36-3 Quantum Theory of Atoms

The Schrödinger Equation in Spherical Coordinates

In quantum theory, the electron is described by its wave function ψ. The probability of finding the electron in some volume dV of space equals the product of the absolute square of the electron wave function $|\psi|^2$ and dV. Boundary conditions on the wave function lead to the quantization of the wavelengths and frequencies and thereby to the quantization of the electron energy.

Consider a single electron of mass m moving in three dimensions in a region in which the potential energy is U. The time-independent Schrödinger equation for such a particle is given by Equation 35-30:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\psi=E\psi \qquad \text{36-19}$$

For a single isolated atom, the potential energy U depends only on the radial distance $r = \sqrt{x^2 + y^2 + z^2}$. The problem is then most conveniently treated using the spherical coordinates r, θ, and ϕ, which are related to the rectangular coordinates x, y, and z by

$$z = r\cos\theta$$

$$x = r\sin\theta\cos\phi$$

$$y = r\sin\theta\sin\phi \qquad \text{36-20}$$

These relations are shown in Figure 36-5. The transformation of the bracketed term in Equation 36-19 is straightforward but involves much tedious calculation, which we will omit. The result is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

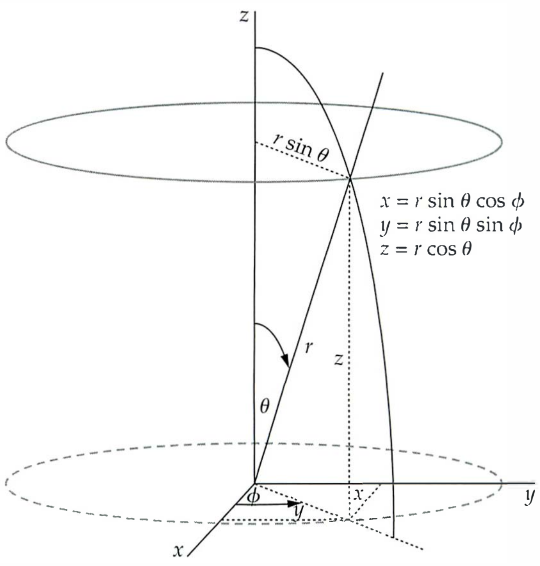

FIGURE 36-5 Geometric relations between spherical coordinates and rectangular coordinates.

Substituting into Equation 36-19 gives

$$-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)-\frac{\hbar^2}{2mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+U(r)\psi=E\psi \qquad \text{36-21}$$

Despite the formidable appearance of this equation, it was not difficult for Schrödinger to solve because it is similar to other partial differential equations in classical physics that had been thoroughly studied. We will not solve this equation but merely discuss qualitatively some of the interesting features of the wave functions that satisfy it.

The first step in the solution of a partial differential equation, such as Equation 36-21, is to separate the variables by writing the wave function $\psi(r, \theta, \phi)$ as a product of functions of each single variable:

$$\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi) \qquad \text{36-22}$$

where R depends only on the radial coordinate r, f depends only on θ, and g depends only on ϕ. When this form of $\psi(r, \theta, \phi)$ is substituted into Equation 36-21, the partial differential equation can be transformed into three ordinary differential equations, one for $R(r)$, one for $f(\theta)$, and one for $g(\phi)$. The potential energy $U(r)$ appears only in the equation for $R(r)$, which is called the **radial equation.** The particular form of $U(r)$ given in Equation 36-19 therefore has no effect on the solutions of the equations for $f(\theta)$ and $g(\phi)$, and therefore has no effect on the angular dependence of the wave function $\psi(r, \theta, \phi)$. These solutions are applicable to any problem in which the potential energy depends only on r.

Quantum Numbers in Spherical Coordinates

In three dimensions, the requirement that the wave function be continuous and normalizable introduces three quantum numbers, one associated with each spatial dimension. In spherical coordinates the quantum number associated with r is labeled n, that associated with θ is labeled ℓ, and that associated with ϕ is labeled m_ℓ.[†] The quantum numbers n_1, n_2, and n_3 that we found in Chapter 35

[†] For simplicity, m_ℓ is sometimes written as m.

for a particle in a three-dimensional square well in rectangular coordinates x, y, and z were independent of one another, but the quantum numbers associated with wave functions in spherical coordinates are interdependent. The possible values of these quantum numbers are

$$n = 1, 2, 3, \ldots$$
$$\ell = 0, 1, 2, 3, \ldots, n-1$$
$$m_\ell = -\ell, (-\ell + 1), \ldots, -2, -1, 0, 1, 2, \ldots, (\ell + 1), \ell \qquad 36\text{-}23$$

QUANTUM NUMBERS IN SPHERICAL COORDINATES

That is, n can be any positive integer; ℓ can be 0 or any positive integer up to $n - 1$; and m_ℓ can have $2\ell + 1$ possible values, ranging from $-\ell$ to $+\ell$ in integral steps.

The number n is called the **principal quantum number.** It is associated with the dependence of the wave function on the distance r and therefore with the probability of finding the electron at various distances from the nucleus. The quantum numbers ℓ and m_ℓ are associated with the angular momentum of the electron and with the angular dependence of the electron wave function. The quantum number ℓ is called the **orbital quantum number.** The magnitude L of the orbital angular momentum $\vec{L}$ is related to the orbital quantum number ℓ by

$$L = \sqrt{\ell(\ell + 1)}\hbar \qquad 36\text{-}24$$

The quantum number m_ℓ is called the **magnetic quantum number.** It is related to the component of the angular momentum along some direction in space. All spatial directions are equivalent for an isolated atom, but placing the atom in a magnetic field results in the direction of the magnetic field being separated out from the other directions. The convention is that the z direction is chosen for the magnetic-field direction. Then the z component of the angular momentum of the electron is given by the quantum condition

$$L_z = m_\ell \hbar \qquad 36\text{-}25$$

This quantum condition arises from the boundary condition on the azimuth coordinate ϕ that the probability of finding the electron at some arbitrary angle ϕ_1 must be the same as that of finding the electron at angle $\phi_1 + 2\pi$ because these are the same points in space.

If we measure the angular momentum of the electron in units of $\hbar$, we see that the angular-momentum magnitude is quantized to the value $\sqrt{\ell(\ell + 1)}$ units and that its component along any direction can have only the $2\ell + 1$ values ranging from $-\ell$ to $+\ell$ units. Figure 36-6 shows a vector-model diagram illustrating the possible orientations of the angular-momentum vector for $\ell = 2$. Note that only specific values of θ are allowed; that is, the directions in space are quantized.

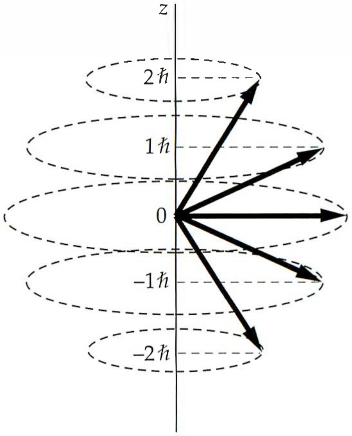

FIGURE 36-6 Vector-model diagram illustrating the possible values of the z component of the angular-momentum vector for the case $\ell = 2$. The magnitude of the angular momentum is $L = \hbar\sqrt{\ell(\ell + 1)} = \hbar\sqrt{2(2 + 1)} = \hbar\sqrt{6}$.

36-4 Quantum Theory of the Hydrogen Atom

We can treat the simplest atom, the hydrogen atom, as a stationary nucleus, a proton, that has a single moving particle, an electron, with kinetic energy $p^2/2m$. The potential energy $U(r)$ due to the electrostatic attraction between the electron and the proton[†] is

$$U(r) = -\frac{kZe^2}{r} \qquad \text{36-26}$$

For this potential-energy function, the Schrödinger equation can be solved exactly. In the lowest energy state, which is the ground state, the principal quantum number n has the value 1, ℓ is 0, and m_ℓ is 0.

Energy Levels

The allowed energies of the hydrogen atom that result from the solution of the Schrödinger equation are

$$E_n = -\frac{mk^2e^4}{2\hbar^2 n^2} = -Z^2\frac{E_0}{n^2}, \quad n = 1, 2, 3, \ldots \qquad \text{36-27}$$

ENERGY LEVELS FOR HYDROGEN

where

$$E_0 = \frac{mk^2e^4}{2\hbar^2} \approx 13.6\text{ eV} \qquad \text{36-28}$$
