## 1. Quantization of Electronic Energies: The Hydrogen atom

The mathematical framework of 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 atoms such as H , $He^+$, $Li^{+2}$ and $Be^{3+.}$ However, this theory was not entirely satisfactory as it failed to provided 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, Schrodinger's wave mechanics has been invoked to one –electron atom.

The time –independent form of Schrodinger equation is

$$H_{op}\psi_{total} = E_{total} \psi_{total} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

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 systems 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 $(x_e, y_e, z_e)$. 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 ,

$$H_{op} = T_{op} + V_{op}$$

$$= \left( -\frac{h^2}{8\pi^2 m_e} \nabla_e^2 - \frac{h^2}{8\pi^2 m_n} \nabla_n^2 \right) - \frac{Ze'^2}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where $e'$ is the electronic charge e in CGS-esu units and is equal to $e/\sqrt{4\pi\epsilon_0}$ in SI units. All symbols have their usual meaning. Substituting Eq.2 in Eq.1 we have

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

$$\ldots\ldots\ldots (3)$$

Eq.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 two particles within the atom. The two equations are

$$-\frac{h^2}{8\pi^2 (m_e + m_n)} \left( \frac{\partial^2}{\partial x_M^2} + \frac{\partial^2}{\partial y_M^2} + \frac{\partial^2}{\partial z_M^2} \right) \psi_M = E_{trans} \psi_M \quad \ldots\ldots\ldots\ldots\ldots(4)$$

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

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

Eq.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 Schrodinger 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 r. The behavior 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 Eq (5). Eq.(4) which describes the motion of the centre of mass will not be dealt here.

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 ( Eq.5) into the spherical polar coordinates r,θ and φ ( Fig1) by using the relations

$$x = r\sin\theta\,\cos\varphi$$
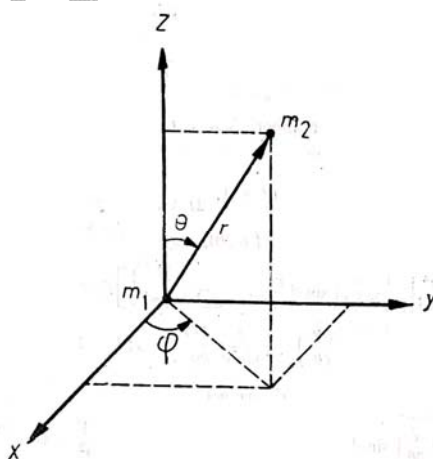$$y = r\sin\theta\,\sin\varphi$$
$$z = r\cos\theta$$



**Fig1: Cartesian and Spherical coordinates**

The transformation is a lengthy and tedious process, and only the transformed expression is given below

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

Where ψ is a function of r,θ and φ. Rearranging the above expression,

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

..........(6)

As usual, the function, $\psi(r,\theta,\varphi)$ may be written as the product of three functions, each dependent on only one of the coordinates, i.e.,

$$\psi(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

...................(7)

Substituting Eq. 7 in Eq. 6

$$\frac{1}{r^2}\left[\Theta\Phi\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right.$$
$$\left. + \frac{R\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}\right] + \frac{8\pi^2\mu}{h^2}\left(\frac{Ze'^2}{r} + E\right)R\,\Theta\,\Phi = 0$$

.......................(8)

Multiplying throughout by $r^2/R\Theta\phi$, we get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$
$$+ \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\varphi^2} + \frac{8\pi^2\mu r^2}{h^2}\left(E + \frac{Ze'^2}{r}\right) = 0$$

Or

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2\mu r^2}{h^2}\left(E + \frac{Ze'^2}{r}\right)$$
$$= -\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}$$

...............(9)

Equality shown in Eq.9 can hold good only when both sides are equal to a constant , say l(l+1). Thus Eq. 9 separates into two equations, one depending only on r and the other on $\theta$ and $\varphi$. These are:

(i) The radial equation:

$$\frac{1}{R} \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{8\pi^2 \mu r^2}{h^2}\left(E + \frac{Ze'^2}{r}\right) = l(l+1) \qquad \text{.....................(10)}$$

(ii) The angular equation :

$$\frac{1}{\Theta \sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi \sin^2\theta} \frac{d^2\Phi}{d\varphi^2} = -l(l+1) \qquad \text{................(11)}$$

Now the angular equation can be further separated into two equations , one depends on θ and the other on φ. This can be done by multiplying Eq. 11 by Sin²θ. On rearranging the terms we get

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = -\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} \qquad \text{................(12)}$$

The two sides of Eq. 12 must be equal to a constant , say **m²**. Thus,

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = m^2 \qquad \text{...........................(13)}$$

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} = -m^2 \qquad \text{...........................(14)}$$

Thus , the Schrodinger eq.6 for the hydrogen-like atoms can be separated into three equations. These are :

(i) Equation involving only r:

$$\frac{1}{R} \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{8\pi^2 \mu r^2}{h^2}\left(E + \frac{Ze'^2}{r}\right) = l(l+1) \qquad \text{.................(10)}$$

(ii) Equation involving only θ:

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = m^2 \qquad \text{.................(13)}$$

(iii) Equation involving only φ:

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} = -m^2 \qquad \text{.................(14)}$$

Now, we consider the acceptable solution of the eq.10, eq.13 and eq.14.

Acceptable Solution of Eq.14

Eq.14 has been solved in connection with the rigid rotator system (**Rigid rotator model –SKR Eq. 36**) Its solution is

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

..........( **Rigid rotator model –SKR Eq. 36**)

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

$$\left(L_z\right)_{op} \left\{\frac{1}{\sqrt{2\pi}} \exp(im\varphi)\right\} = \frac{h}{2\pi i} \frac{\partial}{\partial\varphi}\left\{\frac{1}{\sqrt{2\pi}} \exp(im\varphi)\right\}$$
$$= m\frac{h}{2\pi}\left\{\frac{1}{\sqrt{2\pi}} \exp(im\phi)\right\}$$

……………………….. (15)

Thus , the permitted values of z- component of the angular momentum of the electron are m(h/2π).

## Acceptable Solution of Eq.(13):

Eq. (13) has also been solved in the rigid rotator system (**Rigid rotator model –SKR Eq. 32**).
The solution is

$$\Theta_{l,|m|} = \left[\frac{(2l+1)}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}$$

……………( **Rigid rotator model –SKR Eq. 42**)

Where

$$P_l^{|m|} = (1-\xi^2)^{|m|/2} \frac{d^{|m|}P_l}{d\xi^{|m|}}: \text{Associated Legendre polynomials}$$

…….( **Rigid rotator model –SKR Eq. 39**)

$$P_l = \frac{1}{2^l\,l!} \frac{d^l}{d\xi^l}(\xi^2-1)^l: \text{Legendre polynomials}$$

……………….( **Rigid rotator model –SKR Eq. 40**)

and

$$\xi = \cos\theta$$

The above solutions are obtained provided th following conditions are satisfied.

$$l = 0, 1, 2, 3, \ldots$$

…….( **Rigid rotator model –SKR Eq. 38**)

$$m = 0, \pm1, \pm2, \ldots, \pm l$$

…….( **Rigid rotator model –SKR Eq. 41**)

The quantum number 1 is called the azimuthal quantum number or the subsidiary quantum number and it represents the quantization of the total angular momentum according to equation

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$$L_{op}\,\Theta_{l,|m|} = \sqrt{l(l+1)}\,\frac{h}{2\pi}\,\Theta_{l,|m|}$$

………………….( 16)

## Acceptable Solution of Eq.10

With the help of a suitable transformation of independent variable and from the forms of solutions as the variable approachs zero and infinity, it is possible to write Eq.10 in the following more familiar form, known as associated Laguerre equation.

$$\rho^2\,\frac{d^2L}{d\rho^2} + (j+1-\rho)\,\frac{dL}{d\rho} + (k-j)L = 0$$

…………………..( 17)

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

$$R(r) = s(\rho) = e^{-\rho/2}\,F(\rho) = e^{-\rho/2}\,\rho^l L(\rho)$$

………………..( 18)

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

$$\rho = 2\alpha r \qquad (19)$$
$$j = 2l+1 \qquad (20)$$
$$k = \lambda + l \qquad (21)$$

where

$$\alpha^2 = -8\pi^2\mu E/h^2 \qquad (22)$$
$$\lambda = \frac{4\pi^2\mu Ze'^2}{h^2\alpha} \qquad (23)$$

The solutions of Eq.17 are associated Laguerre polynomials of degree (k-j) and order j, and are given by

$$L \equiv L_k^j = \frac{d^j}{d\rho^j}\,L_k$$

………………….( 24)

Where $L_k$ are the Laguerre polynomials of degree k, given by

$$L_k = e^\rho\,\frac{d^k}{d\rho^k}\,(\rho^k e^{-\rho})$$

………………….( 25)

In order that the associated Laguree polynomials are the acceptable solutions* of Eq.17 the following quantum restriction has to be satisfied.

$$k = 1,2,3,………………\infty$$

………………….( 26)

This quantum restriction leads to the fact that λ which is equal to k-l ( Eq.21) must also be an integer. Let λ be written as n , so that

$$k = n+l$$

………………….( 27)

Thus, the function R as given by Eq. (18) is

$$R = \rho^l e^{-\rho/2}\,L_{n+l}^{2l+1}$$

………………….( 28)

Normalizing the above solution through the expression

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

we get
$$R = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} \rho^l e^{-\rho \cdot 2}\, L_{n+l}^{2l+1} \qquad (29)$$

where
$$\rho = (2\alpha r) = 2\left(\frac{4\pi^2\mu Ze'^2}{nh^2}\right)r = \left(\frac{2Z}{na_0}\right)r \qquad (30)$$

and
$$a_0 = \frac{h^2}{4\pi^2\mu e'^2} \qquad (31)$$

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

The allowed value of n and its relation with l: The constant n is referred to as the principal quantum number. If the associated Laguerre Polynomial ( Eq.24) is not to vanish, we must have

$$j \le k \qquad \qquad \ldots\ldots\ldots\ldots(32)$$

Since j= 2l + 1 and k = n+ l, we have

$$(2l+1) \le (n+l)$$

or $\quad l + 1 \le n$ or $l \le n-1$ $\qquad \qquad \ldots\ldots\ldots\ldots(33)$

Since the allowed values of l are 0, ,1,2,,3….it is obvious that the principal quantum number n cannot have a zero value. The allowed values of n are only positive integer. Thus , we have

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

$$l = 0, 1, 2, 3, \ldots\ldots, (n-1) \qquad \qquad \ldots\ldots\ldots\ldots(34)$$

Expression for the radial function for given values of n and l: The exact form of the function $R_{n,l}(r)$ for the given values of n and l can be determined from Eq. 29 , Eq. 24 and Eq. 25. These equations are

$$R_{n,l} = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} \rho^l\, e^{-\rho/2}\, L_{n+l}^{2l+1} \quad \text{(Eq. 1.7.29)}$$

$$L_{n+l}^{2l+1} = \frac{d^{2l+1}}{d\rho^{2l+1}}\, L_{n+l} \qquad \qquad \text{(Eq. 1.7.24)}$$

and $\quad L_n = e^\rho\, \dfrac{d^n}{d\rho^n}\, (\rho^n\, e^{-\rho})$ $\qquad \qquad$ (Eq. 1.7.25)

where $\quad \rho = \left(\dfrac{2Z}{n\, a_0}\right) r$