2.10* Consider the electron oscillator model for the case in which there is *no field* acting on the atom. Suppose that at $t = 0$ an electron is given the displacement $\mathbf{x}_0$ from equilibrium, and the velocity $\mathbf{v}_0$.

(a) Show that the electron coordinate $\mathbf{x}(t)$ is given by

$$\mathbf{x}(t) = \mathbf{x}_0 \cos \omega_0 t + \frac{\mathbf{v}_0}{\omega_0} \sin \omega_0 t$$

(b) What is the total (kinetic plus potential) energy of the electron?

(c) Using the formula (2.5.14), derive an expression for the rate at which the oscillating electron radiates electromagnetic energy. Give the rate averaged over times long compared with the period of oscillation.

(d) Show that the electron can be expected to radiate away most of its energy in a time

$$\tau = 4\pi\epsilon_0 \left(\frac{2e^2\omega_0^2}{3mc^3}\right)^{-1}$$

This is the classical picture of "spontaneous emission," which we consider in Chapter 7.

(e) Estimate numerically the "radiative lifetime" τ found in part (d) for the case of an electron oscillating at an optical frequency $\nu_0 (= \omega_0/2\pi)$.

2.11 Show that the scattering cross section for radiation of frequency ω much greater than the natural oscillation frequency ω_0 is given by the Thomson formula

$$\sigma(\omega \gg \omega_0) \approx \frac{8\pi}{3} r_0^2 = \frac{8\pi}{3} \left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)^2$$

where $r_0 = e^2/4\pi\epsilon_0 mc^2$ is called the "classical electron radius." What is the magnitude of r_0?

2.12 A typical He–Ne laser operating at 6328 Å contains about five times as much He as Ne, with a total pressure of about one Torr. The length of the gain cell is about 50 cm. Estimate the fraction of laser radiation intensity lost due to Rayleigh scattering in passing a billion times through the gain cell. (Note: For STP Ne the constants in (2.4.9) are $A = 6.66 \times 10^{-5}$ and $B = 2.4 \times 10^{-11}$ cm^2.) This illustrates the fact that Rayleigh scattering is usually very weak in gas laser media.

*Starred problems are somewhat more difficult.

3 CLASSICAL THEORY OF ABSORPTION

3.1 INTRODUCTION

Most objects around us are not self-luminous but are nevertheless visible because they scatter the light that falls upon them. Most objects are *colored*, however, because they absorb light, not simply because they scatter it. The colors of an object typically arise because materials selectively absorb light of certain frequencies, while freely scattering or transmitting light of other frequencies. Thus if an object absorbs light of all visible frequencies, it is black. An object is red if it absorbs all (visible) frequencies except those our eyes perceive to be "red" (wavelengths roughly between about 6300 and 6800 Å), and so on.[1]

The physics of the absorption process is simplest in well-isolated atoms. These are found most commonly in gases. White light propagating through a gas is absorbed at the resonance frequencies of the atoms or molecules, so that one observes gaps in the wavelength distribution of the emerging light. On a spectrogram these gaps appear as bright lines on the dark, exposed background. The gaps, shown as lines in Figure 3.1, correspond to the absorption of sunlight by the atmosphere *of the sun* before the light reaches the earth. The absorbed energy is partially converted into heat (translational kinetic energy of the atoms) when excited atoms (or molecules) which have absorbed radiation collide with other particles. The absorbed radiation is also partially reradiated in all directions at the frequency of the absorbed radiation. This is called resonance radiation, or resonance fluorescence. When the pressure of the gas is increased, collisions may rapidly convert the absorbed radiation into heat before it can be reradiated. In this case the resonance radiation is said to be quenched.

Most atoms have electronic resonance frequencies in the ultraviolet, although resonances in the visible and infrared are not uncommon. Sodium, for instance, has strong absorption lines in the yellow region at 5890 and 5896 Å, the Fraunhofer "D lines," and their position is indicated in Figure 3.1.

Electronic resonances in molecules also tend to lie in the ultraviolet. We have "white" daylight because the atmosphere, consisting mostly of N_2 and O_2, does not absorb strongly at visible frequencies.

In molecules the separate atoms act approximately as if they were connected to each other by springs, so that entire atoms vibrate back and forth. Atoms are of

1. The principal features of the electromagnetic spectrum for our purposes are summarized in Table 3 inside the cover of the book.

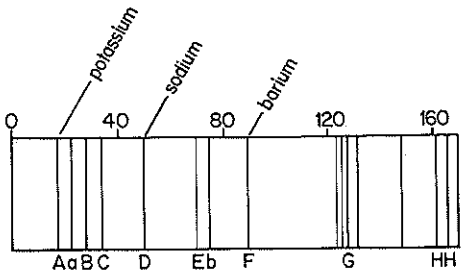

Figure 3.1 Absorption lines of the sun's atmosphere. The Fraunhofer *D* lines of sodium at 5890 and 5896 Å are not resolved in this sketch.

course much more massive (by 10^3–10^5 times) than electrons, and the natural vibrations of molecules are consequently slower. We can estimate, on the basis of this mass difference (Problem 3.1), that molecular vibration frequencies should lie in the infrared portion of the electromagnetic spectrum.

A molecule as a whole can also rotate; the resonance frequencies associated with molecular rotations lie in the microwave portion of the spectrum. Molecules therefore typically have resonances in the ultraviolet, infrared, and microwave regions of the spectrum.

Absorption in liquids and solids is much more complicated than in gases. In liquids and amorphous solids such as glass, the absorption lines have such large widths that they overlap. Water, for example, is obviously transparent in the visible, but absorbs in the near infrared, i.e., at infrared wavelengths not far removed from the visible. Its absorption curve is wide enough, in fact, that it extends into the red edge of the visible. (Figure 3.2) The weak absorption in the red portion of

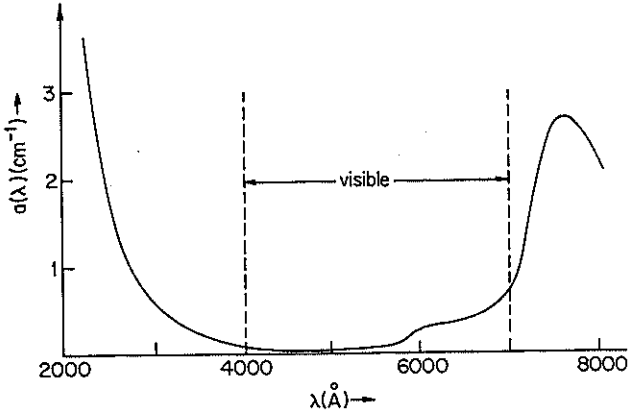

Figure 3.2 Absorption coefficient of water.

the visible spectrum explains why things appear green when one is sufficiently submerged under water.

A broad absorption curve covering all visible wavelengths except those in a particular narrow band is characteristic of the molecules of a dye. The absorbed radiation is converted into heat before it can be reradiated. Such broad absorption curves and fast quenching rates require the high molecular number densities of liquids and solids.

In metals some of the atomic electrons are able to move freely about under the influence of an electromagnetic field. The fact that metals contain these "free" electrons explains, of course, why they are good conductors of electricity. In the *free-electron approximation* we may apply the dispersion formula (2.4.12). The plasma frequency ω_p for metals is usually in the ultraviolet (Problem 3.2). Thus visible frequencies ($\omega < \omega_p$) cannot penetrate into the metal. They are completely reflected, just as AM radio waves are reflected by the ionosphere. This strong reflection gives metals their shine. In a metal like gold there is also absorption, associated with the electrons that remain bound to atoms, and it is this that gives the metal a characteristic color.

In a solid that is a good electrical insulator, the electrons are tightly bound, and consequently the natural oscillation frequencies are high, typically corresponding to wavelengths less than 4000 Å. An insulator, therefore, is usually transparent in the visible but opaque in the ultraviolet. In semiconductors the natural oscillation frequencies are smaller. Silicon, for example, absorbs visible wavelengths (it is black), but transmits radiation of wavelength greater than one micron (1 micron = 1 μm).

Lattice defects (deviations from periodicity) can substantially modify the absorption spectra of crystalline solids. Ruby, for instance, is corundum (Al_2O_3) with an occasional (roughly 0.05% by weight) random substitution of Cr^{+3} ions in place of Al^{+3}. The chromium ions absorb green light and thus ruby is pink, in contrast to the transparency of pure corundum.

The variety of natural phenomena resulting from the selective absorption of certain wavelengths and the transmission of others is too broad to treat here. We mention only one important example, the "greenhouse effect."[2] Visible sunlight is transmitted by the earth's atmosphere and heats (by absorption) both land and water. The warmed earth's surface is a source of thermal radiation, the dominant emission for typical ambient temperatures being in the infrared. This infrared radiation, however, is strongly absorbed by CO_2 and H_2O vapor in the earth's atmosphere, preventing its rapid escape into space. Without this effect, the earth would be a much colder place. An increased burning of fossil fuels could conceivably enhance the greenhouse effect by increasing the level of CO_2 in the atmosphere.

2. The term "greenhouse effect" is actually a misnomer, originating in the observation that the glass in a greenhouse, which is transparent in the visible but opaque to the infrared, plays an absorptive role similar to that of CO_2 and H_2O in the earth's atmosphere. This effect, however, does not contribute significantly to the warming of the air inside a real greenhouse. A real greenhouse mainly prevents cooling by wind currents. This point was demonstrated experimentally by R. W. Wood (1909), although the contrary misconception persists even among scientists.

3.2 ABSORPTION AND THE LORENTZ MODEL

The strength of an electromagnetic field will be reduced in transit through a material medium if the atoms (or molecules) of the medium can absorb radiant energy. More commonly than not, in a wide variety of materials, absorption can be explained by the assumption that the Lorentz electron oscillators introduced in Chapter 2 are subject to a frictional force. The origin of a "frictional" force is itself a subject for discussion, which will be found in Section 3.9. For the moment, however, we will take a frictional force for granted, and explore its consequences.

We simply amend the Newton force law (2.2.18) to read

$$m\frac{d^2\mathbf{x}}{dt^2} = e\mathbf{E}(\mathbf{R}, t) - k_s\mathbf{x} + \mathbf{F}_{\text{fric}} \tag{3.2.1}$$

and we make the simplest assumption compatible with the idea of frictional drag:

$$\mathbf{F}_{\text{fric}} = -b\mathbf{v} = -b\frac{d\mathbf{x}}{dt} \tag{3.2.2}$$

Then the Newton equation of motion (2.3.7) for an electron oscillator in a linearly polarized monochromatic plane wave takes the form

$$\frac{d^2\mathbf{x}}{dt^2} + 2\beta\frac{d\mathbf{x}}{dt} + \omega_0^2\mathbf{x} = \hat{\boldsymbol{\varepsilon}}\frac{e}{m}E_0\cos(\omega t - kz) \tag{3.2.3}$$

where for later convenience we have defined

$$\beta = \frac{b}{2m}$$

As in Chapter 2 we have introduced the natural oscillation frequency

$$\omega_0 = \left(\frac{k_s}{m}\right)^{1/2} \tag{3.2.4}$$

associated with Lorentz's elastic force.

If there is no applied field, Eq. (3.2.3) becomes

$$\frac{d^2\mathbf{x}}{dt^2} + 2\beta\frac{d\mathbf{x}}{dt} + \omega_0^2\mathbf{x} = 0 \tag{3.2.5}$$

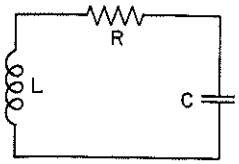

Figure 3.3 An *LRC* circuit. The charge on the capacitor obeys the equation of motion (3.2.6) for a damped oscillator.

This is the equation describing a damped oscillator. A well-known example is an *LRC* circuit (Figure 3.3), where the charge q on the capacitor satisfies the equation

$$\frac{d^2q}{dt^2} + \frac{R}{L}\frac{dq}{dt} + \frac{1}{LC}q = 0 \tag{3.2.6}$$

In this case the natural oscillation frequency and the damping rate are determined by the fundamental parameters of the circuit:

$$\omega_0 = \left(\frac{1}{LC}\right)^{1/2} \tag{3.2.7a}$$

and

$$\beta = \frac{R}{2L} \tag{3.2.7b}$$

The solution of the differential equation (3.2.6) is

$$q(t) = (A\cos\omega_0' t + B\sin\omega_0' t)\,e^{-\beta t} \tag{3.2.8a}$$

where

$$\omega_0' = (\omega_0^2 - \beta^2)^{1/2} \tag{3.2.8b}$$

Under most conditions of interest the oscillator will be significantly underdamped [see Eq. (3.3.10)] and we can replace ω_0' by ω_0. Since (3.2.6) is a second-order linear differential equation, its solution has two constants of integration which are determined by the initial conditions for $q(t)$ and $dq(t)/dt$. We have denoted these two constants by A and B.

If the LRC circuit is driven by a sinusoidal emf (Figure 3.4),

$$V(t) = V_0\cos(\omega t - \theta) \tag{3.2.9}$$

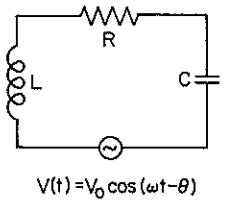

Figure 3.4 An *LRC* circuit with a sinusoidal emf. The charge on the capacitor obeys the equation of motion (3.2.10) for a sinusoidally driven, damped oscillator.

then q satisfies the *forced-oscillator* equation

$$\frac{d^2q}{dt^2} + 2\beta\frac{dq}{dt} + \omega_0^2 q = \frac{V_0}{L}\cos(\omega t - \theta) \tag{3.2.10}$$

where ω_0 and β are given by (3.2.7). This is just a scalar version of the electron oscillator vector equation (3.2.3), with L corresponding to the electron's mass/charge ratio

$$L = \frac{m}{e} \tag{3.2.11}$$

and θ corresponding to the field phase at the position of the atom:

$$\theta = kz = \frac{2\pi z}{\lambda} \tag{3.2.12}$$

In contrast to the homogeneous solution (3.2.8a), which decays to zero, the solution to the forced-oscillator equation (3.2.10) is a steady sinusoidal oscillation with an amplitude depending on ω and ω_0. The amplitude has a maximum when $\omega \approx \omega_0$, and one says that the circuit of Figure 3.4 exhibits a resonance. From (3.2.7a) we see that this resonance condition is met when the capacitance is

$$C = \frac{1}{\omega^2 L} \tag{3.2.13}$$

When the resonance condition is approached by tuning the capacitance to the resonance value (3.2.13), the amplitude of the oscillating current in the circuit increases dramatically, as shown in Figure 3.5. This resonant enhancement is used in simple radio receivers, where a variable capacitor permits tuning to various broadcast frequencies.

The interaction of an atom with a monochromatic field is similarly enhanced when

$$\omega = \omega_0 \tag{3.2.14}$$

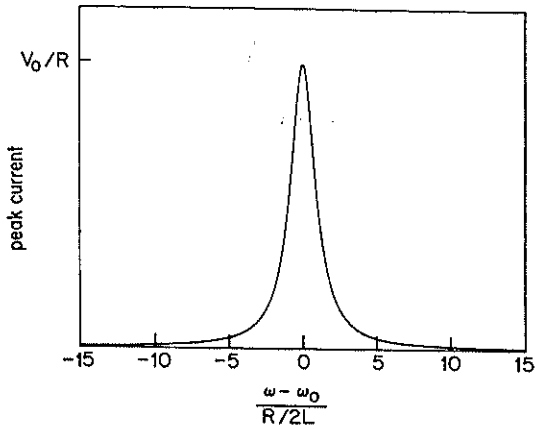

Figure 3.5 The amplitude of the oscillating current in an *LRC* circuit with emf (3.2.9). The current oscillation is at the driving frequency ω, and has maximum amplitude when the resonance condition $\omega = \omega_0 = (1/LC)^{1/2}$ is satisfied.

i.e., when the frequency of the field coincides with a natural oscillation frequency of a bound electron. This enhancement of the interaction is already implied by our result (2.3.14b) for the refractive index. However, that result is obviously undefined if $\omega = \omega_0$. A frictional force in the electron oscillator model allows us to understand formulas like (2.3.14b) even for $\omega = \omega_0$, while also providing the physical mechanism for the absorption of electromagnetic energy.

3.3 COMPLEX POLARIZABILITY AND INDEX OF REFRACTION

The equation (3.2.3) for the electron oscillator with damping is most easily solved by first writing it in complex form:

$$\frac{d^2\mathbf{x}}{dt^2} + 2\beta\frac{d\mathbf{x}}{dt} + \omega_0^2\mathbf{x} = \hat{\boldsymbol{\varepsilon}}\frac{e}{m}E_0\, e^{-i(\omega t - kz)} \tag{3.3.1}$$

where we follow the convention of writing $E_0\cos(\omega t - kz)$ as $E_0\, e^{-i(\omega t - kz)}$. This means that $\mathbf{x}(t)$ in Eq. (3.3.1) is also regarded mathematically as a complex quantity in our calculations, but only its real part is physically meaningful. In other words, we may defer the process of taking the real part of (3.3.1) until *after* our calculations, at which point the real part of our solution for $\mathbf{x}(t)$ is the (real) electron displacement. This approach is standard in solving linear equations, but

there are pitfalls that can arise in nonlinear problems. [See Chapter 17, where modifications of Eq. (3.3.1) are used in an introduction to nonlinear optics.]

We solve (3.3.1) by temporarily writing

$$\mathbf{x}(t) = \mathbf{a}\, e^{-i(\omega t - kz)} \tag{3.3.2}$$

and after inserting this in (3.3.1) we obtain

$$(-\omega^2 - 2i\beta\omega + \omega_0^2)\,\mathbf{a} = \hat{\boldsymbol{\varepsilon}}\frac{e}{m}E_0 \tag{3.3.3}$$

Therefore the assumed solution (3.3.2) satisfies Eq. (3.3.1) if

$$\mathbf{a} = \frac{-\hat{\boldsymbol{\varepsilon}}(e/m)E_0}{\omega^2 - \omega_0^2 + 2i\beta\omega} \tag{3.3.4}$$

and the physically relevant solution is therefore

$$\mathbf{x}(t) = \mathrm{Re}\left(\frac{\hat{\boldsymbol{\varepsilon}}(e/m)E_0\, e^{-i(\omega t - kz)}}{\omega_0^2 - \omega^2 - 2i\beta\omega}\right) \tag{3.3.5}$$

Note that (3.3.5) actually gives only the steady-state solution of (3.3.1). Any solution of the homogeneous version of (3.3.1) can be added to (3.3.5), and the total will still be a solution of (3.3.1). The homogeneous version is

$$\frac{d^2\mathbf{x}_{\mathrm{hom}}}{dt^2} + 2\beta\frac{d\mathbf{x}_{\mathrm{hom}}}{dt} + \omega_0^2\mathbf{x}_{\mathrm{hom}} = 0 \tag{3.3.6}$$

and its general solution is an obvious vectorial extension of (3.2.8a):

$$\mathbf{x}_{\mathrm{hom}} = [\mathbf{A}\cos\omega_0' t + \mathbf{B}\sin\omega_0' t]\, e^{-\beta t} \tag{3.3.7}$$

where again

$$\omega_0' = (\omega_0^2 - \beta^2)^{1/2} \approx \omega_0 \tag{3.3.8}$$

We will usually neglect the homogeneous part of the full solution to (3.3.1). This is obviously an approximation. The approximation is however an excellent one whenever

$$t \gg 1/\beta \tag{3.3.9}$$

Under this condition, $e^{-\beta t} \ll 1$ and we can safely neglect the homogeneous component (3.3.7) because it makes only a short-lived transient contribution to the solution.

Even though the homogeneous damping time, or lifetime $\tau_0 = 1/\beta$, is very short, it is not the shortest time in the problem. Typically the oscillation periods $T = 2\pi/\omega$ and $T_0 = 2\pi/\omega_0$ associated with the natural oscillation frequency ω_0 or the forcing frequency ω are very much shorter. In the case of ordinary optically transparent materials such as atomic vapors, glasses, and many crystals and liquids, both ω_0 and ω are typically in the neighborhood of $10^{15}\ \mathrm{sec}^{-1}$, and β falls in a wide range of much smaller frequencies:

$$\beta \approx 10^6\text{–}10^{12}\ \mathrm{sec}^{-1} \ll \omega_0, \omega \tag{3.3.10}$$

Relations (3.3.9) and (3.3.10), taken together, imply that times of physical interest must be much longer than an optical period:

$$t \gg \beta^{-1} \gg \omega_0^{-1}, \omega^{-1} \tag{3.3.11}$$

That is, steady-state solutions of (3.3.1) are valid for times that are many periods of oscillator vibration ($T_0 = 2\pi/\omega_0$) and forced vibration ($T = 2\pi/\omega$) removed from $t = 0$, but they cannot be used to predict the oscillator's response within the first few cycles after $t = 0$. This is, however, a restriction of no real significance in optical physics, as it is equivalent to

$$t \gg 10^{-15}\ \mathrm{sec}\ (=10^{-3}\ \mathrm{ps}) \tag{3.3.12}$$

This is a time span one or two orders of magnitude smaller than can presently be resolved optically.

The steady-state solution (3.3.5) is very close to the solution (2.3.8) for the undamped oscillator. It implies that the electric field induces in an atom a dipole moment $\mathbf{p} = e\mathbf{x}$, or $\mathbf{p} = \Sigma_j e\mathbf{x}_j$ in the case of many electrons:

$$\mathbf{p} = \mathrm{Re}\left(\hat{\boldsymbol{\varepsilon}}\frac{e^2}{m}\frac{E_0\, e^{-i(\omega t - kz)}}{\omega_0^2 - \omega^2 - 2i\beta\omega}\right) \tag{3.3.13}$$

or

$$\mathbf{p} = \mathrm{Re}\left(\hat{\boldsymbol{\varepsilon}}\frac{e^2}{m}E_0\, e^{-i(\omega t - kz)}\sum_{j=1}^{Z}\frac{1}{\omega_j^2 - \omega^2 - 2i\beta_j\omega}\right)$$

The real part can be found explicitly to be

$$\mathbf{p} = \hat{\boldsymbol{\varepsilon}}\frac{e^2}{m}\left(\frac{(\omega_0^2 - \omega^2)E_0\cos(\omega t - kz) + 2\beta\omega E_0\sin(\omega t - kz)}{(\omega_0^2 - \omega^2)^2 + 4\beta^2\omega^2}\right) \tag{3.3.14}$$

with a corresponding expression for a multielectron system.

Because of the frictional damping (i.e., because $\beta \neq 0$) the dipole moment no longer oscillates completely in phase with the electric field as it did in (2.3.8). The new term proportional to $\sin(\omega t - kz)$ signifies the existence of a phase lag in the dipole response. Thus there is no single real polarizability coefficient that can be identified as the ratio of the dipole moment and the electric field strength.

It is possible nevertheless, and generally very convenient, to introduce a complex polarizability. This is done by recognizing that (3.3.2) can be used to define a complex dipole moment $\mathbf{p}$:

$$\mathbf{p} = e\mathbf{x} = e\mathbf{a}\, e^{-i(\omega t - kz)} \tag{3.3.15}$$

The complex polarizability α is defined by the relation between complex moment and complex field:

$$\mathbf{p} = \alpha(\omega)\, \mathcal{E} E_0\, e^{-i(\omega t - kz)} \tag{3.3.16}$$

In the present case, by comparing (3.3.13) and (3.3.16) we easily identify the complex polarizability of a Lorentzian atom to be

$$\begin{aligned}\alpha(\omega) &= \frac{e^2/m}{\omega_0^2 - \omega^2 - 2i\beta\omega} \\ &= \frac{e^2}{m}\frac{\omega_0^2 - \omega^2 + 2i\beta\omega}{(\omega_0^2 - \omega^2)^2 + 4\beta^2\omega^2}\end{aligned} \tag{3.3.17}$$

or in the case of many electrons,

$$\begin{aligned}\alpha(\omega) &= \sum_{j=1}^{Z} \frac{e^2/m}{\omega_j^2 - \omega^2 - 2i\beta_j\omega} \\ &= \sum_{j=1}^{Z} \frac{e^2}{m}\frac{\omega_j^2 - \omega^2 + 2i\beta_j\omega}{(\omega_j^2 - \omega^2)^2 + 4\beta_j^2\omega^2}\end{aligned} \tag{3.3.18}$$

Given the complex polarizability (3.3.17) or (3.3.18), the complex polarization density is

$$\mathbf{P} = N\mathbf{p} = N\alpha(\omega)\, \mathcal{E} E_0\, e^{-i(\omega t - kz)} \tag{3.3.19}$$

Using this polarization density in the wave equation (2.1.13), together with the complex form of the assumed solution (2.3.1), we obtain

$$\begin{aligned}&\left(-k^2 + \frac{\omega^2}{c^2}\right) \mathcal{E} E_0\, e^{-i(\omega t - kz)} \\ &\quad = -\frac{\omega^2}{c^2}\frac{N\alpha(\omega)}{\epsilon_0}\, \mathcal{E} E_0\, e^{-i(\omega t - kz)}\end{aligned} \tag{3.3.20}$$

Therefore k must satisfy the dispersion relation

$$\begin{aligned}k^2 &= \frac{\omega^2}{c^2}\left(1 + \frac{N\alpha(\omega)}{\epsilon_0}\right) \\ &= \frac{\omega^2}{c^2}\, n^2(\omega),\end{aligned} \tag{3.3.21}$$

just as in Eq. (2.3.13).

In this case, because $\alpha(\omega)$ is complex the refractive index is also a complex number:

$$\begin{aligned}n^2(\omega) &= 1 + \frac{Ne^2/m\epsilon_0}{\omega_0^2 - \omega^2 - 2i\beta\omega} \\ &= 1 + \frac{Ne^2}{m\epsilon_0}\frac{\omega_0^2 - \omega^2 + 2i\beta\omega}{(\omega_0^2 - \omega^2)^2 + 4\beta^2\omega^2} \\ &= \left[n_R(\omega) + in_I(\omega)\right]^2\end{aligned} \tag{3.3.22}$$

The most important consequence of these results is that the electric field in the medium behaves differently from the field discussed in Chapter 2 because $n(\omega)$ is now complex:

$$\begin{aligned}\mathbf{E}(z, t) &= \mathcal{E} E_0\, e^{-i(\omega t - kz)} \\ &= \mathcal{E} E_0\, e^{-i\omega[t - n(\omega)z/c]} \\ &= \mathcal{E} E_0\, e^{-[n_I(\omega)]\omega z/c}\, e^{-i\omega\{t - [n_R(\omega)]z/c\}}\end{aligned} \tag{3.3.23}$$

Note that $\mathbf{E}(z, t)$ is no longer purely oscillatory. Due to $n_I(\omega)$, the field decays with increasing distance of propagation. Since the intensity is proportional to the square of the (real) electric field [recall Eq. (2.6.4) and (2.6.8)], the intensity shows exponential decay with z:

$$I_\omega(z) = I_\omega(0)\, (e^{-[n_I(\omega)]\omega z/c})^2 = I_0\, e^{-a(\omega)z} \tag{3.3.24}$$

where we call $a(\omega)$ the *absorption coefficient* or *extinction coefficient*:

$$\begin{aligned}a(\omega) &= 2\left[n_I(\omega)\right]\omega/c \\ &= \frac{2Ne^2}{\epsilon_0 mc}\sum_j \frac{\beta_j\omega^2}{(\omega_j^2 - \omega^2)^2 + 4\beta_j^2\omega^2}\end{aligned} \tag{3.3.25}$$

As in (2.3.23) we have used $n \approx 1$. This is a very important result, and we will return to it shortly.

The phase velocity of the wave (3.3.23) is $c/n_R(\omega)$. The real part of the com-

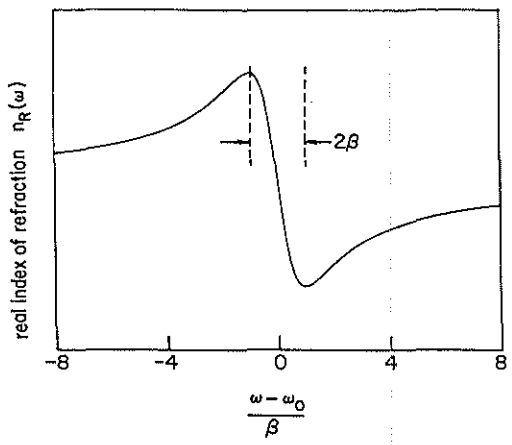

Figure 3.6 Anomalous dispersion curve for a collision-broadened absorption line.

plex refractive index is therefore what would ordinarily be called the "refractive index." This refractive index is plotted versus frequency in Figure 3.6. On the low-frequency side of each resonance frequency, $n_R(\omega)$ increases with increasing frequency, i.e., we have "normal dispersion" (Section 2.4). However, when ω gets within β_j of ω_j, $n_R(\omega)$ begins *decreasing* with increasing frequency. This decrease continues until ω is more than β_j from ω_j on the high-frequency side, whereupon it again increases with increasing frequency. Because most media show normal dispersion at optical frequencies, the negative slope of the dispersion curve near an absorption line was historically termed *anomalous dispersion.*

• Anomalous dispersion was observed by R. W. Wood in 1904. Wood studied the dispersion of light at frequencies near the sodium D lines (5890 and 5896 Å). The basic idea of Wood's experiment is sketched in Figure 3.7. Light enters a tube in which sodium vapor is produced by heating sodium. The vapor pressure decreases upwards in the tube, so that for normal dispersion the light would be bent downward, in the direction of greater density

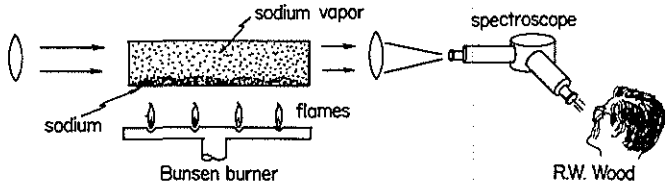

Figure 3.7 One of R. W. Wood's experiments on anomalous dispersion in sodium vapor.

and refractive index. The vapor thus acts as a kind of prism. The light emerging at the other end of the tube is focused onto the entrance slit of a spectroscope. Wood writes:

> On heating the tube, the sodium prism deviates the rays of different wave-length up or down by different amounts, curving the spectrum into two oppositely directed branches. The spectrum on the green side of the D lines will be found to bend down in the spectroscope, which means that the rays are deviated upwards in passing through the sodium tube, since the spectroscope inverts the image of its slit. This means that this phase velocity is greater in the sodium vapor than in vacuo, or the prism acts for these rays like an air prism immersed in water. The red and orange region is deviated in the opposite direction; these rays are therefore retarded by the vapor.

In other words, the refractive index on the low-frequency side of resonance was observed to be greater than unity, whereas on the high-frequency side it was less than unity. This is the behavior shown in Figure 3.6. In fact Wood's measured curve of refractive index versus frequency showed exactly the "anomalous dispersion" form predicted by the electron oscillator model. •

3.4 POLARIZABILITY AND INDEX OF REFRACTION NEAR A RESONANCE

Most of the time we will be primarily interested in the response of the dipoles that are very nearly resonant with an applied field. These dipoles will usually be a small minority of the dipoles present. The sharpness of their resonant response (recall Figure 3.5) makes them particularly important. However, the other dipoles in the far off-resonant "background" can be so numerous that they also make a significant contribution to the polarizability and index of refraction, and we cannot overlook them.

Equation (3.3.18) shows that the polarizability is additive over all dipole response frequencies. Thus we can write

$$\alpha(\omega) = \alpha_b(\omega) + \alpha_r(\omega) \tag{3.4.1}$$

where α_b and α_r are the contributions from "background" and "resonant" dipoles, respectively. The background dipoles may reside in an actual host material, in which the atoms with the resonant dipoles are embedded, or they may be dipoles associated with nonresonant oscillations in the same atoms as the resonant dipoles. In either event, the relations (3.4.1) and (3.3.21) imply

$$n^2(\omega) = 1 + \sum_i \frac{N_{bi}}{\epsilon_0}\alpha_{bi}(\omega) + \frac{N_r}{\epsilon_0}\alpha_r(\omega) \tag{3.4.2}$$

where we have indicated a sum over all background species.

The first two terms in (3.4.2) determine $n_b(\omega)$, the index of refraction of the background or host material. Thus we will write

$$n^2(\omega) = n_b^2(\omega) + \frac{N_r\alpha_r(\omega)}{\epsilon_0}$$
$$= n_b^2(\omega)\left(1 + \frac{N_r\alpha_r(\omega)}{n_b^2(\omega)\,\epsilon_0}\right)$$
$$= n_b^2(\omega)\left(1 + \frac{N_r\alpha_r(\omega)}{\epsilon_b(\omega)}\right) \qquad (3.4.3)$$

where $\epsilon_b = n_b^2\epsilon_0$ is the dielectric permittivity of the background. If the resonant atoms are present in a monatomic beam, then the background material is vacuum or nearly so and the background contributions can largely be ignored. Even in an atomic vapor n_b can be taken to be unity to three or four significant figures. However, in laser physics, the background material is frequently a solid or liquid. For example, the ruby laser operates because of dipoles associated with chromium ions thinly dispersed throughout a solid lattice (the crystal called corundum), and the dye molecules of a dye laser are dissolved in a liquid solvent (for example ethanol). Then n_b is significantly different from unity, typically in the range 1.3–2.0. We will write n_b in place of $n_b(\omega)$ hereafter because the resonances of the background are typically in the infrared or ultraviolet and n_b is effectively constant at optical frequencies.

The resonant dipoles do not make a correspondingly large contribution, since they are usually present in such small concentrations. The concentration of the chromium ions in ruby, for example, may be only 10^{19} per cm^3 or even less, much smaller than typical solid densities. As a consequence the last term in (3.4.3) is typically much smaller than unity. Then the total index of refraction can be expressed compactly as follows:

$$n(\omega) = n_b\left(1 + \frac{N_r\alpha_r(\omega)}{\epsilon_b}\right)^{1/2}$$
$$\approx n_b + \frac{N_r\alpha_r(\omega)}{2n_b\epsilon_0} \qquad (3.4.4)$$

where we have again used $\epsilon_b = n_b^2\epsilon_0$ after expanding the square root and keeping only the first term in the binomial series $(1 + x)^{1/2} = 1 + x/2 + x^2/8 + \cdots$.

Now we must consider what we mean by "near to resonance." Note in (3.3.17) that when $\beta = 0$ the imaginary part of $\alpha(\omega)$ vanishes and the real part reduces to (2.3.10). In any event, if ω is far enough from the resonance frequencies ω_j, we can put $\beta = 0$ without affecting the result appreciably. It should be clear then that "far from resonance" is only a relative term, relative to the damping coefficient β. For any resonance frequency ω_j, then, "far from resonance" means

$$|\omega_j - \omega| \gg \beta_j \qquad (3.4.5a)$$

and "near to resonance" means

$$|\omega_j - \omega| \leq \beta_j \qquad (3.4.5b)$$

A significant contribution to $\alpha(\omega)$ can come from a resonance if the associated β is small enough. Suppose there is one frequency $\omega_j = \omega_0$ close enough to ω to satisfy (3.4.5b) and all others satisfy the off-resonance condition (3.4.5a). For clarity we will label the resonant damping coefficient β without a subscript. Then we can write

$$\alpha_r(\omega) = \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 - 2i\beta\omega}$$

The resonant part of $\alpha(\omega)$ can be written in a still simpler form if ω is close enough to ω_0 to justify the approximation

$$|\omega_0 - \omega| \ll \omega, \omega_0 \qquad (3.4.6)$$

which is always guaranteed in practice whenever the earlier approximation $|\omega_0 - \omega| \leq \beta$ is valid. In this case we can write

$$\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega(\omega_0 - \omega), \qquad (3.4.7)$$

and under this condition we have

$$\alpha_r(\omega) = \frac{e^2/2m\omega}{\omega_0 - \omega - i\beta}. \qquad (3.4.8)$$

When the field frequency ω is far removed from *all* the resonance frequencies ω_j of the medium, the complex polarizability (3.3.17) reduces to the real polarizability (2.3.10). In this case the refractive index predicted by the electron oscillator model has been discussed in Chapter 2. For frequencies ω near to any of the ω_j, however, the friction coefficient β becomes important. For example, it is just because β is not zero that the refractive index does not become infinite whenever $\omega = \omega_j$, as is (erroneously) predicted by (2.3.14).

The real and imaginary parts of the index of refraction can now be identified easily, using (3.4.8) for $\alpha_r(\omega)$, and we find

$$n_R(\omega) = n_{bR} + \frac{Ne^2}{4n_{bR}\epsilon_0 m\omega}\frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \beta^2} \qquad (3.4.9)$$

$$n_I(\omega) = n_{bI} + \frac{Ne^2}{4n_{bR}\epsilon_0 m\omega}\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2} \qquad (3.4.10)$$

Here we have written n_{bR} and n_{bI} for the real and imaginary parts of n_b. Also we have assumed $n_{bR} \gg n_{bI}$. Finally, by comparison with (3.3.25) and (3.4.10), we obtain the absorption coefficient due to the resonance frequency ω_0:

$$\begin{aligned} a(\omega) &= 2n_I(\omega)\,\omega/c \\ &= a_b(\omega) + \frac{Ne^2}{2n_{bR}\epsilon_0 mc}\,\frac{\beta}{(\omega_0-\omega)^2+\beta^2} \end{aligned} \tag{3.4.11}$$

where $a_b(\omega) = 2n_{bI}\,\omega/c$ is the background absorption coefficient.

3.5 LORENTZIAN ATOMS AND RADIATION IN CAVITIES

The Newton–Lorentz equation for the response of an atomic dipole to an applied radiation field was given in (3.2.3) under the assumption that the radiation took the form of a traveling wave. That is, in complex notation, the electric field was assumed to have the form

$$\mathbf{E}(z,t) = \hat{\boldsymbol{\varepsilon}} E_0\, e^{-i(\omega t - kz)} \tag{3.5.1}$$

This is not appropriate for dipoles in cavities, where the electric field takes the form of a standing wave:

$$\mathbf{E}(z,t) = \hat{\boldsymbol{\varepsilon}} E_n \sin k_n z\, e^{-i\omega t} \tag{3.5.2}$$

where

$$k = k_n = n\pi/L, \qquad n = 1, 2, 3, \ldots \tag{3.5.3}$$

as we indicated in Eq. (1.3.2) and derived in Section 2.1.

In this section we will examine the polarizability of atoms exposed to a standing-wave field, and the radiation emitted by these atoms into the cavity. The principal consequences are a new expression for the relation between k and ω and the discovery that a classical laser of Lorentz dipoles can't work.

In free space [recall (2.3.13)] we specified ω and used the coupled Maxwell–Newton equations to find $k = k(\omega)$, and this dispersion relation defined the index of refraction: $n(\omega) = k(\omega)\,c/\omega$, as in (3.3.21). In a cavity, we specify the cavity length L which first determines the wave vector $k = k_n = n\pi/L$ [recall (1.3.2)], but not the frequency ω. We will use the coupled Maxwell–Newton equations to find $\omega = \omega(k_n) \neq \omega_n$. That is, we will find that the presence of dipoles in the cavity will bias ω, the actual oscillation frequency of the field, away from the natural frequency of the cavity mode, $\omega_n = n\pi c/L$.

First we rewrite (3.2.3) using (3.5.2) and obtain

$$\frac{d^2\mathbf{x}}{dt^2} + 2\beta\frac{d\mathbf{x}}{dt} + \omega_0^2\mathbf{x} = \hat{\boldsymbol{\varepsilon}}\frac{e}{m}E_n \sin k_n z\, e^{-i\omega t} \tag{3.5.4}$$

The solution of this equation is the obvious analog of (3.3.2):

$$\mathbf{x} = \mathbf{a} \sin k_n z\, e^{-i\omega t} \tag{3.5.5}$$

where the amplitude $\mathbf{a}$ can be found easily by substitution into (3.5.4). It satisfies (3.3.3) exactly. In other words the atomic polarizability $\alpha(\omega)$ remains as derived in (3.3.17), even though the atoms are in a standing wave.

Next we determine the field amplitude. The appropriate Maxwell wave equation for a cavity is the same as (2.1.13), except that cavity losses can be included by adding an ohmic current $\mathbf{J} = \sigma\mathbf{E}$ to the right side of (2.1.4). Then we obtain

$$\left(\frac{\partial^2}{\partial z^2} - \frac{\sigma}{\epsilon_0 c^2}\frac{\partial}{\partial t} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{E}(z,t) = \frac{1}{\epsilon_0 c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}(z,t) \tag{3.5.6}$$

Here the second term represents the effect of ohmic losses, such as would be due to a finite conductivity σ (Problem 3.3). This is a common method for modeling cavity losses in laser theory.

The polarization is defined to be $\mathbf{P} = N\mathbf{e}\mathbf{x}$, as before, so we can use (3.5.5) to evaluate the derivatives on the right side of (3.5.6) and use (3.5.2) for computing the derivatives on the left side. After differentiating we can cancel the common factor $\hat{\boldsymbol{\varepsilon}} E_n \sin k_n z\, e^{-i\omega t}$ on both sides to get:

$$-k_n^2 + i\left(\frac{\omega\sigma}{\epsilon_0 c^2}\right) + \left(\frac{\omega}{c}\right)^2 = -\left(\frac{\omega}{c}\right)^2 \frac{Ne^2/\epsilon_0 m}{\omega_0^2 - \omega^2 - 2i\beta\omega}$$

Now we use $k_n = \omega_n/c$, and the near-resonance approximation (3.4.7) twice:

$$\omega_0^2 - \omega^2 \approx 2\omega(\omega_0 - \omega) \tag{3.5.7a}$$

$$\omega^2 - \omega_n^2 \approx 2\omega(\omega - \omega_n) \tag{3.5.7b}$$

to get

$$\begin{aligned} \omega - \omega_n + i\frac{\sigma}{2\epsilon_0} &= -\frac{Ne^2}{4\epsilon_0 m}\,\frac{\omega_0 - \omega + i\beta}{(\omega_0-\omega)^2+\beta^2} \\ &= \tfrac{1}{2}(\delta + ig)\,c \end{aligned} \tag{3.5.8}$$

where we have defined g and δ as abbreviations for:

$$g = -\frac{Ne^2}{2\epsilon_0 mc}\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2} \tag{3.5.9}$$

and

$$\delta = -\frac{Ne^2}{2\epsilon_0 mc}\frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \beta^2}$$

$$= \frac{g(\omega_0 - \omega)}{\beta} \tag{3.5.10}$$

We note immediately that all reference to the field amplitude has dropped out in the step from (3.5.6) to the solution (3.5.8), as it did in the similar step between Eqs. (3.3.20) and (3.3.21). What remains is the consistency condition (3.5.8) on the parameters of the interaction. That is, (3.5.8) is the dispersion relation for the cavity.

Let us now solve for g and δ. By matching imaginary parts of (3.5.8) we quickly determine

$$g = \sigma/\epsilon_0 c \tag{3.5.11}$$

Next we look at the real parts of (3.5.8). With the aid of (3.5.10) we find the simple relation

$$\omega_n - \omega = \frac{gc}{2\beta}(\omega - \omega_0) \tag{3.5.12}$$

We can interpret this second relation as a condition on the oscillation frequency ω. Note that if ω is below the cavity frequency ω_n, the left side of (3.5.12) is positive and the right side shows that ω must then lie above the atomic dipole frequency ω_0. Conversely, if ω is above ω_n, then it must be below ω_0. In other words, no matter whether $\omega_0 > \omega_n$ or $\omega_n > \omega_0$, the operating frequency lies between the cavity frequency and the dipole frequency. This is called *frequency pulling*; the interaction with the atomic dipoles pulls the electric field frequency away from the free-space cavity frequency and toward the dipole frequency. An explicit solution of (3.5.12) is

$$\omega = \frac{\beta\omega_n + (gc/2)\omega_0}{\beta + gc/2}$$

$$\approx \omega_n + \frac{gc}{2\beta}(\omega_0 - \omega_n) \qquad (\beta \gg gc/2) \tag{3.5.13}$$

It is possible to give a physical interpretation to the equation for g as well. If we were to allow E_n in Eq. (3.5.2) to be time-dependent, then upon substitution into Maxwell's wave equation (3.5.6) we would obtain a differential equation for $E_n(t)$ instead of the consistency equation (3.5.11). We would find that $E_n(t)$ grows exponentially in time if $g > \sigma/\epsilon_0 c$. Thus gc is the classical *gain coefficient* for the interaction of radiation with atomic dipoles in a cavity (Problem 3.4).

We could go on and formulate immediately a classical theory of laser action. For example, the equality in (3.5.11) gives the value of $g = \sigma/\epsilon_0 c$ at which amplification is first possible. This is the *threshold gain*, usually denoted g_t. Unfortunately, none of this is realistic because (3.5.11) cannot be satisfied. That is, from (3.5.9) we see immediately that g is intrinsically negative. Radiation in the cavity will only be damped and never amplified by classical dipoles. A classical laser theory based on the linear electron oscillator model is not possible.

The negative value of g is inherent in the classical theory. It requires a quantum-mechanical treatment of the light–matter interaction to understand how g can be made positive. Apart from this detail, it is remarkable how much of the present classical formulation survives the transition to quantum theory. For example, except for its sign, the form of the gain coefficient will turn out to be exactly correct. The frequency-pulling equation (3.5.12) is exactly correct as it stands. The threshold condition (3.5.11) is correct. We will find how to make g positive in Chapter 7, and in so doing will find other missing elements of laser theory, such as saturation and power broadening.

3.6 THE ABSORPTION COEFFICIENT

We can associate the energy absorbed from an electromagnetic wave by an atom with the work done by the wave on the Lorentzian oscillators. In classical mechanics the rate at which work is done on an atom when a force $\mathbf{F}$ is exerted on it is $dW_A/dt = \mathbf{F} \cdot \mathbf{v}$. In the electron oscillator model the force exerted on an electron by the monochromatic field (2.3.1) is simply the Lorentz force appearing on the right side of (2.2.18):

$$\mathbf{F}_{\text{em}} = e\hat{\mathcal{E}}E_0 \cos(\omega t - kz) \tag{3.6.1}$$

in which case we can write

$$\frac{dW_A}{dt} = \mathbf{E} \cdot \frac{d\mathbf{p}}{dt} \tag{3.6.2}$$

This expression does not lead to energy absorption by the oscillator if $\mathbf{p}$ is in phase with $\mathbf{E}$. In this section we focus attention on an oscillator near to resonance, for which $\alpha(\omega)$ has a significant imaginary (quadrature) part and for which energy absorption does occur. We can use (3.4.8) to obtain

$$\mathbf{p} = \hat{\boldsymbol{\varepsilon}}\,\frac{e^2}{2m\omega}\,\frac{1}{\omega_0 - \omega - i\beta}\,E_0\,e^{-i(\omega t - kz)} \tag{3.6.3a}$$

which corresponds to the (real) physical moment:

$$\mathbf{p}(t) = \hat{\boldsymbol{\varepsilon}}e\big[U\cos(\omega t - kz) - V\sin(\omega t - kz)\big] \tag{3.6.3b}$$

The coefficients U and V are easily found by computing the real part of (3.6.3a) and comparing with (3.6.3b):

$$U = +\frac{eE_0}{2m\omega}\,\frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \beta^2} \tag{3.6.4}$$

and

$$V = -\frac{eE_0}{2m\omega}\,\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2} \tag{3.6.5}$$

The corresponding solution obtained without damping would have no quadrature component corresponding to V. The existence of the quadrature component is critical to our discussion of absorption, as we now demonstrate. From Eq. (3.6.3b) we obtain

$$\frac{d\mathbf{p}}{dt} = -\omega\hat{\boldsymbol{\varepsilon}}e\big[U\sin(\omega t - kz) + V\cos(\omega t - kz)\big] \tag{3.6.6}$$

Therefore the rate at which the dipole energy changes is given by

$$\begin{aligned}\frac{dW_A}{dt} &= -eE_0\big[\omega U\sin(\omega t - kz)\cos(\omega t - kz) + \omega V\cos^2(\omega t - kz)\big]\\ &= e\omega E_0\big[-\tfrac{1}{2}U\sin(2\omega t - 2kz) - V\cos^2(\omega t - kz)\big]\end{aligned} \tag{3.6.7}$$

Notice that the dipole's energy gain has two distinct contributions. The first term oscillates extremely rapidly and is zero on average, and thus does not give rise to any permanent change in energy. The second term, however, is always positive-definite and corresponds to a steady decrease in field energy with time. Then the rate of change of electromagnetic field energy, equal and opposite to dW_A/dt, is effectively governed by the second term alone:

$$\begin{aligned}\frac{dW_{\text{em}}}{dt} &= e\omega E_0 V\cos^2(\omega t - kz)\\ &= -\frac{e^2}{2m}\,\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2}\,E_0^2\cos^2(\omega t - kz)\end{aligned} \tag{3.6.8}$$

where we have used the expression (3.6.5) for V.

Thus we may express the rate (3.6.8) at which electromagnetic energy is absorbed by an atom in terms of the magnitude of the Poynting vector at the atom [recall (2.6.4)]:

$$\frac{dW_{\text{em}}}{dt} = -\frac{e^2}{2\epsilon_0 mc}\,\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2}\,|\,\mathbf{S}\,| \tag{3.6.9}$$

This result is similar to (2.6.5). Both equations show that dW_{em}/dt is proportional to $|\,\mathbf{S}\,|$. Of course (2.6.5) gives the rate of change of electromagnetic energy in a light beam due to scattering, whereas (3.6.9) gives the rate due to absorption.

The similarity of (3.6.9) to (2.6.5) means that we may define an *absorption cross section*:

$$\sigma(\omega) = \frac{e^2}{2\epsilon_0 mc}\,\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2} \tag{3.6.10}$$

We may follow the same steps, leading from (2.6.6) to the extinction coefficient (2.6.16) due to scattering, to obtain the extinction coefficient due to absorption in a medium of N atoms per unit volume:

$$a(\omega) = N\sigma(\omega) = \frac{Ne^2}{2\epsilon_0 mc}\,\frac{\beta}{(\omega_0 - \omega)^2 + \beta^2} \tag{3.6.11}$$

This extinction coefficient is usually called simply the *absorption coefficient*. The intensity of the incident wave after propagating a distance z into the absorbing medium is

$$I_\omega(z) = I_\omega(0)\,e^{-a(\omega)z} \tag{3.6.12}$$

just as in the case (2.6.15) when the incident wave is attenuated because of scattering.

Equation (3.6.12) is identical to (3.3.24). We have simply obtained the same physical result for the field attenuation due to absorption using two approaches. In the first approach, leading to (3.3.24), absorption was associated with the imaginery part of the complex refractive index. In this section we have obtained the

same result via the rate at which a single atom absorbs energy from the field. The two approaches are equivalent. Keep in mind, however, that the absorption coefficient derived here is physically distinct from the extinction coefficient due to scattering derived in Section 2.6. Both lead to exponential attenuation of intensity, and the total extinction coefficient includes both.

The absorption coefficient is often written in terms of the circular frequency ν,

$$\nu = \omega/2\pi \tag{3.6.13}$$

rather than the angular frequency ω. From (3.6.11), therefore,

$$a(\nu) = \frac{Ne^2}{4\pi\epsilon_0 mc} \frac{\delta\nu_0}{(\nu - \nu_0)^2 + \delta\nu_0^2} \tag{3.6.14}$$

where

$$\nu_0 = \omega_0/2\pi \tag{3.6.15}$$

and

$$\delta\nu_0 = \beta/2\pi \tag{3.6.16}$$

The absorption coefficient (3.6.14) is frequently written in the form

$$a(\nu) = \frac{Ne^2}{4\epsilon_0 mc} L(\nu) \tag{3.6.17}$$

where the lineshape function $L(\nu)$ is defined by

$$L(\nu) = \frac{\delta\nu_0/\pi}{(\nu - \nu_0)^2 + \delta\nu_0^2} \tag{3.6.18}$$

This is called the *Lorentzian function*, and is plotted in Figure 3.8.

The Lorentzian function is a mathematically idealized lineshape in several respects. We have already shown that it is the near-resonance approximation to the more complicated function (3.3.25). The Lorentzian function is defined mathematically for negative frequencies, even though they have no physical significance. It is exactly normalized to unity when integrated over all frequencies, as is easily checked:

$$\int_{-\infty}^{\infty} d\nu\, L(\nu) = \frac{\delta\nu_0}{\pi} \int_{-\infty}^{\infty} \frac{d\nu}{(\nu - \nu_0)^2 + \delta\nu_0^2} = 1 \tag{3.6.19}$$

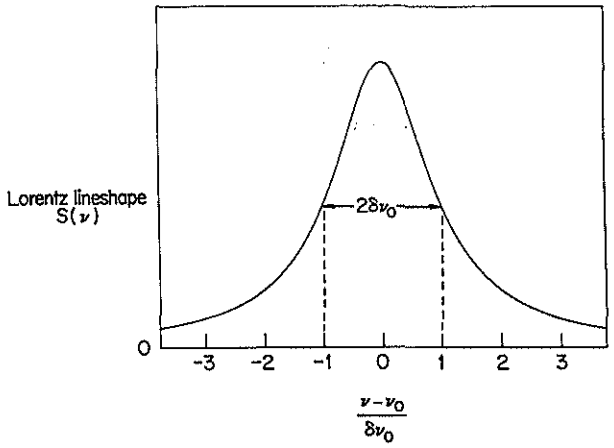

Figure 3.8 The Lorentzian lineshape function.

and the normalization is approximately the same when only the physical, positive frequencies are used. The approximation is excellent for $\delta\nu_0 \ll \nu_0$ [recall (3.3.10)]. In other words, the contribution of the unphysical negative frequencies is negligible because the linewidth is negligible compared with the resonance frequency, and in this sense $L(\nu)$ is physically as well as mathematically normalized to unity.

The maximum value of $L(\nu)$ occurs at the resonance $\nu = \nu_0$:

$$L(\nu)_{\max} = L(\nu_0) = \frac{1}{\pi\delta\nu_0} \tag{3.6.20}$$

At $\nu = \nu_0 \pm \delta\nu_0$ we have

$$L(\nu_0 \pm \delta\nu_0) = \frac{1}{2\pi\delta\nu_0} = \frac{1}{2} L(\nu)_{\max} \tag{3.6.21}$$

Because of this property, $2\delta\nu_0$ is called the width of the Lorentzian function or the *full width at half maximum* (FWHM), and $\delta\nu_0$ is called the *half width at half maximum* (HWHM). The Lorentzian function is fully specified by its width (FWHM or HWHM) and the frequency ν_0 where it peaks. The absorption coefficient is greatest at resonance, where

$$a(\nu = \nu_0) = \frac{Ne^2}{4\pi\epsilon_0 mc\delta\nu_0} \tag{3.6.22}$$

and decreases to half this resonance value when the field is "detuned" from resonance by the half width $\delta\nu_0$ of the Lorentzian function.

Our classical theory thus predicts that the absorption is strongest when the frequency of the light equals one of the natural oscillation frequencies of the bound electrons. Far out in the wings of the Lorentzian, where $|\nu - \nu_0| >> \delta\nu_0$, there is very little absorption. A knowledge of the width $\delta\nu_0$ is therefore essential to a quantitative interpretation of absorption data. In order to determine the numerical magnitude of $\delta\nu_0$ in a given situation, we must consider in some detail the physical origin of this absorption width. This we do in Section 3.9.

We shall see later that $a(\nu)$ does not always have the Lorentzian form (3.6.17). However, it will always be possible to write the absorption coefficient as

$$a(\nu) = a_t S(\nu) \tag{3.6.23}$$

where the lineshape function $S(\nu)$, whatever its form, is normalized to unity:

$$\int_0^\infty d\nu S(\nu) = 1 \tag{3.6.24}$$

With this normalization it follows that

$$\int_0^\infty d\nu a(\nu) = a_t \int_0^\infty d\nu S(\nu) = a_t \tag{3.6.25}$$

The integrated absorption coefficient a_t is convenient because it is independent of the lineshape function $S(\nu)$, which may vary with parameters like pressure, temperature, etc. It thus provides a measure of the inherent absorbing strength of the atoms.

3.7 OSCILLATOR STRENGTH

Even more than the integrated absorption coefficient, the integrated absorption cross section, namely

$$\sigma_t = a_t/N \tag{3.7.1}$$

is a convenient measure of absorption, because it characterizes the inherent absorbing strength of a single atom. From (3.6.23) and (3.6.17) we see that

$$a_t = \frac{Ne^2}{4\epsilon_0 mc} \tag{3.7.2}$$

and therefore

$$\sigma_t = \frac{e^2}{4\epsilon_0 mc} \tag{3.7.3}$$

The numerical value of σ_t is easily computed to be approximately 2.65×10^{-2} cm^2-sec^{-1}. This is a universal value, and according to our theory is applicable to absorption by any atomic material.

Extensive experimental absorption data exist for atomic hydrogen. For example, it is known to absorb strongly at a wavelength of about 1216 Å, with an integrated absorption coefficient of about 1.1×10^{-2} cm^2-sec^{-1}. Thus our classical electron oscillator theory gives a reasonable order of magnitude, although it is far from being quantitatively accurate. However, atoms do not absorb at only one wavelength. Table 3.1 lists some wavelengths at which atomic hydrogen absorbs radiation. Our classical theory gives an integrated absorption cross section (3.7.3) which is independent of ν_0, so that the same numerical value (2.65×10^{-2} cm^2-sec^{-1}) should apply to every wavelength listed in Table 3.1. The second column of Table 3.1 lists the observed integrated cross sections of these absorption lines, while the third column gives the ratio of the observed value for each line to the result (3.7.3) of the classical theory. We see that the classical result comes close to the integrated absorption cross section only for the 1216-Å line.

Before the advent of the quantum theory, this quantitative failure of the classical theory was sidestepped by writing the integrated absorption cross section of a one-electron atom as

$$\sigma_t = \frac{e^2}{4\epsilon_0 mc} f \tag{3.7.4}$$

where the parameter f is called the "oscillator strength," and its values are given by the third column of Table 3.1. In other words, the classical theory was patched up by assigning a different "oscillator strength" to each natural oscillation fre-

TABLE 3.1 Some Integrated Cross Sections of Atomic Hydrogen

Wavelength (Å)	σ_t (actual) (cm^2-sec^{-1})	$f = \frac{\sigma_t \text{ (actual)}}{\sigma_t \text{ (classical theory)}}$
1216	1.10×10^{-2}	0.416
1026	2.10×10^{-3}	0.079
973	7.69×10^{-4}	0.029
950	3.71×10^{-4}	0.014
938	2.07×10^{-4}	0.0078
931	1.27×10^{-4}	0.0048

quency. In fact the integrated absorption cross section for any atom could be written in the form (3.7.4) by making the *ad hoc* replacement

$$\frac{e^2}{m} \to \frac{e^2}{m} f \tag{3.7.5}$$

wherever the quantity on the left appeared. In this way the Lorentz theory (of both absorption and the refractive index) was brought into detailed numerical agreement with experimental results. We will include f in most classical formulas hereafter. Like the natural oscillation frequencies, however, the oscillator strengths had to be taken as empirical parameters, without a theoretical basis. Quantum theory removes both of these defects of Lorentz's model.

3.8 ABSORPTION OF BROADBAND LIGHT

The rate at which the energy W_A of an atom increases due to absorption of electromagnetic energy may be obtained from (3.6.2) or (3.6.9):

$$\frac{dW_A}{dt} = \frac{-dW_{\text{em}}}{dt} = \frac{\pi e^2 f}{2\epsilon_0 mc} \frac{\beta/\pi}{(\omega - \omega_0)^2 + \beta^2} I$$

$$= \frac{\pi e^2 f}{2\epsilon_0 mc} \left(\frac{1}{2\pi} S(\nu) \right) I_\nu \tag{3.8.1}$$

where we have added the subscript ν to remind us that I_ν refers to the intensity of monochromatic radiation at the frequency ν.

Equation (3.8.1) gives the rate of increase of the energy of an atom due to absorption from a monochromatic field of frequency ν. In reality, of course, the applied field will not be perfectly monochromatic. Hereafter we will indicate explicitly the dependence of field quantities on the frequency: $W_{\text{em}} \to W^\nu_{\text{em}}$ and $I \to I_\nu$. The change in atomic energy is due to the action of all the frequency components:

$$\left(\frac{dW_A}{dt} \right)_{\text{total}} = \sum_\nu \left(\frac{-dW^\nu_{\text{em}}}{dt} \right)$$

$$= \frac{e^2 f}{4\epsilon_0 mc} \sum_\nu S(\nu) I_\nu \tag{3.8.2}$$

In many cases of interest the field is composed of a continuous range of frequencies, and the summation in (3.8.2) must be replaced by an integral:

$$\left(\frac{dW_A}{dt} \right)_{\text{total}} \to \frac{e^2 f}{4\epsilon_0 mc} \int_0^\infty S(\nu)\, I(\nu)\, d\nu \tag{3.8.3}$$

where $I(\nu)\, d\nu$ is the intensity of radiation in the frequency band from ν to $\nu + d\nu$.

It is convenient to define a spectral energy density $\rho(\nu)$, such that $\rho(\nu)\, d\nu$ is the electromagnetic energy per unit volume in the same frequency band (Figure 3.9). The total electromagnetic energy per unit volume is then

$$\int_0^\infty \rho(\nu)\, d\nu = \frac{1}{c} \int_0^\infty I(\nu)\, d\nu \tag{3.8.4}$$

Clearly (3.8.3) may be rewritten

$$\left(\frac{dW_A}{dt} \right)_{\text{total}} = \frac{e^2 f}{4\epsilon_0 m} \int_0^\infty S(\nu)\, \rho(\nu)\, d\nu \tag{3.8.5}$$

We can now define "broadband" light as follows. Whenever the spectral energy density $\rho(\nu)$ is a flat, almost constant function of ν compared with the atomic lineshape function $S(\nu)$, we can write

$$\int_0^\infty d\nu\, S(\nu)\, \rho(\nu) \approx \rho(\nu_0) \int_0^\infty d\nu\, S(\nu)$$

$$= \rho(\nu_0) \tag{3.8.6}$$

If $\rho(\nu)$ is perfectly constant, then of course (3.8.6) is an equality. Whether $\rho(\nu)$ is flat enough in its variation to justify the approximation (3.8.6) depends on the lineshape function $S(\nu)$. The narrower the width of $S(\nu)$, the easier it is to satisfy (3.8.6). When this approximation is valid we may say that we have broadband light and broadband absorption, as opposed to the opposite extreme of narrowband (i.e., monochromatic) absorption. Both extremes are limiting cases of (3.8.5).

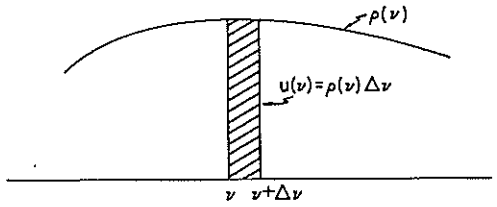

Figure 3.9 The spectral energy density $\rho(\nu)$ is defined so that $u(\nu) = \rho(\nu)\, \Delta\nu$ is the electromagnetic energy per unit volume in the narrow frequency interval from ν to $\nu + \Delta\nu$.

Therefore, the energy absorption rate for an atom exposed to broadband radiation is

$$\frac{dW_A}{dt} = \frac{e^2 f}{4\epsilon_0 m}\rho(\nu_0) \tag{3.8.7}$$

We see that for broadband absorption the rate at which the energy of the atom increases is completely independent of the form of the lineshape function $S(\nu)$, and is simply proportional to the spectral energy density of the field at the dipole's natural oscillation frequency ν_0.

In Table 3.2 we collect the most important results of this section. For simplicity we omit the background refractive index from the equations. This is always an excellent approximation for gaseous media, where n_b is close to unity. However, for solid media the index must be included. We return to this point in our discussion of laser gain in Chapter 10. We have furthermore refrained from specifying the form of the lineshape function $S(\nu)$; the question of different lineshapes is taken up in the following sections. The equations of Table 3.2 are valid for any lineshape function.

TABLE 3.2 Results of the Classical Theory of Absorption by a Medium with N Atoms per Unit Volume.

Energy Absorption Rate of an Atom

$$\frac{dW_A}{dt} = \frac{e^2 f}{4\epsilon_0 m}\int_0^\infty d\nu\, S(\nu)\,\rho(\nu) \qquad (f = \text{oscillator strength})$$

$$\approx \frac{e^2 f}{4\epsilon_0 mc} S(\nu)\, I_\nu \qquad \text{(narrowband radiation)}$$

$$\approx \frac{e^2 f}{4\epsilon_0 m}\rho(\nu_0) \qquad \text{(broadband radiation)}$$

Lineshape Function

$S(\nu)$ peaks at the resonance frequency $\nu = \nu_0$ and

$$\int_0^\infty d\nu\, S(\nu) = 1$$

Attenuation of Intensity for Radiation of Frequency ν

$$I_\nu(z) = I_\nu(0)\, e^{-a(\nu)z}$$

$$a(\nu) = \frac{Ne^2 f}{4\epsilon_0 mc} S(\nu) \qquad \text{(absorption coefficient)}$$

$$a_t = \frac{Ne^2 f}{4\epsilon_0 mc} \qquad \text{(integrated absorption coefficient)}$$

The oscillator strength f has been included by making the replacement (3.7.5), $e^2/m \to e^2 f/m$.

3.9 COLLISIONS AND "FRICTION" IN THE LORENTZ MODEL

In the preceding sections of this chapter we have shown that light is strongly absorbed when it is nearly resonant with one of the natural oscillation frequencies of the molecules of a medium, and that absorption is due to "frictional" processes that damp out dipole oscillations. We have also shown that any frictional force in the Newton equation of an electron oscillator leads to a broadened absorption line, the lineshape being Lorentzian. We did not, however, give any fundamental explanation for the existence of frictional processes. We will now approach the question of absorption and lineshape from a more fundamental viewpoint, focusing our attention on "line broadening" mechanisms in gases, in order to answer the question of the origin of the frictional coefficient β.

It is a well-known result of experiment that, for sufficiently large pressures, the width of an absorption line in a gas increases as the pressure increases. This broadening is due to collisions of the molecules and is therefore called collision broadening, or sometimes pressure broadening. Collision broadening is the most important line-broadening mechanism in gases at atmospheric pressures, and is often dominant at much lower pressures as well. We will begin our study by considering the details of collision broadening.

Our treatment of collision broadening will follow the original approach of Lorentz. We will find, for instance, that a kind of frictional force arises naturally as a result of collisions, and that the damping rate β can be interpreted as simply the collision rate.

Let us consider the effect of collisions on an atom in the electric field of a laser beam. We imagine collisions to occur in billiard-ball fashion, each collision lasting for a time that is very short compared with the time between collisions. We suppose that, immediately prior to a collision, the active electrons in an atom are oscillating along the axis defined by the field polarization, as indicated by (3.3.13). During a collision, the interaction between the two atoms causes a reorientation of the axes of oscillation. Since each atom in a gas may be bombarded by other atoms from any direction, we can assume that *on the average* all orientations of the displacements and velocities of the atomic electrons are equally probable following a collision. This is the assumption made by Lorentz. It is an assumption about the statistics of a large number of collisions, rather than about the details of a single collision.

Consider a gas of atoms at a given time t. Most atoms are not at this moment involved in a collision. Consider in particular those atoms that underwent their most recent collision at the earlier time t_1. According to our (Lorentz's) assump-

tion, the average of the electron displacements and velocities for these atoms vanished at the time t_1, since all orientations of displacement and velocity vectors were equally probable immediately after their collision. We assume that the electrons in those atoms that had their last collision at time t_1 obey the Newton–Lorentz equation (2.3.7), which we write here in complex notation:

$$\frac{d^2\mathbf{x}}{dt^2} + \omega_0^2\mathbf{x} = \hat{\boldsymbol{\varepsilon}}\,\frac{e}{m}\,E_0\,e^{-i(\omega t - kz)} \tag{3.9.1}$$

The electron displacement for a dipole satisfying this equation is obtained by combining the homogeneous and particular solutions in such a way that $\mathbf{x}(t)$ obeys the initial conditions

$$\mathbf{x}(t_1) = \left(\frac{d\mathbf{x}}{dt}\right)_{t=t_1} = 0 \tag{3.9.2}$$

Note that these are initial conditions applying to the "average" atom, since we have assumed that all displacements and velocities are equally likely after a collision. The corresponding solution to (3.9.1) will be written

$$\mathbf{x}(t;\,t_1) = \hat{\boldsymbol{\varepsilon}}\,\frac{eE_0/m}{\omega_0^2 - \omega^2}\left[e^{-i\omega t} - \frac{1}{2}\left(1 + \frac{\omega}{\omega_0}\right)e^{-i\omega_0(t-t_1)}\,e^{-i\omega t_1}\right.$$
$$\left. - \frac{1}{2}\left(1 - \frac{\omega}{\omega_0}\right)e^{i\omega_0(t-t_1)}e^{-i\omega t_1}\right]e^{ikz} \tag{3.9.3}$$

It is easy to verify that (3.9.3) is the desired solution, by checking that it satisfies both (3.9.1) and the initial conditions (3.9.2). This solution will now be taken to represent the average atom. It has this average significance even if it is not applicable to any one of the atoms individually.

We wish to calculate the average electron displacement at time t for atoms in the gas, no matter when their last collision. We can obtain this by summing (3.9.3) over all possible t_1. We only need to know (at time t) the fraction $df\,(t,\,t_1)$ of atoms for which the last collision occurred between t_1 and $t_1 + dt_1$. We show below that this is given by

$$df\,(t,\,t_1) = e^{-(t-t_1)/\tau}\,\frac{dt_1}{\tau} \tag{3.9.4}$$

where τ is the mean time between collisions. The average electron displacement $\langle\,\mathbf{x}(t)\,\rangle$ for any atom at time t is therefore obtained by multiplying (3.9.3) by the fraction (3.9.4) of atoms to which it applies, and then summing (integrating) over all possible values of earlier times t_1:

$$\langle\,\mathbf{x}(t)\,\rangle = \int_{-\infty}^{t}\mathbf{x}(t;\,t_1)\,df\,(t,\,t_1)$$
$$= \hat{\boldsymbol{\varepsilon}}\,\frac{eE_0/m}{\omega_0^2 - \omega^2}\,e^{-i(\omega t - kz)}\left(\frac{1}{\tau}\right)\int_{-\infty}^{t}dt_1\,e^{-(t-t_1)/\tau}$$
$$\times\left[1 - \frac{1}{2}\left(1 + \frac{\omega}{\omega_0}\right)e^{-i(\omega_0-\omega)(t-t_1)} - \frac{1}{2}\left(1 - \frac{\omega}{\omega_0}\right)e^{i(\omega_0+\omega)(t-t_1)}\right] \tag{3.9.5}$$

The required integrals are

$$\int_{-\infty}^{t}dt_1\,e^{-(t-t_1)/\tau} = \tau \tag{3.9.6a}$$

$$\int_{-\infty}^{t}dt_1\,e^{-i(\omega_0-\omega)(t-t_1)}\,e^{-(t-t_1)/\tau} = \frac{-i}{\omega_0-\omega-i/\tau} \tag{3.9.6b}$$

$$\int_{-\infty}^{t}dt_1\,e^{i(\omega_0+\omega)(t-t_1)}e^{-(t-t_1)/\tau} = \frac{i}{\omega_0+\omega+i/\tau} \tag{3.9.6c}$$

The average electron displacement is therefore given by

$$\langle\,\mathbf{x}(t)\,\rangle = \hat{\boldsymbol{\varepsilon}}\,\frac{eE_0/m}{\omega_0^2 - \omega^2}\,e^{-i(\omega t - kz)}$$
$$\times\left[1 + \frac{i}{2\tau}\,\frac{1+\omega/\omega_0}{\omega_0-\omega-i/\tau} - \frac{i}{2\tau}\,\frac{1-\omega/\omega_0}{\omega_0+\omega+i/\tau}\right]$$
$$= \frac{\hat{\boldsymbol{\varepsilon}}(eE_0/m)\,e^{-i(\omega t - kz)}}{\omega_0^2 - \omega^2 - 2i\omega/\tau + 1/\tau^2} \tag{3.9.7}$$

and the corresponding polarizability is

$$\alpha(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2 - 2i\omega/\tau + 1/\tau^2}. \tag{3.9.8}$$

Note that, except for the term $1/\tau^2$, this is the same as (3.3.17) if we identify the frictional coefficient β with the collision rate $1/\tau$.

The main conclusion to be drawn from our collision analysis is obvious. Given the strong inequality

$$\omega\tau \gg 1 \tag{3.9.9}$$

which implies that the mean time between collisions is much longer than an optical period ($\sim 10^{-15}$ sec), and which is an excellent approximation in practice, the last term in the denominator of (3.9.8) can be dropped. Then the effect of collisions is exactly the same as the effect of a frictional damping force if we let

$$\beta = \frac{1}{\tau} = \text{collision rate} \tag{3.9.10}$$

However, we must not lose sight of the statistical nature of our treatment of collisions. We should really say that a frictional term in the Newton equation is justified by the effects of collisions *on the average*. Thus we can give up the artificial notion of friction at the atomic level, but still use all of the results derived from it, if we reinterpret $\mathbf{x}(t)$, U, V, and W_A in Sections 3.5 and 3.6 as *average* values in the sense of (3.9.5). We are thus led to regard the results of Table 3.2 with the Lorentzian lineshape function (3.6.18) as the consequences of collision broadening. The width (HWHM) of this collision-broadened lineshape function is

$$\delta\nu_0 = \frac{\beta}{2\pi} = \frac{1}{2\pi\tau} \tag{3.9.11}$$

The damping term we introduced empirically earlier in (3.2.3) may now be interpreted as the damping of the average electron displacement, i.e.,

$$\frac{d^2}{dt^2}\langle \mathbf{x} \rangle + 2\beta \frac{d}{dt}\langle \mathbf{x} \rangle + \omega_0^2 \langle \mathbf{x} \rangle = \hat{\boldsymbol{\varepsilon}} \frac{e}{m} E_0 e^{-i(\omega t - kz)} \tag{3.9.12}$$

Collision broadening is often described equivalently in terms of a "dephasing" of the electron oscillators, as follows. Immediately after a collision the phase of the electron's oscillation has no correlation with the precollision phase. Collisions have the effect of "interrupting" the phase of oscillation, leading to an overall decay of the average electron displacement from equilibrium (Figure 3.10). The damping rate in (3.9.12) is sometimes called a "dephasing" rate, in order to distinguish it from an "energy decay" rate. The latter would appear as a frictional term in the equation of motion of each electron oscillator as well as in the average equation. In the absence of any inelastic collisions to decrease the energy of the electron oscillators, each oscillator would satisfy the Newton equation (2.3.7) with no damping term. Due to elastic collisions, i.e., collisions which only interrupt the phase of oscillation but do not produce any change in energy, the *average* electron displacement follows equation (3.9.12), which includes damping.

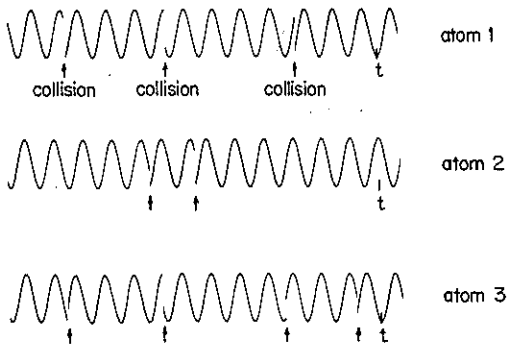

Figure 3.10 Electron oscillations in three different atoms in a gas. Collisions completely interrupt the phase of the oscillation. The average electron displacement associated with all the atoms in the gas therefore decays to zero at a rate given by the inverse of the mean collision time.

• To complete our derivation of (3.9.7), we must prove our assertion (3.9.4). The mean time between collisions, τ, is obviously an average; a given atom certainly does not have collisions in evenly spaced intervals of time τ. We can only say that the *probability* of any given atom having a collision in a small time interval Δt is given by Δt times the mean number of collisions per unit time, $1/\tau$. If at time T there are $\eta(T)$ atoms which have not yet had a collision since the time $T = 0$, then the number of "collisionless" atoms at time $T + \Delta T$ is

$$\eta(T + \Delta T) = \eta(T) - \eta(T)\frac{\Delta T}{\tau} \tag{3.9.13}$$

In words, $\eta(T)$ decreases by the amount $\eta(T)\,\Delta T/\tau$, which is the number of atoms collisionless since the time $T = 0$, times the probability that any one such atom will have a collision in the time interval ΔT. Thus

$$\frac{\eta(T + \Delta T) - \eta(T)}{\Delta T} = -\frac{\eta(T)}{\tau} \tag{3.9.14}$$

The limit $\Delta T \to 0$ gives the simple differential equation

$$\frac{d\eta(T)}{dT} = -\frac{1}{\tau}\eta(T) \tag{3.9.15}$$

with the solution

$$\eta(T) = \eta_0 e^{-T/\tau} \tag{3.9.16}$$

Since η_0 is the total number of atoms in the gas, the quantity

$$P(T) = e^{-T/\tau} \tag{3.9.17}$$

is the probability that a given atom has had no collision for a time T. At $T = 0$, when we begin "looking," this probability is unity. For $T \gg \tau$ it is very small, because in all likelihood the atom will have a collision before many collision times τ have elapsed.

The probability that a given atom will have no collision for a time T, and then have a collision within a time interval dT, is just the product of the probabilities for these two "events", i.e., $P(T)\,dT/\tau$. This is just the fraction $df(T)$, of the total number of atoms, that can be expected to have their *next* collision within the time interval from T to $T + dT$, after we begin "looking" at $T = 0$. If we imagine a movie showing the movements and collisions of the atoms, we can run our film backwards in time and the collisions will exhibit the same statistical behavior. And we will observe the same statistical behavior regardless of where we begin looking.

The atoms at time t that had their last collisions in the interval from t_1 to $t_1 + dt_1$ will be just those having their *next* collision in the same interval when we look at the gas backwards in time beginning at time t. Thus the fraction $df(t, t_1)$ of atoms at time t that had their last collision in an interval dt_1 of $t_1 < t$ will be the same as the fraction of atoms at time t which will have their next collision in an interval dt_1 of t_1 when the film is run backwards. This is just the probability $P(T)\,dt_1/\tau$ found above, with $T = t - t_1$. Thus

$$df(t, t_1) = P(t - t_1)\frac{dt_1}{\tau} = e^{-(t-t_1)/\tau}\frac{dt_1}{\tau} \tag{3.9.18}$$

which is the same as (3.9.4). •

3.10 COLLISION CROSS SECTIONS

We have shown in the preceding section that collisions, on average, can produce the same effect as frictional damping on an electron oscillator. The damping rate β can be identified with the collision rate $1/\tau$. Therefore the magnitude of $1/\tau$ is of direct significance for realistic estimates of line broadening.

The collision rate $1/\tau$ may be expressed in terms of the number density N of atoms, the collision cross section σ between atoms, and the average relative velocity $\overline{v}$ of the atoms. Imagine some particular atom to be at rest and bombarded by a stream of identical atoms of velocity $\overline{v}$. If the number of atoms per unit volume in the stream is N, then the number of collisions per unit time undergone by the atom at rest is $N\sigma\overline{v}$, where the area σ is the *collision cross section* between the atom at rest and an atom in the stream. The number of collisions per second is the same as if all the stream atoms within a cross-sectional area σ collide with the stationary atom. The idea here is exactly the same one used to define scattering and absorption cross sections for incident light.

According to the kinetic theory of gases, an atom of mass m_x has an rms velocity

$$v_{\text{rms}} = \left(\frac{8kT}{\pi m_x}\right)^{1/2} \tag{3.10.1}$$

in a gas in thermal equilibrium at temperature T, where k is Boltzmann's constant.

To obtain the average relative velocity $\overline{v}_{\text{rel}}$ of colliding atoms of masses m_x and m_y in the gas, we replace m_x in (3.10.1) by the reduced mass

$$\mu_{x,y} = \frac{m_x m_y}{m_x + m_y} = \left(\frac{1}{m_x} + \frac{1}{m_y}\right)^{-1} \tag{3.10.2}$$

Thus

$$\overline{v}_{\text{rel}} = \left[\frac{8kT}{\pi}\left(\frac{1}{m_x} + \frac{1}{m_y}\right)\right]^{1/2} \tag{3.10.3}$$

It is convenient to express this in terms of the atomic (or molecular) weights M_x and M_y:

$$\overline{v}_{\text{rel}} = \left[\frac{8RT}{\pi}\left(\frac{1}{M_x} + \frac{1}{M_y}\right)\right]^{1/2} \tag{3.10.4}$$

where R, the universal gas constant, is Boltzmann's constant times Avogadro's number. The collision rate for molecules of type x is therefore

$$\begin{aligned}\frac{1}{\tau} &= \sum_y N(Y)\sigma(X, Y)\,\overline{v}_{\text{rel}}(X, Y) \\ &= \sum_Y N(Y)\sigma(X, Y)\left[\frac{8RT}{\pi}\left(\frac{1}{M_x} + \frac{1}{M_y}\right)\right]^{1/2}\end{aligned} \tag{3.10.5}$$

where the sum is over all species y, including x.

The important "unknowns" in the expression (3.10.5) are the collision cross sections $\sigma(X, Y)$. It often happens that these are not known very accurately. They are difficult to derive theoretically, and experimental determinations are not always unambiguous. The simplest approximation to the cross section is the "hard-sphere" approximation. We write

$$\overline{\sigma}(X, Y) = \frac{\pi}{4}(d_x + d_y)^2 \tag{3.10.6}$$

where d_x and d_y are the "hard-sphere" molecular diameters, estimates of which are sometimes tabulated. $\overline{\sigma}(X, Y)$ is just the area of a circle of diameter $d_x + d_y$, just what we would expect if the molecules acted like spheres of diameters d_x and d_y. For CO_2, for example, the hard-sphere diameter is about 4.00 Å. From (3.10.6), therefore, the hard-sphere cross section for two CO_2 molecules is $\overline{\sigma}(CO_2, CO_2) = 5.03 \times 10^{-15}$ cm^2. For a gas of pure CO_2 at $T = 300$ K we find the

average relative velocity of two colliding CO_2 molecules to be $\bar{v}_{rel} = 5.37 \times 10^4$ cm/sec. The collision rate (3.10.5) in the "hard-sphere" approximation is therefore

$$\frac{1}{\tau} = N(5.03 \times 10^{-15}\ \text{cm}^2)\ (5.37 \times 10^4\ \text{cm/sec})$$

$$= 2.70 \times 10^{-10} N/\text{sec} \tag{3.10.7}$$

where N is the number of CO_2 molecules in a cubic centimeter. For an ideal gas we calculate (Problem 3.5)

$$N = 9.65 \times 10^{18} \frac{P(\text{Torr})}{T} \tag{3.10.8}$$

where $P(\text{Torr})$ is the pressure in Torr (1 atmosphere = 760 Torr) and T is the temperature (K). From (3.10.7), finally, the collision rate for a gas of CO_2 at 300 K is

$$\frac{1}{\tau} = 8.69 \times 10^6 P(\text{Torr})\ \text{sec}^{-1} \tag{3.10.9}$$

Thus at a pressure of 1 atmosphere (760 Torr) we calculate the collision rate

$$\frac{1}{\tau} = 6.60 \times 10^9\ \text{sec}^{-1} \tag{3.10.10}$$

and from (3.9.11) the collision-broadened linewidth

$$\delta\nu_0 = 1.05 \times 10^9\ \text{Hz} \tag{3.10.11}$$

The actual collision-broadened linewidths can be larger, by as much as an order of magnitude or more, than those calculated in the hard-sphere approximation. The value calculated above, however, is reasonable, and it allows us to point out some general features of the collision-broadened linewidths. First we note that the collision rate (3.10.10) is very much smaller than an optical frequency, as assumed in (3.9.9). The linewidth $\delta\nu_0$ is thus also orders of magnitude less than an optical frequency. This explains why we can speak of absorption "lines" in a gas, even though the absorption occurs over a band of frequencies: the band has a width ($\sim 2\delta\nu_0$) that is very small compared with the resonance frequency ν_0.

From (3.10.9) we note that the linewidth is linearly proportional to the pressure. For this reason, experimental results for collision-broadened linewidths are often reported in units such as MHz-Torr^{-1}. The linewidth calculated above, for instance, may be expressed as 1.38 MHz-Torr^{-1} at 300 K.

Our treatment of collision broadening only highlights some general features of a complex subject. In actual calculations we prefer always to use measured values of the collision-broadened linewidths. We note parenthetically that, for the 10.6-μm CO_2 laser line, the linewidth (1.38 MHz-Torr^{-1}) computed above is about three times smaller than the experimentally determined value. It is possible to calculate these widths more accurately, but this will not concern us.

3.11 DOPPLER BROADENING

The Doppler effect was demonstrated for sound waves in 1845 by C. H. D. Buys Ballot, who employed trumpeters performing in a moving train to demonstrate it. The mathematician C. J. Doppler had predicted the effect in 1842. His prediction applied also to light, although Maxwell's electromagnetic theory of light waves was still nearly a quarter of a century away.

Let us consider again a gaseous medium, this time only very weakly influenced by collisions (i.e., β is very small). Every electron oscillator will thus undergo practically undamped oscillation at the field frequency. Nevertheless we will show that, because of the Doppler effect, an absorption line is broadened and its width can be much larger than β. We will find that the lineshape associated with the Doppler effect is not the Lorentzian function (3.6.18), but rather the Gaussian function given in (3.11.6) below.

To an atom moving with velocity $v \ll c$ away from a source of radiation of frequency ν, the frequency of the radiation appears to be shifted:

$$\nu' = \nu\left(1 - \frac{v}{c}\right) \tag{3.11.1}$$

This is the Doppler effect. It implies that a source of radiation (e.g., a laser) exactly resonant in frequency with an absorption line of a stationary atom will not be in resonance with the same absorption line in a moving atom, and the frequency offset is $\delta\nu = (v/c)\nu$. Similarly, a nonresonant absorption line of an atom may be brought *into* resonance with the field as a result of atomic motion. Since the atoms in a gas exhibit a wide variety of velocities, a broad range of different effective resonance frequencies will be associated with a given absorption line. In other words, the absorption line is broadened because of the Doppler effect. The absorption line is thus said to be Doppler-broadened.

For a gas in thermal equilibrium at the temperature T, the fraction $df(v)$ of atoms having velocities between v and $v + dv$ along any one axis is given by the (one-dimensional) Maxwell–Boltzmann distribution,

$$df(v) = \left(\frac{m_x}{2\pi kT}\right)^{1/2} e^{-m_x v^2/2kT} dv \tag{3.11.2}$$

Here again k is the Boltzmann constant and m_x is the mass of an atom or molecule. Because we have assumed that collisions are almost negligible, an atom with resonance frequency ν_0 and velocity v moving away from the source of radiation will only absorb radiation very near to (within $\Delta\nu = \beta/2\pi$ of) the frequency

$$\nu = \nu_0\left(1 + \frac{v}{c}\right) \tag{3.11.3}$$

The fraction of atoms absorbing within the frequency interval from ν to $\nu + d\nu$ is thus equal to the fraction of atoms with velocity in the interval from v to $v + dv$. From (3.11.3) we have

$$v = \frac{c}{\nu_0}(\nu - \nu_0) \tag{3.11.4}$$

and $dv = (c/\nu_0)\, d\nu$. Using (3.11.2) we can determine that this fraction is

$$df_\nu(v) = \left(\frac{m_x}{2\pi kT}\right)^{1/2} e^{-m_x c^2(\nu-\nu_0)^2/2kT\nu_0^2} \left(\frac{c}{\nu_0} d\nu\right) \tag{3.11.5}$$

Since the absorption rate at frequency ν must be proportional to $df_\nu(v)$, we may write the Doppler lineshape function as

$$S(\nu) = \left(\frac{m_x c^2}{2\pi kT\nu_0^2}\right)^{1/2} e^{-m_x c^2(\nu-\nu_0)^2/2kT\nu_0^2} \tag{3.11.6}$$

Since (3.11.2) was normalized to unity when integrated over velocity, (3.11.6) is normalized to unity with respect to the frequency offset (or "detuning") $\nu - \nu_0$, as required by the definition of lineshape function.

By direct computation using (3.11.6) we find

$$\begin{aligned}\int_0^\infty d\nu\, S(\nu) &= S(\nu_0) \int_0^\infty d\nu\, e^{-m_x c^2(\nu-\nu_0)^2/2kT\nu_0^2} \\ &= S(\nu_0) \int_{-\nu_0}^\infty d\mu\, e^{-m_x c^2\mu^2/2kT\nu_0^2} \\ &\approx S(\nu_0) \int_{-\infty}^\infty d\mu\, e^{-m_x c^2\mu^2/2kT\nu_0^2}\end{aligned}$$

$$\begin{aligned}&= S(\nu_0)\left[\frac{\nu_0}{c}\left(\frac{2\pi kT}{m_x}\right)^{1/2}\right] \\ &= 1\end{aligned} \tag{3.11.7}$$

We have used the excellent approximation $kT \ll m_x c^2$ to replace the lower limit of the integral by $-\infty$. Thus we may write

$$S(\nu) = \frac{c}{\nu_0}\left(\frac{m_x}{2\pi kT}\right)^{1/2} e^{-m_x c^2(\nu-\nu_0)^2/2kT\nu_0^2} \tag{3.11.8}$$

It is convenient to define

$$\delta\nu_D = 2\frac{\nu_0}{c}\left(\frac{2kT}{m_x}\ln 2\right)^{1/2} \tag{3.11.9}$$

in terms of which

$$S(\nu) = \frac{1}{\delta\nu_D}\left(\frac{4\ln 2}{\pi}\right)^{1/2} e^{-4(\nu-\nu_0)^2 \ln 2/\delta\nu_D^2}, \tag{3.11.10}$$

and we recognize that $\delta\nu_D$ is the width (FWHM) of the Doppler absorption curve, since

$$S(\nu_0 \pm \tfrac{1}{2}\delta\nu_D) = S(\nu_0)\, e^{-\ln 2} = \tfrac{1}{2} S(\nu_0) \tag{3.11.11}$$

$\delta\nu_D$ is commonly called the *Doppler width* (Figure 3.11). The Doppler width is also often defined in terms of the $1/e$ point of the curve, rather than the half-maximum point. Sometimes it is defined as the half width at half maximum (HWHM) rather than the FWHM. Thus one finds formulas in the literature differing by factors of 2, ln 2, etc. It is important to keep these possible differences in mind when comparing calculations.

The peak of the Doppler curve at $\nu = \nu_0$ has the value

$$S(\nu_0) = \frac{1}{\delta\nu_D}\left(\frac{4\ln 2}{\pi}\right)^{1/2} \tag{3.11.12}$$

where $S(\nu_0)$ is evidently the peak value of $S(\nu)$, for which $\nu = \nu_0$. $S(\nu_0)$ is determined from the normalization condition (3.11.7).

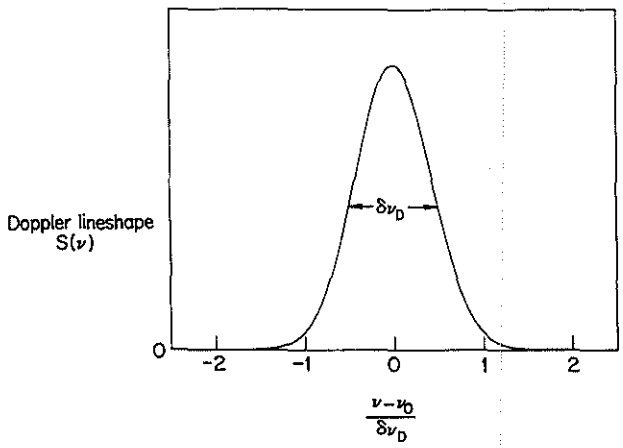

Figure 3.11 The Doppler lineshape function.

In terms of the molecular weight M_x and the wavelength $\lambda_0 = c/\nu_0$ of the absorption line, the Doppler width is

$$\delta\nu_D = \frac{2}{\lambda_0}\left(\frac{2RT}{M_x}\ln 2\right)^{1/2}$$

$$= 2.15 \times 10^{12}\left[\frac{1}{\lambda_0}\left(\frac{T}{M_x}\right)^{1/2}\right] \tag{3.11.13}$$

where λ_0 is expressed in angstroms, M_x in grams, and T in kelvins. In these same units the formula

$$\frac{\delta\nu_D}{\nu_0} \approx 7.16 \times 10^{-7}\left(\frac{T}{M_x}\right)^{1/2} \tag{3.11.14}$$

for the ratio of the Doppler width to the resonance frequency is also useful.

The Doppler width depends only on the transition frequency, the gas temperature, and the molecular weight of the absorbing species. It is therefore much simpler to calculate than the collision-broadened width, which involves the collision cross section. As an example, consider the 6328-Å line of Ne in the He–Ne laser. Since $M_{Ne} \approx 20.18$ g for Ne, we obtain from (3.11.13) the Doppler width

$$\delta\nu_D \approx 1500 \text{ MHz} \tag{3.11.15}$$

for $T = 400$ K. For the 10.6-μm line of CO_2 and the same temperature, however, we find a much smaller Doppler width:

$$\delta\nu_D \approx 61 \text{ MHz} \tag{3.11.16}$$

3.12 THE VOIGT PROFILE

Doppler broadening is an example of what is called *inhomogeneous* broadening. The term inhomogeneous means that individual atoms within a collection of otherwise identical atoms do not have the same resonant response frequencies. Thus atoms in the collection can show resonant response over the available range of frequencies. This is true even though the atoms are nominally identical. In the Doppler case this is because individual (nominally identical) atoms can have different velocities. These different velocities serve as tags or labels for the individual atoms, and any discussion of the behavior of a sample of such atoms must take account of all the velocity labels.

There are other possible inhomogeneities that have the same effect as the Doppler distribution of velocities. For example, impurity atoms embedded randomly in a crystal are subjected to different local crystal fields due to strains and defects. These have the effect of shifting the resonance frequency of each atom slightly differently. The distribution of such shifts acts very much like the Doppler distribution, and gives rise to an inhomogeneous broadening of the absorption line associated with the nominally identical impurity atoms subjected to different local fields in the crystal. This type of random strain broadening is present in the Cr^{3+} line associated with ruby laser light, for example.

The line broadening associated with collisions is different, and is called *homogeneous*. This is because each atom can itself absorb light over a range of frequencies, due to the interruptions of its dipole oscillations by collisions. Since the collisional history of every atom is assumed to be the same, no greater collisional broadening is associated with the collection of atoms than is associated with an individual atom.

In general we cannot characterize an absorption lineshape of a gas as a pure collision-broadened Lorentzian or a pure Doppler-broadened Gaussian. Both phase-interrupting collisions and the Doppler effect may play a role in determining the lineshape. We will now derive the Voigt profile, describing the absorption lineshape when both collision broadening and Doppler broadening must be taken into account.

Equation (3.6.18) gives the collision-broadened lineshape for each atom in the gas. If an atom has a velocity component v moving away from the source of light of frequency $\nu \approx \nu_0$, its absorption curve is Doppler-shifted to

$$S(\nu, v) = \frac{(1/\pi)\delta\nu_0}{(\nu_0 - \nu + v\nu/c)^2 + \delta\nu_0^2} \tag{3.12.1}$$

In other words, the peak absorption for this atom will occur at the field frequency ν such that (3.11.3) is satisfied:

$$\nu \approx \nu_0 + \frac{\nu_0 v}{c} \tag{3.12.2}$$

The lineshape function for the gas is thus obtained by integrating over the velocity distribution (3.11.2):

$$\begin{aligned} S(\nu) &= \int_{-\infty}^{\infty} dv\, S(\nu, v) \left(\frac{M_x}{2\pi RT}\right)^{1/2} e^{-M_x v^2/2RT} \\ &= \left(\frac{M_x}{2\pi RT}\right)^{1/2} \frac{\delta\nu_0}{\pi} \int_{-\infty}^{\infty} \frac{dv\, e^{-M_x v^2/2RT}}{(\nu_0 - \nu + \nu_0 v/c)^2 + \delta\nu_0^2} \\ &= \frac{1}{\pi^{3/2}} \frac{b^2}{\delta\nu_0} \int_{-\infty}^{\infty} \frac{dy\, e^{-y^2}}{(y + x)^2 + b^2} \end{aligned} \tag{3.12.3}$$

where we have made the change of variables (Problem 3.6)

$$x = (4 \ln 2)^{1/2} \frac{\nu_0 - \nu}{\delta\nu_D} \tag{3.12.4}$$

and we have defined

$$b = (4 \ln 2)^{1/2} \frac{\delta\nu_0}{\delta\nu_D} \tag{3.12.5}$$

The lineshape function (3.12.3) is called the *Voigt profile*.

In the case when the applied field is tuned exactly to the resonance frequency ν_0, we have $x = 0$ and therefore

$$S(\nu_0) = \frac{b^2}{\pi^{3/2}\,\delta\nu_0} \int_{-\infty}^{\infty} \frac{dy\, e^{-y^2}}{y^2 + b^2} \tag{3.12.6}$$

The integral may be looked up in a table of integrals. It is found that

$$\int_{-\infty}^{\infty} \frac{dy\, e^{-y^2}}{y^2 + b^2} = \frac{\pi}{b} e^{b^2} \operatorname{erfc}(b) \tag{3.12.7}$$

where

$$\operatorname{erfc}(b) = \frac{2}{\pi^{1/2}} \int_b^{\infty} du\, e^{-u^2} \tag{3.12.8}$$

is the *complementary error function*. From (3.12.6) and (3.12.7), therefore, the lineshape function for the resonance frequency $\nu = \nu_0$ has the value

$$\begin{aligned} S(\nu_0) &= \frac{b^2}{\pi^{3/2}\,\delta\nu_0} \frac{\pi}{b} e^{b^2} \operatorname{erfc}(b) \\ &= \frac{b}{\pi^{1/2}\,\delta\nu_0} e^{b^2} \operatorname{erfc}(b) \\ &= \left(\frac{4 \ln 2}{\pi}\right)^{1/2} \frac{1}{\delta\nu_D} e^{b^2} \operatorname{erfc}(b) \end{aligned} \tag{3.12.9}$$

This function is plotted for several values of the parameter b in Figure 3.12.

$S(\nu_0)$ depends strongly on the ratio of the linewidths for collision and Doppler broadening. When the collision width $\delta\nu_0$ is much greater than the Doppler width $\delta\nu_D$, we have $b \gg 1$. For large values of b it is known that

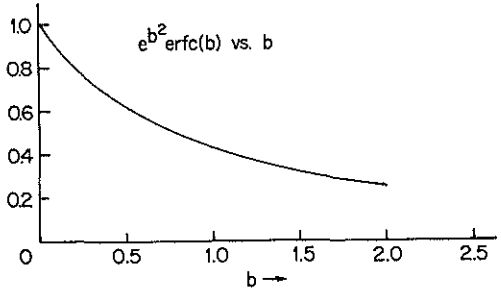

Figure 3.12 The function e^{b^2}erfc (b).

$$e^{b^2}\,\text{erfc}\,(b) \approx \frac{1}{\pi^{1/2}b} \qquad (b \gg 1) \tag{3.12.10}$$

In this "collision-broadened limit," therefore, we have from (3.12.9) the result

$$S(\nu_0) \approx \frac{1}{\pi\delta\nu_0} \qquad (b \gg 1) \tag{3.12.11}$$

which is exactly the result (3.6.20) for the case of pure collision broadening. In the limit in which the Doppler width is much greater than the collision broadened width, on the other hand, we have $b \ll 1$, in which case the function

$$e^{b^2}\,\text{erfc}\,(b) \approx 1 \qquad (b \ll 1) \tag{3.12.12}$$

Then from (3.12.9) we have

$$S(\nu_0) \approx \frac{1}{\delta\nu_D}\left(\frac{4\ln 2}{\pi}\right)^{1/2} \qquad (b \ll 1) \tag{3.12.13}$$

which is the result (3.11.12) for pure Doppler broadening. The limits $\delta\nu_0 \gg \delta\nu_D$ and $\delta\nu_0 \ll \delta\nu_D$ thus reproduce the results for pure collision broadening and pure Doppler broadening, respectively. In general, for arbitrary values of b, $S(\nu_0)$, given by (3.12.9), must be evaluated by using tables of erfc (b).

For the general case of arbitrary values of both the parameter b and the detuning parameter x, the lineshape function $S(\nu)$ given by Eq. (3.12.3) must be evaluated from tabulated values of the more complicated function

$$\int_{-\infty}^{\infty} \frac{dy\, e^{-y^2}}{(y+x)^2 + b^2} = \frac{\pi}{b}\,\text{Re}\left(\frac{i}{\pi}\int_{-\infty}^{\infty}\frac{dy\, e^{-y^2}}{x + y + ib}\right)$$

$$= \frac{\pi}{b}\,\text{Re}\; w(x + ib) \tag{3.12.14}$$

where w is the "error function of complex argument." Numerical values are tabulated in various mathematical handbooks.[3]

In Table 3.3 we summarize our results for collision broadening and Doppler broadening, as well as the more general case of the Voigt profile. Tables 3.2 and 3.3 together summarize the results of our classical theory of absorption. With slight

3. See, for example, M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1971), pp. 325–328.

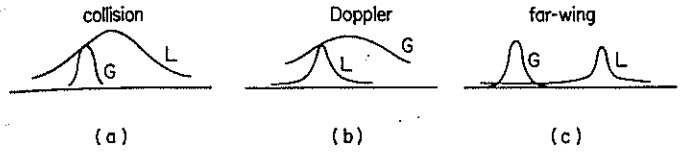

Figure 3.13 Sketch of factors in the integrand of (3.12.3) in three limiting cases: (*a*) collision-broadened limit, (*b*) Doppler-broadened limit, (*c*) far-wing limit.

modifications, these formulas are basically the same as those given by the quantum theory of absorption. The case of *gain*, or "negative absorption," is also described by very similar formulas. Thus the results of our classical theory will prove to be far more relevant to the operation of lasers than one might at first suspect. Indeed, we will refer back to Tables 3.2 and 3.3 in our study of lasers.

• Without going to numerical tables, and even without a study of the asymptotic properties of $w(x + ib)$, it is possible to evaluate the Voigt integral (3.12.3) in several limits because both factors in the integrand are normalized lineshapes themselves. There are three limits of interest, as shown in Figure 3.13.

Collisional Limit ($\delta\nu_0 \gg \delta\nu_D$): In this case $S(\nu, v)$ is very broad and slowly varying compared to the narrow Gaussian velocity distribution (Fig. 3.13*a*). Since the Gaussian is normalized to unity it acts like the delta function $\delta(v)$, and the Voigt integral reduces to the result $S(\nu) = S(\nu, v = 0)$, which is just the original collisional Lorentzian lineshape given in (3.6.18).

Doppler Limit ($\delta\nu_D \gg \delta\nu_0$): In this case the reverse is true (Fig. 3.13*b*), and the collisional function $S(\nu, v)$ acts like the delta function $\delta(\nu_0 - \nu + v\nu/c)$. Thus the Voigt integral gives back the Gaussian function (3.11.10). Except at high pressures or in cases where the Doppler distribution is altered by beam collimation it is usually valid to assume that the inequality $\delta\nu_D \gg \delta\nu_0$ is accurate and the Doppler limit applies.

Far-Wing Limit ($|\nu - \nu_0| \gg \delta\nu_D, \delta\nu_0$): This case refers to the spectral region far from line center, far outside the halfwidths of either the collisional or Doppler factors in the Voigt integrand. Thus the integrand is the product of two peaked functions. Each peak falls in the remote wing of the other function (see Fig. 3.13*c*). Here the qualitative difference between Gaussian and Lorentzian functions is significant. The Gaussian is much more compact. It falls to zero much more rapidly than the Lorentzian. Because the Lorentzian's wings are falling relatively slowly, as $1/\nu^2$ for large ν, it still has nonzero value at the position of the Gaussian peak. However, the value of the Gaussian function is effectively zero by comparison near the Lorentzian's peak. Thus the contribution of the Gaussian function in the Lorentzian wing is much greater than that of the Lorentzian function in the Gaussian wing, and the Voigt integral can be replaced by (3.6.18) in its far wing:

$$S(\nu) \to \frac{\delta\nu_0/\pi}{(\nu - \nu_0)^2} \tag{3.12.15}$$

This result is anomalous in the sense that the lineshape behaves like a Lorentzian in the far wing even if the broadening is principally Doppler, not collisional ($\delta\nu_D \gg \delta\nu_0$). •

TABLE 3.3 Collision, Doppler, and Voigt Lineshapes

Collision-Broadening Lineshape

$$S(\nu) = \frac{(1/\pi)\,\delta\nu_0}{(\nu - \nu_0)^2 + \delta\nu_0^2}$$

$$\delta\nu_0 = \frac{\text{collision rate}}{2\pi}$$

Doppler-Broadening Lineshape

$$S(\nu) = \frac{0.939}{\delta\nu_D}\, e^{-2.77(\nu-\nu_0)^2/\delta\nu_D^2}$$

$$\delta\nu_D = 2.15 \times 10^6 \left[\frac{1}{\lambda_0}\left(\frac{T}{M}\right)^{1/2}\right] \text{MHz}$$

T = gas temperature (K)

M = molecular weight of absorber (g)

λ_0 = wavelength (Å) of absorption line

Voigt Lineshape

$$S(\nu) = \frac{0.939}{\delta\nu_D}\,\text{Re}\, w(x + ib)$$

$$x = 1.67\,\frac{\nu_0 - \nu}{\delta\nu_D}$$

$$b = 1.67\,\frac{\delta\nu_0}{\delta\nu_D}$$

w = error function of complex argument

3.13 EXAMPLE: ABSORPTION BY SODIUM VAPOR

Let us consider an example of the use of Tables 3.2 and 3.3. Consider the 5890-Å absorption line of sodium vapor at 300 K. The Doppler width is

$$\delta\nu_D \approx 2.15 \times 10^{12}\left[\frac{1}{5890}\left(\frac{300}{23}\right)^{1/2}\right] \text{Hz}$$

$$\approx 1300 \text{ MHz} \qquad (3.13.1)$$

since the atomic weight of sodium is $M_{Na} = 23$ g. From tabulated data we can

estimate the collision broadening linewidth of the 5890-Å line in pure sodium vapor at 300 K to be

$$\delta\nu_0 \approx 1700P(\text{Torr}) \text{ MHz} \qquad (3.13.2)$$

The ratio b of Table 3.3 is therefore

$$b \cong 2.2P(\text{Torr}) \qquad (3.13.3)$$

If P(Torr) is less than, say, about 0.1 Torr, we are in the "Doppler regime." In this case the absorption coefficient for narrowband light exactly resonant with the 5890-Å absorption line is found from Table 3.2 at the end of Section 3.8 to be

$$a(\nu_0) = \frac{e^2 f}{4\epsilon_0 mc} N\, S(\nu_0)$$

$$= \frac{e^2 f}{4\epsilon_0 mc} N \frac{1}{\delta\nu_D}\left(\frac{4\ln 2}{\pi}\right)^{1/2} \qquad (3.13.4)$$

For the sodium D lines the oscillator strength—the factor f—is of order unity. In fact the 5890- and 5896-Å lines have oscillator strengths of 0.355 and 0.627, respectively. From (3.13.4), (3.13.1), and (3.10.8), therefore, we obtain

$$a(\nu_0) \approx 2.2 \times 10^5 P(\text{Torr}) \text{ cm}^{-1} \qquad (3.13.5)$$

which is valid provided the pressure is small enough that Doppler broadening prevails. For narrowband light of frequency ν not necessarily equal to ν_0 we have

$$a(\nu) \approx 2.2 \times 10^5 P(\text{Torr})\, e^{-4(\nu-\nu_0)^2 \ln 2/\delta\nu_D^2} \text{ cm}^{-1} \qquad (3.13.6)$$

In Figure 3.14 we have plotted the transmission coefficient

$$\frac{I_\nu(z)}{I_\nu(0)} = e^{-a(\nu)z} \qquad (3.13.7)$$

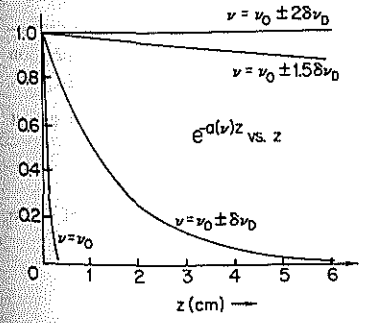

Figure 3.14 Transmission coefficient for 5890-Å radiation in sodium vapor at T = 300 K, $P = 5 \times 10^{-5}$ Torr. In this case the absorption line is Doppler-broadened, with $\delta\nu_0 \approx 1300$ MHz. The four curves illustrate the high selectivity of the absorption process.

for nearly monochromatic light of slightly different frequencies. It is evident that the transmission coefficient has an extremely strong dependence on the detuning $\nu - \nu_0$. The detuning of the field frequency ν by just a very small fraction of ν from the resonance frequency ν_0 results in a very sharp increase in the transmission coefficient. Similar results apply at higher pressures, where collision broadening becomes important.

PROBLEMS

3.1 Assume the "spring constants" k for the binding of electrons in atoms are approximately the same as those for the binding of atoms in molecules. If $\nu \approx 5 \times 10^{14}$ Hz is a typical electronic oscillation frequency, estimate the range of frequencies typical of atomic vibrations in molecules, given typical electron–atom mass differences. Does your estimate indicate that molecular vibrations lie in the infrared region of the spectrum?

3.2 The atomic weight of lithium is 6.939 g, and the density of lithium is 0.534 g/cm^3. Assuming each lithium atom contributes one electron to the "free-electron gas," calculate the plasma frequency ν_p. For what wavelengths would you expect lithium to be transparent? (Note: The transparency of the alkali metals in the ultraviolet was discovered by R. W. Wood in 1933.)

3.3 The addition of an ohmic current density to Maxwell's equations leads to the wave equation (3.5.6). Show this by adding $\mathbf{J} = \sigma\mathbf{E}$ to the right side of (2.1.4) and then retracing the derivation of the wave equation (2.1.13).

3.4* Derive the equation for classical "laser amplification" by substituting (3.5.2) into (3.5.6), allowing E_n to be time-dependent: $E_n = E_n(t)$. It is sufficient to assume that $E_n(t)$ is slowly varying so that terms proportional to d^2E_n/dt^2 can be discarded.

(a) Obtain the equation for dE_n/dt.

(b) Use the approximations and abbreviations given in Eqs. (3.5.7)–(3.5.10) to show that $d|E_n|^2/dt = 0$ if $g = \sigma/\epsilon_0 c$.

(c) Sketch on one graph the behavior of $E_n(t)$ vs. t obtained from the solution of the equation for $d|E_n|^2/dt$ under the (unrealistic) assumption that $g = 2\sigma/\epsilon_0 c$, and the (more realistic) assumption that $g = -2\sigma/\epsilon_0 c$.

3.5 Show that the number of atoms (or molecules) per cm^3 of an ideal gas at pressure P and temperature T is given by (3.10.8).

3.6 **a.** Verify Eq. (3.12.3).

b. Using Eqs. (3.4.9) and (3.4.11), show that in the absence of background atoms

$$n_R(\nu) - 1 = \frac{\lambda_0}{4\pi}\frac{\nu_0 - \nu}{\delta\nu_0}a(\nu), \qquad \lambda_0 = \frac{c}{\nu_0}$$

This equation relates the refractive index near a collision-broadened absorption line to the absorption coefficient.

3.7* Although the relation derived in Problem 3.6 applies to the case of collision broadening, a similar relation holds more generally. Show in the case of a Voigt profile that

$$n_R(\nu) - 1 = \frac{\lambda_0}{4\pi}\frac{\text{Im } w(x + ib)}{\text{Re } w(x + ib)}a(\nu)$$

where w, x, and b are defined in Section 3.12.

[Note: The relation between the refractive index and the absorption coefficient (or, equivalently, between the real and imaginary parts of the complex refractive index) is a special case of the so-called *Kramers–Kronig relations*. Such relations may be derived on very general grounds based on causality.]

3.8 Estimate the absorption coefficient for 5890-Å radiation in sodium vapor containing 2.7×10^{12} atoms/cm^3 at 200°C. [See J. E. Bjorkholm and A. Ashkin, *Phys. Rev. Lett.* **32**, 129 (1974)].

3.9 The CO_2 molecule has strong absorption lines in the neighborhood of $\lambda = 10\ \mu$m. Assuming that the cross sections of CO_2 molecules with N_2 and O_2 molecules are $\sigma(CO_2, N_2) = 120$ Å^2 and $\sigma(CO_2, O_2) = 95$ Å^2, estimate the collision-broadened linewidth for CO_2 in the earth's atmosphere. (Note: since the concentration of CO_2 is very small compared with N_2 and O_2 in air, you may assume that only N_2–CO_2 and O_2–CO_2 collisions contribute to the linewidth.) Compare this with the Doppler width.

3.10 Consider the absorption coefficient $a(\nu_0)$ of a pure gas precisely at resonance. Show that $a(\nu_0)$ is proportional to the number density of atoms when the absorption line is Doppler-broadened, but is independent of the number density when the pressure is sufficiently large that collision broadening is dominant.