Figure 8-10 Vector diagrams representing the rules for adding the quantum numbers $l = 2$ and $s = 1/2$ to obtain the possible values for the quantum numbers j and m_j. *Left:* The maximum possible value of j is obtained when a vector of magnitude l is added to a parallel vector of magnitude s, yielding $j = l + s = 2 + 1/2 = 5/2$. The maximum possible z component of this vector gives the maximum possible value of the quantum number m_j, and the minimum possible z component gives the minimum possible value of m_j. The intermediate values of m_j differ by integers. Thus the possible values are $m_j = -5/2, -3/2, -1/2, 1/2, 3/2, 5/2$. *Right:* A vector of magnitude $l = 2$ is added to an antiparallel vector of magnitude $s = 1/2$ to yield a vector of magnitude $j = l - s = 2 - 1/2 = 3/2$, which represents the minimum possible value of the quantum number j. The possible z components of the vector of magnitude $j = 3/2$, which differ in value by integers, correspond to the possible values $m_j = -3/2, -1/2, 1/2, 3/2$. There are no values of j intermediate between 5/2 and 3/2 since its possible values also may differ only by integers. Note that these diagrams do *not* accurately represent the addition of the angular momenta associated with the quantum numbers.

8-6 SPIN-ORBIT INTERACTION ENERGY AND THE HYDROGEN ENERGY LEVELS

In the first part of this section we shall obtain an expression for the spin-orbit interaction energy in terms of the potential function $V(r)$ and the quantum numbers l, s, and j. In the second part we shall explain how the expression is used to predict the detailed structure of the energy levels of the hydrogen atoms. The expression for the spin-orbit interaction energy will also enter, on several occasions, into our subsequent discussion of multielectron atoms, and it will enter into our discussion of nuclei, since they have very strong spin-orbit interactions.

According to (8-27), the spin-orbit interaction energy is

$$\Delta E = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\,\mathbf{S}\cdot\mathbf{L}$$

To express this in terms of l, s, and j, we first write

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

Taking the dot product of this equality times itself, and employing the fact that $\mathbf{L}\cdot\mathbf{S} = \mathbf{S}\cdot\mathbf{L}$, we have

$$\mathbf{J}\cdot\mathbf{J} = \mathbf{L}\cdot\mathbf{L} + \mathbf{S}\cdot\mathbf{S} + 2\,\mathbf{S}\cdot\mathbf{L}$$

So

$$\mathbf{S}\cdot\mathbf{L} = (\mathbf{J}\cdot\mathbf{J} - \mathbf{L}\cdot\mathbf{L} - \mathbf{S}\cdot\mathbf{S})/2$$

or

$$\mathbf{S}\cdot\mathbf{L} = (J^2 - L^2 - S^2)/2 \tag{8-34}$$

In a quantum state associated with the quantum numbers l, s, and j, each term on the right has a fixed value, and $\mathbf{S}\cdot\mathbf{L}$ has the fixed value

$$\mathbf{S}\cdot\mathbf{L} = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

Thus

$$\Delta E = \frac{\hbar^2}{4m^2c^2}\left[j(j+1) - l(l+1) - s(s+1)\right]\frac{1}{r}\frac{dV(r)}{dr}$$

It should be evident that the spin-orbit energy for the state is the expectation value of this quantity. (See Appendix J for a detailed justification.) That is, the energy arising from the spin-orbit interaction is

$$\overline{\Delta E} = \frac{\hbar^2}{4m^2c^2}\left[j(j+1) - l(l+1) - s(s+1)\right]\overline{\frac{1}{r}\frac{dV(r)}{dr}} \tag{8-35}$$

where the expectation value $\overline{(1/r)\,dV(r)/dr}$ is calculated using the potential function $V(r)$ for the system and the probability density (actually the radial probability density $4\pi r^2 R_{nl}^* R_{nl}$) for the state of interest. As was indicated earlier, (8-35) gives a convenient expression of an important result.

Now we consider the energy levels of the hydrogen atom. In Section 7-5 we obtained the predictions of quantum mechanics for the energy levels of a hydrogen atom in which the spin-orbit interaction is not considered, and found that they are simply the predictions of the Bohr model. In Example 8-3 we estimated the change in the energy of a typical one of these levels due to the presence of the spin-orbit interaction. We found that the energy is shifted up by about one part in 10^4 if $\mathbf{L}$ is approximately parallel to $\mathbf{S}$ (if $j = l + 1/2$), and that it is shifted down about that amount if $\mathbf{L}$ is approximately antiparallel to $\mathbf{S}$ (if $j = l - 1/2$). We also saw that there is obviously no spin-orbit energy shift if $\mathbf{L} = 0$ (if $j = 1/2$).

To obtain quantitative predictions of the hydrogen atom spin-orbit interaction energy-level shifts from the general expression of (8-35), the potential function is equated to the Coulomb potential $V(r) = -e^2/4\pi\epsilon_0 r$, and then the expectation value $\overline{(1/r)\,dV(r)/dr}$ is calculated using the hydrogen atom eigenfunctions. However, before these predictions can be compared with experiments, other effects, of comparable importance in the hydrogen atom, must be taken into account. In discussing Sommerfeld's relativistic modification of the Bohr model in Section 4-10, we estimated that the shift in a typical hydrogen atom energy level, due to the relativistic dependence of mass on velocity, is about one part in 10^4. So this relativistic effect produces energy shifts in the hydrogen atom comparable to those produced by the spin-orbit interaction, which is really also a relativistic effect but a different one. A complete treatment of all the effects of relativity on the energy levels of the hydrogen atom can be given only in terms of the Dirac theory. But results which are almost (i.e., except for $l = 0$ states) complete can be obtained from the Schroedinger theory by adding to the simple hydrogen energy-level formula both the expectation value of the correction to the energy due to the spin-orbit interaction and the expectation value of the correction to the energy due to the dependence of mass on velocity. We shall not do this for two reasons: (1) it would get us into some fairly lengthy calculations, and (2) relativistic effects, other than the spin-orbit interaction, are significant only for hydrogen and a few more atoms of very small atomic number Z. For typical atoms of medium and large values of Z, and the levels involved in their optical spectra, the energy associated with these relativistic effects remains of the order of 10^{-4} times the energy of a level. But we shall see later that the spin-orbit interaction energy increases very rapidly with increasing Z. The spin-orbit interaction is the only effect we have considered that is generally important in a typical atom, and we have already said enough about it here. Therefore, we do no more than present the results

of Dirac's completely relativistic treatment of the hydrogen atom energy levels, which predicts that the energies are

$$E = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \qquad (8\text{-}36)$$

In this equation μ stands for the reduced electron mass, $\mu = mM/(m+M)$, and α is the *fine-structure constant*, $\alpha = e^2/4\pi\epsilon_0\hbar c \simeq 1/137$.

If the student will compare these results of the Dirac theory with the results of the Sommerfeld model expressed in (4-27a) and (4-27b), he will see that they are essentially the same. (Both $j + 1/2$ and n_θ are integers ranging from 1 to n.) Since the Sommerfeld model is based on the Bohr model, it is only a very rough approximation to physical reality. In contrast, the Dirac theory represents an extremely refined expression of our understanding of physical reality. That these two theories lead to essentially the same results for the hydrogen atom is a coincidence that caused much confusion in the 1920s, when the modern quantum theories were being developed. The coincidence occurs because the errors made by the Sommerfeld model, in ignoring the spin-orbit interaction and in using classical mechanics to evaluate the average energy shift due to the relativistic dependence of mass on velocity, happen to cancel for the case of the hydrogen atom.

The energy levels of the hydrogen atom, as predicted by Bohr, Sommerfeld, and Dirac are shown in Figure 8-11. In order to make visible the energy-level splittings,
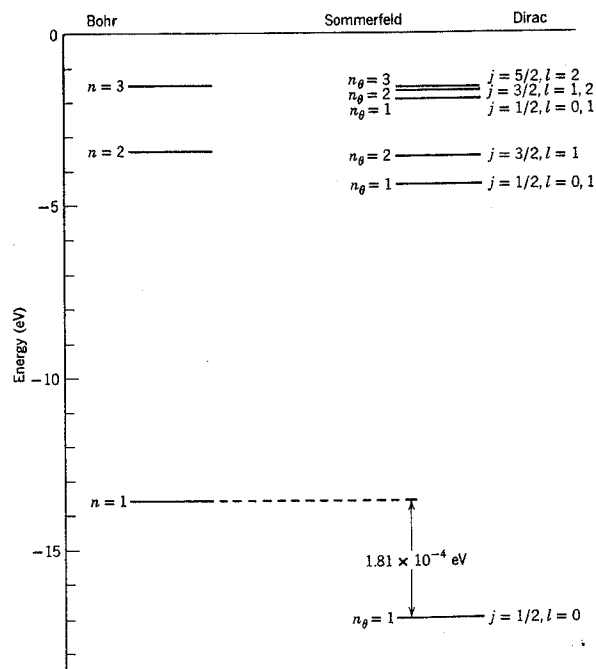

Figure 8-11 The energy levels of the hydrogen atom for $n = 1$, 2, 3 according to Bohr, Sommerfeld, and Dirac. The displacements of the Sommerfeld and Dirac levels from those given by Bohr have been exaggerated by a factor of $(1/\alpha)^2 \simeq (137)^2 \simeq 1.88 \times 10^4$.

called the *fine structure*, the shifts of the Sommerfeld and Dirac energy levels from those given by Bohr have been exaggerated by a factor of $(137)^2 = 1.88 \times 10^4$. Thus the diagrams would be completely to scale if the value of the fine-structure constant α were 1 instead of $\simeq 1/137$. Not shown on the Dirac energy-level diagram are the values of the quantum number m_j, which specify the orientation in space of the atom, since its energy is independent of the orientation if there are no external fields. There is a similar space orientation quantum number in the Sommerfeld model, whose
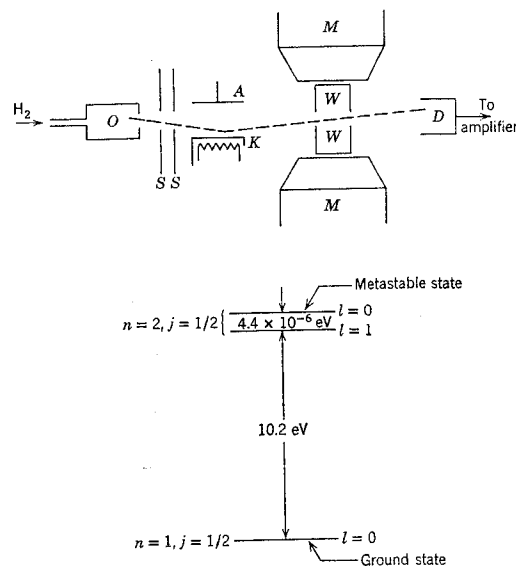

Figure 8-12 The apparatus of Lamb and Retherford. Molecular hydrogen (H_2) entering oven O is largely dissociated into atomic hydrogen which leaves the oven, passing through slits S, S. The arrangement K, A is essentially a vacuum diode, electrons being emitted from heated cathode K and accelerated toward anode A. As the hydrogen passes through this region, some atoms collide with the electrons and are excited into the $n = 2$, $l = 0$ state described in the text. This state is called a metastable state because decay from it to the ground state ($n = 1$, $l = 0$) is highly inhibited by the Δl selection rule and because all other states lie above it except the $n = 2$, $l = 1$, $j = 1/2$ state which, according to the Dirac theory, has exactly the same energy as the metastable state. The experiment showed, however that the $l = 1$ state was in fact about 4.4 μeV below the metastable state. These levels are shown below the apparatus.

The metastable atoms pass out of the collision region K, A and are detected by detector D. Any mechanism which causes these atoms to undergo a transition to the $l = 1$ state (transitions to the ground state are forbidden) will result in a decreased signal from D, which is sensitive only to metastable atoms. Such transitions can be induced by passing the atoms through a region where there is an alternating electric field whose frequency ν is such that $h\nu \simeq 4.4$ μeV, or $\nu \simeq 1060$ MHz. Such an alternating field is provided by a waveguide W,W, through whose walls the beam is passed.

To measure exactly the energy difference (Lamb shift) between the metastable ($l = 0$) and $l = 1$ states (both $n = 2$, $j = 1/2$), we could in principle merely vary the frequency ν, searching for a value that maximized transitions from the former to the latter state, thereby minimizing the signal from D. In practice, the frequency is not easily adjusted and the levels themselves are adjusted instead by a known amount by means of a magnet M,M, this shifting being due to the Zeeman effect.

values are not shown on the Sommerfeld energy levels, since the quantum number is of no consequence unless an external field is applied to the atom. Also not shown are the energy levels of hydrogen measured by optical spectroscopy. They are in very good agreement with the levels of both Sommerfeld and Dirac.

The only difference between the results of these two treatments is that Dirac, but not Sommerfeld, predicts that for most levels there is a degeneracy (in addition to the trivial degeneracy with respect to space orientation just mentioned) because the energy depends on the quantum numbers n and j but not on the quantum number l. Since there are generally two values of l corresponding to the same value of j, the Dirac theory predicts that most levels are really double. This prediction was verified experimentally in 1947 by Lamb, who showed that for $n = 2$ and $j = 1/2$ there are two levels, which actually do not quite coincide. The $l = 0$ level lies above the $l = 1$ level by about one-tenth the separation between that level and the $n = 2$, $j = 3/2$, $l = 1$ level. The experiments involved measuring the frequency of photons absorbed in transitions between the two levels, using the apparatus shown in Figure 8-12. The energy separation between these levels is so small that the frequency is in the micro-wave radio range. Since measurements of radio frequencies can be made very accurately, it is possible to obtain the energy separation to five significant figures. These very accurate measurements of the so-called *Lamb shift* can be explained with precision in terms of the theory of *quantum electrodynamics*, as can the slight departure of the spin g factor from 2 mentioned in Section 8-3. We cannot develop this quite sophisticated theory here, but we shall discuss it in the following section in connection with radiation by excited atoms, and in Chapter 17 in connection with the properties of the elementary particles.

Even with its exaggerated scale, Figure 8-11 cannot show the *hyperfine splitting* of the energy levels, which in hydrogen is due to an interaction between the internal magnetic field produced by the motion of the electron and a spin magnetic dipole moment of the *nucleus*. As nuclear magnetic dipole moments are smaller than electronic magnetic dipole moments by $\sim 10^{-3}$, the hyperfine splitting is smaller than the spin-orbit splitting by the same factor. Nevertheless, we shall see later that this effect can be understood quantitatively in terms of Schroedinger quantum mechanics, and that it can be used to measure nuclear spins and magnetic moments. In fact, every aspect of the behavior of a hydrogen atom can be explained in detail by the theories of quantum physics!

8-7   TRANSITION RATES AND SELECTION RULES

If hydrogen atoms are excited to their higher energy levels, e.g., in collisions with energetic electrons in a gas discharge tube, the atoms will in due course spontaneously make transitions to successively lower energy levels. In each transition between a pair of levels, a photon is emitted of frequency equal to the difference in their energies divided by Planck's constant. The discrete frequencies emitted in all the transitions that take place constitute the "lines" of the spectrum, but measurements show that not all conceivable transitions do take place. Photons are observed only with frequencies corresponding to transitions between energy levels whose quantum numbers satisfy the *selection rules*:

$$\Delta l = \pm 1 \tag{8-37}$$
$$\Delta j = 0, \pm 1 \tag{8-38}$$

That is, transitions take place only between levels whose l quantum numbers differ by one and whose j quantum numbers differ by zero or one. Measurements of the spectra of other one-electron atoms show that these selection rules apply to transitions in all such atoms.

As discussed in Section 4-11, some of the selection rules could be given some justification in the old quantum theory by using the *correspondence principle* to invoke certain restrictions that apply in the classical limit; but the predictions of this technique were not reliable. Furthermore, the old quantum theory had nothing at all to say about atomic *transition rates*. A transition rate is the probability per second that an atom in a certain energy level will make a transition to some other energy level. It is easy to measure a transition rate by measuring the probability per second of detecting a photon of the corresponding frequency, since this is proportional to the intensity of the corresponding spectral line. So it should certainly be possible to calculate a transition rate from atomic theory. An impressive feature of the Schroedinger quantum mechanics is that this can be done with no difficulty, using the atomic eigenfunctions. Of course all the selection rules can be obtained from transition rate calculations, since *a selection rule just specifies which transitions have rates so small that they are not normally observed.*

We have already used elementary quantum mechanics, in Example 5-13 and the discussion following, to develop much of the physical picture that the theory provides for the emission of photons by excited atoms. According to that example, if the wave function describing an atom is the wave function associated with a single quantum state, then the probability density function for the atom will be constant in time. But if the wave function is a mixture of the wave functions associated with two quantum states, corresponding to the two energy levels E_2 and E_1, then the probability density contains terms which oscillate in time at frequency $v = (E_2 - E_1)/h$. Since the atomic electron can be found at any location where the probability density has an appreciable value, the charge it carries is not confined to a particular location. In effect, the atom has a charge distribution which is proportional to its probability density. Thus when the atom is in a mixture of two quantum states its charge distribution oscillates at precisely the frequency of the photon emitted in the transition between the states. This is true since the photon carries away the excess energy $E_2 - E_1$, and so has frequency $v = (E_2 - E_1)/h$.

The simplest aspect of the atom's charge distribution that can be oscillating is the *electric dipole moment*. This is the product of the electron charge and the expectation value of its displacement vector from the essentially fixed massive nucleus. The electric dipole moment is a measure of the separation of the center of the electron charge distribution from the nuclear center of the atom. Even in classical physics, a charge distribution that is constant in time will not emit electromagnetic radiation, while a charge distribution with an oscillating electric dipole moment emits radiation of frequency equal to the oscillation frequency. In fact, an oscillating electric dipole is the most efficient radiator.

We can actually use the classical formula for the rate of emission of energy by an oscillating electric dipole to obtain the important factors in the formula for atomic transition rates. In Appendix B it is shown that the dipole radiates electromagnetic energy at the average rate $\bar{R}$, where

$$\bar{R} = \frac{4\pi^3 v^4}{3\epsilon_0 c^3} p^2 \tag{8-39}$$

with p the amplitude of its oscillating electric dipole moment and v the frequency of oscillation. Since the energy is carried off by photons whose energies are of magnitude hv, the rate of emission of photons, R, is

$$R = \frac{\bar{R}}{hv} = \frac{4\pi^3 v^3}{3\epsilon_0 hc^3} p^2 \tag{8-40}$$

This probability per second that a photon is emitted is just equal to the probability per second that the atom has undergone the transition. Thus R is also the atomic *transition rate*.

Relative to an origin at the essentially fixed nucleus, the electric dipole moment **p** of the one-electron atom is defined as

$$\mathbf{p} = -e\mathbf{r} \qquad (8\text{-}41)$$

where $-e$ is the charge of the electron and **r** is its position vector from the nucleus at the origin. To obtain an expression for the amplitude of the oscillating electric dipole moment of the atom when it is in a mixture of two states, we calculate the expectation value of **p**, using the mixed state probability density obtained in Example 5-13

$$\Psi^*\Psi = c_1^* c_1 \psi_1^* \psi_1 + c_2^* c_2 \psi_2^* \psi_2 + c_2^* c_1 \psi_2^* \psi_1 e^{i(E_2-E_1)t/h} + c_1^* c_2 \psi_1^* \psi_2 e^{-i(E_2-E_1)t/h}$$

There is no way, from the present argument, for us to determine precisely what values of the adjustable constants c_1 and c_2 should be used to specify how much of the two quantum states are mixed together. But the results we seek are independent of their values, as will be seen shortly, so for simplicity we set them both equal to 1. Then we have

$$\Psi^*\Psi = \psi_f^* \psi_f + \psi_i^* \psi_i + \psi_i^* \psi_f e^{i(E_i-E_f)t/h} + \psi_f^* \psi_i e^{-i(E_i-E_f)t/h}$$

where we have replaced the labels 2 and 1 by i and f, for initial and final. As this probability density is not normalized, when we use it to evaluate the expectation value of **p** we obtain only a proportionality, but this will suffice. That is, we have

$$\bar{\mathbf{p}} \propto \int \Psi^*(-e\mathbf{r})\Psi \, d\tau \propto \int \Psi^* e\mathbf{r}\Psi \, d\tau$$

or

$$\bar{\mathbf{p}} \propto \int \psi_f^* e\mathbf{r}\psi_f \, d\tau + \int \psi_i^* e\mathbf{r}\psi_i \, d\tau + e^{i(E_i-E_f)t/h}\int \psi_i^* e\mathbf{r}\psi_f \, d\tau + e^{-i(E_i-E_f)t/h}\int \psi_f^* e\mathbf{r}\psi_i \, d\tau$$

where we have sandwiched the term $e\mathbf{r}$ between the other terms of the integrands to conform with accepted notation, and where the integrals are three-dimensional. Now the first two integrals on the right are not associated with an oscillating $\bar{\mathbf{p}}$; in fact both integrals yield zero. The last two integrals are each multiplied by complex exponentials with a time dependence that oscillates at the frequency $\nu = (1/2\pi)(E_i - E_f)/h = (E_i - E_f)/h$. These two terms describe oscillations in the electric dipole moment expectation value, of amplitude which is measured by the magnitude of the integral in either term. Thus we find that the amplitude of the oscillating electric dipole moment is proportional to the quantity p_{fi}, where

$$p_{fi} \equiv \left| \int \psi_f^* e\mathbf{r}\psi_i \, d\tau \right| \qquad (8\text{-}42)$$

This quantity is called the *matrix element of the electric dipole moment taken between the initial and final states*. Note that its value depends on the behavior of the atom in both the initial state, through ψ_i, and in the final state, through ψ_f^*. This is reasonable because the radiating atom is in a mixture of the two states. Setting the p in (8-40) proportional to p_{fi}, we obtain

$$R \propto \frac{\nu^3 p_{fi}^2}{\epsilon_0 h c^3}$$

where R is the transition rate.

We have obtained the factors ν^3 and p_{fi}^2, as well as the constants $\epsilon_0 h c^3$, in the expression for the transition rate by a partly classical argument. A much more sophisticated argument which uses only Schroedinger quantum mechanics (and is based on the last equation derived in Appendix K) leads to the same result, except that the numerical proportionality constant is determined. The result is

$$R = \frac{16\pi^3 \nu^3 p_{fi}^2}{3\epsilon_0 h c^3} \qquad (8\text{-}43)$$

The same equation can be derived in an even more rigorous manner from the theory of *quantum electrodynamics*, which provides an exact treatment of the quantization properties of electromagnetic fields. Although the results are not different, quantum electrodynamics gives a more complete picture of the emission of photons by excited atoms. In particular, it explains how the radiating atom gets into the mixed state. This happens through a kind of resonance interaction between vibrations of the appropriate frequency, in a surrounding field of electromagnetic radiation, and an atom in the initial state. The interaction induces the charge oscillations of that frequency, which are characteristic of the mixed state, and then the atom emits electromagnetic radiation of the same frequency. The process is indicated schematically in Figure 8-13.

The emission of photons by atoms, under the influence of the photons that comprise an electromagnetic field *applied* to the atom, is a phenomenon called *stimulated emission*. Atoms also emit photons when an electromagnetic field is *not applied*, in a phenomenon called *spontaneous emission*. Quantum electrodynamics shows that spontaneous emission takes place because there is always some electromagnetic field present in the vicinity of an atom, even if a field is not applied! The reason is that the electromagnetic field has an energy content which is *discretely quantized* because the energy, at any particular frequency, is given by the *number* of photons of that frequency. Like any other system with discretely quantized energy, the electromagnetic field has a *zero-point energy*. The quantum electrodynamics shows that there will always be some electromagnetic field vibrations present, of whatever frequency will always be some electromagnetic field vibrations present, of whatever frequency is required to induce the charge oscillations that cause the atom to radiate "spontaneously." We can see that spontaneous and stimulated emission are qualitatively similar. In spontaneous emission, the electromagnetic field surrounding the atom is in its zero-point energy state. In stimulated emission an additional field is applied so that the electromagnetic field surrounding the atom is in a higher energy state. Then more intense field vibrations of the required frequency are present, and there is more chance that the atom will be stimulated to radiate.

From this argument, it is apparent that the transition rate for stimulated emission is proportional to the intensity of the applied electromagnetic field. For intense fields it becomes very large and the atom radiates very efficiently. This has important practical consequences in the *laser*, a device to produce extremely bright beams of coherent light that will be discussed in Chapter 11. In that chapter we shall go more deeply into the relation between stimulated and spontaneous emission, but here we shall consider only spontaneous emission.

The transition rate for spontaneous emission, evaluated in (8-43), is independent of whether or not an external field is applied. It depends only on the properties of the atomic eigenfunctions. Since the eigenfunctions are known, the electric dipole moment matrix elements between various pairs of levels can be obtained by calculating the value of the associated integral (8-42). Then the rates for transitions between these levels can be calculated from (8-43).

Inducing photon

Emitted photon

Before   During   After
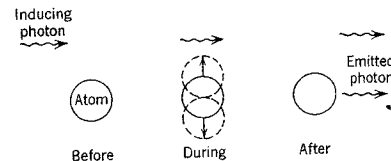
Figure 8-13 A schematic illustration of the emission of a photon by an atom. Electromagnetic radiation impinging on the atom induces dipole charge oscillations in the atom. Then the atom emits electromagnetic radiation.

It is found that the agreement between the predictions and the measurements is quite good, even though the transition rates vary appreciably from one case to the next. For the transition of the hydrogen atom from its first excited state to its ground state, the transition rate has the value $R \simeq 10^8 \text{ sec}^{-1}$. This means that in about 10^{-8} sec the probability that the transition has occurred is about equal to one. It is said that the first excited state has a *lifetime* $t = 1/R \simeq 10^{-8}$ sec. Although the v^3 dependence in (8-43) leads to a range of values of R, the value just quoted is typical of the orders of magnitude encountered in atomic transition rates—except that the transition rates between certain pairs of levels are essentially zero. These are the transitions for which the spectral lines are observed to be absent, or extremely weak. The transition rates are predicted to be zero in these cases because the integral in the electric dipole matrix element yields zero. Thus *the selection rules are a set of conditions on the quantum numbers of the eigenfunctions of the initial and final energy levels, such that the electric dipole matrix elements are zero when calculated with a pair of eigenfunctions whose quantum numbers violate these conditions.*

Example 8-6. When a hydrogen atom is placed in a very strong external magnetic field, the spin-orbit interaction coupling of its orbital angular momentum **L** to its spin angular momentum **S** is overwhelmed, and both vectors precess independently about the direction of the external field with constant z components $L_z = m_l h$ and $S_z = m_s h$. That is, m_l and m_s are good quantum numbers under these circumstances. Spectrum measurements made on such atoms show the existence of a selection rule $\Delta m_l = 0, \pm 1$. Obtain this section rule by evaluating the appropriate electric dipole matrix element.

▶ Written in full, the matrix element is

$$ p_{fi} = \left| \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_f^*(r,\theta,\varphi) e \mathbf{r} \psi_i(r,\theta,\varphi) r^2 \sin\theta \, dr \, d\theta \, d\varphi \right| $$

The triple integral factors into the product of three single integrals. The one that is interesting, because it leads to the selection rule, is

$$ \mathbf{I} = \int_0^{2\pi} \Phi_f^*(\varphi) \mathbf{r} \Phi_i(\varphi) \, d\varphi $$

This is a vector quantity, which has components

$$ I_x = \int_0^{2\pi} \Phi_f^*(\varphi) x \Phi_i(\varphi) \, d\varphi $$

$$ I_y = \int_0^{2\pi} \Phi_f^*(\varphi) y \Phi_i(\varphi) \, d\varphi $$

$$ I_z = \int_0^{2\pi} \Phi_f^*(\varphi) z \Phi_i(\varphi) \, d\varphi $$

If we use the relations

$$ x = r \sin\theta \cos\varphi $$
$$ y = r \sin\theta \sin\varphi $$
$$ z = r \cos\theta $$

which can be verified by inspecting Figure 7-2, and also evaluate $\Phi_i(\varphi)$ and $\Phi_f^*(\varphi)$ from (7-19), we obtain

$$ I_x = r \sin\theta \int_0^{2\pi} \cos\varphi \, e^{i(m_{l_i} - m_{l_f})\varphi} \, d\varphi $$

$$ I_y = r \sin\theta \int_0^{2\pi} \sin\varphi \, e^{i(m_{l_i} - m_{l_f})\varphi} \, d\varphi $$

$$ I_z = r \cos\theta \int_0^{2\pi} e^{i(m_{l_i} - m_{l_f})\varphi} \, d\varphi $$

Any table of definite integrals will show that the integral in I_z equals zero, unless

$$ m_{l_i} - m_{l_f} = 0 \qquad \text{or} \qquad \Delta m_l = 0 $$

The integral in I_x can be rewritten, to yield

$$ I_x = \frac{1}{2} r \sin\theta \int_0^{2\pi} \left[e^{i(m_{l_i} - m_{l_f} - 1)\varphi} + e^{i(m_{l_i} - m_{l_f} + 1)\varphi} \right] d\varphi $$

This definite integral equals zero, unless

$$ m_{l_i} - m_{l_f} = \pm 1 \qquad \text{or} \qquad \Delta m_l = \pm 1 $$

The same result is obtained from the integral in I_y. Therefore, unless $\Delta m_l = 0$, or ± 1, there will be no components of **I** that are not zero. Since this will also be true of the electric dipole matrix element, we have obtained the selection rule. ◄

Physically, the selection rules arise because of symmetry properties of the oscillating charge distribution of the atom. The atom cannot radiate like an electric dipole unless the electric dipole moment of its electron charge distribution is oscillating. A classical analogy is found in a very short antenna, which is center-fed from high frequency sources of alternating current, as illustrated in Figure 8-14. If the leads to the antenna are fed out of phase, so that charge flows into one end at the same time it flows out of the other, the antenna will radiate relatively efficiently. But if
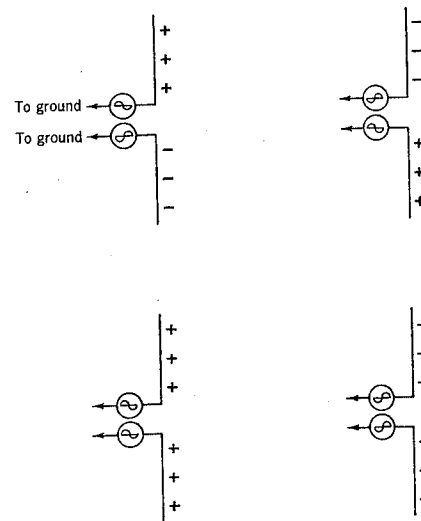
Figure 8-14 *Upper* diagrams: Center-fed antennas driven out of phase. *Lower* diagrams: Driven in phase. *Left* diagrams: The charge distributions are shown at some initial time. *Right* diagrams: At half a period later. The antenna driven in phase will emit very little radiation if its length is short compared to a wavelength, and if the distance to the ground plane is long compared to a wavelength.

the leads are fed in phase, so that charge flows into or out of both ends in unison, the antenna will hardly radiate at all.

Mathematically, it is the symmetry properties of the eigenfunctions in the matrix element that are responsible for the selection rules. Some idea of this can be obtained in an easy way by considering the parities of the eigenfunctions. In Section 6-8 we defined the parity of a one-dimensional eigenfunction as the quantity which describes the behavior of the eigenfunction when the sign of the coordinate is changed. The definition can be extended immediately to three dimensions. That is, eigenfunctions satisfying the relation

$$\psi(-x,-y,-z) = +\psi(x,y,z) \qquad (8\text{-}44)$$

are said to be of *even parity*, and eigenfunctions satisfying the relation

$$\psi(-x,-y,-z) = -\psi(x,y,z) \qquad (8\text{-}45)$$

are said to be of *odd parity*. All eigenfunctions that are bound-state solutions to time-independent Schroedinger equations for a potential that can be written as $V(r)$, like the Coulomb potential, have definite parities, either even or odd. The reason is that the probability densities $\psi^*\psi$ will then have the same value at the point $(-x, -y,-z)$ that they have at the point (x,y,z), which is a requirement of the fact that the potential has the same value at these points.

An example is found in the one-electron atom eigenfunctions of Table 7-2. To see this, inspect Figure 8-15, which shows that when the signs of the rectangular co-ordinates are changed in the *parity operation* the behavior of the spherical polar coodinates is

$$r \to r, \qquad \theta \to \pi - \theta, \qquad \varphi \to \pi + \varphi \qquad (8\text{-}46)$$

By carrying out these changes on several of the eigenfunctions, it is easy to demonstrate that

$$\psi_{nlm_l}(r,\pi - \theta,\pi + \varphi) = (-1)^l\psi_{nlm_l}(r,\theta,\varphi) \qquad (8\text{-}47)$$

The parity is determined by $(-1)^l$; it is even if the orbital angular momentum quantum-number l is even, and odd if l is odd. This is true for *all* eigenfunctions, bound or unbound, of any spherically symmetrical potential $V(r)$, since the only significant assumption that is used to obtain (8-47) is that V can be written as $V(r)$.

Now consider the matrix element of the electric dipole moment

$$P_{fi} = \left| \int \psi_f^* e\mathbf{r}\psi_i\, d\tau \right|$$

The parity of $e\mathbf{r}$ is odd since the vector $\mathbf{r}$ changes into its negative when the signs of the rectangular coordinates are changed. Therefore, if the initial and final eigenfunctions ψ_i and ψ_f are of the same parity, both even or both odd, the entire integrand will be of odd parity. If this is the case the integral will yield zero because the con-
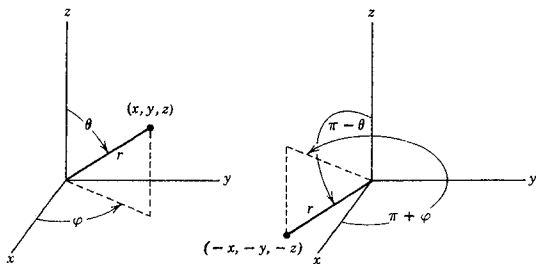

Figure 8-15 Illustrating the parity operation.

tribution from any volume element will be cancelled by the contribution from the diametrically opposite volume element. Then the transition rate will also be zero. Therefore, the parity of the final eigenfunction must differ from the parity of the initial eigenfunction in an electric dipole transition. Since the parities are determined by $(-1)^l$, we can understand why transitions for $\Delta l = 0$, or ± 2, are not allowed, in agreement with the $\Delta l = \pm 1$ selection rule of (8-37). The reason is that in such transitions the parities of the initial and final eigenfunctions would be the same.

Quantum electrodynamics shows, and experiments verify, that a photon carries angular momentum as well as linear momentum. In particular, the theory shows that the angular momentum carried by a photon emitted in an electric dipole transition is, in units of $\hbar$, equal to 1. From this point of view, the total angular momentum quantum number selection rule $\Delta j = 0, \pm 1$ of (8-38) represents the requirements of angular momentum conservation, which is fundamentally a symmetry property, by restricting electric dipole transitions to pairs of states where the change in the total angular momentum of the atom can be compensated for by the angular momentum carried by the photon it emits. (When $\Delta j = 0$ angular momentum conservation is satisfied by a change in the orientation in space of the total angular momentum vector of the atom at the time the photon is emitted.) This point of view also makes it apparent that $\Delta l = \pm 3$ electric dipole transitions cannot occur because they would lead to too large a change in the total angular momentum, even though they would be all right as far as parity is concerned.

It should be mentioned that selection rules do not absolutely prohibit transitions that violate them, but only make such transitions very unlikely. If a transition cannot take place by the normal means of emission of radiation from an oscillating electric dipole moment, there is a very small probability (typically reduced by a factor of about 10^{-4}) that it will take place by emission of radiation from an oscillating magnetic dipole moment. This may occur through oscillations in orientation of electron spin angular momentum and magnetic dipole moment. Transitions can also take place with very small probabilities (typically reduced by approximately a factor of 10^{-6}) by emission of radiation from an oscillating electric quadrupole moment. This involves oscillations in the electron charge distribution of the atom between an elongated ellipsoid and a flattened ellipsoid.

If an atom is excited to a state from which it can return to its ground state only by one of these highly inhibited transitions, it may remain in the excited state for an appreciable fraction of a second, instead of the lifetime of 10^{-8} sec corresponding to the typical transition rate of 10^8 sec^{-1}. The excited state is said to be *metastable*, and the delayed emission of a photon is a form of *phosphorescence*. In practice, phosphorescence of atoms is rarely observed because the metastable state is deexcited, without the emission of a photon, when the atom collides with the wall of its container and gives up its excess energy directly to the atoms of the wall. A process completely analogous to phosphorescence is commonly observed in nuclei, however.

8-8 A COMPARISON OF THE MODERN AND OLD QUANTUM THEORIES

We shall very briefly summarize the last chapters by making a comparison between the modern quantum theories (Schroedinger, Dirac, and quantum electrodynamics) and the old quantum theories (Bohr and Sommerfeld).

One of the most striking aspects of the modern quantum theories is the way they lead progressively to more and more accurate treatments of the hydrogen atom. The Schroedinger theory without electron spin accounts for the energy levels of the atom that are observed in spectroscopic measurements of moderate resolution. Measurements of high resolution reveal the fine-structure splitting of the energy levels. They