Fundamentals of Spectroscopy and Laser Physics

In this chapter we present the fundamental physical definitions and theoretically derived relations that underlie practical laser theory and engineering, and indeed, much of linear optical spectroscopy. Our purpose, however, is not to offer a comprehensive treatment of this topic (see the references for recommended reading) but rather to develop essential understanding in an economical format. To this end, such basic concepts as radiative lifetime, absorption, and polarization dephasing will be initially developed from first principles by using a classical model of the atom. Quantum mechanical aspects of the radiation problem will then be introduced as needed in order to polish the classical results into their useful or more appropriate modern forms.

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1 Classical Charged-Particle Oscillator

1.1 Damped, Undriven Oscillator

As a first approach to understanding the interaction of light with atoms, ions, and molecules we adopt a classical picture of charge oscillation in a microscopic system. Specifically, we first wish to understand simple radiative decay by an excited, undriven, single atom uncomplicated by real-world effects such as collisions or nonradiative transitions and then generalize these results in order to understand electromagnetic absorption in multi-atom ensembles.

Our model atom will consist of a point charge *q* of mass *m* bound in a onedimensional harmonic potential well (see Figure 1). This well is characterized by a spring constant *k*, whereas the charge's displacement from the equilibrium position located at the bottom of the well is denoted by x(t). The electric-dipole moment of this oscillator is thus $\mu(t) = qx(t)$. Newton's equation of motion for the charge may then be written in the form

$$\ddot{\mu} + \gamma \dot{\mu} + \omega_0^2 \mu = 0 \tag{1}$$

where $\omega_0^2 \equiv k/m$ and where we have introduced the damping term $\gamma \dot{\mu}$ in order to quantify the loss of energy by the oscillating charge due to the radiation that it emits. We hasten to emphasize that the form of this damping term has not been rigorously justified but it will be seen later to correspond to our expectations (and what experiments tell us) that the mechanical energy of the oscillator should decay exponentially with time. After solving Eq. (1) for $\mu(t)$, we will see how to relate the radiative damping factor γ to the fundamental parameters of the oscillator, namely q, m, and ω_0^2 .

Although $\mu(t)$ is a real quantity, the linear form of Eq. (1) suggests a recasting of this equation in terms of complex time-varying quantities:

$$\ddot{\tilde{\mu}} + \gamma \dot{\tilde{\mu}} + \omega_0^2 \tilde{\mu} = 0 \tag{2}$$

where the \sim here and hereafter will denote a quantity with both real and imaginary parts. This substitution facilitates the solution of the original Eq. (1) as well as its interpretation as long as we keep in mind that it is the real part of the solution that embodies the physical content. This idea likewise applies to any quantities derived from the complex solution provided that they are related by a strictly *linear* transformation.



Figure 1. Potential energy for a classical charged-particle oscillator of mass m and charge q as a function of displacement x from the equilibrium position at x = 0.

Simple examples of such transformations are multiplication by a (possibly complex) constant and time differentiation. For quantities that depend nonlinearly on physical variables, however, care must be taken to use the real part of the corresponding complex quantities or to apply an appropriately modified mathematical definition. With this in mind the general solution to Eq. (2) is

$$\tilde{\mu}(t) = \mu_0 e^{-(\gamma/2)t - j(\omega_0' t + \phi_0)}$$
(3)

from which $\mu(t) = \operatorname{Re}[\tilde{\mu}(t)]$ is the solution to Eq. (1). In this result, $\mu_0 \cos \phi_0$ is the initial value of the oscillator's (real) dipole moment and ϕ_0 is it's initial phase. The frequency ω'_0 is a substitution for previously defined quantities given by

$$\omega_0' \equiv \sqrt{\omega_0^2 - (\gamma/2)^2} \tag{4}$$

We thus see that the electric-dipole moment oscillates with an amplitude that decays at the rate $\gamma/2$ and at a frequency downshifted from ω_0 , as depicted in Fig. 2. However, for all microscopic radiation and absorption problems discussed in this book (and indeed in nearly all such problems generally), $\gamma \ll \omega_0^*$ and thus to an excellent approximation $\omega'_0 \cong \omega_0$; hence hereafter we will ignore the effect of damping on the oscillator frequency and take $\omega'_0 \equiv \omega_0$.

With the solution Eq. (3) in hand, the mechanical energy of the oscillator – averaged over one oscillation cycle – can be written down:

$$\left\langle W_{osc} \right\rangle_{cycle} = \left\langle \frac{1}{2} k \left(\frac{\mu(t)}{q} \right)^2 + \frac{1}{2} m \left(\frac{\dot{\mu}(t)}{q} \right)^2 \right\rangle_{cycle}$$

$$\equiv \frac{1}{2} \left[\frac{1}{2} (k/q^2) \tilde{\mu}(t) \tilde{\mu}(t)^* + \frac{1}{2} (m/q^2) \dot{\tilde{\mu}}(t) \dot{\tilde{\mu}}(t)^* \right]$$

$$= W_0 e^{-\gamma t}$$

$$(5)$$

where

$$W_{0} \cong \frac{1}{2} \frac{m\omega_{0}^{2}}{q} \mu_{0}^{2}$$
(6)

^{*} A typical rare earth ion radiating in the visible will do so at a damping rate of about 1000 s⁻¹; hence $\gamma / \omega_0 \simeq 10^{-13}$.



Figure 2. Time dependence of the electric dipole moment for a classical charged-particle oscillator as given by Eq. (3).

is the initial energy of the oscillator. The exponential decay of the oscillator's energy thus occurs with a characteristic time constant $\tau = 1/\gamma$. This last result also tells us that the power radiated by the oscillator is

$$P_{rad} = -\frac{d\left\langle W_{osc} \right\rangle_{cycle}}{dt} = W_0 \gamma e^{-\gamma t} \tag{7}$$

On the other hand, classical electromagnetic theory tells us that for an electric dipole oscillating according to the form Eq.(3), the cycle-averaged radiated power is given by

$$P_{rad} = \frac{\mu_0 \omega_0^4}{12\pi\varepsilon_0 c^3} e^{-\gamma t} \tag{8}$$

Equating the LHS's of Eqs. (7) and (8), subject to the definition Eq. (6), yields for the radiative damping rate

$$\gamma = \frac{1}{6\pi\varepsilon_0 c^3} \left(\frac{q^2 \omega_0^2}{m} \right) \tag{9}$$

where for emphasis we have isolated within the parentheses the physical quantities that characterize the oscillator.

Equation (9) is our first fundamental result and tells us these important facts about radiating microscopic systems:

(1) *The radiative damping rate of the oscillator increases with the square of the oscillator frequency*. This fact can also be understood in simple quantum mechanical terms by recalling that according to Fermi's Golden Rule, the rate of transition from an initial state to a continuum of final states is proportional to the density of final states. Since in this context we imagine the atom and electromagnetic field to comprise a coupled, fully quantum system, the density of states factor will be that corresponding to the photon states of the field. By counting up the number of resonant modes falling within a small frequency range in a box-shaped cavity, the reader will discover that the density of states increases with square of the frequency. Spontaneous radiative lifetimes of rare-earth ions will in general decrease dramatically as the frequency increases.

- (2) The radiative damping rate increases with the square of the electric charge of the oscillator. This statement will be found in the quantum mechanical context to be equivalent to the statement that the radiative damping rate increases with the square of the electric-dipole-moment matrix element appropriate to a given transition.
- (3) The radiative damping rate decreases with the mass of the oscillating system. Thus at a fixed frequency and charge for the oscillator, molecular vibrations and rotations will radiate at rates several thousand times slower than an atomic electron. Given that ω_0^2 itself for a molecular vibrational mode will likewise scale inversely as the mass, radiative damping for a vibrational mode will be ~10⁻⁶-10⁻⁷ the rate for an electronic oscillator. Because the damping rate for an allowed atomic visible transition is ~10⁹ s⁻¹ a vibrational mode will typically exhibit a damping rate of ~250 s⁻¹.

The oscillator under study up to this point has been supposed to be isolated in vacuum. A modification of the above results is required when the oscillator is embedded in a transparent dielectric medium (that is, transparent at the oscillator frequency). In this case, the medium will polarize in the presence of the oscillator's constituent charges and in the process produce a dipole moment *larger* than the original dipole moment of the oscillator. The radiated power is thereby increased by the factor $\varepsilon_0 c^3 / \varepsilon c'^3 \equiv n$, where ε is the dielectric constant of the host medium, n is the corresponding index of refraction, and c' = c/n is the speed of light in the medium. Hence the damping rate analogous to Eq. (9) becomes

$$\gamma = \frac{1}{6\pi\varepsilon c^{3}} \left(\frac{q^2 \omega_0^2}{m} \right) \tag{10}$$

1.2 Driven, Damped Oscillator

To proceed further with what the classical oscillator has to say about interactions of atoms with electromagnetic fields, we now consider the response of the oscillator to a driving electric field. The electrostatic potential energy of an electric dipole in the presence of an applied electric field $\mathbf{E}(t)$ is given by

$$V(x) = -\mathbf{\mu} \cdot \mathbf{E}(t) = -qx(t)E_{\mu}(t) \tag{11}$$

where $E_{\mu}(t) = \operatorname{Re}\left[\tilde{E}_{\mu}(t)\right]$ is the projection of the applied field along the axis of the dipole. The equation of motion for the dipole in this case is

$$\ddot{\mu} + (\gamma/m)\dot{\mu} + \omega_0^2 \mu = -(q/m)\frac{\partial V(x)}{\partial x} = \frac{q^2}{m}E_{\mu}(t)$$
(12)

If the electric field varies sinusoidally at angular frequency ω , the applied field $\tilde{E}_{\mu}(t) = \tilde{E}_0 e^{j\omega t}$ and in terms of complex quantities the equation of motion becomes

$$\ddot{\tilde{\mu}} + (\gamma/m)\dot{\tilde{\mu}} + \omega_0^2 \tilde{\mu} = \frac{q^2}{m}\tilde{E}_0 e^{j\omega t}$$
(13)

This equation readily yields the solution (after damping of initial transients)

$$\tilde{\mu}(t) = \frac{q^2}{m} \frac{\tilde{E}_0 e^{j\omega t}}{(\omega_0^2 - \omega^2) + j\gamma\omega}$$
(14)

Since the dipole is radiating electromagnetic energy – in this case at the frequency ω in response to the driving field – this energy must ultimately be supplied by the driving field itself, which tells us that *absorption* is occurring. Inspection of Eq. (14) further reveals that the maximum amplitude of the dipole moment is obtained for a driving frequency ω equal to the natural oscillation frequency ω_0 . Under this resonance condition the absorption of energy from the driving field is maximized.

The absorption of energy by the oscillator can be further quantified by noting that the cycle-averaged power delivered to the oscillator in response to the applied field is given by

$$P_{abs} = \left\langle F_{applied} \dot{x} \right\rangle_{cycle} = \left\langle \operatorname{Re}[q\tilde{E}(t)] \operatorname{Re}[\dot{\tilde{\mu}}(t)/q] \right\rangle_{cycle} = \frac{1}{2} \frac{m\gamma}{q^2} \dot{\tilde{\mu}}(t) \dot{\tilde{\mu}}(t)^*$$

$$= \frac{(qE_0)^2}{2m} \frac{\omega^2 \gamma}{(\omega^2 - \omega_0^2)^2 + (\gamma\omega)^2}$$
(15)

Because we will be almost exclusively concerned with problems involving a near resonance of the driving field with the oscillator, $\omega_0 \approx \omega$ and the above result simplifies in this approximation to

$$P_{abs} \cong \frac{(qE_0)^2}{8m} \frac{\gamma}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$
(16)

Given that the cycle-averaged intensity of the incident radiation that drives the oscillator is $I_{inc} = (1/2)\varepsilon_0 c E_0^2$, the relative absorbed power is

$$P_{rel} = \frac{P_{abs}}{I_{inc}} = \frac{q^2}{4mc\varepsilon_0} \frac{\gamma}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$
(17)

1.2.1 Absorption Cross Section

This last relation leads to the definition of a new spectroscopic quantity called the absorption cross section; it is defined by supposing that the dipole oscillator amounts to a simple hole of area σ_{abs} through which all of the power incident on the hole is absorbed by the oscillator. Hence in accord with Eqs. (16) and (17),

$$P_{abs} \equiv \sigma_{abs} I_{inc} \Longrightarrow \sigma_{abs}(\omega) = \frac{q^2}{4mc\varepsilon_0} \frac{\gamma}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$
(18)

With introduction of the Lorentzian line shape function

$$L(\omega - \omega_0) = \frac{\gamma / 2\pi}{(\omega - \omega_0)^2 + (\gamma / 2)^2}$$
(19)

where $L(\omega - \omega_0)$ has been normalized so that $\int_{-\infty}^{\infty} L(\omega - \omega_0) d\omega = 1$, Eq. (18) becomes

$$\sigma_{abs}(\omega) = \frac{\pi q^2}{2mc\varepsilon_0} L(\omega - \omega_0)$$
⁽²⁰⁾

The finite width of the resonant response of the dipole oscillator to the driving electric field is seen from the above relations to result from the finite magnitude of the damping factor γ . The full frequency width at half maximum of this response is given by $\Delta \omega = \gamma$.

Another way of characterizing the interaction of the dipole with the driving field is obtained by eliminating the detail embodied in the Lorentzian frequency dependence through an integration of the absorption cross section over frequency:

$$\int_{-\infty}^{\infty} \sigma_{abs}(\omega) d\omega = \frac{\pi q^2}{2mc\varepsilon_0}$$
(21)

Note, however, that not only have we accomplished the elimination of the frequency dependence in quantifying electromagnetic absorption in this new way, but we have also eliminated the dependence on the damping term. Equation (21) thus represents a

fundamental way in which to quantify the strength of the interaction between the oscillator and the driving radiation field. It applies to any classical dipole oscillator regardless of the nature of the damping processes that de-excite the oscillator and thus is universally applicable to the understanding of absorption phenomena. As we will show shortly, this statement holds true for even more general damping mechanisms (such as elastic collisions) than those that change the oscillator energy.

1.2.2 Oscillator Strength

In order to make these ideas more formal, we introduce the *absorption oscillator strength*, f_{abs} . This quantity relates the "strength" of the coupling between the dipole and the electromagnetic field relative to a standard oscillator consisting of a single electron of mass m_e and charge e:

$$\int_{-\infty}^{\infty} \sigma_{abs}(\omega) d\omega = \frac{\pi q^2}{2mc\varepsilon_0} = \frac{\pi e^2}{2m_e c\varepsilon_0} f_{abs}$$
(22)

where

$$f_{abs} = \left(\frac{m_e}{m}\right) \left(\frac{q}{e}\right)^2 \tag{23}$$

By virtue of the oscillator strength's independence from the frequency and damping rate, the term might be used in practice to compare the absorption properties of, say, a given ionic impurity embedded in different solid hosts or perhaps different ionic species in identical hosts. In terms of this fundamental quantity, previously defined quantities can be expressed:

$$\gamma = \frac{e^2 \omega_0^2}{6\pi m_e \varepsilon_0 c^3} f_{abs}$$
(24)

and

$$\sigma_{abs}(\omega) = \frac{e^2}{4m_e c\varepsilon_0} \frac{\gamma}{(\omega - \omega_0)^2 + (\gamma/2)^2} f_{abs}$$

$$= \frac{\pi e^2}{2m_e c\varepsilon_0} L(\omega - \omega_0) f_{abs}$$
(25)

1.3 Collisions: Inelastic and Elastic Relaxation

So far we have considered the behavior of an isolated dipole that is unaffected by its surroundings. A more realistic picture includes the possibility that collisions with other particles in the gas phase or interactions with phonons in a solid host will disturb the motion of the dipole. Such disturbances can be divided into two types: i) so called *inelastic* processes, which will either supply or drain energy from the oscillator and *ii*) elastic processes, which will leave the energy of the oscillator unchanged but will interrupt the phase of its motion. Such a division may at first seem artificial, since one might imagine that in any collision of a classical oscillator with another particle it is almost certain that energy will be exchanged. In reality, however, the discrete distribution of allowed internal energy states of bound quantum systems makes it possible to distinguish more sharply inelastic from elastic interactions. For example, in a collision where the joint translational energy of the colliding particles is less than the energy required to promote either particle to a higher excited quantum state, only elastic interactions are possible when both collision partners are in their respective quantum ground states. On the other hand, if one or both of the particles is already in an excited state, a collision could result in the transfer of internal energy to the translational degrees of freedom. Nevertheless, the same idea applies: if the (negative) change of internal energy is large compared with the translational energy of the colliding partners, purely elastic interactions will dominate over inelastic ones.

In any case, we introduce the symbol γ_{nr} in order to quantify the rate at which the energy "state" of the oscillator is changed though *nonradiative* inelastic processes; for simplicity, we will confine attention only to those processes that *reduce* rather than increase the oscillator energy. Hence the total rate of inelastic processes that result in a diminished energy for the oscillator will be denoted by

$$\gamma_i \equiv 1/T_1 = \gamma_{rad} + \gamma_{nr} \tag{26}$$

where $\gamma_{rad} \equiv \gamma$ with γ defined as in Eq. (10); the subscript "rad" here added in order to distinguish radiative from nonradiative relaxation of the oscillator. The symbol T_1 is widely used to quantify the characteristic time scale of energy loss by microscopic systems, thereby giving $W(t) = W_0 e^{-\gamma_t t} \equiv W_0 e^{-t/T_1}$. Because the oscillator is unaware of whether the energy loss occurs by either radiative or nonradiative damping, one then expects that the absorption cross section will become by analogy to Eq. (18)

$$\sigma_{abs}(\omega) = \frac{q^2}{4mc\varepsilon_0} \frac{\gamma_i}{(\omega_0 - \omega)^2 + (\gamma_i/2)^2}$$
(27)

In order to determine the effect of *elastic* processes on the absorption cross section, we first recognize that a single such elastic interaction between atoms and molecules is known to occur in a time period of $\approx 10^{-13}$ s and thus may be considered to good approximation to be instantaneous. The result of the interaction is to establish a new phase for the oscillation that is entirely unrelated to the oscillator phase before the interaction. If the average time between these phase interruptions is τ_e (Figure 3 illustrates this effect in the absence of inelastic damping), it can be shown that the absorption line shape is still of Lorentzian form and is given by

$$\sigma_{abs}(\omega) = \frac{q^2}{4mc\varepsilon_0} \frac{\gamma_{tot}}{(\omega_0 - \omega)^2 + (\gamma_{tot}/2)^2}$$
(28)

where γ_{tot} is the total oscillator damping rate given by

$$\gamma_{tot} = \gamma_{rad} + \gamma_{nr} + 2/\tau_e \tag{29}$$

Values of τ_e range from many seconds or longer for ions in solid hosts at liquid helium temperatures, to 10⁻⁹ s in gases of standard pressure at room temperature, and to 10⁻¹² s for ions in solid hosts at room temperature. In solid-state laser materials τ_e times are much shorter than the radiative or nonradiative relaxation times of the quantum states forming the energy-storing upper level of laser-active transitions; hence the line width in these cases is overwhelmingly dominated by elastic dephasing.

The finite width of the resonant response of the dipole oscillator with respect to the frequency of the driving electric field is seen from the above relations to result from the finite magnitude of the total damping factor γ_{tot} . The full frequency width at half maximum of this response is given by $\Delta \omega = \gamma_{tot}$. In the language of optical spectroscopy, this width is known as the *homogeneous* line width. Those processes that contribute to the value of γ_{tot} , namely, those that directly influence the time dependence of the oscillator's motion, are said to homogeneously broaden the resonant response or equivalently the line width. As for the absorption oscillator strength in the presence of the additional damping processes discussed in this section, the formal similarity of Eq. (28) to Eq. (18) implies that our definition and interpretation of the absorption oscillator strength in Section 1.2.2 holds perfectly well in the more general case. Figure 4



Figure 3. Electric dipole moment of a classical dipole oscillator subject to elastic interactions that interrupt the phase of the oscillation. The average time between interactions is τ_e .



Figure 4. Lorentzian profile of the absorption cross section for a classical dipole oscillator plotted as a function of frequency. The total damping rate is given by $\gamma_{tot} = \gamma_{rad} + \gamma_{nr} + 2 / \tau_e$, where τ_e is the mean time between elastic dephasing events.

plots the absorption cross section for a homogeneously broadened classical dipole oscillator.

1.4 Oscillator Ensembles

1.4.1 Homogeneous Broadening

So far, the absorption and emission properties of only a single oscillator have been considered. Because ultimately we will be concerned with an ensemble of oscillators that will collectively yield the active gain in an upconversion laser, we embark now on a discussion of the elementary absorptive properties of collections of oscillators in three-dimensional space. We suppose these oscillators to be randomly arrayed with a volume number density denoted by N, but for now make the simplifying assumption that the dipole moments are all coaligned parallel to the applied electric field. Consider now an infinitely thin slab of this ensemble and the subsequent absorption of electromagnetic radiation, which impinges on the slab at normal incidence. Keeping in mind the definition of the absorption cross section, the change in the power of the incident radiation on passing through the slab is given by

$$dP = -PN\sigma_{abs}(\omega)dz \tag{30}$$

From this one concludes that the transmitted power, considered as a function of the distance traveled through the medium, is given by

$$P(z) = P_0 e^{-\alpha(\omega)z} \tag{31}$$

where P_0 is the initial power incident on the absorbing ensemble and $\alpha(\omega) \equiv N\sigma_{abs}(\omega)$ is the *absorption coefficient*. Equation (31) is sometimes referred to as Beer's law; through the definition of the absorption cross section, it reveals the connection between the cross section – a microscopic quantity – and a measurable quantity, the transmitted power. If the transmitted power is measured as a function of the frequency of the incident radiation, an *absorption spectrum* results. From this spectrum the frequency dependence of the cross section can be deduced, which through Eq. (22) permits the computation of the oscillator strength. With the latter quantity in hand Eq. (24) then permits the computation of the radiative damping factor. Bear in mind here that we have insisted that all of the oscillators in the medium are identical with identical center frequencies and homogeneous line widths. Thus every oscillator exposed to the applied field responds with equal magnitude depending upon the driving frequency. Such ensembles are therefore called homogeneously broadened, in keeping with our terminology for broadening phenomena for single oscillators. It is precisely the homogeneous line shape function that one would observe in a measurement of the absorption spectrum of a collection of oscillators with the characteristics just named.

1.4.2 Inhomogeneous Broadening

Our oscillators have been thus far idealized to possess identical center frequencies. If the oscillators are in thermal motion, as they are in the gas phase, the Doppler effect will shift the resonant frequencies of the oscillators in accord with their relative motion directly towards and directly away from the propagation direction of the incident radiation. When the Doppler shift is larger than the homogeneous width, one naturally expects that the measured frequency dependence of the absorption coefficient will be broader than what would be found in a homogeneous spectrum – different subpopulations of the thermal ensemble, each of which may be labeled by the apparent resonant frequency as measured in the lab frame, will interact with the incident radiation independently of other subpopulations within the ensemble. This broadening effect on the absorption coefficient is termed *inhomogeneous* broadening in order to emphasize the existence of distinguishable subpopulations with different center frequencies. A mathematically equivalent effect occurs in the solid state: Although when present as embedded impurities, the oscillators are effectively frozen in space so that no Doppler shift of resonant frequencies occurs, random strains within the host material will slightly modify the spring constant of each dipole and thus yield a distribution of resonant frequencies above and below the center frequency of an unperturbed oscillator. For many practical purposes, the resulting distribution of center frequencies is Gaussian in form, thus within a small range of resonant frequencies $d\omega_0$,

$$d\mathbb{N}(\omega_0) = \frac{Ne^{-(\omega_c - \omega_0)^2 / \delta \omega_i^2}}{\sqrt{\pi \delta \omega_i^2}} d\omega_0$$
(32)

gives the number of ions per unit volume of resonant frequency ω_0 , where $\delta\omega_i$ characterizes the width of the Gaussian distribution of resonant frequencies all centered around $\omega = \omega_c$ (see Figure 5). Equations (28) and (32) may be combined to predict the measured frequency dependence of the absorption coefficient in the presence of inhomogeneous broadening:

$$\alpha(\omega) = \int_{-\infty}^{\infty} \mathbb{N}(\omega_0) \sigma_{abs}(\omega) d\omega_0 = \int_{-\infty}^{\infty} \left(\frac{N e^{-(\omega_c - \omega_0)^2 / \delta \omega_i^2}}{\sqrt{\pi \delta \omega_i^2}} \right) \left(\frac{q^2}{4mc\varepsilon_0} \frac{\gamma_{tot}}{(\omega - \omega_0)^2 + (\gamma_{tot} / 2)^2} \right) d\omega_0 \quad (33)$$





Figure 5. The Voigt line shape function. It is comprised of a superposition of Lorentzian line shapes of varying center frequencies.

The resulting line shape is known as the Voigt function; while in general not expressible in closed analytic form it exhibits the following interesting limits. First, in the case where the degree of inhomogeneous broadening is large compared with the homogeneous broadening, *i.e.*, $\delta \omega_i \gg \gamma_{tot}$,

$$\alpha(\omega) = \frac{N\pi q^2}{2mc\varepsilon_0} \frac{e^{-(\omega_c - \omega)^2 / \delta\omega_i^2}}{\sqrt{\pi\delta\omega_i^2}}$$
(34)

Thus the absorption spectrum assumes the frequency dependence of the inhomogeneous distribution function, implying that a single-frequency driving field would interact significantly with only a narrow subpopulation of absorbing oscillators centered very near the frequency of the incident field. In the opposite limit, that is where the inhomogeneous broadening is small in comparison to the homogeneous broadening $(\delta \omega_i \ll \gamma_{tot})$, we recover the homogeneous Lorentzian form of the absorption spectrum,

$$\alpha(\omega) = \frac{N\pi q^2}{2mc\varepsilon_0} \frac{\gamma_{tot}/2\pi}{(\omega - \omega_c)^2 + (\gamma_{tot}/2)^2}$$
(35)

and recognize that as before the incident field will drive each member of the oscillator ensemble identically. In intermediate cases, one finds that near the center frequency ω_c , the oscillators behave as though inhomogeneously broadened with the driving field interacting with a subpopulation whose resonant frequencies are clustered within a frequency width of $\sim \gamma_{tot}$ near the frequency of the incident field. At driving frequencies $\omega >> \delta \omega_i$, however, the incident field overlaps the long Lorentzian tails of all of the oscillators present in the inhomogeneous distribution and the ensemble behaves as though it were homogeneously broadened. Figure 6 shows the line shape functions obtained in these three regimes plotted on a logarithmic scale.

2 Quantum Theory of Resonant Absorption and Stimulated Emission

At this point we have extracted most of what is intuitively useful regarding the classical dipole oscillator and must now invoke quantum mechanics in order to refine our understanding of the optical spectroscopy of real microscopic systems. This will lead us to quantify the process of stimulated emission—an effect not rigorously derivable with classical mechanics—and we will see that this phenomenon is formally identi-



Figure 6. Comparison of line shape functions plotted on a logarithmic scale for varying relative degrees of inhomogeneous and homogeneous broadening. (a) Homogeneous linewidth approaches zero. (b) Inhomogeneous linewidth approaches zero. (c) Inhomogeneous linewidth equivalent to that in (a) and homogeneous linewidth equivalent to that in (b).

cal to absorption. We also find that some modifications are necessary in our definition of the oscillator strength in order to account for the full range of possible transitions in real multilevel atoms.

2.1 The Quantum Two-Level System

2.1.1 Basic Properties

We begin by considering a simple two-level quantum system completely decoupled from either an incident driving field or damping processes (Figure 7). We shall also assume that both of the allowed states are nondegenerate and that we already know the eigenfunctions and eigenvalues of the system Hamiltonian, \hat{H}_0 . These quantities will be denoted by $|a\rangle$, $|b\rangle$, E_a , and E_b , respectively, where $E_b > E_a$. Hence,

and
$$\begin{array}{l}
\hat{H}_{0} | a \rangle = E_{a} | a \rangle \\
\hat{H}_{0} | b \rangle = E_{b} | b \rangle
\end{array}$$
(36)

A general state of this conservative system is thus written

$$\left|\tilde{\psi}_{0}(t)\right\rangle = \tilde{c}_{a}(t)\left|a\right\rangle + \tilde{c}_{b}(t)\left|b\right\rangle \tag{37}$$

where the normalization $\tilde{c}_a(t)\tilde{c}_a^*(t) + \tilde{c}_b(t)\tilde{c}_b^*(t) = 1$ expresses the necessary condition that the system may be found upon measurement to be in either the $|a\rangle$ state or the $|b\rangle$ state, or perhaps more fundamentally that the system itself is stable through all time. Consider now the equation of motion (the Shrödinger equation) for this general state vector:

$$j\hbar \frac{\partial \left|\tilde{\psi}_{0}(t)\right\rangle}{\partial t} = \hat{H}_{0}(t) \left|\tilde{\psi}_{0}(t)\right\rangle \tag{38}$$

Substitution of Eq. (37) into the above equation of motion yields

$$j\hbar \left(\tilde{c}_{a} \left| a \right\rangle + \tilde{c}_{b} \left| b \right\rangle \right) = E_{a} \tilde{c}_{a} \left| a \right\rangle + E_{b} \tilde{c}_{b} \left| b \right\rangle \tag{39}$$

from which orthogonality of the eigenvectors $|a\rangle$ and $|b\rangle$ implies

$$\dot{\tilde{c}}_{a} = -\frac{jE_{a}}{\hbar}\tilde{c}_{a}$$

$$\dot{\tilde{c}}_{b} = -\frac{jE_{b}}{\hbar}\tilde{c}_{b}$$
(40)

Equations (40) yield the straightforward solutions



$$\hbar\omega_{ba} = E_b - E_a$$



Figure 7. Energy level diagram of the quantum two-level system.

$$\tilde{c}_{a}(t) = \tilde{c}_{a}^{\circ} e^{-j\omega_{a}t}$$

$$\tilde{c}_{b}(t) = \tilde{c}_{b}^{\circ} e^{-j\omega_{b}t}$$
(41)

where the quantities $\tilde{c}_{a,b}^{\circ}$ are the initial values of the expansion coefficients in the $|a,b\rangle$ state basis and $\omega_{a,b} \equiv E_{a,b} / \hbar$, respectively. Thus for this isolated system, the general state vector is

$$\left|\tilde{\psi}_{0}(t)\right\rangle = \tilde{c}_{a}^{0} e^{-j\omega_{a}t} \left|a\right\rangle + \tilde{c}_{b}^{0} e^{-j\omega_{b}t} \left|b\right\rangle$$

$$\tag{42}$$

The formalism of quantum mechanics tells us that the probability that the system will be found in the energy eigenstate $|a\rangle$ is

$$P_{a} = \left| \left\langle a \left| \hat{H}_{0} \right| \tilde{\psi}_{0}(t) \right\rangle \right|^{2} = \left| \tilde{c}_{a}^{0} \right|^{2}$$

$$\tag{43}$$

and comparably in the $|b\rangle$ eigenstate

$$P_{b} = \left| \left\langle b \left| \hat{H}_{0} \right| \tilde{\psi}_{0}(t) \right\rangle \right|^{2} = \left| \tilde{c}_{b}^{0} \right|^{2}$$

$$\tag{44}$$

The not unexpected conclusion to be drawn from Eqs. (43) and (44) is that the probabilities for observing the system in either of the two eigenstates are independent of time. Likewise, the expectation value for the total energy of the system is time independent:

$$\langle E \rangle = \left| \left\langle \tilde{\psi}_{0}(t) \left| \hat{H}_{0} \left| \tilde{\psi}_{0}(t) \right\rangle \right|^{2} = \left| \tilde{c}_{a}(t) \right|^{2} E_{a} + \left| \tilde{c}_{b}(t) \right|^{2} E_{b} = \left| \tilde{c}_{a}^{0} \right|^{2} E_{a} + \left| \tilde{c}_{b}^{0} \right|^{2} E_{b}$$
(45)

2.1.2 Electric Dipole Moment Operator

Another observable of interest, one that is of fundamental importance in the theory of electromagnetic interactions with optically active quantum systems, is the electric dipole moment. Taking the hydrogen atom as a concrete example, the electric dipole moment operator is simply $-e\hat{\mathbf{r}}$, where $\hat{\mathbf{r}}$ is the position operator for the electron with the origin of coordinates taken at the nucleus. For a general multielectron atom, the dipole moment becomes $\sum -e\hat{\mathbf{r}}_i$, with the sum being over all electrons in the atom. Note that for three-dimensional microscopic systems like atoms, the dipole moment must be represented in vector form. In all generality, we will therefore denote the electric dipole moment by the vector Hermitian operator $\hat{\mu}$.

Returning to the two-level system, whose general state vector is given in Eq.(42), the expectation value of the dipole moment in general form is written

$$\langle \boldsymbol{\mu} \rangle = \tilde{c}_{a}^{*}(t)\tilde{c}_{a}(t)\boldsymbol{\mu}_{aa} + \tilde{c}_{b}^{*}(t)\tilde{c}_{b}(t)\boldsymbol{\mu}_{bb} + \tilde{c}_{a}^{*}(t)\tilde{c}_{b}(t)\tilde{\boldsymbol{\mu}}_{ab} + \tilde{c}_{b}^{*}(t)\tilde{c}_{a}(t)\tilde{\boldsymbol{\mu}}_{ba} = \left| \tilde{c}_{a}^{0} \right|^{2} \boldsymbol{\mu}_{aa} + \left| \tilde{c}_{b}^{0} \right|^{2} \boldsymbol{\mu}_{bb} + \tilde{c}_{a}^{0*}\tilde{c}_{b}^{0}e^{-j\omega_{ba}t}\tilde{\boldsymbol{\mu}}_{ab} + \tilde{c}_{b}^{0*}\tilde{c}_{a}^{0}e^{j\omega_{ba}t}\tilde{\boldsymbol{\mu}}_{ba}$$

$$(46)$$

where $\tilde{\boldsymbol{\mu}}_{ij} = \langle i | \hat{\boldsymbol{\mu}} | j \rangle$ is the matrix element of the dipole moment operator as represented in the $|a,b\rangle$ basis and where $\omega_{ba} \equiv \omega_b - \omega_a$ will prove later to be the transition frequency between the two eigenstates. The Hermitian character of the operator $\hat{\boldsymbol{\mu}}$ requires that $\boldsymbol{\mu}_{aa}$ and $\boldsymbol{\mu}_{bb}$ be real valued and that $\tilde{\boldsymbol{\mu}}_{ab} = \tilde{\boldsymbol{\mu}}_{ba}^*$, which guarantees that $\langle \boldsymbol{\mu} \rangle$ is real.

Additional general conclusions can be made regarding the values of the matrix elements of the dipole moment operator. Inspection of Eq. (46) for the expectation value in the limit where $\tilde{c}_b^0 \rightarrow 0$ – that is, where the system is initially in the state $|a\rangle$ and remains there for all time – yields

$$\langle \mathbf{\mu} \rangle = \mathbf{\mu}_{aa} \tag{47}$$

Thus $\boldsymbol{\mu}_{aa}$ must be the *permanent* dipole moment of the system when in the $|a\rangle$ state. However, we know from the symmetry properties of real atoms and atomic ions that no nonzero permanent electric dipole moment should exist in pure energy eigenstates, from which we conclude that $\boldsymbol{\mu}_{aa} \equiv 0$. Similarly, $\boldsymbol{\mu}_{bb} \equiv 0$ and thus in matrix form the dipole moment operator in the $|a,b\rangle$ basis may be written

$$\hat{\boldsymbol{\mu}} = \begin{pmatrix} 0 & \tilde{\boldsymbol{\mu}}_{ab} \\ \tilde{\boldsymbol{\mu}}_{ba} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \tilde{\boldsymbol{\mu}}_{ba,x} \\ \tilde{\boldsymbol{\mu}}_{ab,x} & 0 \end{pmatrix} \boldsymbol{e}_{x} + \begin{pmatrix} 0 & \tilde{\boldsymbol{\mu}}_{ba,y} \\ \tilde{\boldsymbol{\mu}}_{ab,y} & 0 \end{pmatrix} \boldsymbol{e}_{y} + \begin{pmatrix} 0 & \tilde{\boldsymbol{\mu}}_{ba,z} \\ \tilde{\boldsymbol{\mu}}_{ab,z} & 0 \end{pmatrix} \boldsymbol{e}_{z}$$
(48)

where for concreteness the vector expansion in terms of the Cartesian unit vectors \mathbf{e}_i has been shown explicitly. Thus Hermiticity of each vector component requires $\tilde{\mu}_{ab,i} = \tilde{\mu}_{ba,i}^*$. With these results in hand, the time dependence of the dipole moment expectation value is seen to oscillate harmonically at the angular frequency ω_{ba} . We see that when the system is in a superposition state constructed from the two energy eigenstates $|a\rangle$ and $|b\rangle$, the dipole moment oscillates at the angular frequency ω_{ba} . Comparing this observation with Eq. (3) for the time evolution of the classical dipole oscillator – ignoring for now the important assumption that we have explicitly excluded damping phenomena in this quantum model—suggests that we identify the quantum two-level system with a dipole oscillator of resonant frequency ω_{ba} . Likewise by analogy with the classical oscillator, one further expects that if the system were exposed to an oscillating electric field of frequency ω_{ba} , such a field would induce transitions between the states

 $|a\rangle$ and $|b\rangle$. In the following we develop the quantum formalism that will allow us to complete this analogy quantitatively.

2.1.3 Radiative Damping of the Undriven Two-Level System

In the absence of explicit coupling between a quantum system and external fields, the expectation value of the system energy remains constant in time and therefore inelastic damping of the system does not occur. Our discussion of the classical oscillator (and real-world experience) tells us to expect that excited atoms will lose energy and decay to their ground states – indeed, we know that a collection of gas phase atoms that are initially prepared in their first excited states will often emit electromagnetic energy (fluorescence) whose measured power decays exponentially with time. However, a rigorous quantum treatment of the fluorescence decay of excited atoms requires us to provide not only a quantum representation of the atom but also of the electromagnetic field to which the atom is coupled. Although in lieu of such a fully quantized theory of atom-field interactions a much simpler semiclassical theory will be developed in detail below, the Hamiltonian for the combined and fully quantized atom-field system would be nevertheless written as

$$\hat{H}_{tot} = \hat{H}_{atom} + \hat{H}_{field} + \hat{H}_{int}$$
(49)

where \hat{H}_{int} quantifies in operator form the interaction energy of the atom and the field. In the event that the atom-field coupling is dominated by the electric-dipole interaction, \hat{H}_{int} is given by

$$\hat{H}_{int} = -\hat{\mu} \cdot \hat{\mathbf{E}} \tag{50}$$

In this expression, $\hat{\mathbf{E}}$ is the quantum-mechanical electric field operator; it is exclusively a function of coordinates – for our purposes unspecified – that are affiliated with the electromagnetic field just as $\hat{\mu}$ exclusively depends on the atom coordinates. Absent an applied field, \hat{H}_{int} thus mediates the energy-conserving decay of an initially excited atom into radiation. More specifically, since the final state of the system consists of the ground state of the atom and an excited state of the field, and since a continuum of possible final field states is available, each of different frequency, Fermi's Golden Rule may be applied to calculate the rate of radiative decay. In the notation of our two-level system just described, and further assuming that the initial state of the system is the general state vector

$$\left|\tilde{\psi}_{i}(t)\right\rangle = \tilde{c}_{a}(t)\left|a\right\rangle + \tilde{c}_{b}(t)\left|b\right\rangle \tag{51}$$

the transition rate is given by

$$W_{\psi_i \to a} = \frac{2\pi}{\hbar} \left| \left\langle \tilde{\psi}_i(t) \left| \left\langle i \right| \hat{H}_{int} \left| f \right\rangle \right| a \right\rangle \right|^2 \rho_f(\hbar \omega_{ba}) = \frac{2\pi}{\hbar} \left| c_b(t) \right|^2 \left| \tilde{\mathbf{\mu}}_{ba} \cdot \left\langle i \right| \hat{\mathbf{E}} \left| f \right\rangle \right|^2 \rho_f(\hbar \omega_{ba})$$
(52)

where *i* and *f* denote the initial and final states of the field and $\rho_f(\hbar\omega_{ba})$ is the density of final field states at the transition energy $\hbar\omega_{ba}$. Note that for the electric-dipole operator we have implicitly used the form Eq.(48). Since the transition rate *is defined* as the time rate of change of the probability that the system be observed in the excited state $|b\rangle$, i.e., $W_{\psi_i \to a} = -d |\tilde{c}_b(t)|^2 / dt$, Eq. (52) assumes the form

$$\frac{d\left|\tilde{c}_{b}(t)\right|^{2}}{dt} = -\gamma_{rad}\left|\tilde{c}_{b}(t)\right|^{2}$$
(53)

where

$$\gamma_{rad} = \frac{2\pi}{\hbar} \left| \tilde{\mathbf{\mu}}_{ba} \cdot \left\langle i \right| \hat{\mathbf{E}} \left| f \right\rangle \right|^2 \rho_f(\hbar \omega_{ba})$$
(54)

is the radiative transition rate between the two states $|b\rangle$ and $|a\rangle$. Insofar as we have assumed that the initial state of the field is the vacuum state (no driving field), and since γ_{rad} is independent of the initial state of the two-level system, γ_{rad} fundamentally characterizes the coupling between the two-level system and the field—it is the direct quantum analog of the classical radiative damping rate. Transitions of this type are termed *spontaneous emission*, since the undriven atom has irreversibly transferred its internal energy to the energy of the field. Einstein introduced a special symbol, the *A* coefficient, to denote the spontaneous emission transition rate; in our example, it is defined by $A_{b\to a} \equiv \gamma_{rad}$. Although we could in principle use Eq. (52) to calculate the Einstein *A* coefficient, we will use a more accessible approach in Section 2.2.4 with the benefit that it will not require quantization of the electromagnetic field.

An important final point to make regarding the spontaneous decay of the twolevel system is that Eq. (52) represents a much more general principle than we have let on: spontaneous radiative transitions aside, *any* type of coupling between the system and a continuum of final states would have led to exponential decay of the excited state. For example, in the event that a first-order interaction with a second (i.e. *nonradiative*) continuum were included in the initial Hamiltonian, decay would occur at a total rate equal to the sum of the individual rates:

$$\gamma = \gamma_{rad} + \gamma_{nr} \tag{55}$$

In all cases, the differential equation Eq. (53) is readily solved to yield

$$\left|\tilde{c}_{b}(t)\right|^{2} = \left|\tilde{c}_{b}^{0}\right|^{2} e^{-\gamma t}$$
(56)

from which the time dependence of the expectation value of the internal energy of the two-level system is

$$\langle E(t) \rangle = \left| \tilde{c}_{a}(t) \right|^{2} E_{a} + \left| \tilde{c}_{b}(t) \right|^{2} E_{b} = E_{a} + \left| \tilde{c}_{b}^{0} \right|^{2} (E_{b} - E_{a}) e^{-\gamma t}$$
 (57)

in direct accord with our classical results.

2.2 Semiclassical RadiationTheory

The purpose of developing a semiclassical theory of radiative interactions with quantum systems is to simplify the derivation of useful results from physical first principles. We also wish to develop a formalism for which inclusion of *elastic* damping processes can be plausibly motivated and included in a natural way. A direct outcome of this procedure will be a quantum theory of the oscillator strength, the absorption cross section, and stimulated emission, the latter subject being of fundamental importance in understanding the workings of lasers. Yet a third objective is to understand the *statistical* behavior of *ensembles* of quantum systems. This is a tall order, so we beg the reader's indulgence in what follows as it departs from the approaches employed in the standard introductory texts on laser physics and engineering. With a minimum of facts to accept on faith, the power of the density-matrix formalism to accomplish in elegant form all three of the tasks just named we hope will encourage the reader to accept the additional level of abstraction.

2.2.1 The Density Matrix

We know from quantum mechanics that the expectation value of an observable \hat{A} for the quantum state $|\psi(t)\rangle$ is given by the rule

$$\left\langle A\right\rangle = \left\langle \psi(t) \left| \hat{A} \right| \psi(t) \right\rangle \tag{58}$$

In terms of a complete set of basis states $|\varphi_n\rangle$ that span the space of all possible solutions to the Shrödinger equation, $\langle A \rangle$ may be written in the form

$$\left\langle A\right\rangle = \left(\sum_{m} \left\langle \varphi_{m} \left| c_{m}^{*}(t) \right\rangle \right) \hat{A}\left(\sum_{n} c_{n}(t) \left| \varphi_{n} \right\rangle \right) = \sum_{m,n} c_{m}^{*}(t) c_{n}(t) \tilde{A}_{mn}$$
(59)

where the $c_n(t)$ are the expansion coefficients of the state vector $|\Psi(t)\rangle$ in the $|\varphi_n\rangle$ basis. If we now take an interest in the average value of the observable \hat{A} over a collection of N identical systems, each labeled with the index i, the latter result naturally suggests

$$\overline{\langle A \rangle} = \frac{1}{N} \sum_{i} \sum_{m,n} c_m^{i*}(t) c_n^i(t) \tilde{A}_{mn}$$
(60)

where the superscript *i* on the expansion coefficients corresponds to the state vector $|\psi_i(t)\rangle$ for the *i*th system. Insofar as the expectation value of the observable \hat{A} will be in general time dependent, especially if classical fields are present or if the particles in the ensemble are mutually interacting, the time rate of change of the mean expectation value is given by

$$\frac{d\overline{\langle A \rangle}}{dt} = \frac{1}{N} \sum_{i} \sum_{m,n} [\dot{\tilde{c}}_{m}^{i*}(t)\tilde{c}_{n}^{i}(t) + \tilde{c}_{m}^{i*}(t)\dot{\tilde{c}}_{n}^{i}(t)]\tilde{A}_{mn}$$
(61)

where we have taken advantage of the fact that the matrix elements \tilde{A}_{mn} are the same for every system in the ensemble. On the other hand, if we take the basis states $|\varphi_n\rangle$ to be the eigenvectors of the Hamiltonian, the Shrödinger equation in terms of the $|\varphi_n\rangle$ basis is

$$i\hbar\sum_{k}\dot{\tilde{c}}_{k}^{i}(t)\left|\varphi_{k}\right\rangle = \sum_{k}\tilde{c}_{k}^{i}(t)\hat{H}\left|\varphi_{k}\right\rangle$$
(62)

from which orthogonality of the $|\varphi_n\rangle$ yields

$$\dot{\tilde{c}}_{n}^{i}(t) = -\frac{i}{\hbar} \sum_{k} \tilde{c}_{k}^{i}(t) \tilde{H}_{nk}$$
(63)

Substitution of Eq. (63) into Eq. (61) gives

$$\frac{d\overline{\langle A\rangle}}{dt} = \frac{1}{N} \frac{j}{\hbar} \sum_{i} \sum_{m,n} \sum_{k} [\tilde{c}_{k}^{i^{*}}(t)\tilde{c}_{n}^{i}(t)\tilde{H}_{km} - \tilde{c}_{m}^{i^{*}}(t)\tilde{c}_{k}^{i}(t)\tilde{H}_{nk}]\tilde{A}_{mn}$$
(64)

We now define the density matrix for the i^{th} single system as

$$\tilde{\rho}_{nm}^{i}(t) = \tilde{c}_{m}^{i*}(t)\tilde{c}_{n}^{i}(t)$$
(65)

which on substitution into Eq. (62) yields

$$\frac{d\langle A\rangle}{dt} = \frac{1}{N} \frac{j}{\hbar} \sum_{i} \sum_{m,n} \sum_{k} [\tilde{\rho}_{nk}^{i}(t)\tilde{H}_{km} - \tilde{H}_{nk}\tilde{\rho}_{km}^{i}(t)]\tilde{A}_{mn}$$
(66)

Performing the sum on k yields

$$\frac{d\langle A\rangle}{dt} = \frac{1}{N} \frac{j}{\hbar} \sum_{i} \sum_{m,n} [\hat{\boldsymbol{\rho}}^{i}(t)\hat{H} - \hat{H}\hat{\boldsymbol{\rho}}^{i}(t)]_{nm} \tilde{A}_{mn} = -\frac{1}{N} \frac{j}{\hbar} \sum_{i} \sum_{m,n} [\hat{H}, \hat{\boldsymbol{\rho}}^{i}(t)]_{nm} \tilde{A}_{mn}$$
(67)

where in the last equality $\begin{bmatrix} \hat{H}, \hat{\rho}^i(t) \end{bmatrix}_{nm}$ denotes the *n*, *m* matrix element of the commutator bracket formed from \hat{H} and $\hat{\rho}^i(t)$. Note that we write the time-dependent density matrix $\hat{\rho}^i(t)$ in bold in order to emphasize the difference between this quantity and ordinary operators. Finally, the sum over the *N* systems can be performed yielding

$$\frac{d\langle A \rangle}{dt} = -\frac{j}{\hbar} \sum_{m,n} \left[\hat{H}, \frac{1}{N} \sum_{i} \hat{\boldsymbol{\rho}}^{i}(t) \right]_{nm} \tilde{A}_{mn} = -\frac{j}{\hbar} \sum_{m,n} \left[\hat{H}, \hat{\boldsymbol{\rho}}(t) \right]_{nm} \tilde{A}_{mn} = \sum_{n} \left(-\frac{j}{\hbar} \left[\hat{H}, \hat{\boldsymbol{\rho}}(t) \right] \hat{A} \right)_{nn} = Tr \left[-\frac{j}{\hbar} \left[\hat{H}, \hat{\boldsymbol{\rho}}(t) \right] \hat{A} \right]$$
(68)

where we define the N-system density matrix

$$\hat{\boldsymbol{\rho}}(t) = \frac{1}{N} \sum_{i=1}^{N} \hat{\boldsymbol{\rho}}^{i}(t)$$
(69)

We can write our original mean expectation value $\overline{\langle A \rangle}$ [Eq.(60)] in terms of $\hat{\rho}(t)$ as well:

$$\overline{\langle A \rangle} = \sum_{m,n} \tilde{\rho}_{nm}(t) \tilde{A}_{mn} = \sum_{n} [\hat{\rho}(t) \hat{A}]_{nn} = Tr[\hat{\rho}(t) \hat{A}]$$
(70)

Thus $\hat{\mathbf{\rho}}(t)$ represents a conventional statistical average over the ensemble; knowledge of this quantity allows us to calculate the mean expectation values [through Eq.(70)] as well as their time rates of change [through Eq. (68)].

Now for the important part: All this algebra is useless unless we have an equation of motion for $\hat{\rho}(t)$ itself! To find this equation, differentiate Eq. (70) with respect to time:

$$\frac{d\overline{\langle A \rangle}}{dt} = Tr[\dot{\hat{\mathbf{p}}}(t)\hat{A}]$$
(71)

and equate this result with the RHS of Eq.(68):

$$Tr[\dot{\hat{\boldsymbol{\rho}}}(t)\hat{A}] = Tr\left[-\frac{j}{\hbar}\left[\hat{H},\hat{\boldsymbol{\rho}}(t)\right]\hat{A}\right]$$
(72)

Because this equation must hold for any time-independent operator \hat{A} , we have

$$\dot{\hat{\boldsymbol{\rho}}}(t) = -\frac{j}{\hbar} \Big[\hat{H}, \hat{\boldsymbol{\rho}}(t) \Big]$$
(73)

With the additional feature of representing a statistical average over the *N*-system ensemble, this last result is really nothing more than a different expression of the same information embodied in the Shrödinger equation of motion. Its real power becomes apparent when we discuss a quantum mechanical system coupled to a continuum of perturbing states, as the following now illustrates.

2.2.2 Damping in the Semiclassical Equations of Motion

We consider a Hamiltonian in this general form:

$$\hat{H}_{tot} = \hat{H}_0 + \hat{H}_{int}(t) + \hat{H}_R(t)$$
(74)

where \hat{H}_0 is meant to denote the unperturbed time-independent Hamiltonian whose eigenstates and eigenvalues we suppose to know before hand, $\hat{H}_{int}(t)$ is a time-dependent interaction Hamiltonian whose explicit form we know how to construct (as, for instance, in the case of an applied sinusoidally varying electric field), while the time-dependent Hamiltonian $\hat{H}_R(t)$ is meant to encapsulate interactions between the system and a reservoir of states comprised of a *large* number of other degrees of freedom. Otherwise, the explicit form of $\hat{H}_R(t)$ is unknown. For example, we can suppose that $\hat{H}_R(t)$ characterizes elastic collisions between the system and other particles. We also assume that an $\hat{H}_R(t)$ can be conceived that would mimic the effects of spontaneous radiative emission or collision induced de-excitation. This is the essence of the semiclassical approach: A full quantum treatment of the states giving rise to damping of the system is

foregone in favor of some ad hoc $\hat{H}_R(t)$ that still depends on system operators but depends only parametrically on the reservoir coordinates. Most importantly, however, the density-matrix approach does not even require us to provide an explicit form of $\hat{H}_R(t)$. Instead, we will make a heuristic argument as to how the existence of $\hat{H}_R(t)$ modifies the equation of motion for the density matrix. This is the fundamental advantage that the density-matrix approach holds over use of the Shrödinger equation in understanding multiparticle systems subject to damping. For the moment, we'll set $\hat{H}_{int}(t)$ to zero in order to develop an equation of motion in the case of pure damping of the excited state. For concreteness, we will also restrict attention to just a single two-level quantum system. In this case, the time derivative of the density matrix becomes

$$\dot{\hat{\boldsymbol{\rho}}} = -\frac{j}{\hbar} \Big[\hat{H}_0, \hat{\boldsymbol{\rho}} \Big] - -\frac{j}{\hbar} \Big[\hat{H}_R, \hat{\boldsymbol{\rho}} \Big]$$
(75)

Assuming now that we choose as basis states the eigenvectors of \hat{H}_0 , the diagonal elements of the first commutator bracket are easily shown to vanish and hence the diagonal elements of $\hat{\hat{\rho}}(t)$ are

$$\dot{\rho}_{ii}(t) = -\frac{j}{\hbar} \Big[\hat{H}_R, \hat{\mathbf{\rho}}(t) \Big]_{ii}$$
(76)

Returning as an example to the two-level system with energy eigenstates $|a\rangle$ and $|b\rangle$, we already know from Eq. (53) for coupling to a damping continuum consisting of a radiation field that

$$\dot{\rho}_{bb}(t) \equiv -\gamma c_b^* c_b = -\gamma \rho_{bb} \tag{77}$$

and thus

$$-\frac{j}{\hbar} \left[\hat{H}_{R}, \mathbf{\rho}(t) \right]_{bb} \equiv -\gamma \rho_{bb}$$
(78)

We also see that necessarily

$$-\frac{j}{\hbar} \left[\hat{H}_{R}, \boldsymbol{\rho}(t) \right]_{aa} = -\gamma (\rho_{aa} - 1) = \gamma \rho_{bb}$$
⁽⁷⁹⁾

As for the off-diagonal elements, the essential assumption of the semiclassical theory is that these are damped in analogous fashion to the diagonal elements, hence

$$-\frac{j}{\hbar} \left[\hat{H}_{R}, \hat{\boldsymbol{\rho}}(t) \right]_{nm} = -\gamma_{nm} \rho_{nm}, \quad n \neq m$$
(80)

This assumption, however, is not as arbitrary as it may at first seem: because $|c_b|^2$ is exponentially damped at the rate γ , c_b will be exponentially damped at the rate $\gamma/2$. The bilinear product $\tilde{\rho}_{ba}(t) = \tilde{c}_a^*(t)\tilde{c}_b(t)$ must exponentially relax to zero at the same rate as c_b since $|\tilde{c}_a|$ is bounded from above. It can be shown quite generally that for purely inelastic damping processes the off-diagonal elements of the density matrix for a two-level system with a stable lower level are

$$\gamma_{ab} = \gamma_{ba} = \gamma / 2 \tag{81}$$

So far, our discussion has established the form of the equation of motion for the density matrix in the case of inter-level relaxation as mediated by a radiative continuum coupled to the system. It is evident from our discussion that exactly analogous results obtain for collision-mediated or other nonradiative inelastic relaxation processes. With regard to *elastic* processes, however, the density matrix formalism provides a natural way to include these effects as well.

Consider the previous result Eq. (46) for the expectation value of the dipole moment for the two-level system:

$$\left\langle \mathbf{\mu} \right\rangle = \tilde{c}_{a}^{*}(t)\tilde{c}_{b}(t)\tilde{\mathbf{\mu}}_{ab} + \tilde{c}_{b}^{*}\tilde{c}_{a}\mathbf{\mu}_{ba} = \rho_{ba}(t)\mathbf{\mu}_{ab} + \rho_{ab}(t)\mathbf{\mu}_{ba}$$
(82)

This expression depends on only the off-diagonal elements of the density matrix. On the other hand, we know from the discussion immediately above that the effect of inelastic collisions that de-excite the state $|b\rangle$ is a commensurate exponential decay of the off-diagonal elements and with them the dipole moment, as seen through Eq. (82). To include the effect of elastic collisions, we simply propose that an additional damping term be added to the equations of motion for the off-diagonal elements that is exactly analogous to the effect of inter-level relaxation. In short,

$$\gamma_{ab} = \gamma_{ba} = \gamma / 2 + \gamma_{elastic} \tag{83}$$

where γ refers to the inelastic portion of the relaxation and $\gamma_{elastic}$ to the elastic portion. The factor of 1/2 does not appear in the latter term because γ quantifies a rate of *population* change rather than a collision rate. This point can be made more concrete by considering a large number of two-level systems whose dipole moments are initially all in phase. In terms of the density matrix, this circumstance corresponds to each one-sys-

tem density matrix being in phase with all the others. The net result is a macroscopic dipole moment equal in magnitude to the sum of the amplitudes of all the dipoles. Since the effect of a single collision is to randomly dephase the quantum state of one of the systems (and hence the expectation value of its dipole moment) with respect to the remaining systems, the average effect of elastic collisions on the total dipole moment of the ensemble will be an exponential decay of dipole moment (or polarization) at a rate exactly equal to the collision rate. Hence

$$\left\langle \boldsymbol{\mu} \right\rangle_{macro} = N \left(\rho_{ba}^{0} \boldsymbol{\mu}_{ab} + \rho_{ab}^{0} \boldsymbol{\mu}_{ba} \right) e^{-(\gamma/2 + \gamma_{elastic})t}$$
(84)

where *N* is the number of systems and ρ_{ij}^0 is the initial value of the one-system offdiagonal density matrix element.

Combining all the pieces, the general equation of motion for the density matrix for an ensemble of freely decaying two-level systems is

$$\begin{pmatrix} \dot{\rho}_{aa} & \dot{\tilde{\rho}}_{ab} \\ \dot{\tilde{\rho}}_{ba} & \dot{\rho}_{bb} \end{pmatrix} = - \frac{j}{\hbar} \begin{pmatrix} 0 & -(E_b - E_a)\tilde{\rho}_{ab} \\ (E_b - E_a)\tilde{\rho}_{ba} & 0 \end{pmatrix} - \begin{pmatrix} \gamma(\rho_{aa} - 1) & (\gamma/2 + \gamma_{elastic})\tilde{\rho}_{ab} \\ (\gamma/2 + \gamma_{elastic})\tilde{\rho}_{ba} & \gamma \rho_{bb} \end{pmatrix}$$
(85)

If we now include the possibility that these systems are exposed to a driving electric field, $\mathbf{E}(t)$, that is

$$\hat{H}_{int} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(t) = \begin{pmatrix} 0 & \hat{\boldsymbol{\mu}}_{ab} \\ \hat{\boldsymbol{\mu}}_{ba} & 0 \end{pmatrix} \cdot \mathbf{E}(t)$$
(86)

then added to the matrix equation above is

$$-\frac{j}{\hbar} \left[\hat{H}_{int}, \hat{\boldsymbol{\rho}} \right] = \frac{j}{\hbar} \begin{pmatrix} \tilde{\rho}_{ba} \tilde{\boldsymbol{\mu}}_{ab} - \tilde{\rho}_{ab} \tilde{\boldsymbol{\mu}}_{ba} & (\rho_{bb} - \rho_{aa}) \tilde{\boldsymbol{\mu}}_{ab} \\ -(\rho_{bb} - \rho_{aa}) \tilde{\boldsymbol{\mu}}_{ba} & -\tilde{\rho}_{ba} \tilde{\boldsymbol{\mu}}_{ab} + \tilde{\rho}_{ab} \tilde{\boldsymbol{\mu}}_{ba} \end{pmatrix} \cdot \mathbf{E}(t)$$
(87)

In all generality then, the time rate of change of the density matrix in the presence of an external field is given by the coupled system of equations

$$\dot{\rho}_{aa} = \frac{j}{\hbar} \left(\tilde{\rho}_{ba} \tilde{\boldsymbol{\mu}}_{ab} - \tilde{\rho}_{ab} \tilde{\boldsymbol{\mu}}_{ba} \right) \cdot \mathbf{E}(t) - \gamma (\rho_{aa} - 1)$$

$$\dot{\rho}_{bb} = -\frac{j}{\hbar} \left(\tilde{\rho}_{ba} \tilde{\boldsymbol{\mu}}_{ab} - \tilde{\rho}_{ab} \tilde{\boldsymbol{\mu}}_{ba} \right) \cdot \mathbf{E}(t) - \gamma \rho_{bb}$$

$$\dot{\tilde{\rho}}_{ab} = \frac{j}{\hbar} (E_b - E_a) \tilde{\rho}_{ab} + \frac{j}{\hbar} (\rho_{bb} - \rho_{aa}) \tilde{\boldsymbol{\mu}}_{ab} \cdot \mathbf{E}(t) - (\gamma / 2 + \gamma_{elastic}) \tilde{\rho}_{ab}$$

$$\dot{\tilde{\rho}}_{ba} = \dot{\tilde{\rho}}_{ab}^*$$
(88)

Equations (88) are what all this work has been driving toward: a semiclassical description of the response of a quantum two-level system to an applied electric field in the presence of inelastic and elastic damping processes. Embedded within the solutions to these equations is a wealth of information regarding electromagnetic interactions with matter, among which of particular interest are quantum theories of absorption and stimulated emission. The equations also lead to a theory of the homogeneous line shape. We now derive these results.

2.2.3 Solutions of the Equations of Motion in the Rate-Equation Limit: Absorption and Stimulated Emission

Our discussion of the classical dipole oscillator suggests that after switching on a sinusoidally varying applied electric field a steady state will evolve in which the mechanical energy of the oscillator remains constant in time while the dipole moment will continue to vary sinusoidally in time in response to the applied field. In the quantum mechanical context, we expect analogous results. In terms of the elements of the density matrix, the diagonal elements therefore will reach constant values after initial transients have damped away and thus $\dot{\rho}_{aa} = \dot{\rho}_{bb} = 0$. On the other hand, even in the presence of damping, the off-diagonal elements must continue to vary in time at a frequency equal to that of the driving field so as to yield a nonzero time-varying value for the field-induced dipole moment [Eq. (3)]. As made explicit below, these observations suggest that a case intermediate between the full time-dependent solutions to Eqs. (88) and the steady-state case may be considered.

We first construct the interaction Hamiltonian appropriate to a monochromatic applied electric field:

$$\hat{H}_{int} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(t) = -\begin{pmatrix} 0 & \hat{\boldsymbol{\mu}}_{ab} \\ \hat{\boldsymbol{\mu}}_{ba} & 0 \end{pmatrix} \cdot \frac{1}{2} \mathbf{E}_0 \left(e^{j\omega t} + e^{-j\omega t} \right)$$

$$= \begin{pmatrix} 0 & \frac{\hat{\boldsymbol{\mu}}_{ab} \cdot \mathbf{E}_0}{2} \left(e^{j\omega t} + e^{-j\omega t} \right) \\ \frac{\hat{\boldsymbol{\mu}}_{ba} \cdot \mathbf{E}_0}{2} \left(e^{j\omega t} + e^{-j\omega t} \right) & 0 \end{pmatrix}$$
(89)

where \mathbf{E}_0 is a real, time-independent vector. We next introduce a standard approximation whose effect is to eliminate rapidly varying, nonresonant components to the solutions. Termed the *rotating-wave approximation*, the approximation consists of simply substituting for the exact interaction Hamiltonian Eq. (89) the modified Hamiltonian

$$\hat{H}'_{int} = \begin{pmatrix} 0 & \frac{\tilde{\mu}_{ab} \cdot \mathbf{E}_0}{2} e^{j\omega t} \\ \frac{\tilde{\mu}_{ba} \cdot \mathbf{E}_0}{2} e^{-j\omega t} & 0 \end{pmatrix}$$
(90)

Note that the essence of the approximation is to discard the "negative-frequency" timevarying portion of the applied electric field, $e^{-j\omega t}$, in $\langle a | \hat{H}_{int} | b \rangle$ while being sure to set $\langle b | \hat{H}'_{int} | a \rangle = \langle a | \hat{H}'_{int} | b \rangle^*$ so that Hermiticity of the interaction Hamiltonian is preserved. The equations of motion Eqs. (88) become under the rotating-wave approximation

$$\dot{\rho}_{aa} = \frac{j}{\hbar} \left(\tilde{\rho}_{ba} \frac{\tilde{\mu}_{ab} \cdot \mathbf{E}_{0}}{2} e^{j\omega t} - \tilde{\rho}_{ab} \frac{\tilde{\mu}_{ba} \cdot \mathbf{E}_{0}}{2} e^{-j\omega t} \right) - \gamma(\rho_{aa} - 1)$$

$$\dot{\rho}_{bb} = -\frac{j}{\hbar} \left(\tilde{\rho}_{ba} \frac{\tilde{\mu}_{ab} \cdot \mathbf{E}_{0}}{2} e^{j\omega t} - \tilde{\rho}_{ab} \frac{\tilde{\mu}_{ba} \cdot \mathbf{E}_{0}}{2} e^{-j\omega t} \right) - \gamma\rho_{bb}$$
(91)a,b,c,d
$$\dot{\tilde{\rho}}_{ab} = \frac{j}{\hbar} (E_{b} - E_{a}) \tilde{\rho}_{ab} + \frac{j}{\hbar} (\rho_{bb} - \rho_{aa}) \frac{\tilde{\mu}_{ab} \cdot \mathbf{E}_{0}}{2} e^{j\omega t} - \Gamma \tilde{\rho}_{ab}$$

$$\dot{\tilde{\rho}}_{ba} = \dot{\tilde{\rho}}_{ab}^{*}$$

where $\Gamma = \gamma/2 + \gamma_{elastic}$ is the total dephasing rate. We now suppose that $\rho_{bb} - \rho_{aa}$ varies sufficiently slowly in time compared with the time variation of the driving field that it can be taken as effectively constant in Eqs. (91). We also suppose that the driving field has been present for a time long compared with the dephasing time $1/\Gamma$. Under these approximations, the so-called rate-equation limit of the equations of motion, Eq. (91)c is easily integrated yielding

$$\tilde{\rho}_{ab} = \frac{\tilde{\mu}_{ab} \cdot \mathbf{E}_0}{2\hbar} (\rho_{bb} - \rho_{aa}) \frac{e^{j\omega t}}{\omega - \omega_0 - j\Gamma}$$
(92)

where $\omega_0 = \omega_{ba} = \hbar^{-1} (E_b - E_a)$ is the resonant frequency of the system. Substitution of the latter result into Eq. (91)b gives:

$$\dot{\rho}_{bb} = -\frac{\left|\tilde{\boldsymbol{\mu}}_{ab} \cdot \mathbf{E}_{0}\right|^{2}}{2\hbar^{2}} \left(\rho_{bb} - \rho_{aa}\right) \frac{\Gamma}{\left(\omega - \omega_{0}\right)^{2} + \Gamma^{2}} - \gamma \rho_{bb}$$
(93)

A similar argument yields

$$\dot{\rho}_{aa} = \frac{\left|\tilde{\boldsymbol{\mu}}_{ab} \cdot \mathbf{E}_{0}\right|^{2}}{2\hbar^{2}} \left(\rho_{bb} - \rho_{aa}\right) \frac{\Gamma}{\left(\omega - \omega_{0}\right)^{2} + \Gamma^{2}} + \gamma \rho_{bb} = -\dot{\rho}_{bb}$$
(94)

2.2.3.1 Absorption

Consider now Eq. (94) for the case of an applied field polarized in the *x* direction and in the limit where ρ_{bb} is initially very small:

$$\dot{\rho}_{aa}(\rho_{bb} \ll 1) = -\frac{\left|\tilde{\boldsymbol{\mu}}_{ab} \cdot E_0 \boldsymbol{e}_x\right|^2}{2\hbar^2} \frac{\Gamma}{\left(\omega - \omega_0\right)^2 + \Gamma^2} = -\frac{\pi \left|\tilde{\boldsymbol{\mu}}_{ab}\right|^2 \cos^2(\theta)}{\hbar^2 \varepsilon_0} \left(\frac{I_{inc}}{c}\right) L(\omega - \omega_0)$$
(95)

where the latter equality has been written in terms of the normalized Lorentzian line shape function [Eq. (19), suitably modified in keeping with our definition of Γ] and the incident optical intensity $I_{inc} = (1/2)\varepsilon_0 cE_0^2$. The angle θ is just the angle between the expectation value of the dipole moment – $\mathbf{\mu}_{ab} = \langle a | \hat{\mathbf{\mu}}_{ab} | b \rangle$ – and the direction of polarization of the incident field, \mathbf{e}_x . Considering next a collection of randomly oriented systems (as would arise in the gas phase or in an amorphous host material) with a number density of *N*, the total rate of change of the population in the $|b\rangle$ state must be

$$\dot{N}_{b} = -N\dot{\rho}_{aa} = N\frac{\pi \left|\tilde{\boldsymbol{\mu}}_{ab}\right|^{2}}{3\hbar^{2}\varepsilon_{0}} \left(\frac{I_{inc}}{c}\right) L(\omega - \omega_{0})$$
(96)

noting that the average of $\cos^2(\theta)$ over all directions in space is 1/3. This result shows that just as in the classical case, the existence of an electric dipole moment in the two-level system must give rise to absorption of energy from the applied field. This energy absorption can be quantified just as before by considering a slab of the material of

thickness dz and noting that the change in power of the incident field on passing at normal incidence through the slab is

$$dI = -\hbar\omega_0 \dot{N}_b dz = -N \frac{\pi\omega_0 \left|\tilde{\boldsymbol{\mu}}_{ab}\right|^2}{3\hbar\varepsilon_0} \left(\frac{I_{inc}}{c}\right) L(\omega - \omega_0) dz$$
(97)

which implies that the absorption cross section in the quantum two-level system is

$$\sigma_{abs}(\omega) = \frac{\pi \omega_0 \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2}{3\hbar \varepsilon_0 c} L(\omega - \omega_0)$$
(98)

and thus that the frequency-integrated cross section is

$$\int_{-\infty}^{\infty} \sigma_{abs}(\omega) d\omega = \frac{\pi \omega_0 \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2}{3\hbar \varepsilon_0 c}$$
(99)

Introducing the quantum absorption oscillator strength in direct analogy with Eq.(22), *i.e.*

$$\int_{-\infty}^{\infty} \sigma_{abs}(\omega) d\omega = \frac{\pi e^2}{2m_e c\varepsilon_0} f_{abs}$$
(100)

implies that

$$f_{abs} = \frac{2m_e \omega_0 \left|\tilde{\boldsymbol{\mu}}_{ab}\right|^2}{3\hbar e^2} \tag{101}$$

A curious feature of this last result is that it appears that the absorption oscillator strength increases linearly with the frequency. This stands in contrast with the result obtained for the classical oscillator, Eq. (23), which showed no frequency dependence at all, a fact that made the oscillator strength such a useful measure with which to compare the strength of different transitions. It seems unreasonable that a quantum theory of the oscillator strength would exhibit such a qualitatively different feature than does the classical theory. In fact, the resolution of this discrepancy is simply that embedded within the squared dipole-moment matrix element is an ω_0^{-1} frequency dependence. While it is not possible to prove this without specifying the precise details of the quantum system under discussion, it is qualitatively reasonable that this be so given that with an increasing energy difference between two energy eigenstates, the less spatial

overlap will exist between the corresponding wave functions. Hence the smaller will be the dipole-moment matrix element. The reader may wish to verify the ω_0^{-1} frequency dependence of the squared dipole-moment matrix element for a specific quantum system; for it's simplicity, the one-dimensional harmonic oscillator is particularly recommended.

As an interesting aside, another important feature of the quantum oscillator strength is that it satisfies a sum rule. For example, with regard to an atom or ion, the oscillator strengths for transitions from the ground state to all excited states sums to a value usually close to unity. If one includes the possibility of optically induced downward transitions, a circumstance to be discussed in detail in the next section, then the oscillator strengths for transitions from *any* initial state to all others will satisfy the same sum rule provided that the oscillator strengths for down-going transitions are taken as negative.

Returning to the main argument, we are now in a position to define the *Einstein B coefficient* for absorption on the $a \rightarrow b$ transition:

$$B_{ab} = \frac{\pi \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2}{3\hbar^2 \varepsilon_0} \tag{102}$$

In terms of the *B* coefficient, the time rate of change of the $|b\rangle$ -state population due to absorption is just

$$\dot{N}_{b} = NB_{ab} \left(\frac{I_{inc}}{c}\right) L(\omega - \omega_{0})$$
(103)

This definition is motivated by a desire to express the transition rate in terms of an *energy density* of the incident radiation, namely I_{inc}/c , rather than its intensity. The rational for such a choice will emerge in Section 2.2.4 below.

2.2.3.2 Stimulated Emission

Much of the previous argument can be applied in considering Eq. (94) in the opposite limit of $\rho_{aa} \ll 1$. The result is

$$\dot{N}_{b} = -N \frac{\pi \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^{2}}{3\hbar^{2} \varepsilon_{0}} \left(\frac{I_{inc}}{c} \right) L(\omega - \omega_{0})$$
(104)

We thus see that in a fashion reciprocal to that of absorption, the applied field drives population out of the excited state into the ground state. But what is crucial regarding this observation is that the driving field is *amplified* in the process. To see this, first recall the classical wave equation for the electric field vector in the presence of a source polarization:

$$\nabla^{2} \mathbf{E}(\mathbf{r},t) - \frac{1}{c^{2}} \frac{\partial^{2} \mathbf{E}(\mathbf{r},t)}{\partial t^{2}} = \frac{4\pi}{c^{2}} \frac{\partial^{2} \mathbf{P}(\mathbf{r},t)}{\partial t^{2}}$$
(105)

In turn, the macroscopic polarization $P(\mathbf{r}, t)$ is given in terms of the density matrix as

$$\mathbf{P}(\mathbf{r},t) = N \left\langle \mathbf{\mu} \right\rangle = N \left(\rho_{ba} \tilde{\mathbf{\mu}}_{ab} + \rho_{ab} \tilde{\mathbf{\mu}}_{ba} \right)$$
(106)

where we suppose that a volume of two-level systems of number density N fills a space labeled by the position vector **r**. Hence

$$\frac{\partial^{2} \mathbf{P}(\mathbf{r},t)}{\partial t^{2}} = N\left(\ddot{\rho}_{ba}\tilde{\mathbf{\mu}}_{ab} + \ddot{\rho}_{ab}\tilde{\mathbf{\mu}}_{ba}\right) \\
= -\omega^{2}\left(\rho_{bb} - \rho_{aa}\right) \left[\frac{\tilde{\mathbf{\mu}}_{ba} \cdot \mathbf{E}_{0}(\mathbf{r})}{2\hbar} \frac{e^{-j\omega t}}{\omega - \omega_{0} + j\Gamma} + \frac{\tilde{\mathbf{\mu}}_{ab} \cdot \mathbf{E}_{0}(\mathbf{r})}{2\hbar} \frac{e^{j\omega t}}{\omega - \omega_{0} - j\Gamma}\right]$$
(107)

Since we already know that for $\rho_{bb} \rightarrow 0$ the electric field amplitude $\mathbf{E}_0(\mathbf{r})$ will decrease as the wave propagates through the medium, the change in sign of $\partial^2 \mathbf{P}(\mathbf{r},t)/\partial t^2$ that is evident in the above expression when $\rho_{aa} \rightarrow 0$ must yield an *increase* in the amplitude. In fact, we see that in all generality that if $\rho_{bb} - \rho_{aa} > 0$, that is, if there is a *population inversion* between the $|b\rangle$ and $|a\rangle$ states, the medium of two-level systems will amplify the applied electromagnetic field. This is the essential physical phenomenon underlying semiclassical laser theory, one that is not predicted by the purely classical theory presented earlier. In exact analogy with the case of absorption, the cross section, oscillator strength, and Einstein *B* coefficient for stimulated emission in the two-level system are readily defined and yield simply

$$\sigma_{se} = \sigma_{abs}, \quad f_{se} = -f_{abs}, \quad B_{ba} = B_{ab} \tag{108}$$

where the minus sign for the stimulated-emission oscillator strength is introduced by convention in order to preserve the oscillator strength sum rules discussed in the previous section. The reciprocity of absorption and amplification in the medium immediately leads to a definition of the *gain coefficient*. In terms of the cross sections, for example, it is given in the case of general ρ_{bb} and ρ_{aa} by

$$g(\omega) = N \left[\sigma_{se}(\omega) \rho_{bb} - \sigma_{abs}(\omega) \rho_{aa} \right] = \sigma_{se}(\omega) N_b - \sigma_{abs}(\omega) N_a$$
(109)

By analogy with the absorption coefficient, the intensity of an applied plane-wave field varies with distance through the medium according to

$$I(z) = I_0 e^{-g(\omega)z} \tag{110}$$

This relation, however, only holds provided that the intensity never becomes so large as to significantly change the local value of N_b . For this reason, $g(\omega)$ in this limit is more precisely termed the *small-signal* gain coefficient.

2.2.3.3 Level Degeneracy

So far, we have neglected the possibility that the states $|a\rangle$ and $|b\rangle$ are degenerate. Level degeneracy can be included in a natural way by simply summing the contributions to absorption or stimulated emission over all possible transitions between the degenerate states of the lower and upper manifolds. For example, in the case of absorption, we can simply insist on continuing to express the absorption coefficient in terms of a cross section defined to embody the effect of multiple transitions to the excited manifold. In other words,

$$\alpha(\omega) = N_a \sigma_{abs}(\omega) = \sum_{i=1}^{g_a} \sum_{j=1}^{g_b} N_{a,i} \sigma_{abs}^{i,j}(\omega)$$
(111)

where $N_{a,i}$ is the population in the i^{th} sublevel of the lower manifold of degenerate states and where

$$\sigma_{abs}^{i,j}(\omega) = \frac{\pi \omega_0 \left| \tilde{\boldsymbol{\mu}}_{ab}^{i,j} \right|^2}{3\hbar \varepsilon_0 c} L(\omega - \omega_0)$$
(112)

is the absorption cross section for a transition from the i^{th} sublevel of the lower manifold to the j^{th} sublevel of the upper manifold. Note that the line shape function $L(\omega - \omega_0)$ is taken to be the *same* for each of the separate sublevel transitions, an assumption that is not rigorously justified, but one that in fact has little practical affect on the results. One reason this can be so is if collisions or other external homogeneous disturbances determine the line width of each sublevel transition rather than a radiative relaxation rate. Another consequence of such disturbances is that the total population in each manifold is equally divided between each of the sublevels, thus giving $N_{a,i} = N_a / g_a$. The absorption coefficient then becomes

$$\alpha(\omega) = \sum_{i=1}^{g_a} \sum_{j=1}^{g_b} \frac{N_a}{g_a} \frac{\pi \omega_0 \left| \tilde{\boldsymbol{\mu}}_{ab}^{i,j} \right|^2}{3\hbar \varepsilon_0 c} L(\omega - \omega_0) = g_a g_b \left(\frac{N_a}{g_a} \right) \frac{\pi \omega_0 \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar \varepsilon_0 c} L(\omega - \omega_0)$$

$$= N_a \frac{g_b \pi \omega_0 \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar \varepsilon_0 c} L(\omega - \omega_0)$$
(113)

where $\langle |\tilde{\mu}_{ab}|^2 \rangle$ is just the dipole moment matrix element averaged over all possible initial and final sublevels. A similar expression results for the small-signal gain coefficient, thus yielding in the case of degenerate lower and upper manifolds absorption and stimulated-emission cross sections of

$$\sigma_{abs}(\omega) = \frac{g_b \pi \omega_0 \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar \varepsilon_0 c} L(\omega - \omega_0)$$
(114)

and

$$\sigma_{se}(\omega) = \frac{g_a \pi \omega_0 \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar \varepsilon_0 c} L(\omega - \omega_0)$$
(115)

and thus the important relation

$$g_b \sigma_{se} = g_a \sigma_{abs} \tag{116}$$

The oscillator strengths and Einstein B coefficients for absorption and stimulated emission are similarly generalized to

$$f_{abs} = \frac{2m_e \omega_0 g_b \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar e^2}, \quad f_{se} = -\frac{2m_e \omega_0 g_a \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar e^2}$$
(117)a,b

and

$$B_{ab} = \frac{\pi g_b \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar^2 \varepsilon_0}, \quad B_{ba} = \frac{\pi g_a \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar^2 \varepsilon_0}$$
(118)a,b

from which one obtains

$$g_b f_{se} = -g_a f_{abs} \tag{119}$$

and

$$g_b B_{ba} = g_a B_{ab} \tag{120}$$

Table 1 gives a list of values for interesting radiative quantities pertinent to important laser transitions.

2.2.4 Relationship between the Einstein *A* and *B* Coefficients

The semiclassical theory of optical transitions that we have used to derive the results of the preceding sections is not applicable to the first-principles calculation of the Einstein A coefficient. As asserted earlier, such a calculation requires quantization of the electromagnetic field. Nevertheless, we expect a relationship between the A and Bcoefficients insofar as they both quantify in different ways the coupling between an optically active microscopic system and the electromagnetic field. This relationship can be rigorously derived through a thermodynamic argument due originally to Einstein.

We consider again a two-level system with lower and upper manifold degeneracies of g_a and g_b , respectively. A gas of these systems is supposed to fill a large box whose interior walls are painted black and whose exterior walls are in contact with a thermal reservoir of temperature T. On the other hand, we idealize the inner walls of the box to be incapable of exchanging energy with the two-level systems as a result of collisions with the walls. We also consider only a very small number density of systems in the box so that mutual collisions are unimportant. Instead, Planck radiation of temperature T within the box will provide the only means by which transitions may be induced between the upper and lower manifolds.

Now in thermodynamic equilibrium, the temperature of the systems is T as well, so that according to elementary statistical mechanics the ratio of the populations in the two manifolds must be

$$\frac{N_b}{N_a} = \frac{g_b}{g_a} e^{-\hbar\omega_0/kT}$$
(121)

However, we know that radiative relaxation out of the excited manifold will deplete the upper state, as will stimulated emission induced by the radiation in the box, while ab-

Transition	Wavelength	Radiative lifetime	Peak stimulated emission cross section	Oscillator strength
HeNe laser transition $3s_2 2p_4$	633 nm	0.7 µs	~10 ⁻¹³ cm ²	0.0047
Nd:YAG laser transition ${}^{4}F_{3/2} {}^{4}I_{3/2}$	1.064 µm	1.22 ms	$4.6 \times 10^{-19} \text{ cm}^2$	~8 × 10 ⁻⁶
Ruby laser transition ${}^{2}E {}^{4}A_{2}$	694 nm	4.3 ms	$2 \times 10^{-20} \text{ cm}^2$	~10 ⁻⁶
Rhodamine 6Gdye laser transition S_1 S_0	620 nm	3.3 ns	$2 \times 10^{-16} \text{ cm}^2$	~1.1

Table 1.Some spectroscopic parameters for common laser systems. [From Siegman (1986)].

sorption of this radiation will repopulate the upper manifold. The essence of the argument then is to equate the rates of radiative down going and up going transitions (the systems are in equilibrium after all!) and further insist that the steady-state populations thereby achieved be related by the ratio Eq. (121).

The first step is to translate the results obtained in Section 2.2.3, which concern transitions induced by a plane monochromatic wave according to

$$\dot{N}_{b} = \left[N_{a}B_{ab} - N_{b}B_{ba}\right] \left(\frac{I}{c}\right) L(\omega - \omega_{0})$$
(122)

into a corresponding equation appropriate to the broad band incoherent radiation in the box. This is easily accomplished by first recalling that I/c is just the energy density of the applied field, suggesting that

$$\Delta \dot{N}_{b}(\omega) = \left[N_{a}B_{ab} - N_{b}B_{ba} \right] \rho_{\omega}(\omega)L(\omega - \omega_{0})\Delta\omega$$
(123)

is the contribution to the time rate of change of the upper-state population due to the presence of Planck radiation within the narrow range of frequencies $\Delta \omega$. This radiation is of spectral energy density $\rho_{\omega}(\omega)$ (units of energy per unit volume per unit frequency interval) at the frequency ω . It is important to recognize in forming this last expression that the energy density of the radiation in the box is a simple arithmetic sum over frequency of the spectral energy density. In other words, the thermal character of the radiation insures that no correlations exist in the electric field at one frequency relative to that at another frequency. Taking Eq. (123) in the limit of $\Delta \omega \rightarrow 0$ and integrating over frequency yields for the radiation-induced total rate of transitions to the upper manifold

$$\dot{N}_{b} = \left[N_{a}B_{ab} - N_{b}B_{ba}\right] \int_{-\infty}^{\infty} \rho_{\omega}(\omega) L(\omega - \omega_{0}) d\omega = \left[N_{a}B_{ab} - N_{b}B_{ba}\right] \rho_{\omega}(\omega_{0})$$
(124)

In obtaining this result, the slow variation of $\rho_{\omega}(\omega)$ with frequency relative to the width of the normalized line shape function has been used to write the second equality. Including now the contribution due to spontaneous transitions, the total rate of change of the upper manifold population is

$$\dot{N}_{b} = \left[N_{a}B_{ab} - N_{b}B_{ba}\right]\rho_{\omega}(\omega_{0}) - A_{ba}N_{b}$$
(125)

Having now included all the processes capable of changing the upper manifold population density, thermodynamic equilibrium requires that $\dot{N}_b = 0$ and thus Eq. (125) is easily solved for the ratio of the upper and lower manifold population densities:

$$\frac{N_b}{N_a} = \frac{B_{ab}}{B_{ba} + A_{ba} / \rho_\omega(\omega_0)}$$
(126)

With the help of Eq. (121), this leads to

$$\frac{B_{ab}}{B_{ba} + A_{ba} / \rho_{\omega}(\omega_0)} = \frac{g_b}{g_a} e^{-\hbar\omega_0/kT}$$
(127)

Now making use of the relation $B_{ab} = (g_b / g_a)B_{ba}$, Eq. (127) can be solved for the ratio of the *A* and *B* coefficients to give

$$\frac{A_{ba}}{B_{ba}} = \rho_{\omega}(\omega_0) \left(e^{\hbar \omega_0 / kT} - 1 \right)$$
(128)

All we need at this point is an expression for the spectral energy density of Planck radiation, $\rho_{\omega}(\omega_0)$. This is given by

$$\rho_{\omega}(\omega_0) = \frac{\hbar \omega_0^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega_0/kT} - 1}$$
(129)

Although we will not derive this result here, the general form of the spectral energy density can be understood by recognizing that it is a product of three terms: The first is just the energy of a photon at frequency ω_0 ($\hbar\omega_0$), the second term is the number of photons actually present in a radiation mode of frequency ω_0 , namely, the Bose-Einstein occupation factor $(e^{\hbar\omega_0/kT}-1)^{-1}$, and the third term is the density of such modes of frequency ω_0 (number per unit frequency), which we know from simple counting arguments to scale as $2\omega_0^2$ (the factor of 2 is due to the existence of two independent polarizations). The remaining constant factor of $\pi^{-2}c^{-3}$ merely converts the general scaling of the mode degeneracy to units of modes per unit volume (of the box) per unit frequency interval. Combining Eqs. (128) and (129) finally yields

$$\frac{A_{ba}}{B_{ba}} = \frac{\hbar\omega_0^3}{\pi^2 c^3}$$
(130)

Equation (118)b allows us to write the A coefficient in terms of more fundamental quantities of the two-level system:

$$A_{ba} = 1/\tau_{rad} = \frac{g_a \omega_0^3 \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar \pi c^3 \varepsilon_0}$$
(131)

Indeed, a host of relationships between Einstein coefficients, cross sections, lifetimes, dipole moments, and oscillator strengths may be written down with the results developed above. A summary of these is given in Table 2.

2.3 Absorption and Emission in the Solid State: Generalizations of the Einstein Relations

2.3.1 Method of Reciprocity

Both homogeneous and inhomogeneous broadening effects in the solid state are much more pronounced than in the gas phase, particularly at room temperature. As a result, otherwise well-separated spectral lines merge into a single feature or band with a complex spectral profile. In these circumstances, it is convenient to treat such complex features as single units by introducing absorption and stimulated emission cross sections applicable to the feature as a whole. This approach is especially helpful, for example, when very fast thermal equilibration within a manifold of closely spaced energy levels makes this manifold effectively degenerate. That is, rather than keep track of the individual populations found in each member sublevel, it is possible to assign to the manifold as a whole a single population that is equal to the sum of the individual sublevel populations. If, moreover, the homogeneous line width is larger than the inhomogeneous width (a common occurrence for rare-earth impurities in crystals at room temperature and often effectively the case for glass host materials as well), the manifold will behave as if it were homogeneously broadened.

We can make these qualitative ideas more formal as follows. Consider Figure 8, which shows the energy-level diagram for an impurity ion in a solid host at some nonzero temperature *T*. The level structure consists of a pair of well-separated manifolds; each separately consists of closely spaced levels that are thermally well coupled to one another. The number of distinct sublevels (any one of which may itself be degenerate) is designated by D_a for the lower manifold and D_b for the upper manifold. One then defines a total absorption cross section for this system in a manner analogous to our discussion in Section 2.2.3.3 for degenerate states:

	A_{ba}	B_{ab}	$\left< \left \tilde{\mu}_{ab} \right ^2 \right>$	${f}_{abs}$
A_{ba}		$\frac{g_a}{g_b} \frac{\hbar \omega_0^3}{\pi^2 c^3} B_{ab}$	$\frac{g_a \omega_0^3}{3\hbar\pi c^3 \varepsilon_0} \left< \left \tilde{\mu}_{ab} \right ^2 \right>$	$\frac{g_a}{g_b} \frac{\omega_0^2 e^2}{2\pi c^3 m_e \varepsilon_0} f_{abs}$
B_{ab}	$\frac{g_b}{g_a}\frac{\pi^2 c^3}{\hbar\omega_0^3}A_{ba}$		$\frac{\pi g_b}{3\hbar^2 \varepsilon_0} \left< \left \tilde{\mu}_{ab} \right ^2 \right>$	$\frac{\pi e^2}{2m_e\varepsilon_0\hbar\omega_0}f_{abs}$
$\left< \left \tilde{\mu}_{ab} \right ^2 \right>$	$\frac{3\hbar\pi c^3\varepsilon_0}{g_a\omega_0^3}A_{ba}$	$\frac{3\hbar^2\varepsilon_0}{\pi g_b}B_{ab}$		$\frac{3\hbar e^2}{2m_e\omega_0g_b}f_{abs}$
$\sigma_{abs}(\omega)$	$\frac{g_b}{g_a}\frac{\pi^2 c^2}{\omega_0^2}A_{ba}L(\omega-\omega_0)$	$\frac{\hbar\omega_0}{c}B_{ab}L(\omega-\omega_0)$	$\frac{g_b \pi \omega_0 L(\omega - \omega_0)}{3\hbar \varepsilon_0 c} \left\langle \left \tilde{\mu}_{ab} \right ^2 \right\rangle$	$\frac{\pi e^2 L(\omega - \omega_0)}{2m_e \varepsilon_0 c} f_{abs}$
f_{abs}	$\frac{g_b}{g_a} \frac{2\pi c^3 m_e \varepsilon_0}{\omega_0^2 e^2} A_{ba}$	$\frac{2m_e\varepsilon_0\hbar\omega_0}{\pi e^2}B_{ab}$	$\frac{2m_e\omega_0g_b}{3\hbar e^2}\left<\left \tilde{\mu}_{ab}\right ^2\right>$	

Table 2. Relationships Between Fundamental Radiation Quantities Algebraic relations in terms of symbols defined in the text are given for radiative transitions between degenerate states $|a\rangle$ and $|b\rangle$ with energies such that $E_b - E_a - \hbar\omega_0$ and level degeneracies g_a and g_b , respectively. Angle brackets enclosing the squared dipole-moment matrix element indicate an average over all sublevel-to-sublevel transitions within each degenerate manifold. Except for the Einstein *A* coefficient and the dipole moment, all quantities refer to absorption, *i.e.* the *a b* transition. Relations for quantities referring to stimulated emission may be obtained with the help of the expressions $g_b f_{se} = g_a f_{abs}$, $g_b B_{ba} = g_a B_{ab}$, and $g_b \sigma_{se} = g_a \sigma_{abs}$. For analogous expressions in a medium of refractive index *n*, substitute c / n for *c* and $\varepsilon = n \tilde{\varepsilon}_0$ for ε_0 .



Figure 8. Energy level diagram and total absorption cross section for a multilevel system comprised of two well separated manifolds denoted by $|a\rangle$ and $|b\rangle$. Each manifold, in turn, is comprised of D_a and D_b distinct sublevels, respectively, any one of which may be degenerate.

$$\sigma_{abs}^{tot}(\omega) = \frac{1}{N_a} \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} N_{a,i} \sigma_{abs}^{ij}(\omega)$$
(132)

where N_a is the total population density of the lower manifold, $N_{a,i}$ is the population density of the *i*th sublevel of the lower manifold, and $\sigma_{abs}^{ij}(\omega)$ is the absorption cross section for transitions from the g_a^i -fold degenerate *i*th sublevel in the lower manifold to the g_j -fold degenerate *j*th sublevel in the upper manifold.

By hypothesis, however, the sublevels in either the lower or the upper manifold are thermally well coupled to one another and thus $N_{a,i} \equiv N_a g_i e^{-E_i/kT} / Z_a$, where $Z_a = \sum_{i=1}^{D_a} g_i e^{-E_i/kT}$ is the partition function for the lower manifold (with the zero of energy defined at the *i* = 1 sublevel). The above expression may be then rewritten as

$$\sigma_{abs}^{tot}(\omega) = \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} g_i \sigma_{abs}^{ij}(\omega) \frac{e^{-E_i/kT}}{Z_a}$$
(133)

We hence arrive at an expression for the total cross section of a broadband absorption feature affiliated with the inter-manifold transition $a \rightarrow b$. As in the case of a single inter-level transition, this cross section makes no reference to the individual population densities of the separate sublevels, nor, for that matter, to the manifold population density as a whole. While we will continue to assume that each individual sublevel-to-sublevel transition $i \rightarrow j$ is homogeneously broadened, an exactly analogous expression may be derived in the case of inhomogeneous broadening. In the former case, however, we see that a narrowband source illuminating the impurity system at a fixed frequency effectively interacts with all impurities simultaneously, that is, it is as if the multilevel impurity were homogeneously broadened over the *entire* absorption band and not just within individual sublevel transitions. The only new complication is that this newly defined total cross section exhibits a more complex temperature dependence in accord normalized Boltzmann factor $e^{-E_i/kT}/Z_a$.

An exactly analogous generalization of the stimulated emission cross section is readily derived:

$$\sigma_{se}^{tot}(\omega) = \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} g_j \sigma_{se}^{ji}(\omega) \frac{e^{-E_j/kT}}{Z_b}$$
(134)

where in this case the partition function Z_b for the upper manifold is defined with the zero of energy set at the j = 1 sublevel.

It is now possible to derive a useful relationship between these two generalized cross sections based on the fundamental *reciprocity* relation $g_a^i \sigma_{abs}^{ij} \equiv g_b^j \sigma_{se}^{ji}$ [Eq. (116)] found earlier:

$$\sigma_{se}^{tot}(\omega) = \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} g_j g_j \sigma_{abs}^{ij}(\omega) \left(\frac{e^{-E_i/kT}}{Z_a} \frac{Z_a}{e^{-E_i/kT}} \right) \frac{e^{-E_j/kT}}{Z_b}$$
$$= \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} g_j g_j \sigma_{abs}^{ij}(\omega) \frac{e^{-E_i/kT}}{Z_a} \frac{Z_a}{Z_b} e^{-(E_j-E_i)/kT}$$
$$= \sigma_{abs}^{tot}(\omega) \frac{Z_a}{Z_b} e^{-(E_0-\hbar\omega)/kT}$$
(135)

where E_0 is the energy spacing between the lowest lying (i=1) sublevel of the lower manifold and the lowest lying (j=1) sublevel of the upper manifold, as shown in Figure 8. Note for this result that in the limit $T \rightarrow 0$ one recovers the previous result Eq. (116).

This remarkable result, originally derived by McCumber (1964), gives us a way of calculating the stimulated-emission cross section for a complex band by performing a simple absorption measurement and applying Eq. (135). All that we are required to know are the sublevel energies and the temperature.

2.3.2 Füchtbauer-Ladenburg Relation

Another result useful for determining the stimulated-emission cross section in broadband systems can be derived by first forming an expression for the normalized line shape function for the emission band:

$$G(\omega) = \frac{\sum_{i=1}^{D_a} \sum_{j=1}^{D_b} \frac{N_{b,i}}{N_b \tau_{ji}} L(\omega - \omega_0^{ji})}{1/\tau_{rad}}$$
(136)

In this expression, we assume that a total population density N_b resides in the upper manifold, in which case the radiative lifetime of the manifold as a whole (assuming a branching ratio of 1 for transitions to the lower manifold) is given by

$$1/\tau_{rad} = \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} \frac{N_{b,i}}{N_b \tau_{ji}}$$
(137)

The quantity $L(\omega - \omega_0^{ji})$ is the normalized Lorentzian line shape function for emission on the $j \rightarrow i$ sublevel transition with center frequency ω_0^{ji} . This function is identical to the normalized absorption line shape owing to the reciprocity relation $g_b^j \sigma_{abs}^{ij}(\omega) \equiv g_a^i \sigma_{se}^{ji}(\omega)$; it may be more intuitively understood in terms of the relation

$$L(\omega - \omega_0^{ji}) = \frac{S^{ji}(\omega)/\hbar\omega}{\int_0^\infty \frac{S^{ji}(\omega)}{\hbar\omega} d\omega}$$
(138)

where $S^{ji}(\omega)$ is the emission spectrum of the $j \rightarrow i$ sublevel transition in units of watts per unit radial frequency. Thus $G(\omega)$ is the same normalized quantity defined for the emission band as a whole.

Equation (136) can be transformed to give an expression for the total emission cross section:

$$\frac{G(\omega)}{\tau_{rad}} = \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} \frac{N_{b,i}}{N_b \tau_{ji}} L(\omega - \omega_0^{ji})$$

$$= \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} \frac{e^{-E_j/kT}}{Z_b} \frac{g_b^j g_a^i (\omega_0^{ji})^3 \left\langle \left| \tilde{\boldsymbol{\mu}}_{ab} \right|^2 \right\rangle}{3\hbar \pi c^3 \varepsilon_0} L(\omega - \omega_0^{ji})$$

$$= \sum_{i=1}^{D_a} \sum_{j=1}^{D_b} g_b^j \frac{e^{-E_j/kT}}{Z_b} \left(\frac{\omega_0^{ji}}{\pi c} \right)^2 \sigma_{se}^{ji}(\omega)$$
(139)

If one now replaces the term ω_0^{ji} in the above sum by a suitably defined average emission frequency ω_0^{av} for the band, the approximate result is

$$\sigma_{se}^{tot}(\omega) = \frac{G(\omega)}{\tau_{rad}} \left(\frac{\pi c}{\omega_0^{av}}\right)^2 \tag{140}$$

This approximation is typically good to a few percent for visible transitions of rareearth ions in insulators.

Equation (140) thus represents a second means by which the stimulated-emission cross section can be found indirectly in terms of more easily measured quantities. In this case, these quantities are the normalized emission line shape function $G(\omega)$ and the radiative lifetime of the upper manifold. In some circumstances, the latter quantity may

prove more difficult to measure than in others. For example, if the branching ratio to the lower manifold is significantly different than unity or if the rate of nonradiative transitions between the two manifolds is large, then additional auxiliary measurements will be needed in order to apply Eq. (140). Of course, an absorption measurement may be used to indirectly determine τ_{rad} .

3 References

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