CHAPTER - 6

Hydrogen Atom & Rigid Rotor

Quantization of Electronic Energy:

Necessity of Replacing Bohr's Theory :

The mathematical framework of the Bohr's theory was based on the basic assumption of quantization of orbital angular momentum of the electron. It was seen earlier that this theory led to the quantization of electronic energies which formed the basis for explaining the experimental spectra of hydrogen like species such as H, He^{+}, Li^{2+} and Be^{3+}. However, this theory was not entirely satisfactory as it failed to provide an interpretation of relative line intensities in the hydrogen spectrum and also failed completely when it was applied to explain the energies and spectra of more complex atoms. In this section, we consider the application of Schrodinger's wave theory to one-electron atom. In the subsequent section, it will be shown how the principles of this theory can be applied, in a more approximate way, to many electron atoms.

Setting of Schrodinger Equation :

The time independent form of Schrodinger equation is

$$\mathrm{H_{op}}\ \psi_{\mathrm{total}} = \mathrm{E_{total}}\ \psi_{\mathrm{total}} \qquad ...(1)$$

where $\mathrm{H_{op}}$ is the Hamiltonian operator, $\mathrm{E_{total}}$ is the total nonrelativistic energy and ψ_{total} is the wave function for the total system. Since the hydrogen like system contain two particles, namely, nucleus and electron, it is obvious that the wave function ψ_{total} depends on the six coodinate variables, three for the electron (x_e, y_e, z_e) and three for the nucleus (x_n, y_n, z_n), both sets of coordinates refer to the common origin. The Hamiltonian operator consists of two terms, viz. the kinetic and potential energy terms. The kinetic energy operator will contain two terms, one for the electron and one for the nucleus. Thus, we have

$$H_{op} = T_{op} + V_{op} = \left(-\frac{h^2}{8\pi^2 m_e}\nabla_e^2 - \frac{h^2}{8\pi^2 m_n}\nabla_n^2\right) - \frac{Ze^2}{(4\pi\varepsilon_o)r} \qquad ...(2)$$

All symbols have their usual meanings. Substituting equation (2) in equation (1), we have

$$\left[-\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right)-\frac{h^2}{8\pi^2 m_n}\left(\frac{\partial^2}{\partial x_n^2}+\frac{\partial^2}{\partial y_n^2}+\frac{\partial^2}{\partial z_n^2}\right)-\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi_{total} = E_{total}\ \psi_{total} \qquad ...(3)$$

Equation (3) can be broken into two simpler equations, one involving the free movement of the centre of mass of the atom in space and the other involving the relative motion of the electron with respect to the nucleus within the atom. The two equations are

$$-\frac{h^2}{8\pi^2(m_e+m_n)}\left(\frac{\partial^2}{\partial x_c^2}+\frac{\partial^2}{\partial y_c^2}+\frac{\partial^2}{\partial z_c^2}\right)\psi_M = E_{trans}\psi_M \qquad ...(4)$$

and $$\left[-\frac{h^2}{8\pi^2\mu_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi_e = E\psi_e \qquad ...(5)$$

with $E_{trans} + E = E_{total}$

Equation (4) is simply the Schrodinger equation for a free particle of mass $(m_e + m_n)$, E_{trans} is the translational kinetic energy associated with the free movement of the centre of mass of the atom through space.

Equation (5) is the Shrodinger equation which represents the system in which a particle of reduced mass μ is revolving around the stationary nucleus of positive charge Z at a distance of *r*. The behaviour of this electron can be described by the function ψ_e and E is the corresponding energy of the electron. The allowed values of electronic energies can be obtained by solving equation (5) and equation (4) which describes the motion of the centre of mass is of the same form as that of the particle in a three dimensional box.

Since, the mass of the nucleus is very high as compared to the mass of the electron, the reduced mass of the entire system is very nearly equal to the mass of the electron. Also, the centre of mass of the entire system lies almost at the nucleus. Hence, equation (5) very well describes the motion of electron with respect to the nucleus.

Schrodinger Equation in Terms of Spherical Polar Coordinates:

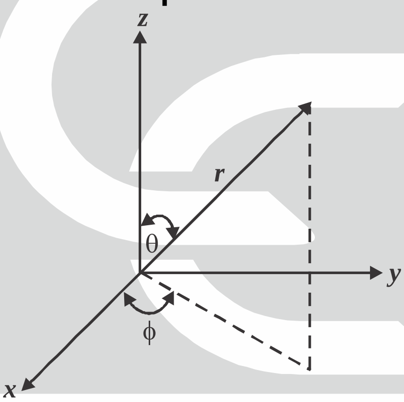

Figure: The polar coordinate system for the motion of electron in hydrogen atom.

The solution of Schrödinger equation becomes very much simplified if the equation is expressed in the coordinate system that reflects the symmetry of the system. In the present case the potential energy is spherically symmetric (*V* depends only on *r*), and thus, it is convenient to transform the Schrodinger equation (5) into the spherical polar coordinates *r*, θ and φ by using the relations

$$x = r\sin\theta\cos\varphi;\quad y = r\sin\theta\sin\varphi;\quad z = r\cos\theta$$

Transforming the Schrödinger equation into spherical polar coordinates using the above relations results in:

$$\left[-\frac{h^2}{8\pi^2\mu r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}-\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi = E\psi$$

where ψ is a function of *r*, θ and φ

Splitting of Schrodinger Equation:

Rearranging the above expression, we get

$$\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\psi + \frac{8\pi^2\mu}{h^2}\left(\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right)\psi = 0$$

Multiplying throughout by r^2 and rearranging the resultant expression, we get

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{8\pi^2\mu r^2}{h^2}\left\{\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right\}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi=0 \quad ...(6)$$

Since the operator is made up of two terms, one depending on the variable r and the other on the variables θ and φ taken together, we can write the wave function ψ as

$$\psi_{r,\theta,\varphi}=R_{r,}Y_{\theta,\varphi} \quad ...(7)$$

The function Y is known as spherical harmonics. Substituting equation (7) in equation (6) we get

$$Y_{\theta,\varphi}\frac{d}{dr}\left(r^2\frac{d}{dr}R_r\right)+\frac{8\pi^2\mu r^2}{h^2}\left[\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right]R_rY_{\theta,\varphi}$$

$$+R_r\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_{\theta,\varphi}=0 \quad ...(8)$$

Dividing throghout by $R_r\ Y_{\theta,\varphi}$, we get

$$\left[\frac{1}{R_r}\frac{d}{dr}\left(r^2\frac{d}{dr}R_r\right)+\frac{8\pi^2\mu r^2}{h^2}\left\{\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right\}\right]$$

$$=-\left[\frac{1}{Y_{\theta,\varphi}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\theta,\varphi}\right] \quad ...(9)$$

Equality shown in equation (9) holds good only when both sides are equal to a constant say, $\ell(\ell+1)$. Thus equation (9) separates into two equations, one depending only on *r* and the other on θ and φ. These are :
Equation involving the variable *r*

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)=\ell(\ell+1) \quad ...(10)$$

Equation involving the angles θ and φ

$$\frac{1}{Y_{\theta,\varphi}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\theta,\varphi}=-\ell(\ell+1) \quad ...(11)$$

Multiplying equation (1) by $\sin^2\theta$ and rearranging the resultant expression, we get

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\ell(\ell+1)\sin^2\theta+\frac{\partial^2}{\partial\varphi^2}\right]Y_{\theta,\varphi}=0 \quad ...(12)$$

Since the operator in equation (11) consists of two terms. one depending on θ and the other on φ, we can write the wave function $Y_{\theta,\varphi}$ as $Y_{\theta,\varphi}=\Theta_\theta\ \Phi_\varphi$
With this, equation (12) becomes

$$\Phi_\varphi\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_\theta}{d\theta}\right)+\ell(\ell+1)\sin^2\theta\ \Theta_\theta\Phi_\varphi+\Theta_\theta\frac{d^2}{d\varphi^2}\Phi_\varphi=0$$

Dividing throughout by $\Theta_\theta \Phi_\varphi$ and rearranging, we get

$$\frac{\sin\theta}{\Theta_\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_\theta}{d\theta}\right)+\ell(\ell+1)\sin^2\theta=-\frac{1}{\Phi_\varphi}\frac{d^2\Phi_\varphi}{d\varphi^2} \quad ...(13)$$

The two sides of equation (12) must be equal to a constant, say m^2. Thus, we have

$$\frac{\sin\theta}{\Theta_\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_\theta}{d\theta}\right)+\ell(\ell+1)\sin^2\theta=m^2 \quad ...(14)$$

and $$\frac{1}{\Phi_\varphi}\frac{d^2\Phi_\varphi}{d\varphi^2}=-m^2 \quad ...(15)$$

Three Split Expressions of the Schrodinger Equation :

Thus, the Schrodinger equation (6) for the hydrogen like species can be separated into three equations. These are :

- Equation involving only r

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)=\ell(\ell+1) \quad ...(16)$$

- Equation involving only θ

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\ell(\ell+1)\sin^2\theta=m^2 \quad ...(17)$$

- Equation involving only φ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m^2 \quad ...(18)$$

We now consider the acceptable solutions of equations (16), (17) and (18).

Solutions of Φ-dependent equation :

Solving equation (18) results in the following normalized wavefunctions:

$$\Phi_m=\frac{1}{\sqrt{2\pi}}\exp(im\varphi); \qquad m=0,\pm1,\pm2,..... \quad ...(19)$$

The constant m is called the magnetic quantum number and it represents the quantization of the z-component of the angular momentum since

$$\hat{L}_z\left\{\frac{1}{\sqrt{2\pi}}\exp(im\varphi)\right\}=\frac{h}{2\pi i}\frac{\partial}{\partial\varphi}\left\{\frac{1}{\sqrt{2\pi}}\exp(im\varphi)\right\}$$

$$=m\frac{h}{2\pi}\left\{\frac{1}{\sqrt{2\pi}}\exp(im\varphi)\right\} \quad ...(20)$$

Thus, the permitted values of z-component of the angular momentum of the electron are given by the expression $m(h/2\pi)$.

Solutions of θ-Dependent Equation:

Solving equation (17) results in the following function:

$$\Theta_{\ell,|m|}=\left[\frac{(2\ell+1)}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2}P_\ell^{|m|}(\xi) \quad ...(21)$$

where, $P_\ell^{|m|}(\xi) = \left(1-\xi^2\right)^{|m|/2} \dfrac{d^{|m|}P_\ell}{d\xi^{|m|}}(\xi)$: Associated Legendre Polynomials ...(22)

$$P_\ell(\xi) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{d\xi^\ell}\left(\xi^2-1\right)^\ell \quad : \text{Legendre polynomials} \qquad ...(23)$$

and $\xi = \cos\theta$

These solutions are obtained provided the following conditions are satisfied.

$\ell = 0, 1, 2, 3, ...$

$m = 0, \pm 1, \pm 2, ..., \pm \ell$

The quantum number ℓ is called the azimuthal quantum number or the subsidiary quantum number and it represents the quantization of the square of total angular momentum according to the equation

$$\hat{L}^2\Theta_{\ell,|m|} = \ell(\ell+1)\left(\frac{h}{2\pi}\right)^2 \Theta_{\ell,|m|} \qquad ...(24)$$

Solution of ρ-Dependent Equation :

With the help of a suitable transformation of independent variable and from the forms of solutions as the variable approaches zero and infinity, it is possible to write the radial equation into the following more familiar form, known as associated Laguerre equation.

$$\rho^2\frac{d^2L}{d\rho^2} + (j+1-\rho)\frac{dL}{d\rho} + (K-j)L = 0 \qquad ...(25)$$

where the function R is related to the function L through the following transformation scheme.

$$R(r) = s(\rho) = e^{-\rho/2}F(\rho) = e^{-\rho/2}\rho^\iota L(\rho) \qquad ...(26)$$

The terms ρ, j and k are given by

$$\rho = 2\alpha r \qquad ...(27)$$

$$j = 2\ell + 1 \qquad ...(28)$$

$$k = \lambda + 1 \qquad ...(29)$$

where $$\alpha^2 = -\frac{8\pi^2\mu E}{h^2} \qquad ...(30)$$

$$\lambda = \frac{4\pi^2\mu Z e^2}{(4\pi\varepsilon_0)h^2\alpha} \qquad ...(31)$$

The solution of equation (25), as determined by the power series method, is the associated Laguerre polynomial of degree (k–j) and order j, and is given by

$$L \equiv L_k^j = \frac{d^j}{d\rho^j}L_k \qquad ...(32)$$

where L_k, the Laguerre polynomial of degree k, is given by

$$L_k = e^\rho \frac{d^k}{d\rho^k}\left(\rho^k e^{-\rho}\right) \qquad ...(33)$$