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 $\mathbf{r}$, and p_x, p_y, p_z are the components of $\mathbf{p}$.

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

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

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

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

or

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

Similarly, the expectation value of L^2 is

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

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

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

We have

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

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

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

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

and we obtain the answer

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

◀

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

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

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

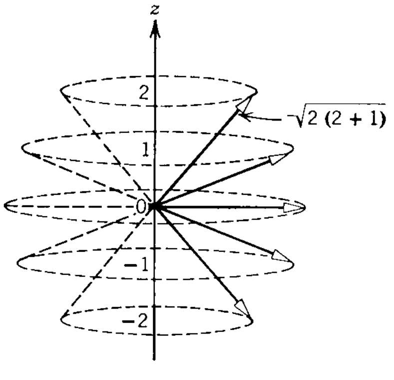

FIGURE 7-12

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), $\overline{L_z^2} = \bar{L}_z^2$, 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), $L_{z_{\text{op}}}\psi_{nlm_l} = m_l\hbar\psi_{nlm_l}$, to calculate $\overline{L_z^2}$. According to the three-dimensional extension of the prescription for calculating expectation values, we have

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

This immediately gives

$$\overline{L_z^2} = \int \psi_{nlm_l}^* L_{z_{\text{op}}}^2 \psi_{nlm_l} \, d\tau$$

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 $L_{z_{\text{op}}}^2$ obtained from that dynamical quantity is thus the product of two operators of the form $L_{z_{\text{op}}}$. Therefore

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

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

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

Thus each operation of $L_{z_{\text{op}}}$ 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

$$L_{z_{\text{op}}}^2 \psi_{nlm_l} = (m_l\hbar)^2 \psi_{nlm_l}$$

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), $L_{z_{\rm op}}\psi_{nlm_l} = m_l\hbar\psi_{nlm_l}$ and $L^2_{\rm op}\psi_{nlm_l} = l(l+1)\hbar^2\psi_{nlm_l}$. The equations state the surprising facts that the result of operating on the one-electron atom eigenfunction ψ_{nlm_l} with the differential operator $L_{z_{\rm op}}$ is simply to multiply that eigenfunction by the constant $m_l\hbar$, while the result of operating on it with the differential operator $L^2_{\rm op}$ 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 $L_{x_{\rm op}}$ or $L_{y_{\rm op}}$ 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

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

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

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*

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

where $f_{\rm op}$ 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 $e_{\rm op}$ for the total energy. Thus we have

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

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 $e_{\rm op}$.

The general relation of (7-51) is called an *eigenvalue equation*, ψ is said to be an *eigenfunction of the operator $f_{\rm op}$*, 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 $e_{\rm op}$ 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)?