TABLE 8-1
HYDROGEN ATOM WAVE FUNCTIONS.

Spectroscopic Notation	$\psi_{n,\ell,m_\ell}(r,\theta,\phi)$
$1s$	$\psi_{1,0,0} = \dfrac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
$2s$	$\psi_{2,0,0} = \dfrac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \dfrac{r}{a_0}\right) e^{-r/2a_0}$
$2p\ (m_\ell = 0)$	$\psi_{2,1,0} = \dfrac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(\dfrac{r}{a_0}\right) e^{-r/2a_0} \cos\theta$
$2p\ (m_\ell = +1)$	$\psi_{2,1,1} = \dfrac{1}{8\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r}{a_0}\right) e^{-r/2a_0} \sin\theta\, e^{i\phi}$
$2p\ (m_\ell = -1)$	$\psi_{2,1,-1} = \dfrac{1}{8\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r}{a_0}\right) e^{-r/2a_0} \sin\theta\, e^{-i\phi}$
$3s$	$\psi_{3,0,0} = \dfrac{1}{81\sqrt{3\pi}\, a_0^{3/2}} \left(27 - \dfrac{18r}{a_0} + \dfrac{2r^2}{a_0^2}\right) e^{-r/3a_0}$
$3p\ (m_\ell = 0)$	$\psi_{3,1,0} = \dfrac{2}{81\sqrt{2\pi}\, a_0^{3/2}} \left(\dfrac{6r}{a_0} - \dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \cos\theta$
$3p\ (m_\ell = +1)$	$\psi_{3,1,1} = \dfrac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{6r}{a_0} - \dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin\theta\, e^{i\phi}$
$3p\ (m_\ell = -1)$	$\psi_{3,1,-1} = \dfrac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{6r}{a_0} - \dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin\theta\, e^{-i\phi}$
$3d\ (m_\ell = 0)$	$\psi_{3,2,0} = \dfrac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \left(\dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \left(3\cos^2\theta - 1\right)$
$3d\ (m_\ell = +1)$	$\psi_{3,2,1} = \dfrac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin\theta \cos\theta\, e^{i\phi}$
$3d\ (m_\ell = -1)$	$\psi_{3,2,-1} = \dfrac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin\theta \cos\theta\, e^{-i\phi}$
$3d\ (m_\ell = +2)$	$\psi_{3,2,2} = \dfrac{1}{162\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin^2\theta\, e^{2i\phi}$
$3d\ (m_\ell = -2)$	$\psi_{3,2,-2} = \dfrac{1}{162\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin^2\theta\, e^{-2i\phi}$

The boundary condition that the wave function $R(r)$ go to zero at infinity causes the integer n to appear (compare to the particle in a box, the finite square-well, and the harmonic oscillator). The solutions to the radial equation (see Table 8-1 and Appendix H) are polynomials in r times an exponential, e^{-r/na_0}, where n is the principal quantum number. The radial equation (8.39) contains a term with d^2R/dr^2. This second derivative with respect to r produces a term proportional to $1/n^2$. This leads to solutions for the electron energy proportional to $1/n^2$. The energy levels in the hydrogen atom are quantized. We give each energy level a serial number n and write

$$E_n = -\frac{\alpha^2 mc^2}{2n^2} = -\frac{13.6\,\text{eV}}{n^2}, \qquad (8.40)$$

where n is a positive integer $(1, 2, 3, \ldots)$. According to the Schrödinger equation, the energy levels do not depend on the values of the quantum numbers ℓ and m_ℓ. For example, the $2s$ and $2p$ states have the same energy even though they have different radial probability distributions. Figure 8-6 shows the energy levels of an electron in the hydrogen atom.

FIGURE 8-4 Probability of finding the electron as a function of radius for a hydrogen atom in the second excited state.
There are three possible states: $n=3$ and $\ell=0$ called the $3s$ state, $n=3$ and $\ell=1$ called the $3p$ state, or $n=3$ and $\ell=2$ called the $3d$ state. The area under each curve is normalized to unity.
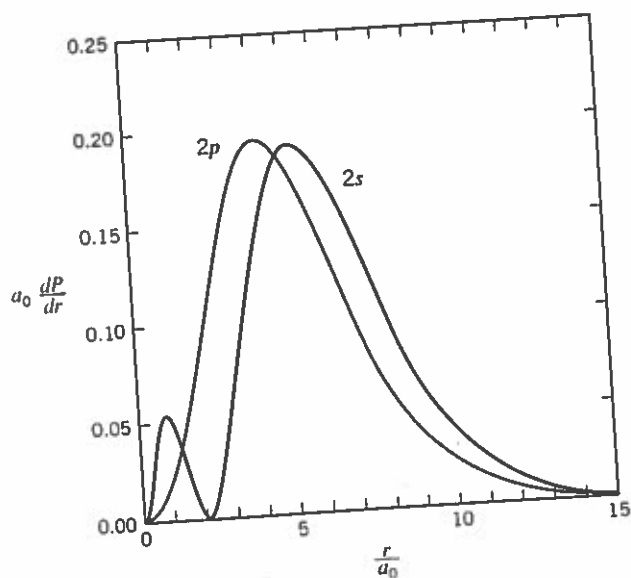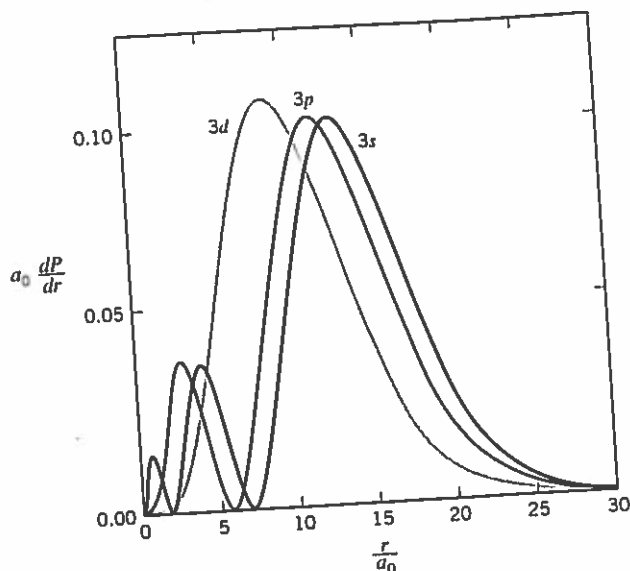

FIGURE 8-3 Probability of finding the electron as a function of radius for a hydrogen atom in the first excited state.
There are two possible states: $n=2$ and $\ell=0$ called the $2s$ state, or $n=2$ and $\ell=1$ called the $2p$ state. The area under each curve is normalized to unity.

EXAMPLE 8-7

Use the wave functions in Table 8-1 to calculate the energies of the $2s$ and $2p$ states.

SOLUTION:

The radial wave function for the $2s$ state is

$$R_{2,0} = C_0 \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0},$$

where C_0 is a constant. The derivatives are

$$\frac{dR_{2,0}}{dr} = C_0 \left(-\frac{1}{a_0} \right) e^{-r/2a_0}$$

$$+ C_0 \left(2 - \frac{r}{a_0} \right) \left(-\frac{1}{2a_0} \right) e^{-r/2a_0}$$

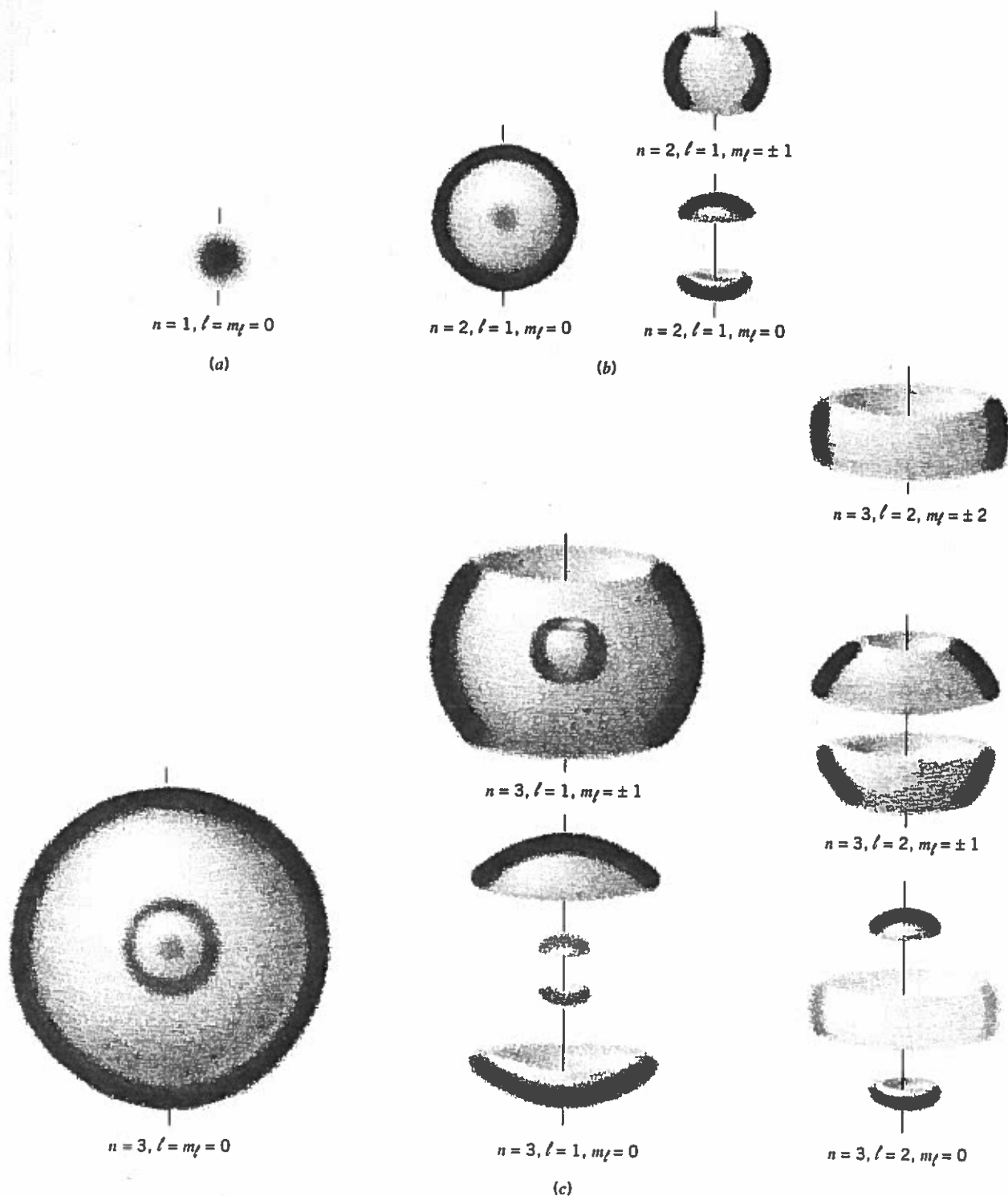$$= C_0 \left(\frac{r}{2a_0^2} - \frac{2}{a_0} \right) e^{-r/2a_0},$$

and

$n = 1, \ell = m_\ell = 0$

(a)

$n = 2, \ell = 1, m_\ell = 0$

$n = 2, \ell = 1, m_\ell = \pm 1$

$n = 2, \ell = 1, m_\ell = 0$

(b)

$n = 3, \ell = m_\ell = 0$

$n = 3, \ell = 1, m_\ell = \pm 1$

$n = 3, \ell = 1, m_\ell = 0$

$n = 3, \ell = 2, m_\ell = \pm 2$

$n = 3, \ell = 2, m_\ell = \pm 1$

$n = 3, \ell = 2, m_\ell = 0$

(c)

FIGURE 8-5 Sketches of $|\psi|^2$ for the hydrogen atom in three dimensions:
(a) the $n = 1$ state, (b) the $n = 2$ states, and (c) the $n = 3$ states. After R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*, Wiley (copyright © 1985).
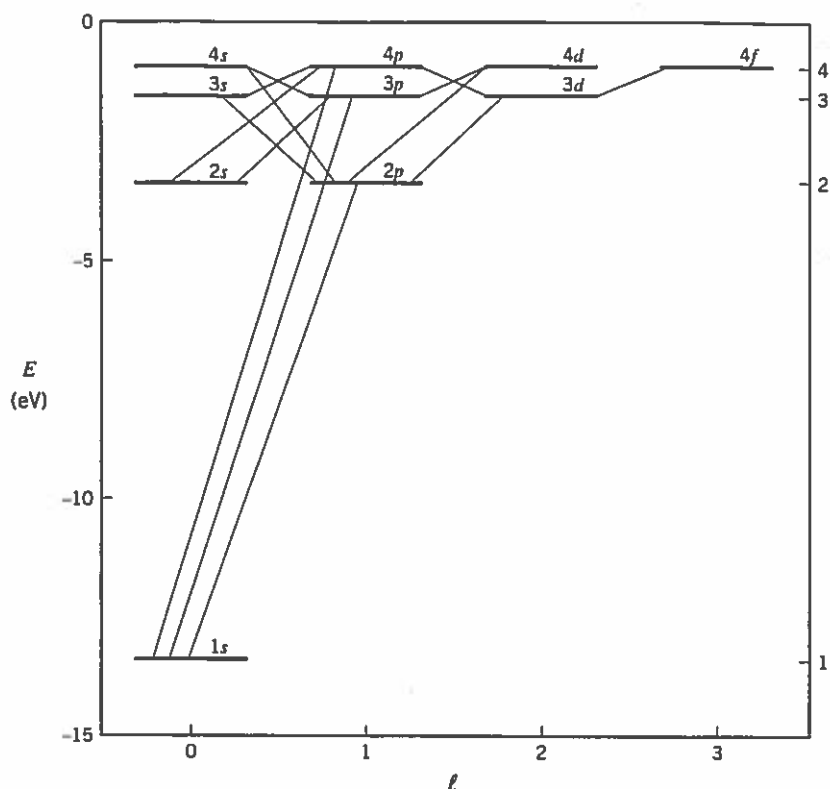
FIGURE 8-6 Energy levels in the hydrogen atom.
The favored transitions are those in which ℓ changes by ± 1.

$$\frac{d}{dr}\left(r^2\frac{dR_{2,0}}{dr}\right)$$

$$= C_0\left(\frac{3r^2}{2a_0{}^2} - \frac{4r}{a_0}\right)e^{-r/2a_0}$$

$$+ C_0\left(\frac{r^3}{2a_0{}^2} - \frac{2r^2}{a_0}\right)\left(\frac{-1}{2a_0}\right)e^{-r/2a_0}$$

$$= C_0\left(-\frac{4r}{a_0} + \frac{5r^2}{2a_0{}^2} - \frac{r^3}{4a_0{}^3}\right)e^{-r/2a_0} .$$

The radial equation (8.39) with $\ell = 0$ is

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = -\frac{2mke^2r}{\hbar^2}R - \frac{2mEr^2}{\hbar^2}R .$$

Therefore, the radial equation gives

$$C_0\left(-\frac{4r}{a_0} + \frac{5r^2}{2a_0{}^2} - \frac{r^3}{4a_0{}^3}\right)e^{-r/2a_0}$$

$$= -\frac{2mke^2}{\hbar^2}C_0\left(2r - \frac{r^2}{a_0}\right)e^{-r/2a_0}$$

$$- \frac{2mE_2}{\hbar^2}C_0\left(2r^2 - \frac{r^3}{a_0}\right)e^{-r/2a_0} .$$

Comparison of the r terms gives the Bohr radius,

$$a_0 = \frac{\hbar^2}{mke^2} .$$

Comparison of the r^3 terms gives the electron energy,

$$E_2 = -\frac{\hbar^2}{8ma_0{}^2} = -\frac{1}{8}mc^2\alpha^2 .$$

Comparison of the r^2 terms gives no extra information but shows that the solution works. The radial wave function for the 2p state is

$$R_{2,1} = C_1 \frac{r}{a_0} e^{-r/2a_0},$$

where C_1 is a constant. The derivatives are

$$\frac{dR_{2,1}}{dr} = C_1 \left(\frac{1}{a_0} \right) e^{-r/2a_0} + C_1 \left(\frac{r}{a_0} \right) \left(-\frac{1}{2a_0} \right) e^{-r/2a_0}$$

$$= C_1 \left(\frac{1}{a_0} - \frac{r}{2a_0^2} \right) e^{-r/2a_0},$$

and

$$\frac{d}{dr} \left(r^2 \frac{dR_{2,1}}{dr} \right)$$

$$= C_1 \left(\frac{2r}{a_0} - \frac{3r^2}{2a_0^2} \right) e^{-r/2a_0}$$

$$+ C_1 \left(\frac{r^2}{a_0} - \frac{r^3}{2a_0^2} \right) \left(\frac{-1}{2a_0} \right) e^{-r/2a_0}$$

$$= C_1 \left(\frac{2r}{a_0} - \frac{2r^2}{a_0^2} + \frac{r^3}{4a_0^3} \right) e^{-r/2a_0}.$$

The radial equation (8.39) with $\ell=1$ is

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = -\frac{2mke^2 r}{\hbar^2} R - \frac{2mEr^2}{\hbar^2} R + 2R.$$

Therefore, the radial equation gives

$$C_1 \left(\frac{2r}{a_0} - \frac{2r^2}{a_0^2} + \frac{r^3}{4a_0^3} \right) e^{-r/2a_0}$$

$$= -\frac{2mke^2}{\hbar^2} \left(C_1 \frac{r^2}{a_0} \right) e^{-r/2a_0}$$

$$- \frac{2mE_2}{\hbar^2} \left(C_1 \frac{r^3}{a_0} \right) e^{-r/2a_0} + 2C_1 \frac{r}{a_0} e^{-r/2a_0}.$$

The r terms cancel, the r^2 terms give the Bohr radius, and the r^3 terms give the energy:

$$E_2 = -\frac{\hbar^2}{8ma_0^2} = -\frac{1}{8} mc^2 \alpha^2.$$

The energies of the 2s and 2p states are identical. The energy does not depend on the quantum number ℓ. ∎

The Orbital Angular Momentum Quantum Number, ℓ

The quantum number ℓ has appeared in the solution for the angular dependence $P(\theta)$. The separation constant C_r is equal to the product of two consecutive nonnegative integers that we write as $\ell(\ell+1)$. This separation constant also appears in the radial equation (8.39) which we may write as

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right)$$

$$+ \left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{ke^2}{r} \right] R = ER. \quad (8.41)$$

The solution for radial motion should depend only on the coordinate r. The total energy E that appears in the radial equation is the kinetic plus the potential energy. The kinetic energy contains both radial motion ($p_r^2/2m$) and orbital motion ($L^2/2mr^2$), where L is the *orbital angular momentum*. We may write the electron energy as

$$E = \frac{p^2}{2m} + V = \left(\frac{p_r^2}{2m} + \frac{L^2}{2mr^2} \right) - \frac{ke^2}{r}, \quad (8.42)$$

and the radial equation (8.41) becomes

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right)$$

$$+ \left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{p_r^2}{2m} - \frac{L^2}{2mr^2} \right] R = 0. (8.43)$$

Thus, we see that we have a *pure* radial equation if

$$\frac{L^2}{2mr^2} = \frac{\ell(\ell+1)\hbar^2}{2mr^2}, \quad (8.44)$$

or

$$L^2 = \ell(\ell+1)\hbar^2. \quad (8.45)$$

Orbital angular momentum is quantized.

The quantum number ℓ specifies the orbital angular momentum of the electron. Zero orbital angular momentum corresponds to spherical symmetry since the separation constant (8.34) is zero and there is no angular dependence. There is a limit on how large ℓ may be for a given value of n. The solution requires that $\ell < n$. For example, if $n = 1$ then $\ell = 0$, that is, there is no $1p$ state. If ℓ is not equal to zero, the wave function vanishes at the origin (see Table 8-1 and Figure 8-5) and the wave function is proportional to r^ℓ.

The Magnetic Quantum Number, m_ℓ

The quantum number m_ℓ has appeared in the solution for $F(\phi)$. The separation constant C_ϕ is equal to minus one times the square of an integer (m_ℓ). The minimum value of m_ℓ is $-\ell$ and the maximum value is ℓ.

For the $2p$ wave functions, there are three possibilities for m_ℓ: -1, 0, and $+1$. For $m_\ell = 0$, the wave function (see Table 8-1) is proportional to $\cos\theta$ and the electron is most likely to be found near the z axis. We can see from Figure 8-5 that the *average* of the z component of angular momentum (L_z) is zero when $m_\ell = 0$. It turns out that the z component of angular momentum is *exactly* zero when $m_\ell = 0$. For $m_\ell = +1$ or $m_\ell = -1$, the wave function is proportional to $\sin\theta$ and the electron is most likely to be found near the x-y plane. The exact value of L_z is $\hbar$ for $m_\ell = +1$ and $-\hbar$ for $m_\ell = -1$. We summarize these results with

$$L_z = m_\ell \hbar, \qquad (8.46)$$

where m_ℓ may take on integer values from $-\ell$ to ℓ. The total number of states for a given value of ℓ is $2\ell + 1$. The z direction is special in spherical coordinates because the polar angle is measured with respect to the z axis. All of the wave functions squared are symmetric about the z axis, that is, $|\psi|^2$ does not depend on ϕ. The quantization condition (8.46) is similar to that used in the Bohr model, where the electron is assumed to have a circular trajectory. In this case, the z direction is the direction perpendicular to the plane of the orbit. In the Bohr model, the minimum value of $|L_z|$ is $\hbar$, whereas in the Schrödinger formulation (8.46) it is zero.

If both the total angular momentum and the z component of angular momentum are quantized, then the angular momentum cannot point in an arbitrary direction in space. Angular momentum quantization is observable when there is a magnetic field that selects a special direction in space. The magnetic field causes a shift in the atomic energy level by an amount that is proportional to the quantum number m_ℓ. We shall discuss the reason for this in the next section. Thus, m_ℓ is known as the *magnetic* quantum number. Angular momentum quantization is illustrated in Figure 8-7, where we plot L_z versus $(L_x^2 + L_y^2)^{1/2}$. (Note that $L_x^2 + L_y^2 = L^2 - L_z^2$.)

The uncertainty principle tells us that we may not simultaneously know the exact values of any two components of the angular momentum. For example, if L_x and L_y were known exactly, then we would know the exact trajectory, position, and momentum of the particle in the x-y plane. If the z component of angular momentum (8.46) is known exactly, then nothing is known about the azimuthal angle. Both the magnitude of the electron orbital angular momentum L and the z component L_z may be specified exactly. The direction of **L** is not known; however, **L** is constrained to lie on a cone (Figure 8-8).

The solution to the Schrödinger equation gives three quantum numbers for an electron in the hydrogen atom. The primary quantum number n gives the electron energy,

$$E_n = -\frac{13.6 \text{ eV}}{n^2},$$

where $n = 1, 2, 3, \ldots$ The orbital quantum number ℓ gives the electron orbital angular momentum,

$$L = \sqrt{\ell(\ell+1)}\,\hbar,$$

where $\ell = 0, 1, 2, 3, \ldots n-1$. The magnetic quantum number m_ℓ gives the z component of orbital angular momentum,

$$L_z = m_\ell \hbar,$$

where $m_\ell = -\ell, -\ell+1, \ldots 0, \ldots \ell-1, \ell$.

---

* *Challenging*

Operators in Quantum Mechanics

The Schrödinger equation may be written as

$$\frac{1}{2m}\left(\mathbf{p}^{\text{opp}}\right)^2 \psi + V\psi = E\psi, \qquad (8.47)$$

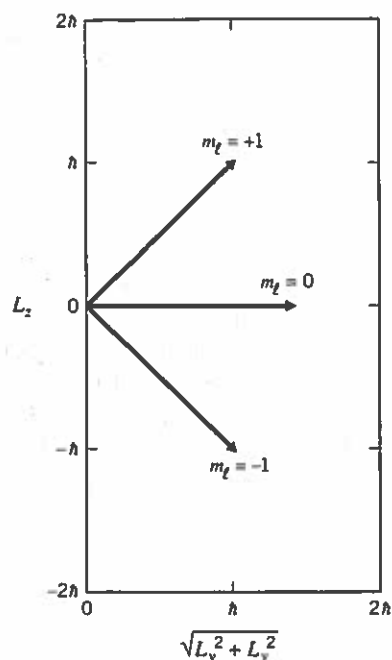where the symbol $\mathbf{p}^{\text{opp}}$ is defined to be

FIGURE 8-7 Angular momentum quantization for $\ell = 1$.
When the orbital quantum number is one, the orbital angular momentum is $L = \sqrt{2}\,\hbar$. There are only three possibilities for the z component of orbital angular momentum: $-\hbar$, 0, or $\hbar$. Thus, the total angular momentum vector cannot point in any arbitrary direction. This effect is observable when the atom is placed in an external magnetic field, which serves to define a specific direction.
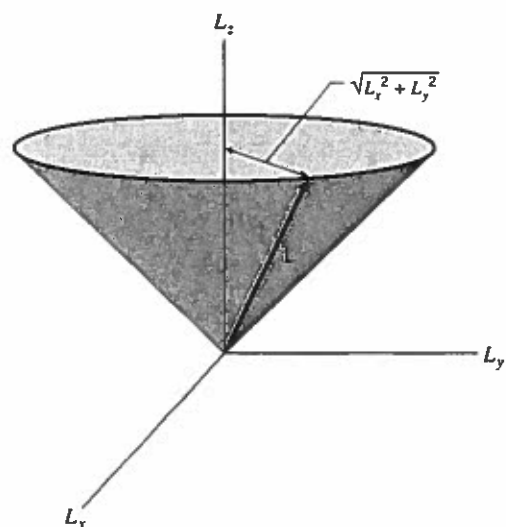

FIGURE 8-8 Relationship between L and L_z.
Both the magnitude of the electron orbital angular momentum and the z component may be specified exactly. The exact direction of **L** is not known but is constrained to lie on a cone.

$$\mathbf{p}^{\text{opp}} \equiv -i\hbar\nabla. \tag{8.48}$$

The symbol $\mathbf{p}^{\text{opp}}$ is called the momentum *operator*. In the Schrödinger equation (8.47) the square of an operator means that the operation is applied twice.

The operator for the z component of angular momentum $\mathbf{L}_z^{\text{opp}}$ is

$$\mathbf{L}_z^{\text{opp}} = x\mathbf{p}_y - y\mathbf{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{8.49}$$

From the definition of spherical coordinates (see problem 15), we get

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$= \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial \phi}, \tag{8.50}$$

and

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}$$

$$= \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial \phi}. \tag{8.51}$$

Therefore, $\mathbf{L}_z^{\text{opp}}$ (8.49) may be written

$$\mathbf{L}_z^{\text{opp}} = -i\hbar\frac{\partial}{\partial \phi}. \tag{8.52}$$

Applying $\mathbf{L}_z^{\text{opp}}$ to the hydrogen atom wave functions determines the value of L_z,

$$\mathbf{L}_z^{\text{opp}}\psi_{n,\ell,m_\ell} = -i\hbar\frac{\partial \psi_{n,\ell,m_\ell}}{\partial \phi}$$

$$= (-i\hbar)(im_\ell)\psi_{n,\ell,m_\ell}$$

$$= m_\ell\hbar\psi_{n,\ell,m_\ell}. \tag{8.53}$$

The hydrogen atom wave functions have a definite angular momentum given by

$$L_z = m_\ell\hbar. \tag{8.54}$$

Similarly, the operators for the other components of angular momentum (see problem 15) are

$$L_x{}^{opp} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\theta\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right), \quad (8.55)$$

and

$$L_y{}^{opp} = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \frac{\cos\theta\sin\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right). \quad (8.56)$$

The total angular momentum operator L^{opp} may be constructed from the component operators, $L_x{}^{opp}$, $L_y{}^{opp}$, and $L_z{}^{opp}$:

$$\left(L^{opp}\right)^2 = \left(L_x{}^{opp}\right)^2 + \left(L_y{}^{opp}\right)^2 + \left(L_z{}^{opp}\right)^2, \quad (8.57)$$

which reduces to (see problem 16)

$$\left(L^{opp}\right)^2$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. (8.58)$$

The angular momentum operator applied twice gives the angular portion of the ∇^2 operator times $\hbar$. Therefore, the solution to the Schrödinger equation gives

$$\left(L^{opp}\right)^2\psi_{n,\ell,m_\ell}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi_{n,\ell,m_\ell}$$

$$= \ell(\ell+1)\hbar^2\psi_{n,\ell,m_\ell}. \quad (8.59)$$

Thus, the value of L^2 is $\ell(\ell+1)\hbar^2$.

EXAMPLE 8-8

The average value of an observable quantity $<O>$ whose corresponding operator is O^{opp} is given by the expression

$$\langle O \rangle = \iiint_V dV\,\psi^* O^{opp}\,\psi.$$

Calculate the average kinetic energy of an electron in the ground state of the hydrogen atom.

SOLUTION:
The average kinetic energy is given by

$$\left\langle\frac{p^2}{2m}\right\rangle = \frac{1}{2m}\iiint_V dV\,\psi^*\left(p^{opp}\right)^2\psi$$

$$= \frac{1}{2m}\iiint_V dV\,\psi^*\left(-i\hbar\nabla\right)^2\psi$$

$$= -\frac{\hbar^2}{2m}\iiint_V dV\,\psi^*\nabla^2\psi.$$

For the ground state,

$$\psi = Ce^{-r/a_0}$$

and

$$\nabla^2\psi = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}Ce^{-r/a_0}\right)$$

$$= C\left(\frac{1}{a_0{}^2} - \frac{2}{a_0 r}\right)e^{-r/a_0}.$$

where $c^2 = 1/\pi a_0{}^3$. The average kinetic energy is

$$\left\langle\frac{p^2}{2m}\right\rangle = -\frac{\hbar^2}{2m}\iiint_V dV\left[\frac{C^2 e^{-2r/a_0}}{a_0{}^2} - \frac{2C^2 e^{-2r/a_0}}{a_0 r}\right]$$

$$= \left(-\frac{\hbar^2}{2ma_0{}^2}\right)\left(\frac{1}{\pi a_0{}^3}\right)4\pi\int_0^\infty dr\,r^2 e^{-2r/a_0}$$

$$+ \left(\frac{\pi\hbar^2}{ma_0}\right)\left(\frac{1}{\pi a_0{}^3}\right)4\pi\int_0^\infty dr\,r e^{-2r/a_0}$$

$$= -\frac{\hbar^2}{2ma_0{}^2} + \frac{\hbar^2}{ma_0{}^2}$$

$$= \frac{\hbar^2}{2ma_0{}^2} = \frac{1}{2}\alpha^2 mc^2 = 13.6\,\text{eV}.$$

The *average* value of the kinetic energy plus the *average* value of the potential energy is equal to the energy of the state

$$\left\langle\frac{p^2}{2m}\right\rangle + \left\langle-\frac{ke^2}{r}\right\rangle = E_n. \quad \blacksquare$$

*

8-4 INTRINSIC ANGULAR MOMENTUM

The Schrödinger equation in three dimensions has given us three quantum numbers (n, ℓ, and m_ℓ) for the description of an electron in a hydrogen atom. In spite of the great success of the Schrödinger equation in explaining much of the structure of the hydrogen atom, experiments tell us that the Schrödinger theory of the hydrogen atom is not complete! To appreciate where the Schrödinger theory fails, we proceed with a more detailed discussion of the angular momentum of the electron in the hydrogen atom.

Electron Angular Momentum and Magnetic Moment

The electron in the hydrogen atom does not have a classical trajectory; the wave properties of the electron are inconsistent with such an interpretation. The electron is described by a probability density given by the square of the wave function. The probability density is peaked near $n^2 a_0$ for the nth state. If there is no angular (θ) dependence to the probability density, then there is no net orbital angular momentum of the electron, $L = 0$. If there is a θ dependence of the probability density, then there is a nonzero value of orbital angular momentum. For example, if the probability density is maximum at $z = 0$ and $(x^2+y^2)^{1/2}$ = constant, corresponding to a ring in the x-y plane, then there is a net angular momentum in the z direction (either positive or negative). This is the case for the $2p$ state when $m_\ell = +1$ or -1 (see Figure 8-5). In the classical limit, the probability density is a delta function corresponding to an electron traveling in a circle either clockwise or counterclockwise with an orbital angular momentum, $L = mvr$. In the quantum interpretation, all we can say is that at any given time the electron can interact or be found near the ring with a fixed energy E and a fixed orbital angular momentum L. The electron is moving with a characteristic speed $v \approx \alpha c$ and the result of this motion constitutes a net orbital angular momentum.

A moving charge corresponds to a current and a magnetic moment. Consider a loop of current (I) enclosing an area (A) in the x-y plane. The classical magnetic moment is

$$\mu = IA. \tag{8.60}$$

The orientation of the magnetic moment vector is perpendicular to the loop. For a circulating charge (q) the time-averaged current is

$$I = \frac{q}{T}, \tag{8.61}$$

where T is the period of revolution. Kepler's law states that the area swept out per time is a constant,

$$\frac{A}{T} = \frac{L}{2m}. \tag{8.62}$$

For a displacement $d\mathbf{r}$ along the path (see Figure 8-9),

$$dA = \frac{1}{2}|\mathbf{r} \times d\mathbf{r}|, \tag{8.63}$$

so

$$\frac{dA}{dt} = \frac{1}{2}\left|\mathbf{r} \times \frac{d\mathbf{r}}{dt}\right| = \frac{\left|\mathbf{r} \times \left(m\dfrac{d\mathbf{r}}{dt}\right)\right|}{2m} = \frac{L}{2m}, \tag{8.64}$$

and

$$\frac{A}{T} = \frac{L}{2m}. \tag{8.65}$$

This is easily verified for a circular orbit where $L = mvr$, $T = 2\pi r/v$ and $A = \pi r^2$. The magnetic moment of a moving charge is

$$\mu = IA = \left(\frac{q}{T}\right)\left(\frac{TL}{2m}\right) = \frac{q}{2m}L. \tag{8.66}$$

The direction of μ is along the direction of L,

$$\boldsymbol{\mu} = \frac{q}{2m}\mathbf{L}. \tag{8.67}$$

By writing the magnetic moment in terms of orbital angular momentum, we have circumvented the need to know the exact trajectory of the charge. This is just the situation of our knowledge of the motion of an electron in the atom: the orbital angular momentum is well-defined but the exact motion of the electron is not well-defined. Note that for electrons $q = -e$ so that the direction of the magnetic moment is opposite the direction of the orbital angular momentum:
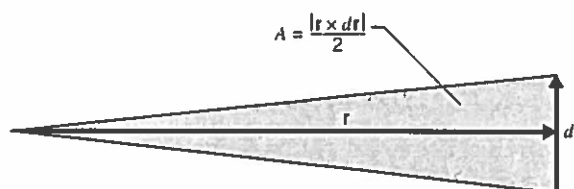

FIGURE 8-9 Kepler's law.

$$\mu = -\frac{e}{2m}\mathbf{L}. \qquad (8.68)$$

An electron with orbital angular momentum L is a tiny electromagnet.

The ratio $-e/2m$ is commonly called the electron *gyromagnetic* ratio. The gyromagnetic ratio is the magnetic moment divided by the orbital angular momentum. The smallest unit of angular momentum is $\hbar$. The *Bohr magneton* (μ_B) is defined as

$$\mu_B \equiv \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \; A \cdot m^2$$

$$= 5.788 \times 10^{-5} \; eV/T. \qquad (8.69)$$

Since the magnetic moment is proportional to the orbital angular momentum, the direction of the magnetic moment vector μ is restricted (see Figure 8-7). Therefore, we may write the z component of μ as

$$\mu_z = -\frac{e}{2m}L_z = -\mu_B m_\ell. \qquad (8.70)$$

A magnet placed in a magnetic field experiences a torque (τ),

$$\tau = \frac{d\mathbf{L}}{dt} = \mu \times \mathbf{B} = \frac{q}{2m}\mathbf{L} \times \mathbf{B}, \qquad (8.71)$$

which tends to align μ with $\mathbf{B}$. This is illustrated in Figure 8-10. This results in a precession when μ is not parallel $\mathbf{B}$ because the change in angular momentum is perpendicular to both $\mathbf{L}$ and $\mathbf{B}$. This is analogous to a spinning top in a gravitational field. The frequency of precession ω_L, called the *Larmor* frequency (see problem 35), is

$$\omega_L = \frac{eB}{2m}. \qquad (8.72)$$

The potential energy of the magnetic dipole in an external magnetic field is

$$V = -\mu \cdot \mathbf{B}. \qquad (8.73)$$

The energy of an electron in an external field (B_z) is shifted by

$$\Delta E = \mu_z B_z = \hbar \omega_L m_\ell. \qquad (8.74)$$

The Stern-Gerlach Experiment

According to the analysis of the preceding section, an atom in the s state ($\ell = 0$ and $m_\ell = 0$), has no energy shift
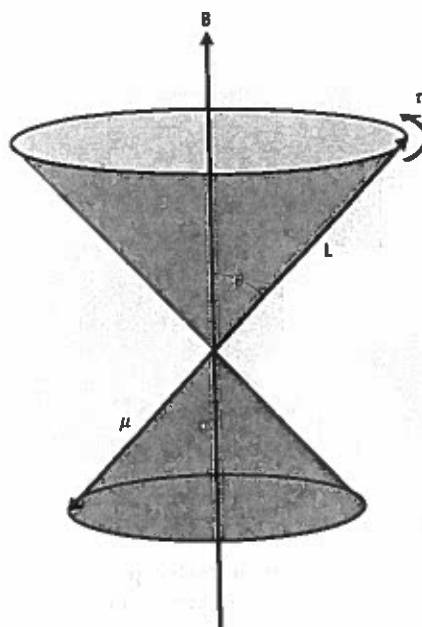

FIGURE 8-10 An electron with orbital angular momentum L in a magnetic field (B).

when placed in an external magnetic field. In 1921 Otto Stern and Walter Gerlach performed an experiment that proved this not to be correct. Stern and Gerlach chose to experiment with the silver atom because it could be readily detected by photographic techniques. The silver atom behaves like the hydrogen atom; a single outer electron moves in a Coulomb potential generated by a charge e due to 47 protons and 46 inner electrons. The orbital angular momentum of the outer electron in the ground state is zero. The structure of multielectron atoms is discussed in the next chapter.

Stern and Gerlach directed a beam of silver atoms into a region where the magnetic field was nonuniform, as indicated in Figure 8-11. The force on the atom is in the direction of the magnetic field gradient and has a magnitude (F_z),

$$F_z = -\mu_z \frac{\Delta B}{\Delta z}. \qquad (8.75)$$

After passing through the nonuniform field, the beam of silver atoms was observed to be split in two, as shown in Figure 8-12. The Stern-Gerlach experiment shows that the silver atom has two possible values for the z component of the magnetic moment (μ_z).
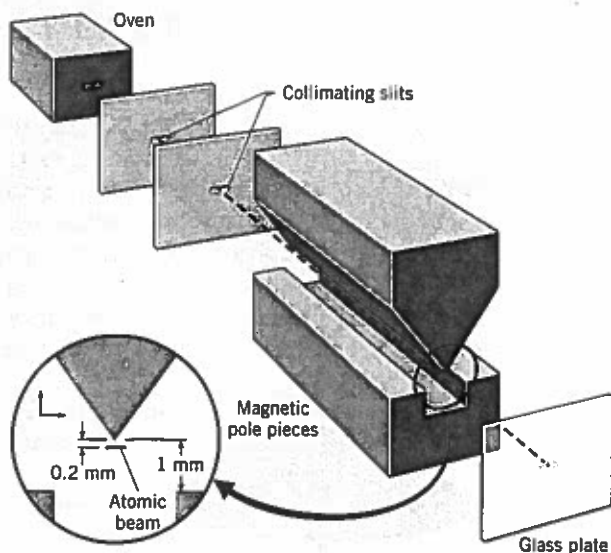
FIGURE 8-11 The Stern-Gerlach experiment.
A beam of atoms enters a region where the magnetic field varies in the direction transverse to the velocity (v) of the atoms. There is a force on the atoms that depends on the orientation of the magnetic moment (μ). The number of paths that the atoms may follow through the magnetic field region is equal to the number of possible orientations of μ. For the case $\mu = 0$, there is no force on the atoms. For atoms with a single electron in the $\ell = 0$ state, two possible deflections are observed corresponding to two possible orientations of μ. This magnetic moment is generated by the intrinsic angular momentum of the electron. After R. L. Sproull and W. A. Phillips, *Modern Physics: The Quantum Physics of Atoms, Solids, and Nuclei*, Wiley (copyright © 1985).

Intrinsic Angular Momentum

Recall that the total number of states for a given value of the orbital angular momentum quantum number ℓ is given by the number of possibilities for the quantum number m_ℓ, which is $2\ell + 1$. The Stern-Gerlach experiment shows that atoms in the s state ($\ell = 0$) are split into *two states* in a magnetic field. In 1925 Samuel A. Goudsmit and George E. Uhlenbeck postulated that the electron had an *intrinsic* angular momentum. The intrinsic angular momentum causes the electron to behave like a tiny magnet even when the orbital angular momentum is zero. We assign the electron an additional quantum number (s), called the *intrinsic angular momentum* quantum number,
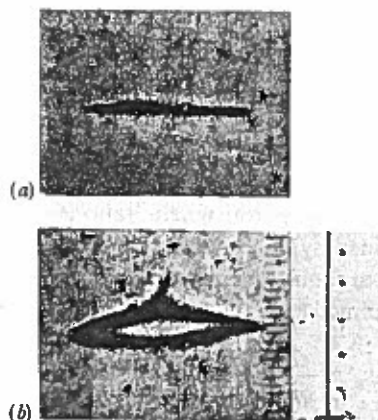
$$s = \frac{1}{2}, \qquad (8.76)$$

corresponding to the

FIGURE 8-12 Results from the Stern-Gerlach experiment.
(*a*) A beam of silver atoms from a hot oven is deposited on a piece of glass and detected by photographic techniques. (*b*) The beam passes through a region of nonuniform magnetic field before reaching the detector. The beam is split into two due to interaction of the magnetic moment of the atom with the magnetic field. The magnetic moment of the silver atom is caused by the intrinsic angular momentum of the electron. (Photos courtesy of Dr. Vera Rubin.)

$$2s + 1 = 2 \qquad (8.77)$$

states. The intrinsic angular momentum quantum number is commonly referred to as the *spin* quantum number. The term "spin" is somewhat misleading since the electron is not really "spinning" like a top. Intrinsic angular momentum is a purely quantum mechanical effect with no classical analogy. The magnitude of the intrinsic angular momentum is

$$S = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar, \qquad (8.78)$$

analogous to the orbital angular momentum L (8.45). The z component of the intrinsic angular momentum is

$$S_z = m_s \hbar, \qquad (8.79)$$

where $m_s = -1/2$ or $1/2$, analogous to L_z (8.46).

Corresponding to the intrinsic angular momentum, the electron has an intrinsic magnetic moment,

$$\mu_z = -\frac{e}{2m}g\,S, \qquad (8.80)$$

where the factor g accounts for the intrinsic charge-to-mass ratio of the electron. (The g factor for orbital

motion is 1.) The g factor is measured to be very nearly equal to 2:

$$g \approx 2, \qquad (8.81)$$

The small deviation from 2 is discussed further in Section 8-9. The intrinsic magnetic moment (8.80) is a fundamental property of the electron analogous to the electric charge.

The total magnetic moment of an electron in an atom is

$$\mu = -\frac{e}{2m}(L + gS) \approx -\frac{e}{2m}(L + 2S). \quad (8.82)$$

In the Stern-Gerlach experiment, the silver atom behaves like an atom with one electron because net orbital angular momentum of the inner electrons is zero and the net intrinsic angular momentum of the inner electrons is zero. The quantum numbers L and S of the atom are given by the quantum numbers of the outer electron. In the ground state, the orbital angular momentum of the outer electron is zero ($L = 0$). The magnetic moment of the atom is given by the magnetic moment of the outer electron

$$\mu = -\frac{e}{2m}g\,S \approx -\frac{e}{m}S. \qquad (8.83)$$

The intrinsic angular momentum vector (S) specifies the magnetic moment. The vector S can point in one of two directions, as indicated in Figure 8-13:

$$\mu_z = -\frac{e}{m}m_s\hbar. \qquad (8.84)$$

Since m_s can be $+1/2$ or $-1/2$, the value of μ_z can be $-\mu_B$ or $+\mu_B$. There are two possibilities for the direction of the force, and the beam of silver atoms is split into two when it passes through the region of nonuniform magnetic field.

The electron has an internal degree of freedom, specified by the quantum numbers $s = 1/2$ and m_s, not predicted by the Schrödinger equation. The electron has an intrinsic angular momentum

$$S = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\,\hbar,$$

and z component

$$S_z = m_s\hbar,$$
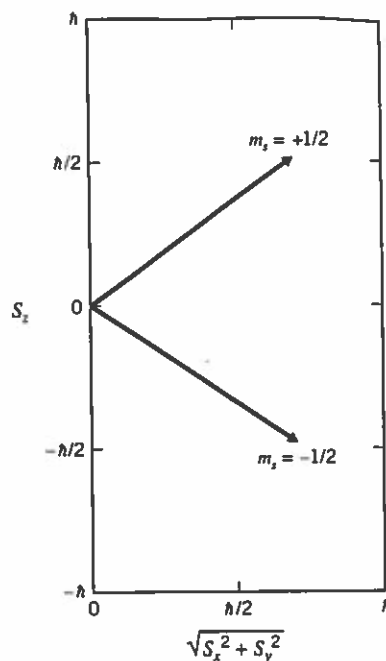
where $m_s = -1/2$ or $+1/2$.

FIGURE 8-13 Angular momentum quantization for an atom with one outer electron in an $\ell = 0$ state.
The total angular momentum is not zero because the electron has an intrinsic angular momentum. The z component (S_z) of the intrinsic angular momentum can be $\hbar/2$ or $-\hbar/2$. The total angular momentum (S) is $\sqrt{3}\hbar/2$.

8-5 TOTAL ANGULAR MOMENTUM

The total angular momentum (J) is the vector sum of the orbital and intrinsic parts,

$$J = L + S. \qquad (8.85)$$

The total angular momentum (J) is conserved in all interactions, and not necessarily L or S individually. The total angular momentum has the value

$$J = \sqrt{j(j+1)}\,\hbar, \qquad (8.86)$$

where the possible values of j are $|\ell-s|$, $|\ell-s|+1,\ldots |\ell+s|$. The z component of angular momentum has the value

$$J_z = m_j\hbar, \qquad (8.87)$$

where the possible values of m_j are $-j$, $-j+1$, $-j+2,\ldots j$.

In the spectroscopic notation for the atomic states, we often label the value of the total angular momentum quantum number (j) with a subscript following the letter code for orbital angular momentum. Thus, the two 2p

states of hydrogen (see Example 8-10) are called $2p_{1/2}$ (for $j = 1/2$) and $2p_{3/2}$ (for $j = 3/2$).

EXAMPLE 8-9

What is the total angular momentum (J) and z component (J_z) for an electron in the ground state of hydrogen?

SOLUTION:

The orbital angular momentum quantum number is

$$\ell = 0.$$

The intrinsic angular momentum quantum number is

$$s = \frac{1}{2}.$$

There is only one possibility for the total angular momentum quantum number:

$$j = \ell + s = \frac{1}{2}.$$

There are two possible values for the quantum number m_j: $-1/2$ and $1/2$. The total electron angular momentum is

$$J = \sqrt{j(j+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar.$$

The possible values of the z component of angular momentum are $-\hbar/2$ or $\hbar/2$. ∎

The observed total angular momentum of the electron in the ground state of hydrogen is

$$J = \frac{\sqrt{3}}{2}\hbar. \tag{8.88}$$

This value of total angular momentum is between that predicted by the Bohr model ($J = \hbar$) and the Schrödinger equation ($J = 0$). The relativistic formulation of the wave equation of the electron was made in 1927 by Paul A. M. Dirac. The *Dirac equation* correctly predicts the angular momentum of the electron (see Table 8-2).

EXAMPLE 8-10

What are the possible values for the total angular momentum (J) for an electron in a p state?

SOLUTION:

First we determine the possible values of the total angular momentum quantum number (j). The orbital quantum number is

TABLE 8-2
TOTAL ANGULAR MOMENTUM OF THE ELECTRON IN THE GROUND STATE OF HYDROGEN.

Theory	*Angular Momentum*
Bohr Model	$\hbar$
Schrödinger Equation	0
Dirac Equation	$\frac{\sqrt{3}}{2}\hbar$

$$\ell = 1.$$

The intrinsic angular momentum quantum number is

$$s = \frac{1}{2}.$$

The possible values of j are $1/2$ or $3/2$. Thus,

$$J = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \frac{\sqrt{3}}{2}\hbar,$$

or

$$J = \sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)}\,\hbar = \frac{\sqrt{15}}{2}\hbar. \quad ∎$$

The intrinsic angular momentum vector S and the orbital angular momentum vector L are shown in Figure 8-14.

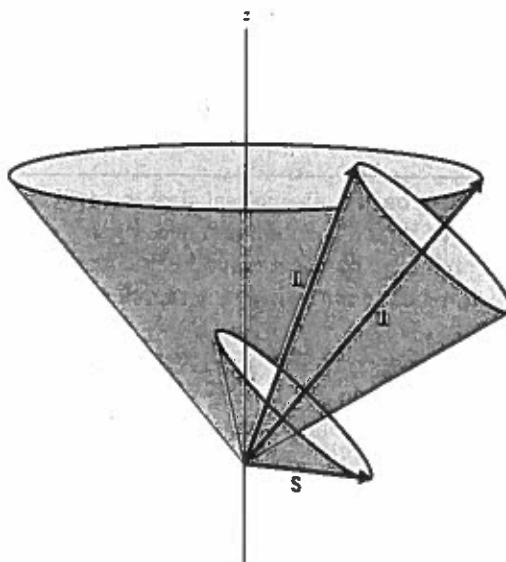FIGURE 8-14 The angular momentum vectors L, S, and J.

The vectors **L** and **S** precess about **J** such that the resultant vector **J** has a fixed magnitude and a fixed z component. The vector **J** precesses about the z axis. The addition of angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, for $\ell = 1$ and $s = 1/2$ is shown in Figure 8-15.

8-6 THE SPIN–ORBITAL INTERACTION: FINE STRUCTURE

If the orbital angular momentum is not zero, then the orbital motion of the electron creates an internal magnetic field ($\mathbf{B}_{int}$). In the rest frame of the electron, the proton appears as a cloud with an angular momentum (**L**). The internal magnetic field is oriented in the same direction as the orbital angular momentum. The portion of electron

magnetic moment (μ_s) due to the electron intrinsic angular momentum (**S**) interacts with this internal magnetic field, causing an energy shift (ΔE). The size of this energy shift is

$$\Delta E = -\mu_s \cdot \mathbf{B}_{int}$$

$$= \frac{e}{2m} g\mathbf{S} \cdot \mathbf{B}_{int} = C\,\mathbf{S} \cdot \mathbf{L}, \qquad (8.89)$$

where C is a positive constant. The amount of energy shift depends on the orientation of the electron intrinsic angular momentum vector (**S**) with respect to **L**. If **S** is aligned with **L**, then the energy shift is positive, whereas if **S** is antialigned with **L**, then the energy shift is negative. Consider the $2p$ states of hydrogen. The energy shift is negative for the case where $\mathbf{S} \cdot \mathbf{L}$ is negative, which cor-
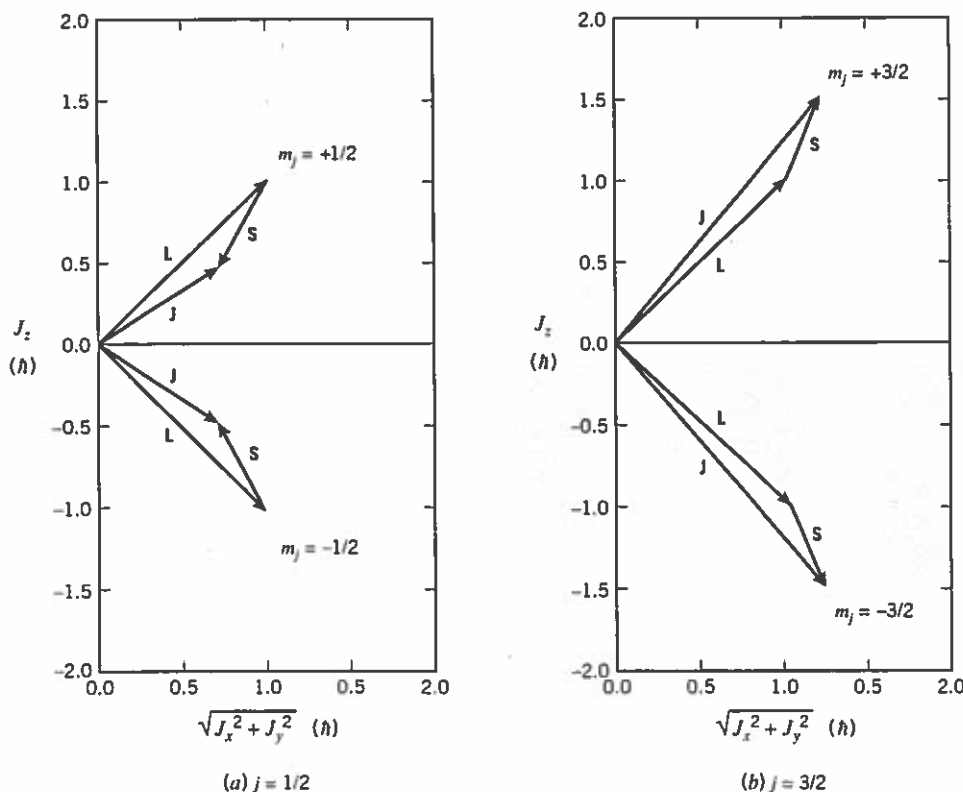

$(a)\ j = 1/2$

$(b)\ j = 3/2$

FIGURE 8-15 The total angular momentum, J=L+S, for a p state electron.
The total angular momentum is the vector sum of the orbital (**L**) and the intrinsic (**S**) angular momentum. For a p state, $\ell = 1$, corresponding to an orbital angular momentum of $\sqrt{2}\hbar$. The electron spin quantum number is $1/2$, corresponding to an intrinsic angular momentum of $\sqrt{3}\hbar/2$. The two possibilities for the total angular momentum quantum number are $(a)\ j = 1/2$ or $(b)\ 3/2$ corresponding to $J = \sqrt{3}\hbar/2$ or $\sqrt{15}\hbar/2$. The smaller value of J corresponds to **L** and **S** being approximately antialigned, and the larger value of J corresponds to **L** and **S** being approximately aligned.

responds to the smaller value of $\mathbf{J}$ ($j = 1/2$). The energy shift is positive for the case where $\mathbf{S} \cdot \mathbf{L}$ is positive, which corresponds to the larger value of $\mathbf{J}$ ($j = 3/2$). Thus, the $2p$ states of hydrogen are split into two states, with the $2p_{3/2}$ state having a larger energy than the $2p_{1/2}$ state. Note that there is no fine-structure splitting of the $s_{1/2}$ state because $L = 0$. The fine structure splitting of hydrogen is shown in Figure 8-16.

The amount of fine-structure splitting is tiny compared to the $2p$ energy level (-3.4 eV). We may make an estimate of the fine-structure energy splitting by using the Bohr model of the atom. The magnetic field due to a current I is given by Ampère's law

$$\oint_L d\mathbf{l} \cdot \mathbf{B} = \frac{4\pi k I}{c^2}. \tag{8.90}$$

(a)

(b)

$$\begin{array}{ccc} & & \\ 656.1 & 656.2 & 656.3 \end{array}$$
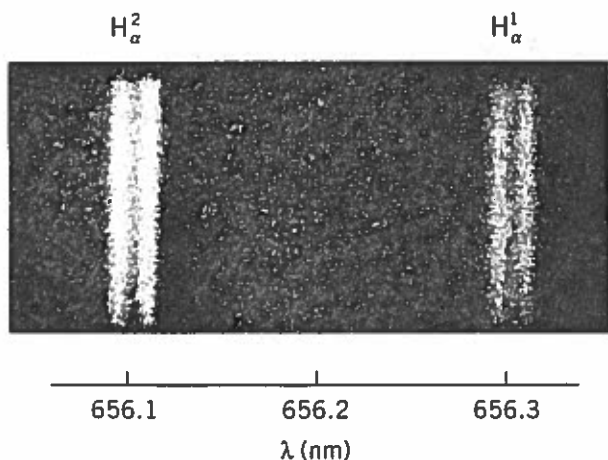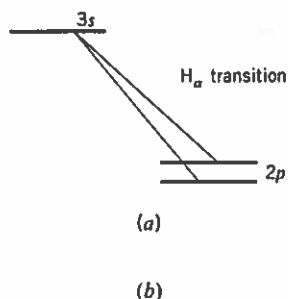
λ (nm)

FIGURE 8-16 The fine structure of hydrogen.
(a) The $2p$ state of hydrogen is split by the spin-orbital interaction. This results in the splitting of the H_α ($3s \rightarrow 2p$) transition into two lines. The order of magnitude of the energy splitting is 1 eV times α^2. (b) Observation of fine-structure splitting in hydrogen (H^1_α) and deuterium (H^2_α). After H. E. White, *Introduction to Atomic Spectra*, McGraw-Hill (1934). Photo by Lewis and Spedding.

The magnetic field at the center of a current loop of radius r is

$$B = \left(\frac{4\pi k}{c^2}\right)\left(\frac{I}{2r}\right). \tag{8.91}$$

The current is equal to the charge times the frequency of revolution

$$I = \frac{ev}{2\pi r}, \tag{8.92}$$

where v is the electron speed. The field at the center of the current loop is

$$\begin{aligned} B &= \left(\frac{4\pi k}{c^2}\right)\left(\frac{I}{2r}\right) \\ &= \left(\frac{4\pi k}{c^2}\right)\left(\frac{ev}{4\pi r^2}\right) = \frac{kev}{c^2 r^2}. \end{aligned} \tag{8.93}$$

An estimate of the energy shift is

$$\begin{aligned} \Delta E &\approx \frac{e}{2m} g \mathbf{S} \cdot \mathbf{B} \approx \left(\frac{e}{2m}\right)(2)\left(\frac{\hbar}{2}\right)\left(\frac{kev}{c^2 r^2}\right) \\ &= \alpha\left(\frac{v}{c}\right)\left(\frac{\hbar^2}{2mr^2}\right), \end{aligned} \tag{8.94}$$

For an electron in the $n = 2$ Bohr orbit, the speed is given by

$$\frac{v}{c} = \frac{\alpha}{2}, \tag{8.95}$$

and the radius of the orbit is

$$r = 4a_0 = \frac{4\hbar c}{\alpha mc^2}. \tag{8.96}$$

Thus, we may write the estimate of the energy shift as

$$\Delta E = \alpha\left(\frac{\alpha}{2}\right)\left(\frac{\hbar^2 \alpha^2 m^2 c^4}{32 m\hbar^2 c^2}\right) \approx \frac{\alpha^4 mc^2}{64}. \tag{8.97}$$

The energy shift is proportional to α^4, whereas the energy level without the shift is proportional to α^2. For this reason, the constant α has historically been referred to as the *fine-structure constant*. The energy shift is ΔE for the $2p_{3/2}$ state and $-\Delta E$ for the $2p_{1/2}$ state. The estimate of the energy splitting between the $2p_{1/2}$ and $2p_{3/2}$ states is

$$E_{2P_{3/2}} - E_{2P_{1/2}} \approx 2\,\Delta E \approx (2)\frac{5.1 \times 10^5 \text{ eV}}{(64)(137)^4}$$

$$\approx 4.5 \times 10^{-5} \text{ eV.} \qquad (8.98)$$

* Challenging

Closer Look at the Energy Shifts

We have made an estimate of the energy splitting (8.98) between the 2p states of hydrogen using the Bohr model. We now reexamine this fine-structure splitting in light of the interpretation of **J** as the total angular momentum. The total angular momentum is a *constant of the motion* in the hydrogen atom. If there was no spin–orbital interaction, then the intrinsic angular momentum **S** and the orbital angular momentum **L** would also both be constants of the motion. The presence of the spin–orbital interaction destroys this because there is a torque acting on both **S** and **L** that changes their directions!

In the rest frame of the electron, the magnetic field due to the motion of the proton may be written in terms of the orbital angular momentum:

$$\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{E}}{c^2} = \frac{ke\mathbf{L}}{mc^2 r^3}, \qquad (8.99)$$

so that the energy shift (8.89) for a level with principle quantum number n may be written in terms of the average value of **S** • **L**:

$$\Delta E_n = -\langle \mu \cdot \mathbf{B} \rangle = \left\langle \left(\frac{e}{2m}\right)(2\mathbf{S}) \cdot \left(\frac{ke\mathbf{L}}{mc^2 r^3}\right)\right\rangle$$

$$= \frac{ke^2}{m^2 c^2}\left\langle \frac{\mathbf{S} \cdot \mathbf{L}}{r^3}\right\rangle. \qquad (8.100)$$

Our expression for ΔE_n is not exact because there are relativistic corrections. We shall first proceed with the evaluation of ΔE_n and return later to these relativistic corrections.

The spin–orbital interaction causes a change or *perturbation* in the wave functions; however, the interaction causes such a small shift in the energy levels (8.98) that we may use the unperturbed wave functions to calculate the average of **S** • **L**/r^3. Therefore,

$$\left\langle \frac{\mathbf{S} \cdot \mathbf{L}}{r^3}\right\rangle = \iiint\limits_V dV\ \psi^* \frac{\mathbf{S} \cdot \mathbf{L}}{r^3}\psi. \qquad (8.101)$$

Since all of the radial dependence of the wave function is contained in $R_{n,\ell}(r)$ and the angular momentum part **S** • **L** does not depend on r, we have

$$\left\langle \frac{\mathbf{S} \cdot \mathbf{L}}{r^3}\right\rangle = \left[\int_0^\infty dr\ r^2 R_{n,\ell}^2(r)\frac{1}{r^3}\right]$$

$$\times \left[\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\ P_{\ell,m_\ell}(\theta)e^{-im_\ell\phi}\right.$$

$$\left. \mathbf{S} \cdot \mathbf{L} P_{\ell,m_\ell}(\theta)e^{im_\ell\phi}\right]. \qquad (8.102)$$

The average of **S** • **L**/r^3 is $1/r^3$ averaged over the radial part of the wave function and **S** • **L** averaged over the angular part. The average value of $1/r^3$ depends on the quantum numbers n and ℓ. The evaluation of the average of $1/r^3$ is straightforward although somewhat tedious. The result is

$$\left\langle \frac{1}{r^3}\right\rangle = \frac{2}{a_0^3 n^3 \ell(\ell+1)(2\ell+1)}. \qquad (8.103)$$

To compute the average of **S** • **L** over the angular part we write out the square of the total angular momentum vector:

$$J^2 = \mathbf{J} \cdot \mathbf{J} = (\mathbf{L}+\mathbf{S}) \cdot (\mathbf{L}+\mathbf{S})$$

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

$$= L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}. \qquad (8.104)$$

Therefore,

$$\langle \mathbf{S} \cdot \mathbf{L}\rangle = \frac{1}{2}\langle J^2 - L^2 - S^2\rangle. \qquad (8.105)$$

The average value of J^2, L^2, and S^2 are determined by the quantum numbers j, ℓ, and s so that

$$\langle \mathbf{S} \cdot \mathbf{L}\rangle$$

$$= \frac{j(j+1)\hbar^2 - \ell(\ell+1)\hbar^2 - s(s+1)\hbar^2}{2}. \qquad (8.106)$$

The value of s is 1/2 and there are two possible values for j: $\ell+1/2$ or $\ell-1/2$ unless $\ell = 0$ in which case $j = 1/2$. Therefore, the two possible values of $\langle \mathbf{S} \cdot \mathbf{L}\rangle$ are for $j = \ell + 1/2$,

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \frac{\ell \hbar^2}{2}, \tag{8.107}$$

and for $j = \ell - 1/2$,

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = -\frac{(\ell+1)\hbar^2}{2} \tag{8.108}$$

provided that ℓ is not zero. Putting these results together, for $j = \ell + 1/2$ we have

$$\left\langle \frac{\mathbf{S} \cdot \mathbf{L}}{r^3} \right\rangle = \left[\frac{2}{a_0{}^3 n^3 \ell(\ell+1)(2\ell+1)} \right] \left[\frac{\ell \hbar^2}{2} \right]$$

$$= \frac{\hbar^2}{a_0{}^3 n^3 (\ell+1)(2\ell+1)}, \tag{8.109}$$

and for $j = \ell - 1/2$ we have

$$\left\langle \frac{\mathbf{S} \cdot \mathbf{L}}{r^3} \right\rangle$$

$$= \left[\frac{2}{a_0{}^3 n^3 \ell(\ell+1)(2\ell+1)} \right] \left[-\frac{(\ell+1)\hbar^2}{2} \right]$$

$$= -\frac{\hbar^2}{a_0{}^3 n^3 \ell(2\ell+1)}, \tag{8.110}$$

provided that ℓ is not zero. Using $E_n = -mc^2\alpha^2/2n^2$, the energy shift (8.100) for $j = \ell + 1/2$ is

$$\Delta E_n = \frac{ke^2 \hbar^2}{m^2 c^2 a_0{}^3 n^3 (\ell+1)(2\ell+1)}$$

$$= \frac{\alpha^4 mc^2}{n^3 (\ell+1)(2\ell+1)}$$

$$= -\frac{2 E_n \alpha^2}{n(\ell+1)(2\ell+1)}, \tag{8.111}$$

and for $j = \ell - 1/2$ is

$$\Delta E_n = -\frac{ke^2 \hbar^2}{m^2 c^2 a_0{}^3 n^3 \ell(2\ell+1)}$$

$$= -\frac{\alpha^4 mc^2}{n^3 \ell(2\ell+1)} = \frac{2 E_n \alpha^2}{n\ell(2\ell+1)}, \tag{8.112}$$

provided that ℓ is not zero.

We now discuss the relativistic corrections to the energy shifts. The first is due to the fact that the orbital time calculated in the rest frame of the electron is not equal to the orbital time calculated in the rest frame of the proton due to time dilation. The angular frequency in the rest frame of the electron is L/mr^2. The angular frequency in the rest frame of the proton is $L/\gamma mr^2$, where $\gamma = (1-v^2/c^2)^{-1/2}$. The difference in the two angular frequencies (ω_T) is

$$\omega_T = \frac{L}{\gamma mr^2} - \frac{L}{mr^2} = \frac{L}{mr^2} \left(\frac{1}{\sqrt{1-\dfrac{v^2}{c^2}}} - 1 \right)$$

$$\approx \frac{Lv^2}{2mr^2c^2} = \frac{ke^2 L}{2m^2c^2r^3}, \tag{8.113}$$

where we have used $mv^2/r = ke^2/r^2$ to eliminate v. Therefore, the angular momentum vector precesses at the frequency ω_T, a phenomenon called *Thomas precession*. Thomas precession causes an energy shift that has the opposite sign of ΔE_n (8.100). The magnitude of the shift can be obtained by examining the Larmor precession frequency of $\mathbf{S}$ in an external field $\mathbf{B}$, which is

$$\omega_L = -g\frac{eB}{2m} = -\frac{eB}{m} = -\frac{ke^2 L}{m^2 c^2 r^3}. \tag{8.114}$$

We see that ω_T is one-half as large as ω_L so that the energy shift due to Thomas precession (ΔE_T) is

$$\Delta E_T = -\frac{\Delta E_n}{2}. \tag{8.115}$$

A second type of relativistic correction arises because we have approximated the kinetic energy as $p^2/2m$. The expression for the kinetic energy is

$$E_k = \sqrt{\left(mc^2\right)^2 + \left(pc\right)^2} - mc^2$$

$$\approx \frac{(pc)^2}{2mc^2} - \frac{(pc)^4}{8\left(mc^2\right)^3}. \tag{8.116}$$

Since the order of magnitude of the electron speed is αc, the correction will be proportional to α^4, that is, it is the same order of magnitude as ΔE_n. We need to calculate the average value of the correction to the kinetic energy, which may be written

$$\Delta E_r = \left\langle \frac{(pc)^4}{8(mc^2)^3} \right\rangle$$

$$= \frac{1}{2mc^2} \left\langle \left(\frac{p^2}{2m}\right)^2 \right\rangle = \frac{\left\langle (E_n - V)^2 \right\rangle}{2mc^2}$$

$$= \frac{E_n^2 + \left\langle V^2 \right\rangle - 2E_n \left\langle V \right\rangle}{2mc^2}. \qquad (8.117)$$

This calculation is straightforward:

$$\Delta E_r = \frac{E_n^2}{2mc^2}$$

$$+ \frac{1}{2mc^2} \iiint_V dV \psi^* \left(-\frac{ke^2}{r}\right)^2 \psi$$

$$- \frac{E_n}{mc^2} \iiint_V dV \psi^* \left(-\frac{ke^2}{r}\right) \psi. \qquad (8.118)$$

The result depends on n and ℓ:

$$\Delta E_r = -\frac{\alpha^2 E_n}{4n^2}\left(3 - \frac{8n}{2\ell+1}\right). \qquad (8.119)$$

The complete first-order corrections to the energy level shifts are

$$\Delta E_{tot} = \Delta E_n + \Delta E_T + \Delta E_r$$

$$= -\frac{\alpha^2 E_n}{4n^2}\left(3 - \frac{8n}{2j+1}\right), \qquad (8.120)$$

which is valid for both $j = \ell+1/2$ and $j = \ell-1/2$ (see problem 36). For the ground state of hydrogen, $n = 1$ and $j = 1/2$ and the energy shift is

$$\Delta E_{1s_{1/2}} = -\frac{\alpha^2 (13.6\,\text{eV})}{4} = -1.8 \times 10^{-4}\ \text{eV}. \qquad (8.121)$$

For the first excited state, $n = 2$ and $j = 1/2$ or $j = 3/2$. The energy shifts are

$$\Delta E_{2s_{1/2}} = \Delta E_{2p_{1/2}} = -\frac{5\alpha^2 (13.6\,\text{eV})}{64}$$

$$= -5.6 \times 10^{-5}\ \text{eV}, \qquad (8.122)$$

and

$$\Delta E_{2p_{3/2}} = -\frac{\alpha^2 (13.6\,\text{eV})}{64} = -1.1 \times 10^{-5}\ \text{eV}. \qquad (8.123)$$

The energy splitting between the $2p_{3/2}$ and $2p_{1/2}$ states is

$$\Delta E_{2p_{3/2}} - \Delta E_{2p_{1/2}} = 4.5 \times 10^{-5}\ \text{eV}. \qquad (8.124)$$

These energy shifts are summarized in Figure 8-17. *

Hyperfine Structure

The proton also has an intrinsic angular momentum. We have seen the contribution of the proton intrinsic angular momentum to the electron–proton scattering cross section (see Chapter 6). There is also an interaction of the electron intrinsic angular momentum with the proton intrinsic angular momentum in the hydrogen atom. This interaction produces a *hyperfine structure* in the ground state of hydrogen ($1s_{1/2}$ state) because the energy of the state in which the electron has $m_j = 1/2$ has a slightly higher energy than the state in which the electron has $m_j = -1/2$. When hydrogen makes the transition between the two states, the wavelength of the emitted radiation is 0.21 meter. Detection of radiation at a wavelength of 0.21 meter is used as a signature for the presence of hydrogen in outer space.

8-7 ATOMIC TRANSITIONS AND SELECTION RULES

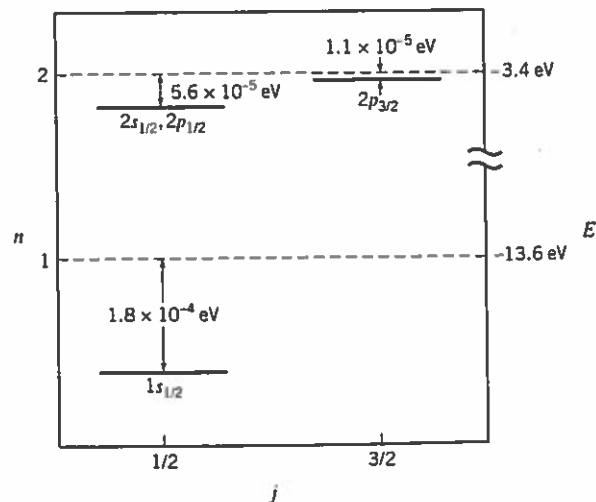The photon has an intrinsic angular momentum characterized by the quantum number,

FIGURE 8-17 The fine structure of hydrogen.

$$s = 1. \qquad (8.125)$$

There are only two possibilities for the quantum number m_s: $m_s = +1$ or $m_s = -1$, corresponding to the two photon polarizations. (The value $m_s = 0$ is not allowed by special relativity; this is related to the fact that there exists no frame where the photon is at rest.) Angular momentum conservation places restrictions on the allowed atomic transitions involving the absorption or emission of a photon. These restrictions may be expressed in terms of the allowed changes in the quantum numbers of the electron. The restrictions are called *selection rules*. If a selection rule is not satisfied, then the transition is either forbidden or suppressed.

The selection rule on the electron orbital angular momentum is that ℓ must change by one unit:

$$\Delta \ell = \pm 1. \qquad (8.126)$$

The change in the magnetic quantum number must be

$$\Delta m_\ell = 0 \quad \text{or} \quad \pm 1. \qquad (8.127)$$

In addition, the electron intrinsic angular momentum magnetic quantum number (m_s) must not change

$$\Delta m_s = 0, \qquad (8.128)$$

and the change in the electron total angular momentum quantum number (j) must be

$$\Delta j = 0 \quad \text{or} \quad \pm 1, \qquad (8.129)$$

with the restriction that the transition $j = 0 \rightarrow j = 0$ is forbidden.

8-8 THE ZEEMAN EFFECT

If a hydrogen atom is placed in an external magnetic field, the magnetic moment of the electron in the atom will interact with the field causing an energy shift:

$$\Delta E = -\mu \cdot \mathbf{B}. \qquad (8.130)$$

When the external magnetic field is much larger than the fields inside the atom, this energy shift (8.130) will dominate over the spin–orbital interaction. As usual, we choose the z direction to be direction of the field, so that

$$\Delta E = -\mu_z B_z = \frac{e}{2m}\left(L_z + 2S_z\right)B_z$$

$$= \frac{e\hbar}{2m}\left(m_\ell + 2m_s\right)B_z. \qquad (8.131)$$

The splitting of energy levels in an external magnetic field was first observed by Pieter Zeeman in 1896 and is known as the *Zeeman effect*. The Zeeman effect for strong fields was studied by F. Paschen and E. Back and is referred to as the *Paschen-Back effect*. The Paschen-Back effect for hydrogen is illustrated in Figure 8-18. The p states are split into five states, and the s states are split into two states. The $s \rightarrow p$ transitions are split into two triplets of lines according to the selection rule $\Delta m_s = 0$. The triplet from the hydrogen H_α transition measured by Paschen and Back is shown in Figure 8-18c. The Zeeman effect is discussed further in Chapter 9.

EXAMPLE 8-11

Into how many states does the $3d$ state of hydrogen divide in a strong external magnetic field?

SOLUTION:

The value of the orbital angular momentum quantum number is

$$\ell = 2.$$

The possible values of m_ℓ are $-2, -1, 0, 1$, and 2. The possible values of $2m_s$ are -1, and 1. The possible values of $(m_\ell + 2m_s)$ are $-3, -2, -1, 0, 1, 2$, and 3. Therefore, the $3d$ state is split into 7 states in the strong external magnetic field. ∎

EXAMPLE 8-12

Calculate the magnetic field strength needed to make an upward fractional energy shift ($\Delta E/E$) of 10^{-4} on the $3d_{5/2}$ state of hydrogen.

SOLUTION:

The energy of the $3d$ state is

$$E_3 = \frac{-13.6\,\text{eV}}{9}.$$

The energy shift is

$$\Delta E = \frac{\left(10^{-4}\right)(13.6\,\text{eV})}{9}.$$

The quantum numbers of the electron are $\ell = 2$, $s = 1/2$ and $j = 5/2$. The maximum shift will occur when $m_j = 5/2$ corresponding to $m_\ell = 2$ and $m_s = 1/2$, so

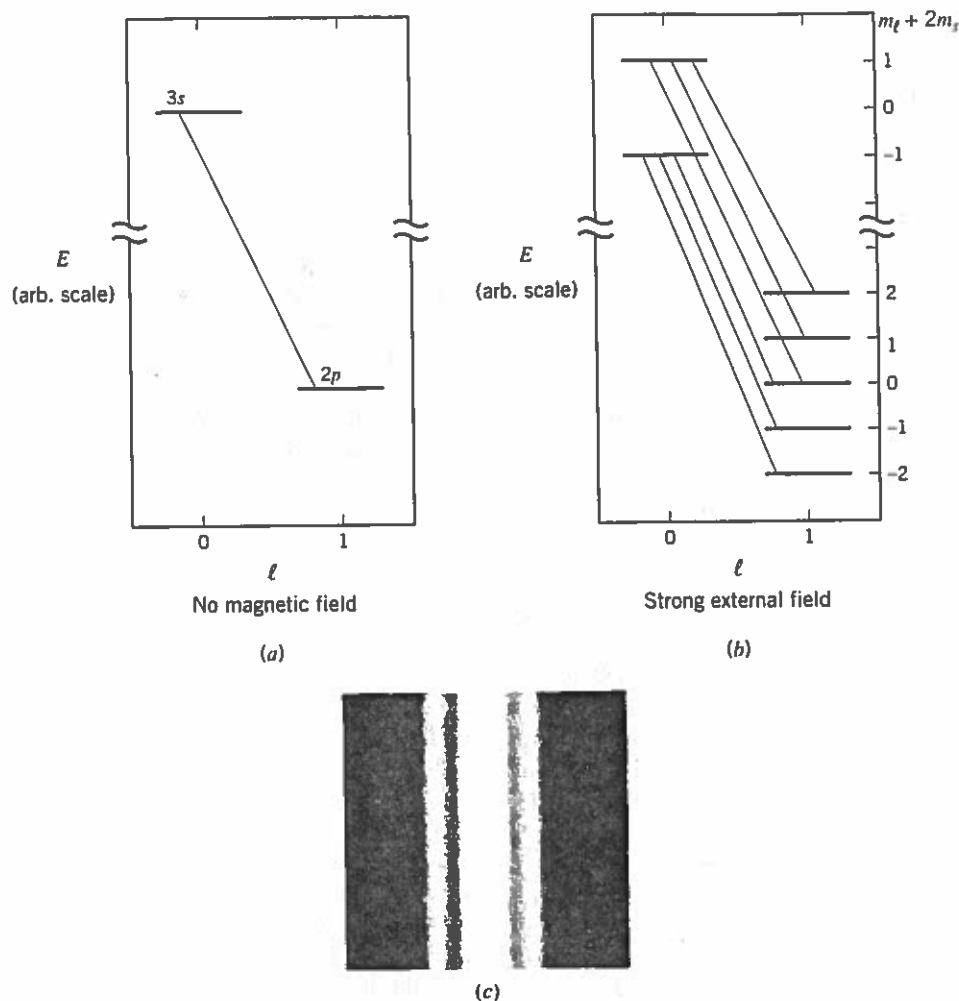$$m_\ell + 2m_s = 3.$$

The magnetic field is

FIGURE 8-18 The Paschen-Back effect.
(a) The 2p and 3s states of hydrogen with no external magnetic field, neglecting fine structure. (b) In a strong external magnetic field (compared to the internal magnetic field), the energy shift of each state is proportional to $m_l + 2m_s$, which splits the the 2p state into 5 states and the 3s state into 2 states. For the 3s $\rightarrow$ 2p transitions (H$_\alpha$) , there is a selection rule $\Delta m_s = 0$ corresponding to the 6 transitions shown. There are only 3 unique photon energies. (c) First observation of the hydrogen H$_\alpha$ transition in a strong magnetic field showing 3 photon lines. From F. Paschen and E. Back *Ann. d. Phys.* **39**, 897 (1912).

$$B = \frac{\Delta E}{3\mu_B} = \frac{\left(10^{-4}\right)\left(\dfrac{3.6\,\text{eV}}{9}\right)}{(3)\left(5.79 \times 10^{-5}\ \text{eV/T}\right)} \approx 0.23\,\text{T}. \quad \blacksquare$$

*** Challenging**

8-9 THE LAMB SHIFT

The electron in a hydrogen atom interacts with itself by emission and absorption of photons as indicated in Figure 8-19. The effect of this self-interaction is to cause a "smearing" of the electron over a distance scale of approximately 0.1 fm. This effect is observable when

the electron is very close to the proton. In this case, the "smeared" electron has a slightly weaker attraction to the proton compared to an "unsmeared" electron. This means that a state where the electron has a higher probability of being near the proton will have a slightly higher energy. (It will take slightly less energy to remove the electron because the force is weaker.) Therefore, the hydrogen $2s_{1/2}$ state has a slightly higher energy than the $2p_{1/2}$ state (see Figure 8-3). This energy shift due to the self-interaction of the electron is called the *Lamb shift*, after Willis Lamb, who first accurately measured it in 1951. The magnitude of the Lamb shift can be calculated to many significant figures, and comparison with measurement of the energy level differences provides the most powerful quantitative test of the quantum theory of electrodynamics. It proves that the picture of the electron as continually emitting and absorbing photons is the correct one!

An extremely stringent test of quantum electrodynamics comes from the accurate calculation of the difference in energy of the $2s_{1/2}$ and $2p_{1/2}$ levels in the hydrogen atom. Part of the energy difference arises from the self interaction of the electron causing a deviation of g from 2. We have seen that the spin–orbital correction to the energy depends on the total angular momentum
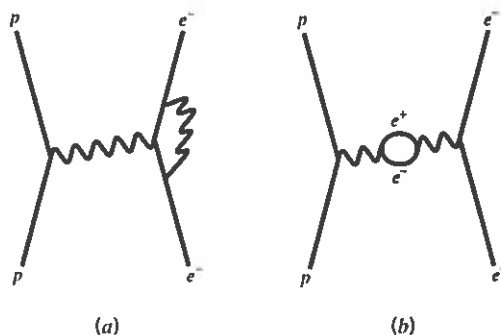

(a)   (b)

FIGURE 8-19 Feynman diagrams for the electron self-interaction.
Two diagrams (*a*) and (*b*) with amplitude of order α^2 are shown. The electron interacts with itself by emitting and absorbing photons, causing the electron g factor to differ slightly from 2. Interations of the type shown in diagram (*b*) cause a small amount of charge screening of the proton from the electron, resulting in a slightly weaker force when the electron is in the immediate vicinity of the proton. Because the wave function of the $2s$ state is finite at $r = 0$ compared to the wave function of the $2p$ state, which vanishes at $r = 0$, the force on an electron in the $2s$ state is smaller than an electron in the $2p$ state, and the energy of the $2s$ state is slightly larger than the energy of the $2p$ state.

quantum number (j). In the $2s_{1/2}$ state, $j = 1/2$ comes from the electron intrinsic angular momentum, whereas in the $2p_{1/2}$ state, $j = 1/2$ comes from one unit of orbital angular momentum minus one-half unit of intrinsic angular momentum. If g is exactly equal to 2, then the z component of electron magnetic moment due to intrinsic angular momentum is exactly equal to the z component of electron magnetic moment due to one unit of orbital angular momentum. For $g = 2$ the energies of the states of fixed n depend only on the total angular momentum quantum number j and not the addition of ℓ and s producing j.

The first-order correction to g (in powers of α) is calculated in quantum electrodynamics to be

$$g \approx 2 + \frac{\alpha}{\pi}, \tag{8.133}$$

or

$$\frac{g-2}{2} \approx \frac{\alpha}{2\pi}. \tag{8.134}$$

Thus, g is slightly smaller than 2 and the $2p_{1/2}$ state is slightly smaller in energy than the $2s_{1/2}$ state.

The difference in energy levels was first measured by Willis E. Lamb. The energy shift is indicated in Figure 8-20. In his experiment, Lamb formed a beam of hydrogen atoms in the $2s_{1/2}$ state. These atoms cannot make transitions to the $1s_{1/2}$ state because of the selection rule, $\Delta\ell = \pm 1$. (The electromagnetic classical analogy is that a spherically symmetric charge and current distribution cannot radiate.) The atoms can make transitions to the $2p$ levels, and from there to the $1s$ ground state. Lamb put his hydrogen atoms in a magnetic field so that the energy levels were split by the Zeeman effect. He then exposed the atoms to radio waves of a fixed frequency (2395 MHz) and varied the magnetic field while measuring the transitions

$$2s \rightarrow 2p \rightarrow 1s. \tag{8.135}$$

Lamb used his data to determine the zero magnetic field energy separation of the $2s_{1/2}$ and $2p_{1/2}$ states. Expressed as the frequency of a transition photon, this splitting is

$$f = 1057\,\text{MHz}, \tag{8.136}$$

or

$$\Delta E = hf = \left(4.136 \times 10^{-15}\,\text{eV}\cdot\text{s}\right)\left(1.057 \times 10^{9}\,\text{s}^{-1}\right)$$
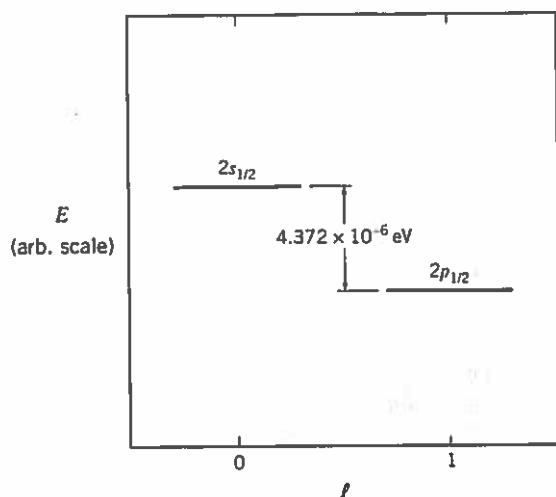$$= 4.372 \times 10^{-6}\,\text{eV}. \tag{8.137}$$

FIGURE 8-20 The Lamb shift in hydrogen.
The spin–orbital interaction gives corrections to the energy levels in the hydrogen atom that depend only on the quantum numbers n and j. The $2s_{1/2}$ and the $2p_{1/2}$ states of hydrogen have the same energy after applying this correction. The gyromagnetic factor (g) of the electron is slightly greater than 2 so that a component of spin angular momentum of $g\hbar/2$ contributes more to the electron magnetic moment than a component of orbital angular momentum $\hbar$. This causes the $2s_{1/2}$ state to have a slightly higher energy than the $2p_{1/2}$ state. The factor g can be calculated to many decimal places so that the measurement of the energy difference of the $2s_{1/2}$ and $2p_{1/2}$ states provides a precision test of quantum electrodynamics.

This energy difference is about 1/10 as large as the energy splitting between the $2p$ states due to the spin–orbital interaction. The Lamb shift has been measured to many decimal places, and comparison with higher order calculations of quantum electrodynamics shows perfect agreement!   *

CHAPTER 8: PHYSICS SUMMARY

- The solution to the Schrödinger equation with a Coulomb potential energy gives a quantitatively correct description of the energy levels and electron probability distributions of the hydrogen atom (apart from small corrections due to the effects of intrinsic angular momentum and relativity).

- The boundary conditions on the hydrogen atom wave functions lead to quantization of energy (E), angular momentum (L), and the projection of angu-

lar momentum in any given direction (L_z). The quantization conditions are:

$$E_n = -\frac{13.6\,\text{eV}}{n^2},$$

where n is a positive integer (1, 2, 3, ...),

$$L = \sqrt{\ell(\ell+1)}\,\hbar,$$

where ℓ is an integer less than n (0, 1, 2, 3, ... $n-1$), and

$$L_z = m_\ell \hbar,$$

where m_ℓ is an integer from $-\ell$ to ℓ.

- A complete description of the physics of the hydrogen atom must include the intrinsic angular momentum of the electron, which has a fixed value of

$$S = \frac{\sqrt{3}\hbar}{2},$$

corresponding to a spin quantum number $s = 1/2$. The component of intrinsic angular momentum in any given direction (S_z) is quantized ($S_z = \hbar/2$ or $S_z = -\hbar/2$) corresponding to $m_s = 1/2$ or $m_s = -1/2$.

- The total angular momentum of an atomic electron is the vector sum of its orbital angular momentum and its intrinsic angular momentum:

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

- The notation used for atomic states is nl_j, where n and j are the principal and total angular momentum quantum numbers and l is a letter (s, p, d, or f) that represents the value of the orbital angular momentum quantum number: s for $\ell = 0$, p for $\ell = 1$, d for $\ell = 2$, and f for $\ell = 3$.

- The magnetic moment of an electron in an atom is

$$\mu = -\frac{e}{2m}(\mathbf{L} + g\mathbf{S}),$$

where the gyromagnetic factor (g) of the electron is very nearly equal to 2.

- There is a contribution to the fine-structure splitting of p states in atoms caused by the interaction of the electron spin with the internal magnetic field due to the electron orbital angular momentum. The order of magnitude of the splitting is α^2 times the energy of the state.