

Atomic Radiation

In previous chapters, we discussed the emission of radiation in atomic transitions without considering why these transitions should occur at all. We *assumed* that an atom may change from a higher energy state to a lower energy state, while emitting the energy difference in the form of radiation; and this assumption is certainly in accord with the experimental facts. But the Schrödinger equation contains no term which *requires* that such transitions occur; as far as this equation is concerned, an atom might remain in an excited state forever. Thus we need a theory which demands that transitions take place, and which tells us how to calculate their probability of occurrence.

In Section 3.4, we saw how to estimate a transition probability by making use of the classical expression for the rate of radiation of energy from an accelerated charge. Fundamentally we should do the same thing in developing a quantum theory of radiation. We must take the classical equations for the electric and magnetic fields—Maxwell's equations—and quantize them, so that these equations, which are known to be correct when large numbers of photons are present, may be extended into the domain in which very few photons are present.

Unfortunately, the process of quantizing Maxwell's equations is too sophisticated for this book, so we shall settle for an approximate treatment which gives good results. By means of a *time-dependent* perturbation theory, developed along the same lines as the time-independent theory of Section 8.1, we can calculate the effect of *external fields* in *inducing* transitions from one state to another. We can then use a thermodynamic argument to relate the induced transition rate to the probability that a *spontaneous* transition will occur in the absence of a field. This approach does not answer the fundamental question of why an atom makes a spontaneous transition, but it does enable us to calculate the transition rate with some degree of accuracy and assurance.

We shall find that the transition probabilities often turn out to be zero in such calculations. This fact leads us to the formulation of selection rules to determine which transitions are likely to occur. In many cases a transition probability is not absolutely zero, but it is calculated to be zero only because of the approximation made in the calculation. Such transitions are said to be "forbidden." We shall study the nature of these approximations, and thereby estimate the probabilities of various forbidden transitions relative to the probabilities of allowed transitions.

Finally, we shall see how these rules apply to the operation of the maser and the laser, and we shall study some of the properties of these remarkable devices.

10.1 TIME-DEPENDENT PERTURBATION THEORY; TRANSITION RATES

Time dependent perturbation theory is developed in a way which is quite similar to the development of time independent perturbation theory (Section 8.1). We assume that the potential energy contains a small time dependent perturbing term $v(x, t)$, and that without the addition of this term the Schrödinger equation may be solved exactly. Since the potential is time dependent, we begin with the *time-dependent* Schrödinger equation (instead of the time independent equation as in Section 8.1), and we write

$$[H_0 + v(x, t)]\psi'_n = i\hbar \frac{\partial \psi'_n}{\partial t} \quad (1)$$

where, as before, H_0 is the H operator (the Hamiltonian, or energy operator) for the unperturbed system, so that

$$H_0 \psi_t = i\hbar \frac{\partial \psi_t}{\partial t} \quad (2)$$

As in Section 8.1, we can now write each function ψ_n' as a linear combination of the functions ψ_l ; but we must now allow the coefficients to be *time dependent*¹:

$$\psi_n' = \sum_l a_{nl}(t) \psi_l \quad (3)$$

Thus Eq. (1) becomes, with the insertion of Eq. (3),

$$[H_0 + v(x, t)] \sum_l a_{nl}(t) \psi_l = i\hbar \frac{\partial}{\partial t} \sum_l a_{nl} \psi_l \quad (4)$$

[Compare with Eqs. (2) and (3) in Section 8.1.]

If we carry out the indicated differentiation term-by-term on the right-hand side, we obtain

$$H_0 \left(\sum_l a_{nl}(t) \psi_l \right) + v(x, t) \left(\sum_l a_{nl}(t) \psi_l \right) = i\hbar \left[\sum_l \left(\dot{a}_{nl} \psi_l + a_{nl} \frac{\partial \psi_l}{\partial t} \right) \right] \quad (5)$$

The first series on the left may be written as $\sum_l a_{nl} H_0 \psi_l$, because the operator H_0 does not operate on the time variable. However, from Eq. (2) we see that this series is equal to $i\hbar \sum_l a_{nl} (\partial \psi_l / \partial t)$, so we may eliminate these two series from Eq. (5) to obtain

$$v(x, t) \sum_l a_{nl} \psi_l = i\hbar \sum_l \dot{a}_{nl} \psi_l \quad (6)$$

We are now in a position to find the rate of change of a_{nl} , by solving for \dot{a}_{nl} ; this will eventually tell us the transition probability which we seek. We proceed as in finding the coefficients a_{ml} in Section 8.1; we multiply each side of Eq. (6) by ψ_m^* , a *particular* wavefunction, and we then integrate over all space, to obtain

$$\int \sum_l a_{nl} \psi_m^* v(x, t) \psi_l d\tau = i\hbar \int \sum_l \dot{a}_{nl} \psi_m^* \psi_l d\tau$$

which we integrate term-by-term as we did with similar expressions in Section 8.1. Because \dot{a}_{nl} has no space dependence, and the wavefunctions ψ_l are orthogonal to one another, the only nonzero term on the right-hand side is the one for which $l = m$. (Remember that l is the running index in the summation, whereas m is a fixed number.) Inserting the time dependence of ψ_m ,

$$\psi_m = u_m(x) e^{-iE_m t/\hbar}$$

we find that

$$\dot{a}_{nm} = -\frac{i}{\hbar} \sum_l a_{nl} e^{-i(E_l - E_m)t/\hbar} v_{ml} \quad (7)$$

where, as in Section 8.1, we use the abbreviation $v_{ml} = \int u_m^* v u_l d\tau$.

¹ At any given time t_1 , ψ_n' is a linear combination of the ψ_l , with coefficients a_{nl} , which may be determined by time independent perturbation theory. But since $v(x, t)$ changes with time, the expansion coefficients will, in general, be different at some other time t_2 .

Equation (7) is still exact; except for the time dependence, it is very similar to Eq. (6) in Section 8.1; and like that equation, it contains too many unknown quantities to be useful as it stands. So we make the *approximation* that $v(x, t)$ is a *small perturbation* of the original system. This means that the eigenfunctions of the perturbed system differ very slightly from the unperturbed eigenfunctions, so that, as in Section 8.1, one of the coefficients, a_{nn} , is approximately equal to 1 at all times, and the other coefficients are very small.² In that case, we can neglect all terms on the right-hand side of Eq. (7) except the one for which $l = n$, and we can thus find the time dependence of the small coefficient a_{nm} :

$$\dot{a}_{nm} \approx -\frac{i}{\hbar} e^{-i(E_n - E_m)t/\hbar} v_{mn} \quad (8)$$

If we know $v(x, t)$ for all x and t , we can now integrate Eq. (8) to find $a_{nm}(t)$, and the behavior of the system is determined, to the extent that our approximation is valid and each coefficient $a_{nm} \ll 1$ for $m \neq n$.

At this point, we should pause to point out the differences as well as the similarities between time-dependent and time-independent perturbation theory. The *methods* used are quite similar, but the *goals* are different. In Section 8.1, we were trying to calculate a shift in an energy level, but here we are not concerned with such shifts; rather, we are concerned with the *transitions* which the perturbation causes to occur between the unperturbed levels. It is possible to adopt this point of view only because the perturbation is not applied for an infinite period of time, so that after the perturbation is turned off, one can make a measurement which places the system in one of the *unperturbed* levels. We can say that the following sequence of events may occur:

1. The system is initially in an unperturbed state whose wavefunction is ψ_n ; its energy is E_n , one of the energy eigenvalues of the unperturbed Schrödinger equation.
2. The perturbation is "turned on" at time $t = 0$, so that the system is, for $t > 0$, described by the *perturbed* Schrödinger equation, with a different set of eigenfunctions and energy levels. The wavefunction becomes ψ'_n , which may be expanded in terms of the unperturbed eigenfunctions by means of the coefficients $a_{nm}(t)$. Since the perturbation is small, the new wavefunction ψ'_n never differs greatly from the old wavefunction ψ_n during the time that the perturbation is on; that is, $a_{nn}(t) \simeq 1$, and the other coefficients a_{nm} are very small.
3. The perturbation is turned off at time $t = t'$, and the energy of the system is determined again. At this point, the system is again described by the

² Obviously, when the coefficients are time dependent, there is some question as to how long they can remain small. We shall discuss this implied limitation on the *time of application of the perturbation* in a moment.

unperturbed Schrödinger equation, so that the wavefunction must again be one of the unperturbed wavefunctions; it may be the original wavefunction ψ_n , or it may be a different wavefunction ψ_m . In the latter case, we say that the perturbation has *induced a transition*. According to Postulate 3 (Section 6.3), the probability that the wavefunction will be ψ_m is given by $|a_{nm}(t')|^2$ —the absolute square of the coefficient of ψ_m in the expansion of the wavefunction ψ'_m , which is the wavefunction of the system at the time of the measurement. Thus $|a_{nm}(t')|^2$ is the probability of a transition from an initial state with wavefunction ψ_n to a final state with wavefunction ψ_m .

Now we would like to integrate Eq. (8) in order to evaluate $a_{nm}(t')$ and thus determine the transition probability as a function of the time t' . To do this, we need to know the time-dependent potential $v(x, t)$ so that we can find the matrix element v_{nm} . We recall that we set out to solve the problem of an atom in an external electromagnetic field, so let us compute the potential energy of an atomic electron in such a field; this will enable us to derive many properties of atomic radiation.

Dipole Radiation. Let us consider radiation whose wavelength is much greater than the diameter of the atoms involved. This is a reasonable thing to do, because we know that the shortest wavelength emitted by a hydrogen atom is more than 1000 times the diameter of the hydrogen atom. For such radiation, the field does not vary appreciably over the dimensions of the atom, and we can as a first approximation assume that the field is constant over the atom. That is, the field varies only in time, not space. (This is known as the dipole approximation, which gives results valid for electric dipole radiation; later we shall see what happens when this approximation is abandoned.) For simplicity, we shall consider monochromatic (single frequency) radiation, which is polarized along the x axis; it will be easy to generalize the results to unpolarized radiation with a continuous frequency spectrum. We therefore write the x component of the electric field³ as

$$E_x = E_{0x} \cos \omega t$$

where E_{0x} is a constant. It is more convenient to rewrite this field in the complex notation:

$$E_x = \frac{1}{2} E_{0x} (e^{i\omega t} + e^{-i\omega t})$$

By definition, the potential energy of a charge q in this field is $v(x, t) = -q \int E_x dx$; and since E_{0x} is a constant, we can immediately evaluate this integral to obtain

$$v(x, t) = -\frac{1}{2} E_{0x} qx (e^{i\omega t} + e^{-i\omega t})$$

³ Here we neglect the interaction between the electron and the *magnetic* field. This is reasonable, because the speed of the electron is of order $0.01c$, and at such a speed the magnetic interaction energy is of order 0.01 times the electric interaction energy.

Inserting this expression into Eq. (8), we obtain (with q equal to the electron charge of $-e$)

$$\dot{a}_{nm}(t) = -\frac{ieE_{0x}}{2\hbar} [e^{i(E_m - E_n + \hbar\omega)t/\hbar} + e^{i(E_m - E_n - \hbar\omega)t/\hbar}] x_{mn} \quad (9)$$

where we have used the abbreviation $x_{mn} = \int u_m^* x u_n d\tau$, the integral being over all space as before.

To find the value of $a_{nm}(t)$ at time t' (when the external field is "turned off"), we integrate Eq. (9) from $t = 0$ to $t = t'$. Using the initial condition $a_{nm}(0) = 0$ ($n \neq m$), we have

$$a_{nm}(t') = \frac{1}{2} x_{mn} eE_{0x} \left[\frac{1 - e^{i(E_m - E_n + \hbar\omega)t'/\hbar}}{E_m - E_n + \hbar\omega} + \frac{1 - e^{i(E_m - E_n - \hbar\omega)t'/\hbar}}{E_m - E_n - \hbar\omega} \right] \quad (10)$$

Because of the expressions $E_m - E_n + \hbar\omega$ and $E_m - E_n - \hbar\omega$ in the denominators, a graph of the coefficient $a_{nm}(t')$ would be peaked at $E_n - E_m = \pm \hbar\omega$. Thus we find a large transition probability when the energy difference between the two states is equal to the energy of a quantum of the applied field—that is, just when the Bohr condition is satisfied.

But we see here that E_m may be *greater* or *less* than E_n by the amount $\hbar\omega$. If E_m is greater than E_n , we have the well-known situation in which the atom has absorbed energy from the field; absorption of a photon has excited the atom from a lower energy state to a higher energy state. But if E_m is *smaller* than E_n , the atom has emitted energy as a result of the perturbation; a photon striking the atom has *stimulated* the emission of a *second* photon. This *stimulated emission*, which *deexcites* the atom and causes the external field to *gain* energy, is the phenomenon responsible for the operation of the maser and the laser.

To evaluate the probability $|a_{nm}(t')|^2 = a_{nm}^*(t')a_{nm}(t')$, let us consider the case in which $E_m - E_n \simeq \hbar\omega$, so that the first term of Eq. (10) is much smaller than the second term, and the first term may therefore be neglected. Direct multiplication then yields [after use of the formula $\cos \theta = 1 - 2 \sin^2(\theta/2)$]

$$|a_{nm}(t')|^2 = e^2 E_{0x}^2 |x_{mn}|^2 \frac{\sin^2 \frac{(E_m - E_n - \hbar\omega)t'}{2\hbar}}{(E_m - E_n - \hbar\omega)^2} \quad (11)$$

Two features of this expression require some explanation. One is the sinusoidal time dependence plotted in Fig. 1, which seems to indicate that the transition probability oscillates as time passes. However, because of the presence of the expression $(E_m - E_n - \hbar\omega)$ in the denominator, this oscillation is not quite what it seems, as we shall see.

The second feature, which is closely connected with the first, is the nonzero probability of transitions for which $E_m - E_n = \hbar\omega$ —that is, transitions for which the change in energy of the atom is *not* equal to the energy of a photon

for a field of angular frequency ω . Thus, either the law of conservation of energy is being violated, or else there is a possibility that the photons in the radiation field may have energies not equal to $\hbar\omega$.

Fortunately for the law of conservation of energy, we can easily see that the latter is the case. Our analysis requires that the perturbation—the radiation field—be turned on for a *finite time* t' , and in that case the wave cannot possibly be monochromatic. A Fourier analysis⁴ of a sine wave which is suddenly turned on at $t = 0$ and turned off again at $t = t'$ would show a sinusoidal distribution of frequencies which is consistent with expression (11). (See Problem 2.) Thus there is no conflict with either the law of conservation of energy or the condition that a photon's energy is $\hbar\omega$. Furthermore, if we let $t' \rightarrow \infty$ in Eq. (11), we see that the wave becomes truly monochromatic; the function $\sin^2[\frac{1}{2}(\omega_{nm} - \omega)t']/\hbar^2(\omega_{nm} - \omega)^2$ approaches zero for all frequencies except the frequency $\omega = \omega_{nm} = (E_m - E_n)/\hbar$. (Refer again to Fig. 1.)

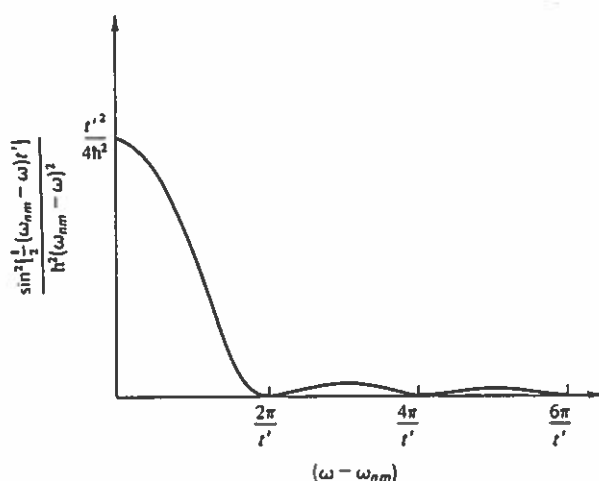


Fig. 1 The function $\sin^2[\frac{1}{2}(\omega_{nm} - \omega)t']/\hbar^2(\omega_{nm} - \omega)^2$, which appears in Eq. (11), plotted versus angular frequency ω . Notice that the overwhelming contribution to the function comes from the region $0 < |\omega - \omega_{nm}| < 2\pi/t'$, and the width of this region goes to zero as $t' \rightarrow \infty$. Because the height of the curve is proportional to t'^2 , and the width is proportional to $1/t'$, the area under the curve is proportional to t' . This area represents the total transition probability in a radiation field containing a uniform distribution of frequencies in the neighborhood of $\omega = \omega_{nm}$.

⁴ See Section 4.3.

Let us now consider the more general case, in which the radiation field cannot be represented by the function $E_{0x} \cos \omega t$ at any time, but rather contains a *superposition* of such fields, with the various values of ω forming a *continuous spectrum*. In such a case, Eq. (11) can still be used to describe a component of that spectrum with any given frequency ω , but since the frequencies form a continuous spectrum, we cannot speak of the amplitude of any single frequency. (There are now an *infinite* number of possible frequencies, so the amplitude of any *single* frequency must be zero.) Therefore we rewrite Eq. (11) in terms of an energy density function $\rho(\omega)$, such that $\int_{\omega_1}^{\omega_2} \rho(\omega) d\omega$ is the energy density of radiation between the frequencies ω_1 and ω_2 . It is easy to do this, because Eq. (11) is already expressed in terms of an energy density. According to classical electromagnetic theory, the quantity $\frac{1}{2}\epsilon_0 E_{0x}^2$ is the average energy density in an electric field of the form originally assumed.⁵ Thus we set $\frac{1}{2}\epsilon_0 E_{0x}^2$ equal to $\rho(\omega) d\omega$, and we replace E_{0x}^2 in Eq. (11) by $2\rho(\omega) d\omega/\epsilon_0$. Then we find the total transition probability T_{nm} , resulting from the entire spectrum of radiation, by integrating the resulting expression over all frequencies:

$$T_{nm} = |a_{nm}(t')|^2 = 2e^2 |x_{mn}|^2 \int_0^\infty \frac{\sin^2[\frac{1}{2}(\omega - \omega_{nm})t']}{\epsilon_0 \hbar^2 (\omega - \omega_{nm})^2} \rho(\omega) d\omega$$

The integrand here is the product of the energy density distribution $\rho(\omega)$ and the peaked function $\sin^2[\frac{1}{2}(\omega - \omega_{nm})t']/\hbar^2(\omega - \omega_{nm})^2$, which is characteristic of the atom and of the duration of the perturbation. Let us suppose that the distribution $\rho(\omega)$ varies much more slowly than the sharply peaked function by which it is multiplied. Then $\rho(\omega)$ is nearly constant over the small range of values of ω for which the integrand is nonzero, so that we can replace $\rho(\omega)$ by its value at $\omega = \omega_{nm}$, and remove it from the integral, with no loss of accuracy. With the further substitution $z = \frac{1}{2}(\omega - \omega_{nm})t'$, the expression becomes

$$|a_{nm}(t')|^2 = \frac{e^2 \rho(\omega_{nm}) |x_{mn}|^2 t'}{\hbar^2 \epsilon_0} \int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2} dz$$

or, since

$$\int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2} dz = \pi$$

the transition probability is

$$T_{nm} = |a_{nm}(t')|^2 = \frac{\pi e^2 \rho(\omega_{nm}) |x_{mn}|^2 t'}{\hbar^2 \epsilon_0} \quad (12)$$

⁵ The energy density in a constant electric field of magnitude E_{0x} is equal to $\frac{1}{2}\epsilon_0 E_{0x}^2$ (mks). In a field which varies as $\cos \omega t$, the time average energy density is only one-half as great, but there is an equal amount of energy in the magnetic field which always accompanies an oscillating electric field.

We must remember that Eq. (12) holds for radiation which is polarized along the x axis. In the general case, when radiation is incident upon the atom from all directions and with random polarization, T_{nm} must include equal contributions from x_{mn} , y_{mn} , and z_{mn} , so that

$$T_{nm} = \frac{\pi e^2 \rho(\omega_{nm}) t'}{3 \hbar^2 \epsilon_0} [|x_{mn}|^2 + |y_{mn}|^2 + |z_{mn}|^2] \quad (13)$$

where the factor of 3 has been introduced into the denominator because each polarization direction is assumed to contribute $\frac{1}{3}$ of the intensity.

Equation (13) and its derivation contain some features which you might have expected, and some other features which are not so obvious, as follows:

1. The induced transition probability is proportional to the energy density of the incident radiation. This is certainly reasonable.
2. T_{nm} is also proportional to the sum of the absolute squares of the matrix elements x_{mn} , y_{mn} , and z_{mn} . This is also reasonable, and it has an analogy in classical theory. The expression $ex_{mn} = e \int u_m^* x u_n d\tau$ is the x component of the so-called *dipole moment between states n and m* ; the y and z components of the dipole moment are expressed in an analogous manner. The designation "dipole moment" comes from the classical expression for the dipole moment of a charge distribution of charge density ρ ; the x component of the classical expression is $\int x \rho d\tau$.⁶ We see the connection between the two expressions by writing the charge density produced by a single electron whose wavefunction is u_n ; the charge density equals the electron charge e times the probability density $u_n^* u_n$, so that the dipole moment has x component $e \int x u_n^* u_n d\tau$. This expression differs from the one given above only in the fact that a single wavefunction u_n is involved, rather than the wavefunctions u_n and u_m . But under the influence of the perturbation, the electron in a sense *occupies both states n and m simultaneously*, so it is reasonable to find that an analogous expression for the dipole moment becomes $e \int u_m^* x u_n d\tau$. Because of this connection with the classical expression for dipole moment, the results obtained here are said to describe *electric dipole radiation*, which classically results from a changing dipole moment. (We shall see in Section 9.3 that the matrix elements x_{mn} , y_{mn} , and z_{mn} determine the electric dipole *selection rules* for absorption and emission of radiation by atoms; a zero matrix element indicates that the corresponding transition is "forbidden." In that section we shall also have something to say about the other possible types of radiation.)

⁶ We use ρ here as a standard symbol for density; it is not to be confused with the *energy density* $\rho(\omega)$ of the radiation field.

3. T_{nm} is directly proportional to the time t' during which the perturbation is applied. Thus we can refer to T_{nm}/t' as a *constant transition probability per unit time*. This result requires some thought. Obviously, we cannot expect T_{nm} to increase indefinitely in this manner. The first-order perturbation theory used here is valid only for times such that $T_{nm} \ll 1$. But there are many real situations in which this condition is satisfied. For example, if the energy density of the radiation is small, we can suppose that the atom is exposed to only one photon at a time. Then the radiation impinging on the atom does not form a continuous wave, but is turned on when a photon reaches the atom and is turned off when the photon has passed. After the photon has passed, the atom is again unperturbed, and it must be found in one of its unperturbed states. If the time between turning on and off is short, the probability that a transition will occur is small enough so that first-order perturbation theory gives a valid result. (Of course, the transition probability also depends on the energy density of the radiation field; but this energy density can be quite small, because the energy of a photon can be spread out over many atoms, so that the probability of an interaction with any one atom is very small.)

Uncertainty Relation for Energy and Time. Let us return to the second feature of Eq. (11)—the fact that a field of the form $E_0 \cos \omega t$, applied for a finite time t' , can induce transitions such that $E_n - E_m \neq \hbar\omega$. We saw that, as t' is increased, the maximum difference between $\hbar\omega$ and the transition energy ($E_m - E_n$) becomes smaller; Fig. 1 shows that

$$\hbar\omega - (E_m - E_n) \lesssim \frac{2\pi}{t'} \hbar$$

Now suppose that we attempt to measure the energy difference $E_m - E_n$ for a given atom. We might do this by applying a field of angular frequency ω and observing whether or not the atom absorbs energy from the field; we could vary ω and eventually observe an absorption of energy. The value of ω at which energy was absorbed would have to be considered equal to the quantity $(E_m - E_n)/\hbar$. But we see from Fig. 1 that we could in this way obtain a value of $E_m - E_n$ which is in error by as much as

$$\Delta E = \frac{2\pi}{t'} \hbar \simeq \frac{\hbar}{t'}$$

This example shows a special case of the so-called *uncertainty relation for energy and time*, which states that

$$(\Delta E)(\Delta t) \geq \hbar/2$$

where ΔE is the uncertainty in the energy of a system, and Δt is the time interval over which the energy is measured. This relation, which is parallel to the relation $(\Delta p_x)(\Delta x) \geq \hbar/2$ for momentum and position, has its origin in the same basic fact—that a wave packet of finite length must contain a superposition of different frequencies (wavelengths). In the case we are considering here, the wave packet is that of a *photon* of the radiation field which is inducing a transition, but the same mathematical laws must govern this wave packet as well as an electron wave packet. The principle is a general one which applies to any measurement of energy, just as the position–momentum uncertainty relation is valid for any method of measurement.

Notice that the energy–time uncertainty relation, like the position–momentum uncertainty relation, is in the form of an *inequality*. Equality is achieved only for a Gaussian wave packet in either case.

10.2 SPONTANEOUS TRANSITIONS

As we said at the beginning of this chapter, there is no mechanism in the Schrödinger equation to provide for a finite lifetime for an excited state. In Section 10.1, we found that an atom in an excited state could be induced to go to the ground state, if it is bathed in radiation of the resonant frequency. But we still have no mechanism for a transition to the ground state in the absence of an external field, although we know that such transitions must occur. As mentioned above, such a mechanism could be developed by quantization of the radiation field, but we are not about to do that here.

Instead, we shall rely on a trick, developed in 1917 by Einstein, which enables one to calculate the rate of spontaneous transitions from knowledge of the rate of induced transitions. The relation between the two rates is obtained from elementary thermodynamical considerations.

Consider a collection of atoms which can exchange energy only by means of radiation. The atoms are in thermal equilibrium, inside a cavity whose walls are kept at a constant temperature. Because the system is in thermal equilibrium, each atom must be emitting and absorbing radiation at the same rate, if one averages over a sufficiently long time (such as 1 sec). Let P_{nm} be the probability that a given atom will go from the n th state to the m th state in a short time dt . This probability must be proportional to the probability p_n that the atom is in the n th state to begin with, multiplied by the transition probability T_{nm} [which for dipole radiation is given by Eq. (13)]:

$$P_{nm} = T_{nm} p_n$$

More generally, P_{nm} may be written as

$$P_{nm} = A_{nm} \rho(\omega_{nm}) p_n dt \quad (14)$$

which expresses the fact that T_{nm} must be proportional to the radiation density $\rho(\omega_{nm})$, the time interval dt [which was denoted by t' in Eq. (13)], and other factors, incorporated into the coefficient A_{nm} , which depend on matrix elements.

Let us consider the case in which $E_n < E_m$, so that the transition from n to m involves absorption of a photon. We must recognize the possibility that the radiation field may induce a transition *downward* from state m to state n , if an atom is initially in state m . The probability of such a downward transition may be written as

$$P_{mn} = A_{mn} \rho(\omega_{nm}) p_m dt$$

but because of the symmetry of the equations leading to Eq. (13), we know that $A_{mn} = A_{nm}$ and $\omega_{mn} = \omega_{nm}$, so that

$$P_{mn} = A_{nm} \rho(\omega_{nm}) p_m dt \quad (15)$$

Notice that P_{nm} does *not* equal P_{mn} , because $p_n > p_m$; the n th state, being lower in energy, is more heavily populated, according to the Boltzmann factor (Section 1.1).

But we know, because the system is in equilibrium, that the *total* number of transitions from n to m must equal the *total* number of transitions from m to n . Since the *induced* transition probabilities are *unequal*, there must be additional transitions from state m to state n which are *spontaneous*. The spontaneous transition probability by definition does not depend on the energy density of the externally applied field; this probability may be written $B_{nm} p_m dt$, where B_{nm} is the quantity which we wish to calculate.

The total transition probability from m to n is therefore equal to $P_{mn} + B_{nm} p_m dt$, and this total should equal the transition probability P_{nm} . Thus, from Eqs. (14) and (15), we have

$$\rho(\omega_{nm}) p_n A_{nm} = \rho(\omega_{nm}) p_m A_{nm} + p_m B_{nm}$$

or

$$B_{nm} = \rho(\omega_{nm}) A_{nm} \left[\frac{p_n}{p_m} - 1 \right]$$

But the population of a state of energy E is proportional to the Boltzmann factor $e^{-E/kT}$, so the ratio p_n/p_m may be written

$$\begin{aligned} \frac{p_n}{p_m} &= e^{(E_m - E_n)/kT} \\ &= e^{\hbar\omega_{nm}/kT} \end{aligned}$$

Thus

$$B_{nm} = \rho(\omega_{nm}) A_{nm} (e^{\hbar\omega_{nm}/kT} - 1) \quad (16)$$

The factor $\rho(\omega_{nm})$ in Eq. (16) is illusory, because B_{nm} by definition does not depend on the energy density of the radiation field. We can eliminate this factor by recalling the assumption made at the beginning of this section that

the atoms are in thermal equilibrium inside a cavity. In such a case we have an expression for the energy density inside the cavity; it was derived as a function of ν in Section 3.1 (Eq. 5). Writing it in terms of ω yields

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

Substitution of this expression into Eq. (16) yields an expression for B_{nm} involving only A_{nm} and known constants:

$$B_{nm} = \frac{\hbar\omega_{nm}^3}{\pi^2 c^3} A_{nm} \quad (17)$$

Returning to Eq. (13) to evaluate A_{nm} , we finally find that the spontaneous transition probability in time dt is equal to

$$\frac{1}{3} \frac{e^2 \omega_{nm}^3}{\pi \epsilon_0 c^3 \hbar} (|x_{mn}|^2 + |y_{mn}|^2 + |z_{mn}|^2) dt = \lambda dt \quad (18)$$

where λ , the decay constant, is the probability of decay per unit time (for times dt such that $\lambda dt \ll 1$).

Exponential Decay Law. In studying spontaneous transitions, we must remember that the emitted photon exhibits the same wave-particle duality that appears in other atomic phenomena. In making the transition, the atom oscillates back and forth between the initial state and the final state, and thus generates an electromagnetic wave. But it is characteristic in the analysis of such quantum processes that we cannot isolate the behavior of the system under study from the behavior of the *measuring instrument* used to observe that system. Thus the transition is *observed* as a *discontinuous* process, because the emitted *wave* interacts with a measuring instrument as a *photon*.

The term "measuring instrument" is to be interpreted in the broadest possible sense. The matter surrounding each atom acts as the measuring instrument, as it absorbs the photon emitted by the atom. Now consider the problem of determining the time at which each atom makes its transition. This determination is based upon the interaction of a photon with the measuring instrument. We can say that the instrument tests the atom at the end of each time interval dt ; it either absorbs a photon or it does not, during that time interval. That is, the test shows one of only two possible results: Either the transition has occurred, or it has not. There is no way for the measuring instrument to find the atom in the in-between state of oscillation which produces the wave, because a measurement must always find the atom to be in an eigenstate. If the transition has *not* occurred at the time of the measurement, then the atom is *indistinguishable from other excited atoms*, regardless of how long it had been in the excited state before the measurement was made.

Thus, although the transition probability as given by Eq. (18) is directly

proportional to the time interval dt , the total number of transitions does *not* build up linearly with time. At the end of any given time interval, there are fewer atoms left in the excited state than there were at the beginning of that interval; each of these atoms has exactly the same transition probability in the subsequent time interval that it had in the first time interval, but since there are fewer atoms, there are fewer transitions per unit time as time goes by. We can express this quantitatively as follows: Let state m be the first excited state and state n be the ground state, and let N be the number of atoms in the excited state at any given time. Then in the next short time interval dt , N will change by an amount dN given by

$$dN = -N\lambda dt$$

where λ is the decay constant defined in Eq. (18). We can find N for any time t by integrating this equation as follows:

$$\begin{aligned} dN/N &= -\lambda dt \\ \ln N &= -\lambda t + \text{constant} \\ N &= N_0 e^{-\lambda t} \end{aligned} \quad (19)$$

where N_0 must be the number of excited atoms at time $t = 0$. The form of this expression is independent of the choice of the zero of time; no matter how long the atoms have been in the excited state, one can arbitrarily set $t = 0$, and the number left at any subsequent time is related to the number at the (arbitrary) $t = 0$ by Eq. (19) (see Fig. 2).

In a time interval $t_{\frac{1}{2}}$ such that $e^{-\lambda t_{\frac{1}{2}}} = \frac{1}{2}$, the number of excited atoms is reduced by a factor of 2. Therefore the *half-life* of the excited state is given by $\lambda t_{\frac{1}{2}} = \ln 2$, or $t_{\frac{1}{2}} = 0.7/\lambda$. We often refer also to the *mean lifetime* of the state, which is the average, or mean, of the times which a large collection of atoms would spend in the excited state. By following the same mathematical pro-

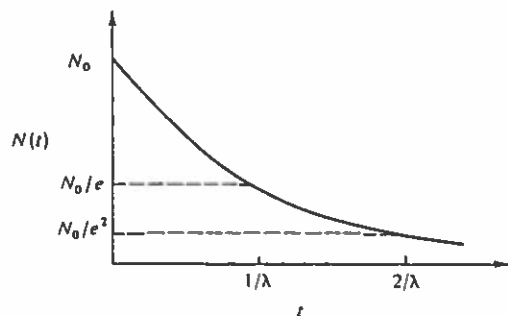


Fig. 2. Number N of excited atoms remaining as a function of time, if N_0 are present at time $t = 0$. In each time interval of $1/\lambda$, the number remaining is divided by e .

cedure used in Section 1.1 to find the mean free path of an atom, one can show that the mean lifetime τ is related to λ by

$$\tau = \frac{1}{\lambda}$$

You must realize, of course, that the decay process follows the laws of probability. It cannot be predicted exactly how many of a given collection of atoms will decay in any given time interval. For example, when there are only two excited atoms, the binomial distribution shows (Appendix A) that the probability is $\frac{1}{4}$ that both will decay in the next half-life, the probability is $\frac{1}{2}$ that one of them will decay, and the probability is $\frac{1}{4}$ that neither of them will decay.

Because an atom lives for a limited time in an excited state, the uncertainty relation $\Delta E \Delta t \geq \hbar/2$ imposes a fundamental limitation on the accuracy with which the energy of such a state can be defined. A short-lived state is said to be broader than a longer-lived state, because the atom can absorb a broader spectrum of frequencies in being excited to such a state. Thus each energy level in each atom is defined only to an accuracy which is permitted by the uncertainty relation for the lifetime of that state.⁷ Observation of the "width" of a state can actually be used to obtain a rough estimate of the state's lifetime, in cases where the state is too short lived for its lifetime to be measured directly (see Chapters 15 and 16).

10.3 SELECTION RULES

Let us now turn our attention to the "dipole" matrix elements x_{mn} , y_{mn} , z_{mn} . If we can evaluate these, it is a simple matter to use Eq. (18) to determine the spontaneous transition probability, or to use Eq. (13) to find the induced transition probability. The evaluation is particularly easy for many pairs of states, because it happens that the matrix elements x_{mn} , y_{mn} , and z_{mn} are all equal to zero. In such cases the transition is said to be *forbidden* for dipole radiation. We have already seen that certain transitions were forbidden by selection rules developed empirically by spectroscopists (Section 7.3 and Chapter 9); now we are able to derive some of these rules.

The simplest example is the selection rule for the magnetic quantum number m :⁸

$$\Delta m = \pm 1 \text{ or } 0$$

⁷ Of course, a definite amount of energy is absorbed and the same amount is re-emitted in each case (energy is conserved), but this amount can vary by ΔE from one event to another, or from one atom to another, because of the width of the energy level. The frequency corresponding to energy ΔE is called the *natural linewidth*.

⁸ At this point, there is a slight risk of confusion between the quantum number m and the subscript m used as an index to identify the state. But we must run some such risk, because any letter that we could use as an index has already been assigned some other meaning.

which was necessary to explain the number of lines observed in the Zeeman effect (Section 9.2). This rule may be derived by considering only the wavefunction's ϕ dependence $e^{im\phi}$. If the wavefunction of the initial state is proportional to $e^{im\phi}$, and that of the final state is proportional to $e^{im'\phi}$, then the matrix element z_{mn} is proportional to

$$\int_0^{2\pi} e^{-im'\phi} z e^{im\phi} d\phi \quad (20)$$

But z is equal to $r \cos \theta$, so it may be removed from the integral, and the integral then vanishes at both limits, as long as $m' \neq m$. Thus transitions for which $m' \neq m$ cannot be induced by radiation which is polarized in the z direction, nor can such transitions occur spontaneously with the emission of light polarized in that direction; there is a *selection rule*

$\Delta m = 0$ for light polarized in the z direction.

For example, in the normal Zeeman effect (Section 1.2 and 9.2), the unshifted line results from a transition in which $\Delta m = 0$, so the light must be polarized in the z direction (the direction of B). This line is not emitted along the z direction, because light waves are transverse.

If we replace z by x or y in expression (20), we find a different rule. With $x = r \sin \theta \cos \phi$, the integral may be written

$$\int_0^{2\pi} e^{-im'\phi} \cos \phi e^{im\phi} d\phi$$

We can evaluate this integral most easily by means of the substitution

$$\cos \phi = \frac{1}{2} (e^{i\phi} + e^{-i\phi})$$

which yields

$$\frac{1}{2} \left[\int_0^{2\pi} e^{i(m-m'+1)\phi} d\phi + \int_0^{2\pi} e^{i(m-m'-1)\phi} d\phi \right]$$

The first integral is zero unless $m - m' = -1$; the second integral is zero unless $m - m' = +1$. Thus, for radiation polarized in the x direction, the selection rule is

$$\Delta m = \pm 1$$

and it is easy to show that radiation polarized in the y direction obeys the same rule. Thus we have, considering all possible polarizations, the rule

$$\Delta m = \pm 1 \quad \text{or} \quad 0$$

for electric dipole radiation.

Again, the selection rule is manifest in the polarizations observed in the

normal Zeeman effect. The shifted lines emitted in the y direction are polarized in the x direction; those emitted in the x direction are polarized in the y direction; and those emitted in the z direction are circularly polarized (see problem 6). (In the anomalous effect, *some* of the shifted lines come from $\Delta m = 0$ transitions and are polarized in the z direction.)

The selection rule on l , $\Delta l = \pm 1$, can be derived in much the same manner as was the rule for m . If $P_l^{|m|}(\cos\theta)$ is the θ dependence of the wavefunction for the initial state, and $P_{l'}^{|m|}(\cos\theta)$ is the θ dependence of the wavefunction for the final state, then for each matrix element the integral on θ vanishes unless $l' - l = \pm 1$. The general derivation of this result requires the use of two formulas involving the associated Legendre functions $P_l^{|m|}(\cos\theta)$; we state these without proof⁹:

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

$$\sin\theta P_l^{|m|} = \frac{P_{l+1}^{|m+1|} - P_{l-1}^{|m+1|}}{2l + 1}$$

Given these formulas, derivation of the selection rule is straightforward, and is left as an exercise.

Parity. The above selection rules were derived by using the specific wavefunctions of the hydrogen atom. But there is a more general rule which does not depend on any specific wavefunction; the rule is that *the parity of the wavefunction must change in an electric dipole transition*.¹⁰ The reason for the rule is quite simple. If the initial state wavefunction and the final state wavefunction have the same parity, then the product of the two functions must have even parity (which is not changed by taking the complex conjugate of the final state wavefunction). Multiplying this function by x , y , or z yields a product which has odd parity, and the integral of a function of odd parity over all space is zero. Thus the matrix element always vanishes if the initial state and the final state have the same parity.

The rule that parity must change is, of course, satisfied in any one-electron transition for which $\Delta l = \pm 1$, because the parity of the associated Legendre function is even if l is even, and it is odd if l is odd. But there are other situations in which the parity selection rule imposes *additional restrictions* on the transitions. For example, in a multi-electron atom, when two electrons are involved in a transition, the sum of the l -values must change from odd to even or from even to odd. We may understand this rule by reference to the

⁹ These formulas may be derived from a generating function for the Legendre polynomials. See, for example, L. Schiff, "Quantum Mechanics" p. 72 and p. 258. McGraw-Hill, New York, 1949.

¹⁰ See Section 5.6 for a discussion of parity of wavefunctions.

Ca spectrum (Chapter 9, Fig. 2). There can be a transition from a 4p3d state (odd) to 3d4s or 4s4s (both even), but not to 4s4p (odd). Such a transition is forbidden even though it may satisfy the selection rule $\Delta L = \pm 1$ for the resultant angular momentum; for example, the transition 4p3d $^3D \rightarrow 4s3p$ 3P is forbidden. (A state such as 4p3d 3D is often designated as $^3D^o$, the superscript o indicating odd parity.)

EXAMPLE PROBLEM 1 (*Selection Rules for the Simple Harmonic Oscillator*). Derive a selection rule for the simple one-dimensional harmonic oscillator by computing the matrix elements x_{mn} for the appropriate wavefunctions.

Solution. We require the matrix element $x_{mn} = \int u_m^* x u_n dx$. But it is not necessary to carry out a detailed computation, because we only need to know when x_{mn} is equal to zero. Therefore we make use of the orthogonality of the harmonic oscillator wavefunctions, by introducing the stepping operators $(d/dx) - ax$ and $(d/dx) + ax$, which convert one wavefunction into another (see Section 5.7). We can express the variable x in terms of these operators as

$$x = \frac{1}{2a} \left[\left(\frac{d}{dx} + ax \right) - \left(\frac{d}{dx} - ax \right) \right]$$

Thus we may write

$$x_{mn} = \frac{1}{2a} \left[\int u_m^* \left(\frac{d}{dx} + ax \right) u_n dx - \int u_m^* \left(\frac{d}{dx} - ax \right) u_n dx \right]$$

It was shown in Section 5.7 that

$$\left(\frac{d}{dx} - ax \right) u_n = \alpha u_{n+1}$$

and

$$\left(\frac{d}{dx} + ax \right) u_n = \beta u_{n-1}$$

where α and β are normalizing constants, and the subscripts indicate the value of the n quantum number. So we have

$$x_{mn} = \frac{1}{2a} \left[\alpha \int u_m^* u_{n+1} dx + \beta \int u_m^* u_{n-1} dx \right]$$

The orthogonality of the wavefunctions then requires that x_{mn} be zero unless $m = n + 1$ or $m = n - 1$. Thus the selection rule is $\Delta n = \pm 1$. Notice that this rule agrees with the comments in Section 5.7 about the correspondence principle; transitions for which Δn is greater than 1 would not involve photons whose frequency is equal to the frequency of oscillation.

Occurrence of Forbidden Transitions. The selection rules which we have just examined are not absolute laws. It is found that some of the "forbidden" transitions actually do occur, although they occur far less often than the allowed transitions. How is this possible? We must not forget that these rules were derived on the basis of the dipole *approximation*, in which it is assumed that (1) the electric field is uniform over the entire atom, and (2) the magnetic energy has a negligible effect. These assumptions were made because a uniform electric field can have an effect which is much greater than the effect of the associated magnetic field or the effect of nonuniformity in the electric field. But if the effect of the uniform field on a given state is nil, then obviously other effects can no longer be neglected.

(a) *Electric Quadrupole and Higher Multipole Radiation.* Let us first consider the effect of nonuniformity of the electric field. To do this, we must write the field as $E_{0x} \cos(kx - \omega t)$, where as usual the wavelength λ is equal to $2\pi/k$. We can display the difference between this expression and the previous one ($E_{0x} \cos \omega t$) most easily by writing it in exponential form as follows:

$$\begin{aligned}\cos(kx - \omega t) &= \text{Re}[e^{i(kx - \omega t)}] \\ &= \text{Re}[e^{ikx} e^{-i\omega t}] \\ &= \text{Re}[\{1 + ikx + (ikx)^2/2! + (ikx)^3/3! + \cdots\} e^{-i\omega t}]\end{aligned}$$

where $\text{Re} []$ denotes the real part of $[]$. The dipole approximation is now seen to be equivalent to replacing e^{ikx} by 1—that is, neglecting ikx and higher order terms in the series expansion of e^{ikx} . This is reasonable when the wavelength is long, for then $kx \ll 1$ over the dimensions of the atom. But if this procedure yields a null result, then it is logical to make the approximation $e^{ikx} \approx 1 + ikx$; retaining the second term may lead to a nonzero result for the transition probability. To test this possibility, we must determine the potential energy when the electric field is proportional to x .

As before, we find the energy from the integral of the electric field. Integrating along the x direction, we find the potential energy to be proportional to x^2 . Therefore the matrix element needed to determine T_{nm} [Eq. (12)] is of the form $\int u_m^* x^2 u_n d\tau$, or $(x^2)_{mn}$ rather than x_{mn} . When we consider all possible directions of polarization for the radiation, and when we integrate the field along all possible directions, we find that matrix elements of the form $(y^2)_{mn}$, $(x^2)_{mn}$, $(xy)_{mn}$, $(yz)_{mn}$, and $(zx)_{mn}$ also can contribute to T_{nm} . Just as the elements x_{mn} , y_{mn} , and z_{mn} are in the form of components of the electric *dipole* moment *vector*, the six elements listed above— $(x^2)_{mn}$, $(y^2)_{mn}$, ...—are in the form of the components of a second rank *tensor*, called the electric *quadrupole* moment between states n and m . When these matrix elements are