

The probability that energy level E is occupied is given by the Fermi-Dirac distribution

$$(E) = \frac{1}{\exp[(E - E_f)/k_{\rm B}T] + 1},$$
 (12.1-10)

where E_f is a constant known as the Fermi energy. This distribution has a maximum value of unity, which indicates that the energy level E is definitely occupied. f(E) decreases monotonically as E increases, assuming the value $\frac{1}{2}$ at $E = E_f$. Although f(E) is a distribution (sequence) of probabilities rather than a probability density function, when $E \gg E_f$ it behaves like the Boltzmann distribution

$$P(E) \propto \exp\left[-\frac{E-E_f}{k_BT}\right],$$

as is evident from (12.1-10). The Fermi-Dirac and Boltzmann distributions are compared in Fig. 12.1-11. The Fermi-Dirac distribution is discussed in further detail in Chap. 15.

12.2 INTERACTIONS OF PHOTONS WITH ATOMS

A. Interaction of Single-Mode Light with an Atom

As is known from atomic theory, an atom may emit (create) or absorb (annihilate) a photon by undergoing downward or upward transitions between its energy levels, conserving energy in the process. The laws that govern these processes are described in this section.

Interaction Between an Atom and an Electromagnetic Mode

Consider the energy levels E_1 and E_2 of an atom placed in an optical resonator of volume V that can sustain a number of electromagnetic modes. We are particularly interested in the interaction between the atom and the photons of a prescribed radiation mode of frequency $v = v_0$, where $hv_0 = E_2 - E_1$, since photons of this energy match the atomic energy-level difference. Such interactions are formally studied by the use of quantum electrodynamics. The key results are presented below, without proof. Three forms of interaction are possible—spontaneous emission, absorption, and stimulated emission.

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Figure 12.2-1 Spontaneous emission of a photon into the mode of frequency ν by an atomic transition from energy level 2 to energy level 1. The photon energy $h\nu = E_2 - E_1$.

Spontaneous Emission

If the atom is initially in the upper energy level, it may drop spontaneously to the lower energy level and release its energy in the form of a photon (Fig. 12.2-1). The photon energy $h\nu$ is added to the energy of the electromagnetic mode. The process is called **spontaneous emission** because the transition is independent of the number of photons that may already be in the mode.

hv

In a cavity of volume V, the probability density (per second), or rate, of this spontaneous transition depends on ν in a way that characterizes the atomic transition.



The function $\sigma(\nu)$ is a narrow function of ν centered about the atomic resonance frequency ν_0 ; it is known as the **transition cross section**. The significance of this name will become apparent subsequently, but it is clear that its dimensions are area (since $p_{\rm ap}$ has dimensions of second⁻¹). In principle, $\sigma(\nu)$ can be calculated from the Schrödinger equation; the calculations are usually so complex, however, that $\sigma(\nu)$ is usually determined experimentally rather than calculated. Equation (12.2-1) applies separately to every mode. Because they can have different directions or polarizations, more than one mode can have the same frequency ν .

The term "probability density" signifies that the probability of an emission taking place in an incremental time interval between t and $t + \Delta t$ is simply $p_{sp} \Delta t$. Because it is a probability density, p_{sp} can be greater than 1 (s⁻¹), although of course $p_{sp} \Delta t$ must always be smaller than 1. Thus, if there are a large number N of such atoms, a fraction of approximately $\Delta N = (p_{sp} \Delta t)N$ atoms will undergo the transition within the time interval Δt . We can therefore write $dN/dt = -p_{sp}N$, so that the number of atoms $N(t) = N(0) \exp(-p_{sp}t)$ decays exponentially with time constant $1/p_{sp}$, as illustrated in Fig. 12.2-2.



Figure 12.2-2 Spontaneous emission into a single mode causes the number of excited atoms to decrease exponentially with time constant $1/p_{sp}$.



Absorption

energy level 2.

If the atom is initially in the lower energy level and the radiation mode contains a photon, the photon may be absorbed, thereby raising the atom to the upper energy level (Fig. 12.2-3). The process is called absorption. Absorption is a transition induced by the photon. It can occur only when the mode contains a photon.

The probability density for the absorption of a photon from a given mode of frequency ν in a cavity of volume V is governed by the same law that governs spontaneous emission into that mode,

$$p_{ab} = \frac{c}{V}\sigma(\nu). \qquad (12.2-2)$$

However, if there are n photons in the mode, the probability density that the atom absorbs one photon is n times greater (since the events are mutually exclusive), i.e.,



Stimulated Emission

Finally, if the atom is in the upper energy level and the mode contains a photon, the atom may be stimulated to emit another photon into the same mode. The process is known as stimulated emission. It is the inverse of absorption. The presence of a photon in a mode of specified frequency, direction of propagation, and polarization stimulates the emission of a duplicate ("clone") photon with precisely the same characteristics as the original photon (Fig. 12.2-4). This photon amplification process is the phenomenon underlying the operation of laser amplifiers and lasers, as will be shown in later chapters. Again, the probability density $p_{\rm st}$ that this process occurs in a cavity of volume V is governed by the same transition cross section,

hw

$$p_{\rm st} = \frac{c}{V} \sigma(\nu). \tag{12.2-4}$$

Figure 12.2-4 Stimulated emission is a process whereby a photon hv stimulates the atom to emit a clone photon as it undergoes a downward transition.



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(12.2-5)

As in the case of absorption, if the mode originally carries n photons, the probability density that the atom is stimulated to emit an additional photon is



After the emission, the radiation mode carries n + 1 photons. Since $P_{st} = P_{ab}$, we use the notation W, for the probability density of both stimulated emission and absorption.

Since spontaneous emission occurs in addition to the stimulated emission, the total probability density of the atom emitting a photon into the mode is $p_{sp} + P_{st} =$ $(n + 1)(c/V)\sigma(v)$. In fact, from a quantum electrodynamic point of view, spontaneous emission may be regarded as stimulated emission induced by the zero-point fluctuations of the mode. Because the zero-point energy is inaccessible for absorption, Pab is proportional to n rather than to (n + 1).

The three possible interactions between an atom and a cavity radiation mode (spontaneous emission, absorption, and stimulated emission) obey the fundamental relations provided above. These should be regarded as the laws governing photon-atom interactions, supplementing the rules of photon optics provided in Chap. 11. We now proceed to discuss the character and consequences of these rather simple relations in some detail.

The Lineshape Function

The transition cross section $\sigma(v)$ specifies the character of the interaction of the atom with the radiation. Its area,

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

which has units of cm²-Hz, is called the transition strength or oscillator strength, and represents the strength of the interaction. Its shape governs the relative magnitude of the interaction with photons of different frequencies. The shape (profile) of $\sigma(\nu)$ is readily separated from its overall strength by defining a normalized function with units of Hz⁻¹ and unity area, $g(\nu) = \sigma(\nu)/S$, known as the lineshape function, so that $\int_0^\infty g(v) dv = 1$. The transition cross section can therefore be written in terms of its strength and its profile as

 σ

$$(\nu) = Sg(\nu).$$
 (12.2-6)

The lineshape function $g(\nu)$ is centered about the frequency where $\sigma(\nu)$ is largest (viz., the transition resonance frequency ν_0) and drops sharply for ν different from ν_0 . Transitions are therefore most likely for photons of frequency $\nu \approx \nu_0$. The width of the function $g(\nu)$ is known as the transition linewidth. The linewidth $\Delta \nu$ is defined as the full width of the function $g(\nu)$ at half its maximum value (FWHM). In general, the width of $g(\nu)$ is inversely proportional to its central value (since its area is unity),

$$\Delta \nu \propto \frac{1}{g(\nu_0)}.$$
(12.2-7)



It is also useful to define the peak transition cross section, which occurs at the resonance frequency, $\sigma_0 = \sigma(\nu_0)$. The function $\sigma(\nu)$ is therefore characterized by its height σ_0 , width $\Delta \nu$, area S, and profile $g(\nu)$, as Fig. 12.2-5 illustrates.

B. Spontaneous Emission

Total Spontaneous Emission into All Modes

Equation (12.2-1) provides the probability density p_{sp} for spontaneous emission into a specific mode of frequency ν (regardless of whether the mode contains photons). As shown in Sec. 9.1C, the density of modes for a three-dimensional cavity is $M(\nu) = k \pi \nu^2 / c^3$. This quantity approximates the number of modes (per unit volume of the cavity per unit bandwidth) that have the frequency ν ; it increases in quadratic fashion. An atom may spontaneously emit *one* photon of frequency ν into *any* of these modes, as shown schematically in Fig. 12.2-6.

The probability density of spontaneous emission into a single prescribed mode must therefore be weighted by the modal density. The overall spontaneous emission probability density is thus

$$P_{\rm sp} = \int_0^\infty \left[\frac{c}{V}\sigma(\nu)\right] [VM(\nu)] d\nu = c \int_0^\infty \sigma(\nu) M(\nu) d\nu.$$

For simplicity, this expression assumes that spontaneous emission into modes of the same frequency ν , but with different directions or polarizations, is equally likely.

Because the function $\sigma(\nu)$ is sharply peaked, it is narrow in comparison with the function $M(\nu)$. Since $\sigma(\nu)$ is centered about ν_0 , $M(\nu)$ is essentially constant at $M(\nu_0)$,



Figure 12.2-6 An atom may spontaneously emit a photon into any one (but only one) of the many modes with frequencies $\nu \approx \nu_0$.

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so that it can be removed from the integral. The probability density of spontaneous emission of one photon into any mode therefore becomes

$$P_{\rm sp} = M(\nu_0)cS = \frac{8\pi S}{\lambda^2},$$
 (12.2-8)

where $\lambda = c/\nu_0$ is the wavelength in the medium. We define a time constant t_{sp} , known as the spontaneous lifetime of the $2 \rightarrow 1$ transition, such that $1/t_{sp} = P_{sp} = M(\nu_n)cS$. Thus

 $= \frac{1}{t_{sp}},$ (12.2-9)
Probability Density of
Spontaneous Emission
of One Photon into Any Mode

which, it is important to note, is independent of the cavity volume V. We can therefore express S as

$$S = \frac{\lambda^2}{8\pi t_{so}};$$
 (12.2-10)

consequently, the transition strength is determined from an experimental measurement of the spontaneous lifetime t_{sp} . This is useful because an analytical calculation of S would require knowledge about the quantum-mechanical behavior of the system and is usually too difficult to carry out.

Typical values of t_{sp} arc $\approx 10^{-8}$ s for atomic transitions (e.g., the first excited state of atomic hydrogen); however, t_{sp} can vary over a large range (from subpicoseconds to minutes).

EXERCISE 12.2-1

Frequency of Spontaneously Emitted Photons. Show that the probability density of an excited atom spontaneously emitting a photon of frequency between ν and $\nu + d\nu$ is $P_{up}(\nu) d\nu = (1/t_{up})g(\nu) d\nu$. Explain why the spectrum of spontaneous emission from an atom is proportional to its lineshape function $g(\nu)$ after a large number of photons have been emitted.

Relation Between the Transition Cross Section and the Spontaneous Lifetime The substitution of (12.2-10) into (12.2-6) shows that the transition cross section is related to the spontaneous lifetime and the lineshape function by

$$\sigma(\nu) = \frac{\lambda^2}{8\pi t_{sp}} g(\nu).$$
(12.2-11)
Transition
Cross Section

(12.2-12)

Furthermore, the transition cross section at the central frequency ν_0 is

$$\sigma_0 \equiv \sigma(\nu_0) = \frac{\lambda^2}{8\pi t_{\rm sp}}g(\nu_0).$$

Because $g(\nu_0)$ is inversely proportional to $\Delta \nu$, according to (12.2-7), the peak transition cross section σ_0 is inversely proportional to the linewidth $\Delta \nu$ for a given t_{sn} .

C. Stimulated Emission and Absorption

Transitions Induced by Monochromatic Light

We now consider the interaction of single-mode light with an atom when a stream of photons impinges on it, rather than when it is in a resonator of volume V as considered above. Let monochromatic light of frequency ν , intensity I, and mean photon-flux density (photons/cm²-s)

$$\phi = \frac{I}{h\nu} \tag{12.2-13}$$

interact with an atom having a resonance frequency ν_0 . We wish to determine the probability densities for stimulated emission and absorption $W_i = P_{ab} = P_{st}$ in this configuration.

The number of photons n involved in the interaction process is determined by constructing a volume in the form of a cylinder of area A and height c whose axis is parallel to the direction of propagation of the light (its k vector). The cylinder has a volume V = cA. The photon flux across the cylinder base is ϕA (photons per second). Because photons travel at the speed of light c, within one second all of the photons within the cylinder cross the cylinder base. It follows that at any time the cylinder contains $n = \phi A$, or

$$n = \phi \frac{V}{c}$$
, (12.2-14)

photons so that $\phi = (c/V)n$. To determine W_i , we substitute (12.2-14) into (12.2-3) to obtain

$$W_i - \phi \sigma(\nu).$$
 (12.2-15)

It is apparent that $\sigma(\nu)$ is the coefficient of proportionality between the probability density of an induced transition and the photon-flux density. Hence the name "transition cross section": ϕ is the photon flux per cm², $\sigma(\nu)$ is the effective cross-sectional area of the atom (cm²), and $\phi\sigma(\nu)$ is the photon flux "captured" by the atom for the purpose of absorption or stimulated emission.

Whereas the spontaneous emission rate is enhanced by the many modes into which an atom can decay, stimulated emission involves decay only into modes that contain photons. Its rate is enhanced by the possible presence of a large number of photons in few modes.

Transitions in the Presence of Broadband Light

Consider now an atom in a cavity of volume V containing multimode polychromatic light of spectral energy density $\rho(\nu)$ (energy per unit bandwidth per unit volume) that is broadband in comparison with the atomic linewidth. The average number of photons in the v to v + dv band is $\rho(v)Vdv/hv$, each with a probability density $(c/V)\sigma(v)$ of initiating an atomic transition, so that the overall probability of absorption or stimulated emission is

$$W_{i} = \int_{0}^{\infty} \frac{\varrho(\nu)V}{h\nu} \left[\frac{c}{V} \sigma(\nu) \right] d\nu.$$
(12.2-16)

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Since the radiation is broadband, the function $\rho(\nu)$ varies slowly in comparison with the sharply peaked function $\sigma(v)$. We can therefore replace $\varrho(v)/v$ under the integral with $\rho(\nu_0)/\nu_0$ to obtain

$$W_i = \frac{\varrho(\nu_0)}{h\nu_0} c \int_0^\infty \sigma(\nu) \, d\nu = \frac{\varrho(\nu_0)}{h\nu_0} cS.$$

Using (12.2-10), we have

$$W_{i} = \frac{\lambda^{3}}{8\pi h t_{c0}} \varrho(\nu_{0}), \qquad (12.2-17)$$

where $\lambda = c/\nu_0$ is the wavelength (in the medium) at the central frequency ν_0 . The approach followed here is similar to that used for calculating the probability density of spontaneous emission into multiple modes, which gives rise to $P_{sp} = M(\nu_0)cS$. Defining

$$\overline{n} = \frac{\lambda^3}{8\pi h} \varrho(\nu_0),$$

which represents the mean number of photons per mode, we write (12.2-17) in the convenient form $W_i =$

$$\frac{n}{t_{sp}}$$
. (12.2-18)

The interpretation of \bar{n} follows from the ratio $W_i/P_{sp} = \varrho(\nu_0)/h\nu_0 M(\nu_0)$. The probability density W_i is a factor of \bar{n} greater than that for spontaneous emission since each of the modes contains an average of \overline{n} photons.

Einstein's A and B Coefficients

Einstein did not have knowledge of (12.2-17). However, based on an analysis of the exchange of energy between atoms and radiation under conditions of thermal equilibrium, he was able to postulate certain expressions for the probability densities of the different kinds of transitions an atom may undergo when it interacts with broadband radiation of spectral energy density $\rho(\nu)$. The expressions he obtained were as follows:

$$P_{ip} = \mathbb{A}$$
(12.2-19)

$$W_i = \mathbb{B}\varrho(\nu_0).$$
Einstein's Postulate

The constants $\mathbb A$ and $\mathbb B$ are known as Einstein's A and B coefficients. By a simple comparison with our expressions (12.2-9) and (12.2-17), the A and B coefficients are identified as



so that

$$\frac{\mathbb{B}}{\mathbb{A}} = \frac{\lambda^3}{8\pi h}.$$
(12.2-23)

It is important to note that the relation between the \mathbb{A} and \mathbb{B} coefficients is a result of the microscopic (rather than macroscopic) probability laws of interaction between an atom and the photons of each mode. We shall present an analysis similar to that of Einstein in Sec. 12.3.

EXAMPLE 12.2-1. Comparison Botween Rates of Spontaneous and Stimulated Emission. Whereas the rate of spontaneous emission for an atom in the upper state is constant (at $A = 1/r_{sp}$), the rate of simulated emission in the presence of broadband light $Bq(\nu_p)$ is proportional to the spectral energy density of the light $g(\nu_p)$. The two rates are equal when $q(\nu_p) = \lambda/R = 8\pi\hbar/\lambda^2$; for greater spectral energy densities, the rate of simulated emission exceeds that of spontaneous emission. If $\lambda = 1 \ \mu$ m, for example, $\lambda/B = 1.66 \times 10^{-16} \ J/m^2$ ·Hz. This corresponds to a linewidth $\Delta \nu = 10^7$ Hz, the optical intensity at which the stimulated emission rate equals the spontaneous emission rate is 50 W/m² or 5 mW/cm².

Summary

An atomic transition is characterized by its resonance frequency ν_0 , its spontaneous lifetime t_{sp} , and its lineshape function $g(\nu)$, whose width is the linewidth $\Delta \nu$. The transition cross section is



Spontaneous Emission

 If the atom is in a cavity of volume V in the upper level, the probability density (per second) of emitting spontaneously into one *prescribed* mode of frequency v is

$$p_{\rm sp} = \frac{c}{V} \sigma(\nu). \tag{12.2-1}$$

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 The probability density of spontaneous emission into any of the available modes is

 $P_{\rm sp} =$

• The probability density of emitting into modes lying only in the frequency band between ν and $\nu + d\nu$ is $P_{sp}(\nu) d\nu - (1/t_{sp})g(\nu) d\nu$. The spectrum of spontaneously emitted light is therefore proportional to the lineshape function $g(\nu)$.

Stimulated Emission and Absorption

If the atom in the cavity is in the upper level and a radiation mode contains n
photons, the probability density of emitting a photon into that mode is

$$W_i = n \frac{c}{V} \sigma(\nu). \tag{12.2-5}$$

If the atom is instead in the lower level, and a mode contains n photons, the probability of absorption of a photon from that mode is also given by (12.2-5).

If instead of being in a cavity the atom is illuminated by a monochromatic beam of light of frequency v, with mean photon-flux density & (photons per second per unit area), the probability density of stimulated emission (if the atom is in the upper level) or absorption (if the atom is in the lower level) is

$$W_i = \phi \sigma(\nu). \tag{12.2-15}$$

If the light illuminating the atom is polychromatic but narrowband in comparison with the atomic linewidth, and has a mean photon-flux spectral density \u03c6_{\u03c6} (photons per second per unit area per unit frequency), the probability density of stimulated emission/absorption is

$$W_i = \int \phi_{\nu} \sigma(\nu) \, d\nu. \qquad (12.2-24)$$

 If the light illuminating the atom has a spectral energy density Q(v) that is broadband in comparison with the atomic linewidth, the probability density of stimulated emission / absorption is

W,

$$= \mathbb{B}\varrho(\nu_0), \qquad (12.2-20)$$

where $\mathbb{B} = (\lambda^3 / 8\pi h t_{sp})$ is the Einstein B coefficient.

In all of these formulas, $c = c_o/n$ is the velocity of light, $\lambda = \lambda_o/n$ is the wavelength of light in the atomic medium, and n is the refractive index.

D. Line Broadening

Because the lineshape function g(v) plays an important role in atom-photon interactions, we devote this subsection to a brief discussion of its origins. The same lineshape function is applicable for spontaneous emission, absorption, and stimulated emission

Lifetime Broadening

Atoms can undergo transitions between energy levels by both radiative and nonradiative means. Radiative transitions result in photon absorption and emission. Nonradiative transitions permit energy transfer by mechanisms such as lattice vibrations, inelastic collisions among the constituent atoms, and inelastic collisions with the walls of the vessel. Each atomic energy level has a lifetime r, which is the inverse of the rate at which its population decays, radiatively or nonradiatively, to all lower levels.

The lifetime τ_2 of energy level 2 shown in Fig. 12.2-1 represents the inverse of the rate at which the population of that level decays to level 1 and to all other lower energy levels (none of which are shown in the figure), by either radiative or nonradiative means. Since $1/t_{\rm sp}$ is the radiative decay rate from level 2 to level 1, the overall decay rate $1/\tau_2$ must be more rapid, i.e., $1/\tau_2 \ge 1/t_{\rm sp}$, so that $\tau_2 \le t_{\rm sp}$. The lifetime τ_1 of level 1 is defined similarly. Clearly, if level 1 is the lowest allowed energy level (the ground state), $\tau_1 = \infty$.

Lifetime broadening is, in essence, a Fourier transform effect. The lifetime τ of an energy level is related to the time uncertainty of the occupation of that level. As shown in Appendix A, the Fourier transform of an exponentially decaying harmonic function of time $e^{-t/2\tau}e^{i2\pi\nu\omega}$, which has an energy that decays as $e^{-t/\tau}$ (with time constant τ), is proportional to $1/(1 + j4\pi(\nu - \nu_0)\tau)$. The full width at half-maximum (FWHM) of the magnitude of this Lorentzian function of frequency is $\Delta\nu = 1/2\pi\tau$. This spectral uncertainty corresponds to an energy spread $\Delta E = h/2\pi\tau$. An energy level with lifetime τ therefore has an energy spread $\Delta E = h/2\pi\tau$, provided that we can model the decay process as a simple exponential. In this picture, spontaneous emission can be viewed in terms of a damped harmonic oscillator which generates an exponentially decaying harmonic function.

Thus, if the energy spreads of levels 1 and 2 are $\Delta E_1 = h/2\pi\tau_1$ and $\Delta E_2 = h/2\pi\tau_2$, respectively, the spread in the energy difference, which corresponds to the transition between the two levels, is

$$\Delta E = \Delta E_1 + \Delta E_2 = \frac{h}{2\pi} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) = \frac{h}{2\pi} \frac{1}{\tau},$$
 (12.2-25)

where $\tau^{-1} = (\tau_1^{-1} + \tau_2^{-1})$ and τ is the transition lifetime. The corresponding spread of the transition frequency, which is called the lifetime-broadening linewidth, is therefore

$$\Delta \nu = \frac{1}{2\pi} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right).$$
 (12.2-26)
Lifetime-Broadening

This spread is centered about the frequency $\nu_0 = (E_2 - E_1)/h$, and the lineshape function has a Lorentzian profile,

$$g(\nu) = \frac{\Delta \nu / 2\pi}{(\nu - \nu_0)^2 + (\Delta \nu / 2)^2}.$$
 (12.2-27)
Lorentzian Lineshape
Experimental

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Figure 12.2-7 Wavepacket emissions at random times from a lifetime broadened atomic system with transition lifetime τ . The light emitted has a Lorentzian power spectral density of width $\Delta \nu = 1/2\pi \tau$.

The lifetime broadening from an atom or a collection of atoms may be more generally modeled as follows. Each of the photons emitted from the transition represents a wavepacket of central frequency ν_0 (the transition resonance frequency), with an exponentially decaying envelope of decay time 2τ (i.e., with energy decay time equal to the transition lifetime τ), as shown in Fig. 12.2-7. The radiated light is taken to be a sequence of such wavepackets emitted at random times. As discussed in Example 10.1-1, this corresponds to random (partially coherent) light whose power spectral density is precisely the Lorentzian function given in (12.2-27), with $\Delta \nu = 1/2\pi\tau$.

The value of the Lorentzian lineshape function at the central frequency ν_0 is $g(\nu_0) = 2/\pi\Delta\nu$, so that the peak transition cross section, given by (12.2-12), becomes

$$\sigma_{0} = \frac{\lambda^{2}}{2\pi} \frac{1}{2\pi t_{sp} \Delta \nu} \,. \tag{12.2-28}$$

The largest transition cross section occurs under ideal conditions when the decay is entirely radiative so that $\tau_2 - t_{sp}$ and $1/\tau_1 = 0$ (which is the case when level 1 is the ground state from which no decay is possible). Then $\Delta \nu = 1/2\pi t_{sp}$ and

$$_{0} = \frac{\lambda^{2}}{2\pi}$$
, (12.2-29)

indicating that the peak cross-sectional area is of the order of one square wavelength. When level 1 is not the ground state or when nonradiative transitions are significant,



Figure 12.2-8 A sinewave interrupted at the rate f_{col} by random phase jumps has a Lorentzian spectrum of width $\Delta \nu = f_{col}/\pi$.

 $\Delta\nu$ can be $\gg 1/t_{sp}$ in which case σ_0 can be significantly smaller than $\lambda^2/2\pi$. For example, for optical transitions in the range $\lambda = 0.1$ to $10 \ \mu\text{m}$, $\lambda^2/2\pi \approx 10^{-11}$ to 10^{-7} cm², whereas typical values of σ_0 for optical transitions fall in the range 10^{-20} to 10^{-11} cm² (see .e.g., Table 13.2-1 on page 480).

Collision Broadening

Inelastic collisions, in which energy is exchanged, result in atomic transitions between energy levels. This contribution to the decay rates affects the lifetimes of all levels involved and hence the linewidth of the radiated field, as indicated above.

Elastic collisions, on the other hand, do not involve energy exchange. Rather, they cause random phase shifts of the wavefunction associated with the energy level, which in turn results in a random phase shift of the radiated field at each collision time. Collisions between atoms provide a source of such line broadening. A sinewave whose phase is modified by a random shift at random times (collision times), as illustrated in Fig. 12.2-8, exhibits spectral broadening. The determination of the spectrum of such a randomly dephased function is a problem that can be solved using the theory of random processes. The spectrum turns out to be Lorentzian, with width $\Delta \nu = f_{\rm col}/\pi$, where $f_{\rm col}$ is the collision rate (mean number of collisions per second).[†]

Adding the linewidths arising from lifetime and collision broadening therefore results in an overall Lorentzian lineshape of linewidth



Inhomogeneous Broadening

Lifetime broadening and collision broadening are forms of homogeneous broadening that are exhibited by the atoms of a medium. All of the atoms are assumed to be identical and to have identical lineshape functions. In many situations, however, the different atoms constituting a medium have different lineshape functions or different center frequencies. In this case we can define an average lineshape function

$$\bar{g}(\nu) = \langle g_{\beta}(\nu) \rangle,$$
 (12.2-31)

where $\langle \cdot \rangle$ represents an average with respect to the variable β , which is used to label

[†]See, e.g., A. E. Siegman, Lasers, University Science Books, Mill Valley, CA, 1986, Sec. 3.2.



Figure 12.2-9 The average lineshape function of an inhomogeneously broadened collection of atoms.

those atoms with lineshape function $g_{\beta}(\nu)$. Thus $g_{\beta}(\nu)$ is weighted with the fraction of the atomic population having the property β , as shown in Fig. 12.2-9.

One inhomogeneous broadening mechanism is Doppler broadening. As a result of the Doppler effect, an atom moving with velocity v along a given direction exhibits a spectrum that is shifted by the frequency $\pm (v/c)v_0$, where v_0 is its central frequency, when viewed along that direction. The shift is in the direction of higher frequency (- sign) if the atom is moving toward the observer, and in the direction of lower frequency shift is $\pm (v_{\mu}/c)v_0$, where v_1 is the component of velocity parallel to the direction of observation. Since a collection of atoms in a gas exhibits a distribution of velocities, the light they emit exhibits a range of frequencies, resulting in Doppler broadening, as illustrated in Fig. 12.2-10.

In the case of Doppler broadening, the velocity v therefore plays the role of the parameter $\beta_i \,\overline{g}(v) = \langle g_v(v) \rangle$. Thus if $p(v) \, dv$ is the probability that the velocity of a given atom lies between v and v + dv, the overall inhomogeneous Doppler-broadened lineshape is (see Fig. 12.2-11)

$$\bar{g}(\nu) = \int_{-\infty}^{\infty} g\left(\nu - \nu_0 \frac{v}{c}\right) p(v) dv.$$
 (12.2-32)



Figure 12.2-10 The radiated frequency is dependent on the direction of atomic motion relative to the direction of observation. Radiation from atom 1 has higher frequency than that from atoms 3 and 4. Radiation from atom 2 has lower frequency.





EXERCISE 12.2-2

Doppler-Broadened Lineshape Function

(a) The component of velocity v of atoms of a gas along a particular direction is known to have a Gaussian probability density function

$$p(\mathbf{v}) = \frac{1}{\sqrt{2\pi}\sigma_{\mathbf{v}}} \exp\left(-\frac{\mathbf{v}^2}{2\sigma_{\mathbf{v}}^2}\right),$$

where $\sigma_v^2 = k_B T/M$ and M is the atomic mass. If each atom has a Lorentzian natural lineshape function of width $\Delta \nu$ and central frequency ν_0 , derive an expression for the average lineshape function $\tilde{g}(\nu)$.

(b) Show that if $\Delta\nu\ll\nu_0\sigma_v/c,\ \bar{g}(\nu)$ may be approximated by the Gaussian lineshape function

$$(\nu) = \frac{1}{\sqrt{2\pi}\sigma_D} \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma_D^2}\right],$$
 (12.2-33)

where

$$v_0 \frac{\sigma_v}{c} = \frac{1}{\lambda} \left(\frac{k_B T}{M}\right)^{1/2}$$
. (12.2-34)

The full-width half-maximum (FWHM) Doppler linewidth $\Delta \nu_D$ is then

oD .

$$\Delta \nu_D = (8 \ln 2)^{1/2} \sigma_D \approx 2.35 \sigma_D. \qquad (12.2-35)$$

(c) Compute the Doppler linewidth for the $\lambda_{\varphi} = 632.8$ nm transition in Ne, and for the $\lambda_{\varphi} = 10.6 \ \mu m$ transition in CO₂ at room temperature, assuming that $\Delta \nu \ll \nu_{g}\sigma_{\nu}/c$. These transitions are used in the H=-Ne and CO₂ lasers, respectively.

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$$\sigma_0 = \frac{\lambda^2}{8\pi} \left(\frac{4\ln 2}{\pi}\right)^{1/2} \frac{1}{t_{sp} \Delta \nu_D}$$

$$\approx 0.94 \frac{\lambda^2}{8\pi} \frac{1}{t_{sp} \Delta \nu_D}.$$
(12.2-36)

Compare with (12.2-28) for the Lorentzian lineshape function.

Many atom-photon interactions exhibit broadening that is intermediate between purely homogeneous and purely inhomogeneous. Such mixed broadening can be modeled by an intermediate lineshape function known as the Voight profile.

*E. Laser Cooling and Trapping of Atoms

The broadening associated with the Doppler effect often masks the natural lineshape function; the magnitude of the latter is often of interest. One way to minimize Doppler broadening is to use a carefully controlled atomic beam in which the velocities of the atoms are well regulated. However, the motion of atoms can also be controlled by means of radiation pressure (see Sec. 11.1C).

Photons from a laser beam of narrow linewidth, tuned above the atomic line center, can be absorbed by a beam of atoms moving toward the laser beam. After absorption, the atom can return to the ground state by either stimulated or spontaneous emission. If it returns by stimulated emission, the momentum of the emitted photon is the same as that of the absorbed photon, leaving the atom with no net change of momentum. If it returns by spontaneous emission, on the other hand, the direction of photon emission is random so that repeated absorptions result in a net decrease of the atomic momentum in the direction pointing toward the laser beam. The result is a decrease in the velocity of those atoms, as shown schematically in Fig. 12.2-12. Ultimately, the



Figure 12.2-12 The thermal velocity distribution (dashed curve) and the laser-cooled distribution (solid curve).