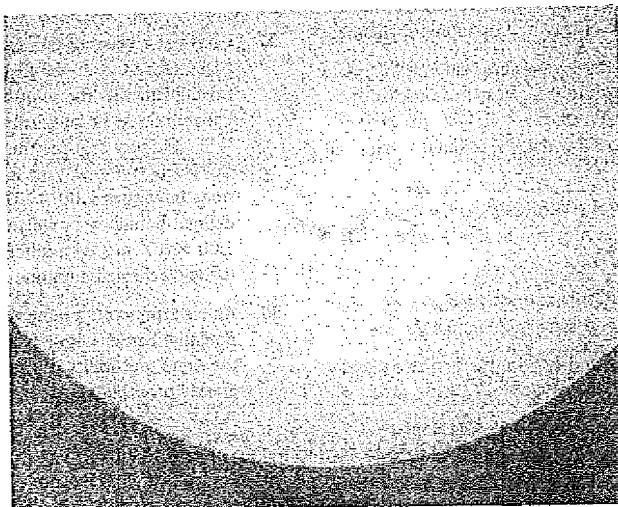


## CHAPTER 6

# Quantum Theory of the Hydrogen Atom



The strong magnetic fields associated with sunspots were detected by means of the Zeeman effect. Sunspots appear dark because they are cooler than the rest of the solar surface, although quite hot themselves. The number of spots varies in an 11-year cycle, and a number of terrestrial phenomena follow this cycle.

- 6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM
  - Symmetry suggests spherical polar coordinates
- 6.2 SEPARATION OF VARIABLES
  - A differential equation for each variable
- 6.3 QUANTUM NUMBERS
  - Three dimensions, three quantum numbers
- 6.4 PRINCIPAL QUANTUM NUMBER
  - Quantization of energy
- 6.5 ORBITAL QUANTUM NUMBER
  - Quantization of angular-momentum magnitude
- 6.6 MAGNETIC QUANTUM NUMBER
  - Quantization of angular-momentum direction

- 6.7 ELECTRON PROBABILITY DENSITY
  - No definite orbits
- 6.8 RADIATIVE TRANSITIONS
  - What happens when an electron goes from one state to another
- 6.9 SELECTION RULES
  - Some transitions are more likely to occur than others
- 6.10 ZEEMAN EFFECT
  - How atoms interact with a magnetic field

The first problem that Schrödinger tackled with his new wave equation was that of the hydrogen atom. He found the mathematics heavy going, but was rewarded by the discovery of how naturally quantization occurs in wave mechanics: "It has its basis in the requirement that a certain spatial function be finite and single-valued." In this chapter we shall see how Schrödinger's quantum theory of the hydrogen atom achieves its results, and how these results can be interpreted in terms of familiar concepts.

## 6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM

*Symmetry suggests spherical polar coordinates*

A hydrogen atom consists of a proton, a particle of electric charge  $+e$ , and an electron, a particle of charge  $-e$  which is 1836 times lighter than the proton. For the sake of convenience we shall consider the proton to be stationary, with the electron moving about in its vicinity but prevented from escaping by the proton's electric field. As in the Bohr theory, the correction for proton motion is simply a matter of replacing the electron mass  $m$  by the reduced mass  $m'$  given by Eq. (4.22).

Schrödinger's equation for the electron in three dimensions, which is what we must use for the hydrogen atom, is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0 \quad (6.1)$$

The potential energy  $U$  here is the electric potential energy

$$\text{Electric potential energy} \quad U = -\frac{e^2}{4\pi\epsilon_0 r} \quad (6.2)$$

of a charge  $-e$  when it is the distance  $r$  from another charge  $+e$ .

Since  $U$  is a function of  $r$  rather than of  $x, y, z$ , we cannot substitute Eq. (6.2) directly into Eq. (6.1). There are two alternatives. One is to express  $U$  in terms of the cartesian coordinates  $x, y, z$  by replacing  $r$  by  $\sqrt{x^2 + y^2 + z^2}$ . The other is to express Schrödinger's equation in terms of the spherical polar coordinates  $r, \theta, \phi$  defined in Fig. 6.1. Owing to the symmetry of the physical situation, doing the latter is appropriate here, as we shall see in Sec. 6.2.

The spherical polar coordinates  $r, \theta, \phi$  of the point  $P$  shown in Fig. 6.1 have the following interpretations:

Spherical polar coordinates  $r = \text{length of radius vector from origin } O \text{ to point } P$   
 $= \sqrt{x^2 + y^2 + z^2}$

$\theta = \text{angle between radius vector and } +z \text{ axis}$

$= \text{zenith angle}$

$$= \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$= \cos^{-1} \frac{z}{r}$$

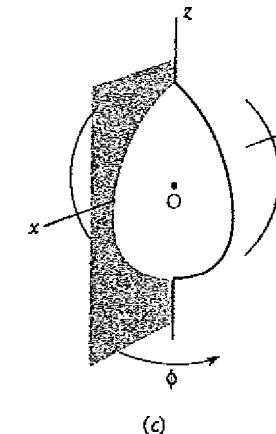
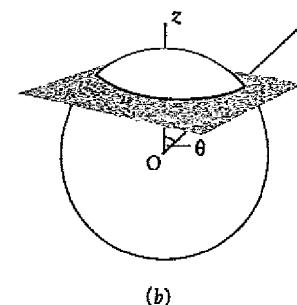
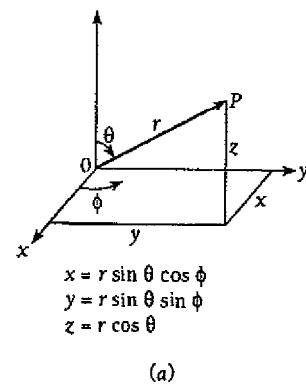


Figure 6.1 (a) Spherical polar coordinates. (b) A line of constant zenith angle  $\theta$  on a sphere is a circle whose plane is perpendicular to the  $z$  axis. (c) A line of constant azimuthal angle  $\phi$  is a circle whose plane includes the  $z$  axis.

$$\begin{aligned}
 \phi &= \text{angle between the projection of the radius vector in the } xy \\
 &\text{plane and the } +x \text{ axis, measured in the direction shown} \\
 &= \text{azimuth angle} \\
 &= \tan^{-1} \frac{y}{x}
 \end{aligned}$$

On the surface of a sphere whose center is at  $O$ , lines of constant zenith angle  $\theta$  are like parallels of latitude on a globe (but we note that the value of  $\theta$  of a point is not the same as its latitude;  $\theta = 90^\circ$  at the equator, for instance, but the latitude of the equator is  $0^\circ$ ). Lines of constant azimuth angle  $\phi$  are like meridians of longitude (here the definitions coincide if the axis of the globe is taken as the  $+z$  axis and the  $+x$  axis is at  $\phi = 0^\circ$ ).

In spherical polar coordinates Schrödinger's equation is written

$$\begin{aligned}
 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) \\
 + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (6.3)
 \end{aligned}$$

Substituting Eq. (6.2) for the potential energy  $U$  and multiplying the entire equation by  $r^2 \sin^2 \theta$ , we obtain

$$\begin{aligned}
 \text{Hydrogen atom} \quad & \sin^2 \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) \\
 & + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0 \quad (6.4)
 \end{aligned}$$

Equation (6.4) is the partial differential equation for the wave function  $\psi$  of the electron in a hydrogen atom. Together with the various conditions  $\psi$  must obey, namely that  $\psi$  be normalizable and that  $\psi$  and its derivatives be continuous and single-valued at each point  $r, \theta, \phi$ , this equation completely specifies the behavior of the electron. In order to see exactly what this behavior is, we must solve Eq. (6.4) for  $\psi$ .

When Eq. (6.4) is solved, it turns out that three quantum numbers are required to describe the electron in a hydrogen atom, in place of the single quantum number of the Bohr theory. (In Chap. 7 we shall find that a fourth quantum number is needed to describe the spin of the electron.) In the Bohr model, the electron's motion is basically one-dimensional, since the only quantity that varies as it moves is its position in a definite orbit. One quantum number is enough to specify the state of such an electron, just as one quantum number is enough to specify the state of a particle in a one-dimensional box.

A particle in a three-dimensional box needs three quantum numbers for its description, since there are now three sets of boundary conditions that the particle's wave function  $\psi$  must obey:  $\psi$  must be 0 at the walls of the box in the  $x$ ,  $y$ , and  $z$  directions independently. In a hydrogen atom the electron's motion is restricted by the inverse-square electric field of the nucleus instead of by the walls of a box, but the electron is

nevertheless free to move in three dimensions, and it is accordingly not surprising that three quantum numbers govern its wave function also.

## 6.2 SEPARATION OF VARIABLES

*A differential equation for each variable*

The advantage of writing Schrödinger's equation in spherical polar coordinates for the problem of the hydrogen atom is that in this form it may be separated into three independent equations, each involving only a single coordinate. Such a separation is possible here because the wave function  $\psi(r, \theta, \phi)$  has the form of a product of three different functions:  $R(r)$ , which depends on  $r$  alone;  $\Theta(\theta)$  which depends on  $\theta$  alone; and  $\Phi(\phi)$ , which depends on  $\phi$  alone. Of course, we do not really know that this separation is possible yet, but we can proceed by assuming that

$$\text{Hydrogen-atom} \quad \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (6.5)$$

wave function

and then seeing if it leads to the desired separation. The function  $R(r)$  describes how the wave function  $\psi$  of the electron varies along a radius vector from the nucleus, with  $\theta$  and  $\phi$  constant. The function  $\Theta(\theta)$  describes how  $\psi$  varies with zenith angle  $\theta$  along a meridian on a sphere centered at the nucleus, with  $r$  and  $\phi$  constant (Fig. 6.1c). The function  $\Phi(\phi)$  describes how  $\psi$  varies with azimuth angle  $\phi$  along a parallel on a sphere centered at the nucleus, with  $r$  and  $\theta$  constant (Fig. 6.1b).

From Eq. (6.5), which we may write more simply as

$$\psi = R\Theta\Phi$$

we see that

$$\begin{aligned}\frac{\partial\psi}{\partial r} &= \Theta\Phi \frac{\partial R}{\partial r} = \Theta\Phi \frac{dR}{dr} \\ \frac{\partial\psi}{\partial\theta} &= R\Phi \frac{\partial\Theta}{\partial\theta} = R\Phi \frac{d\Theta}{d\theta} \\ \frac{\partial^2\psi}{\partial\phi^2} &= R\Theta \frac{\partial^2\Phi}{\partial\phi^2} = R\Theta \frac{d^2\Phi}{d\phi^2}\end{aligned}$$

The change from partial derivatives to ordinary derivatives can be made because we are assuming that each of the functions  $R$ ,  $\Theta$ , and  $\Phi$  depends only on the respective variables  $r$ ,  $\theta$ , and  $\phi$ .

When we substitute  $R\Theta\Phi$  for  $\psi$  in Schrödinger's equation for the hydrogen atom and divide the entire equation by  $R\Theta\Phi$ , we find that

$$\begin{aligned}\frac{\sin^2\theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} \\ + \frac{2mr^2 \sin^2\theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0 \quad (6.6)\end{aligned}$$

The third term of Eq. (6.6) is a function of azimuth angle  $\phi$  only, whereas the other terms are functions of  $r$  and  $\theta$  only.

Let us rearrange Eq. (6.6) to read

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad (6.7)$$

This equation can be correct only if both sides of it are equal to the same constant, since they are functions of different variables. As we shall see, it is convenient to call this constant  $m_l^2$ . The differential equation for the function  $\phi$  is therefore

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2 \quad (6.8)$$

Next we substitute  $m_l^2$  for the right-hand side of Eq. (6.7), divide the entire equation by  $\sin^2 \theta$ , and rearrange the various terms, which yields

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \quad (6.9)$$

Again we have an equation in which different variables appear on each side, requiring that both sides be equal to the same constant. This constant is called  $l(l+1)$ , once more for reasons that will be apparent later. The equations for the functions  $\Theta$  and  $R$  are therefore

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) = l(l+1) \quad (6.10)$$

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = l(l+1) \quad (6.11)$$

Equations (6.8), (6.10), and (6.11) are usually written

$$\text{Equation for } \Phi \quad \frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0 \quad (6.12)$$

$$\text{Equation for } \Theta \quad \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (6.13)$$

$$\text{Equation for } R \quad \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$$

Each of these is an ordinary differential equation for a single function of a single variable. Only the equation for  $R$  depends on the potential energy  $U(r)$ .

We have therefore accomplished our task of simplifying Schrödinger's equation for the hydrogen atom, which began as a partial differential equation for a function  $\psi$  of three variables. The assumption embodied in Eq. (6.5) is evidently valid.

### 6.3 QUANTUM NUMBERS

#### *Three dimensions, three quantum numbers*

The first of these equations, Eq. (6.12), is readily solved. The result is

$$\Phi(\phi) = A e^{im_l \phi} \quad (6.15)$$

As we know, one of the conditions that a wave function—and hence  $\Phi$ , which is a component of the complete wave function  $\psi$ —must obey is that it have a single value at a given point in space. From Fig. 6.2 it is clear that  $\phi$  and  $\phi + 2\pi$  both identify the same meridian plane. Hence it must be true that  $\Phi(\phi) = \Phi(\phi + 2\pi)$ , or

$$A e^{im_l \phi} = A e^{im_l (\phi + 2\pi)}$$

which can happen only when  $m_l$  is 0 or a positive or negative integer ( $\pm 1, \pm 2, \pm 3, \dots$ ). The constant  $m_l$  is known as the **magnetic quantum number** of the hydrogen atom.

The differential equation for  $\Theta(\theta)$ , Eq. (6.13), has a solution provided that the constant  $l$  is an integer equal to or greater than  $|m_l|$ , the absolute value of  $m_l$ . This requirement can be expressed as a condition on  $m_l$  in the form

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

The constant  $l$  is known as the **orbital quantum number**.

The solution of the final equation, Eq. (6.14), for the radial part  $R(r)$  of the hydrogen-atom wave function  $\psi$  also requires that a certain condition be fulfilled. This condition is that  $E$  be positive or have one of the negative values  $E_n$  (signifying that the electron is bound to the atom) specified by

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \left( \frac{1}{n^2} \right) = \frac{E_1}{n^2} \quad n = 1, 2, 3, \dots \quad (6.16)$$

We recognize that this is precisely the same formula for the energy levels of the hydrogen atom that Bohr obtained.

Another condition that must be obeyed in order to solve Eq. (6.14) is that  $n$ , known as the **principal quantum number**, must be equal to or greater than  $l + 1$ . This requirement may be expressed as a condition on  $l$  in the form

$$l = 0, 1, 2, \dots, (n - 1)$$

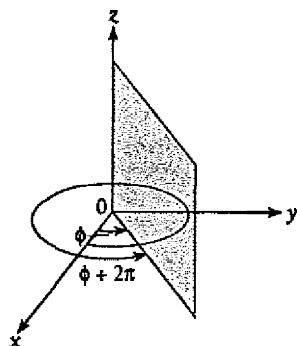


Figure 6.2 The angles  $\phi$  and  $\phi + 2\pi$  both identify the same meridian plane.

Hence we may tabulate the three quantum numbers  $n$ ,  $l$ , and  $m_l$  together with their permissible values as follows:

Principal quantum number	$n = 1, 2, 3, \dots$
Orbital quantum number	$l = 0, 1, 2, \dots, (n - 1)$
Magnetic quantum number	$m_l = 0, \pm 1, \pm 2, \dots, \pm l$

It is worth noting again the natural way in which quantum numbers appear in quantum-mechanical theories of particles trapped in a particular region of space.

To exhibit the dependence of  $R$ ,  $\Theta$ , and  $\Phi$  upon the quantum numbers  $n$ ,  $l$ ,  $m_l$ , we may write for the electron wave functions of the hydrogen atom

$$\psi = R_n l \Theta_{lm_l} \Phi_{m_l} \quad (6.18)$$

The wave functions  $R$ ,  $\Theta$ , and  $\Phi$  together with  $\psi$  are given in Table 6.1 for  $n = 1, 2$ , and 3.

Table 6.1 Normalized Wave Functions of the Hydrogen Atom for  $n = 1, 2$ , and 3\*

$n$	$l$	$m_l$	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	$\pm 2$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

\*The quantity  $a_0 = 4\pi\epsilon_0\hbar^2/m\epsilon^2 = 5.292 \times 10^{-11}$  m is equal to the radius of the innermost Bohr orbit.

**Example 6.1**

Find the ground-state electron energy  $E_1$  by substituting the radial wave function  $R$  that corresponds to  $n = 1, l = 0$  into Eq. (6.14).

**Solution**

From Table 6.1 we see that  $R = (2/a_0^{3/2})e^{-r/a_0}$ . Hence

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

and

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = \left( \frac{2}{a_0^{7/2}} - \frac{4}{a_0^{5/2} r} \right) e^{-r/a_0}$$

Substituting in Eq. (6.14) with  $E = E_1$  and  $l = 0$  gives

$$\left[ \left( \frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}} \right) + \left( \frac{me^2}{\pi\epsilon_0\hbar a_0^{3/2}} - \frac{4}{a_0^{5/2}} \right) \frac{1}{r} \right] e^{-r/a_0} = 0$$

Each parenthesis must equal 0 for the entire equation to equal 0. For the second parenthesis this gives

$$\begin{aligned} \frac{me^2}{\pi\epsilon_0\hbar^2 a_0^{3/2}} - \frac{4}{a_0^{5/2}} &= 0 \\ a_0 &= \frac{4\pi\epsilon_0\hbar^2}{me^2} \end{aligned}$$

which is the Bohr radius  $a_0 = r_1$  given by Eq. (4.13)—we recall that  $\hbar = h/2\pi$ . For the first parenthesis,

$$\begin{aligned} \frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}} &= 0 \\ E_1 &= -\frac{\hbar^2}{2ma_0^2} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \end{aligned}$$

which agrees with Eq. (6.16).

## 6.4 PRINCIPAL QUANTUM NUMBER

### *Quantization of energy*

It is interesting to consider what the hydrogen-atom quantum numbers signify in terms of the classical model of the atom. This model, as we saw in Chap. 4, corresponds exactly to planetary motion in the solar system except that the inverse-square force holding the electron to the nucleus is electrical rather than gravitational. Two quantities are conserved—that is, maintain a constant value at all times—in planetary motion: the scalar total energy and the vector angular momentum of each planet.

Classically the total energy can have any value whatever, but it must, of course, be negative if the planet is to be trapped permanently in the solar system. In the quantum theory of the hydrogen atom the electron energy is also a constant, but while it may have any positive value (corresponding to an ionized atom), the only negative

values the electron can have are specified by the formula  $E_n = E_1/n^2$ . The quantization of electron energy in the hydrogen atom is therefore described by the principal quantum number  $n$ .

The theory of planetary motion can also be worked out from Schrödinger's equation, and it yields a similar energy restriction. However, the total quantum number  $n$  for any of the planets turns out to be so immense (see Exercise 11 of Chap. 4) that the separation of permitted levels is far too small to be observable. For this reason classical physics provides an adequate description of planetary motion but fails within the atom.

## 6.5 ORBITAL QUANTUM NUMBER

### *Quantization of angular-momentum magnitude*

The interpretation of the orbital quantum number  $l$  is less obvious. Let us look at the differential equation for the radial part  $R(r)$  of the wave function  $\psi$ :

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$$

This equation is solely concerned with the radial aspect of the electron's motion, that is, its motion toward or away from the nucleus. However, we notice the presence of  $E$ , the total electron energy, in the equation. The total energy  $E$  includes the electron's kinetic energy of orbital motion, which should have nothing to do with its radial motion.

This contradiction may be removed by the following argument. The kinetic energy KE of the electron has two parts,  $KE_{\text{radial}}$  due to its motion toward or away from the nucleus, and  $KE_{\text{orbital}}$  due to its motion around the nucleus. The potential energy  $U$  of the electron is the electric energy

$$U = -\frac{e^2}{4\pi\epsilon_0 r} \quad (6.2)$$

Hence the total energy of the electron is

$$E = KE_{\text{radial}} + KE_{\text{orbital}} + U = KE_{\text{radial}} + KE_{\text{orbital}} - \frac{e^2}{4\pi\epsilon_0 r}$$

Inserting this expression for  $E$  in Eq. (6.14) we obtain, after a slight rearrangement,

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ KE_{\text{radial}} + KE_{\text{orbital}} - \frac{\hbar^2 l(l+1)}{2mr^2} \right] R = 0 \quad (6.19)$$

If the last two terms in the square brackets of this equation cancel each other out, we shall have what we want: a differential equation for  $R(r)$  that involves functions of the radius vector  $r$  exclusively.

We therefore require that

$$KE_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2mr^2} \quad (6.20)$$

Since the orbital kinetic energy of the electron and the magnitude of its angular momentum are respectively

$$KE_{\text{orbital}} = \frac{1}{2}mv_{\text{orbital}}^2 \quad L = mv_{\text{orbital}}r$$

we may write for the orbital kinetic energy

$$KE_{\text{orbital}} = \frac{L^2}{2mr^2}$$

Hence, from Eq. (6.20),

$$\frac{L^2}{2mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2}$$

Electron angular momentum

$$L = \sqrt{l(l+1)}\hbar \quad (6.21)$$

With the orbital quantum number  $l$  restricted to the values

$$l = 0, 1, 2, \dots, (n-1)$$

The electron can have only the angular momenta  $L$  specified by Eq. (6.21). Like total energy  $E$ , angular momentum is both conserved and quantized. The quantity

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ J} \cdot \text{s}$$

is thus the natural unit of angular momentum.

In macroscopic planetary motion, as in the case of energy, the quantum number describing angular momentum is so large that the separation into discrete angular momentum states cannot be experimentally observed. For example, an electron (or, for that matter, any other body) whose orbital quantum number is 2 has the angular momentum

$$\begin{aligned} L &= \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar \\ &= 2.6 \times 10^{-34} \text{ J} \cdot \text{s} \end{aligned}$$

By contrast the orbital angular momentum of the earth is  $2.7 \times 10^{40} \text{ J} \cdot \text{s}$ .

### Designation of Angular-Momentum States

It is customary to specify electron angular-momentum states by a letter, with  $s$  corresponding to  $l = 0$ ,  $p$  to  $l = 1$ , and so on, according to the following scheme:

Angular-momentum states	$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \dots$
	$s \quad p \quad d \quad f \quad g \quad h \quad i \dots$

**Table 6.2 Atomic Electron States**

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

This peculiar code originated in the empirical classification of spectra into series called sharp, principal, diffuse, and fundamental which occurred before the theory of the atom was developed. Thus an  $s$  state is one with no angular momentum, a  $p$  state has the angular moment  $\sqrt{2}\ h$ , and so forth.

The combination of the total quantum number with the letter that represents orbital angular momentum provides a convenient and widely used notation for atomic electron states. In this notation a state in which  $n = 2, l = 0$  is a  $2s$  state, for example, and one in which  $n = 4, l = 2$  is a  $4d$  state. Table 6.2 gives the designations of electron states in an atom through  $n = 6, l = 5$ .

## 6.6 MAGNETIC QUANTUM NUMBER

### *Quantization of angular-momentum direction*

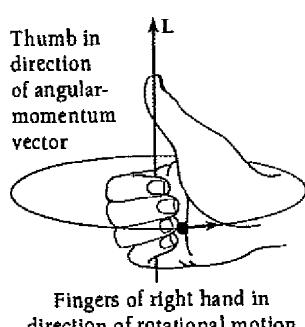


Figure 6.3 The right-hand rule for angular momentum.

The orbital quantum number  $l$  determines the magnitude  $L$  of the electron's angular momentum  $L$ . However, angular momentum, like linear momentum, is a vector quantity, and to describe it completely means that its direction be specified as well as its magnitude. (The vector  $L$ , we recall, is perpendicular to the plane in which the rotational motion takes place, and its sense is given by the right-hand rule: When the fingers of the right hand point in the direction of the motion, the thumb is in the direction of  $L$ . This rule is illustrated in Fig. 6.3.)

What possible significance can a direction in space have for a hydrogen atom? The answer becomes clear when we reflect that an electron revolving about a nucleus is a minute current loop and has a magnetic field like that of a magnetic dipole. Hence an atomic electron that possesses angular momentum interacts with an external magnetic field  $B$ . The magnetic quantum number  $m_l$  specifies the direction of  $L$  by determining the component of  $L$  in the field direction. This phenomenon is often referred to as space quantization.

If we let the magnetic-field direction be parallel to the  $z$  axis, the component of  $L$  in this direction is

$$\text{Space quantization} \quad L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad (6.22)$$

The possible values of  $m_l$  for a given value of  $l$  range from  $+l$  through 0 to  $-l$ , so that the number of possible orientations of the angular-momentum vector  $L$  in a magnetic field is  $2l + 1$ . When  $l = 0$ ,  $L_z$  can have only the single value of 0; when  $l = 1$ ,  $L_z$  may be  $\hbar, 0$ , or  $-\hbar$ ; when  $l = 2$ ,  $L_z$  may be  $2\hbar, \hbar, 0, -\hbar$ , or  $-2\hbar$ ; and so on.

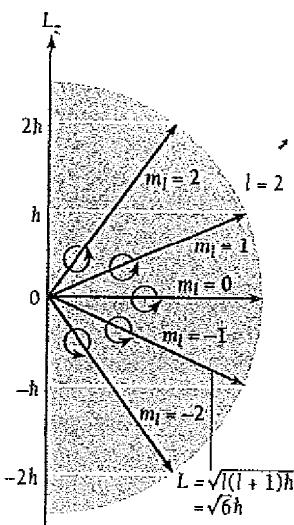


Figure 6.4 Space quantization of orbital angular momentum. Here the orbital quantum number is  $l = 2$  and there are accordingly  $2l + 1 = 5$  possible values of the magnetic quantum number  $m_l$ , with each value corresponding to a different orientation relative to the  $z$  axis.

The space quantization of the orbital angular momentum of the hydrogen atom is shown in Fig. 6.4. An atom with a certain value of  $m_l$  will assume the corresponding orientation of its angular momentum  $L$  relative to an external magnetic field if it finds itself in such a field. We note that  $L$  can never be aligned exactly parallel or antiparallel to  $B$  because  $L_z$  is always smaller than the magnitude  $\sqrt{l(l+1)\hbar}$  of the total angular momentum.

In the absence of an external magnetic field, the direction of the  $z$  axis is arbitrary. What must be true is that the component of  $L$  in *any* direction we choose is  $m_l\hbar$ . What an external magnetic field does is to provide an experimentally meaningful reference direction. A magnetic field is not the only such reference direction possible. For example, the line between the two H atoms in the hydrogen molecule  $H_2$  is just as experimentally meaningful as the direction of a magnetic field, and along this line the components of the angular momenta of the H atoms are determined by their  $m_l$  values.

### The Uncertainty Principle and Space Quantization

Why is only one component of  $L$  quantized? The answer is related to the fact that  $L$  can never point in any specific direction but instead is somewhere on a cone in space such that its projection  $L_z$  is  $m_l\hbar$ . Were this not so, the uncertainty principle would be violated. If  $L$  were fixed in space, so that  $L_x$  and  $L_y$  as well as  $L_z$  had definite values, the electron would be confined to a definite plane. For instance, if  $L$  were in the  $z$  direction, the electron would have to be in the  $xy$  plane at all times (Fig. 6.5a). This can occur only if the electron's momentum component  $p_z$  in the  $z$  direction is infinitely uncertain, which of course is impossible if it is to be part of a hydrogen atom.

However, since in reality only one component  $L_z$  of  $L$  together with its magnitude  $L$  have definite values and  $|L| > |L_z|$ , the electron is not limited to a single plane (Fig. 6.5b). Thus there is a built-in uncertainty in the electron's  $z$  coordinate. The

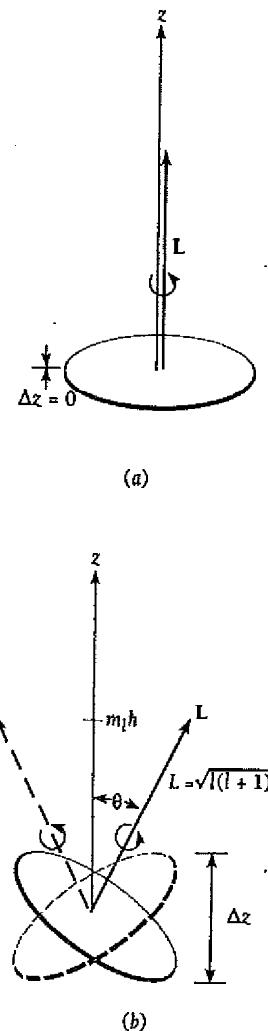


Figure 6.5 The uncertainty principle prohibits the angular momentum vector  $L$  from having a definite direction in space.

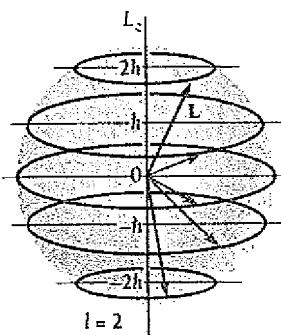


Figure 6.6 The angular momentum vector  $\mathbf{L}$  precesses constantly about the  $z$  axis.

direction of  $\mathbf{L}$  is not fixed, as in Fig. 6.6, and so the average values of  $L_x$  and  $L_y$  are 0, although  $L_z$  always has the specific value  $m\hbar$ .

## 6.7 ELECTRON PROBABILITY DENSITY

### No definite orbits

In Bohr's model of the hydrogen atom the electron is visualized as revolving around the nucleus in a circular path. This model is pictured in a spherical polar coordinate system in Fig. 6.7. It implies that if a suitable experiment were performed, the electron would always be found a distance of  $r = n^2 a_0$  (where  $n$  is the quantum number of the orbit and  $a_0$  is the radius of the innermost orbit) from the nucleus and in the equatorial plane  $\theta = 90^\circ$ , while its azimuth angle  $\phi$  changes with time.

The quantum theory of the hydrogen atom modifies the Bohr model in two ways:

- 1 No definite values for  $r$ ,  $\theta$ , or  $\phi$  can be given, but only the relative probabilities for finding the electron at various locations. This imprecision is, of course, a consequence of the wave nature of the electron.
- 2 We cannot even think of the electron as moving around the nucleus in any conventional sense since the probability density  $|\psi|^2$  is independent of time and varies from place to place.

The probability density  $|\psi|^2$  that corresponds to the electron wave function  $\psi = R\Theta\Phi$  in the hydrogen atom is

$$|\psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2 \quad (6.23)$$

As usual the square of any function that is complex is to be replaced by the product of the function and its complex conjugate. (We recall that the complex conjugate of a function is formed by changing  $i$  to  $-i$  whenever it appears.)

From Eq. (6.15) we see that the azimuthal wave function is given by

$$\Phi(\phi) = Ae^{im\phi}$$

The azimuthal probability density  $|\Phi|^2$  is therefore

$$|\Phi|^2 = \Phi^* \Phi = A^2 e^{-im\phi} e^{im\phi} = A^2 e^0 = A^2$$

The likelihood of finding the electron at a particular azimuth angle  $\phi$  is a constant that does not depend upon  $\phi$  at all. The electron's probability density is symmetrical about the  $z$  axis regardless of the quantum state it is in, and the electron has the same chance of being found at one angle  $\phi$  as at another.

The radial part  $R$  of the wave function, in contrast to  $\Phi$ , not only varies with  $r$  but does so in a different way for each combination of quantum numbers  $n$  and  $l$ . Figure 6.8 contains graphs of  $R$  versus  $r$  for  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  states of the hydrogen atom. Evidently  $R$  is a maximum at  $r = 0$ —that is, at the nucleus itself—for all  $s$  states, which correspond to  $L = 0$  since  $l = 0$  for such states. The value of  $R$  is zero at  $r = 0$  for states that possess angular momentum.

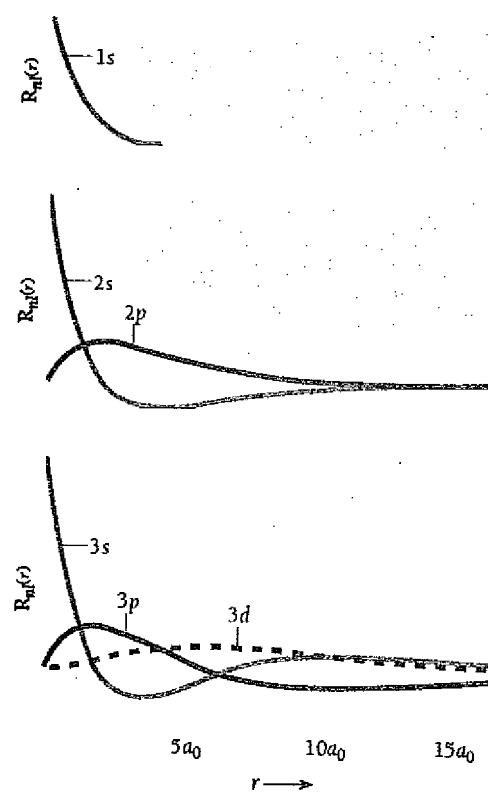


Figure 6.8 The variation with distance from the nucleus of the radial part of the electron wave function in hydrogen for various quantum states. The quantity  $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 0.053$  nm is the radius of the first Bohr orbit.

### Probability of Finding the Electron

The *probability density* of the electron at the point  $r, \theta, \phi$  is proportional to  $|\psi|^2$ , but the *actual probability* of finding it in the infinitesimal volume element  $dV$  there is  $|\psi|^2 dV$ . In spherical polar coordinates (Fig. 6.9),

$$\begin{aligned} dV &= (dr)(r d\theta)(r \sin \theta d\phi) \\ \text{Volume element} &= r^2 \sin \theta dr d\theta d\phi \end{aligned} \quad (6.24)$$

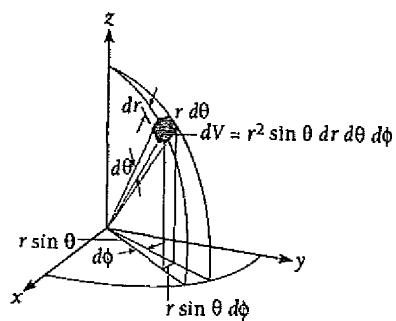


Figure 6.9 Volume element  $dV$  in spherical polar coordinates.

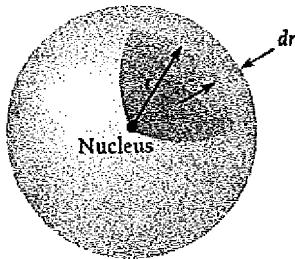


Figure 6.10 The probability of finding the electron in a hydrogen atom in the spherical shell between  $r$  and  $r + dr$  from the nucleus is  $P(r) dr$ .

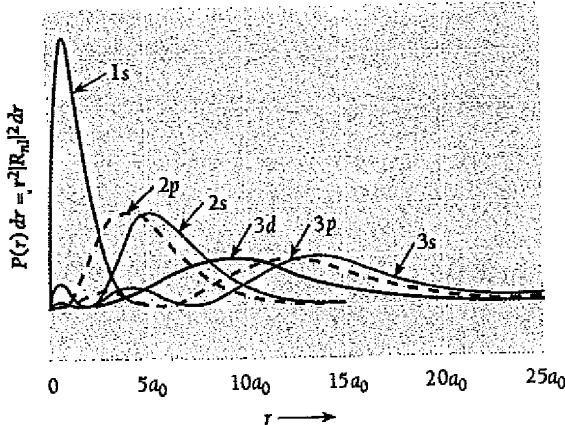


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between  $r$  and  $r + dr$  from the nucleus for the quantum states of Fig. 6.8.

As  $\Theta$  and  $\Phi$  are normalized functions, the actual probability  $P(r) dr$  of finding the electron in a hydrogen atom somewhere in the spherical shell between  $r$  and  $r + dr$  from the nucleus (Fig. 6.10) is

$$\begin{aligned} P(r) dr &= r^2 |R|^2 dr \int_0^\pi |\Theta|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi \\ &= r^2 |R|^2 dr \end{aligned} \quad (6.25)$$

Equation (6.25) is plotted in Fig. 6.11 for the same states whose radial functions  $R$  were shown in Fig. 6.8. The curves are quite different as a rule. We note immediately that  $P$  is not a maximum at the nucleus for  $s$  states, as  $R$  itself is, but has its maximum a definite distance from it.

The most probable value of  $r$  for a  $1s$  electron turns out to be exactly  $a_0$ , the orbital radius of a ground-state electron in the Bohr model. However, the average value of  $r$  for a  $1s$  electron is  $1.5a_0$ , which is puzzling at first sight because the energy levels are the same in both the quantum-mechanical and Bohr atomic models. This apparent discrepancy is removed when we recall that the electron energy depends upon  $1/r$  rather than upon  $r$  directly, and the average value of  $1/r$  for a  $1s$  electron is exactly  $1/a_0$ .

### Example 6.2

Verify that the average value of  $1/r$  for a  $1s$  electron in the hydrogen atom is  $1/a_0$ .

#### Solution

The wave function of a  $1s$  electron is, from Table 6.1,

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^{3/2}}}$$

Since  $dV = r^2 \sin\theta dr d\theta d\phi$  we have for the expectation value of  $1/r$

$$\begin{aligned}\left\langle \frac{1}{r} \right\rangle &= \int_0^\infty \left( \frac{1}{r} \right) |\psi|^2 dV \\ &\approx \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi\end{aligned}$$

The integrals have the respective values

$$\begin{aligned}\int_0^\infty r e^{-2r/a_0} dr &= \left[ \frac{a_0^2}{4} e^{-2r/a_0} - \frac{r}{2} e^{-2r/a_0} \right]_0^\infty = \frac{a_0^2}{4} \\ \int_0^\pi \sin\theta d\theta &= [-\cos\theta]_0^\pi = 2 \\ \int_0^{2\pi} d\phi &= [2\phi]_0^{2\pi} = 2\pi\end{aligned}$$

Hence  $\left\langle \frac{1}{r} \right\rangle = \left( \frac{1}{\pi a_0^3} \right) \left( \frac{a_0^2}{4} \right) (2)(2\pi) = \frac{1}{a_0}$

### Example 6.3

How much more likely is a 1s electron in a hydrogen atom to be at the distance  $a_0$  from the nucleus than at the distance  $a_0/2$ ?

#### Solution

According to Table 6.1 the radial wave function for a 1s electron is

$$R = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

From Eq. (6.25) we have for the ratio of the probabilities that an electron in a hydrogen atom be at the distances  $r_1$  and  $r_2$  from the nucleus

$$\frac{P_1}{P_2} = \frac{r_1^2 |R_1|^2}{r_2^2 |R_2|^2} = \frac{r_1^2 e^{-2r_1/a_0}}{r_2^2 e^{-2r_2/a_0}}$$

Here  $r_1 = a_0$  and  $r_2 = a_0/2$ , so

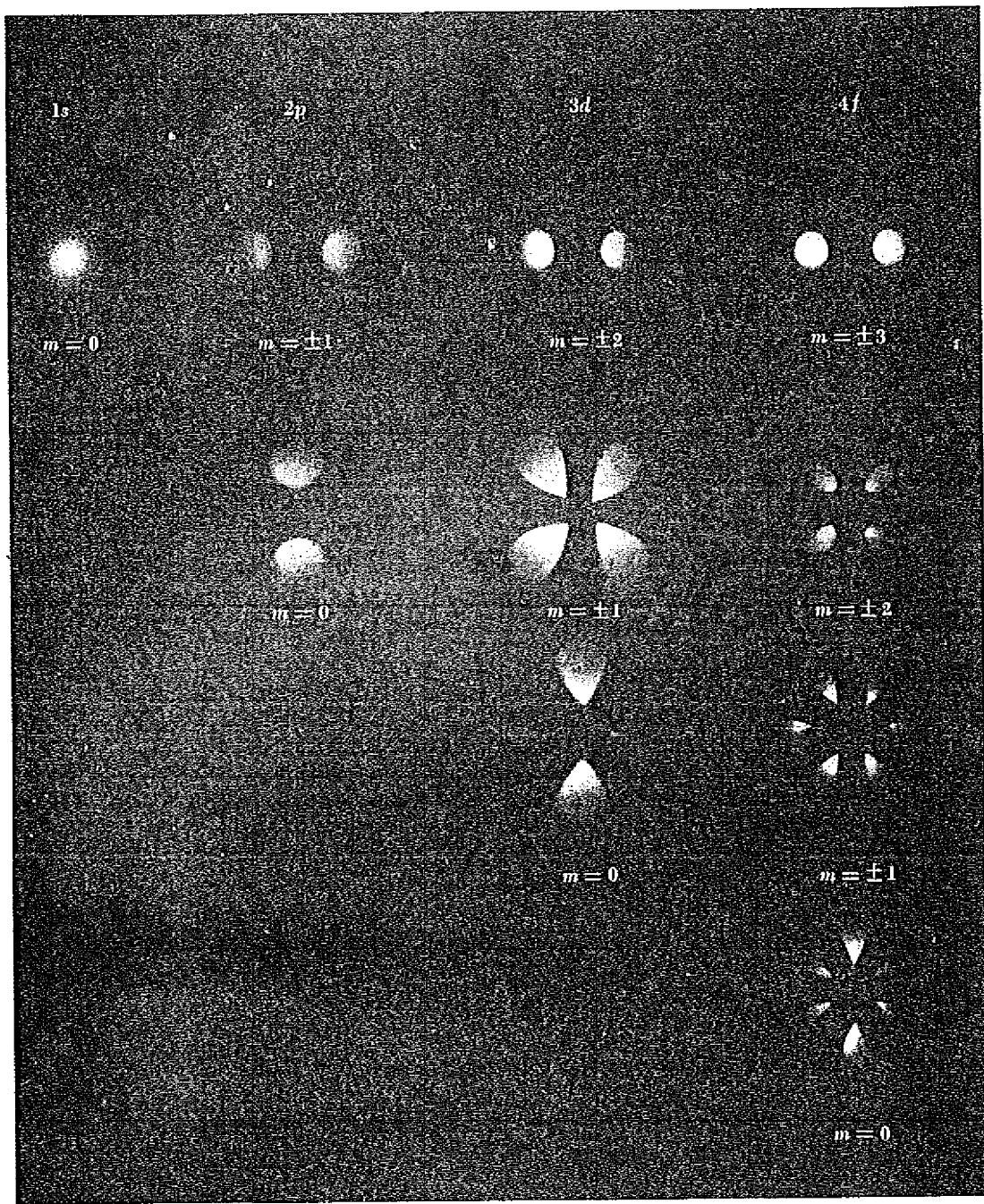
$$\frac{P_{a_0}}{P_{a_0/2}} = \frac{(a_0)^2 e^{-2}}{(a_0/2)^2 e^{-1}} = 4e^{-1} = 1.47$$

The electron is 47 percent more likely to be  $a_0$  from the nucleus than half that distance (see Fig. 6.11).

### Angular Variation of Probability Density

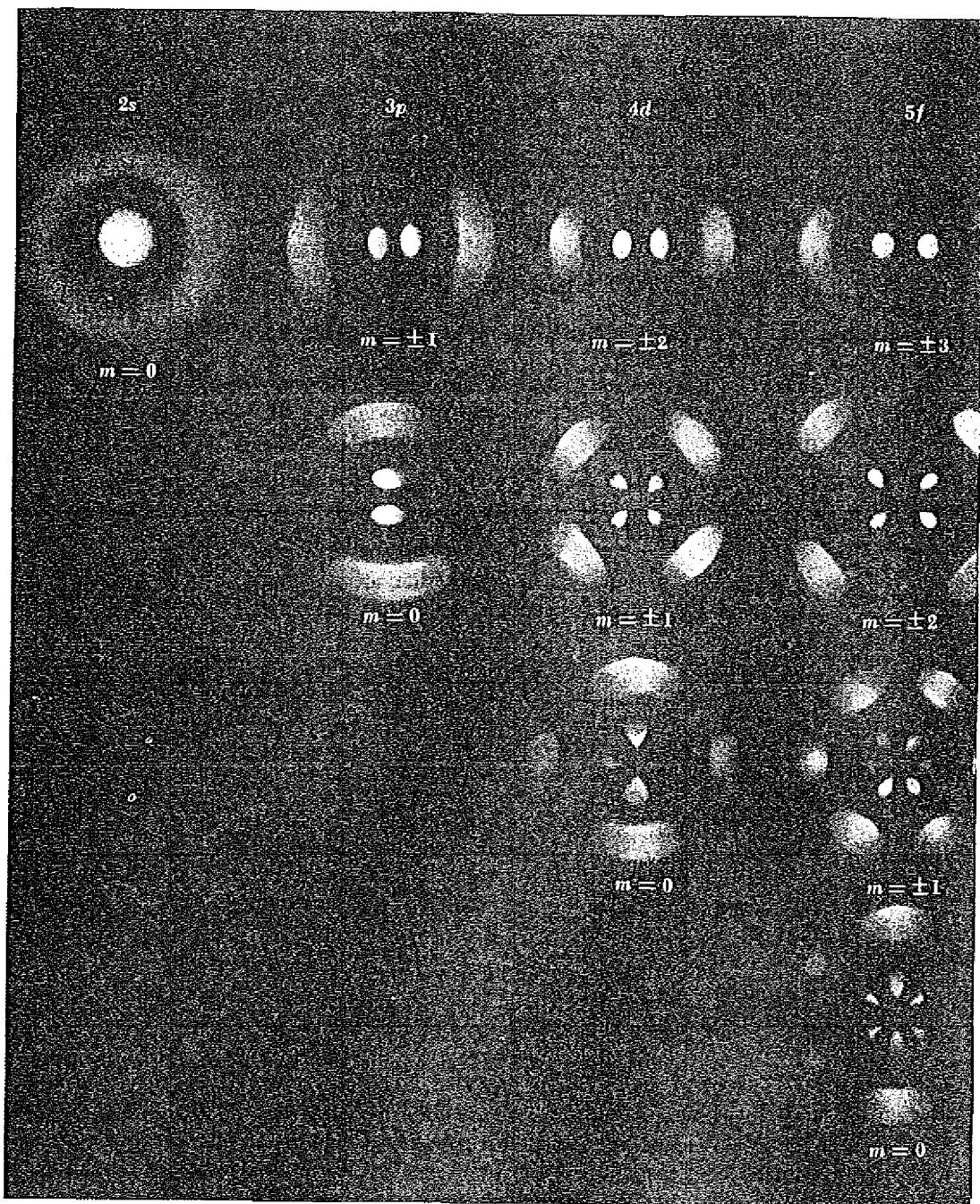
The function  $\Theta$  varies with zenith angle  $\theta$  for all quantum numbers  $l$  and  $m_l$  except  $l = m_l = 0$ , which are  $s$  states. The value of  $|\Theta|^2$  for an  $s$  state is a constant;  $\frac{1}{2}$ , in fact. This means that since  $|\Phi|^2$  is also a constant, the electron probability density  $|\psi|^2$  is

spherically symmetric; it has the same value at a given  $r$  in all directions. Electrons in other states, however, do have angular preferences, sometimes quite complicated ones. This can be seen in Fig. 6.12, in which electron probability densities as functions of  $r$



**Figure 6.12** Photographic representation of the electron probability-density distribution  $|\psi|^2$  for several energy states. These may be regarded as sectional views of the distribution in a plane containing the polar axis, which is vertical and in the plane of the paper. The scale varies from figure to figure.

and  $\theta$  are shown for several atomic states. (The quantity plotted is  $|\psi|^2$ , not  $|\psi|^2 dV$ .) Since  $|\psi|^2$  is independent of  $\phi$ , we can obtain a three-dimensional picture of  $|\psi|^2$  by rotating a particular representation about a vertical axis. When this is done, we see that the probability densities for s states are spherically symmetric whereas those for other



states are not. The pronounced lobe patterns characteristic of many of the states turn out to be significant in chemistry since these patterns help determine the manner in which adjacent atoms in a molecule interact.

A look at Figure 6.12 also reveals quantum-mechanical states that resemble these of the Bohr model. The electron probability-density distribution for a  $2p$  state with  $m_l = \pm 1$ , for instance, is like a doughnut in the equatorial plane centered at the nucleus. Calculation shows the most probable distance of such an electron from the nucleus to be  $4a_0$ —precisely the radius of the Bohr orbit for the same principal quantum number  $n = 2$ . Similar correspondences exist for  $3d$  states with  $m_l = \pm 2$ ,  $4f$  states with  $m_l = \pm 3$ , and so on. In each of these cases the angular momentum is the highest possible for that energy level, and the angular-momentum vector is as near the  $z$  axis as possible so that the probability density is close to the equatorial plane. Thus the Bohr model predicts the most probable location of the electron in one of the several possible states in each energy level.

## 6.8 RADIATIVE TRANSITIONS

*What happens when an electron goes from one state to another*

In formulating his theory of the hydrogen atom, Bohr was obliged to postulate that the frequency  $\nu$  of the radiation emitted by an atom dropping from an energy level  $E_m$  to a lower level  $E_n$  is

$$\nu = \frac{E_m - E_n}{h}$$

It is not hard to show that this relationship arises naturally in quantum mechanics. For simplicity we shall consider a system in which an electron moves only in the  $x$  direction.

From Sec. 5.7 we know that the time-dependent wave function  $\Psi_n$  of an electron in a state of quantum number  $n$  and energy  $E_n$  is the product of a time-independent wave function  $\psi_n$  and a time-varying function whose frequency is

$$\nu_n = \frac{E_n}{h}$$

Hence

$$\Psi_n = \psi_n e^{-(iE_n/h)t} \quad \Psi_n^* = \psi_n^* e^{+(iE_n/h)t} \quad (6.26)$$

The expectation value  $\langle x \rangle$  of the position of such an electron is

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x \Psi_n^* \Psi_n dx = \int_{-\infty}^{\infty} x \psi_n^* \psi_n e^{[i(E_n/h) - (iE_n/h)]t} dx \\ &= \int_{-\infty}^{\infty} x \psi_n^* \psi_n dx \end{aligned} \quad (6.27)$$

The expectation value  $\langle x \rangle$  is constant in time since  $\psi_n$  and  $\psi_n^*$  are, by definition, functions of position only. The electron does not oscillate, and no radiation occurs. Thus quantum mechanics predicts that a system in a specific quantum state does not radiate, as observed.

We next consider an electron that shifts from one energy state to another. A system might be in its ground state  $n$  when an excitation process of some kind (a beam of radiation, say, or collisions with other particles) begins to act upon it. Subsequently we find that the system emits radiation corresponding to a transition from an excited state of energy  $E_m$  to the ground state. We conclude that at some time during the intervening period the system existed in the state  $m$ . What is the frequency of the radiation?

The wave function  $\Psi$  of an electron that can exist in both states  $n$  and  $m$  is

$$\Psi = a\Psi_n + b\Psi_m \quad (6.28)$$

where  $a^*a$  is the probability that the electron is in state  $n$  and  $b^*b$  the probability that it is in state  $m$ . Of course, it must always be true that  $a^*a + b^*b = 1$ . Initially  $a = 1$  and  $b = 0$ ; when the electron is in the excited state,  $a = 0$  and  $b = 1$ ; and ultimately  $a = 1$  and  $b = 0$  once more. While the electron is in either state, there is no radiation, but when it is in the midst of the transition from  $m$  to  $n$  (that is, when both  $a$  and  $b$  have nonvanishing values), electromagnetic waves are produced.

The expectation value  $\langle x \rangle$  that corresponds to the composite wave function of Eq. (6.28) is

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x(a^*\Psi_n^* + b^*\Psi_m^*)(a\Psi_n + b\Psi_m) dx \\ &= \int_{-\infty}^{\infty} x(a^2\Psi_n^*\Psi_n + b^*a\Psi_m^*\Psi_n + a^*b\Psi_n^*\Psi_m + b^2\Psi_m^*\Psi_m) dx \end{aligned} \quad (6.29)$$

Here, as before, we let  $a^*a = a^2$  and  $b^*b = b^2$ . The first and last integrals do not vary with time, so the second and third integrals are the only ones able to contribute to a time variation in  $\langle x \rangle$ .

With the help of Eqs. (6.26) we expand Eq. (6.29) to give

$$\begin{aligned} \langle x \rangle &= a^2 \int_{-\infty}^{\infty} x\psi_n^*\psi_n dx + b^*a \int_{-\infty}^{\infty} x\psi_m^*e^{+(iE_m/\hbar)t} \psi_n e^{-(iE_n/\hbar)t} dx \\ &\quad + a^*b \int_{-\infty}^{\infty} x\psi_n^*e^{+(iE_n/\hbar)t} \psi_m e^{-(iE_m/\hbar)t} dx + b^2 \int_{-\infty}^{\infty} x\psi_m^*\psi_m dx \end{aligned} \quad (6.30)$$

Because

$$e^{i\theta} = \cos \theta + i \sin \theta \quad \text{and} \quad e^{-i\theta} = \cos \theta - i \sin \theta$$

the two middle terms of Eq. (6.30), which are functions of time, become

$$\begin{aligned} \cos\left(\frac{E_m - E_n}{\hbar}\right)t \int_{-\infty}^{\infty} x[b^*a\psi_m^*\psi_n + a^*b\psi_n^*\psi_m] dx \\ + i \sin\left(\frac{E_m - E_n}{\hbar}\right)t \int_{-\infty}^{\infty} x[b^*a\psi_m^*\psi_n - a^*b\psi_n^*\psi_m] dx \end{aligned} \quad (6.31)$$

The real part of this result varies with time as

$$\cos\left(\frac{E_m - E_n}{\hbar}\right)t = \cos 2\pi\left(\frac{E_m - E_n}{h}\right)t = \cos 2\pi\nu t \quad (6.32)$$

The electron's position therefore oscillates sinusoidally at the frequency

$$\nu = \frac{E_m - E_n}{\hbar} \quad (6.33)$$

When the electron is in state  $n$  or state  $m$  the expectation value of the electron's position is constant. When the electron is undergoing a transition between these states, its position oscillates with the frequency  $\nu$ . Such an electron, of course, is like an electric dipole and radiates electromagnetic waves of the same frequency  $\nu$ . This result is the same as that postulated by Bohr and verified by experiment. As we have seen, quantum mechanics gives Eq. (6.33) without the need for any special assumptions.

## 6.9 SELECTION RULES

*Some transitions are more likely to occur than others*

We did not have to know the values of the probabilities  $a$  and  $b$  as functions of time, nor the electron wave functions  $\psi_n$  and  $\psi_m$ , in order to find the frequency  $\nu$ . We need these quantities, however, to calculate the chance a given transition will occur. The general condition necessary for an atom in an excited state to radiate is that the integral

$$\int_{-\infty}^{\infty} x \psi_n \psi_m^* dx \quad (6.34)$$

not be zero, since the intensity of the radiation is proportional to it. Transitions for which this integral is finite are called **allowed transitions**, while those for which it is zero are called **forbidden transitions**.

In the case of the hydrogen atom, three quantum numbers are needed to specify the initial and final states involved in a radiative transition. If the principal, orbital, and magnetic quantum numbers of the initial state are  $n'$ ,  $l'$ ,  $m_l'$ , respectively, and those of the final state are  $n$ ,  $l$ ,  $m_l$ , and  $u$  represents either the  $x$ ,  $y$ , or  $z$  coordinate, the condition for an allowed transition is

$$\text{Allowed transitions} \quad \int_{-\infty}^{\infty} u \psi_{n,l,m_l} \psi_{n',l',m_l'}^* dV \neq 0 \quad (6.35)$$

where the integral is now over all space. When  $u$  is taken as  $x$ , for example, the radiation would be that produced by a dipole antenna lying on the  $x$  axis.

Since the wave functions  $\psi_{n,l,m_l}$  for the hydrogen atom are known, Eq. (6.35) can be evaluated for  $u = x$ ,  $u = y$ , and  $u = z$  for all pairs of states differing in one or more quantum numbers. When this is done, it is found that the only transitions between states of different  $n$  that can occur are those in which the orbital quantum number  $l$  changes by  $\pm 1$  and the magnetic quantum number  $m_l$  does not change or changes by  $\pm 1$ . That is, the condition for an allowed transition is that

$$\Delta l = \pm 1 \quad (6.36)$$

$$\text{Selection rules} \quad \Delta m_l = 0, \pm 1 \quad (6.37)$$

The change in total quantum number  $n$  is not restricted. Equations (6.36) and (6.37) are known as the **selection rules** for allowed transitions (Fig. 6.13).

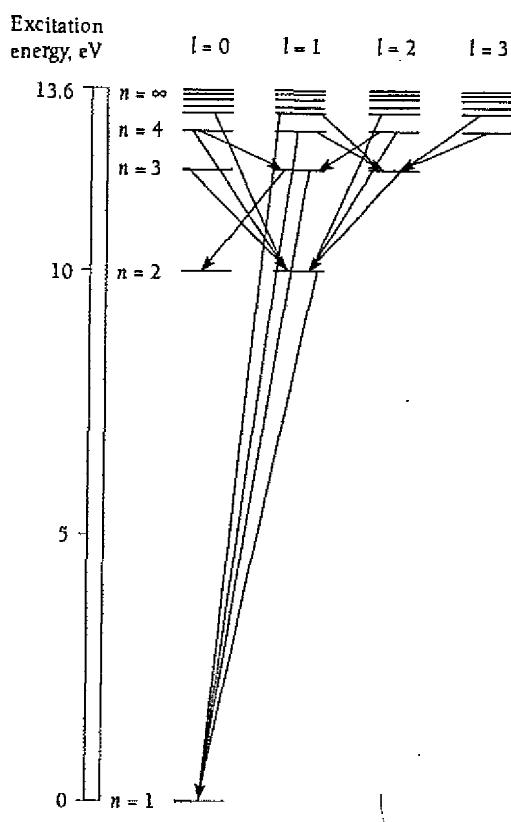


Figure 6.13 Energy-level diagram for hydrogen showing transitions allowed by the selection rule  $\Delta l = \pm 1$ . In this diagram the vertical axis represents excitation energy above the ground state.

The selection rule requiring that  $l$  change by  $\pm 1$  if an atom is to radiate means that an emitted photon carries off the angular momentum  $\pm \hbar$  equal to the difference between the angular momenta of the atom's initial and final states. The classical analog of a photon with angular momentum  $\pm \hbar$  is a left or right circularly polarized electromagnetic wave, so this notion is not unique with quantum theory.

### Quantum Electrodynamics

The preceding analysis of radiative transitions in an atom is based on a mixture of classical and quantum concepts. As we have seen, the expectation value of the position of an atomic electron oscillates at the frequency  $\nu$  of Eq. (6.33) while passing from an initial eigenstate to another one of lower energy. Classically such an oscillating charge gives rise to electromagnetic waves of the same frequency  $\nu$ , and indeed the observed radiation has this frequency. However, classical concepts are not always reliable guides to atomic processes, and a deeper treatment is required. Such a treatment, called **quantum electrodynamics**, shows that the radiation emitted during a transition from state  $m$  to state  $n$  is in the form of a single photon.

In addition, quantum electrodynamics provides an explanation for the mechanism that causes the "spontaneous" transition of an atom from one energy state to a lower one. All electric and

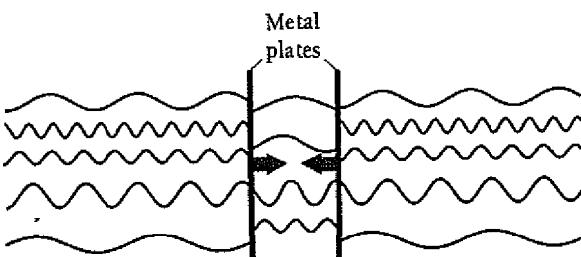


Figure 6.14 Two parallel metal plates exhibit the Casimir effect even in empty space. Virtual photons of any wavelength can strike the plates from the outside, but photons trapped between the plates can have only certain wavelengths. The resulting imbalance produces inward forces on the plates.

magnetic fields turn out to fluctuate constantly about the  $E$  and  $B$  that would be expected on purely classical grounds. Such fluctuations occur even when electromagnetic waves are absent and when, classically,  $E = B = 0$ . It is these fluctuations (often called "vacuum fluctuations" and analogous to the zero-point vibrations of a harmonic oscillator) that induce the apparently spontaneous emission of photons by atoms in excited states.

The vacuum fluctuations can be regarded as a sea of "virtual" photons so short-lived that they do not violate energy conservation because of the uncertainty principle in the form  $\Delta E \Delta t \geq \hbar/2$ . These photons, among other things, give rise to the Casimir effect (Fig. 6.14), which was proposed by the Dutch physicist Hendrik Casimir in 1948. Only virtual photons with certain specific wavelengths can be reflected back-and-forth between two parallel metal plates, whereas outside the plates virtual photons of all wavelengths can be reflected by them. The result is a very small but detectable force that tends to push the plates together.

Can the Casimir effect be used as a source of energy? If the parallel plates are released, they would fly together and thereby pick up kinetic energy from the vacuum fluctuations that would become heat if the plates were allowed to collide. Unfortunately not much energy is available in this way: about half a nanojoule ( $0.5 \times 10^{-9}$  J) per square meter of plate area.



**Richard P. Feynman** (1918–1988) was born in Far Rockaway, a suburb of New York City, and studied at the Massachusetts Institute of Technology and Princeton. After receiving his Ph.D. in 1942, he helped develop the atomic bomb at Los Alamos, New Mexico, along with many other young physicists. When the war was over, he went first to Cornell and, in 1951, to the California Institute of Technology.

In the late 1940s Feynman made important contributions to quantum electrodynamics, the relativistic quantum theory that describes the electromagnetic interaction between charged particles. A serious problem in this theory is the presence of infinite quantities in its results, which in the procedure called renormalization are removed by subtracting other infinite quantities. Although this step is mathematically dubious and still leaves some physicists uneasy, the final theory has proven

extraordinarily accurate in all its predictions. An unrepentant Feynman remarked, "It is not philosophy we are after, but the behavior of real things," and compared the agreement between quantum electrodynamics and experiment to finding the distance from New York to Los Angeles to within the thickness of a single hair.

Feynman articulated the feelings of many physicists when he wrote: "We have always had a great deal of difficulty understanding the world view that quantum mechanics represents . . . I cannot define the real problem, therefore I suspect there's no real problem, but I'm not sure there's no real problem."

In 1965 Feynman received the Nobel Prize together with two other pioneers in quantum electrodynamics, Julian Schwinger, also an American, and Sin-Itiro Tomonaga, a Japanese. Feynman made other major contributions to physics, notably in explaining the behavior of liquid helium near absolute zero and in elementary particle theory. His three-volume *Lectures on Physics* has stimulated and enlightened both students and teachers since its publication in 1963.

## 6.10 ZEEMAN EFFECT

### *How atoms interact with a magnetic field*

In an external magnetic field  $B$ , a magnetic dipole has an amount of potential energy  $U_m$  that depends upon both the magnitude  $\mu$  of its magnetic moment and the orientation of this moment with respect to the field (Fig. 6.15).

The torque  $\tau$  on a magnetic dipole in a magnetic field of flux density  $B$  is

$$\tau = \mu B \sin \theta$$

where  $\theta$  is the angle between  $\mu$  and  $B$ . The torque is a maximum when the dipole is perpendicular to the field, and zero when it is parallel or antiparallel to it. To calculate the potential energy  $U_m$  we must first establish a reference configuration in which  $U_m$  is zero by definition. (Since only changes in potential energy are ever experimentally observed, the choice of a reference configuration is arbitrary.) It is convenient to set  $U_m = 0$  when  $\theta = \pi/2 = 90^\circ$ , that is, when  $\mu$  is perpendicular to  $B$ . The potential energy at any other orientation of  $\mu$  is equal to the external work that must be done to rotate the dipole from  $\theta_0 = \pi/2$  to the angle  $\theta$  that corresponds to that orientation. Hence

$$\begin{aligned} U_m &= \int_{\pi/2}^{\theta} \tau d\theta = \mu B \int_{\pi/2}^{\theta} \sin \theta d\theta \\ &= -\mu B \cos \theta \end{aligned} \quad (6.38)$$

When  $\mu$  points in the same direction as  $B$ , then  $U_m = -\mu B$ , its minimum value. This follows from the fact that a magnetic dipole tends to align itself with an external magnetic field.

The magnetic moment of the orbital electron in a hydrogen atom depends on its angular momentum  $L$ . Hence both the magnitude of  $L$  and its orientation with respect to the field determine the extent of the magnetic contribution to the total energy of the atom when it is in a magnetic field. The magnetic moment of a current loop has the magnitude

$$\mu = IA$$

where  $I$  is the current and  $A$  the area it encloses. An electron that makes  $f$  rev/s in a circular orbit of radius  $r$  is equivalent to a current of  $-ef$  (since the electronic charge is  $-e$ ), and its magnetic moment is therefore

$$\mu = -ef\pi r^2$$

Because the linear speed  $v$  of the electron is  $2\pi fr$  its angular momentum is

$$L = mvr = 2\pi mfr^2$$

Comparing the formulas for magnetic moment  $\mu$  and angular momentum  $L$  shows that

Electron magnetic moment

$$\mu = -\left(\frac{e}{2m}\right)L \quad (6.39)$$

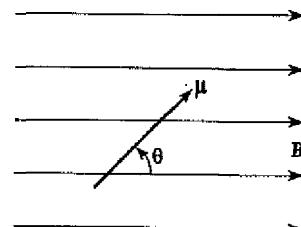


Figure 6.15 A magnetic dipole of moment  $\mu$  at the angle  $\theta$  relative to a magnetic field  $B$ .

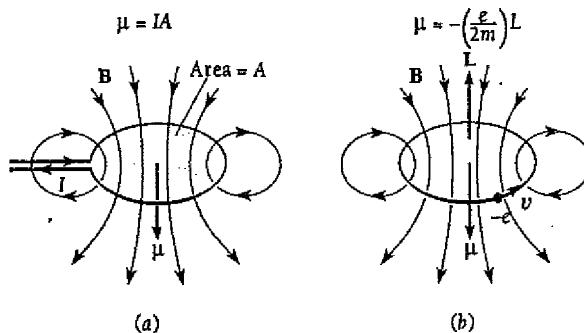


Figure 6.16 (a) Magnetic moment of a current loop enclosing area  $A$ . (b) Magnetic moment of an orbiting electron of angular momentum  $L$ .

for an orbital electron (Fig. 6.16). The quantity  $(-e/2m)$ , which involves only the charge and mass of the electron, is called its **gyromagnetic ratio**. The minus sign means that  $\mu$  is in the opposite direction to  $L$  and is a consequence of the negative charge of the electron. While the above expression for the magnetic moment of an orbital electron has been obtained by a classical calculation, quantum mechanics yields the same result. The magnetic potential energy of an atom in a magnetic field is therefore

$$U_m = \left(\frac{e}{2m}\right)LB \cos \theta \quad (6.40)$$

which depends on both  $B$  and  $\theta$ .

### Magnetic Energy

From Fig. 6.4 we see that the angle  $\theta$  between  $L$  and the  $z$  direction can have only the values specified by

$$\cos \theta = \frac{m_l}{\sqrt{l(l+1)}}$$

with the permitted values of  $L$  specified by

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

To find the magnetic energy that an atom of magnetic quantum number  $m_l$  has when it is in a magnetic field  $B$ , we put the above expressions for  $\cos \theta$  and  $L$  in Eq. (6.40) to give

$$\text{Magnetic energy} \quad U_m = m_l \left(\frac{e\hbar}{2m}\right)B \quad (6.41)$$

The quantity  $e\hbar/2m$  is called the **Bohr magneton**:

$$\text{Bohr magneton} \quad \mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T} = 5.788 \times 10^{-5} \text{ eV/T} \quad (6.42)$$

In a magnetic field, then, the energy of a particular atomic state depends on the value of  $m_l$  as well as on that of  $n$ . A state of total quantum number  $n$  breaks up into several substates when the atom is in a magnetic field, and their energies are slightly more or slightly less than the energy of the state in the absence of the field. This phenomenon

leads to a "splitting" of individual spectral lines into separate lines when atoms radiate in a magnetic field. The spacing of the lines depends on the magnitude of the field.

The splitting of spectral lines by a magnetic field is called the Zeeman effect after the Dutch physicist Pieter Zeeman, who first observed it in 1896. The Zeeman effect is a vivid confirmation of space quantization.

Because  $m_l$  can have the  $2l + 1$  values of  $+l$  through 0 to  $-l$ , a state of given orbital quantum number  $l$  is split into  $2l + 1$  substates that differ in energy by  $\mu_B B$  when the atom is in a magnetic field. However, because changes in  $m_l$  are restricted to  $\Delta m_l = 0, \pm 1$ , we expect a spectral line from a transition between two states of different  $l$  to be split into only three components, as shown in Fig. 6.17. The normal Zeeman effect consists of the splitting of a spectral line of frequency  $\nu_0$  into three components whose frequencies are

$$\nu_1 = \nu_0 - \mu_B \frac{B}{h} = \nu_0 - \frac{e}{4\pi m} B \quad (6.43)$$

Normal Zeeman  
effect

$$\nu_2 = \nu_0$$

$$\nu_3 = \nu_0 + \mu_B \frac{B}{h} = \nu_0 + \frac{e}{4\pi m} B$$

In Chap. 7 we will see that this is not the whole story of the Zeeman effect.

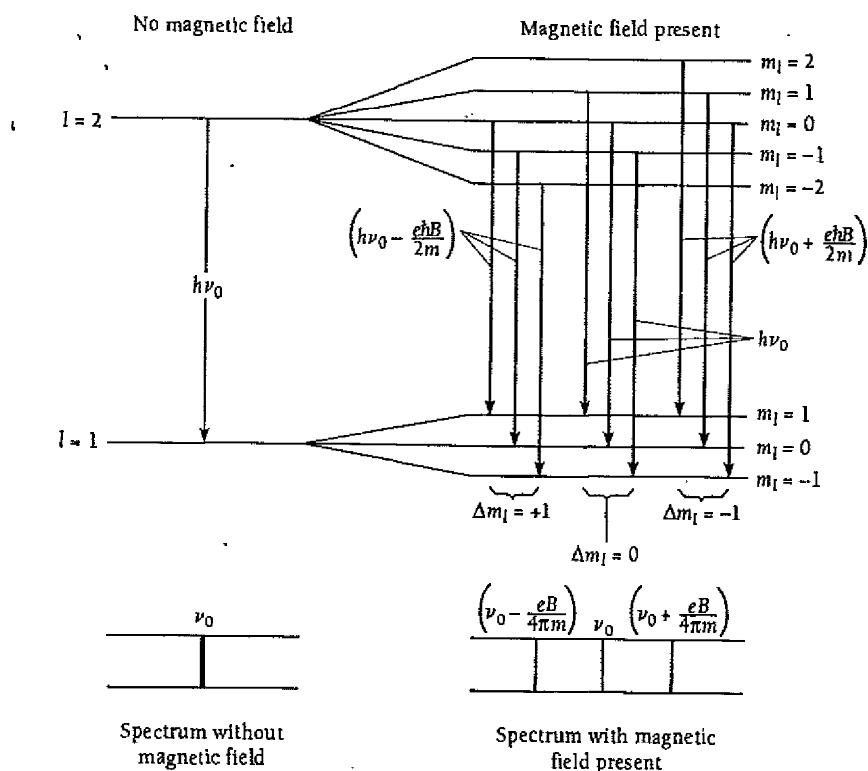


Figure 6.17 In the normal Zeeman effect a spectral line of frequency  $\nu_0$  is split into three components when the radiating atoms are in a magnetic field of magnitude  $B$ . One component is  $\nu_0$  and the others are less than and greater than  $\nu_0$  by  $eB/4\pi m$ . There are only three components because of the selection rule  $\Delta m_l = 0, \pm 1$ .

**Example 6.4**

A sample of a certain element is placed in a 0.300-T magnetic field and suitably excited. How far apart are the Zeeman components of the 450-nm spectral line of this element?

**Solution**

The separation of the Zeeman components is

$$\Delta\nu = \frac{eB}{4\pi m}$$

Since  $\nu = c/\lambda$ ,  $d\nu = -c d\lambda/\lambda^2$ , and so, disregarding the minus sign,

$$\begin{aligned}\Delta\lambda &= \frac{\lambda^2 \Delta\nu}{c} = \frac{eB\lambda^2}{4\pi mc} \\ &= \frac{(1.60 \times 10^{-19} \text{ C})(0.300 \text{ T})(4.50 \times 10^{-7} \text{ m})^2}{(4\pi)(9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})} \\ &= 2.83 \times 10^{-12} \text{ m} = 0.00283 \text{ nm}\end{aligned}$$

**EXERCISES**

To strive, to seek, to find, and not to yield. —Alfred, Lord Tennyson

**6.3 Quantum Numbers**

1. Why is it natural that three quantum numbers are needed to describe an atomic electron (apart from electron spin)?
2. Show that

$$\Theta_{20}(\theta) = \frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$$

is a solution of Eq. (6.13) and that it is normalized.

3. Show that

$$R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

is a solution of Eq. (6.14) and that it is normalized.

4. Show that

$$R_{21}(r) = \frac{1}{2\sqrt{6}a_0^{5/2}} \frac{r}{a_0} e^{-r/2a_0}$$

is a solution of Eq. (6.14) and that it is normalized.

5. In Exercise 12 of Chap. 5 it was stated that an important property of the eigenfunctions of a system is that they are orthogonal to one another, which means that

$$\int_{-\infty}^{\infty} \psi_n^* \psi_m dV = 0 \quad n \neq m$$

Verify that this is true for the azimuthal wave functions  $\Phi_{ml}$  of the hydrogen atom by calculating

$$\int_0^{2\pi} \Phi_{m_l}^* \Phi_{m_l} d\phi$$

for  $m_l \neq m'_l$ .

6. The azimuthal wave function for the hydrogen atom is

$$\Phi(\phi) = A e^{im\phi}$$

Show that the value of the normalization constant  $A$  is  $1/\sqrt{2\pi}$  by integrating  $|\Phi|^2$  over all angles from 0 to  $2\pi$ .

**6.4 Principal Quantum Number****6.5 Orbital Quantum Number**

7. Compare the angular momentum of a ground-state electron in the Bohr model of the hydrogen atom with its value in the quantum theory.
8. (a) What is Schrödinger's equation for a particle of mass  $m$  that is constrained to move in a circle of radius  $R$ , so that  $\psi$  depends only on  $\phi$ ? (b) Solve this equation for  $\psi$  and evaluate the normalization constant. (Hint: Review the solution of Schrödinger's equation for the hydrogen atom.) (c) Find the possible energies of the particle. (d) Find the possible angular momenta of the particle.

### 6.6 Magnetic Quantum Number

9. Under what circumstances, if any, is  $L_z$  equal to  $L^2$ ?
10. What are the angles between  $L$  and the  $z$  axis for  $l = 1$ ? For  $l = 2$ ?
11. What are the possible values of the magnetic quantum number  $m_l$  of an atomic electron whose orbital quantum number is  $l = 4$ ?
12. List the sets of quantum numbers possible for an  $n = 4$  hydrogen atom.
13. Find the percentage difference between  $l$  and the maximum value of  $L_z$  for an atomic electron in  $p$ ,  $d$ , and  $f$  states.

### 6.7 Electron Probability Density

14. Under what circumstances is an atomic electron's probability-density distribution spherically symmetric? Why?
15. In Sec. 6.7 it is stated that the most probable value of  $r$  for a 1s electron in a hydrogen atom is the Bohr radius  $a_0$ . Verify this.
16. At the end of Sec. 6.7 it is stated that the most probable value of  $r$  for a 2p electron in a hydrogen atom is  $4a_0$ , which is the same as the radius of the  $n = 2$  Bohr orbit. Verify this.
17. Find the most probable value of  $r$  for a 3d electron in a hydrogen atom.
18. According to Fig. 6.11,  $P dr$  has two maxima for a 2s electron. Find the values of  $r$  at which these maxima occur.
19. How much more likely is the electron in a ground-state hydrogen atom to be at the distance  $a_0$  from the nucleus than at the distance  $2a_0$ ?
20. In Section 6.7 it is stated that the average value of  $r$  for a 1s electron in a hydrogen atom is  $1.5a_0$ . Verify this statement by calculating the expectation value  $\langle r \rangle = \int r|\psi|^2 dV$ .
21. The probability of finding an atomic electron whose radial wave function is  $R(r)$  outside a sphere of radius  $r_0$  centered on the nucleus is

$$\int_{r_0}^{\infty} |R(r)|^2 r^2 dr$$

- (a) Calculate the probability of finding a 1s electron in a hydrogen atom at a distance greater than  $a_0$  from the nucleus.  
 (b) When a 1s electron in a hydrogen atom is  $2a_0$  from the nucleus, all its energy is potential energy. According to classical physics, the electron therefore cannot ever exceed the distance  $2a_0$  from the nucleus. Find the probability  $r > 2a_0$  for a 1s electron in a hydrogen atom.
22. According to Fig. 6.11, a 2s electron in a hydrogen atom is more likely than a 2p electron to be closer to the nucleus than

$r = a_0$  (that is, to be between  $r = 0$  and  $r = a_0$ ). Verify this by calculating the relevant probabilities.

23. Unsöld's theorem states that for any value of the orbital quantum number  $l$ , the probability densities summed over all possible states from  $m_l = -l$  to  $m_l = +l$  yield a constant independent of angles  $\theta$  or  $\phi$ ; that is,

$$\sum_{m_l=-l}^{+l} |\Theta|^2 |\Phi|^2 = \text{constant}$$

This theorem means that every closed subshell atom or ion (Sec. 7.6) has a spherically symmetric distribution of electric charge. Verify Unsöld's theorem for  $l = 0$ ,  $l = 1$ , and  $l = 2$  with the help of Table 6.1.

### 6.9 Selection Rules

24. A hydrogen atom is in the 4p state. To what state or states can it go by radiating a photon in an allowed transition?
25. With the help of the wave functions listed in Table 6.1 verify that  $\Delta l = \pm 1$  for  $n = 2 \rightarrow n = 1$  transitions in the hydrogen atom.
26. The selection rule for transitions between states in a harmonic oscillator is  $\Delta n = \pm 1$ . (a) Justify this rule on classical grounds. (b) Verify from the relevant wave functions that the  $n = 1 \rightarrow n = 3$  transition in a harmonic oscillator is forbidden whereas the  $n = 1 \rightarrow n = 0$  and  $n = 1 \rightarrow n = 2$  transitions are allowed.
27. Verify that the  $n = 3 \rightarrow n = 1$  transition for the particle in a box of Sec. 5.8 is forbidden whereas the  $n = 3 \rightarrow n = 2$  and  $n = 2 \rightarrow n = 1$  transitions are allowed.

### 6.10 Zeeman Effect

28. In the Bohr model of the hydrogen atom, what is the magnitude of the orbital magnetic moment of an electron in the  $n$ th energy level?
29. Show that the magnetic moment of an electron in a Bohr orbit of radius  $r_n$  is proportional to  $\sqrt{r_n}$ .
30. Example 4.7 considered a muonic atom in which a negative muon ( $m = 207m_e$ ) replaces the electron in a hydrogen atom. What difference, if any, would you expect between the Zeeman effect in such atoms and in ordinary hydrogen atoms?
31. Find the minimum magnetic field needed for the Zeeman effect to be observed in a spectral line of 400-nm wavelength when a spectrometer whose resolution is 0.010 nm is used.
32. The Zeeman components of a 500-nm spectral line are 0.0116 nm apart when the magnetic field is 1.00 T. Find the ratio  $e/m$  for the electron from these data.