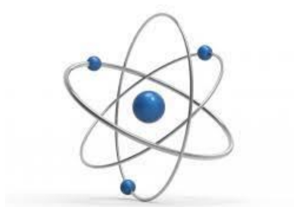
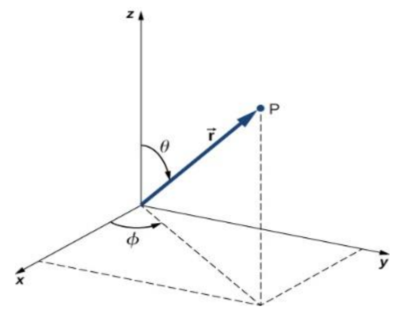
Chapter Six

Spherically Symmetric Potentials and Hydrogenic Atoms

We shall now turn our attention to the study of the motion of a particle in a potential $V(r)$ which depends only on the magnitude r of the position vector $\vec{r}$ of the particle with respect to some origin. Such a potential is called a *spherically symmetric potential* or a *central potential*. This is one of the most important problems in quantum mechanics and forms the starting point of the application of quantum mechanics to the understanding of atomic and nuclear structure.





8.1 Separation of the Wave Equation into Radial and Angular Parts

If m is the mass of the particle, then its Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad \ldots(8.1)$$

Since $V(r)$ is spherically symmetric, it is most convenient to use the spherical polar coordinates. Expressing the ∇^2 operator in spherical polar coordinates, the Hamiltonian (8.1) becomes

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r) \qquad \ldots(8.2)$$

The representation of the square of the angular momentum operator in spherical polar coordinates is given by

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad \ldots(8.3)$$

We may write

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2 r^2}\right] + V(r) \qquad \ldots(8.4)$$

The time-independent Schrödinger equation for the particle can be written as

$$H\psi(r) = E\psi(r) \qquad \ldots(8.5)$$

or $$\left[-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2 r^2}\right\} + V(r)\right]\psi(r,\ \theta,\ \phi) = E\psi(r,\ \theta,\ \phi)$$

or $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{2m}{\hbar^2}[E - V(r)]\ \psi(r,\ \theta,\ \phi) = \frac{L^2}{\hbar^2 r^2}\psi(r,\ \theta,\ \phi) \qquad \ldots(8.6)$$

This equation can be solved by using the method of separation of variables. Let us write

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

Substituting into (8.6),

$$\frac{Y(\theta,\phi)}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}[E - V(r)]\ R(r)Y(\theta,\ \phi) = \frac{R(r)}{\hbar^2 r^2}\ L^2\ Y(\theta,\ \phi)$$

Dividing by $R(r)Y(\theta,\ \phi)/r^2$,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}[E - V(r)] = \frac{1}{\hbar^2 Y}\ L^2 Y(\theta,\ \phi) \qquad \ldots(8.7)$$

The left-hand side of this equation depends only on r and the right-hand side depends only on θ and ϕ. Therefore, both sides must be equal to a constant. Calling this constant λ, we obtain the ***radial equation***

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\{E - V(r)\} - \frac{\lambda}{r^2}\right]R(r) = 0 \qquad \ldots(8.8)$$

and the ***angular equation***

$$L^2 Y(\theta,\ \phi) = \lambda\hbar^2 Y(\theta,\ \phi) \qquad \ldots(8.9)$$

8.1.1 The Angular Equation

Equation (8.9) is an eigenvalue equation for the operator L^2. We recall from chapter 7 that physically acceptable solutions of this equation are obtained for

…(8.10)

$$\lambda = l(l+1),\ l = 0,\ 1,\ 2,\ \ldots$$

Thus, the eigenvalues of L^2 that corresponding eigenfunctions are the spherical harmonics $Y_{lm_l}(\theta,\phi)$ defined in (7.20) and (7.21). The spherical harmonics $Y_{lm_l}(\theta,\phi)$ are also eigenfunctions of the z-component of the angular momentum L_z such that

$$\begin{aligned} L^2\ Y_{lm_l}(\theta,\ \phi) &= l(l+1)\hbar^2\ Y_{lm_l}(\theta,\ \phi), \\ L_z\ Y_{lm_l}(\theta,\ \phi) &= m_l\hbar\ Y_{lm_l}(\theta,\ \phi), \\ l &= 0,\ 1,\ 2,\ \ldots; \\ m_l &= -l,\ -l+1,\ ..0,\ \ldots,\ l-1,\ l. \end{aligned} \qquad \ldots(8.11)$$

The magnitude of **L** in state Y_{lm_l} is $\sqrt{l(l+1)}\hbar$ and the possible values of the projection L_z are the $(2l+1)$ values of $m_l\hbar$.

The state $Y_{lm_l}(\theta,\phi)$ has the parity of l.

8.1.2 The Radial Equation

Substituting (8.10) into (8.8), the radial equation becomes

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right] R(r) = 0 \qquad \ldots(8.12)$$

If we put, $R(r) = u(r)/r$

then the equation for the new radial function $u(r)$ is

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right] u(r) = 0 \qquad \ldots(8.13)$$

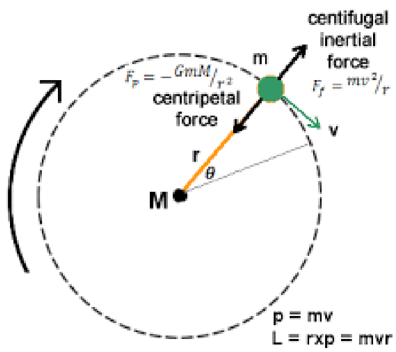
This equation shows that the radial motion is similar to the one-dimensional motion of a particle in the "effective" potential consequence

$$V_{\text{eff}} = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \qquad \ldots(8.14)$$

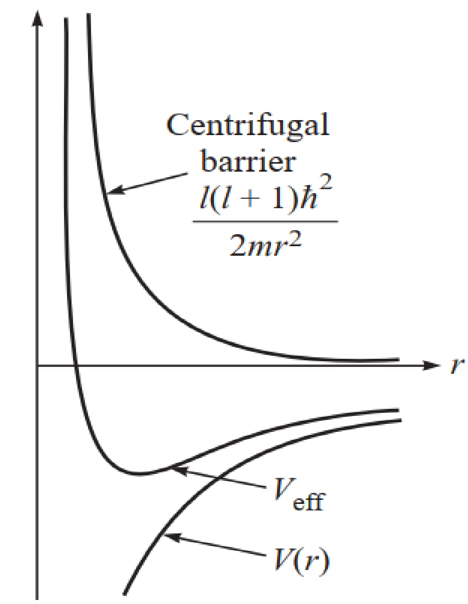
The additional term $l(l+1)\hbar^2/2mr^2$ is due to the "centrifugal barrier" which is a consequence of the non-zero angular momentum. This can be understood as follows: According to classical mechanics, if a particle has angular momentum L about an axis, then its angular velocity is

$$\omega = \frac{L}{mr^2}$$

where r is the distance of the particle from the axis. The “centrifugal force” on the particle is



$$mr\omega^2 = \frac{L^2}{mr^3}$$

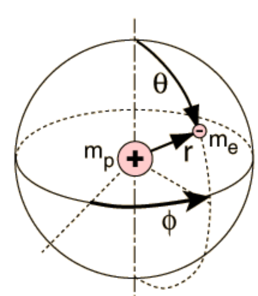


Shapes of the centrifugal barrier, effective potential and Coulomb potential.

8.2 Reduction of a Two-Body Problem to an Equivalent One-Body Problem

In what follows we shall solve the radial equation for a hydrogenic atom, which consists of a nucleus and an electron interacting via the attractive Coulomb force which depends on the magnitude of the distance between the two.

For a two-body system, if the potential energy depends only on the coordinates of one particle relative to the other, then the problem can be reduced to an equivalent one-body problem along with a uniform translational motion of the center of mass of the two-body system.



Consider two particles, of masses m_1 and m_2, interacting via a potential $V(r_1 - r_2)$ which depends only upon the relative coordinate $r_1 - r_2$.

The time-independent Schrödinger equation for the system is,

$$\left[-\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} + V(\mathbf{r}_1 - \mathbf{r}_2)\right]\Psi(\mathbf{r}_1,\ \mathbf{r}_2) = E\ \Psi(\mathbf{r}_1,\ \mathbf{r}_2) \qquad \ldots(8.15)$$

where E is the total energy of the system. Let us now introduce the *relative coordinate*

$$\boldsymbol{r} = \boldsymbol{r_1} - \boldsymbol{r_2} \qquad \ldots(8.16)$$

and the *center of mass* coordinate

$$R = \frac{m_1\boldsymbol{r_1} - m_2\boldsymbol{r_2}}{m_1 + m_2} \qquad \ldots(8.17)$$

A simple calculation will show that

$$-\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} \qquad \ldots(8.18)$$

where

$$M = m_1 + m_2 \qquad \ldots(8.19)$$

and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \ldots(8.20)$$

The quantity μ is called the *reduced mass* of the two-particle system. The Schrödinger Equation (8.15) becomes

$$\left[-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\Psi(\mathbf{R},\ \mathbf{r}) = E\ \Psi(\mathbf{R},\ \mathbf{r}) \qquad \ldots(8.21)$$

Now, since the potential $V(\boldsymbol{r})$ depends only on the relative coordinate, the wave function $\Psi(\boldsymbol{R},\boldsymbol{r})$ can be written as a product of functions of $\boldsymbol{R}$ and $\boldsymbol{r}$:

$$\Psi(\mathbf{R},\ \mathbf{r}) = \Phi(\mathbf{R})\ \psi(\mathbf{r}) \qquad \ldots(8.22)$$

Substituting into (8.21) it can be easily shown that the functions $\Phi(R)$ and $\Psi(r)$ satisfy, respectively, the equations

$$-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) = E_{\mathbf{R}}\Phi(\mathbf{R}) \qquad \ldots(8.23)$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\psi(\mathbf{r}) = E_{\mathbf{r}}\psi(\mathbf{r}) \qquad \ldots(8.24)$$

Equation (8.23) describes the motion of the center of mass. It says that the center of mass moves as a free particle of mass M and energy $E_{\boldsymbol{R}}$.

Equation (8.24) describes the relative motion of the particles. It says that the relative motion is same as that of a particle of mass μ moving in the potential $V(\boldsymbol{r})$. Clearly

$$E = E_{\boldsymbol{R}} + E_{\boldsymbol{r}} \qquad \ldots(8.25)$$

By separating the center-of-mass motion, the solution of the problem gets considerably simplified.