

# 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<sup>+</sup>, Li<sup>2+</sup> and Be<sup>3+</sup>. 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

$$H_{op} \Psi_{total} = E_{total} \Psi_{total} \quad \dots(1)$$

where  $H_{op}$  is the Hamiltonian operator,  $E_{total}$  is the total nonrelativistic energy and  $\Psi_{total}$  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  $\Psi_{total}$  depends on the six coordinate 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

$$H_{op} = T_{op} + V_{op} = \left( -\frac{h^2}{8\pi^2 m_e} \nabla_e^2 - \frac{h^2}{8\pi^2 m_n} \nabla_n^2 \right) - \frac{Ze^2}{(4\pi\epsilon_0)r} \quad \dots(2)$$

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

$$\left[ -\frac{h^2}{8\pi^2 m_e} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{h^2}{8\pi^2 m_n} \left( \frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2} \right) \right] \Psi_{total} = E_{total} \Psi_{total} \quad \dots(3)$$

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

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

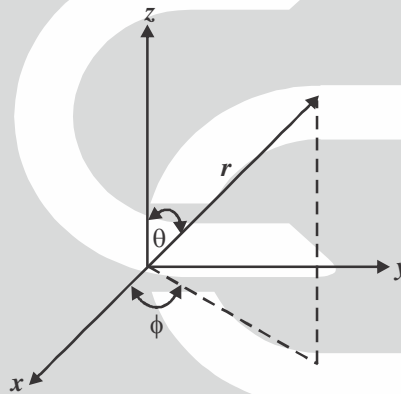
and 
$$\left[ -\frac{h^2}{8\pi^2 \mu_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi_e = E\psi_e \quad \dots(5)$$

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 an electron of reduced mass  $\mu$  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  $\psi_e$  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.

**Schrodinger Equation in Terms of Spherical Polar Coordinates:**



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

The solution of Schrodinger 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 field is spherical symmetry ( $V$  depends only on  $r$ ), and thus, it is convenient to transform the Schrodinger equation (5) into the spherical polar coordinates  $r, \theta$  and  $\phi$  by using the relations

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

The transformation is lengthly and tedious process, and only the transformed expression is given below :

$$\left[ -\frac{h^2}{8\pi^2 \mu r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi = E\psi$$

where  $\psi$  is a function of  $r, \theta$  and  $\phi$

**Splitting of Schrodinger Equation:**

Rearranging the above expression, we get

$$\frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \psi + \frac{8\pi^2 \mu}{h^2} \left( \frac{Ze^2}{(4\pi\epsilon_0)r} + E \right) \psi = 0$$

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

$$\left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{8\pi^2 \mu r^2}{h^2} \left\{ \frac{Ze^2}{(4\pi\epsilon_0)r} + E \right\} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \psi = 0 \quad \dots(6)$$

Since the operator is made up of two terms, one depending on the variable  $r$  and the other on the variables  $\theta$  and  $\phi$  taken together, we can write the wave function  $\psi$  as

$$\psi_{r,\theta,\phi} = R_r Y_{\theta,\phi} \quad \dots(7)$$

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

$$Y_{\theta,\phi} \frac{d}{dr} \left( r^2 \frac{d}{dr} R_r \right) + \frac{8\pi^2 \mu r^2}{h^2} \left[ \frac{Ze^2}{(4\pi\epsilon_0)r} + E \right] R_r Y_{\theta,\phi} + R_r \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y_{\theta,\phi} = 0 \quad \dots(8)$$

Dividing throughout by  $R_r Y_{\theta,\phi}$ , we get

$$\left[ \frac{1}{R_r} \frac{d}{dr} \left( r^2 \frac{d}{dr} R_r \right) + \frac{8\pi^2 \mu r^2}{h^2} \left\{ \frac{Ze^2}{(4\pi\epsilon_0)r} + E \right\} \right] = - \left[ \frac{1}{Y_{\theta,\phi}} \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right\} Y_{\theta,\phi} \right] \quad \dots(9)$$

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  $\theta$  and  $\phi$ . These are :

Equation involving the variable  $r$

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} \left( E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) = \ell(\ell+1) \quad \dots(10)$$

Equation involving the angles  $\theta$  and  $\phi$

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

Multiplying equation (11) by  $\sin^2\theta$  and rearranging the resultant expression, we get

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

Since the operator in equation (11) consists of two terms, one depending on  $\theta$  and the other on  $\phi$ , we can write the wave function  $Y_{\theta,\phi}$  as  $Y_{\theta,\phi} = \Theta_\theta \Phi_\phi$

With this, equation (12) becomes

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

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

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

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

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

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

### 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  $r$

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} \left( E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) = \ell(\ell+1) \quad \dots(16)$$

- ◆ Equation involving only  $\theta$

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

- ◆ Equation involving only  $\varphi$

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

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

### Solutions of $\Phi$ -dependent equation :

Equation (17) has already been solved in connection with the rigid rotator system. Its solution is

$$\Phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\varphi); \quad m = 0, \pm 1, \pm 2, \dots \quad \dots(19)$$

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

$$\begin{aligned} \hat{L}_z \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} &= \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} \\ &= m \frac{h}{2\pi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} \end{aligned} \quad \dots(20)$$

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 $\theta$ -Dependent Equation:

Equation (17) has also been solved in the rigid rotator system. The solution is

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

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

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

and  $\xi = \cos \theta$

These solutions are obtained provided the following conditions are satisfied.

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

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

The quantum number  $\ell$  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

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

### Solution of $\rho$ -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 in the following more familiar form, known as associated Laguerre equation.

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

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

$$R(r) = s(\rho) = e^{-\rho/2} F(\rho) = e^{-\rho/2} \rho^j L(\rho) \quad \dots(26)$$

The terms  $\rho$ ,  $j$  and  $k$  are given by

$$\rho = 2\alpha r \quad \dots(27)$$

$$j = 2\ell + 1 \quad \dots(28)$$

$$k = \lambda + 1 \quad \dots(29)$$

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

$$\lambda = \frac{4\pi^2 \mu Z e^2}{(4\pi\epsilon_0) h^2 \alpha} \quad \dots(31)$$

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

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

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

$$L_k = e^\rho \frac{d^k}{d\rho^k} (\rho^k e^{-\rho}) \quad \dots(33)$$

In order that the associated Laguerre polynomial is the acceptable solution of equation (25) the following quantum restriction has to be satisfied.

$$k = 1, 2, 3, \dots, \infty \quad \dots(34)$$

Acceptable solutions, as usual, means that the wave function  $L(\rho)$  should be a well-behaved function and should vanish as  $\rho \rightarrow \infty$ . The latter condition requires that the polynomial must be restricted to a finite number of terms.

This quantum restriction leads to the fact that  $\lambda$  which is equal to  $k - \ell$  (equation (29)) must also be an integer. Let  $\lambda$  be written as  $n$ , so that

$$k = n + \ell \quad \dots(35)$$

### Expression of the Normalized R Functions:

Thus, the function  $R$  as given by equation (26) is

$$R = \rho^\ell e^{-\rho/2} L_{n+\ell}^{2\ell+1} \quad \dots(36)$$

Normalizing the above solution through the expression

$$\int_0^\infty R^* R r^2 dr = 1$$

we get 
$$R = - \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{1/2} \rho^\ell e^{-\rho/2} L_{n+\ell}^{2\ell+1} \quad \dots (37)$$

where 
$$\rho = (2\alpha r) = 2 \left( \frac{4\pi^2 \mu Z e^2}{nh^2 (4\pi\epsilon_0)} \right) r = \left( \frac{2Z}{na_0} \right) r \quad \dots (38)$$

and 
$$a_0 = \frac{h^2 (4\pi\epsilon_0)}{4\pi^2 \mu e^2} \quad \dots (39)$$

### Allowed Values of $n$ and its Relation with $l$ :

The constant  $n$  is referred to as the principal quantum number. If the associated Laguerre polynomial (equation 32) is not to vanish, we must have

$$j \leq k \quad \dots (40)$$

Since  $j = 2\ell + 1$  and  $k = n + \ell$ , we have

$$(2\ell + 1) \leq (n + \ell)$$

Or 
$$\ell + 1 \leq n \quad \text{or} \quad \ell \leq n - 1 \quad \dots (41)$$

Since the allowed values of  $\ell$  are  $1, 2, 3, \dots$ , it is obvious that the principal quantum number  $n$  cannot have a zero value. The allowed values of  $n$  are only positive integers. Thus, we have

$$n = 1, 2, 3, 4, \dots$$

$$\ell = 0, 1, 2, 3, \dots, (n - 1) \quad \dots (42)$$

**Expressions for the Function  $R_{n,\ell}$  :**

The exact form of the function  $R_{n,\ell}(r)$  for the given values of  $n$  and  $\ell$  can be determined from equations (37), (32) and (33). These equations are

$$R_{n,\ell} = - \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{1/2} \rho^\ell e^{-\rho/2} L_{n+\ell}^{2\ell+1} \quad \dots (43)$$

$$L_{n+\ell}^{2\ell+1} = \frac{d^{2\ell+1}}{d\rho^{2\ell+1}} L_{n+\ell} \quad \dots (44)$$

and  $L_{n+\ell} = e^\rho \frac{d^{n+\ell}}{d\rho^{n+\ell}} (\rho^{n+\ell} e^{-\rho})$  where,  $\rho = \left( \frac{2Z}{na_0} \right) r$  ... (45)

**Virial theorem for hydrogen atom:**

Potential,  $V \propto r^{-1} \Rightarrow V \propto x^b \Rightarrow b = -1$

$$2\langle T \rangle = b\langle V \rangle \Rightarrow 2\langle T \rangle = -\langle V \rangle$$

$$\Rightarrow \frac{\langle T \rangle}{\langle V \rangle} = -\frac{1}{2} \Rightarrow \langle E \rangle = \langle T \rangle + \langle V \rangle$$

$$\Rightarrow \frac{\langle E \rangle}{\langle V \rangle} = \frac{-\frac{1}{2}\langle V \rangle + \langle V \rangle}{\langle V \rangle} = \frac{1}{2} \Rightarrow \frac{\langle E \rangle}{\langle V \rangle} = \frac{1}{2}$$

where, E = total energy

T = kinetic energy

V = potential energy.

$V = -2T$  (Virial Theorem for Hydrogen atom)

**Degeneracy in H-atom:**

(1) If spin is not included degeneracy =  $n^2$  (where,  $n$  is principle quantum number)

(2) If spin is included degeneracy =  $2n^2$

**PROBLEMS ON HYDROGEN ATOM**

1. The two radial nodes in the 3s radial function of H atom occur at the distances R1 and R2 from the nucleus. The three radial nodes in the 4s orbital occur at R3, R4 and R5. The order of these distances is given by

(a)  $R3 < R1 < R4 < R2 < R5$  (b)  $R1 < R3 < R4 < R2 < R5$

(c)  $R3 < R1 < R2 < R4 < R5$  (d)  $R3 < R1 < R4 < R5 < R2$

**Soln.** For 3s-radial function total radial nodes =  $n-l-1 = 3-0-1 = 2$  for 4s-radial function total radial nodes =  $n-l-1 = 4-0-1 = 3$ .

$$\Psi_{3s} = \left( \frac{Z}{a_0} \right)^{3/2} \frac{1}{81\sqrt{3}\pi} \left[ 27 - 18\frac{Zr}{a_0} + 2\left( \frac{Zr}{a_0} \right)^2 \right] e^{-Zr/3a_0}$$

$$\Psi_{4s} = \left( \frac{Z}{a_0} \right)^{3/2} \frac{1}{1536\sqrt{\pi}} \left[ 192 - 144\frac{Zr}{a_0} + 24\left( \frac{Zr}{a_0} \right)^2 - \left( \frac{Zr}{a_0} \right)^3 \right] e^{-Zr/4a_0}$$