7

One-Electron Atoms

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7-1 Introduction

In this chapter we begin our quantum mechanical study of atoms by treating the simplest case, the *one-electron atom*. This is also the most important case. For instance, the one-electron atom hydrogen is of historical importance because it was the first system which Schroedinger treated with his theory of quantum mechanics. We shall see that the eigenvalues which the theory predicts for the hydrogen atom agree with those predicted by the Bohr model and observed by experiment. This provided the first verification of the Schroedinger theory.

There is much more to the Schroedinger theory of the one-electron atom than its prediction of the eigenvalues, because it also predicts the eigenfunctions. Using the eigenfunctions, we shall learn about the following properties of the atom: (1) the probability density functions, which give us detailed pictures of the structure of the atom that do not violate the uncertainty principle as do the precise orbits of the Bohr model, (2) the orbital angular momenta of the atom, which were incorrectly predicted by the Bohr model, (3) the electron spin and other effects of relativity on the atom, which were also incorrectly predicted by the Bohr model, and (4) the rates at which the atom makes transitions from its excited states to its ground state—measurable quantities that were not predictable at all by the Bohr model.

Above and beyond its historical and intrinsic importance, the Schroedinger theory of the one-electron atom is of great practical importance because it forms the foundation of the quantum mechanical treatment of all multielectron atoms, as well as of molecules and nuclei. In later chapters this will become very apparent.

The one-electron atom is the simplest bound system that occurs in nature. But it is more complicated than the systems we have dealt with in the preceding chapters because it contains *two particles*, and because it is *three dimensional*. The system consists of a positively charged nucleus and a negatively charged electron, moving under the influence of their mutual Coulomb attraction and bound together by that attraction. The three-dimensional character of the system allows it to have angular momentum. We shall see that interesting new quantum mechanical phenomena arise as a consequence. Quantum mechanical phenomena involving angular momentum could not arise in our earlier considerations, which dealt with only one-dimensional systems.

The three-dimensional character of the atom causes difficulty because it complicates the mathematical procedures that must be used in its treatment. However, the procedures are straightforward extensions of the simpler ones we have used on one-dimensional systems, so no conceptual problems should arise. We shall avoid practical problems by avoiding the actual solution of the more difficult equations. And certain other details, of interest to some but not all students, will be relegated to appendices. We shall present in this chapter enough of the mathematics to make it apparent how it is related to that used in the preceding chapters. But here we shall emphasize the physical considerations underlying the mathematics, the results which it yields, and the interpretation of the results.

The fact that the one-electron atom contains two particles causes no difficulty at all, if use is made of the reduced mass technique. This technique, discussed in Section

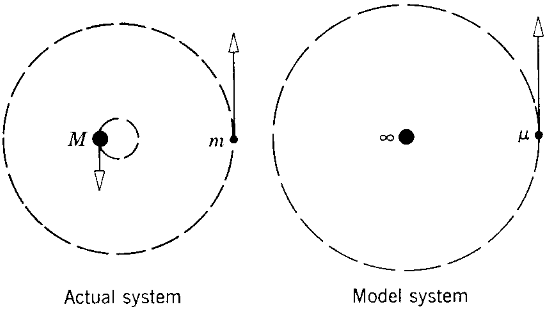

FIGURE 7-1

Left: In an actual one-electron atom, an electron of mass m and nucleus of mass M move about their fixed center of mass. *Right:* In the equivalent model atom, a particle of reduced mass μ moves about a stationary nucleus of infinite mass.

4-7, models the actual atom by an atom in which the nucleus is infinitely massive and the electron has the *reduced mass* μ given by

$$\mu = \left(\frac{M}{m + M}\right)m \tag{7-1}$$

where m is the true mass of the electron and M is the true mass of the nucleus. The reduced mass electron moves about the infinitely massive nucleus with the same electron-nucleus separation as in the actual atom. Since the infinitely massive nucleus must be completely stationary, it is necessary to treat *only* the motion of the reduced mass electron in the model atom, and the problem is therefore simplified from one involving a pair of moving particles to one involving only a single moving particle.

In classical mechanics, the motion of the reduced mass electron about the stationary nucleus in the model atom exactly duplicates the motion of the electron relative to the nucleus in the actual atom. Furthermore, the total energy of the model atom, which is just the total energy of its reduced mass electron, equals the total energy of the actual atom in a frame of reference in which its center of mass is at rest. The student may have seen a proof of these results of classical mechanics in connection with the motion of a planet about the sun, or some other system involving the motion of two particles. It is not difficult to prove that the same results are obtained in quantum mechanics, but we shall not bother to do so here. Figure 7-1 indicates the behavior of the electron and the nucleus in the actual atom and in the model atom. In both cases the center of mass of the atom is at rest.

7-2 Development of the Schroedinger Equation

We consider, therefore, an electron of reduced mass μ which is moving under the influence of the *Coulomb potential*

$$V = V(x,y,z) = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}} \tag{7-2}$$

where x, y, z are the rectangular coordinates of the electron of charge $-e$ relative to the nucleus, which is fixed at the origin. The square root in the denominator is just the electron-nucleus separation distance r. The nuclear charge is $+Ze$ ($Z = 1$ for neutral hydrogen, $Z = 2$ for singly ionized helium, etc.).

As a first step, we must develop the Schroedinger equation for this three-dimensional system. We do this by using the procedure indicated in Section 5-4. We first write the classical expression for the total energy E of the system

$$\frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x,y,z) = E \tag{7-3}$$

The quantities p_x, p_y, p_z are the x, y, z components of the linear momentum of the electron. Thus the first term on the left is the kinetic energy of the system, while the second term is its potential energy. Now we replace the *dynamical quantities* p_x, p_y, p_z, and E, by their associated *differential operators*, using an obvious three-dimensional extension of the scheme in (5-32). This gives us the *operator equation*

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z) = i\hbar\frac{\partial}{\partial t} \tag{7-4}$$

Operating with each term on the *wave function*

$$\Psi = \Psi(x,y,z,t) \tag{7-5}$$

we obtain the *Schroedinger equation* for the system

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2\Psi(x,y,z,t)}{\partial x^2} + \frac{\partial^2\Psi(x,y,z,t)}{\partial y^2} + \frac{\partial^2\Psi(x,y,z,t)}{\partial z^2}\right] + V(x,y,z)\Psi(x,y,z,t) = i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} \tag{7-6}$$

It is often convenient to write this as

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{7-7}$$

where we use the symbol

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{7-8}$$

which is called the *Laplacian operator*, or "del squared," in rectangular coordinates.

Many of the properties of the three-dimensional Schroedinger equation, and of the wave functions which are its solutions, can be obtained by obvious extensions of the properties developed in the preceding chapters. For instance, it is easy to show by the technique of separation of variables, used in Section 5-5, that since the potential function $V(x,y,z)$ does not depend on time there are solutions to the Schroedinger equation which have the form

$$\Psi(x,y,z,t) = \psi(x,y,z)e^{-iEt/\hbar} \tag{7-9}$$

where the *eigenfunction* $\psi(x,y,z)$ is a solution to the *time-independent Schroedinger equation*

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z) \tag{7-10}$$

Note that in three dimensions this equation is a *partial* differential equation because it contains three independent variables, the space coordinates x, y, z.

7-3 Separation of the Time-Independent Equation

The time-independent Schroedinger equation for the Coulomb potential can be solved by making repeated applications of the technique of separation of variables to split

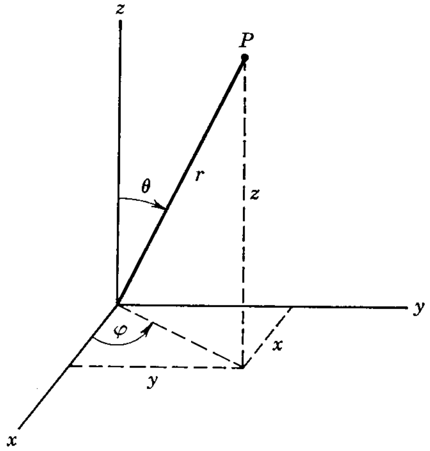

FIGURE 7-2

The spherical coordinates r, θ, φ of a point P, and its rectangular coordinates x, y, z.

the partial differential equation into a set of three ordinary differential equations, each involving only one coordinate, and then using standard procedures to solve these equations. However, separation of variables *cannot* be carried out when *rectangular coordinates* are employed because the Coulomb potential energy is a function $V(x,y,z) = -Ze^2/4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}$ of all three of these coordinates. Separation of variables will not work in rectangular coordinates because the potential itself cannot be split into terms, each of which involves only one such coordinate.

The difficulty is removed by changing to *spherical polar coordinates*. These are the coordinates r, θ, φ, illustrated in Figure 7-2. The length of the straight line connecting the electron with the origin (the nucleus) is r, and θ and φ are the polar and azimuthal angles specifying the orientation of that line. Now the distance between the electron and the nucleus is just r. So in spherical polar coordinates the Coulomb potential can be expressed as a function of a single coordinate $r = \sqrt{x^2 + y^2 + z^2}$, as follows

$$V = V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r} \tag{7-11}$$

Because of this great simplification in the form of the potential, it then becomes possible to carry out the separation of variables on the time-independent Schroedinger equation, as we shall soon see.

The space derivatives in the time-independent Schroedinger equation also change form when the coordinates are changed from rectangular to spherical. A straightforward, but tedious, application of the rules of differential calculus shows that the time-independent Schroedinger equation can be written as

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\varphi) + V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{7-12}$$

where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) \tag{7-13}$$

is the Laplacian operator in the spherical polar coordinates r, θ, φ. For the details of the coordinate transformation leading to (7-12) and (7-13), the student should consult Appendix I. A comparison of the forms of the Laplacian operator in rectangular and spherical polar coordinates, (7-8) and (7-13), shows that we have simplified the expression of the potential energy function at the expense of considerably complicating the expression of the Laplacian operator in the time-independent Schroedinger equation that must be solved.

Nevertheless, the change of coordinates is worthwhile because it will allow us to find solutions to the time-independent Schroedinger equation of the form

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi) \tag{7-14}$$

That is, we shall show that there are solutions $\psi(r,\theta,\varphi)$ to (7-12) that split into products of three functions, $R(r)$, $\Theta(\theta)$, and $\Phi(\varphi)$, each of which depends on only one of the coordinates. The advantage lies in the fact that these three functions can be found by solving *ordinary* differential equations. We show this by substituting the product form, $\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$, into the time-independent Schroedinger equation obtained by evaluating the Laplacian operator in (7-12) from (7-13). This yields

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R\Theta\Phi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 R\Theta\Phi}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial R\Theta\Phi}{\partial\theta}\right)\right] + V(r)R\Theta\Phi = ER\Theta\Phi$$

Carrying out the partial differentiations, we have

$$-\frac{\hbar^2}{2\mu}\left[\frac{\Theta\Phi}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\varphi^2} + \frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + V(r)R\Theta\Phi = ER\Theta\Phi$$

In this equation we have written the partial derivative $\partial R/\partial r$ as the total derivative dR/dr since the two are equivalent because R is a function of r alone. The same comment applies to the other derivatives. If we now multiply through by $-2\mu r^2\sin^2\theta/R\Theta\Phi\hbar^2$, and transpose, we obtain

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta[E - V(r)]$$

As the left side of this equation does not depend on r or θ, whereas the right side does not depend on φ, their common value cannot depend on any of these variables. The common value must therefore be a constant, which we shall find it convenient to designate as $-m_l^2$. Thus we obtain two equations by setting each side equal to this constant

$$\frac{d^2\Phi}{d\varphi^2} = -m_l^2\Phi \tag{7-15}$$

and

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2[E - V(r)] = -\frac{m_l^2}{\sin^2\theta}$$

By transposing, we can rewrite the second equation as

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}[E - V(r)] = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

Since we have here an equation whose left side does not depend on one of the variables and whose right side does not depend on the other, we conclude again that both sides must equal a constant. It is convenient to designate this constant as $l(l+1)$. Thus we obtain, by setting each side equal to $l(l+1)$, two more equations

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta \tag{7-16}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}[E - V(r)]R = l(l+1)\frac{R}{r^2} \tag{7-17}$$

We see that the assumed product form of the solution, $\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$, is valid because it works! We also see that the problem has been reduced to that of solving the ordinary differential equations, (7-15), (7-16), and (7-17), for $\Phi(\varphi)$, $\Theta(\theta)$, and $R(r)$.

In solving these equations, we shall find that the equation for $\Phi(\varphi)$ has *acceptable* solutions only for *certain values of* m_l. Using these values of m_l in the equation for $\Theta(\theta)$, it turns out that this equation has *acceptable* solutions only for *certain values of* l. With these values of l in the equation for $R(r)$, this equation is found to have *acceptable* solutions only for *certain values of the total energy* E; that is, the energy of the atom is quantized.

7-4 Solution of the Equations

Consider (7-15) for $\Phi(\varphi)$. By differentiation and substitution, the student may easily verify that it has a particular solution

$$\Phi(\varphi) = e^{im_l\varphi}$$

(The discussion following Example 7-5 explains why this particular solution is used.) Here we must, for the first time, explicitly consider the requirement of Section 5-6 that the eigenfunctions be *single valued.* This demands that the function $\Phi(\varphi)$ be single valued, and the demand must be considered explicitly because the azimuthal angles $\varphi = 0$ and $\varphi = 2\pi$ are actually the same angle. Thus, we must require that $\Phi(\varphi)$ has the same value at $\varphi = 0$ as it does at $\varphi = 2\pi$, that is

$$\Phi(0) = \Phi(2\pi)$$

Evaluating the exponential in the particular solution $\Phi(\varphi)$, we obtain

$$e^{im_l0} = e^{im_l2\pi}$$

or

$$1 = \cos m_l2\pi + i \sin m_l2\pi$$

The requirement is satisfied only if the absolute value of m_l has one of the values

$$|m_l| = 0, 1, 2, 3, \ldots \tag{7-18}$$

In other words, m_l can be only a positive or negative *integer*. Thus the set of functions which are *acceptable* solutions to (7-15) are

$$\Phi_{m_l}(\varphi) = e^{im_l\varphi} \tag{7-19}$$

where m_l has one of the integral values specified by (7-18). The *quantum number* m_l is used as a subscript to identify the specific form of an acceptable solution.

In solving (7-16) for the functions $\Theta(\theta)$, the procedure is very nearly the same as that used to obtain analytical solutions of the time-independent Schroedinger equation for the simple harmonic oscillator potential. Interested students are referred to Appendix H, which explains this quite lengthy procedure. Here we shall only quote the results. It is found that solutions to (7-16) which are *acceptable* (remain finite) are obtained only if the constant l is equal to one of the *integers*

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \ldots \tag{7-20}$$

The acceptable solutions can be written

$$\Theta_{lm_l}(\theta) = \sin^{|m_l|}\theta\, F_{l|m_l|}(\cos\theta) \tag{7-21}$$

The $F_{l|m_l|}(\cos\theta)$ are polynomials in $\cos\theta$, which have forms that depend on the value of the *quantum number* l and on the absolute value of the quantum number m_l. Thus it is necessary to use both of these quantum numbers to identify the functions $\Theta_{lm_l}(\theta)$ that are acceptable solutions to the equation. Examples of these functions will be presented in Section 7-6.

The procedure used in the solution of (7-17) for the functions $R(r)$ is also very similar to that used for the simple harmonic oscillator potential. It is found that there are bound-state solutions which are *acceptable* (remain finite) only if the constant E (the total energy) has one of the values E_n, where

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \tag{7-22}$$

In this expression the *quantum number n* is one of the *integers*

$$n = l + 1, l + 2, l + 3, \ldots \tag{7-23}$$

The acceptable solutions are most conveniently written as

$$R_{nl}(r) = e^{-Zr/na_0}\left(\frac{Zr}{a_0}\right)^l G_{nl}\left(\frac{Zr}{a_0}\right) \tag{7-24}$$

where the parameter a_0 is

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \tag{7-25}$$

The $G_{nl}(Zr/a_0)$ are polynomials in Zr/a_0, with different forms for different values of n and l. Thus both of these quantum numbers are required to identify the different functions $R_{nl}(r)$ that are acceptable solutions to the equation. But the allowed values E_n of the total energy carry only the quantum number n as a label since they depend only on the value of that quantum number. Examples of the functions $R_{nl}(r)$ will be presented in Section 7-6.

7-5 Eigenvalues, Quantum Numbers, and Degeneracy

One of the important results of the Schroedinger theory of the one-electron atom is the prediction of (7-22) for the allowed values of total energy of the bound states of the atom. Comparing this prediction for the eigenvalues

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

with the predictions of the Bohr model (see (4-18)), we find that *identical* allowed energies are predicted by these treatments. Both predictions are in excellent agreement with experiment. Schroedinger's derivation of (7-22) provided the first convincing verification of his theory of quantum mechanics. Figure 7-3 illustrates the Coulomb potential $V(r)$ for the one-electron atom, and its *eigenvalues* E_n.

What is the relation between the Coulomb potential and its eigenvalues, and the potentials studied in Chapter 6 and their eigenvalues? One obvious difference is that the quantum mechanical calculations leading to the eigenvalues of the Coulomb potential are appreciably more complicated. But the Coulomb potential is an exact description of a real three-dimensional system. The potentials previously treated are approximate descriptions of idealized one-dimensional systems, which are designed to simplify the calculations. Part of the complication for the Coulomb potential is also due to its spherical symmetry, which forces the use of spherical polar coordinates instead of rectangular coordinates.

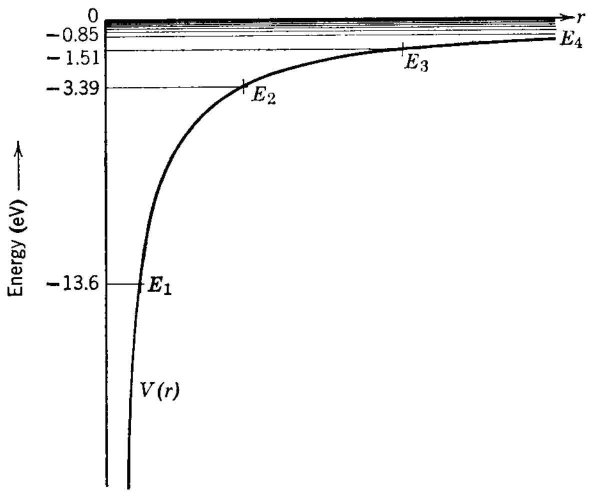

FIGURE 7-3

The Coulomb potential $V(r)$ and its eigenvalues E_n. For large values of n the eigenvalues become very closely spaced in energy since E_n approaches zero as n approaches infinity. Note that the intersection of $V(r)$ and E_n, which defines the location of one end of the classically allowed region, moves out as n increases. Not shown in this figure is the continuum of eigenvalues at positive energies corresponding to unbound states.

The similarities are much more fundamental than the differences. For the Coulomb potential, as for any other binding potential, the allowed total energies of a particle bound to the potential are *discretely quantized.* Figure 7-4 makes a comparison between the allowed energies for a Coulomb potential and for several one-dimensional binding potentials. In this figure the Coulomb potential represents a crosscut along a diameter through the one-electron atom. Note that all the binding potentials have a *zero-point energy.* That is, in all cases the lowest allowed value of total energy lies above the minimum value of the potential energy. Associated with its zero-point energy, the one-electron atom has a zero-point motion like other systems described by binding potentials. In the following section we shall see that this phenomena can give us a basic explanation of the stability of the ground state of the atom.

Although the eigenvalues of the one-electron atom depend on only the quantum number n, the eigenfunctions depend on all three quantum numbers n, l, m_l since they are products of the three functions $R_{nl}(r)$, $\Theta_{lm_l}(\theta)$, and $\Phi_{m_l}(\varphi)$. *The fact that three*

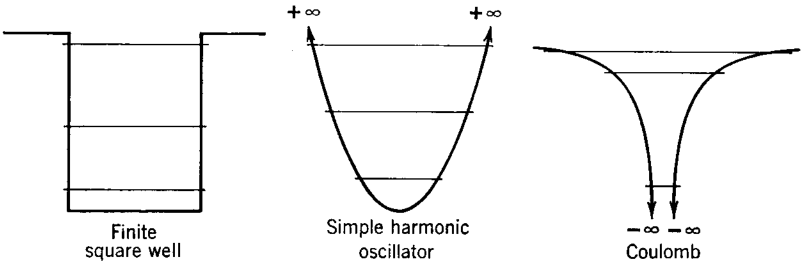

FIGURE 7-4

A comparison between the allowed energies of several binding potentials. The three-dimensional Coulomb potential is shown in a cross-sectional view along a diameter; the other potentials are one-dimensional.

quantum numbers arise is a consequence of the fact that the time-independent Schroedinger equation contains three independent variables, one for each space coordinate. Gathering together the conditions which the quantum numbers satisfy, we have

$$\begin{aligned} |m_l| &= 0, 1, 2, 3, \ldots \\ l &= |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \ldots \\ n &= l + 1, l + 2, l + 3, \ldots \end{aligned} \tag{7-26}$$

These conditions are more conveniently expressed as

$$\begin{aligned} n &= 1, 2, 3, \ldots \\ l &= 0, 1, 2, \ldots, n - 1 \\ m_l &= -l, -l + 1, \ldots, 0, \ldots, +l - 1, l \end{aligned} \tag{7-27}$$

Example 7-1. Show that the conditions of (7-27) are equivalent to those of (7-26).

According to (7-26) the minimum value of l is equal to $|m_l|$, and the minimum value of $|m_l|$ is 0. Thus the minimum value of l is 0 and the minimum value of n, which is equal to $l + 1$, is $0 + 1 = 1$. Since n increases by integers without limit, the possible values of n are $n = 1, 2, 3, \ldots$. For a given n, the maximum value of l is the one satisfying the relation $n = l + 1$, that is, $l = n - 1$. Consequently the possible values of l are $l = 0, 1, 2, \ldots, n - 1$. Finally, for a given l, the largest value which $|m_l|$ can assume is $|m_l| = l$. Thus the maximum value of m_l is $+l$ and the minimum value is $-l$, and it can assume only the values $m_l = -l, -l + 1, \ldots, 0, \ldots, +l - 1, +l$. ◀

Because of its role in specifying the total energy of the atom, n is sometimes called the *principal* quantum number. Because the azimuthal, or orbital, angular momentum of the atom depends on l, as we shall soon see, l is sometimes called the *azimuthal* quantum number. We shall also see that if the atom is in an external magnetic field there is a dependence of its energy on m_l. Consequently, m_l is sometimes called the *magnetic* quantum number.

The conditions of (7-27) make it apparent that for a given value of n there are generally several different possible values of l and m_l. Since the form of the eigenfunctions depends on all three quantum numbers, it is apparent that there will be situations in which two or more completely different eigenfunctions correspond to exactly the same eigenvalue E_n. As the eigenfunctions described the behavior of the atom, we see that it has states with *completely different behavior* that nevertheless have the *same total energy*. In physics the word used to characterize this phenomenon is *degeneracy*, and eigenfunctions corresponding to the same eigenvalue are said to be *degenerate*. There is little relation to the common usage of the word; degenerate eigenfunctions are not at all reprehensible!

Degeneracy also occurs in classical mechanics and in the related old quantum theory. In the discussion of elliptical orbits of the Bohr-Sommerfeld atom in Section 4-10, we indicated that the total energy of the atom is independent of the semiminor axis of the ellipse. Thus the atom has states with very different behavior, that is, with the electron traveling in very different orbits, which nevertheless have the same total energy. Exactly the same phenomenon occurs in planetary motion. This classical degeneracy is comparable to the l degeneracy that arises in the quantum mechanical one-electron atom. The energy of a Bohr-Sommerfeld atom, or of a planetary system, is also independent of the orientation in space of the plane of the orbit. This is comparable to the m_l degeneracy of the quantum mechanical atom.

In either classical or quantum mechanics, degeneracy is a result of certain properties of the potential energy function that describes the system. In the quantum

TABLE 7-1. Possible Values of l and m_l for $n = 1, 2, 3$

n	1	2		3		
l	0	0	1	0	1	2
m_l	0	0	$-1, 0, +1$	0	$-1, 0, +1$	$-2, -1, 0, +1, +2$
Number of degenerate eigenfunctions for each l	1	1	3	1	3	5
Number of degenerate eigenfunctions for each n	1	4		9		

mechanical one-electron atom, the degeneracy with respect to m_l arises because the potential depends only on the coordinate r, so the potential is spherically symmetrical and the total energy of the atom is independent of its orientation in space. The l degeneracy is a consequence of the particular form of the r dependence of the Coulomb potential.

If an external magnetic field is applied to the atom, then its total energy *will* depend on its orientation in space because of an interaction between currents in the atom and the applied field. We shall study this later, and we shall find that the orientation in space is determined by the quantum number m_l. Thus in an external magnetic field the degeneracy with respect to m_l is removed and the atom has different energy levels for different m_l values. If the external magnetic field is gradually reduced in intensity, the dependence of the total energy of the atom on m_l is reduced in proportion. When the field is reduced to zero the energy levels that correspond to different values of m_l degenerate into a single energy level, and the corresponding eigenfunctions become degenerate.

Many properties of alkali atoms can be discussed in terms of the motion of a single "valence" electron in a potential which is spherically symmetrical, but which does not have the $1/r$ behavior of the Coulomb potential. The energy of this electron *does* depend on l. Thus the degeneracy with respect to l is removed if the form of the r dependence of the potential is changed. We shall study this phenomenon on a number of occasions later in this book, and in the process more insight into the origin of the l degeneracy of the Coulomb potential will be obtained.

From (7-27) it is easy to see how many degenerate eigenfunctions there are, for an isolated one-electron atom, which correspond to a particular eigenvalue E_n. The possible values of the quantum numbers for $n = 1$, 2, and 3 are shown in Table 7-1. Inspection of this table makes it apparent that:

1. For each value of n, there are n possible values of l.
2. For each value of l, there are $(2l + 1)$ possible values of m_l.
3. For each value of n, there are a total of n^2 degenerate eigenfunctions.

7-6 Eigenfunctions

The mathematical techniques used in quantum mechanics to obtain (7-22) for the eigenvalues of the one-electron atom are, admittedly, quite complicated compared to

TABLE 7-2. Some Eigenfunctions for the One-Electron Atom

Quantum Numbers			
n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\theta e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\theta$
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\theta e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$
3	2	± 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin\theta\cos\theta e^{\pm i\varphi}$
3	2	± 2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin^2\theta e^{\pm 2i\varphi}$

those used in the Bohr model to obtain the same equation. Putting aside questions concerning the logical consistency of the postulates of the Bohr model, it is still reasonable to question whether all the extra work involved in the quantum mechanical treatment of the one-electron atom is justified by the results obtained. The answer is, overwhelmingly, yes! We can now find out much more about the one-electron atom than we possibly can from the Bohr model, because we have the *eigenfunctions* as well as the eigenvalues. The eigenfunctions contain a wealth of additional information about the properties of the atom. The remainder of this chapter, and the following chapter, will be devoted largely to studying the eigenfunctions and extracting this information from them.

We know that the eigenfunctions are formed by taking the product

$$\psi_{nlm_l}(r,\theta,\varphi) = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\varphi)$$

We also know, from (7-19), (7-21), and (7-23) that for any bound state

$$\Phi_{m_l}(\varphi) = e^{im_l\varphi}$$

$$\Theta_{lm_l}(\theta) = \sin^{|m_l|}\theta\,(\text{polynomial in }\cos\theta)$$

and

$$R_{nl}(r) = e^{-(\text{constant})r/n}\,r^l(\text{polynomial in } r)$$

All the eigenfunctions have basically the same mathematical structure, except that with increasing values of n and l the polynomials in r and $\cos\theta$ become increasingly more complicated. Table 7-2 lists the one-electron atom eigenfunctions for the first three values of n. They are expressed in terms of the parameter

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 0.529 \times 10^{-10}\,\text{m} = 0.529\,\text{Å}$$

which the student may recognize as equal to the radius of the smallest orbit of a Bohr hydrogen atom. The multiplicative constant in front of each eigenfunction has been adjusted so that it is normalized. In other words, the integral over all space of the corresponding probability density function equals one, so that in each quantum state there is probability one of finding the atomic electron somewhere.

Example 7-2. Verify that the eigenfunction ψ_{211}, and the associated eigenvalue E_2, satisfy the time-independent Schroedinger equation, (7-12), for the one-electron atom with $Z = 1$.

Since the differential equation is linear in ψ, for the purposes of this verification we can ignore completely the multiplicative constant $1/8\pi^{1/2}a_0^{5/2}$, and write the eigenfunction as

$$\psi = re^{-r/2a_0}\sin\theta e^{i\varphi}$$

This is the simplest case with a nontrivial dependence on all three coordinates. Nevertheless, the verification of this case should give the student some confidence in the validity of all the eigenfunctions quoted in Table 7-2.

Before beginning, let us introduce the convenient notation

$$\psi = f(r,\varphi)\sin\theta = f\sin\theta$$

and

$$\psi = g(\theta,\varphi)\,re^{-r/2a_0} = gre^{-r/2a_0}$$

This notation will be useful in evaluating the derivatives that enter in (7-12), which is

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)\right] + V\psi = E\psi$$

First we calculate

$$\frac{\partial\psi}{\partial\theta} = \frac{\partial}{\partial\theta}(f\sin\theta) = f\cos\theta$$

$$\sin\theta\frac{\partial\psi}{\partial\theta} = f\sin\theta\cos\theta$$

$$\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) = f(\cos^2\theta - \sin^2\theta)$$

$$\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) = \frac{f}{r^2}\left(\frac{\cos^2\theta - \sin^2\theta}{\sin\theta}\right)$$

Next we calculate

$$\frac{\partial^2\psi}{\partial\varphi^2} = (i)^2\psi = -\psi = -f\sin\theta$$

$$\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} = -\frac{f}{r^2\sin\theta}$$

Adding these two results, we obtain

$$\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$= \frac{f}{r^2\sin\theta}(\cos^2\theta - \sin^2\theta - 1) = -\frac{2f\sin^2\theta}{r^2\sin\theta} = -\frac{2f\sin\theta}{r^2} = -\frac{2\psi}{r^2}$$

Then we calculate

$$\frac{\partial\psi}{\partial r} = g\left(e^{-r/2a_0} - \frac{r}{2a_0}e^{-r/2a_0}\right)$$

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

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = g\left(2re^{-r/2a_0} - \frac{r^2}{2a_0}e^{-r/2a_0} - \frac{3r^2}{2a_0}e^{-r/2a_0} + \frac{r^3}{4a_0^2}e^{-r/2a_0}\right)$$

$$= 2gre^{-r/2a_0}\left(1 - \frac{r}{a_0} + \frac{r^2}{8a_0^2}\right) = 2\left(1 - \frac{r}{a_0} + \frac{r^2}{8a_0^2}\right)\psi$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = 2\left(\frac{1}{r^2} - \frac{1}{ra_0} + \frac{1}{8a_0^2}\right)\psi$$

Substituting this term, and the term coming from the θ and φ derivatives, into the differential equation that is supposed to be satisfied, we obtain

$$-\frac{\hbar^2}{2\mu}\left[2\left(\frac{1}{r^2} - \frac{1}{ra_0} + \frac{1}{8a_0^2}\right) - \frac{2}{r^2}\right]\psi + V\psi = E\psi$$

or

$$\frac{\hbar^2}{\mu a_0}\left(\frac{1}{r} - \frac{1}{8a_0}\right) + V = E$$

Now

$$E = E_2 = -\frac{\mu e^4}{8(4\pi\epsilon_0)^2\hbar^2}$$

Also

$$V = -\frac{e^2}{4\pi\epsilon_0 r}$$

and

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

So we have

$$\frac{\hbar^2}{\mu}\frac{\mu e^2}{4\pi\epsilon_0\hbar^2}\left(\frac{1}{r} - \frac{\mu e^2}{8(4\pi\epsilon_0)\hbar^2}\right) - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{\mu e^4}{8(4\pi\epsilon_0)^2\hbar^2}$$

Since inspection demonstrates that this equation is satisfied identically, we have completed the verification. ◀

7-7 Probability Densities

We begin to extract information from the one-electron atom eigenfunctions by studying the forms of the corresponding *probability density functions*

$$\Psi^*\Psi = \psi^*_{nlm_l}e^{iE_nt/\hbar}\psi_{nlm_l}e^{-iE_nt/\hbar} = \psi^*_{nlm_l}\psi_{nlm_l} = R^*_{nl}\Theta^*_{lm_l}\Phi^*_{m_l}R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

As these are functions of three coordinates, we cannot directly plot them in two dimensions. Nevertheless, we can study their three-dimensional behavior by considering separately their dependence on each coordinate. We treat first the r dependence in terms of the *radial probability density* $P(r)$, defined so that $P(r)\,dr$ is the probability of finding the electron at any location with radial coordinate between r and $r + dr$. By integrating the probability density $\Psi^*\Psi$, which is a probability per unit volume, over the volume enclosed between spheres of radii r and $r + dr$, it is easy to show that

$$P_{nl}(r)\,dr = R^*_{nl}(r)R_{nl}(r)r^2\,dr \tag{7-28}$$

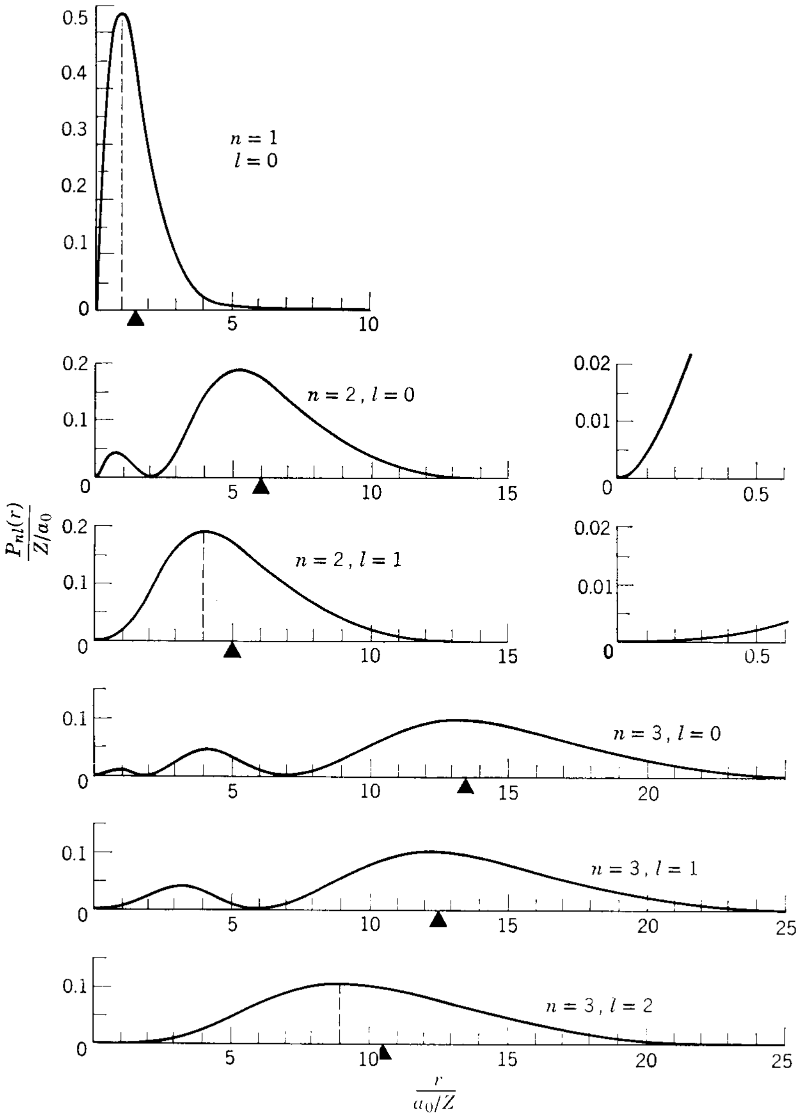

FIGURE 7-5

The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-31). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{\text{max}} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{\text{Bohr}} = n^2 a_0/Z$, which is indicated by the location of the dashed line.

The factor of r^2 is present on the right side because the volume enclosed between the spheres is proportional to that factor. The use of the quantum numbers n and l as labels to specify the form of a particular radial probability density function is obviously appropriate, but the form of these functions does not depend on the quantum number m_l. Figure 7-5 plots several $P_{nl}(r)$, using dimensionless quantities for each axis.

Inspection of the figure shows that the radial probability densities, for each set of the pertinent quantum numbers, have appreciable values only in reasonably restricted ranges of the radial coordinate. Thus, when the atom is in one of its quantum states, specified by a particular set of its quantum numbers, there is a high probability that the radial coordinate of the electron will be found within a reasonably restricted range. The electron would quite probably be found within a certain so-called *shell* contained within two concentric spheres centered on the nucleus. A study of the figure will demonstrate that the characteristic radii of these shells is determined primarily by the quantum number n, although there is a small l dependence.

This property can be seen in a more quantitative way by using the expectation value of the radial coordinate of the electron to characterize the radius of the shell. An obvious extension of the arguments of Section 5-4 to three dimensions shows that the expectation value is given by the expression

$$\overline{r_{nl}} = \int_0^\infty r P_{nl}(r)\,dr$$

If the integral is evaluated, this yields

$$\overline{r_{nl}} = \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\} \tag{7-29}$$

The values of $\overline{r_{nl}}$ are indicated in Figure 7-5 with small triangles. It is apparent that $\overline{r_{nl}}$ depends primarily on n, since the l dependence is suppressed by the factor of $1/2$ and the factor of $1/n^2$ in (7-29).

An interesting comparison can be made between (7-29) and (4-16)

$$r_{\text{Bohr}} = \frac{n^2 a_0}{Z}$$

which gives the radii of the circular orbits of a Bohr atom. Quantum mechanics shows that the radii of the shells are of approximately the same size as the radii of the circular Bohr orbits. These radii increase rapidly with increasing n. The basic reason is that the total energy E_n of the atom becomes more positive with increasing n, so the region of the coordinate r for which E_n is greater than $V(r)$ expands with increasing n, as can be seen in Figure 7-3. That is, the shells expand with increasing n because the classically allowed regions expand.

Example 7-3. (a) Calculate the location at which the radial probability density is a maximum for the ground state of the hydrogen atom. (b) Next calculate the expectation value for the radial coordinate in this state. (c) Then interpret these results in terms of the results of measurements of the location of the electron in the atom.

(a) The radial probability density for the $n = 1$, $l = 0$ ground state is

$$P_{10}(r) = R_{10}^*(r)R_{10}(r)r^2$$

We take $R_{10}(r)$ from the r-dependent factor of the first eigenfunction listed in Table 7-2, with $Z = 1$, and obtain

$$P_{10}(r) = e^{-r/a_0}\,e^{-r/a_0}\,r^2 = e^{-2r/a_0}\,r^2$$

We have ignored normalization (i.e., for simplicity taken the multiplicative constant equal to one) since it has no effect on what we are about to do. This is to find the maximum in $P_{10}(r)$ by evaluating its derivative with respect to r and setting the result equal to zero. That is

$$\frac{dP_{10}(r)}{dr} = -\frac{2}{a_0}\,e^{-2r/a_0}\,r^2 + e^{-2r/a_0}\,2r$$

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

The solution to the equation we have obtained is

$$1 - \frac{r}{a_0} = 0$$

or

$$r = a_0$$

This is the location of the maximum in the radial probability density.

(b) To calculate the expectation value of the radial coordinate r, we evaluate (7-29), with $n = 1, l = 0$, and $Z = 1$. We obtain

$$\overline{r_{10}} = a_0\{1 + (1/2)\}\ [1] = 1.5a_0$$

(c) We have found that the expectation value of r is somewhat larger than the value of r at which the radial probability density is a maximum. The reason is that the radial probability density is asymmetrical about its maximum in such a way that there is a small, but not negligible, probability of finding fairly large values of r in measurements of the location of the electron in the atom. So, although the most likely location of the electron is at $r = a_0$ (i.e., at the ground state Bohr orbit radius), the average value obtained in measurements of the location is $\bar{r} = 1.5a_0$. All these features can be seen by inspecting the top curve of Figure 7-5. ◀

Example 7-4. In its ground state, the size of the hydrogen atom can be taken to be the radius of the $n = 1$ shell for $Z = 1$, which is essentially $a_0 = 4\pi\epsilon_0\hbar^2/\mu e^2 \simeq 0.5$ Å. Show that this fundamental atomic dimension can be obtained directly from consideration of the uncertainty principle.

The form of the potential function

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

tends to cause the atom to collapse since the smaller the distance from the electron to the nucleus the more negative is the potential energy. This tendency is opposed by the effect of the uncertainty principle, as follows.

If the electron is located within a region of size R, then any component of its linear momentum must have an uncertainty of approximately

$$\Delta p = \frac{\hbar}{R}$$

This uncertainty reflects the fact that the linear momentum of magnitude p can be in any direction, so the components can have values ranging from $-p$ to $+p$. Thus the uncertainty in any component of the linear momentum also satisfies approximately the relation

$$\Delta p = p$$

Therefore, the electron must have a kinetic energy approximately equal to

$$K = \frac{p^2}{2\mu} = \frac{(\Delta p)^2}{2\mu} = \frac{\hbar^2}{2\mu R^2}$$

We see that the kinetic energy becomes more positive with decreasing R, which opposes the effect of the potential energy to cause collapse.

If the size of the atom is R, its potential energy is approximately

$$V = \frac{-e^2}{4\pi\epsilon_0 R}$$

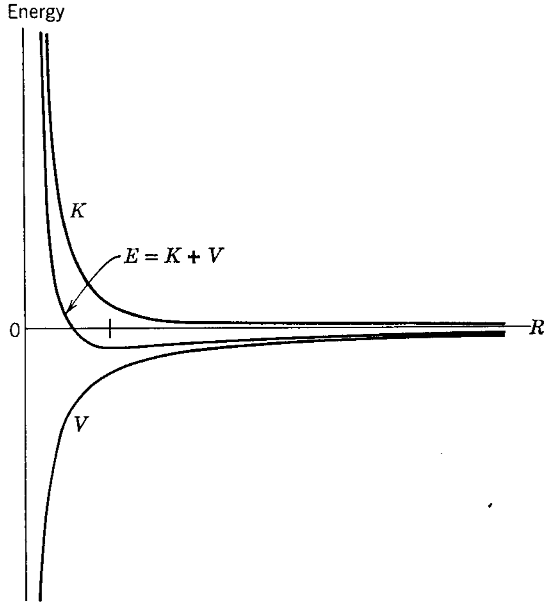

FIGURE 7-6

The qualitative behavior of the kinetic energy K, potential energy V and total energy E of a hydrogen atom, as functions of the size R of the atom. For small R, K increases more rapidly than V decreases because $K \propto 1/R^2$ while $V \propto -1/R$. For large R, K becomes negligible compared to V. As a result, E has a minimum at a certain value of R (indicated by the mark on the R axis), and at this size the atom is most stable.

Then the total energy of the atom is approximately

$$E = K + V = \frac{\hbar^2}{2\mu R^2} - \frac{e^2}{4\pi\epsilon_0 R}$$

Obeying the common tendency of all physical systems to be as stable as possible, the atom will adjust its size so as to minimize its total energy. The existence of an optimum size can be seen qualitatively by inspecting Figure 7-6, which plots K, V, and E as functions of R. (Note that R is *not* the radial coordinate; it is the size of the atom which we are treating as a variable in order to determine its optimum value.) We can find the most energetically favorable size quantitatively by differentiating E with respect to R, and setting the derivative equal to zero. That is

$$\frac{dE}{dR} = -\frac{2\hbar^2}{2\mu R^3} + \frac{e^2}{4\pi\epsilon_0 R^2} = 0$$

Solving this equation for R, we find

$$R = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = a_0$$

the size which gives minimum total energy, and therefore the most stable atom.

The uncertainty principle governs the minimum size of the atom because its governs its minimum energy. This is the zero-point energy of the ground state, which has a size that arises from its zero-point motion. These simple ideas provide a very satisfactory answer to the question of the stability of the ground state of the atom. And this is particularly so if we also consider the discussion following Example 5-13, which shows that in its ground state the atom does not radiate. ◀

Figure 7-5 shows that the *details* of the structure of the radial probability density functions do depend on the value of the quantum number l. For a given n, the function has a single strong maximum when l takes on its largest possible value; but additional weaker maxima develop inside the strong one when l takes on smaller values. Generally, these weaker maxima are not so important. However, there is a related property that can be very important. Inspection of the figure, particularly the expanded plots for $n = 2, l = 0$, and $n = 2, l = 1$, will demonstrate that the radial probability density functions have appreciable values near the origin at $r = 0$ only for $l = 0$. This means that only for $l = 0$ will there be an appreciable probability of finding the electron near the nucleus.

Another way of seeing this property is to consider the probability density, $\Psi^*\Psi = \psi^*\psi$, itself. Inspection of the eigenfunctions listed in Table 7-2 will show that for values of r which are small compared to a_0/Z, where the exponential term is slowly varying, the radial dependence of all the eigenfunctions has the behavior

$$\psi \propto r^l \qquad r \rightarrow 0 \quad (7\text{-}30)$$

This behavior can easily be verified by direct substitution into (7-17), the equation that determines the radial dependence of the ψ. As a consequence, the radial dependence of the probability densities for small r is

$$\psi^*\psi \propto r^{2l} \qquad r \rightarrow 0 \quad (7\text{-}31)$$

From this it follows that the value of $\psi^*\psi$ in a small volume near $r = 0$ is relatively large only for $l = 0$, and decreases very rapidly with increasing l. The reason is that $r^0 \gg r^2 \gg r^4 \gg \ldots$, for $r \rightarrow 0$.

We see that there is some probability that the electron will be near the nucleus if $l = 0$, but very much less probability that this will happen if $l = 1$, and even less if $l = 2$, etc. This can have important effects in certain circumstances because the potential energy of the atom becomes very large in magnitude if the electron is near the nucleus. We shall see later that this is particularly true for the case of multielectron atoms, which have essentially the same property. In fact the r^l behavior of the eigenfunctions for small r is of predominant importance in the structure of multielectron atoms. We shall also see later that the r^l behavior is due physically to the angular momentum of the atom, which depends on l.

Now let us proceed to the study of the *angular* dependence of the probability density functions

$$\psi^*_{nlm_l}\psi_{nlm_l} = R^*_{nl}R_{nl}\Theta^*_{lm_l}\Theta_{lm_l}\Phi^*_{m_l}\Phi_{m_l}$$

From (7-19) we have

$$\Phi^*_{m_l}(\varphi)\Phi_{m_l}(\varphi) = e^{-im_l\varphi}e^{im_l\varphi} = 1$$

Thus the probability density does not depend on the coordinate φ. The three-dimensional behavior of $\psi^*_{nlm_l}\psi_{nlm_l}$ is therefore completely specified by the product of the quantity $R^*_{nl}(r)R_{nl}(r) = P_{nl}(r)/r^2$ and the quantity $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$, which plays the role of a directionally dependent modulation factor.

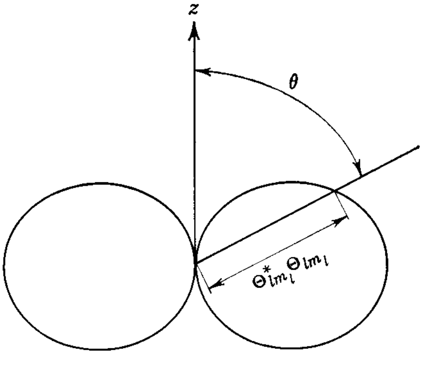

FIGURE 7-7

A polar diagram of the factor which determines the directional dependence of the one-electron atom probability density.

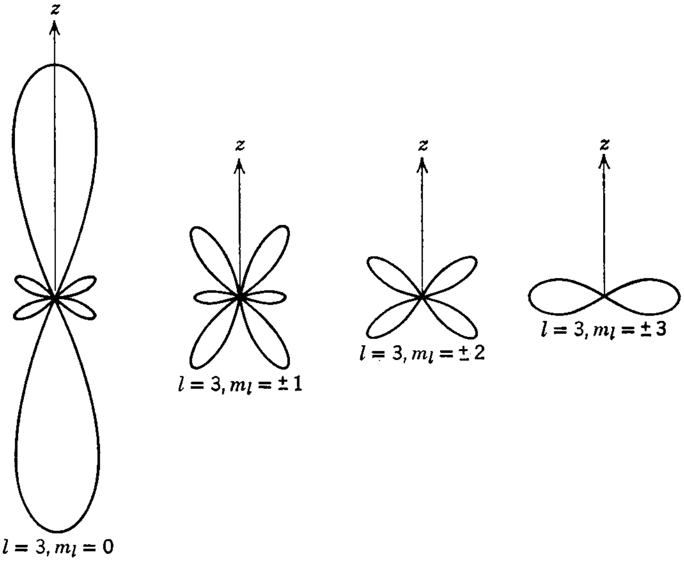

FIGURE 7-8

Polar diagrams of the directional dependence of the one-electron atom probability densities for $l = 3$; $m_l = 0, \pm 1, \pm 2, \pm 3$.

The form of the factor $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$ is conveniently presented in terms of polar diagrams, of which one is shown in Figure 7-7. The origin of the diagram is at the point $r = 0$ (the nucleus), and the z axis is taken along the direction from which the angle θ is measured. The distance from the origin to the curve, measured at the angle θ, is equal to the value of $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$ for that angle. Such a diagram can also be thought of as representing the complete directional dependence of $\psi^*_{nlm_l}\psi_{nlm_l}$ by visualizing the three-dimensional surface obtained by rotating the diagram about the z axis through the 360° range of the angle φ. The distance, measured in the direction specified by the angles θ and φ, from the origin to a point on the surface, is equal to $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)\Phi^*_{m_l}(\varphi)\Phi_{m_l}(\varphi)$ for those values of θ and φ.

In Figure 7-8 we illustrate an example of the dependence of the form of $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$ on the quantum number m_l, by a set of polar diagrams for $l = 3$, and the seven possible values of m_l for this value of l, i.e., for $m_l = -3, -2, -1, 0, 1, 2, 3$. Note the way in which the region of concentration of $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$, and therefore $\psi^*_{nlm_l}\psi_{nlm_l}$, shifts from the z axis to the plane perpendicular to the z axis as the absolute value of m_l increases. Some features of the dependence of $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$ on the quantum number l are indicated in Figure 7-9 in terms of a set of polar diagrams for $m_l = \pm l$ and $l = 0, 1, 2, 3, 4$. In the case $n = 1$, $l = m_l = 0$, which is the ground state of the atom, $\psi^*_{nlm_l}\psi_{nlm_l}$ depends on neither θ nor φ and the probability density is spherically symmetrical. For the other states, the concentration of probability density in the plane perpendicular to the z axis, when $m_l = \pm l$, becomes more and more pronounced with increasing l. Figure 7-10 is an attempt to overcome the limitations of the two-dimensional printed page using shading to represent the three-dimensional appearance of the probability density functions for various states of the one-electron atom.

The probability density functions displayed in these figures generally have a set of spherical and conical surfaces, defined by certain values of r and θ, on which they equal zero. These nodal surfaces are analogous to the nodal points at which the

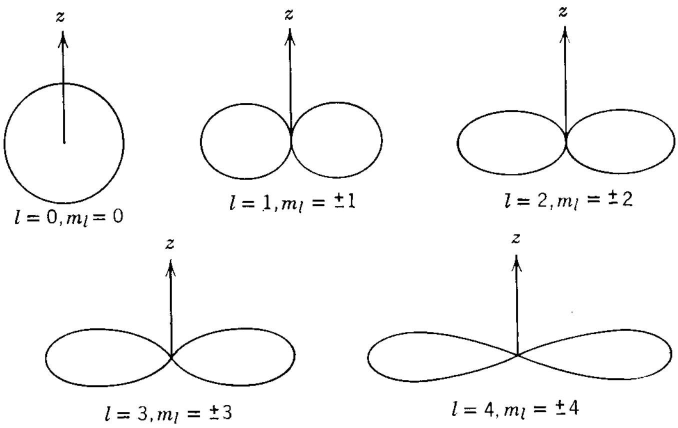

FIGURE 7-9

Polar diagrams of the directional dependence of the one-electron probability densities for $l = 0, 1, 2, 3, 4$; $m_l = \pm l$.

probability density for a particle bound in a one-dimensional potential equals zero (see, for example, Figure 6-32). They are a consequence of the fact that the wave functions for a bound particle must be standing waves with fixed nodes.

However, if a collection of hydrogen atoms has been completely isolated from its environment, it is not possible to then make measurements on the locations of the electron in each atom, knowing that they are all in a quantum state with a particular set of quantum numbers n, l, m_l, and thereby locate the nodal surfaces for that state. If it could be done it would certainly be remarkable, because it would allow the determination of the direction of the z axis. And this would amount to finding for each atom a preferred direction in a space which should be spherically symmetrical, because the Coulomb potential of the atom $V = -Ze^2/4\pi\epsilon_0 r$ is spherically symmetrical. In fact, it cannot be done because it is generally not possible to observe any of the probability density patterns of Figure 7-10 in actual measurements on *free* atoms (i.e., atoms in the complete absence of external magnetic or electric fields). The only exception is the spherically symmetrical state for $n = 1$, $l = m_l = 0$. The reason is that, with the exception of the state just mentioned, every state is degenerate with several other states of the same n value. Because the energies of atoms in degenerate states are identical, it is not possible experimentally to separate them from each other with techniques that leave the probability density unchanged. Thus, all that can be measured is the average probability density of the atoms for the entire set of states which are degenerate with each other. It turns out that the probability density functions, when averaged together in this manner, always yield a spherically symmetrical function.

Example 7-5. Evaluate the average of the probability density functions for the set of degenerate states corresponding to the energy E_2.

We have

$$\frac{1}{4}\,[\psi^*_{200}\psi_{200} + \psi^*_{21-1}\psi_{21-1} + \psi^*_{210}\psi_{210} + \psi^*_{211}\psi_{211}]$$

$$= \frac{1}{128\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Zr/a_0}\left[\left(2 - \frac{Zr}{a_0}\right)^2 + \left(\frac{Zr}{a_0}\right)^2\left(\frac{1}{2}\sin^2\theta + \frac{1}{2}\sin^2\theta + \cos^2\theta\right)\right]$$

$$= \frac{1}{128\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Zr/a_0}\left[\left(2 - \frac{Zr}{a_0}\right)^2 + \left(\frac{Zr}{a_0}\right)^2\right] \qquad (7\text{-}32)$$

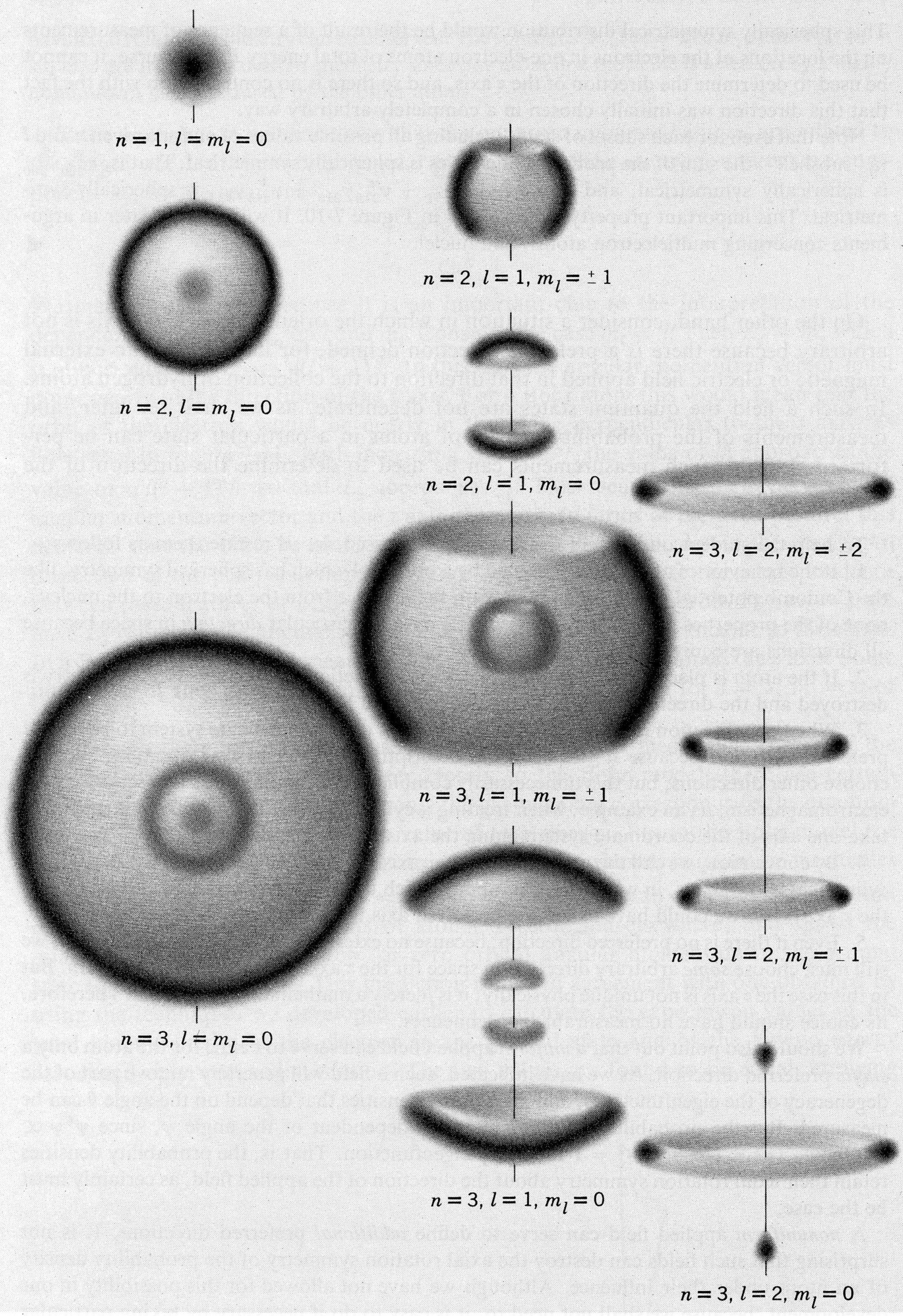

FIGURE 7-10

An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the *z* axis. If all the probability densities for a given *n* and *l* are combined, the result is spherically symmetrical.

This spherically symmetrical distribution would be the result of a sequence of measurements on the locations of the electrons in one-electron atoms of total energy E_2. Of course, it cannot be used to determine the direction of the z axis, and so there is no contradiction with the fact that this direction was initially chosen in a completely arbitrary way.

Note that even for each subset of states including all possible values of m_l for a given n and l (a "subshell") the sum of the probability densities is spherically symmetrical. That is, $\psi^*_{200}\psi_{200}$ is spherically symmetrical, and also $\psi^*_{21-1}\psi_{21-1} + \psi^*_{210}\psi_{210} + \psi^*_{211}\psi_{211}$ is spherically symmetrical. This important property is illustrated in Figure 7-10. It will be used later in arguments concerning multielectron atoms, and nuclei. ◀

On the other hand, consider a situation in which the orientation of the z axis is not arbitrary because there *is* a preferred direction defined, for instance, by an external magnetic or electric field applied in that direction to the collection of hydrogen atoms. In such a field the quantum states are not degenerate, as we shall see later, and measurements of the probability density of atoms in a particular state can be performed. In fact, such measurements can be used to determine the direction of the external field.

To help the student understand the ideas just discussed, let us restate them as follows:

1. If the behavior of an atom is governed by a potential which has spherical symmetry, like the Coulomb potential which depends only on the *distance* from the electron to the nucleus, none of the properties of the atom should single out any particular *direction* in space because all directions are equivalent.
2. If the atom is placed in an external electric or magnetic field, the spherical symmetry is destroyed and the direction defined by the external field becomes unique.
3. When one direction is unique, we choose one axis of our coordinate system to be in that preferred direction because it simplifies the description of the physical situation. We can choose other directions, but this unnecessarily complicates the mathematical description. (In electromagnetism, as an example, when treating a cylindrical wire it is very advantageous to take one axis of the coordinate system along the axis of the cylinder.)
4. By convention, we call the preferred axis the z axis. (The convention probably comes from cylindrical coordinates, in which the axis about which the angular coordinate varies is called the z axis.) But we could have called the preferred axis the x or y axis, just as well.
5. Even if there is no preferred direction, because no external field is applied to the atom, we still must choose *some* arbitrary direction in space for the z axis of our coordinate system. But in this case the z axis is not unique physically; it is merely a mathematical construct. Therefore, its choice should have no measurable consequences.

We should also point out that a *uniform* applied field can serve to define for the atom only a *single* preferred direction. As we have indicated, such a field will generally remove part of the degeneracy of the eigenfunctions, and probability densities that depend on the angle θ can be measured. But the probability densities remain independent of the angle φ, since $\psi^*\psi \propto \Phi^*_{m_l}(\varphi)\Phi_{m_l}(\varphi) = e^{-im_l\varphi}e^{im_l\varphi} = 1$ for every eigenfunction. That is, the probability densities retain their axial rotation symmetry about the direction of the applied field, as certainly must be the case.

A *nonuniform* applied field can serve to define *additional* preferred directions. It is not surprising that such fields can destroy the axial rotation symmetry of the probability density of an atom under their influence. Although we have not allowed for this possibility in our development, because we shall not need to, it is easy to do if necessary by taking particular solutions to (7-15) in the form $\Phi_{m_l}(\varphi) = \cos m_l\varphi$ or $\Phi_{m_l}(\varphi) = \sin m_l\varphi$, instead of in the form we have taken. With no applied field, or with uniform applied field, the eigenfunction associated with $\cos m_l\varphi$ is degenerate with the eigenfunction associated with $\sin m_l\varphi$, so measurement of the probability density will always yield a φ-independent combination $\propto \cos^2 m_l\varphi + \sin^2 m_l\varphi = 1$, just as with the eigenfunctions that we use. In the nonuniform applied field the degeneracy can be removed, however, and probability densities that do not have axial rotation symmetry can be observed. The solutions $\Phi_{m_l}(\varphi) = \cos m_l\varphi$ and $\Phi_{m_l}(\varphi) = \sin m_l\varphi$ are frequently used in chemistry since one atom in a molecule is acted on by a highly nonuniform field produced by the other atoms.

In the next section we shall show that the quantum numbers l and m_l are related to the magnitude L of the orbital angular momentum of the electron, and to its z component L_z, by the relations

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

We mention this now because it is an important clue to the interpretation of the dependence of $\psi^*_{nlm_l}\psi_{nlm_l}$ on l and m_l. Consider the case $m_l = l$. Then $L_z = l\hbar$, which is almost equal to $L = \sqrt{l(l+1)}\,\hbar$. In this case the angular momentum vector must point nearly in the direction of the z axis. For a Bohr atom this would mean that the orbit of the electron would lie nearly in the plane perpendicular to the z axis, as illustrated in Figure 7-11. With increasing values of l, the value of $l\hbar$ approaches the value of $\sqrt{l(l+1)}\,\hbar$, so that L_z approaches L. This means the angle between the angular momentum vector and the z axis decreases. In terms of the Bohr picture, this demands that the orbit lie more nearly in the plane perpendicular to the z axis. An inspection of the polar diagrams of Figure 7-9 will demonstrate the correspondence between these features of $\psi^*_{nlm_l}\psi_{nlm_l}$ and the picture of a Bohr orbit. For $m_l = 0$ we have $L_z = 0$, and the angular momentum vector must be perpendicular to the z axis. In a Bohr atom this would mean that the plane of the orbit contained the z axis. Some indication of this behavior can be seen in the polar diagram for $l = 3$, $m_l = 0$ of Figure 7-8.

Although there are many points at which the quantum mechanical theory of the one-electron atom corresponds quite closely to the Bohr model, there are certain striking differences. In both treatments the ground state corresponds to the quantum number $n = 1$, and it has the same value of total energy. But in the Bohr model the orbital angular momentum for this state is $L = n\hbar = \hbar$, whereas in quantum mechanics it is $L = \sqrt{l(l+1)}\,\hbar = 0$, since $l = 0$ when $n = 1$. There is an overwhelming amount of evidence, from measurements of atomic spectra and elsewhere, that shows the quantum mechanical prediction for zero orbital angular momentum in the ground state to be the correct one. This prediction is also in agreement with one obtained by using the techniques we developed earlier to calculate the expectation values of the total kinetic energy of the electron in the ground state and of the kinetic energy associated only with radial motion. The two values are found to be equal, implying

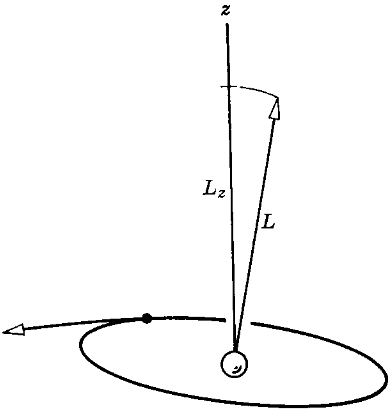

FIGURE 7-11
A Bohr orbit lying in a plane nearly perpendicular to the z axis.

that the motion is entirely radial in that state. If the Bohr model were modified in a way that would allow for zero angular momentum states, the orbit for such a state would be a radial oscillation in which the electron passes directly through the nucleus, and the oscillation could take place along any direction in space. This would correspond, in a sense, to a spherical symmetrical probability density or charge distribution, similar to that which is predicted by quantum mechanics and is observed experimentally. Nevertheless, it is difficult to visualize the motion of an electron in the ground state of the quantum mechanical atom. That is, it is difficult to make an analogy to a classical picture, such as the Bohr picture. But this situation is not unique; it is equally difficult to visualize the motion of an electron traveling through a two-slit diffraction apparatus.

7-8 Orbital Angular Momentum

We shall now proceed to justify the relations

$$L_z = m_l\hbar \tag{7-33}$$

$$L = \sqrt{l(l+1)}\,\hbar \tag{7-34}$$

between the quantum numbers m_l and l, and the z component L_z and magnitude L of the angular momentum of an electron in its "orbital" motion about the center of an atom. The justification will take a little effort, but it will be well worth it. We have just seen that these relations are very useful in interpreting the angular dependence of the probability density functions for a one-electron atom. As we continue our study of quantum physics, we shall see that the angular momentum relations are extremely important in the study of all atoms (and nuclei). The basic reason is that in most circumstances the z component and magnitude of the angular momenta of the particles in microscopic systems remain constant. From a classical point of view, this happens because in most systems the particles move in spherically symmetrical potentials that cannot exert torques on them. We shall find that, of all the quantities that can be used to describe atoms (and nuclei), angular momentum and total energy are about the only ones that do remain constant. A consequence is that most experiments on such systems involve measuring angular momentum and total energy. Therefore, quantum mechanics must be able to make predictions about angular momentum, as well as total energy. Another parallel between these two is that both are quantized. In other words, the relations of (7-33) and (7-34), stating that L_z and L have the *precise* values $m_l\hbar$ and $\sqrt{l(l+1)}\,\hbar$, are quantization relations just like the energy quantization relation stating that the total energy E of a one-electron atom has the precise values $-\mu Z^2e^4/(4\pi\epsilon_0)^2 2\hbar^2 n^2$. Angular momentum quantization is certainly as important as energy quantization. The only reason that it has not appeared before in our treatment of Schroedinger quantum mechanics is that the treatment was restricted to one-dimensional systems. Of course, angular momentum is the dynamical quantity that sets real three-dimensional systems apart from one-dimensional idealizations in which it has no meaning.

The *angular momentum* of a particle, relative to the origin of a certain coordinate system, is the vector quantity $\mathbf{L}$ defined by the equation

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{7-35a}$$

where $\mathbf{r}$ is the position vector of the particle relative to the origin, and $\mathbf{p}$ is the linear momentum vector for the particle. By evaluating the components in rectangular coordinates of the vector, or cross, product, it is easy to show that the three rectangular components of **L** are

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \end{aligned} \tag{7-35b}$$

where x, y, z are the components of **r**, and p_x, p_y, p_z are the components of **p**.

In order to study the *dynamical quantity* angular momentum in quantum mechanics, we construct the associated *operators*. This is done by replacing p_x, p_y, p_z by their quantum mechanical equivalents $-i\hbar\,\partial/\partial x$, $-i\hbar\,\partial/\partial y$, $-i\hbar\,\partial/\partial z$, according to an obvious three-dimensional extension of (5-32). Thus the operators for the three components of angular momentum are

$$\begin{aligned} L_{x_{\text{op}}} &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_{y_{\text{op}}} &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_{z_{\text{op}}} &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned} \tag{7-36}$$

Because we must use spherical polar coordinates, these expressions must be transformed into these coordinates. Appendix I shows how this can be done. The results are

$$\begin{aligned} L_{x_{\text{op}}} &= i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ L_{y_{\text{op}}} &= i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ L_{z_{\text{op}}} &= -i\hbar\frac{\partial}{\partial\varphi} \end{aligned} \tag{7-37}$$

We shall also be interested in the square of the magnitude of the angular momentum vector **L**, which is

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

As is indicated in Appendix I, in spherical polar coordinates the associated operator is

$$L^2_{\text{op}} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{7-38}$$

The first step in deriving the angular momentum quantization equations involves using the operators to calculate the expectation values of the z component of **L**, and of the square of its magnitude, for an electron in the n, l, m_l quantum state of a one-electron atom. According to the three-dimensional extension of the prescription of (5-34), the expectation value L_z is

$$\overline{L_z} = \int_0^\infty\int_0^\pi\int_0^{2\pi} \Psi^* L_{z_{\text{op}}}\Psi r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

The quantity $r^2 \sin\theta\, dr\, d\theta\, d\varphi$ is the element of volume in spherical polar coordinates, and the integrations are taken over the complete ranges of all three coordinates. Because it will simplify the notation, without causing confusion, we shall write this expression as

$$\overline{L_z} = \int \Psi^* L_{z_{\text{op}}} \Psi \, d\tau$$

Here $d\tau$ stands for the three-dimensional volume element $r^2 \sin\theta \, dr \, d\theta \, d\varphi$, and $\int$ stands for the three definite integrals $\int_0^\infty \int_0^\pi \int_0^{2\pi}$. The same shorthand notation will be used in the remainder of this chapter, and in the following chapters. Continuing our calculation of $\overline{L_z}$, by expressing the wave function as a product of the eigenfunction and the exponential time factor we obtain

$$\overline{L_z} = \int e^{iE_n t/\hbar} \psi^*_{nlm_l} L_{z_{\text{op}}} e^{-iE_n t/\hbar} \psi_{nlm_l} \, d\tau$$

or

$$\overline{L_z} = \int \psi^*_{nlm_l} L_{z_{\text{op}}} \psi_{nlm_l} \, d\tau \tag{7-39}$$

Similarly, the expectation value of L^2 is

$$\overline{L^2} = \int \psi^*_{nlm_l} L^2_{\text{op}} \psi_{nlm_l} \, d\tau \tag{7-40}$$

To evaluate the integrals in the two numbered equations above, we must first evaluate $L_{z_{\text{op}}} \psi_{nlm_l}$ and $L^2_{\text{op}} \psi_{nlm_l}$.

Example 7-6. Evaluate $L_{z_{\text{op}}} \psi_{nlm_l}$, where $L_{z_{\text{op}}} = -i\hbar \, \partial/\partial\varphi$, and where ψ_{nlm_l} is a one-electron atom eigenfunction.

We have

$$L_{z_{\text{op}}} \psi_{nlm_l} = -i\hbar \frac{\partial \psi_{nlm_l}}{\partial \varphi}$$

Since

$$\psi_{nlm_l} = R_{nl}(r) \Theta_{lm_l}(\theta) \Phi_{m_l}(\varphi)$$

we obtain

$$-i\hbar \frac{\partial \psi_{nlm_l}}{\partial \varphi} = R_{nl}(r) \Theta_{lm_l}(\theta) \left[-i\hbar \frac{d\Phi_{m_l}(\varphi)}{d\varphi} \right]$$

According to (7-19)

$$\Phi_{m_l}(\varphi) = e^{im_l\varphi}$$

so

$$\frac{d\Phi_{m_l}(\varphi)}{d\varphi} = im_l e^{im_l\varphi} = im_l \Phi_{m_l}(\varphi)$$

Thus

$$\begin{aligned} i\hbar \frac{\partial \psi_{nlm_l}}{\partial \varphi} &= R_{nl}(r) \Theta_{lm_l}(\theta) [-i\hbar i m_l \Phi_{m_l}(\varphi)] \\ &= m_l \hbar R_{nl}(r) \Theta_{lm_l}(\theta) \Phi_{m_l}(\varphi) \end{aligned}$$

and we obtain the answer

$$L_{z_{\text{op}}} \psi_{nlm_l} = m_l \hbar \psi_{nlm_l} \tag{7-41}$$

◀

Although we do not have a concise expression for the functions $\Theta_{lm_l}(\theta)$, which must be differentiated to evaluate $L^2_{\text{op}} \psi_{nlm_l}$, we know that these functions satisfy the differential equation (7-16). Using this fact, it is not difficult to show that

$$L^2_{\text{op}} \psi_{nlm_l} = l(l+1)\hbar^2 \psi_{nlm} \tag{7-42}$$

Using (7-41) from Example 7-6 in (7-39), which is

$$\overline{L_z} = \int \psi^*_{nlm_l} L_{z_{\text{op}}} \psi_{nlm_l} \, d\tau$$

it is trivial to evaluate $\overline{L_z}$. We have

$$\overline{L_z} = m_l \hbar \int \psi^*_{nlm_l} \psi_{nlm_l} \, d\tau$$

But we know that this integral has the value one because it is equal to the probability density integrated over all space, i.e., the probability of finding the electron somewhere. Thus we obtain

$$\overline{L_z} = m_l \hbar \tag{7-43}$$

In a similar fashion we use (7-42) in (7-40), which is

$$\overline{L^2} = \int \psi^*_{nlm_l} L^2_{\text{op}} \psi_{n\ m_l} \, d\tau$$

to obtain

$$\overline{L^2} = l(l+1)\hbar^2 \int \psi^*_{nlm_l} \psi_{nlm_l} \, d\tau$$

$$\overline{L^2} = l(l+1)\hbar^2 \tag{7-44}$$

Let us compare the results of our expectation value calculations, (7-43) and (7-44), with the quantization relations we are trying to verify, that can be written

$$L_z = m_l \hbar \tag{7-45}$$

$$L^2 = l(l+1)\hbar^2 \tag{7-46}$$

The former are certainly consistent with the latter, but they are not proofs of the latter. The quantization relations make stronger statements about the values of L_z and L^2. These relations say that *any* measurement of the angular momentum of an electron in the n, l, m_l state of the atom will *always* yield $L_z = m_l \hbar$ and $L^2 = l(l+1)\hbar^2$ since, in that state, these quantities have *precisely* the values quoted. But the expectation value relations say only that the values quoted will be obtained on the average, that is, when the results of a large number of measurements of L_z and L^2 are averaged.

To complete the proof of the quantization relations is a matter of continuing along the line we have been following. For example, by calculating the expectation value of some power of L_z, say the square L_z^2, it is found that $\overline{L_z^2} = (m_l \hbar)^2$. This immediately leads to the conclusion that not only must L_z equal $m\hbar$ on the average, i.e., $\overline{L_z} = m_l \hbar$, but that L_z must equal $m\hbar$ always, i.e., $L_z = m_l \hbar$. The point is that if L_z fluctuated about its average $m_l \hbar$ it would not be possible to obtain $\overline{L_z^2} = (m_l \hbar)^2$ because when averaging a power of L_z higher than the first more weight is given to fluctuations above the average than to fluctuations below the average. In order to proceed with our interpretation of the angular momentum of one-electron atoms, we defer the details of this proof to the following section. There we shall also obtain the interesting conclusion that L_x and L_y, the x and y components of the orbital angular momentum, do *not* obey quantization relations.

The fact that ψ_{nlm_l} does not describe a state with a definite x and y component of orbital angular momentum, because these quantities are not quantized, is mysterious from the point of view of classical mechanics. According to the angular momentum conservation law of classical mechanics, the orbital angular momentum vector of an electron moving under the influence of a spherically symmetrical potential $V(r)$ of a one-electron atom in free space would be completely fixed in direction and magnitude, and all three components of the vector would have definite values. The reason is that there would be no torques acting on the electron. The fact that this result is not obtained in the quantum mechanical theory is a consequence of the fact that there is an uncertainty principle relation which states that no two components of an angular momentum can be known simultaneously with complete precision. Because the z component of orbital angular momentum has the precise value $m_l\hbar$, the relation requires that the values of the x and y components be indefinite. Upon evaluating $\overline{L_x}$ and $\overline{L_y}$, the average values of these components, it is found that both equal zero. Thus the orientation of the orbital angular momentum vector of an electron moving in a spherically symmetrical potential must be constantly changing in such a way that its x and y components fluctuate about an average value of zero, while its z component and magnitude remain fixed. This result might be called the *quantum mechanical orbital angular momentum conservation law*.

Many of the properties of the orbital angular momentum can be conveniently represented in terms of vector diagrams. Consider the set of states having a common value of the quantum number l. For each of these states the length of the orbital angular momentum vector, in units of $\hbar$, is $L/\hbar = \sqrt{l(l+1)}$. In the same units, the z component of this vector is $L_z/\hbar = m_l$. The z component can assume any integral value from $L_z/\hbar = -l$ to $L_z/\hbar = +l$, depending on the value of m_l. The case of $l = 2$ is illustrated in Figure 7-12. The figure depicts the angular momentum vectors for each of the five states corresponding to the five possible values of m_l for this value of l. Since in any one of these states L_x and L_y fluctuate about their average values of zero, the vectors describing the state precess randomly in the conical surface surrounding the z axis, satisfying the quantum mechanical angular momentum conservation law. The actual orientation in space of the angular momentum vector is known with the greatest precision for the states with $m_l = \pm l$. But even for these states there is some uncertainty since the vector can be anywhere on a cone of half-angle $\cos^{-1}[l/\sqrt{l(l+1)}]$. In the classical limit $l \to \infty$, and this angle becomes vanishingly small. Thus, in the classical limit the angular momentum vector for the states $m_l = \pm l$ is constrained to lie almost along the z axis and is therefore essentially fixed in space. This agrees with the behavior predicted by the classical theory, i.e., with the classical orbital angular momentum conservation law.

The quantum number m_l determines the space orientation of the orbital angular momentum vector of the one-electron atom. Therefore, in a sense it determines the orientation in space of the atom itself. As the spherically symmetrical Coulomb potential implies that there is no preferred direction in the space in which the atom is

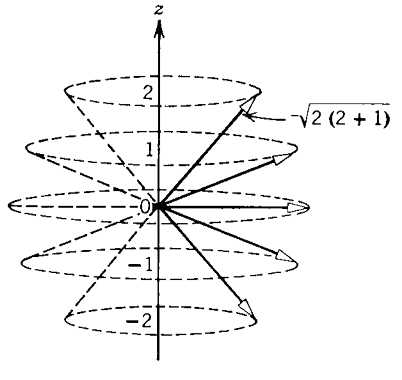

FIGURE 7-12

Representing the angular momentum vectors (measured in units of $\hbar$) for the possible states with $l = 2$. In each state the vector precesses randomly about the z axis, maintaining a constant magnitude and a constant z component.

situated, we can understand why the theory predicts that the total energy of the atom does not depend on m_l, which determines this orientation. Thus we can understand why the eigenfunctions are degenerate with respect to the quantum number m_l. The energy of the atom simply does not depend on its orientation in empty space.

7-9 Eigenvalue Equations

Here we shall complete the derivation, started in the previous section, of the orbital angular momentum quantization conditions. Then we shall generalize the results of the derivation to point out an interesting feature of Schroedinger's theory of quantum mechanics.

To study the quantization of the orbital angular momentum, we focus attention first on its z component, L_z. Now, if the z component quantization condition of (7-45) is valid, then any measurement of L_z will always yield the same precise value specified by that quantization condition

$$L_z = m_l\hbar \tag{7-47}$$

Furthermore, measurements of some higher power of L_z, say the square L_z^2, will always yield the same value $L_z^2 = (m_l\hbar)^2$. As a consequence, the expectation value of the square of L_z will be just $\overline{L_z^2} = (m_l\hbar)^2$. Note that, since we also have $\overline{L_z} = m_l\hbar$, this means

$$\overline{L_z^2} = \overline{L_z}^2 \tag{7-48}$$

That is, the expectation value of the square of L_z equals the square of the expectation value of L_z, if the quantization condition of (7-47) is valid.

On the other hand, if (7-47) is not valid then measurements of L_z can lead to various values, subject, however, to the constraint that the values average out to yield $m_l\hbar$ because we have proven in (7-43) that $\overline{L_z} = m_l\hbar$ in any case. If the measured values of L_z fluctuate about the average value $m_l\hbar$, then the expectation value of the square of L_z will no longer equal the square of $m_l\hbar$. The reason is that when averaging a higher power of L_z, like its square L_z^2, we give much more weight to the cases in which L_z is larger than $\overline{L_z}$, and much less weight to the equally numerous cases in which L_z is smaller than $\overline{L_z}$. In this situation $\overline{L_z^2} \neq (m_l\hbar)^2$, so $\overline{L_z^2} \neq \overline{L_z}^2$.

An example is shown in Table 7-3, which applies the ideas just discussed to calculating the square of the average, and the average of the squares, of the ages of a group of children whose individual ages are 1, 2, and 3 years. Inspection of the table shows that when the ages are first squared, and then averaged, a larger result is obtained than when the ages are first averaged, and then squared. This will be true in any case in which a power of the ages higher than the first is averaged, and in which the ages fluctuate. But if all the children in the group have ages

TABLE 7-3. The Square of the Average, and the Average of the Squares, of a Set of Fluctuating Numbers

$$A = 1, 2, 3$$

$$\overline{A} = \frac{1+2+3}{3} = \frac{6}{3} = 2$$

$$\overline{A}^2 = 4$$

$$A^2 = 1, 4, 9$$

$$\overline{A^2} = \frac{1+4+9}{3} = \frac{14}{3} = 4.67$$

$$\Delta A \equiv \sqrt{\overline{A^2} - \overline{A}^2} = \sqrt{4.67 - 4} = \sqrt{0.67} = 0.82$$

TABLE 7-4. The Square of the Average, and the Average of the Squares, of a Set of Nonfluctuating Numbers

$$\begin{aligned}
A &= 2, 2, 2 \\
\bar{A} &= \frac{2+2+2}{3} = \frac{6}{3} = 2 \\
\bar{A}^2 &= 4 \\
A^2 &= 4, 4, 4 \\
\overline{A^2} &= \frac{4+4+4}{3} = \frac{12}{3} = 4 \\
\Delta A &\equiv \sqrt{\overline{A^2} - \bar{A}^2} = \sqrt{4-4} = 0
\end{aligned}$$

precisely equal to each other, and therefore to the average age, then it makes no difference in which order the operations are carried out and the average of the squares equals the square of the averages. An example of that situation is shown in Table 7-4.

For another illustration of these ideas, consider the quantity $\Delta x = \sqrt{\overline{x^2} - \bar{x}^2}$. As mentioned in Example 5-10, this quantity is used as a measure of the fluctuations that would be observed in measurements of the x coordinate of a particle. If there were no fluctuations, then $\overline{x^2} = \bar{x}^2$. But the uncertainty principle demands that there be fluctuations in x (which are larger the smaller the fluctuations in the linear momentum p). As a result $\overline{x^2} > \bar{x}^2$, and the difference between $\overline{x^2}$ and $\bar{x}^2$ increases as the fluctuations in x increase so $\sqrt{\overline{x^2} - \bar{x}^2}$ is a measure of these fluctuations.

Now, it is easy to prove the validity of the relation expressed by (7-48), $\overline{L_z^2} = \overline{L_z}^2$, and therefore also the validity of the quantization condition $L_z = m_l\hbar$ of (7-47). To do this we twice use (7-41), $L_{z_{op}}\psi_{nlm_l} = m_l\hbar\psi_{nlm_l}$, to calculate $\overline{L_z^2}$. According to the three-dimensional extension of the prescription for calculating expectation values, we have

$$\overline{L_z^2} = \int \Psi^* L^2_{z_{op}} \Psi \, d\tau$$

This immediately gives

$$\overline{L_z^2} = \int \psi^*_{nlm_l} L^2_{z_{op}} \psi_{nlm_l} \, d\tau$$

The dynamical quantity L_z^2 is the product of two factors of the form L_z

$$L_z^2 = L_z \cdot L_z$$

According to the expectation value prescription, the operator $L^2_{z_{op}}$ obtained from that dynamical quantity is thus the product of two operators of the form $L_{z_{op}}$. Therefore

$$L^2_{z_{op}}\psi_{nlm_l} = L_{z_{op}} \cdot L_{z_{op}}\psi_{nlm_l}$$

In other words, $L^2_{z_{op}}\psi_{nlm_l}$ means that $L_{z_{op}}$ operates twice on ψ_{nlm_l}. But according to (7-41)

$$L_{z_{op}}\psi_{nlm_l} = m_l\hbar \, \psi_{nlm_l}$$

Thus each operation of $L_{z_{op}}$ on ψ_{nlm_l} yields the same function ψ_{nlm_l}, multiplied by a constant factor $m_l\hbar$. Therefore, the result of two operations is simply to multiply ψ_{nlm_l} by two factors of $m_l\hbar$. That is

$$L^2_{z_{op}}\psi_{nlm_l} = (m_l\hbar)^2\psi_{nlm_l}$$

Knowing this, we immediately obtain

$$\begin{aligned}\overline{L_z^2} &= \int \psi^*_{nlm_l}(m_l\hbar)^2\psi_{nlm_l}\,d\tau \\ &= (m_l\hbar)^2\int \psi^*_{nlm_l}\psi_{nlm_l}\,d\tau \\ &= (m_l\hbar)^2 \\ &= \overline{L_z}^2\end{aligned}$$

where we have made use of the fact that the integral over all space of $\psi^*_{nlm_l}\psi_{nlm_l}$ equals one because of the normalization condition. Since we have verified (7-48), we have completed our verification of the quantization condition $L_z = m_l\hbar$. The proof of the validity of the quantization condition $L^2 = l(l+1)\hbar^2$ is carried through in a completely parallel manner.

Note that these proofs depend on (7-41) and (7-42), $L_{z_{\text{op}}}\psi_{nlm_l} = m_l\hbar\psi_{nlm_l}$ and $L^2_{\text{op}}\psi_{nlm_l} = l(l+1)\hbar^2\psi_{nlm_l}$. The equations state the surprising facts that the result of operating on the one-electron atom eigenfunction ψ_{nlm_l} with the differential operator $L_{z_{\text{op}}}$ is simply to multiply that eigenfunction by the constant $m_l\hbar$, while the result of operating on it with the differential operator L^2_{op} is simply to multiply it by the constant $l(l+1)\hbar^2$. These results are certainly not typical of what happens when a differential operator operates on a function. For instance, if we operate on a function, say $f(x) = x^2$, with the differential operator d/dx, we obtain a very different function $f'(x) = 2x$. As another example, it is not difficult to show that the results of operating on ψ_{nlm_l} with the operators $L_{x_{\text{op}}}$ or $L_{y_{\text{op}}}$ is to produce new functions of r, θ, φ in which these variables enter quite differently from the way they enter in the function ψ_{nlm_l}. That is

$$L_{x_{\text{op}}}\psi_{nlm_l} \neq (\text{const})\psi_{nlm_l} \tag{7-49}$$

$$L_{y_{\text{op}}}\psi_{nlm_l} \neq (\text{const})\psi_{nlm_l} \tag{7-50}$$

The ideas that we have developed, in the process of verifying the angular momentum quantization conditions, can be extended to provide a deeper insight into the theory of Schroedinger quantum mechanics. They can also be used to lead into the more sophisticated theories, such as Heisenberg's *matrix mechanics*. We must leave these matters for more advanced books. Here we shall say only that the properties associated with (7-41) and (7-42) are perfectly general. That is, *whenever the dynamical quantity f has the precise value F in the quantum state described by the function ψ, then that function satisfies the relation*

$$f_{\text{op}}\psi = F\psi \tag{7-51}$$

where f_{op} is the operator corresponding to f.

We shall also show that the time-independent Schroedinger equation can be written in the form of (7-51). To do this, consider the time-independent Schroedinger equation in rectangular coordinates

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi$$

Rewrite it as

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi$$

By comparing (7-3) with (7-4), we see that the square bracket is just the operator e_{op} for the total energy. Thus we have

$$e_{\text{op}}\psi = E\psi$$

Here E is one of the precise allowed values of the total energy of the system described by the potential V. The system is also described by the total energy operator e_{op}.

The general relation of (7-51) is called an *eigenvalue equation*, ψ is said to be an *eigenfunction of the operator* f_{op}, and F is said to be the corresponding *eigenvalue*. This is the same terminology as is used in the particular case of the eigenvalue equation for the total energy operator—that is, in the case of the time-independent Schroedinger equation. The total energy operator e_{op} is sometimes called the *Hamiltonian.*

These considerations lead to the important conclusion that, since (7-49) and (7-50) show ψ_{nlm_l} is not an eigenfunction of the operators $L_{x_{\text{op}}}$ or $L_{y_{\text{op}}}$, the corresponding dynamical quantities L_x and L_y do not have precise values in the one-electron atom. That is, L_x and L_y do not obey quantization conditions.

QUESTIONS

1. If a hydrogen atom were not at rest, but moving freely through space, how would the quantum mechanical description of the atom be modified?
2. Since it is well known that the Coulomb potential has a much simpler form in spherical polar coordinates, why did we begin our treatment of the one-electron atom in rectangular coordinates?
3. In what important equations of classical physics does the Laplacian operator enter?
4. Would the results of the calculations be affected if we took different forms for the separation constants that arise in the splitting of the time-independent Schroedinger equation, for the one-electron atom, into three ordinary differential equations?
5. Why must $\Phi(\varphi)$ be single valued? How does this lead to the restriction that m_l must be an integer?
6. What would happen if we took $e^{-im_l\varphi}$ as the particular solution to the $\Phi(\varphi)$ equation? What about $\cos m_l\varphi$ or $\sin m_l\varphi$?
7. Why do three quantum numbers arise in the treatment of the (spinless) one-electron atom?
8. Can you say what the functions $\Theta(\theta)$ and $\Phi(\varphi)$ would be like if V were a function of r, but not proportional to $-1/r$? (This is the case for the valence electron of an alkali atom.)
9. Just what is degeneracy?
10. What is the relation between the size of a Bohr atom and the size of a Schroedinger atom?
11. What is the fundamental reason why the size of the hydrogen atom in its ground state has the value it does?
12. For a one-electron atom in free space, what would be the mathematical consequences of changing the choice of direction of the z axis? The physical consequences? What if the atom is in an external electric or magnetic field?
13. Why does a uniform electric or magnetic field define only one unique direction is space?
14. How do the predictions of the Bohr and Schroedinger treatments of the hydrogen atom (ignoring spin and other relativistic effects) compare with regard to the location of the electron, its total energy, and its orbital angular momentum?
15. Devise an explanation for the obvious relation between the last two terms of the Laplacian operator, in spherical polar coordinates, and the operator for the square of the magnitude of the orbital angular momentum.
16. Using the connection between L and l, explain physically why $\psi^*\psi$ is very small near $r = 0$, unless $l = 0$.
17. Exactly why do we say that for a hydrogen atom in free space the orbital angular momentum vector precesses randomly about the z axis (ignoring spin)?

18. What is the quantum mechanical orbital angular momentum conservation law?

19. Is every eigenfunction of angular momentum magnitude necessarily also an eigenfunction of total energy? Is the reciprocal statement true?

20. Are examples of eigenvalue equations found in classical physics? If so, what are they?

PROBLEMS

1. Using the technique of separation of variables, show that there are solutions to the three-dimensional Schroedinger equation for a time-independent potential, which can be written

$$\Psi(x,y,z,t) = \psi(x,y,z)e^{-iEt/\hbar}$$

where $\psi(x,y,z)$ is a solution to the time-independent Schroedinger equation.

2. Verify that $\Phi(\varphi) = e^{im_l\varphi}$ is the solution to the equation for $\Phi(\varphi)$, (7-15).

3. Hydrogen, deuterium, and singly ionized helium are all examples of one-electron atoms. The deuterium nucleus has the same charge as the hydrogen nucleus, and almost exactly twice the mass. The helium nucleus has twice the charge of the hydrogen nucleus, and almost exactly four times the mass. Make an accurate prediction of the ratios of the ground state energies of these atoms. (Hint: Remember the variation in the reduced mass.)

4. (a) Evaluate, in electron volts, the energies of the three levels of the hydrogen atom in the states for $n = 1, 2, 3$. (b) Then calculate the frequencies in hertz, and the wavelengths in angstroms, of all the photons that can be emitted by the atom in transitions between these levels. (c) In what range of the electromagnetic spectrum are these photons?

5. Verify by substitution that the ground state eigenfunction ψ_{100}, and the ground state eigenvalue E_1, satisfy the time-independent Schroedinger equation for the hydrogen atom.

6. (a) Extend Example 7-4 to obtain from the uncertainty principle a prediction of the total energy of the ground state of the hydrogen atom. (b) Compare with the energy predicted by (7-22).

7. (a) Calculate the location at which the radial probability density is a maximum for the $n = 2, l = 1$ state of the hydrogen atom. (b) Then calculate the expectation value of the radial coordinate in this state. (c) Explain the physical significance of the difference in the answers to (a) and (b). (Hint: See Figure 7-5.)

8. (a) Calculate the expectation value $\bar{V}$ for the potential energy in the ground state of the hydrogen atom. (b) Show that in the ground state $E = \bar{V}/2$, where E is the total energy. (c) Use the relation $E = K + V$ to calculate the expectation value $\bar{K}$ of the kinetic energy in the ground state, and show that $\bar{K} = -\bar{V}/2$. These relations are obtained for any state of motion of any quantum mechanical (or classical) system with a potential in the form $V(r) \propto -1/r$. They are sometimes called the *virial theorem.*

9. (a) Calculate the expectation value $\bar{V}$ of the potential energy in the $n = 2, l = 1$ state of the hydrogen atom. (b) Do the same for the $n = 2, l = 0$ state. (c) Discuss the results of (a) and (b), in connection with the virial theorem of Problem 8, and explain how they bear on the origin of the l degeneracy.

10. By substituting into the equation for $R(r)$, (7-17), the form $R(r) \propto r^l$, show that it is a solution for $r \rightarrow 0$. (Hint: Ignore terms that become negligible relative to others as $r \rightarrow 0$.)

11. Show that the sum of hydrogen atom probability densities for the $n = 3$ quantum states, analogous to the sum in Example 7-5, is spherically symmetrical.

12. Show that $\Phi(\varphi) = \cos m_l\varphi$, and $\Phi(\varphi) = \sin m_l\varphi$, are particular solutions to the equation for $\Phi(\varphi)$, (7-15).

13. By using the techniques of Appendix I show that $L_{x_{\text{op}}}$ has the form stated in (7-37).

14. Prove that $L^2_{\text{op}}\psi_{nlm_l} = l(l+1)\hbar^2\psi_{nlm_l}$. (Hint: Use the differential equation satisfied by $\Theta_{lm_l}(\theta)$, (7-16).)

15. We know that $\psi = e^{ikx}$ is an eigenfunction of the total energy operator e_{op} for the one-dimensional problem of the zero potential. (a) Show that it is also an eigenfunction of the linear momentum operator p_{op}, and determine the associated momentum eigenvalue. (b) Repeat for $\psi = e^{-ikx}$. (c) Interpret what the results of (a) and (b) mean concerning measurements of the linear momentum. (d) We also know that $\psi = \cos kx$ and $\psi = \sin kx$ are eigenfunctions of the zero potential e_{op}. Are they eigenfunctions of p_{op}? (e) Interpret the results of (d).

16. All four of the functions $e^{im_l\varphi}$, $e^{-im_l\varphi}$, $\cos m_l\varphi$, and $\sin m_l\varphi$ are particular solutions to the equation for $\Phi(\varphi)$, (7-15) (see Problem 12). (a) Find which are also eigenfunctions of the operator for the z component of angular momentum $L_{z_{\text{op}}}$. (b) Interpret your results.

17. A particle of mass μ is fixed at one end of a rigid rod of negligible mass and length R. The other end of the rod rotates in the x-y plane about a bearing located at the origin, whose axis is in the z direction. This two-dimensional "rigid rotator" is illustrated in Figure 7-13. (a) Write an expression for the total energy of the system in terms of its angular momentum L. (Hint: Set the constant potential energy equal to zero, and then express the kinetic energy in terms of L.) (b) By introducing the appropriate operators into the energy equation, convert it into the Schroedinger equation

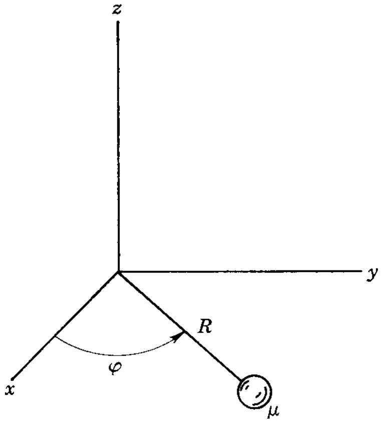

FIGURE 7-13

The rigid rotator moving in the x-y plane considered in Problem 17.

$$-\frac{\hbar^2}{2I}\frac{\partial^2\Psi(\varphi,t)}{\partial\varphi^2} = i\hbar\frac{\partial\Psi(\varphi,t)}{\partial t}$$

where $I = \mu R^2$ is the rotational inertia, or moment of inertia, and $\Psi(\varphi, t)$ is the wave function written in terms of the angular coordinate φ and the time t. (Hint: Since the angular momentum is entirely in the z direction, $L = L_z$ and the corresponding operator is $L_{z_{\text{op}}} = -i\hbar\partial/\partial\varphi$.)

18. By applying the technique of separation of variables, split the rigid rotator Schroedinger

equation of Problem 17 to obtain: (a) the time-independent Schroedinger equation

$$-\frac{\hbar^2}{2I}\frac{d^2\Phi(\varphi)}{d\varphi^2} = E\Phi(\varphi)$$

and (b) the equation for the time dependence of the wave function

$$\frac{dT(t)}{dt} = -\frac{iE}{\hbar}T(t)$$

In these equations $E =$ the separation constant, and $\Phi(\varphi)T(t) = \Psi(\varphi, t)$, the wave function.

19. (a) Solve the equation for the time dependence of the wave function obtained in Problem 18. (b) Then show that the separation constant E is the total energy.

20. Show that a particular solution to the time-independent Schroedinger equation for the rigid rotator of Problem 18 is $\Phi(\varphi) = e^{im\varphi}$ where $m = \sqrt{2IE}/\hbar$.

21. (a) Apply the condition of single valuedness to the particular solution of Problem 20. (b) Then show that the allowed values of the total energy E for the two-dimensional quantum mechanical rigid rotator are

$$E = \frac{\hbar^2 m^2}{2I} \qquad |m| = 0, 1, 2, 3, \ldots$$

(c) Compare the results of quantum mechanics with those of the old quantum theory obtained in Problem 34 of Chapter 4. (d) Explain why the two-dimensional quantum mechanical rigid rotator has no zero-point energy. Also explain why it is not a completely realistic model for a microscopic system.

22. Normalize the functions $\Phi(\varphi) = e^{im\varphi}$ found in Problem 21.

23. (a) Calculate the expectation value of the angular momentum, $\overline{L}$, for a two-dimensional rigid rotator in a typical quantum state, using the eigenfunctions found in Problem 22. (b) Then calculate $\overline{L^2}$ and $\overline{L}^2$, and interpret what your results have to say about the values of L that would be obtained in a series of measurements on the system.