4.2 RIGID ROTATOR

Free Axis Rigid Rotator

A rigid rotator is a system of two particles connected by a light rigid rod *i.e.* distance between the particles is always constant. Fig. 4.1 shows the rigid rotator of masses m_1 and m_2 a distance r apart.

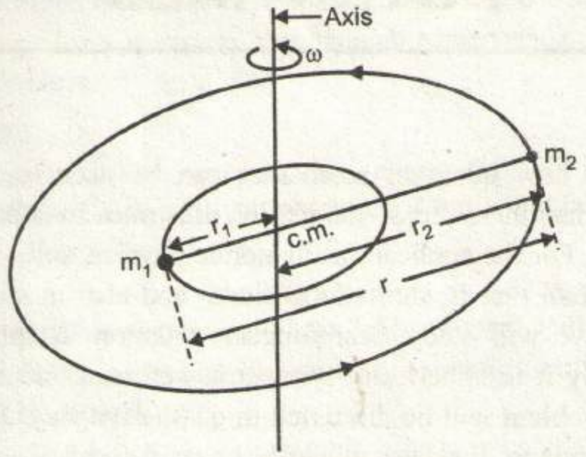


Fig. 4.1 : Rigid rotator

The axis of rotation is passing through the centre of mass of rigid rotator and perpendicular to the length of the rod. The orientation of axis of rotation in space can be along any direction, so this is called free axis rigid rotator. The moment of inertia about an axis passing through centre of mass and perpendicular to the line joining of m_1 and m_2 is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{...(4.2)}$$

where r_1 and r_2 are distances of m_1 and m_2 respectively from centre of mass. Since the mass is equally distributed about centre of mass, we have

$$m_1 r_1 = m_2 r_2$$

and $$r = r_1 + r_2$$

$\therefore$ $$r_1 = \frac{m_2}{m_1} r_2$$

and $$r = \frac{m_2}{m_1} r_2 + r_2 = \frac{m_1 + m_2}{m_1} r_2$$

or $$r_2 = \frac{m_1}{m_1 + m_2} r$$

Similarly $$r_1 = \frac{m_2}{m_1 + m_2} r$$

Using r_1 and r_2 in equation (4.2), we get

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

The reduced mass of the system is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{... (4.3)}$$

and moment of inertia of the system about the free axis is

$$I = \mu r^2 \qquad \dots (4.4)$$

Equation (4.4) states that the rotation of a rigid rotator is equivalent to the rotation of a single particle of mass μ at perpendicular distance r from the axis of rotation.

Classically the kinetic energy of rotation is

$$E = \frac{1}{2} I\omega^2$$

where ω is the angular velocity.

Since angular momentum is $L = I\omega$, we can write

$$E = \frac{L^2}{2I} \qquad \dots (4.5)$$

The rigid rotator can have any value of ω between 0 to ∞. Therefore, energy spectrum is continuous.

Now, we will solve the problem quantum mechanically. Schrödinger's time independent equation in spherical polar co-ordinates is given as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}[E-V]\psi = 0$$

Multiplying throughout by r^2, we get

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2}{\hbar^2}[E-V]\psi = 0$$

Since the rigid rotator is free to rotate in any plane and no force acting on it, its potential energy $V = 0$. Therefore,

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2 E}{\hbar^2}\psi = 0$$

But r = constant, therefore, the first term on right hand side of above equation is $\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = 0$. Hence we get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2 E}{\hbar^2}\psi = 0 \qquad \dots (4.6)$$

Since $I = \mu r^2$, we get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2IE}{\hbar^2}\psi = 0 \qquad \dots (4.7)$$

Equation (4.7) can be solved by separation of variables method. Let us assume

$$\psi(\theta, \phi) = F(\theta)\, G(\phi) = FG \qquad \dots (4.8)$$

Using in equation (4.6), we get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial FG}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 FG}{\partial\phi^2} + \frac{2IE}{\hbar^2}FG = 0$$

Let, $\lambda = \frac{2IE}{\hbar^2}$ ... (4.9)

Therefore,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial FG}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 FG}{\partial\phi^2}+\lambda FG=0$$

$$\frac{G}{\sin\theta}\frac{\partial}{\partial F}\left(\sin\theta\frac{\partial F}{\partial\theta}\right)+\frac{F}{\sin^2\theta}\frac{\partial^2 G}{\partial\phi^2}+\lambda FG=0$$

Multiplying above equation throughout by $\sin^2\theta$ and dividing by FG, we get

$$\frac{\sin\theta}{F}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial F}{\partial\theta}\right)+\frac{1}{G}\frac{\partial^2 G}{\partial\phi^2}+\lambda\sin^2\theta=0$$

or $$\frac{\sin\theta}{F}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial F}{\partial\theta}\right)+\lambda\sin^2\theta=-\frac{1}{G}\frac{\partial^2 G}{\partial\phi^2} \quad \ldots (4.10$$

Left hand side of above equation depends upon θ only and right hand side depends on ϕ only. This is possible only when both sides are equal to some constant say m_l^2. Therefore, we get

$$\frac{\sin\theta}{F}\frac{d}{d\theta}\left(\sin\theta\frac{dF}{d\theta}\right)+\lambda\sin^2\theta=m_l^2 \quad \ldots (4.11$$

and $$-\frac{1}{G}\frac{d^2G}{d\phi^2}=m_l^2 \quad \ldots (4.12$$

Equation (4.12) can be written as

$$\frac{d^2G}{d\phi^2}+m_l^2 G=0 \quad \ldots (4.13$$

The general solution of equation (4.13) can be written as

$$G(\phi)=A\,e^{im_l\phi} \quad \ldots (4.14$$

where m_l can be positive or negative integer. The range of ϕ is from 0 to 2π. The constant A ca be obtained by normalisation condition *i.e.*

$$\int_0^{2\pi} G^*G\,d\phi=1$$

$$\therefore \quad \int_0^{2\pi} A^*e^{-im_l\phi}A\,e^{im_l\phi}d\phi=1$$

$$|A|^2\int_0^{2\pi} d\phi=1$$

or $$|A|^2\,2\pi=1$$

This gives $$|A|=\frac{1}{\sqrt{2\pi}}$$

$$\therefore \quad G(\phi)=\frac{1}{\sqrt{2\pi}}\,e^{im_l\phi} \quad \ldots (4.1$$

s the wave function (4.15) must be acceptable solution (*i.e.* single valued and continuous), e must have $G(\phi) = G(\phi + 2\pi)$. Because rotating ϕ by 2π, we are again at the same point.

$$\frac{1}{\sqrt{2\pi}}\, e^{im_l\phi} = \frac{1}{\sqrt{2\pi}}\, e^{im_l(\phi + 2\pi)}$$

$$e^{i2\pi m_l} = 1$$

$$\cos(2\pi m_l) + i\sin(2\pi m_l) = 1$$

is gives $\qquad \cos(2\pi m_l) = 1 \quad \text{and} \quad \sin(2\pi m_l) = 0$

is is possible only when

$$2\pi m_l = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi \ldots\ldots$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots \qquad \ldots (4.16)$$

uation (4.11) can be written as

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dF}{d\theta}\right) + \left(\lambda - \frac{m_l^2}{\sin^2\theta}\right)F = 0 \qquad \ldots (4.17)$$

is equation can be solved by following substitution.

$$\cos\theta = x, \text{ then } -\sin\theta\, d\theta = dx$$

$$-\frac{d}{dx} = \frac{1}{\sin\theta}\frac{d}{d\theta}$$

$$\sin\theta\frac{dF}{d\theta} = \frac{\sin^2\theta}{\sin\theta}\frac{dF}{d\theta} = -(1 - x^2)\frac{dF}{dx}$$

ing in equation (4.17), we get

$$-\frac{d}{dx}\left(-(1 - x^2)\frac{dF}{dx}\right) + \left[\lambda - \frac{m_l^2}{(1 - x^2)}\right] = 0$$

$$(1 - x^2)\frac{d^2F}{dx^2} - 2x\frac{dF}{dx} + \left[\lambda - \frac{m_l^2}{(1 - x^2)}\right] = 0 \qquad \ldots (4.18)$$

is is associated Legendre's equation. For a given value of m_l, it has acceptable solution hen $\lambda = l(l + 1)$, where l is a positive integer given as

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \ldots\ldots$$

ith equation (4.16), we get

$$l = 0, 1, 2, 3, 4, \ldots\ldots \qquad \ldots (4.19)$$

erefore, we can write equation (4.18) as

$$(1 - x^2)\frac{d^2F}{dx^2} - 2x\frac{dF}{dx} + \left[l(l+1) - \frac{m_l^2}{(1 - x^2)}\right] = 0$$

e general solution of above equation is associated Legendre polynomials $P_l^{m_l}(x)$ given as

$$P_l^{m_l}(x) = (1 - x^2)^{|m_l|/2}\frac{d^{|m_l|}}{dx^{|m_l|}}P_l(x)$$

$P_l(x)$ are Legendre polynomials.

Hence general solution of equation (4.17) is

$$F_l^{m_l}(\theta) = B\, P_l^{m_l}(\cos\theta) \qquad \text{... (4.18)}$$

where B is normalization constant and is given by

$$B = \sqrt{\frac{(2l+1)}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}}$$

Thus, the total wave function is

$$\psi(\theta, \phi) = F_l^{m_l}(\theta)\, G m_l(\phi)$$

or

$$\psi(\theta, \phi) = \frac{1}{\sqrt{2\pi}}\sqrt{\frac{(2l+1)}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}}\; P_l^{m_l}(\cos\theta)\; e^{im_l\phi} \qquad \text{...(4.19)}$$

From equation (4.9), we have

$$\lambda = \frac{2IE}{\hbar^2}$$

$$\therefore \qquad \frac{2IE}{\hbar^2} = l(l+1)$$

Thus the corresponding eigen value is

$$E_l = \frac{l(l+1)\hbar^2}{2I} \qquad \text{... (4.20)}$$

When

$l = 0, \quad E_0 = 0$

$l = 1, \quad E_1 = 2\frac{\hbar^2}{2I} = 2B$

$l = 2, \quad E_1 = 6\frac{\hbar^2}{2I} = 6B$

$l = 3, \quad E_1 = 12\frac{\hbar^2}{2I} = 12B$

and so on…

where $B = \frac{\hbar^2}{2I}$.

The energy level E_0 is called the ground state energy of rigid rotator. The subsequent levels E_1, E_2, E_3 etc. are called first, second, third etc. energy levels.

The energy level diagram is shown in Fig. 4.2.

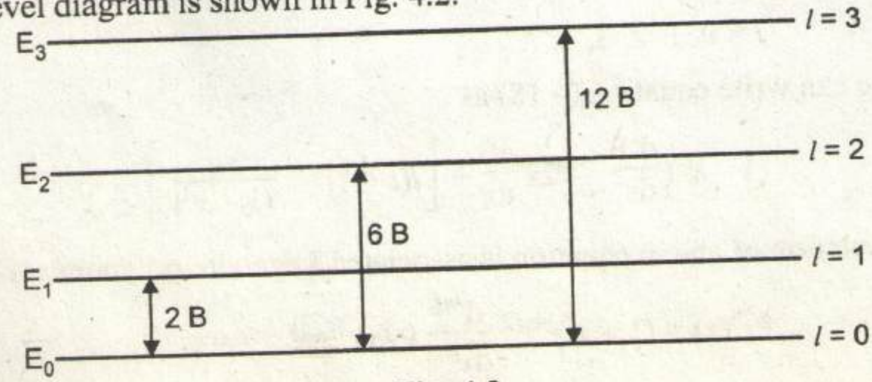
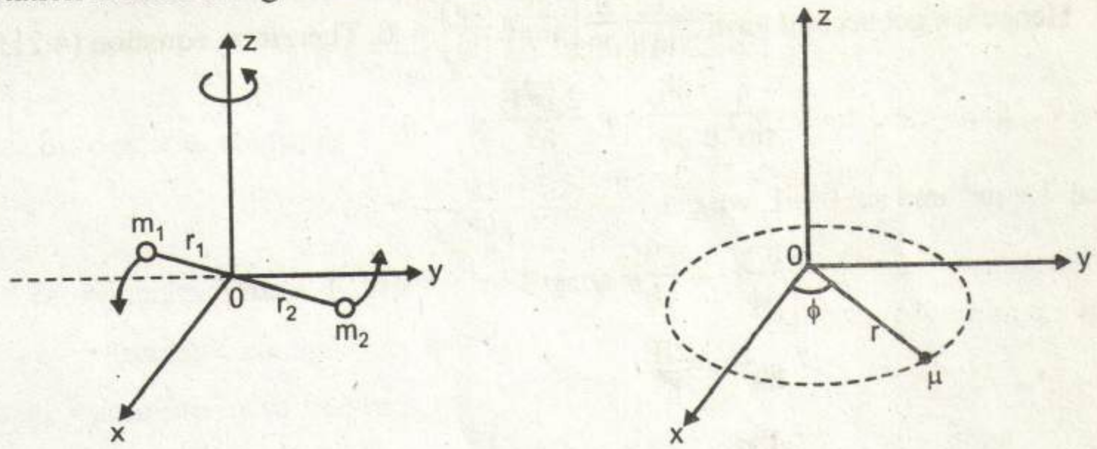


Fig. 4.2

It is seen that the difference between successive energy levels increases with increase in l. Also the spectrum is discrete one. The discrete nature energy levels is confirmed experimentally.

Fixed Axis Rigid Rotator

Suppose that a rigid rotator with its centre of mass at the origin rotate in the XY plane and axis of rotation is fixed along Z-axis as shown in Fig. 4.3.



(a) Fixed axis rotator **(b) Equivalent system**

Fig. 4.3

The reduced mass of the system is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{... (4.3)}$$

and moment of inertia of the system about the axis of rotation is

$$I = \mu r^2 \quad \text{... (4.4)}$$

To obtain eigen functions and eigen values, we will apply Schrödinger's time independent equation in spherical polar co-ordinates. It is given by

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}[E - V]\,\psi = 0$$

Multiplying throughout by r^2, we get

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2}{\hbar^2}[E - V]\,\psi = 0$$

Since the rigid rotator is free to rotate in any plane and no force acting on it, its potential energy V = 0. Therefore,

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2 E}{\hbar^2}\,\psi = 0 \quad \text{... (4.21)}$$

But r = constant, therefore, the first term on right hand side of above equation i
$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = 0$. Also the rotator is rotating in fixed XY plane *i.e.* angle made by r with the Z-axi

$\theta = 90°$. Hence we get second term $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) = 0$. Therefore, equation (4.21) becomes

$$\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2 E}{\hbar^2}\psi = 0 \qquad \text{... (4.22}$$

Since $I = \mu r^2$ and $\sin\theta = 1$, we get

$$\frac{d^2\psi}{d\phi^2} + \frac{2IE}{\hbar^2}\psi = 0 \qquad \text{... (4.23}$$

Let $$m_l^2 = \frac{2IE}{\hbar^2} \qquad \text{... (4.24}$$

$$\therefore \quad \frac{d^2\psi}{d\phi^2} + m_l^2\psi = 0 \qquad \text{... (4.25}$$

The general solution of equation (4.25) is given by

$$\psi(\phi) = A\,e^{im_l\phi} \qquad \text{... (4.25}$$

where m_l can be positive or negative integer. The range of ϕ is from 0 to 2π. The constant A ca be obtained by normalisation condition and it is given by

$$|A| = \frac{1}{\sqrt{2\pi}}$$

$$\therefore \quad \psi(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{im_l\phi} \qquad \text{... (4.26}$$

As the wave function (4.26) must be acceptable solution (*i.e.* single valued and continuous then we must have $G(\phi) = G(\phi + 2\pi)$. Because rotating ϕ by 2π, we are again at the same point.

$$\therefore \quad e^{im_l\phi} = e^{im_l(\phi+2\pi)}$$

or $$e^{i2\pi m_l} = 1$$

$$\therefore \quad \cos(2\pi m_l) + i\sin(2\pi m_l) = 1$$

This gives $\cos(2\pi m_l) = 1$ and $\sin(2\pi m_l) = 0$

This is possible only when

$$2\pi m_l = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi \ldots\ldots$$

$$\therefore \quad m_l = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots \qquad \text{... (4.27}$$

From equation (4.24), we get

$$E = \frac{m_l^2\hbar^2}{2I} \qquad \text{... (4.2}$$

Equation (4.28) gives the energy eigen value for the fixed axis rigid rotator.

(2) θ-part equation :

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dF}{d\theta}\right)+\left(l(l+1)-\frac{m_l^2}{\sin^2\theta}\right)F = 0 \qquad \ldots (4.33)$$

(3) ϕ-part equation :

$$\frac{d^2G}{d\phi^2}+m_l^2\,G=0 \qquad \ldots (4.34)$$

Solution of ϕ-part equation is given as

$$G(\phi)=\frac{1}{\sqrt{2\pi}}\,e^{im_l\phi} \qquad \ldots (4.35)$$

The constant m_l must be positive or negative integer. This is because G and its derivative must be continuous and single valued in the domain $0 \le \phi \le 2\pi$.

We have

$$m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \ldots\ldots. \qquad \ldots (4.36)$$

m_l is known as *magnetic quantum number*.

As we know that equation (4.33) is associated Legendre equation, its solution is

$$F_l^{m_l}(\theta) = B\,P_l^{m_l}(\cos\theta) \qquad \ldots (4.37)$$

where $P_l^{m_l}(\cos\theta)$ is associated Legendre polynomials and B is normalization constant. B can be obtained by condition of normalization of equation (4.37) in the range $0 \le \theta < \le \pi$. It is given by

$$B=\sqrt{\frac{(2l+1)}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}} \qquad \ldots (4.38)$$

and l is positive integer given as

$$l = |m_l|, |m_l|+1, |m_l|+2, |m_l|+3, \ldots\ldots\ldots \qquad \ldots (4.39)$$

Substituting equation (4.30) in equation (4.32), we get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_o r}-\frac{l(l+1)}{r^2}\right]R = 0 \qquad \ldots (4.40)$$

The effective potential is

$$V_{eff} = -\frac{e^2}{4\pi\varepsilon_o r}+\frac{l(l+1)}{r^2}$$

With the given value of l, it is found that there are bound state solutions for equation (4.40) which are acceptable (*i.e.* single valued, continuous and finite) solutions only if the total energy E has one of the values E_n, where

$$E_n = -\frac{\mu e^4}{(4\pi\varepsilon_o)^2\, 2\hbar^2 n^2} \qquad \ldots (4.41)$$

where n is the integer and can have values

$$n = l+1, l+2, l+3, \ldots\ldots\ldots \qquad \ldots (4.42)$$

With l from equation (4.39) and m_l from equation (4.36), we get

$$n = 1, 2, 3, 4, 5, \ldots\ldots\ldots\ldots \qquad \ldots(4.43)$$

The acceptable solution of radial part equation (4.40) is more conveniently be written as

$$R_{nl}(r) = C\, e^{-\alpha r}(\alpha r)^l\, L(\alpha r) \qquad \ldots(4.44)$$

where

$L(\alpha r)$ is polynomial in (αr)

$\alpha = \frac{1}{na_0}$ where a_0 is Bohr's radius given by $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$

and C is normalization constant.

Therefore the general eigen function of the hydrogen atom is

$$\psi(r, \theta, \phi) = N\, e^{-\alpha r}(\alpha r)^l\, L(\alpha r)\, P_l^{m_l}(\cos\theta)\, e^{im_l\phi} \qquad \ldots(4.45)$$

where N is normalization constant and is given by

$$N = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}} \cdot \sqrt{\frac{(2l+1)}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}} \cdot \frac{1}{\sqrt{2\pi}}$$

Some of the eigen functions are listed in Table 4.2.

Table 5.2

n	l	m_l	$\psi_{nlm_l}(r, \theta, \phi)$	
1	0	0	$\Psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$	Ground state
2	0	0	$\Psi_{200} = \frac{1}{4\sqrt{2\pi a_0^3}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	
2	1	0	$\Psi_{210} = \frac{1}{4\sqrt{2\pi a_0^3}}\left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos\theta$	First excited state
2	1	±1	$\Psi_{21\pm1} = \frac{1}{8\sqrt{\pi a_0^3}}\left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$	
3	0	0	$\Psi_{300} = \frac{1}{81\sqrt{3\pi a_0^3}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/2a_0}$	
3	1	0	$\Psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi a_0^3}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/2a_0} \cos\theta$	Second excited state
3	1	±1	$\Psi_{31\pm1} = \frac{1}{81\sqrt{\pi a_0^3}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$	

Eigen values :

The solution of radial part of the hydrogen atom shows that the allowed values of total energy of bound state is

$$E_n = -\frac{\mu e^4}{(4\pi\varepsilon_o)^2\, 2\hbar^2 n^2} = -\frac{13.6}{n^2}\ \text{eV}$$

which is same as predicted by Bohr's theory. Both quantum mechanical predictions and Bohr's predictions are in exact agreement with the experimental results.

Quantum numbers :

The energy eigen values depend on the quantum number 'n' only. But the eigen functions depend on three quantum numbers n, l, m_l since they are products of three functions $R_{nl}(r)$, $F_l^{m_l}(\theta)$ and $G_{m_l}(\phi)$. These three quantum numbers arise because Schrödinger's time independent equation contains three variables r, θ and ϕ, one for each space co-ordinate.

From equations (4.36), (4.39) and (4.42), the conditions for three quantum numbers

$$m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \ldots\ldots$$

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \ldots\ldots$$

and $$n = l + 1, l + 2, l + 3, \ldots\ldots$$

These conditions more conveniently can be written as

$$n = 0, 1, 2, 3, 4, \ldots\ldots$$

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

and $$m_l = -l, -l+1, -l+2, \ldots\ldots -1, 0, +1, \ldots\ldots l+1, l.$$

The role of 'n' is in specifying the energy eigen value E_n as given by equation (4.41), it is sometimes called *principal quantum number*. As the orbital angular momentum number depends on quantum number l, it is also called *orbital quantum number*. If an atom is placed in an external magnetic field, its energy depends on m_l. Consequently m_l is also called *magnetic quantum number*.

Thus, for a given n, l takes values as 0, 1, 2, ……(n – 1) and for a given l, m_l takes values as $-l, -l+1, -l+2, \ldots\ldots -1, 0, +1, \ldots\ldots l+1, l$.

Another quantum number is spin quantum number. It has two possible values of orientation $m_s = \pm\frac{1}{2}$.

Degeneracy :

For a given value of principal quantum number n, the energy of the atomic level is fixed as predicted by the Bohr's theory. But for a given value of n there are generally several different values of l and for each l there are different values of m_l. As the eigen functions depend on n, l and m_l, we have a number of possible eigen functions corresponding to a given energy eigen value E_n. Behaviour of the atom is described by the eigen functions. So the atom has different states having completely different states for given n with the same energy eigen values. This is referred as *degeneracy* of the level, and the eigen functions corresponding to the same energy are called *degenerate*.

As m_l takes values $-l, -l+1, -l+2, \ldots\ldots -1, 0, +1, \ldots\ldots l+1, l$ that is $(2l + 1)$ values. Each l takes values as 0, 1, 2, …. (n – 1). Therefore, for each n the number of independent eigen functions will be

$$\sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = n^2$$

Thus for each n there are n^2 corresponding degenerate eigen functions.