}\psi_{i\mathbf{k}}(\mathbf{r})$, is multiples of 2π (see definition just before Eq. (23.22)). This is obeyed by the expression in terms of the imaginary part of the log, which is a trigonometric function. As discussed in the text, Ω in Eq. (23.14) is not gauge invariant; however, the special choice of change of phase by the factor $\mathrm{e}^{-\mathbf{ik}\cdot\mathbf{T}_m}$ is just a translation, and the definition in Eq. (23.14) is such that there is no change in Ω with a translation. Some algebra is required to show that in terms of the formulas, but it is left for the reader. Detailed derivations are in Marzari and Vanderbilt [900].

Exercise 23.7 Show that Ω_I in Eq. (23.25) is positive using the definition of the $\mathbf{M}$ matrices and the fact that the overlap of Bloch functions at different $\mathbf{k}$ points must be less than unity.

Solution:
This is easily shown for a single band where the matrices reduce to scalars and noting that the overlap on neighboring points cannot exceed unity. The general case is explained in Marzari and Vanderbilt [900].

Exercise 23.8 Explain why it is not possible to make $\widetilde{\Omega}$ vanish in higher dimensions.

(a) First show that the *projected* operators $\{\hat{P}\hat{x}\hat{P}, \hat{P}\hat{y}\hat{P}, \hat{P}\hat{z}\hat{P}\}$ do not commute. Show this is equivalent to the statement that $\hat{x}$ and $\hat{P}$ do not commute. Then show that $\hat{x}$ and $\hat{P}$ do not commute.

(b) Use the fact that non-commuting operators cannot be simultaneously diagonalized to complete the demonstration.

Solution:
In general two position operators commune with one another. However, a position operator x does not commute with the projection P. This is because projecting the wavefuntions and then multiplying by x (xP) is different from multiplying by x and then projecting (Px). For Px the result is clearly within the projected manifold of occupied states, whereas xP clearly is not since multiplication by x in general brings in components of the unoccupied states. A full discussion is explained in Marzari and Vanderbilt [900].

NOTE: Explain better here?

Exercise 23.9 Demonstrate that it is possible to find functions with $\widetilde{\Omega} = 0$ in one dimension by explicitly minimizing $\widetilde{\Omega}$ for a one-band, nearest-neighbor tight-binding model with overlap (see definitions in Section 14.5):

$$H_{i,i\pm1} = t; \quad S_{i,i\pm1} = s, \tag{S.158}$$

where $S_{i,i} = 1$.

(a) First consider the case with $s = 0$: show that in this artificial model the minimum spread is the spread of the basis function. However, one can also choose more delocalized states, e.g., the eigenstates.

(b) For $s \neq 0$, find the minimum spread Ω_I as a function of t. Show it is greater than in part (a). For explicit evaluation of the spread Ω_I, use (21.23) with the eigenvectors given by analytic solution of the Schrödinger equation and the sum over k done approximately on a regular grid of values in one dimension.

Solution:

The solution of part (a) is the same as in Exercise 23.1.

For part (b) the proof follows the same approach as in Exercise 23.2. The spread is larger because it extends to the functions centered on neighboring site. The explicit evaluation can be done analytically but not done here!

Exercise 23.10 See exercises in Chapter 26 for solutions for the two-site model in Fig. 26.2, which is also used in Exercise 23.11 and 23.12.

Solution:

See those Exs.

Exercise 23.11 This exercise is to construct maximally localized Wannier functions for the one-dimensional ionic dimer model in Fig. 26.2 using the fact that the gauge-dependent term in it can be made to vanish.

(a) Let $t_1 = t_2$ so that each atom is at a center of symmetry. Show that the maximally localized Wannier function for the lower band is centered on the atom with lower energy ε_A or ε_B, and the function for the upper band is centered on the atom with higher energy. (Hint: If there is a center of inversion the periodic part of the Bloch functions can be made real.)

(b) Similarly, there are two centers of inversion if $\varepsilon_A = \varepsilon_B$ and $t_1 \neq t_2$. Show that in this case the Wannier functions are centered respectively on the strong and the weak bonds between the atoms.

(c) In each of the cases above, calculate the maximally localized Wannier function as a sum of localized basis functions. The eigenfunctions can be calculated analytically and the Wannier functions constructed using the definition in (21.3) and approximating the integral by a sum over a regular grid of k points. (This can be done with a small computer code. Note that the grid spacing must be small for a small gap between the bands.)

Solution:

The first two parts can be answered by noting that in each case there are two centers of inversion and there are two bands that are symmetric ($\varepsilon_k = \pm|\varepsilon_k|$) about a zero of energy determined by the average energy $(\varepsilon_A + \varepsilon_B)/2$ or average hopping $(t_1 + t_2)/2$. This means that one can chose two Wannier functions for the two bands that are identical except that are centered on the two different centers of inversion. It follows that the lower energy must be the function for the lower band, centered on atom with lower energy or the strong bond. The only remaining thing needed is that the maximally localized functions can be chosen in this way.

The full solution of the functions requires a numerical calculation as pointed out in part (c). It can be done by band since the problem involves only 2x2 matrices or with a small code like that used to calculate the Berry phases later in the book.

Exercise 23.12 Using the model of Exercise 23.11 and the methods described in Section 23.3, construct a computer code to calculate the centers of the Wannier functions in a general case, $\varepsilon_A \neq \varepsilon_B$ and $t_1 \neq t_2$. This can be used to find polarization and effective charges as described in Exercises 24.8 and 24.9.

Exercise 23.13 Construct the maximally localized Wannier function for the lowest band in the one-dimensional continuum model of Exercise 12.5. Show that the function is centered at the minimum of the potential. Calculate the functions using the analytic expressions for the Bloch functions and the same approach as in Exercise 23.11, part (c).

Solution:

Computational problem not solved here.

Exercise 23.14 See Exercise 15.6 for a project to construct Wannier functions in one dimension.

Solution:

Computational problem not solved here.

Exercise 23.15 Show that $\mathbf{U}^{\mathbf{k}}$, defined in Eq. (23.27), is unitary if $\mathbf{W}^{\mathbf{k}}$ is antihermitian, i.e., $W_{ij} = -W_{ji}^*$.

Solution:

The definition of a unitary matrix is one that obeys $U^*U = UU^* = 1$. Thus if $U = e^W$. then $e^{W^*}e^W = 1$. Then $e^{-W^*} = e^W$ and $-W^* = W$ which means W is anti-hermitian. An example is the scalar case where W must be a purely imaginary phase factor in order for $|e^W| = 1$.

Exercise 23.16 Show that the gradient, Eq. (23.31), follows from the definitions. To do this, verify the operator commutation relations, and note that $\mathrm{Tr}[\hat{X}'\hat{X}_D] = 0,$ etc.

Solution:

This is just a matter of matrix algebra. It is worked out in the references given in text and I have not written out the steps.

NOTE: Explain this better?!

Exercise 23.17 Show that the minimization of the functional $\Omega[A] + C_a \mathrm{min}\{\Omega_a[A, X]\}$ leads to the desired solution of a non-singular transformation to non-orthogonal orbitals. Hint: Use the conditions stated following Eq. (18.33) and the relations given in Equation (23.32)–Equation (23.35).

Solution:

This is also matrix algebra which may be tedious. It is useful for a practical approach to finding non-orthogonal functions, and is especially important in the order-N methods where it is very important to have functions as localized as possible, and non-orthogonal functions can greatly reduice the computational time. The methods are described in Section 18.6 where there are references to the compact derivation by Yang [746] and Liu [774]. They are also important in the real space approach in disordered systems (which has a lot in common with the order-N methods) in Silvestrelli [902] and Berghold [903].

Solutions for Chapter 24

This was in Ch. 22 in first edition. Exs. are the same.

Exercise 24.1 Verify that the well-known expression for a dipole moment, Eq. (24.3), follows from the definition of the polarization field, Eq. (24.1), with the boundary condition given.

Solution:

Often Eq. (24.3) is taken to be the definition and here we want to see that ir follows from Eq. (24.1) if the n and $\mathbf{P}$ are restricted to a finite region and zero outside. This can be done a a scalar equation for each directing by integration by parts:

$$\int dx\ d(uv)/dx = (uv)|_{-\infty}^{\infty} = 0 = \int dx\ [u(dv/dx) + (du/dx)v],$$

where we have required u and v to be zero at the limits. Choosing $u = x$ and $v = P$, and using Eq. (24.1) where $dP/dx = -n$, we have

$$\int dx\ (du/dx)P = \int dx\ P = \int dx\ (u(dP/dx) = \int dx\ xn.$$

Since $\int P$ is the total dipole moment, this is the desired relation Eq. (24.3).

There are two lessons from this exercise that reveal the quandaries that have plagued the theory of polarization in condensed matter. First, the choice $u = x$ is the source of the difficulty; what does one do with the usual approach to treat condensed matter as the limit of a system that extends to infinity where x is unbounded? The other is that the integral converges only if P is required to vanish outside the system; however, the definition is only i terms of the derivative of P so that its absolute value id not defined by Eq. (24.1). It seems we had a circular definition where we added a requirement to define the absolute value of P in order to determine the absolute value of P. This makes sense for a finite system. What about an infinite system? These are the quandaries resolved only recently.

Exercise 24.2 Show that expressions (24.7) and (24.8) for the expectation values in terms of the commutators follow from the definition of $\hat{H}(\mathbf{k}, \lambda)$.

Solution:

This is really just a clarification of where the commutator means. Since the derivatives are operators acting on all functions to the right (or left) the commutator is just the restriction the the derivative acts only on the hamiltonian H. This interpretation leads to (24.8) and to (24.7) with the definition of $H(\mathbf{k})$. On the other hand, since the wavefunctions in the expression are eigenvectors of $H(\mathbf{k})$ one can let the H operator act to the left or right to see that

$$\langle u^{\lambda}_{\mathbf{k}i}|[\partial/\partial\mathbf{k}\ \hat{H}(\mathbf{k},\lambda) - \hat{H}(\mathbf{k},\lambda)\ \partial/\partial\mathbf{k}]|u^{\lambda}_{\mathbf{k}j}\rangle = \langle u^{\lambda}_{\mathbf{k}i}|[\varepsilon^{\lambda}_{\mathbf{k}i} - \varepsilon^{\lambda}_{\mathbf{k}j}]|\partial u^{\lambda}_{\mathbf{k}j}/\partial\mathbf{k}\rangle \qquad \text{(S.159)}$$

and similarly for the λ derivative.

Exercise 24.3 Show that Eq. (24.9) follows from the previous equations as stated in the text. Hint: Use completeness relations to eliminate excited states.

Solution:

Putting the results of the previous problem into Eq. (24.5) and Eq. (24.6), we can see that the factors of energy differences cancel in the numerator and denominator and lead to the desired result Eq. (24.9).

Exercise 24.4 Show that the dipole moment averaged over all possible cells vanishes in any crystal.

Solution:

Even though we have argued that the equation for the dipole is problematic in a crystal, it can be argued that the expression in Eq. 24.3 is well defined if the dipole is averaged over all choices of the origin for the position vector $\mathbf{r}$, i.e., if we replace $\mathbf{r}$ by $\mathbf{r} - \mathbf{r}_0$ and average over $\mathbf{r}_0$ in a cell it is well defined and clearly zero since it averages over all possible expressions for the dipole with charges to the left and right equally.

Exercise 24.5 Define a "localization gap" $E_{\rm L}$ by turning Eq. (24.19) into an equality: $\xi^2 \equiv \hbar^2/(2m_e E_{\rm L})$.

(a) Using the f sum rule and Eq. (24.17), show that E_L can be expressed as the first inverse moment of the optical conductivity distribution:

$$E_L^{-1} = \frac{1}{\hbar}\frac{\int \omega^{-1}\sigma'(\omega)\mathrm{d}\omega}{\int \omega^0\sigma'(\omega)\mathrm{d}\omega}.$$

(b) Use the f sum rule and the Kramers–Krönig expression for $\epsilon(0)$ to show that the Penn gap defined in D. R. Penn, "Wave-Number-Dependent Dielectric Function of Semiconductors, Phys. Rev. 128, 2093 (1962) [941] $E_{\rm Penn}$ defined via the relation $\epsilon(0) = 1 + (\hbar\omega_p/E_{\rm Penn})$, where ω_p is the plasma frequency, can be expressed as the second inverse moment:

$$E_{\rm Penn}^{-2} = \frac{1}{\hbar^2}\frac{\int \omega' {-2}\sigma'(\omega)\mathrm{d}\omega}{\int \omega^0\sigma'(\omega)\mathrm{d}\omega}.$$

(c) Using the results of (a) and (b), show that inequalities ((24.19)) and ((24.20)) can be recast in a compact form as follows:

$$E_{\rm Penn}^2 \geq E_{\rm L}E_{\rm gap}^{\rm min} \geq (E_{\rm gap}^{\rm min})^2.$$

Solution:

The solution for the first two parts is a matter of using the relation to the plasma frequency given in Exercise E.2 and realizing the mistakes in the equations! The symbol ω^0 should be ω. The Eq for $E_{\rm Penn}$ is dimensionally incorrect. There is a latex erropr. It should be

$$E_{\rm Penn}^{-2} = \frac{1}{\hbar^2}\frac{\int \omega'^{-2}\sigma'(\omega)\mathrm{d}\omega}{\int \omega^0\sigma'(\omega)\mathrm{d}\omega}.$$

The second inequality follows from the fact that an average gaps is always greater then the minimum gap. The first inequality follows from the powers of ω in the expressions for $E_{\rm Penn}^2$, $E_{\rm L}$, and $E_{\rm gap}^{\rm min}$?

ADD MORE?

ADD MORE?

Exercise 24.6 Find a reasonable estimate and upper and lower bounds for $\sum_{\alpha=1}^{3}\xi_\alpha^2$ using gaps and dielectric constants of typical semiconductors and the expressions given in

Exercise 24.5. The lowest direct gaps can be taken from Sgiarovell, et al. [942] or other sources and values of the dielectric functions can be found in texts such as Marder, Kittel or Ashcroft [300, 285, 280], e.g., $\epsilon \approx 12$ in Si.

Solution:

This is a matter of checking values for representative cases.

ADD MORE? ADD MORE?

Exercise 24.7 It is also instructive to calculate values of the average "Penn gap" in the 1962 paper by Penn [941] which is defined in **Exercise 24.5**. The Penn gap is an estimate of the average gap in the optical spectrum and is directly related to the inequalities in Exercises 24.5 and 24.6. As an example, find the gap in Si with $\epsilon \approx 12$ and compare with the minimum direct gap. Find values for other semiconductors as well, using standard references or [941].

Solution:

This is a matter of checking values for representative cases. Also check **Exercise 24.5**.

ADD MORE? ADD MORE?

Exercise 24.8 Construct a small computer code to calculate the electronic contribution to the polarization from the Berry phase expressions given in Section 24.3 for the one-dimensional ionic dimer model of Fig. 26.2 in a general case, $\varepsilon_A \neq \varepsilon_B$ and $t_1 \neq t_2$. Compare with the calculations of the centers of the Wannier function found in Exercise 23.12.

Solution:

This is a computational problem not solved here.

Exercise 24.9 The effective charge, Eq. (E.20), is defined by the change in the polarization induced by displacement on an atom. An important part of the charge is the "dynamical" electronic contribution that results from changes in the electronic wavefunctions in addition to rigid displacements. A simple model for this is given by the one-dimensional ionic dimer model of Fig. 26.2. Consider $\varepsilon_A \neq \varepsilon_B$ and let $t_1 = t + \delta t$ and $t_2 = t - \delta t$. A change in δt causes a change in polarization in addition to any change due to rigid displacement of ionic charges. For a given $\Delta\varepsilon \equiv \varepsilon_A - \varepsilon_B$ calculate $\delta \mathbf{P}/\delta t$ for small δt using computer codes for the Berry phase (**Exercise 24.8**) or the centers of the Wannier functions (**Exercise 23.12**). Show that the contribution to the effective charge can be large and have either sign (depending on the variation of t with displacement), which can explain large "anomalous effective charges" as described in Section 24.5.

Solution:

The calculation of the Berry phase requires a computation, but we can see the physical effect with out computation. The charge is moved to the left or right since the perturbation is not symmetrical around each atom, i.e., the center of inversion is broken. In a real crystal there is an effect of displacement of the positive nuclei and in addition this displacement of the electrons that depends up the way the band structure varies as the atoms are displaced. It can be in either direction and large or smaller than the nuclear component of the effective charge.

Exercise 24.10 Consider the one-dimensional continuum model of Exercise 12.5 for which Wannier functions are found in Exercise 23.13. The polarization is zero since the crystal has a center of inversion and the eigenfunctions can be chosen to be real. If the entire crystal is shifted rigidly a distance Δx, so that $V(x) \to V_0 \cos(2\pi(x - \Delta x)/a)$, the origin is not at the center of inversion and the eigenfunctions are not real. Using the Berry phase expressions in Section 24.3, show that the change in the electronic contribution to the polarization is $\Delta P = -2|e|\Delta x/a$. The interpretation of this simple result is that the electrons simply move rigidly with the potential. Give the reasons that this shift does not actually lead to a net polarization since in a real crystal this electronic term is exactly cancelled by the contribution of the positive nuclei which shift rigidly.

Solution:

This is a variation of the previous problem in terms of Wannier functions. The transformation from the Berry phase expressions in the previous problem to Wannier is a rigorous transformation bevause it is really just a different interpretaion of the quations because *the Wannier functions are defined by the same Berry phase expressions!* A quantitative calculation requires a computation, but we can see the physical effect that the displacements of the centers of Wannier functions is the charge in electronic polarization is we multiply by the charge e. It is just another way of dealing with the problem in a real crystal where there is a sum of displacement of the positive nuclei and negative electrons.

Solutions for Chapter 25
This is a new Chapter in second edition

Exercise 25.1 Apply same arguments as in Exercise P.1 to show that $\langle u_k|\partial_k u_k\rangle$ is purely imaginary.

Solution:
Since the norm $\langle u_k|u_k\rangle = 1$ is normalized, the derivative $\partial_k\langle u_k|u_k\rangle = 0$. Thus $\langle u_k|\partial_k u_k\rangle + \langle\partial_k u_k|u_k\rangle = 0$. The two terms are complex conjugates of one another, and therefore each is purely imaginary.

Exercise 25.2 See Exercise P.2 for the general form of Berry curvature. Apply the arguments to derive the first equality in expression for $\Omega(\mathbf{k})$ in Eq. (25.8) from the previous expressions the Berry phases. Discuss how added factors of 2π might occur in crystals. Show that the second equality follows from the normalization condition for the Bloch functions.

Solution:
Note that in Eq. (25.8) ∂_x means ∂_{k_x}, etc. The formulas are expressed in a form where $\mathbf{k}$ is a continuous function, but a way to derive the result is to consider a small box of size $Deltak_x \times \Delta k_y$, where the value $\langle u|\partial_x u\rangle$ and $\langle u|\partial_y u\rangle$ can be taken to be constant along each edge, and then take the limit. Thus the clockwise line integral is the sum of the differences (bottom - top) + (right - left) which is $\left[\langle u|\partial_x u\rangle|_{k_y} - \langle u|\partial_x u\rangle|_{k_y+\Delta k_y}\right]\Delta k_x + \left[\langle u|\partial_y u\rangle|_{k_x+\Delta k_x} - \langle u|\partial_y u\rangle|_{k_x}\right]\Delta k_y$. Taking the limit leads to the differential expression in the middle expression in Eq. (25.8). Taking into account that $\langle u|\partial_x u\rangle$ is purely imaginary leads to the form at the right in Eq. (25.8).

This is a consequence of the same analysis as used in Section D.1 where the change in the ground state wavefunctions is only by mixing in the unoccupied states. See also Exercise C.1.

Exercise 25.3 In Section P.7 it is pointed out that one way the to treat the monopole is to define two different smooth gauges for the northern and southern hemispheres and "glue" them together, which is allowed because the Berry phase is defined modulo 2π. The integer factor of 2π is the Chern number. The winding around the cylinder results from a smooth variation across the Brillouin zone. Discuss the way this is analogous when we "glue" together the two ends of the cylinder to describe the behavior of the Berry phase on the torus that is the Brillouin zone (or the torus defined by a cyclic variable λ.

Solution:
This is an elegant way to relate the problem of two bands defined on the BZ which is a torus show at the right in Fig. 25.1. The torus is a closed surface with an inside and an outside that is essential for the arguments on Chern numbers and for the conclusions about whether the zero of the hamiltonian is inside or outside the surface. However, it is often easier to visualize the BZ as a cylinder shown at the center if the figure. It is MUCH easier to draw the winding around the cylinder than around the torus! And it makes clearer the relation to the linear shift of the centers of the Wannier functions in real space. The relation is that forcing all properties including the wavefunction to be periodic means they are the same at the two ends which in equivalent to the torus. For the wavefunction, the phase can

wind as illustrated in the top part of Fig. 25.2, which means that there is a zero point inside the torus as illustrated in Fig. 26.6. The same arguments apply for action of the pump in a periodic crystal with no surfaces, where the torus represents one unit cell of a crystal; a cycle of the pump translates the electrons by one cell which is the same as pumping through each cell or equivalently around the torus.

Solutions for Chapter 26

This is a new Chapter in second edition

Exercise 26.1 Derive the expression for the hamiltonian for the two-site model Fig. 26.2 in Eq. (26.4) and the eigenvalues $\varepsilon(k)$ given after Eq. (26.4). Show that the results are the same if the cell is chosen with B sites on the left and A on the right.

Solution:

This exercise illustrates the subtleties of using this model to illustrate the bulk-boundary effect. Any 2x2 hamiltonian can be expressed in the form of Eq. (26.4) with the zero of energy chosen to be midway between the two site energies. As stated in the text the choices of $t(k)$ depend upon the choice of the cell and the choice of the $exp(ikR)$ factors. As is clear from the solution for the eigenvalues multiplying t by any factor $exp(ikX)$ leaves the eigenvalues unchanged. A simple way to choose $t(k)$ is to tom define the cell as in the text with the choice that the phase factors are only between cells. Then it is clear that the two choice of the cell lead to $t(k) = t_1 + t_2 exp(-ika)$ or $t(k) = t_1 exp(-ika) + t_2$ depending on whether t_2 or t_1 is the intercell term. There are many choice with the same dispersion curves for the bulk crystal (or any finite crystal with periodic boundary conditions and no surfaces), but the eigenvectors are different. This is the essential point that one must make a choice and use it consistently. The effects of forming a surface appear when it ends on an A atom or a B atom, and the relation to the bulk Berry phase (which depends upon the eigenvectors) depends upon using the phases of the eigenvectors consistently.

Exercise 26.2 Consider the one-dimensional tight-binding model with two atoms per cell labeled A and B. If the basis is one s state on each atom, the model can denoted pictorially by Fig. 26.2 where $\varepsilon_A, \varepsilon_B$ are the on-site energies and t_1, t_2 the hopping matrix elements. By varying the parameters, this model describes a symmetric ionic crystal ($\varepsilon_A \neq \varepsilon_B$, $t_1 = t_2$), a molecular elemental crystal ($\varepsilon_A = \varepsilon_B$, $t_1 \neq t_2$), and any ionic/molecular combination. Derive the bands as a function of the parameters and show that there is a gap between the two bands for all cases except the one-atom/cell limit where $\varepsilon_A = \varepsilon_B$, $t_1 = t_2$. See Exercise 26.1 for a related exercise and Exercises 23.11, 23.12, 24.8, and 24.9 for examples of Wannier functions, polarization, and effective charges using this model.

Solution:

See the answer for Exercise 26.1 where the eigenvalues given after Eq. (26.4). This is an example of the fact that the bands repel and do not cross in the middle of the BZ, and the only possibile places where a degeneracy (no gap)can occur are $k = 0$ and $k = \pi/a$. The only case where there is no gap is where the primitive cell contains only one atom and there is a half filled band if there is one electron per atom. In that case the two-atom cell is just an artificial construction with no gap.

Exercise 26.3 Show the transformation of the calculations in Exercise 26.2 to the $s - p$ model in Fig. 26.3 using the relations given in Section 26.2.

Solution:

The most compact way to describe the relation is that the eigenvalues are plus and minus the magnitude os the $\mathbf{h}$ vector in Eqs. (26.6) - 26.8. It is not an exact mapping of the dispersion but rather another possible form, which is more flexible with more parameters.

It is more messy to write out the equations, where the determinant equation $|H(\mathbf{k}) - \varepsilon|$ with $H(\mathbf{k})$ given by Eq. (26.5) becomes

$$(\varepsilon_p + 2t_{pp}\cos(ka) - \varepsilon)(\varepsilon_s + 2t_{ss}\cos(ka) - \varepsilon) - 4(t_{sp}\sin(ka))^2 = 0. \tag{S.160}$$

Exercise 26.4 Derive the equations for of the dispersion curves for the one-dimensional lattice illustrated in Fig. 26.4 and show that the bands have the normal and inverted order respectively in the two cases.

Solution:

This is a matter of solving the quadratic equation from the previous problem or using a computer program such as the TBPW code.It is easier to determine whether the system is normal or inverted since one needs only the symmetry of the eigenvectors at $k = 0$ and $k = \pi/a$. At those points $sin(ka) = 0$, $cos(0) = 1$, and $cos(\pi) = -1$. All that is required is to checked if the states at $\varepsilon_p + 2t_{pp}$, $\varepsilon_s + 2t_{ss}$ and $\varepsilon_p - 2t_{pp}$, $\varepsilon_s - 2t_{ss}$ have exchanged order.

Exercise 26.5 See Exercise 14.14 for a related problem of an A-B model with p states on the B sites.

Exercise 26.6 Show that the Berry phase takes the value π (mod(2 π)) for the case where the oval encloses the origin. Explain how this relates to the fact that the wavefunction for a fermion changes sign for a 2π rotation. See also Exercise 28.7 for Weyl points.

This should have been emphasized more. Many instructive points. Change in future reprinting?

Solution:

(NOTE: There is much in common with Exercise P.3 and P.4 which have a sequence of three and four states.)

The Berry phase is phase of the lowest eigenfunction *accumulated* as k varies from $-\pi/a$ to $+\pi/a$. It may seem like one merely has to know the phase at two points and take the difference. *this is NOT true. The phase of the eigenfunction at any point is undefined!* One way to find the change accumulated along the path is to follow the discrete set of points that define a path and calculate the change in phase from one point to the next using the log formula Eq. (25.1); a physically meaningful result can occur only if it is a closed path. Others ways the find the Berry phase include the mathematical transformations for a continuous variation of k with the result that there is no way to have a globally continuous phase of the eigenfunction if the path encircles a zero point where the gap vanishes.

A calculation using the discrete formulation Eq. (25.1) is easily done with a small computer program which is left to the reader. However, it is more instructive to go through the arguments by hand with a small number of points and a few examples to see how the result comes about. Even for a small number it is not hard to conclude what the answer must be since the only possibilities are 0 or π mod(2π). One can choose a simple hamiltonian and vary the form to show that the result depends only on whether the path encircles a zero.

Consider the $s - p$ model in Eq. (26.7) with $u = 0$, $\Delta = 0$ and $d = w = 1$ which forms a circle in the h_2, h_3 plane as shown in the left side of Fig. S.4. Consider four k points 0, $\pi/2a$, π/a, $3\pi/2a$, where the hamiltonians $H(k)$ are:

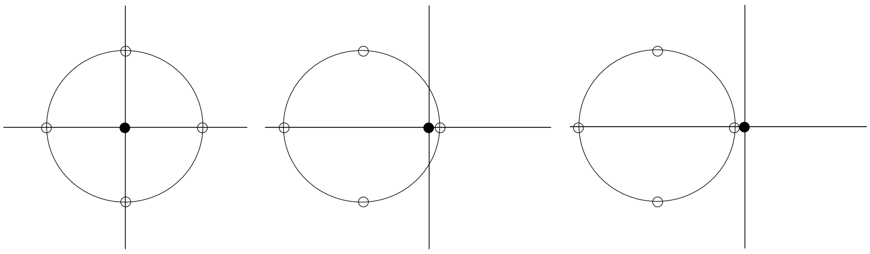


Figure S.4. Path for evaluation of Berry phase in Exercise 26.6.

$$\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}, \begin{bmatrix}0 & i\\ -i & 0\end{bmatrix}, \begin{bmatrix}-1 & 0\\ 0 & 1\end{bmatrix}, \begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}. \tag{S.161}$$

One choice of eigenvalues are ± 1 at each point and eigenvector for the lowest energy -1 are:

$$\begin{bmatrix}0\\ 1\end{bmatrix}, \begin{bmatrix}-i\\ 1\end{bmatrix}, \begin{bmatrix}1\\ 0\end{bmatrix}, \begin{bmatrix}i\\ 1\end{bmatrix}. \tag{S.162}$$

The expression Eq. (25.1) for the accumulated phase around the loop

$$\phi = -\mathrm{Im}\ln[\langle u_0|u_1\rangle\langle u_1|u_2\rangle\langle u_2|\ldots|u_{N-2}\rangle\langle\langle u_{N-2}|u_{N-1}\rangle\langle u_{N-1}|u_0\rangle], \tag{S.163}$$

gives

$$\phi = -[0\ +\ \pi/2\ +\ \pi/2\ +\ 0] = -\pi \tag{S.164}$$

which is a change of sign. It is easy to verify that choosing a different phase for eigenvectors at each point does not affect the result.

To see that the result depends on whether the zero point is inside or outside the path one can consider $\Delta = 1 \pm \delta$ where δ is a small, $\delta << 1$, as shown at the right in Fig. S.4. The calculations are now messier at $\pi/2a$ since the calculation of eigenvalues requires solving a quadratic equation (not very hard!) but the result can be appreciated by considering only the eigenvector for the point at the right for $k = \pi/a$ where the hamiltonian is

$$\begin{bmatrix}+\delta & 0\\ 0 & -\delta\end{bmatrix}. \tag{S.165}$$

The eigenvector for the lowest state can be chosen to be real

$$\begin{bmatrix}1\\ 0\end{bmatrix},\ \text{if } \delta > 0,\ \text{or}\ \begin{bmatrix}0\\ 1\end{bmatrix},\ \text{if } \delta < 0. \tag{S.166}$$

It is easy to verify that the result is the same as in the previous case(change of sign) for $\delta > 0$ since the eigenvector at $k = \pi/a$ is the same. For $\delta < 0$ (the circle does not include the zero point of $|\mathbf{h}|$, the eigenvector is flipped and it is easy to see that the result is

$$\phi = -[0 \ + \ 0 \ + \ 0 \ + \ 0] = 0, \tag{S.167}$$

i.e., no change of sign.
Finally, we can see that these results hold for any set of points that include or do not include the zero! This is because the eigenvectors at $k = 0$ and $k = \pi/a$ always can be chosen to be real. If the eigenvectors do not exchange between 0 and π/a, the eigenvectors are the same and we always get the result $\phi = 0$. If the eigenvectors exchange ($\delta < 0$) and the zero is included in the path. Furthermore, the result is the same for any set of eigenvectors and any set of points that include the $k = 0$ and $k = \pi/a$ points; this can be seen directly if the vectors for k and $-k$ are conjugates which is always a possible choice for a hermitian hamiltonian. Thus we finally have answered the question! We needed the proof for many points since it is only in the limit of many points that the curve is continuous and it is well-defined to say if the path includes the zero point or not.

Very instructive that it is exact!

Exercise 26.7 Derive the analytic solution for the surface state wavefunction as it decays into the crystal for the two-site model. Hint: first show that the state has non-zero amplitude only on A sites if the crystal is terminated on an A site (and similarly for B sites). The solution can be found in [967].

Solution:
The solution follows from the condition that the hamiltonian is terminated at the surface, i.e., it ends with t_1 or t_2 bonds. It is not difficult and it is given in detail in the paper by Pershoguba and Yakovenko, Phys. Rev. B 86, 075304 2012 [967].

Exercise 26.8 Use the results of Exercise 26.7 to explain why the two end states in Fig. 26.4 are degenerate even though the calculation is for a finite size crystal.

Solution:
The proof comes from the solution in the previous proble. As shown in [967], the surface state has non-zero amplitude only on alternate sites, eiethr A or B sites. Thus the two states from the two ends are on different sites they are orthogonal.

Exercise 26.9 In the text is worked out the pump using the 2-site model Eq. (26.8) and a cycle of parameters as shown in Fig. 26.7. Find an equivalent cycle using the $s-p$ model Eq. (26.7) and show that there are equivalent results for the pump.

Solution:
For the $s-p$ model Eq. (26.7) the symmetry is broken only if u is non-zero. In the 2-site model it is clear that if t_1
$neqt_2$ ten the symmetry is broken around a site. That happens in the $s-p$ model if there is interaction of s and p on a site. Thus the cycle is a variation of $\Delta = \varepsilon_p - \varepsilon_s$ and u such that each varies from positive to negative in a cyclic fashion. Physically tey are the same and the exact form can be seen by the relation of the forms for the vector $\mathbf{h}$ in Eqs. (26.6) - 26.8. The results are qualitatively the same if the variation of $\Delta, t_1 - t_2$ is replaced by Δ, u.

Exercise 26.10 Show that a narrow armchair ribbon is an insulator with no edge bands. It is useful to check Exercise 27.9 which shows the gap vanishes in the limit of a wide ribbon, but there are no edge bands.

Solution:

See Exercise 27.9 where it is shown that there is only a point where there the gap vanishes as a function of k parallel to the strip for the infinite width strip. For a finite width, there are a discrete set of bands and a gap, with no edge state.

Exercise 26.11 The counting of the winding numbers is done in the paper of Cao, et al. [236]. The exercise is to go through the arguments in the paper to find the winding numbers as a function of width, and the show that the 7 and the 9 atom ribbons are different.

Solution:

See the paper as suggested in the Exercise. This requires extensive calculations and it is appropriate only to read the paper to see the results.

Exercise 26.12 Show that a junction between two ribbons with different winding numbers has an interface state. The simplest example is the two-site model in Fig. 26.2 with $\Delta = 0$ which is the Su-Schrieffer-Heeger (SSH) model (PRl 42, 1698 (1979) [954]. The famous result is is that there is a bound state an interface between two sections, one with $t_1 > t_2$ and the other with $t_1 < t_2$.

Solution:

There is always an interface state so long as the bulk on each side is insulating and there are different widing numbers. This follows because the difference in winding numbers is a difference Berry phase which means a shift in the relative positions of the Wannier centers on the two sides that means the occupied states must include an extra state at the interface. It may or may not be in the gap. It is midgap if the system has electron hole symmetry everywhere including the interface, but in general is is shifted and may not be a state in the gap. This can also cars in terms of the arguments for the pump: a fraction of the cycle corresponds to a partial shift and if there are integer winding numbers there are integer states that appear at the interface.

CHECK to be sure this is all correct.

Exercise 26.13 This exercise is at two levels. One is to explain the qualitative behavior of the pump shown in Figs. 26.7 and Fig. 26.8. Explain why a cycle that does not enclose the zero point in the upper left figure in Fig. 26.7 is not a pump. The second level is to do a calculation to derive the results. This can be done using available tight-binding codes for a large finite system. Verify that a pump transfers a state from one ene to the other.

Solution:

It is straightforward using the connection of the Berry phase and the shift in the Wannier center. The Berry phase is illustrated in Fig. 25.2 in a way that shows that it can very by multiples of 2π (a shift of the electrons by one lattice constant) or it can return to itself with no shift. A shift corresponds to the loop in the upper left of figure, and no shift results if it does not enclose the zero. The calculation and the proof are actually the same as in Exercise 26.6 where the logic and the proof by induction is given.

Solutions for Chapter 27
This is a new Chapter in second edition

Exercise 27.1 Show that the matrix $W_{mn}(\mathbf{K}_a) = \langle u_{m-\mathbf{K}_a}|\mathcal{T})|u_{n\mathbf{K}_a}\rangle$ defined after Eq. (27.4) is skew symmetric (a matrix with $A_{ij} = -A_{ji}$). Check the original paper by Fu and Kane, Phys. Rev. B, 76, 045302 (2007) [972] and summarize the derivation of the formula involving Pfafians.

Solution:

The operation for time reversal $\mathcal{T}$ is conjugation with a spin flip. The spin operation can be written $i\sigma_y$ which flips the spin and changes the sign of one component and $\mathcal{T}^2 = -1$. (If there were no spin–orbit interaction, the set of up spin functions are flipped to down spin functions that are orthogonal so that the W's would be zero.)

The derivation of the formula in terms of Pfafians is in [972] and the earlier paper by Kane and Mele PRL 95, 146802 (2005) [86]. The arguments are related to the variation of the wavefunctions in a way that is related to the simpler derivations for the case where there is a center of inversion, but they are more general. See also the book by Vanderbilt [918].

Derivation referred to original refs and Vanderbilt book.

Exercise 27.2 Work out explicitly for yourself the conclusion that all cases reduce to even or odd and the relation to the Shockley problem stated in Section 27.4.

Solution:

Meant for the reader to do!

Exercise 27.3 Show that for zero spin–orbit interaction the bands for the square lattice have the general form shown in the left figure in Fig. 27.6 with degeneracies at high symmetry points as shown.

Solution:

The purpose of this problem is to examine what can be established just from symmetry. The basis is one s and two p states and spin is not relevant. Since there is a center of inversion, at Γ the s and p states do not mix. Since there ios 4-fold rotation symmetry the p state must be degenerate. The same at the M point (π,π). Along the line from Γ to X the s state mixes with one of the p states and not with the other, e.g., s mixes with p_x along the line $(0,0)$ to $(\pi,0)$. Along Γ to M the s state mixes with one p states. (This model obscures some features of the bands. The flat bands and the near degeneracy of the p bands along part of the line from Γ to M are artifacts of this model with only nearest neighbor $pp\sigma$ matrix elements.)

Exercise 27.4 Show that the bands do not cross at general **k**-points and the parities of the bands at the TRIM lead to a Z_2 odd state for any non-zero spin–orbit interaction. Give an example of a gauge transformation can change the parity at any one point, but the product remains the same. (Hint: There are more than one centers of inversion.) Show also that the definition in terms of Pfaffians gives the same result.

Solution:

The bands do not cross at general k-points in the surface BZ because they have the same symmetry. To see this it is sufficient to notice that the only symmetries for the surface

(a one-dimensional edge) are time-reversal and inversion in the direction parallel to the surface. Only at the TRIM are states with k and $-k$ the same (modulo $2\pi/a$) and $k\uparrow$ and $-k\downarrow$ are degenerate by symmetry.
An example of a gauge that affects each TRIM point and leaves the total invariant is a choice of the center of inversion at the center of the cell between atoms in the bulk.
NOTE: NOT FINISHED showing the Pfaffian result. See note - not finished

Exercise 27.5 Find the value of the ratio that leads to a zero gap for the model in used in Fig. 27.9. This can be done with a relatively simple calculation for the bulk bands at the zone boundary. Does the result agree with the transition point in Fig. 27.9?

Solution:
This is "relatively simple" since one can decide on the point in the BZ where the bulk band gap must vanish (the zone boundary) with no calculations; however, it still involves a 3×3 matrix since the is a competition between the spin–orbit interaction and the ratio of x and y matrix elements.

The 3×3 matrix matrix is the hamiltonian give in the text and the SO interactionfor p states given for example in the solution of thew next problem, but simplified here sine it is only two dimension.
NOTE: NOT FINISHED - left to reader to solve 3x3 problem. See note - not finished

Exercise 27.6 Starting with the full sp^3 model on a honeycomb lattice, show that in a model appropriate for graphene with only p_z states near the Fermi energy and nearest neighbor hopping, derive the perturbation expressions for the effects of spin–orbit interaction. Show that in the approximation that spin is conserved ($\uparrow$ or $\downarrow$), this leads to an effective hamiltonian with complex second-neighbor hopping. Hint: Even if there is no direct hopping to second-neighbors, show that there is hopping to a second neighbor due to spin–orbit interaction on the atom that is in between - a second-order effect. Estimate the size of the interaction using the spin–orbit interaction for the atom which can be found in the literature, and show that the final effect is indeed extremely small.

Solution:
The π bands are purely p_z is there is no spin–orbit interaction. There is no matrix element with p_x and p_y which have opposite parity in the z direction. However, spin–orbit interaction adds a term that mixes p_x, p_y and p_z. Since it is a small perturbation it is sufficient to consider the effective matrix element for two spin up p_z states on second neighbors due to the spin–orbit interaction on the atom between them. Note that the intermediate state is not purely spin up.
The matrix element for coupling of the $p_z\uparrow$ and the $p_{x,}\downarrow$ states on an atom are given by the expression at the right in Eq. (14.12),

$$H_{SO}(\downarrow\uparrow) = \begin{bmatrix} 0 & 0 & \zeta \\ 0 & 0 & -i\zeta \\ -\zeta & i\zeta & 0 \end{bmatrix}. \tag{S.168}$$

Since the first-neighbor hopping t is spin-independent, the effective second-neighbor hopping is second order in H_{SO}. For hopping to the neighbor at an angle of $-\pi/6$ to the right is the zz component of the matrix

$$H_2(\uparrow\uparrow) = t^2 H^{SO}_{1,0} * H^{SO}_{cos(-\pi/6),sin(-\pi/6)}/\Delta E^3, \tag{S.169}$$

where ΔE is the difference of z and x, y energies. This is

$$H_2(\uparrow\uparrow) = \frac{\zeta^2 t^2}{\Delta E^3} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & -i \\ -1 & i & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & c-is \\ 0 & 0 & -ic+s \\ -c+is & ic-s & 0 \end{bmatrix}, \tag{S.170}$$

where $c = cos(-\pi/6)$ and $s = sin(-\pi/6)$. Taking the zz component we find

$$H_2(\uparrow\uparrow)_{zz} = \frac{\zeta^2 t^2}{\Delta E^3} 2isin(-\pi/6)^2 = -i\frac{\zeta^2 t^2}{2\Delta E^3}. \tag{S.171}$$

CHECK!

CHECK Exercise 27.6. Be sure ΔE^3 imag. parts are correct?

Note that the effect is opposite for left and right hopping and is zero for straight-ahead hopping. Time reversal symmetry is obeyed since the oppiste happens for the opposite spin.

Exercise 27.7 Show that in the bismuthene system described in Section 27.9 the spin–orbit interaction is first-order effect, i.e., it does not require other bands. Calculate the eigenvalues at at high symmetry points for a nearest neighbor hopping model and estimate the size of the effects. Compare with the observations in the 2017 Science paper by Reis, et al. [979].

Solution:

This is described in detail in the supplementary material for [979]. Here we give a summary. (In the opinion of the author) is sufficient for understanding the problem.)

In this case the states near the Fermi energy are primarily p_x and p_y and we consider the system as purely two dimensional ignoring p_z bands that are in the bonding states with the substrate.

If we first consider the $p_x - p_y$ bands ignoring the spin–orbit interaction then we must consider two states per site and two sites A and B per cell of the honeycomb lattice. The on-site energies for p_x and p_y are the same by symmetry since there are three-fold rotations around each site. In a nearest-neighbor model there are only AB matrix elements that are $V_{pp\sigma}$ and $V_{pp\pi}$. It is straightforward to the basis can be chosen as in the square lattice as $p_x \pm ip_y$. If we approximate the system then we can consider only the

IS THIS USEFUL? z component of the spin is conserved and the problem decouples into two distinct bands with spin up and down respectively (like two Chern insulator states) split by $\pm\zeta$. which are split by the spin–orbit interaction into $J_z = 3/2$ and $J_z = 1/2$.

Exercise 27.8 Show that a wide strip of graphene with a zigzag edge has an edge state like that shown in left side of Fig. 27.14. The answer is given in the text and this exercise is to verify the statements.

Solution:

Left for reader to over statements in text.

Exercise 27.9 An armchair edge is one that ends on pairs of atoms. It is the same as the edges on the nanoribbon in Fig. 26.9 for the case where the ribbon is very wide. (It is also the same as an end of a nanotube in Fig. 14.7.) Show that the projected bulk density of states has only one point is the surface BZ where the gap vanishes, and there is no surface state. See also Exercise 26.10 for a narrow nanoribbon.

Solution:

A wide armchair nanoribbon corresponds to a buld crystal oriented as shown in the figure. Consider the corresponding BZ and projection in the direct perpendicular to the edge in the figure. It is straightforward to see that the projection has only one point in the surface BZ with zero gap.

Solutions for Chapter 28

This is a new Chapter in second edition

Exercise 28.1 Consider a bilayer formed by bringing together two planes each with Z_2 odd. For each plane there are two oppositely circulating currents. Give the arguments that with weak coupling no gap should vanish in the bulk, and the counting rules for even and odd number of crossings in Section 27.4 imply that this is a Z_2-even case. Sketch how this could happen by considering anti-crossing points between weakly coupled bands.

Solution:

As shown in Section 27.4 for a single layer states at k=0 must be degenerate so there is no gap at any energy in the gap. However, if there are two layers, there are two bands, even and odd at high symmetry points. They are shifted in energy and cross at points in the BZ at non-zero k where they can mix and create a gap. Note that there are special cases where the states are even and off at all k and the states do not mix, but there depend on the crystal symmetry and hamiltonian and are not generic.

Exercise 28.2. Show that the cases marked $(0; 011)$ and $(0; 111)$ in Fig. 28.1 correspond to stacks of planes along other directions in the crystal.

Solution:

The cases marked $(0; 011)$ and $(0; 111)$ in Fig. 28.1 each have black dots in a line so that the crystal can eb viewed as a stack of planes perpendicular to those lines.

Exercise 28.3 Describe explicitly how one can ensure the vanishing of an energy gap for some range of hamiltonians in three dimensions but not two. Hint: for $\mathbf{k}$ in three dimensions, the condition $h_1(\mathbf{k}) = 0$ can occur for a two-dimensional surface. Continue the argument to reach the conclusion.

Solution:

This is a matter of filling in the steps in the arguments. The condition for a gap in the BZ not at a symmetry point is that both real and imag. parts of $H(\mathbf{k})$ vanish. In 2D, there are only two variables k_x and k_y and in general there is only be one point where both vanish. But in 3D there are three variables k_x, k_y and k_z; for a range of hamiltonians, there can be a point in where the two conditions are satisfied.

Exercise 28.4 Show that in the absence of a magnetic field ($b = 0$) the expression Eq. (28.4) reduces to a Dirac-like equation with the speed of light c replaced by v. The addition of a Zeeman term $b\sigma_z$ completes the derivation of Eq. (28.4). Also derive Eq. (28.5).

Solution:

For $b = 0$ the equations are linear in $\mathbf{k}$ as shown in Eq. (28.3) with energies that are symmetric plus and minus. Derivation of Eq. (28.5) is a matter of carrying through the equations using the Pauli matrices for σ and τ. Thus this involves 4×4 matrices, which can be simplified to 2×2 by inspection. See the nice discussion in the RMP review by Armitage [986] Sec. 3B.

Exercise 28.5 Solve for the energies for three cases: (1) $m = b = 0$; (2) $m = 1,\ b = 0.5$; and (3) $m = 0.5,\ b = 1.0$. Show that these parameters lead to the results with the form shown in Fig. 28.6. (These are three of the cases that are shown in fig. 2 of [986])

Solution:
This is a matter of carrying through the equations using the Pauli matrices for σ and τ. Thus this involves 4×4 matrices, which can be simplified to 2×2 by inspection.

Exercise 28.6 Show that near the zero-gap nodes, the hamiltonian has the form of the Weyl hamiltonian in Eq. (28.1).
Solution:
This is follows since near the zero gap point the energies are linear with $\mathbf{k}$ with the form $\mathbf{k} \cdot \boldsymbol{\sigma}$, as derived in the previous exercises.

Exercise 28.7 Go through the arguments to convince yourself that this problem is indeed the same as the problem for spins. See also Exercise 26.6 for the one-dimensional two-band problem.
Solution:
This is meant to be a problem to work out yourself, and to see that it is the same as the reason the two-band problems can be cast in terms of Pauli matrices in Chap. 26, the relation to spin in App. P, sech as in Sec. P.7, and so forth.

Solutions for Appendix A
Same as in first edition

Exercise A.1 Show that Eq. (A.5) follows from (A.3), and that application of the expression to the Thomas–Fermi approximation leads to expression (6.4).

Solution:
See Exercise 6.1.

Exercise A.2 Derive the form of the variational expression in (A.10) involving the gradient terms.

Solution:
This expression follows from the previous two equations using integration by parts. To prove integration by parts one must show the boundary terms vanish which follows for a finite system since the functions vanish outside the system and for periodic systems since the boundary terms vanish for integration over a periodic cell.

Solutions for Appendix C [No exercises for Appendix B]

Exercise C.1 Show that the requirement that Ψ is normalized is sufficient to prove $A_{ii} = 0$. Hint: Use the fact that any derivative of $\langle \Psi || \Psi \rangle$ must vanish.

Solution:
The normalization condition is $\langle \Psi | \Psi \rangle = 1$. The perturbed wavefunction is $\Psi + \delta\Psi$ which must be normalized $\langle \Psi + \delta\Psi | \Psi + \delta\Psi \rangle = 1$. Thus to first order $\langle \Psi | \delta\Psi \rangle + \langle \delta\Psi | \Psi \rangle = 0$. If the wavefunction is real each term must vanish $\langle \Psi | \delta\Psi \rangle = \langle \delta\Psi | \Psi \rangle = 0$. This is sufficient for the desired proof for any matrix element for a Hermitian operator and a physical quantity such as the density, energy, force, etc., which must be real.

This is an example of the consequence of normalization that occurs for any variation of the hamiltonian. For example see Section D.1 where the change in the ground state wavefunctions is only by mixing in the unoccupied states. Another example is the construction of basis functions in Exercise 17.1 for the variations as a function of energy. The normalization requirement leads to the consequence that the expression $\langle \psi | \partial_x \psi \rangle$ is purely imaginary which is used in several places in the expressions for the Berry phase and Berry connection (see Exercise P.2 and Exercise 25.2).

Exercise C.2 Derive the equation for nuclear motion, (C.7), from (C.4) using the assumption of the adiabatic approximation as described before (C.7).

Solution:
This is really just following the prescription to define the equations and to recognize that the adiabatic approximation is that the occupied electronic wavefunctions vary as a function of the positions of the nuclei but they do not change order, i.e., there is no exchange where empty states become filled and vice versa. This is violated if there is level crossing, e.g., in a molecule, where the adiabatic approximation fails.

Exercise C.3 For small nuclear displacements about their equilibrium positions, show that (C.7) leads to harmonic oscillator equations.

Solution:
This is also just a simple exercise that depends upon U acting a a potential that is a function of nuclear positions and expanding the second order. Note that U has a subscript i for the electronic state. This is a general expression that holds for ground and excited states so long as the states do not cross. The normal case for solids is that i is the ground state for the electrons that varies as the atoms move but alays the instantaneous ground state.

Exercise C.4 For a simple diatomic molecule treated in the harmonic approximation, show that (C.7) leads to the well-known result that the ground state energy of the nuclear–electron system is $E_{min} + \frac{1}{2}\hbar\omega$, where ω is the harmonic oscillator frequency.

Solution:
This is a standard problem in undergraduate quantum mechanics not worked out here. The energies of the harmonic oscillator are $(n + 1/2)\hbar\omega$.

Solutions for Appendix D

Exercise D.1 Derive the general form of the density response function χ_n in Fourier space, (D.8). This applies to any function, periodic or non-periodic.

Solution:
The expression Eq. (D.8) is general since any function can be expressed in the terms of Fourier components. It is just a transform of the expression in Eq. (D.5) and it follows from integrating the expression in Eq. (D.5) with $e^{i\mathbf{q}\cdot\mathbf{r}}e^{i\mathbf{q}'\cdot\mathbf{r}'}$. In a crystal Eq. (D.8) simplifies as indicated after the equation.

Exercise D.2 Derive the second form given in (D.14) from the first expression. Hint: Move all terms involving χ to the left-hand side, solve for χ in terms of χ^0 and K, and invert both sides of the equation.

Solution:
This is a matter of knowing what to do and some algebra. Following the hint, the first step is $\chi[1-\chi^0K]=\chi^0$ and the rest is algebra. The first expression in Eq. (D.14) is must useful to see that χ diverges if $\chi^0K=1$ and the second brings out the correction to χ^0, which is most easily expressed in terms of the inverses.

Exercise D.3 See Exercise 7.20 for the way in which the response function can be used to analyze the form of the energy functionals near the minimum.

Solution:
See Exercise 7.20.

Exercise D.4 Show that the response of a harmonic oscillator, Eq. (D.16), obeys the KK relations. Hint: The key point is the sign of the damping term that corresponds to energy loss, i.e., $\Gamma > 0$. See Exercise D.5 for an explanation.

Solution:
This is an example where one should first go to the general analysis in the next problem. It follows from the general theory of complex variable that the KK relations hold for any function with no poles in the upper half-plane, and we understand the definition of a principal part.

Exercise D.5 Derive the KK relations, Eq. (D.18), from the analytic properties of the response functions. Causality requires that all poles as a function of complex frequency z be in the lower plane $\Im z < 0$. Hint: An integral along the real axis can be closed in the upper plane with a contour that is at $|z| \to \infty$. Since the contour encloses no poles, the line integral vanishes; also the integral at infinity vanishes. The integral along the axis can be broken into the principal value parts and the residue parts leading to Eq. (D.18). See the book by Pines and also material in the book by Marder [297, 300].

Solution:
The KK expressions are widely used for response functions and can be found in many places. In addition to the references given a good deception is in Kittel. (In the 6th edition

of Kittel it is Eqs. 10 -20 in Ch. 11. It may be different in other editions. There Kittel gives the explicit integrals for the principal parts in addition to the analysis in the complex plane. The contour integral along the real axis and closed at high frequency in the upper or lower planes is equal to $2\pi i$ times the sum of residues for the poles. The integral in the upper half plane vanishes as explained in the problem, so that the contour integral vanishes. But due to factor $1/(\omega - \omega')$ there is a pole of the real axis in the integrand. The integral over ω' can be divided into the principal parts plus a segment that goes around the point $\omega = \omega'$ in the upper plane. The latter is $1/2$ the integral around the pole $\pi i \chi(\omega)$. Since the total integral must be zero, the real and imaginary parts of the integral lead to the two equations for the relation of the real and imaginary parts given in the KK expressions.

Exercise D.6 Derive the formula (D.36) for energy to third order from the preceding equations.

There is an error in Eq. (D.36) in the text. Somehow the tex file was messed up the Eq. is completely wrong. It was correct in the first edition (in Ch. 3). This correct equation is (note definition of $\bar{H}$ given below):

$$\begin{aligned} 0 = &\langle \psi^{(3)} | \bar{H}^{(0)} | \psi^{(0)} \rangle \\ &+ \langle \psi^{(2)} | \bar{H}^{(1)} | \psi^{(0)} \rangle + \langle \psi^{(2)} | \bar{H}^{(0)} | \psi^{(1)} \rangle \\ &+ \langle \psi^{(1)} | \bar{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(1)} | \bar{H}^{(1)} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \bar{H}^{(0)} | \psi^{(2)} \rangle \\ &+ \langle \psi^{(0)} | \bar{H}^{(3)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \bar{H}^{(2)} | \psi^{(1)} \rangle + \langle \psi^{(0)} | \bar{H}^{(1)} | \psi^{(2)} \rangle + \psi^{(0)} | \bar{H}^{(0)} | \psi^{(3)} \rangle, \end{aligned} \tag{S.172}$$

where we have defined $\bar{H}^{(j)} = \hat{H}^{(j)} - \varepsilon^{(j)}$ for each order j to simplify the notation.

Solution:

This equation is used to derive the expression in (D.36) for the energy to third order $\varepsilon^{(3)}$ using the condition the each row and column sum to zero. The desired result follows by requiring the sum of the last line the be zero. We can use the fact that $\bar{H}^{(0)} | \psi^{(o)} \rangle = 0$ to see that the last term is zero. The first term is $\langle \psi^{(0)} | \bar{H}^{(3)} | \psi^{(0)} \rangle = \langle \psi^{(0)} | (\hat{H}^{(3)} - \varepsilon^{(3)}) | \psi^{(0)} \rangle = \langle \psi^{(0)} | \hat{H}^{(3)} | \psi^{(0)} \rangle - \varepsilon^{(3)}$. The term involving $\psi^{(2)}$ can be replaced by terms involving only $\psi^{(0)}$ and $\psi^{(1)}$ using the third row and third column, with the result that $\langle \psi^{(0)} | \bar{H}^{(1)} | \psi^{(2)} \rangle = \langle \psi^{(1)} | \bar{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(1)} | \bar{H}^{(1)} | \psi^{(1)} \rangle = \langle \psi^{(1)} | \bar{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(1)} | (\hat{H}^{(1)} - \varepsilon^{(1)}) | \psi^{(1)} \rangle$. Combining these results leads to (D.36). In summary, the trick is that the terms involving $\psi^{(2)}$ can be replaced by ones that involve only $\psi^{(0)}$ and $\psi^{(1)}$ and the eigenvalue to first order $\varepsilon^{(1)}$ which is determined by $\psi^{(0)}$ and $\psi^{(1)}$. The generalization of this analysis leads to the general results for $2n + 1$ theorem.

It is useful to note that the higher order terms $\hat{H}^{(2)}$, $\hat{H}^{(3)}$, etc., arise only in a system with an effective hamiltonian that changes due to the changes in the wavefunctions, i.e., a self-consistent Kohn–Sham problem. For a perturbation in a text-book case with a fixed $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$, there are no tems like $\hat{H}^{(2)}$ or $\hat{H}^{(3)}$.

Exercise D.7 Exercise 20.10 considers the variational principle in perturbation theory applied to a system composed of two springs. Let each spring have a non-linear term $\frac{1}{2}\gamma_1(x_1 - x_0)^3$ and similarly for spring 2. Find an explicit expression for the change in energy to third order due to the applied force.

Solution:

This is a poor choice of a problem! One reason is that it is not clearly stated that we want to quantum solution for the oscillators. See also below for why it is rather trivial as stated.

The system in reduces to two harmonic oscillators. If $k_1 = k_2$ the result is two degenerate oscillators. If they are different, one can always transform to two independent oscillators and the non-linear term is the same for each. Therefore we need analyze only one oscillator that can be defined by $E = \frac{1}{2}kx^2 + \frac{1}{2}\gamma x^3$.

As stated in the pervious problem solution, the higher order terms $\hat{H}^{(2)}$, $\hat{H}^{(3)}$, etc., arise only in a system with an effective hamiltonian such as a self-consistent Kohn–Sham problem. Here we have only $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$. The energy is given by

$$\varepsilon^{(3)} = \langle \psi^{(1)} | \hat{H}^{(1)} - \varepsilon^{(1)} | \psi^{(1)} \rangle. \tag{S.173}$$

This problem is rather trivial because the perturbation in odd the first order change in energy is zero, and the change in wavefunction is odd, $\langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle = 0$. So the third order term t vanishes. There is a second order term given by the usual perturbation expression, which does not illustrate the $2n + 1$ theorem!

Solutions for Appendix E

Exercise E.1 Derive Eq. (E.12) for the dielectric tensor at high frequency using only the fact that electrons respond as free particles at sufficiently high frequency. It may be helpful to relate to the high-frequency limit of the harmonic oscillator response function given in Section D.4.

Solution:
At high frequency the electrons respond as a system of charged particles that are free, i.e., independent of the lattice, and the analysis is given in Section 5.5. At high frequency the electrons act like an oscillator with frequency ω_P and the dielectric function approaches $\epsilon \to 1 - \omega_P^2/\omega^2$, as given in Eq. (E.12).

Exercise E.2 Show that the f sum rule, (E.13), follows from the high-frequency behavior in Equation (E.12) and the Kramers-Kronig relations, (D.18).

Solution:
From the first of Kramers-Kronig relations in Eq. (D.18), we can see that in the limit of high frequency

$$\mathrm{Re}\chi(\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\mathrm{Im}\chi(\omega')}{\omega - \omega'} \to -\frac{1}{\pi\omega}\int_{-\infty}^{\infty} \mathrm{d}\omega' \mathrm{Im}\chi(\omega')(1 + \omega'/\omega). \qquad \text{(S.174)}$$

Using the expression valid at high frequency $\epsilon - 1 \to -\omega_P^2/\omega^2$, where $\epsilon - 1$ is the response function, we find

$$\int_0^{\infty} \mathrm{d}\omega' \mathrm{Im}\epsilon(\omega')\omega' = \frac{\pi}{2}\omega_P^2, \qquad \text{(S.175)}$$

where we have used the fact that the imaginary part of the repones function is odd in frequency to transform to an integral over positive frequencies. (The integral over $\mathrm{Im}\epsilon(\omega')$ is zero and over $\omega'\mathrm{Im}\epsilon(\omega')$ is twice the integral from 0 to ∞.)

Exercise E.3 Show that Eq. (E.15) results from the definition of internal and external charges in Eq. (E.4) and the definition of ϵ^{-1} in Eq. (E.14).

Solution:
This exercise is really just the definitions and some algebra. The idea is that ϵ^{-1} defined in the left equation in Eq. (E.14) is the change in the total internal field per unit external field. Since the total is external plus internal, we arrive at the delta function plus the internal response which is V_C times χ defined in Eq. (D.9). The equations following Eq. (D.9) show useful relations, but they are not really needed.

Exercise E.4 The expression for the macroscopic dielectric function, Eq. (E.17), can be derived by carefully applying the definition that it is the ratio of external to total internal fields given in Eq. (E.17) *for the case where there are no short wavelength external fields*, $V_{\mathrm{ext}}(\mathbf{q} + \mathbf{G}, \omega) = 0$ for $\mathbf{G} \neq 0$, and using the definition that the inverse function is the response to external fields. Use these facts to derive Eq. (E.17).

Solution:

The definition of the macroscopic dielectric constant is the ratio of macroscopic applied external field to macroscopic internal field. There are no applied microscopic external fields (fields that vary of the scale of the unit cell and defined by non-zero $\mathbf{G}$ components); but there may be generated microscopic internal fields. Thus the useful approach is to find the response to the external field which is given by ϵ^{-1}; this includes macroscopic and microscopic internal fields and we define the dielectric constant by taking only the macroscopic part of the internal fields. Thus

$$V_{int}(\mathbf{G}) = \epsilon^{-1}(\mathbf{G}, 0)V_{ext}(0) \tag{S.176}$$

so that

$$V_{int}(0) = \epsilon^{-1}(0, 0)V_{ext}(0) \tag{S.177}$$

and

$$\epsilon_{macro} = V_{ext}(0)/V_{int}(0) = 1/\epsilon^{-1}(0, 0). \tag{S.178}$$

A detailed derivation with the relation to $\epsilon(0, 0)$ and local field corrections is given in Pick, R., Cohen, M. H. and Martin, R. M., "Microscopic theory of force constants in the adiabatic approximation," *Phys. Rev. B* 1:910–920, 1970.

Solutions for Appendix F

As stated below, there is a mistake in the second edition that two problems (Ex F.6 and 7 in the first ed.) are omitted. They are computational problems so solutions are not given, but it leaves out the instruction to make a code and it changes the numbering.

Exercise F.1 Show that the potential in (F.4) has zero average value as claimed. As a hint in the reasoning, the final term can be considered as the limit $G \to 0$ of the middle term.

Solution:
The average value is the integral over a cell. Since the terms with non-zero $\mathbf{G}$ vanish, the only thing is consider is the integral of $\mathbf{r}$ of the first term and the last term. It is a matter of integrating over the $erfc$ terms to show that these terms cancel to give an average value of zero. See, for example, thye paper by Frasewr, et al., Phys. Rev. B, 53, 1814 (1996) [1018].

Exercise F.2 Discuss the values of the Madelung constant in Table F.1. Compare these with the result of the previous problem. Why are the values larger or smaller? Rationalize the variation of α among the structures.

Solution:
This exercise was meant to be after Exercise F.3. It should say to compare with the result of Exercise F.3.

This is a qualitative discussion question. The value for a close-packed system should be close to the value for the neutral sphere since the system can be considered to be a sum of neutral Wigner-Seitz cells, each of which can be approximated as spherical. indeed this is the case as shown in the bottom line of the table. However, the simple cubic lattice has higher energy and the diamond lattice yet higher because the near-neighbor positive nuclei are closer together and the Wigner-Seitz cells are further from a spherical shape.

Exercise F.3 The problem of a point charge at the center of a sphere with a neutralizing uniform charge density can be solved analytically. Derive the expressions given for the potential, (F.9) and energy, (F.10). Hint: Use the knowledge that the potential due to the uniform distribution must vary as r^2 (Why?) and that the last term in (F.9) has been chosen to make $V = 0$ at the boundary for the neutral cell (Why?). (Related analysis is given for the Wigner interpolation formula for electron correlation energy by Pines [297], p. 92–94.)

Solution:
The fact that the potential due to the uniform charge density is proportional to r^2 is one of the classic problems in freshman physics that the gravitational potential inside the earth is proportional to r^2. It results from the fact that the electric field at point r is $E(r) n_{inside}(r)/r^2$ where $n_{inside}(r)$ is the total charge inside the sphere of radius r, which is Zr^3/R^3 where Z is the total charge. Thus $V(r) = \int E(r)dr = \frac{Z}{2} Zr^2/R^3$. This leads to the expression in (F.9) with the choice that the total potential is zero at the boundary. This follows from the definition that the potential is zero at infinity and field is zero outside the neutral sphere. Thus the integral of the field to from infinity to R is zero. In the expression

for the energy in (F.10) the first term is the ion interacting withe the uniform density. (Note that e is negative in the formulas in text. It is omitted here.))

The energy is the sum of the nucleus-electron term and el-el interaction. Since the unform density is $n = Z/(4\pi R^3/3) = Z\frac{3}{4\pi R^3}$, E_{ne} is

$$E_{ne} = -Z^2 \int 4\pi r^2 drn/r = Z^2 \frac{3}{R^3}\frac{1}{2}R^2 = -\frac{3}{2}\frac{Z^2}{R} \tag{S.179}$$

The self-interaction of the uniform density is the one-half the integral of the density times the potential due to the density given in (F.9)

$$E_{ee} = \frac{1}{2}\int 4\pi r^2 drnV(r) = -\frac{1}{2}Z^2\frac{3}{R^3}\int r^2 dr(\frac{r^2}{R^3} - \frac{3}{2R}) = -\frac{3}{2}(\frac{1}{10R} - \frac{1}{2R}). \tag{S.180}$$

The expressions can be put in the form of (F.9) with some algebra, and the main result is that the total energy is (F.9),

$$E_{tot} = -\frac{9}{10}Z^2. \tag{S.181}$$

Exercise F.4 Show that the two expressions for the Ewald energy, (F.6) and (F.7), are equivalent. As a first step in the proof show that the right-hand side of (F.7) is real. Hint: Expand exponentially and use the cosine addition formula $\cos(A - B) = \cos A \cos B + \sin A \sin B$.

Solution:

The result follows by applying the relation $\cos(A - B) = \cos A \cos B + \sin A \sin B$ to the left side where A and B correspond the τ_s and $\tau_{s'}$. The right side is $\cos A \cos B + \sin A \sin B$, using the same relation that A and B correspond to τ_s and $\tau_{s'}$, plus cross terms $icos(A)sin(B)$ that are imaginary, which must vanish in order for the sum to be real. This is due to the condition stated before that the cell must be chosen so there is no net polarization, i.e., $\sum Z_s \tau_s = 0$. In an ionic crystal this may seem tricky to do. For example for a cell with two atoms of charge ± 1, one can choose the origin at the ion with charge -1 ($\tau_1 = 0$ so the sin term is zero) and the ion with charge $+1$ considered to be at the cell boundaries with charge $+1/2$. Then the sum is centered on the origin and the sum of sin terms is zero.
(NOTE: In fact, this is one of the clever ways that convergence sums purely in real space can be generated by summing over neutral cells such as this.)

Check that this choice is really needed!

Exercise F.5 Explain the meanings of the terms in real and reciprocal space in (F.6) in terms of the physical interactions of gaussian charge distributions, and verify the statements made in the interpretation following (F.7).

Solution:
The first line of Eq. (F.6) is only conditionally convergent. Each of the terms for s and

s' diverges. The next lines provide a well-defined result where the sum in real space is the difference between the sum for point charges and the the sum for gaussian charges, which converges.The sum over non-zero $\mathbf{G}$ also converges; it is the energy of the gaussian charges except for the $\mathbf{G} = 0$ term. As explained following Eq. (F.6), the first term in the last line removes the self term. Finally all the convergence problems are swept into the $\mathbf{G} = 0$ term, and the last term is the limit for $\mathbf{q} \to 0$

There is a mistake in the second edition. Before the following exercises there should be an exercise to construct a program to perform Ewald sums given in Eq. (F.4), or find a program. (It is not a difficult job to make such a program.) It to be used in the following problems Exercise F.6 to Exercise F.11. These are numerical problems not solved explicitly here, except for the analytic part of Exercise F.7.

Exercise F.6 For a chosen simple crystal structure calculate the energy versus lattice constant a. Show that it varies as $1/a$. From the slope of energy vesus volume, calculate the pressure. Check that this agrees with the pressure given by the stress theorem, Eq. (F.13).

Solution:
Computation exercise not worked out here.

Exercise F.7 Show analytically that in the simple crystal structures in Table F.1, the force on each atom vanishes. Verify this numerically using the force theorem.

Solution:
The analytic demonstration is that for a crystal with atoms at a center of inversion the sum for the force involves equal and opposite forces that sum to zero. For the diamond and zinc blende structure the sum of forces due to neighbors in a tetrahedral symmetry also sums to zero.

The remaining problems are computations and solutions are not given here.

Exercise F.8 Construct a crystal with two atoms per cell, e.g., diatomic molecules with spacing d placed on an fcc lattice with lattice constant a. Calculate the energy for several values of d; from the slope calculate the force on an atom and compare with the force found using the force theorem, (F.11).

Exercise F.9 Following the previous problem, calculate the stress using the stress theorem, Eq. (F.13), and compare with the slope of the energy versus lattice constant a. Give the analytic proof that the stress is given by scaling *both* d and a, and also show this numerically by direct calculation.

Exercise F.10 Consider a molecule represented by plus and minus charges so that it has a dipole moment. Place the molecules on a simple cubic lattice and evaluate the Ewald energy. Now make the cell long in one direction so that it is orthorhombic with $a = b \ll c$. (Be sure that the program sums over sufficient vectors in both real and reciprocal space for this anisotropic case.) Find the energy for dipoles along the c direction and for dipoles oriented along a. Are they different? Why? What does this have to do with Chapter 24?

Exercise F.11 Modify the program to calculate the potential at an arbitrary point. For the case in the problem above with dipoles along the c direction, show that the potential has the dipole offset given by Eq. (F.22). Vary the in-plane lattice constant $a = b$ (but still with $a = b \ll c$) and show the point stated in Section F.5 that variation of the fields in the plane decreases exponentially as a function of distance from the plane of dipoles.

Solutions for Appendix G

Exercise G.1 Show that for particles interacting via two-body central potentials the contribution to the stress tensor is given by the generalized virial expression Eq. (G.6). Further, transform the expression to the symmetric form Eq. (G.7).

Solution:
The so0lution to this and the next exercise are not written out here. They are given in detail in the paper Nielsen, O. H. and Martin, R. M., "Quantum-mechanical theory of stress and force," *Phys. Rev.* B 32(6):3780–3791, 1985. The key aspects are that the effect of the strain dilation is proportional to the position $\mathbf{r}$ of a particle and the change in energy is the force times displacement as in Eq. (G.6). This would be an unphysical expression except for the fact that there is always an equal and opposite force on the other atom in the pair; for short range forces this means only local relative dilations matter and not the absolute position. This is shown explicitly in the symmetric form Eq. (G.7) which explicitly sums over the pair and the dilation of the distance between the atoms in the pair. Eq. (G.7) can be derived by carefully counting the equal and opposite forces on the atoms in each pair.

Exercise G.2 Derive the expression, (G.8), for the Hartree contribution to the stress tensor.

Solution:
As stated in the previous problem, the detailed deviation is in the paper by Nielsen and Martin. The dilation is expressed in terms of the reciprocal lattice in analogy to expressions in real space. The geometrical factors $\frac{\mathbf{G}_\alpha \mathbf{G}_\beta}{G^2}$ are analogous to the factors in the real space expression.

Exercise G.3 Using the argument of the scaling of reciprocal space, show that the kinetic contribution to the stress can be written in the form (G.10), which is convenient for plane wave calculations.

Solution:
The kinetic energy in k-space is very straightforward. Because it is simple k^2 the dilation of space is isotropic and has the same form in all cases that given in the text. It is the same in classical virial theorem in thermodynamic where the kinetic energy is proportional to velocity squared. See the Nielsen paper for more description.

Exercise G.4 Find the elastic constant $C = \mathrm{d}^2E/\mathrm{d}L^2$ and the internal strain parameter Γ defined by Eq. (G.14) for a one-dimensional chain of diatomic molecules. The atoms in a molecule are spaced a distance R_1 and are connected by a spring with constant K_1; spacing between the molecules is R_2 and they are connected by a spring with constant K_2. The cell length is $L = R_1 + R_2$. Show that the system has the expected behavior that the molecules are incompressible for $K_1 \gg K_2$.

Solution:
This is really the same as the first steps in the solution of Exercise 20.10. Recasting the expressions there using the symbols defined in this problem, the energy can be expressed

in terms of the length $L = R_1 + R_2$ and $R_2 - R_1 \equiv y$. The value of y in the unstrained system is not relevant since the energy involves only changes from equilibrium, dL and dy,

$$E = \frac{1}{2}K_1(dL/2 - dy)^2 + \frac{1}{2}K_2(dL/2 + dy)^2 = \frac{1}{2}(K_1 + K_2)(dy^2 + (dL/2)^2) + (K_2 - K_1)(dL/2)dy. \tag{S.182}$$

Here it is most useful to define $\gamma = dy/(dL/2)$, so that

$$E = \left[\frac{1}{2}(K_1 + K_2)(1 + \gamma^2) + (K_2 - K_1)2\gamma\right](dL/2)^2. \tag{S.183}$$

The parameter γ is an internal strain that is determined by minimizing the energy as L is varied. Thus

$$dE/d\gamma = [(K_1 + K_2)\gamma + (K_2 - K_1)]\,(dL/2)^2 = 0 \tag{S.184}$$

from which it follows that

$$\gamma = (K_2 - K_1)/(K_1 + K_2), \tag{S.185}$$

which is the expected result. $\gamma = 0$ means no internal strain and the two springs change the same. For large spring constant $K_1, \gamma \to -1$ which means no compression of the molecule.

Exercise G.5 Show that in any crystal with one atom per cell the internal strain is zero by symmetry.

Solution:
There are many ways to see this. All ways depend on the fact that in a crystal with one atom per cell, every atom is at a center of inversion symmetry. Since there is no force by symmetry the atoms do not move from their site as the distance beteen atoms is scaled. Another way to see it is simple that there is only one parameter and there no inetrnal degree of freedom.

Exercise G.6 As an example of the condition in the previous problem, show that for the molecular chain in Exercise G.4, internal strain vanishes for $R_1 = R_2$ and $K_1 = K_2$. For a homonuclear case, this means one atom per cell. Note that the internal strain is still zero for a diatomic ionic crystal with two different atoms so long as $R_1 = R_2$ and $K_1 = K_2$.

Solution:
The answer is given above.

Exercise G.7 Show that it is *impossible* to have a chain with three inequivalent atoms per cell and still have zero internal strain.

Solution:
The more correct statement is the requirement that there are three atoms per PRIMITIVE cell, i.e., not an artificial supercell. Then if there are three inequivalent atoms, each one has two inequivalent neighbors. Thus it cannot be at a center of inversion. It follows that the porions are not determined by symmetry and they will change under stress. One can

invent special cases where the forces vanish but those are of vanishing probability in real systems.

Solutions for Appendix H

Exercise H.1 Show that $\sum_{i=1}^{N} |\nabla\phi_i(\mathbf{r})|^2 = -\sum_{i=1}^{N} \phi_i(\mathbf{r})\nabla^2\phi_i(\mathbf{r})$ follows from the requirement $\sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 = 1$ at all $(\mathbf{r})$.
Hint: Use Eqs. (H.10) and (H.11).

Solution:
The key is the requirement stated in the exercise. We write out the equations for a single function and it easily generalizes to a sum of functions. Because of the way $\phi(\mathbf{r})$ is defined in Eq. (H.10)
$\nabla|\phi(\mathbf{r})|^2 = \phi(\mathbf{r})\nabla\phi*(\mathbf{r}) + \nabla\phi(\mathbf{r})\nabla\phi*(\mathbf{r}) = 0$
and $\nabla^2|\phi(\mathbf{r})|^2 = 2\nabla\phi(\mathbf{r})\nabla\phi*(\mathbf{r}) + \phi(\mathbf{r})\nabla^2\phi*(\mathbf{r}) + \nabla^2\phi(\mathbf{r})\phi*(\mathbf{r}) = 0$
Using the fact that the expressions are real leads to the desired result.

Exercise H.2 Show that the excess fermion kinetic energy density in Eq. (H.13) follows from Eq. (H.11). The previous problem may be helpful.

Solution:
This follows directly from the previous problem. The fact that this is the excess kinetic energy due to fermions is that for bosons in the ground state ϕ_i is a constant for all i so that the derivatives are non-zero only for fermions.

Exercise H.3 Show that Eq. (H.17) follows from the definitions of the terms in the energy density given before and the Kohn–Sham equation for the eigenvalues.

Solution:
This expression for energy density follows from the same arguments as for the total energy in . The energy can be expressed as either kinetic plus potential energies or as the sum of eigenvalues minus the Hartree term that is double counted in the sum of eigenvalues plus the difference of the total xc energy and the potential times density.

Exercise H.4 Show that the formulas for the stress given by Nielsen and Martin [162] in their Eqs. (33) and (34) can be written in the form of Eq. (H.21), using definition Eq. (H.10).

Solution:
With apologies to the readers for errors. In the first edition, there was some TEX error that caused the equation reference to be wrong. The correct number is Eq. H.20 as given in the second edition. In addition, those are not the right equations in the Nielsen paper. The relevant expressions are (30a) - (30e). The relation to Eq. (H.21) is that for electrons and nuclei, the ion-ion, ion-electron and electron-electron Hartree terms can all be gathered into the Maxwell density in terms of the total electric field given in the last line in Eq. (H.21). The xc term is the same and the kinetic energy term in Eq. (H.21) is the same except it is expressed in the way that separates the boson and excess fermion terms.

Solutions for Appendix I

Exercise I.1 Show that the expression, Eq. (I.4), for an energy difference to first order follows from the form of the energy functional given in Eq. (7.26). Use this result with the special choice for the change in potential to derive the final result, Eq. (I.5).

Solution:
This is really a exercise that depends only upon the fact that the form of the Functional is stationary w.r.t. the potential and that we have freedom to choose the change in potential. Thus the solution is a summary of why this is the case.
To really appreciate the result one needs to realize that the change in the sum of eigenvalues is the change taking into account the effective potential, which is given explicitly in Eq. (I.4).

Exercise I.2 Using the fact that ψ_i is a solution of the Kohn–Sham equations in a spherical geometry, show that the potential can be eliminated and the expression for pressure can be written in terms of the wavefunction and its derivatives as in Eq. (I.8). Also show that there is an added term for exchange and correlation that can be written in the form in Eq. (I.8) in the local approximation. Hint: The first part can be done by partial integration and the second is the correction due to the fact that the potential is not fixed as the spherical system is scaled.

Solution:
This is closely related to Exercise 10.10 and the other exercises there. We can use the expressions in terms of the wavefunctions given in Section 10.7.
The pressure is the change in energy per unit change in volume which in a spherical geometry is $d[(4\pi/3)r^3 = Sdr$ where S is the area. The derivation is given in the paper by Liberman [496] who refers to Slater [1026] for the derivation of the equation. Note the Salter paper is in issue 1 of JCP in 1933.

Solutions for Appendix L [No exercises for Appendices J and K]

The solutions in this section can be found in standard texts that are referenced in this chapter.

Exercise L.1 Derive the leading error in the finite difference approximation to the second derivative that is $O(h^2)$ and is given explicitly in Eq. (L.2).

Exercise L.2 Derive the Numerov expressions (L.3) and (L.4) and show the leading error in the solutions are, respectively, $O(h^4)$ and $O(h^6)$.

Exercise L.3 Show that the conjugate gradient minimization equations, (L.8) and (L.9), follow from differentiating the functional and assuming it is quadratic. Then derive the key equation, (L.10), that if each direction is made conjugate to the previous one, then it is also conjugate to all previous directions. This can be shown by induction given that each direction is defined to be conjugate to the previous direction and it is a linear combination only of the new steepest descent gradient and the previous direction, as in Eq. (L.11).

Exercise L.4 For the quadratic functional (L.6), show that the conjugate directions (L.12) are also given by (L.13).

Consider a two-dimensional case $F(x, y) = Ax^2 + By^2$, with $B = 10A$. Show that the CG method reaches the exact minimum in two steps, starting from any point (x, y), whereas SD does not. What is the value of F in the SD method after two steps starting from $x = 1;\ y = 1$.

Exercise L.6 As the simplest three-dimensional example, consider $F(x, y, z) = Ax^2 + By^2 + Cz^2$, and show that the third direction $\mathbf{d}^3$ is conjugate to the first direction $\mathbf{d}^1 = \mathbf{g}^1$.

Exercise L.7 Make a short computer program to do the CG minimization of a function $F = \mathbf{G} \cdot \mathbf{x} + \mathbf{x} \cdot \mathbf{G} \cdot \mathbf{x}$ in any dimension for any $\mathbf{G}$ and $\mathbf{H}$.

Exercise L.8 The Broyden method generates a new approximation to the inverse Jacobian $\mathbf{J}_i^{-1}$ at each step i based on the conditions outlined before Eq. (L.24). Verify that $\mathbf{J}_i^{-1}$, defined by Eq. (L.24), satisfies (L.22) and that $\mathbf{J}_i^{-1} - \mathbf{J}_{i-11}^{-1}$ gives a null result when acting on any residual orthogonal to $\delta\mathbf{R}_i$.

Solutions for Appendix M

NOTE: The references for recursion in the text are to books. One reference online that is useful is The recursive solution of the Schrödinger equation, Roger Haydock, Computer Physics Communications 20, 11-16 (1980).

Exercise M.1 Show by induction that each vector ψ_n generated by the Lanczos algorithm is orthogonal to *all* the other vectors, and that the hamiltonian has tridiagonal form, Eq. (M.10). Regarding the problem that orthogonality is guaranteed only for infinite numerical precision, show how errors in each step can accumulate in the deviations from orthogonality.

Solution: The solution can be found in standard texts that are referenced in this chapter.

Exercise M.2 The solution for the eigenvalues of the tridiagonal matrix H in Eq. (M.10) is given by $|H_{ij} - \lambda\delta_{ij}| = 0$, which is polynomial $P_M(\lambda)$ of degree *M*. This may be solved in a recursive manner starting with the subdeterminant with $M = 1$. The first two polynomials are $P_1(\lambda) = \alpha_1 - \lambda$ and $P_2(\lambda) = (\alpha_2 - \lambda)P_1(\lambda) - \beta_2^2$. Show that the general relation for higher polynomials is

$$P_n(\lambda) = (\alpha_n - \lambda)P_{n-1}(\lambda) - \beta_n^2[P_{n-2}(\lambda)], \tag{S.186}$$

and thus that the solution can be found by root tracing (varying λ successively to reach condition $P_M(\lambda) = 0$ in computer time proportional to M for each eigenvalue.

Solution: The solution can be found in standard texts that are referenced in this chapter.

Exercise M.3 Consider a plane wave calculation with the wavefunction limited to Fourier components with $|\mathbf{G}| < |\mathbf{G}_{\mathrm{max}}|$. Show that all Fourier components of the external potential and the Hartree potential are given exactly (with no "aliasing") by the FFT algorithm, so long as the FFT extends to $|2\mathbf{G}_{\mathrm{max}}|$. For the non-linear exchange–correlation potential, show that there is no exact expression and that the expressions are "reasonable."

Solution: This is an important point for electronic structure calculations. This is explicitly for plane wanes but related issues happen for other bases.

The idea is straightforward. Squaring a wavefunction is get a density means that the density extends to $|2\mathbf{G}_{\mathrm{max}}|$. An FFT transforms a grid of data with size N^3 (in 3 dimensions) in reciprocal space to N^3 points in real space, and vice versa. Thus a plane wave calculation expresses each wavefunction in terms of Fourier components with $|\mathbf{G}| < |\mathbf{G}_{\mathrm{max}}|$. The square has components to $|2\mathbf{G}_{\mathrm{max}}|$ for the density and the potential is found by multiplying by $1/G^2$. This must be padded with zeros to define points on a parallelpiped that encloses the sphere with radius $|2\mathbf{G}_{\mathrm{max}}|$ (the double grid). Operations can be carried out on this grid, such as multiplying the wavefunction by the potential. Finally, the key is that the kinetic energy is restricted to the second derivation of the wavefunction in the original basis, which is a type of smoothing operation on the expressions on the double grid.

For an operation that is not limited to the double grid this introduces errors. An example is the LDA where the potential at point $\mathbf{R}$ is proportional to $n(\mathbf{R})^{1/3}$.

Solutions for Appendix P [No exercises for for Appendices N and O]
New App in second edition

Exercise P.1 Show that $\langle u_x|\partial_x u_x\rangle$ needed in Eq. (P.3) is purely imaginary.

Solution:

The solution is the same as for Exercise 25.1 with k replaced by x.

Exercise P.2 Derive the first equality in expression for $\Omega(\mathbf{k})$ in Eq. (P.12) from the expressions for the Berry phases in the previous equations. Discuss when there might be added factors of 2π. Show that the second equality follows from the normalization condition for the wave functions.

Solution:

The solution is the same as for Exercise 25.2 with k_x, k_y replaced by x, y.

Exercise P.3 Work out the expressions for the eigenvectors Eq. (P.20) and verify the result $\phi = \pi/4$.

Solution:

For the set of states for the path leads to the Berry phase (see Eq. (P.19))

$$\phi = -Im\ln[\langle\uparrow z|\uparrow x\rangle\langle\uparrow x|\uparrow y\rangle\langle\uparrow y|\uparrow z\rangle] = -[0+\pi/4+0] = -\pi/4, \tag{S.187}$$

which is half the solid angle of $\pi/2$. NOTE: The sign of ϕ is a convention.

Exercise P.4 Calculate the Berry phase for the loop with four states from $\hat{\mathbf{z}}$ to $\hat{\mathbf{x}}$ to $-\hat{\mathbf{z}}$ to $\hat{\mathbf{y}}$ and back to $\hat{\mathbf{z}}$.

Solution:

The the path visits the south pole there is a state $|\downarrow z\rangle$ between the x and y states and the Berry phase becomes

$$\phi = -Im\ln[\langle\uparrow z|\uparrow x\rangle\langle\uparrow x||\downarrow z\rangle\langle\downarrow z|\rangle\uparrow y\rangle\langle\uparrow y|\uparrow z\rangle] = -[0+0+\pi/2+0] = -\pi/2, \tag{S.188}$$

which is half the solid angle of π.

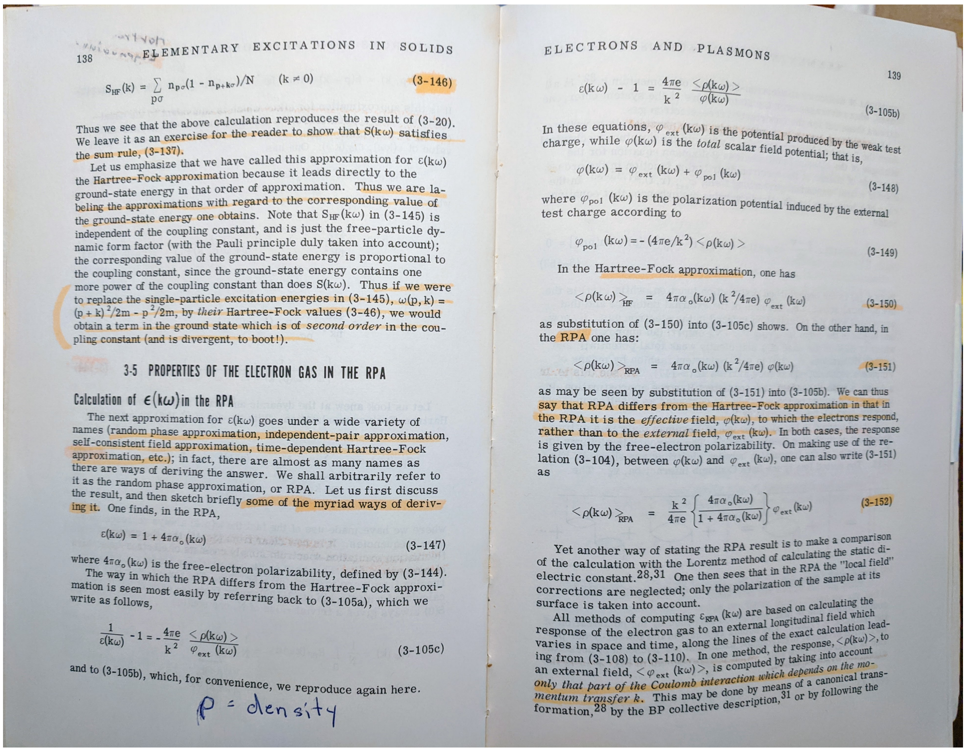
NOTE: This is very similar to the analysis in Exercise 26.6 which involves a sequence of four states. There the exchange of the eigenstates from the case with the singularity inside to outside the circle is a change of Berry phase from $\pi/2$ to zero. Here this is analogous to the change between two paths: the one considered in this exercise that visits the south pole (z,x,-z,y) with solid angle π and Berry phase $\pi/2$, and another that returns to the north pole (z,x,z,y) with solid angle and Berry phase zero.

Appendix T

Solution for Exercise 5.18. Pages from Pines book [297]

This appendix are contains added solutions that are placed here because they are long. They are referred to in the main list of solutions.

Solution for Exercise 5.18. Pages from Pines book [297] that provide the integrals to find the Lindhard dielectric function for the homogeneous electron gas (5.38). These are copied from the book I used as a grad student in 1960s.



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$$S_{HF}(k) = \sum_{p\sigma} n_{p\sigma}(1 - n_{p+k\sigma})/N \qquad (k \neq 0) \tag{3-146}$$

Thus we see that the above calculation reproduces the result of (3-20). We leave it as an exercise for the reader to show that $S(k\omega)$ satisfies the sum rule, (3-137).

Let us emphasize that we have called this approximation for $\varepsilon(k\omega)$ the Hartree-Fock approximation because it leads directly to the ground-state energy in that order of approximation. Thus we are labeling the approximations with regard to the corresponding value of the ground-state energy one obtains. Note that $S_{HF}(k\omega)$ in (3-145) is independent of the coupling constant, and is just the free-particle dynamic form factor (with the Pauli principle duly taken into account); the corresponding value of the ground-state energy is proportional to the coupling constant, since the ground-state energy contains one more power of the coupling constant than does $S(k\omega)$. Thus if we were to replace the single-particle excitation energies in (3-145), $\omega(p, k) = (p + k)^2/2m - p^2/2m$, by *their* Hartree-Fock values (3-46), we would obtain a term in the ground state which is of *second order* in the coupling constant (and is divergent, to boot!).

3-5 PROPERTIES OF THE ELECTRON GAS IN THE RPA

Calculation of $\epsilon(k\omega)$ in the RPA

The next approximation for $\varepsilon(k\omega)$ goes under a wide variety of names (random phase approximation, independent-pair approximation, self-consistent field approximation, time-dependent Hartree-Fock approximation, etc.); in fact, there are almost as many names as there are ways of deriving the answer. We shall arbitrarily refer to it as the random phase approximation, or RPA. Let us first discuss the result, and then sketch briefly some of the myriad ways of deriving it. One finds, in the RPA,

$$\varepsilon(k\omega) = 1 + 4\pi\alpha_o(k\omega) \tag{3-147}$$

where $4\pi\alpha_o(k\omega)$ is the free-electron polarizability, defined by (3-144).

The way in which the RPA differs from the Hartree-Fock approximation is seen most easily by referring back to (3-105a), which we write as follows,

$$\frac{1}{\varepsilon(k\omega)} - 1 = -\frac{4\pi e}{k^2}\,\frac{<\rho(k\omega)>}{\varphi_{ext}(k\omega)} \tag{3-105c}$$

and to (3-105b), which, for convenience, we reproduce again here.

ρ = density

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$$\varepsilon(k\omega) - 1 = \frac{4\pi e}{k^2}\,\frac{<\rho(k\omega)>}{\varphi(k\omega)} \tag{3-105b}$$

In these equations, $\varphi_{ext}(k\omega)$ is the potential produced by the weak test charge, while $\varphi(k\omega)$ is the *total* scalar field potential; that is,

$$\varphi(k\omega) = \varphi_{ext}(k\omega) + \varphi_{pol}(k\omega) \tag{3-148}$$

where $\varphi_{pol}(k\omega)$ is the polarization potential induced by the external test charge according to

$$\varphi_{pol}(k\omega) = -(4\pi e/k^2)<\rho(k\omega)> \tag{3-149}$$

In the Hartree-Fock approximation, one has

$$<\rho(k\omega)>_{HF} = 4\pi\alpha_o(k\omega)\,(k^2/4\pi e)\,\varphi_{ext}(k\omega) \tag{3-150}$$

as substitution of (3-150) into (3-105c) shows. On the other hand, in the RPA one has:

$$<\rho(k\omega)>_{RPA} = 4\pi\alpha_o(k\omega)\,(k^2/4\pi e)\,\varphi(k\omega) \tag{3-151}$$

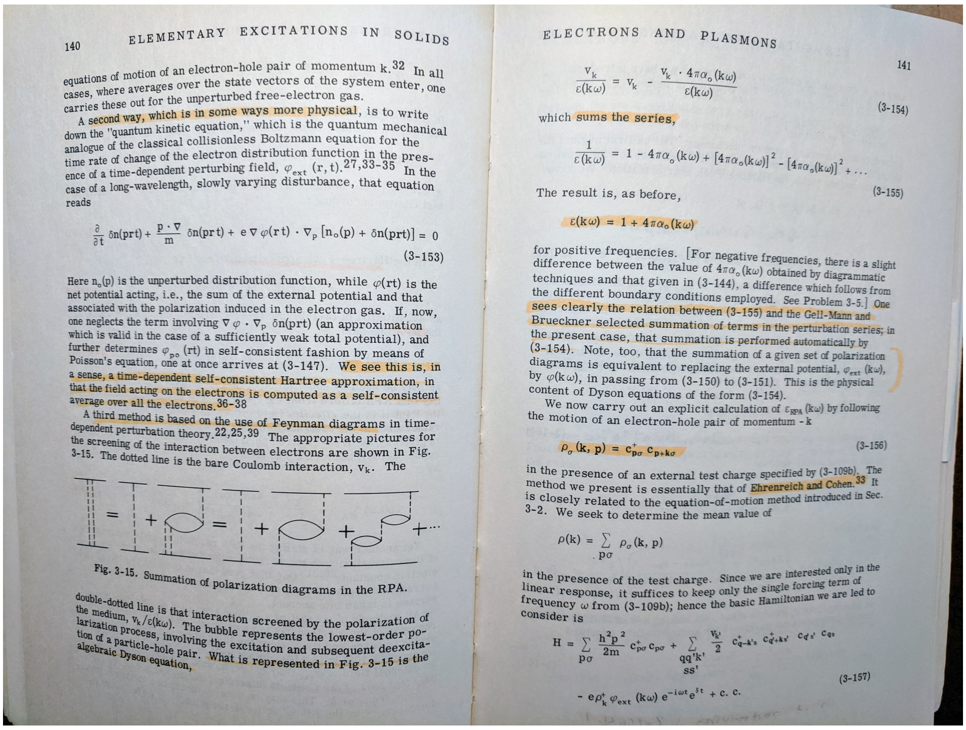
as may be seen by substitution of (3-151) into (3-105b). We can thus say that RPA differs from the Hartree-Fock approximation in that in the RPA it is the *effective* field, $\varphi(k\omega)$, to which the electrons respond, rather than to the *external* field, $\varphi_{ext}(k\omega)$. In both cases, the response is given by the free-electron polarizability. On making use of the relation (3-104), between $\varphi(k\omega)$ and $\varphi_{ext}(k\omega)$, one can also write (3-151) as

$$<\rho(k\omega)>_{RPA} = \frac{k^2}{4\pi e}\left\{\frac{4\pi\alpha_o(k\omega)}{1 + 4\pi\alpha_o(k\omega)}\right\}\varphi_{ext}(k\omega) \tag{3-152}$$

Yet another way of stating the RPA result is to make a comparison of the calculation with the Lorentz method of calculating the static dielectric constant.[28,31] One then sees that in the RPA the "local field" corrections are neglected; only the polarization of the sample at its surface is taken into account.

All methods of computing $\varepsilon_{RPA}(k\omega)$ are based on calculating the response of the electron gas to an external longitudinal field which varies in space and time, along the lines of the exact calculation leading from (3-108) to (3-110). In one method, the response, $<\rho(k\omega)>$, to an external field, $<\varphi_{ext}(k\omega)>$, is computed by taking into account *only that part of the Coulomb interaction which depends on the momentum transfer k.* This may be done by means of a canonical transformation,[28] by the BP collective description,[31] or by following the

Figure T.1. Section on RPA - 1.



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equations of motion of an electron-hole pair of momentum k.[32] In all cases, where averages over the state vectors of the system enter, one carries these out for the unperturbed free-electron gas.

A second way, which is in some ways more physical, is to write down the "quantum kinetic equation," which is the quantum mechanical analogue of the classical collisionless Boltzmann equation for the time rate of change of the electron distribution function in the presence of a time-dependent perturbing field, $\varphi_{ext}(r, t)$.[27,33-35] In the case of a long-wavelength, slowly varying disturbance, that equation reads

$$\frac{\partial}{\partial t}\delta n(prt) + \frac{p \cdot \nabla}{m}\delta n(prt) + e\nabla\varphi(rt)\cdot\nabla_p\left[n_o(p) + \delta n(prt)\right] = 0 \tag{3-153}$$

Here $n_o(p)$ is the unperturbed distribution function, while $\varphi(rt)$ is the net potential acting, i.e., the sum of the external potential and that associated with the polarization induced in the electron gas. If, now, one neglects the term involving $\nabla\varphi\cdot\nabla_p\,\delta n(prt)$ (an approximation which is valid in the case of a sufficiently weak total potential), and further determines $\varphi_{po}(rt)$ in self-consistent fashion by means of Poisson's equation, one at once arrives at (3-147). We see this is, in a sense, a time-dependent self-consistent Hartree approximation, in that the field acting on the electrons is computed as a self-consistent average over all the electrons.[36-38]

A third method is based on the use of Feynman diagrams in time-dependent perturbation theory.[22,25,39] The appropriate pictures for the screening of the interaction between electrons are shown in Fig. 3-15. The dotted line is the bare Coulomb interaction, v_k. The double-dotted line is that interaction screened by the polarization of the medium, $v_k/\varepsilon(k\omega)$. The bubble represents the lowest-order polarization process, involving the excitation and subsequent deexcitation of a particle-hole pair. What is represented in Fig. 3-15 is the algebraic Dyson equation,

Fig. 3-15. Summation of polarization diagrams in the RPA.

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$$\frac{v_k}{\varepsilon(k\omega)} = v_k - \frac{v_k\cdot 4\pi\alpha_o(k\omega)}{\varepsilon(k\omega)} \tag{3-154}$$

which sums the series,

$$\frac{1}{\varepsilon(k\omega)} = 1 - 4\pi\alpha_o(k\omega) + \left[4\pi\alpha_o(k\omega)\right]^2 - \left[4\pi\alpha_o(k\omega)\right]^2 + \dots \tag{3-155}$$

The result is, as before,

$$\varepsilon(k\omega) = 1 + 4\pi\alpha_o(k\omega)$$

for positive frequencies. [For negative frequencies, there is a slight difference between the value of $4\pi\alpha_o(k\omega)$ obtained by diagrammatic techniques and that given in (3-144), a difference which follows from the different boundary conditions employed. See Problem 3-5.] One sees clearly the relation between (3-155) and the Gell-Mann and Brueckner selected summation of terms in the perturbation series; in the present case, that summation is performed automatically by (3-154). Note, too, that the summation of a given set of polarization diagrams is equivalent to replacing the external potential, $\varphi_{ext}(k\omega)$, by $\varphi(k\omega)$, in passing from (3-150) to (3-151). This is the physical content of Dyson equations of the form (3-154).

We now carry out an explicit calculation of $\varepsilon_{RPA}(k\omega)$ by following the motion of an electron-hole pair of momentum -k

$$\rho_\sigma(k, p) = c^+_{p\sigma}c_{p+k\sigma} \tag{3-156}$$

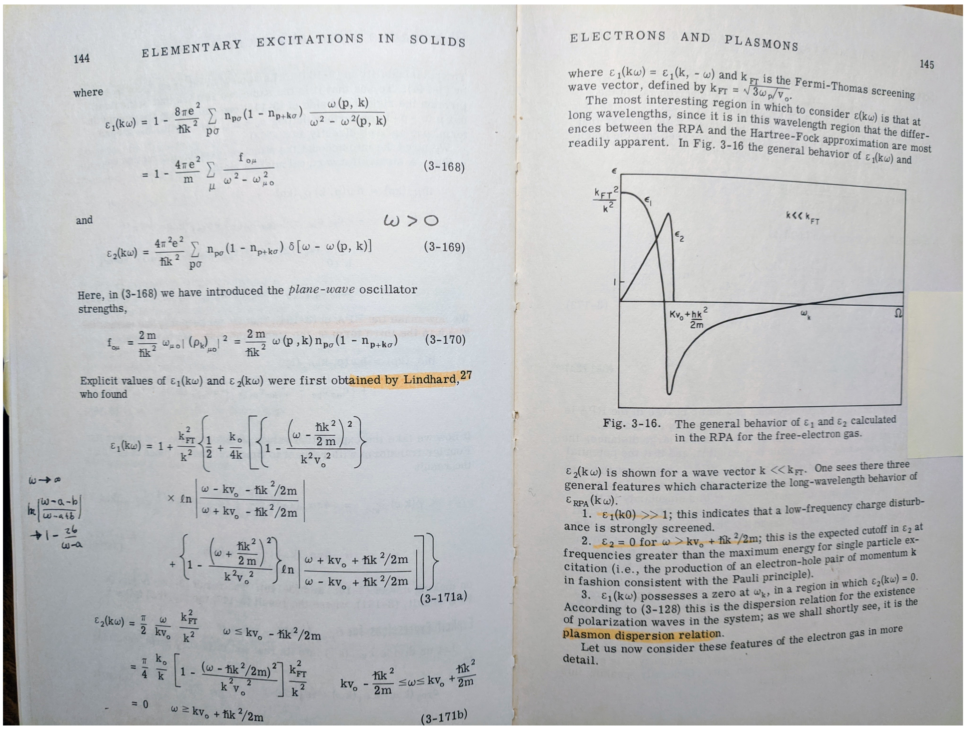
in the presence of an external test charge specified by (3-109b). The method we present is essentially that of Ehrenreich and Cohen.[33] It is closely related to the equation-of-motion method introduced in Sec. 3-2. We seek to determine the mean value of

$$\rho(k) = \sum_{p\sigma}\rho_\sigma(k, p)$$

in the presence of the test charge. Since we are interested only in the linear response, it suffices to keep only the single forcing term of frequency ω from (3-109b); hence the basic Hamiltonian we are led to consider is

$$H = \sum_{p\sigma}\frac{h^2p^2}{2m}c^+_{p\sigma}c_{p\sigma} + \sum_{\substack{qq'k'\\ss'}}\frac{v_{k'}}{2}c^+_{q-k's}c^+_{q'+ks'}c_{q's'}c_{qs} - e\rho^+_k\varphi_{ext}(k\omega)e^{-i\omega t}e^{\delta t} + c.c. \tag{3-157}$$

Figure T.2. Section on RPA - 2.



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where

$$\varepsilon_1(k\omega) = 1 - \frac{8\pi e^2}{\hbar k^2}\sum_{p\sigma} n_{p\sigma}(1-n_{p+k\sigma})\frac{\omega(p,k)}{\omega^2-\omega^2(p,k)}$$

$$= 1 - \frac{4\pi e^2}{m}\sum_{\mu}\frac{f_{o\mu}}{\omega^2-\omega^2_{\mu o}} \qquad (3\text{-}168)$$

and

$\omega > 0$

$$\varepsilon_2(k\omega) = \frac{4\pi^2 e^2}{\hbar k^2}\sum_{p\sigma} n_{p\sigma}(1-n_{p+k\sigma})\,\delta[\omega-\omega(p,k)] \qquad (3\text{-}169)$$

Here, in (3-168) we have introduced the *plane-wave* oscillator strengths,

$$f_{o\mu} = \frac{2m}{\hbar k^2}\omega_{\mu o}|(\rho_k)_{\mu o}|^2 = \frac{2m}{\hbar k^2}\omega(p,k)\,n_{p\sigma}(1-n_{p+k\sigma}) \qquad (3\text{-}170)$$

Explicit values of $\varepsilon_1(k\omega)$ and $\varepsilon_2(k\omega)$ were first obtained by Lindhard,[27] who found

$$\varepsilon_1(k\omega) = 1 + \frac{k_{FT}^2}{k^2}\left\{\frac{1}{2} + \frac{k_o}{4k}\left[\left\{1-\frac{\left(\omega-\frac{\hbar k^2}{2m}\right)^2}{k^2v_o^2}\right\}\times \ln\left|\frac{\omega-kv_o-\hbar k^2/2m}{\omega+kv_o-\hbar k^2/2m}\right| + \left\{1-\frac{\left(\omega+\frac{\hbar k^2}{2m}\right)^2}{k^2v_o^2}\right\}\ln\left|\frac{\omega+kv_o+\hbar k^2/2m}{\omega-kv_o+\hbar k^2/2m}\right|\right]\right\} \qquad (3\text{-}171a)$$

$\omega \to \infty$

$\ln\left|\frac{\omega-a-b}{\omega-a+b}\right| \to 1-\frac{2b}{\omega-a}$

$$\varepsilon_2(k\omega) = \frac{\pi}{2}\frac{\omega}{kv_o}\frac{k_{FT}^2}{k^2} \qquad \omega \le kv_o - \hbar k^2/2m$$

$$= \frac{\pi}{4}\frac{k_o}{k}\left[1-\frac{(\omega-\hbar k^2/2m)^2}{k^2v_o^2}\right]\frac{k_{FT}^2}{k^2} \qquad kv_o-\frac{\hbar k^2}{2m} \le \omega \le kv_o+\frac{\hbar k^2}{2m}$$

$$= 0 \qquad \omega \ge kv_o + \hbar k^2/2m \qquad (3\text{-}171b)$$

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where $\varepsilon_1(k\omega) = \varepsilon_1(k,-\omega)$ and k_{FT} is the Fermi-Thomas screening wave vector, defined by $k_{FT} = \sqrt{3}\,\omega_p/v_o$.

The most interesting region in which to consider $\varepsilon(k\omega)$ is that at long wavelengths, since it is in this wavelength region that the differences between the RPA and the Hartree-Fock approximation are most readily apparent. In Fig. 3-16 the general behavior of $\varepsilon_1(k\omega)$ and

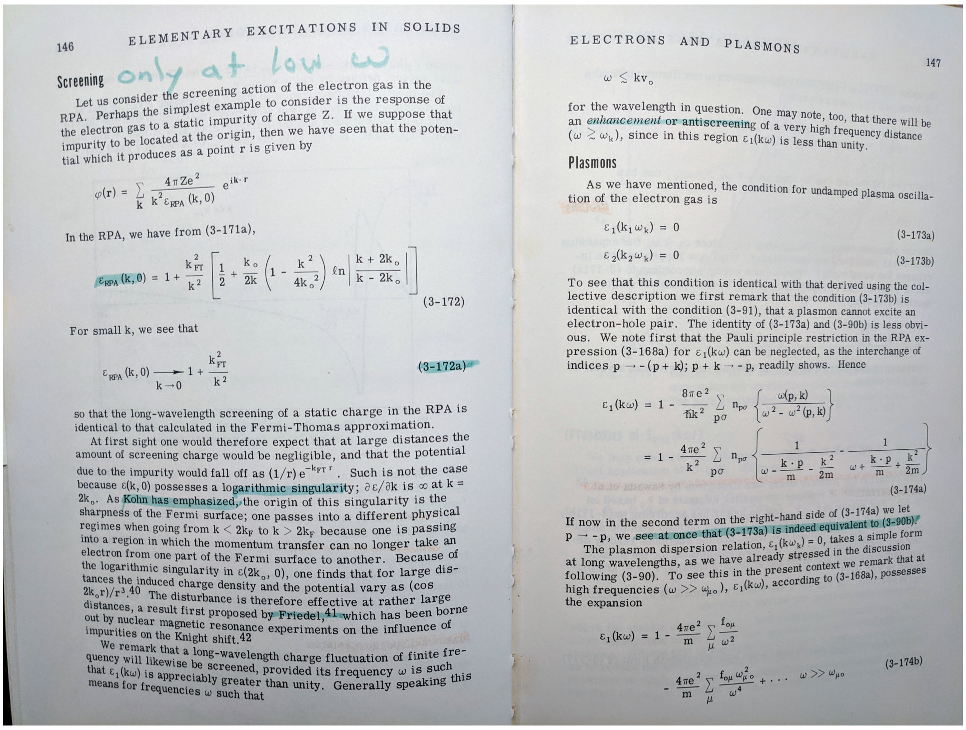
Fig. 3-16. The general behavior of ε_1 and ε_2 calculated in the RPA for the free-electron gas.

$\varepsilon_2(k\omega)$ is shown for a wave vector $k \ll k_{FT}$. One sees there three general features which characterize the long-wavelength behavior of $\varepsilon_{RPA}(k\omega)$.

1. $\varepsilon_1(k0) \gg 1$; this indicates that a low-frequency charge disturbance is strongly screened.
2. $\varepsilon_2 = 0$ for $\omega > kv_o + \hbar k^2/2m$; this is the expected cutoff in ε_2 at single particle ex- frequencies greater than the maximum energy for single particle excitation (i.e., the production of an electron-hole pair of momentum k in fashion consistent with the Pauli principle).
3. $\varepsilon_1(k\omega)$ possesses a zero at ω_k, in a region in which $\varepsilon_2(k\omega) = 0$. According to (3-128) this is the dispersion relation for the existence of polarization waves in the system; as we shall shortly see, it is the plasmon dispersion relation.

Let us now consider these features of the electron gas in more detail.

Figure T.3. Section on RPA - 3.



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Screening only at low ω

Let us consider the screening action of the electron gas in the RPA. Perhaps the simplest example to consider is the response of the electron gas to a static impurity of charge Z. If we suppose that impurity to be located at the origin, then we have seen that the potential which it produces as a point r is given by

$$\varphi(\mathrm{r}) = \sum_{\mathrm{k}} \frac{4\pi Z e^2}{k^2 \varepsilon_{RPA}(k,0)} e^{i\mathrm{k}\cdot\mathrm{r}}$$

In the RPA, we have from (3-171a),

$$\varepsilon_{RPA}(k,0) = 1 + \frac{k_{FT}^2}{k^2}\left[\frac{1}{2} + \frac{k_o}{2k}\left(1 - \frac{k^2}{4k_o^2}\right)\ell n\left|\frac{k+2k_o}{k-2k_o}\right|\right] \tag{3-172}$$

For small k, we see that

$$\varepsilon_{RPA}(k,0) \xrightarrow[k\to 0]{} 1 + \frac{k_{FT}^2}{k^2} \tag{3-172a}$$

so that the long-wavelength screening of a static charge in the RPA is identical to that calculated in the Fermi-Thomas approximation.

At first sight one would therefore expect that at large distances the amount of screening charge would be negligible, and that the potential due to the impurity would fall off as $(1/r)e^{-k_{FT}r}$. Such is not the case because $\varepsilon(k,0)$ possesses a logarithmic singularity; $\partial\varepsilon/\partial k$ is ∞ at $k = 2k_o$. As Kohn has emphasized, the origin of this singularity is the sharpness of the Fermi surface; one passes into a different physical regimes when going from $k < 2k_F$ to $k > 2k_F$ because one is passing into a region in which the momentum transfer can no longer take an electron from one part of the Fermi surface to another. Because of the logarithmic singularity in $\varepsilon(2k_o, 0)$, one finds that for large distances the induced charge density and the potential vary as $(\cos 2k_o r)/r^3$.[40] The disturbance is therefore effective at rather large distances, a result first proposed by Friedel,[41] which has been borne out by nuclear magnetic resonance experiments on the influence of impurities on the Knight shift.[42]

We remark that a long-wavelength charge fluctuation of finite frequency will likewise be screened, provided its frequency ω is such that $\varepsilon_1(k\omega)$ is appreciably greater than unity. Generally speaking this means for frequencies ω such that

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$$\omega \lesssim kv_o$$

for the wavelength in question. One may note, too, that there will be an *enhancement* or antiscreening of a very high frequency distance $(\omega \gtrsim \omega_k)$, since in this region $\varepsilon_1(k\omega)$ is less than unity.

Plasmons

As we have mentioned, the condition for undamped plasma oscillation of the electron gas is

$$\varepsilon_1(k_1\omega_k) = 0 \tag{3-173a}$$

$$\varepsilon_2(k_2\omega_k) = 0 \tag{3-173b}$$

To see that this condition is identical with that derived using the collective description we first remark that the condition (3-173b) is identical with the condition (3-91), that a plasmon cannot excite an electron-hole pair. The identity of (3-173a) and (3-90b) is less obvious. We note first that the Pauli principle restriction in the RPA expression (3-168a) for $\varepsilon_1(k\omega)$ can be neglected, as the interchange of indices $p \to -(p+k)$; $p + k \to -p$, readily shows. Hence

$$\begin{aligned}\varepsilon_1(k\omega) &= 1 - \frac{8\pi e^2}{\hbar k^2}\sum_{p\sigma} n_{p\sigma}\left\{\frac{\omega(p,k)}{\omega^2 - \omega^2(p,k)}\right\}\\ &= 1 - \frac{4\pi e^2}{k^2}\sum_{p\sigma} n_{p\sigma}\left\{\frac{1}{\omega - \frac{k\cdot p}{m} - \frac{k^2}{2m}} - \frac{1}{\omega + \frac{k\cdot p}{m} + \frac{k^2}{2m}}\right\}\end{aligned} \tag{3-174a}$$

If now in the second term on the right-hand side of (3-174a) we let $p \to -p$, we see at once that (3-173a) is indeed equivalent to (3-90b).

The plasmon dispersion relation, $\varepsilon_1(k\omega_k) = 0$, takes a simple form at long wavelengths, as we have already stressed in the discussion following (3-90). To see this in the present context we remark that at high frequencies $(\omega >> \omega_{\mu o})$, $\varepsilon_1(k\omega)$, according to (3-168a), possesses the expansion

$$\begin{aligned}\varepsilon_1(k\omega) &= 1 - \frac{4\pi e^2}{m}\sum_{\mu}\frac{f_{o\mu}}{\omega^2}\\ &\quad - \frac{4\pi e^2}{m}\sum_{\mu}\frac{f_{o\mu}\,\omega_{\mu o}^2}{\omega^4} + \cdots \qquad \omega >> \omega_{\mu o}\end{aligned} \tag{3-174b}$$

Figure T.4. Section on RPA - 4.

Appendix U

Solution of Exercise 8.5 part b - 2-site Hubbard model

This appendix are contains added solutions that are placed here because they are long. They are referred to in the main list of solutions.

Solution of Exercise Exercise 8.5 part b in Electronic Structure, Second Ed.

(This is the Exact Solution of the Two Site Hubbard Dimer from homework in UIUC Course 598 SCM Fall 2004 Homework 4 by Luke Shulenburger)

The Hamiltonian for this system is:

$$\hat{H} = t\sum_{\sigma}(\hat{a}^{\dagger}_{1\sigma}\hat{a}_{2\sigma} + \hat{a}^{\dagger}_{2\sigma}\hat{a}_{1\sigma}) + U(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{2\uparrow}\hat{n}_{2\downarrow})$$

In the following, I will find the solutions of the hamiltonian for 0, 1, 2, 3 and 4 electrons.

(i) **0 electrons**

In this case, the solution is just the vacuum, $|0\rangle$, which has energy 0.

(ii) **1 electron**

For one electron, the interaction terms (involving U) are all zero. This means that the eigenstates are the eigenstates of the kinetic energy operator. They are degenerate with respect to spin. The solutions $\frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\uparrow} + \hat{a}^{\dagger}_{2\uparrow})|0\rangle$ and $\frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\downarrow} + \hat{a}^{\dagger}_{2\downarrow})|0\rangle$ have energy t, and the solutions $\frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\uparrow} - \hat{a}^{\dagger}_{2\uparrow})|0\rangle$ and $\frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\downarrow} - \hat{a}^{\dagger}_{2\downarrow})|0\rangle$ have energy -t.

(iii) **2 electrons**

In this case, there are two electrons. In determining the solutions, it is convenient to choose a basis that consists of antisymmetrized products of single particle states on individual sites with a given spin. It is also convenient to separate this basis out into the four states that have $s_z = 0$, which are $\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{1\downarrow}|0\rangle$, $\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\downarrow}|0\rangle$, $\hat{a}^{\dagger}_{2\uparrow}\hat{a}^{\dagger}_{1\downarrow}|0\rangle$, $\hat{a}^{\dagger}_{2\uparrow}\hat{a}^{\dagger}_{2\downarrow}|0\rangle$, and the two states that have a nonzero s_z, which are $\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\uparrow}|0\rangle$, and $\hat{a}^{\dagger}_{1\downarrow}\hat{a}^{\dagger}_{2\downarrow}|0\rangle$.

Looking at this basis, the first thing to notice is that when the Hamiltonian acts on the states for which s_z is nonzero, the result is zero. In fact there is a degenerate subspace of this problem with energy 0, spanned by the states $\hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\uparrow}|0\rangle$, and $\hat{a}^{\dagger}_{1\downarrow}\hat{a}^{\dagger}_{2\downarrow}|0\rangle$.

The situation is slightly more difficult for the states with $s_z = 0$. To make the notation a bit easier, adopt the following notation: $|1\rangle = \hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{1\downarrow}|0\rangle$, $|2\rangle = \hat{a}^{\dagger}_{1\uparrow}\hat{a}^{\dagger}_{2\downarrow}|0\rangle$, $|3\rangle = \hat{a}^{\dagger}_{2\uparrow}\hat{a}^{\dagger}_{1\downarrow}|0\rangle$, and $|4\rangle = \hat{a}^{\dagger}_{2\uparrow}\hat{a}^{\dagger}_{2\downarrow}|0\rangle$. In this notation, the Hamiltonian becomes:

$$\hat{H} = t\left[(|2\rangle + |3\rangle)(\langle 1| + \langle 4|) + (|1\rangle + |4\rangle)(\langle 2| + \langle 3|)\right] + U(|1\rangle\langle 1| + |4\rangle\langle 4|)$$

In matrix form this is:

$$\begin{bmatrix} U & t & t & 0 \\ t & 0 & 0 & t \\ t & 0 & 0 & t \\ 0 & t & t & U \end{bmatrix}$$

Diagonalization of this matrix gives the following states as solutions:

$$\frac{1}{\sqrt{2}}(|1\rangle - |4\rangle)$$
$$\frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$$
$$\sqrt{\frac{4t^2}{U^2+16t^2+U\sqrt{16t^2+U^2}}}(|1\rangle - \frac{U+\sqrt{16t^2+U^2}}{4t}|2\rangle - \frac{U+\sqrt{16t^2+U^2}}{4t}|3\rangle + |4\rangle)$$
$$\sqrt{\frac{4t^2}{U^2+16t^2-U\sqrt{16t^2+U^2}}}(|1\rangle - \frac{U-\sqrt{16t^2+U^2}}{4t}|2\rangle - \frac{U-\sqrt{16t^2+U^2}}{4t}|3\rangle + |4\rangle)$$

That respectively have eigenvalues: U, 0, $\frac{U-\sqrt{16t^2+U^2}}{2}$, and $\frac{U+\sqrt{16t^2+U^2}}{2}$
These solutions have interesting interpretations in two limits. First in the case where $U >> t$, the solutions become:

$$\frac{1}{\sqrt{2}}(|1\rangle - |4\rangle)$$
$$\frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$$
$$\frac{1}{\sqrt{2}}(|2\rangle + |3\rangle)$$
$$\frac{1}{\sqrt{2}}(|1\rangle + |4\rangle)$$

That respectively have eigenvalues: U, 0, 0, U. This sets an energy scale whereby only the second two solutions are accessible. These solutions correspond to a spin system that is antiferromagnetic with opposite spin electrons sitting on the two sites.
The other case with an interesting interpretation is when $t >> U$. In this case the solutions become:

$$\frac{1}{\sqrt{2}}(|1\rangle - |4\rangle)$$
$$\frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$$
$$\frac{1}{2}(|1\rangle + |2\rangle + |3\rangle + |4\rangle)$$
$$\frac{1}{2}(|1\rangle - |2\rangle - |3\rangle + |4\rangle)$$

That respectively have eigenvalues: U, 0, 2t, -2t. In this case we see bonding and antibonding character in the last two states, with the last state being the bonding state of the system.

(iv) **3 electrons**

There is a trick that will allow us to see that the solution to a system of three electrons is the same a system of one electron with a suitably defined zero of Energy. The trick is to define the vacuum state to be the state with four electrons. To maintain consistancy, the anhillation operators become creation operators because they create holes from the vacuum. The creation operators become anhillation operators because they anhillate the vacuum. Under this change, the Hamiltonian becomes:

$$\begin{aligned}\hat{H} &= t\sum_{\sigma}(\hat{a}_{1\sigma}\hat{a}^{\dagger}_{2\sigma} + \hat{a}_{2\sigma}\hat{a}^{\dagger}_{1\sigma}) + U(\hat{a}_{1\uparrow}\hat{a}^{\dagger}_{1\uparrow}\hat{a}_{1\downarrow}\hat{a}^{\dagger}_{1\downarrow} + \hat{a}_{2\uparrow}\hat{a}^{\dagger}_{2\uparrow}\hat{a}_{2\downarrow}\hat{a}^{\dagger}_{2\downarrow}) \\ &= -t\sum_{\sigma}(\hat{a}^{\dagger}_{1\sigma}\hat{a}_{2\sigma} + \hat{a}^{\dagger}_{2\sigma}\hat{a}_{1\sigma}) + U(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{2\uparrow}\hat{n}_{2\downarrow} - 2)\end{aligned}$$

If we take the view that we are creating holes, particles that have opposite mass of an electron, it makes sense that the kinetic energy part of the hamiltonian will have the opposite sign. Furthermore we can arbitrarily redefine the zero of energy to be 2U. Under these changes, this Hamiltonian for holes becomes equivalent to the Hamiltonian for electrons that we started with.

Now, creating 3 electrons from the vacuum produces the same physical state as creating 1 hole from our new vacuum. In this sense, the solution for three electrons is equivalent to the solution for one electron, we just have to remember that the particles we talk about are holes, not electrons. The solutions are:

$$\begin{gathered}\frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\uparrow} + \hat{a}^{\dagger}_{2\uparrow}) \\ \frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\downarrow} + \hat{a}^{\dagger}_{2\downarrow}) \\ \frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\uparrow} - \hat{a}^{\dagger}_{2\uparrow}) \\ \frac{1}{\sqrt{2}}(\hat{a}^{\dagger}_{1\downarrow} - \hat{a}^{\dagger}_{2\downarrow})\end{gathered}$$

the eigenvalues of these states are $2U - t$, $2U - t$, $2U + t$, and $2U + t$ respectively.

(v) **4 electrons**

Using the same trick as in the 3 electron case, we realize that this is the same as the zero electron case where we have just redefined the state to be the vacuum of our hole system. Its energy is 2U.

Commented out solution of Anderson Imp. model in HF approx.

Appendix Z

Errata in Second Edition

Major Errors (below are more minor errata)

Chapter 23 - first two exercises

There is an error in these Exs. and they are stated in a way are much harder than they need to be.

The periodic part of the Bloch function $u_{\mathbf{k}}(\mathbf{r})$ is NOT independent of $\mathbf{k}$ as stated. (Also the exercises would have been simpler to work in terms of ψ instead of in terms of u.) See the solutions for discussion.

Errata identified in 2020 after book is in press

∗∗∗

CHECK THE FOLLOWING IS CORRECT!

Error in Monkhorst Pack points. It should be integrated exactly up to $(N_i - 1)\mathbf{T}_i$ instead of $N_i\mathbf{T}_i$

∗∗∗

Error in Eq. (5.32): 0.899 should be $0.814^2 = 0.663$ I have no idea where 0.899 came from This problem is worked out in Ashcroft and Mermin p. 410-414, which agrees with the corrected result. See also Exercise 5.17 solution. The correct equation is

$$\frac{r_s}{a_0} = 0.81 + \sqrt{0.66 + 3.31\left(\frac{R_c}{a_0}\right)^2}, \tag{Z.1}$$

which is the same as Eq. (5.32) corrected and rounded to fewer decimal places.

∗∗∗

In Eq. (9.13) (8.27) in first ed.), on the right hand side there should be ψ^* not ψ.

∗∗∗

In Eq 10.8, the factor of ℓ/2 should be 1/2.

∗∗∗

In Eq 10.23, the subscript $r - r_0$ is a typo. The expression the left side is evaluated at $r = r_0$.

∗∗∗

At the end of Ex. 11.2 omit the phrase "at other energies at most $\propto \varepsilon_k - \varepsilon_0$."

***

In Exercise 18.7 Eq. numbers in part (c) should be (18.23) and (18.24).

***

CHECK

CHECK: Is the line before Eq. 27.4 correct where it states “invariant”?

***

After Eq. 27.4 and in Ex 27. the expression for W has an extra paren: “T)” should be “T” where T is the time reversal operator. The usual symbol is Θ.

***

Error in lines before Eq. C.4. $\Psi_m i$ should be Ψ_i.

***

There is an error in Eq. (D.36) in the text. Somehow the tex file was messed up the Eq. is completely wrong. It was correct in the first edition (in Ch. 3). This correct equation is (note definition of $\bar{H}$ given below):

$$\begin{aligned} 0 = {} & \langle\psi^{(3)}|\bar{H}^{(0)}|\psi^{(0)}\rangle \\ & + \langle\psi^{(2)}|\bar{H}^{(1)}|\psi^{(0)}\rangle + \langle\psi^{(2)}|\bar{H}^{(0)}|\psi^{(1)}\rangle \\ & + \langle\psi^{(1)}|\bar{H}^{(2)}|\psi^{(0)}\rangle + \langle\psi^{(1)}|\bar{H}^{(1)}|\psi^{(1)}\rangle + \langle\psi^{(1)}|\bar{H}^{(0)}|\psi^{(2)}\rangle \\ & + \langle\psi^{(0)}|\bar{H}^{(3)}|\psi^{(0)}\rangle + \langle\psi^{(0)}|\bar{H}^{(2)}|\psi^{(1)}\rangle + \langle\psi^{(0)}|\bar{H}^{(1)}|\psi^{(2)}\rangle + \psi^{(0)}|\bar{H}^{(0)}|\psi^{(3)}\rangle, \end{aligned} \tag{Z.2}$$

where we have defined $\bar{H}^{(j)} = \hat{H}^{(j)} - \varepsilon^{(j)}$ for each order j to simplify the notation.

***

There are errors in Exercise H.4. In the first edition, the equation reference to be wrong. The correct number is Eq. H.20 as given in the second edition. In addition, those are not the right equations in the Nielsen paper. The relevant expressions are (30a) - (30e).

***

In Eq. (I.4) the last term should be $\left\{V^{\mathrm{CC}}_{A+B}(\mathbf{r}) + \epsilon_{\mathrm{xc}}[n(\mathbf{r})] - V_{\mathrm{eff}}(\mathbf{r})\right\}$