

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  $r$  = length of radius vector from origin  $O$  to point  $P$

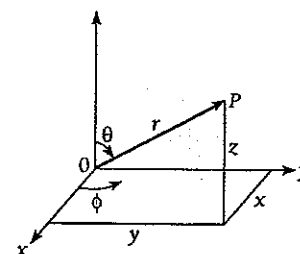
$$= \sqrt{x^2 + y^2 + z^2}$$

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

= zenith angle

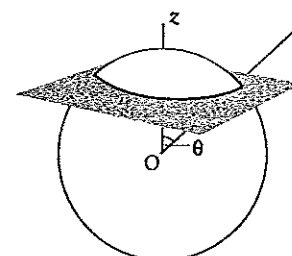
$$= \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

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

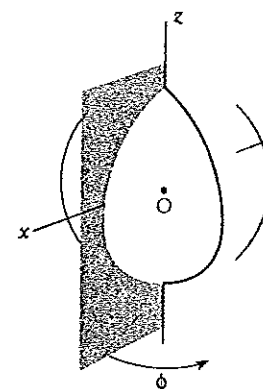


$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

(a)



(b)



(c)

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 azimuth angle  $\phi$  is a circle whose plane includes the  $z$  axis.

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

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

Hydrogen-atom  
wave function

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (6.5)$$

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

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

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

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

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

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

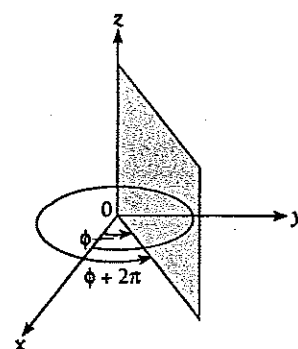


Figure 6.2 The angles  $\phi$  and  $\phi + 2\pi$  both identify the same meridian plane.

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

$$\begin{aligned} \text{Principal quantum number} & n = 1, 2, 3, \dots \\ \text{Orbital quantum number} & l = 0, 1, 2, \dots, (n-1) \\ \text{Magnetic quantum number} & m_l = 0, \pm 1, \pm 2, \dots, \pm l \end{aligned} \quad (6.17)$$

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  $n$ ,  $l$ ,  $m$ , we may write for the electron wave functions of the hydrogen atom

$$\psi = R_{nl} \Theta_{lm_l} \Phi_{m_l} \quad (6.18)$$

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	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
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  $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$  m is equal to the radius of the innermost Bohr orbit.