DEGENERACY AND NONDEGENERACY:

(i) Degeneracy: *It is seen from equation (3) and equation (4), for several combination of quantum numbers we have same energy eigen value but different eigen functions. Such states and energy levels are called* ***Degenerate State.***

The three combination of quantum numbers (112), (121) and (211), which gives same eigen value but different eigen functions are called **3 fold degenerate state.**

> **Note:** If we have 6 combinations to give the same energy level and 6 eigen functions, it is called 6 fold-degenerate state.

(ii) Non-Degeneracy: *For various combinations of quantum number if we have same energy eigen value and same (one) eigen function then such states and energy levels are called* ***Non-Degenerate State.***

There is another basic type of motion that is of great interest in atomic and molecular problems; it is the rotational motion. It crops up whenever we have to deal with motion of a particle under the influence of a central field of force, for example, the motion of an electron around the nucleus of an atom.

For a single particle executing such a motion, the Schrodinger equation can be solved exactly. We shall consider in this chapter first the rotational motion of a particle in a plane (particle in a ring) and then in three dimensions (particle on a sphere); we shall use these results for the case of a rotating diatomic molecule.

6.1 PARTICLE IN A RING

6.1.1 The Schrodinger Equation and the Wave Functions

Consider a particle of mass m rotating in a circle of radius r in the xy plane. If the potential energy (V) of the particle is zero (*i.e.*, it is unacted upon by any external force), the Hamiltonian in the simplest form can be written as,

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \quad ...(6.1)$$

Since the motion is circular, it will be more convenient to express $\hat{H}$ in polar coordinates (r, φ). The cartesian coordinates x and y are related to polar coordinates r and φ as,

$$x = r\cos\varphi, \; y = r\sin\varphi \quad ...(6.2)$$

where φ is the angular variable which varies from 0 to 2π and the radius, r, is constant. Hence, Equation (6.1) in polar coordinates becomes,

$$\hat{H} = -\frac{h^2}{8\pi^2 mr^2}\left(\frac{\partial^2}{\partial \varphi^2}\right) = -\frac{h^2}{8\pi^2 I}\left(\frac{\partial^2}{\partial \varphi^2}\right) \text{ (See Appendix 1)} \quad ...(6.3)$$

where $I = mr^2$ is the moment of inertia. The eigenfunction $F(\varphi)$, or simply F, will be a function of φ only; so the Schrodinger equation is given by,

$$-\frac{h^2}{8\pi^2 I}\cdot\frac{d^2 F}{d\varphi^2} = EF \quad ...(6.4)$$

or

$$\frac{d^2 F}{d\varphi^2} + M^2 F = 0 \quad ...(6.5)$$

where

$$M^2 = \frac{8\pi^2 IE}{h^2} \quad ...(6.6)$$

The Equation (6.5) is quite familiar (cf. particle in a one-dimensional box). Its solutions (the wave functions) are:

$$\left.\begin{array}{l} F = N \sin M\varphi \\ F' = N' \cos M\varphi \end{array}\right] \quad \text{...(6.7)}$$

as the real set, and $$F'' = A \exp(\pm iM\varphi) \quad \text{...(6.8)}$$

as the imaginary set. The trigonometric forms (6.7) are also called "circular harmonics".

Equations (6.7) and (6.8) are equivalent in view of the theorem,

$$\exp(\pm iM\varphi) = \cos M\varphi \pm i \sin M\varphi \quad \text{...(6.9)}$$

The functions (6.7) and (6.8) are finite and continuous for all values of φ and M. They are single-valued too, since the angles φ and $\varphi + 2\pi$ represent the same point, and the property of single-valuedness demands that,

$$F(\varphi) = F(\varphi + 2\pi)$$

Using the real set Equation (6.7), we get

$$\sin M\varphi = \sin M(\varphi + 2\pi)$$

or

$$\cos M\varphi = \cos M(\varphi + 2\pi)$$

This is possible only if $M = 0, \pm 1, \pm 2, \ldots$ [put, for example, $M = +1$; then $\sin M\varphi = \sin \varphi$; and $\sin M(\varphi + 2\pi) = \sin \varphi$. Similarly,

$$A \exp(iM\varphi) = A \exp(iM(\varphi + 2\pi)) = A \exp(iM\varphi) \cdot \exp(i\, 2\pi M)$$

$$\exp(i\, 2\pi M) = 1, \text{ or } \cos 2\pi M + i \sin 2\pi M = 1 \text{ only if } M = 0, \pm 1, \pm 2$$

As regards boundary conditions, there is no barrier to the particle's motion as long as it is on the ring, and so there is no condition for the wave function to vanish at any point. (For $M = 0$, $N \sin M\varphi = 0$ but $N' \cos M\varphi = N'$).

[*Exercise:* Show that $F = N \sin \phi/2$ is not acceptable even though

$$\sin \phi/2 = \sin 1/2 (\phi + 2\pi)$$

Let $$F = \sin \phi/2 \text{ and } F' = \sin \frac{1}{2}(\phi + 2\pi) \text{ then } \frac{dF}{d\varphi} = \frac{1}{2}\cos \phi/2, \text{ and}$$

$$\frac{dF'}{d\varphi} = \frac{1}{2}\cos(\varphi/2 + \pi)$$

$$= \frac{1}{2}\left(\cos\frac{\varphi}{2}\cos\pi - \sin\frac{\varphi}{2}\sin\pi\right) = -\frac{1}{2}\cos\frac{\varphi}{2}$$

Since $\frac{dF}{d\varphi} \neq \frac{dF'}{d\varphi}$, there is discontinuity].

6.1.1.1 Normalisation and Orthogonality

The normalisation factor N can be determined as follows:

$$\int_0^{2\pi} (N \sin M\varphi)^2\, d\varphi = 1$$

or $$N^2 \int_0^{2\pi} \sin^2 M\varphi \, d\varphi = N^2 \int_0^{2\pi} \left(\frac{1 - \cos 2M\varphi}{2} \right) d\varphi = 1$$

or $$N^2 \cdot \pi = 1 \text{ or } N = 1/\sqrt{\pi}$$

Similarly, $$N' = 1/\sqrt{\pi}$$

The normalised real set of wave functions are

$$F = \frac{1}{\sqrt{\pi}} \sin M\varphi \text{ and } F = \frac{1}{\sqrt{\pi}} \cdot \cos M\varphi \quad ...(6.10)$$

For $$M = 0, \; F' = \frac{1}{\sqrt{\pi}} \quad ...(6.11)$$

For the imaginary set,

$$\int_0^{2\pi} A^* \exp \mp (iM\varphi), \; A \exp (\pm \, iM\varphi) \cdot d\varphi = 1$$

or $$\int_0^{2\pi} |A|^2 \, d\varphi = 1 \text{ or } |A|^2 \cdot 2\pi = 1 \text{ or } |A| = \frac{1}{\sqrt{2\pi}}$$

Hence $$F'' = \frac{1}{\sqrt{2\pi}} \exp \; (\pm \, iM\varphi) \quad ...(6.12)$$

For $$M = 0, \; F'' = \frac{1}{\sqrt{2\pi}} \quad ...(6.13)$$

It is not difficult to show that the functions (6.10) and (6.12), for example, are orthogonal sets as, for example,

$$\frac{1}{\pi} \int_0^{2\pi} \sin \varphi \cdot \cos \varphi \, d\varphi = 0$$ (see the table of integrals)

[*Exercise:* Show that $\frac{1}{\sqrt{2\pi}} \exp (iM\varphi)$ and $\frac{1}{\sqrt{2\pi}} \exp (-\, iM\varphi)$ are orthogonal.

$$\int_0^{2\pi} (e^{iM\varphi})^* \cdot e^{-iM\varphi} \cdot d\varphi = \int_0^{2\pi} e^{-\, iM\varphi} \cdot e^{-\, iM\varphi} \cdot d\varphi$$

$$= \left[\frac{e^{-\, 2iM\varphi}}{-\, 2iM} \right]_0^{2\pi} = 0 \;]$$

It is seen that except for $M = 0$ the functions (6.10) and (6.12) constitute doubly degenerate real and imaginary sets of wave functions respectively. The degeneracy is inherent in any system that involves rotational motion.

6.1.1.1 Quantisation of Energy

The expression (6.6) can be rearranged to give the expression for energy as,

$$E = \frac{M^2 h^2}{8\pi^2 I} \qquad ...(6.14)$$

Thus, the energy is quantised in units of $h^2/8\pi^2 I$, the parameter M being the "rotational quantum number".

For $M = 0$, $E = 0$, *i.e.*, the rotating particle does not have zero point energy.

6.2 PARTICLE ON A SPHERE

The Spherical Angular Coordinates

The position of a particle on the surface of a sphere of radius r is more conveniently determined in terms of two angular variables (coordinates)—φ, called the azimuthal angle, and θ, called the zenith angle. The angle φ is the angle measured in the xy plane between the x axis and the projection of the line r joining the particle (P) with the centre of the sphere (Figure 6.1); it varies from 0 to 2π. The angle θ is the angle between the line r and the z axis; it varies from 0 to π.

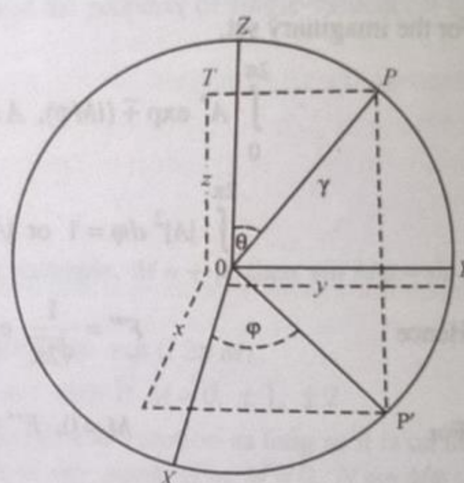

Figure 6.1 : The angular coordinates θ and φ

6.2.1.1 The Schrodinger Equation

Since the particle rotates in three dimensions the Hamiltonian in cartesian coordinates, if potential energy V is zero, is

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{h^2}{8\pi^2 m}\nabla^2 \qquad ...(6.15)$$

where x, y and z are the coordinates of the particle at any point. However, with the present form of the Hamiltonian, the Schrodinger equation cannot be solved by the method of separation of variables as the variables x, y and z do not vary independently of each other here. The equation can be solved by transforming Equation (6.15) into one involving θ and φ by making use of the relation between cartesian (x, y, z) and angular (θ, φ) variables given below.

$$x = r\sin\theta\cos\varphi,\ y = r\sin\theta\sin\varphi,\ z = r\cos\theta \qquad ...(6.16)$$

The transformation, then, is a straightforward application of the theory of partial derivatives but is lengthy. We give only the final expression here. (For complete derivation see Appendix 1).

$$\nabla^2 = \frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right) \qquad ...(6.17)$$

Since r is constant, $\frac{\partial}{\partial r} = \frac{\partial^2}{\partial r^2} = 0$.

$$\therefore \quad \hat{H} = -\frac{h^2}{8\pi^2 m}\left[\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \quad ...(6.18)$$

The Schrodinger equation, $\hat{H}\psi = E\psi$ becomes

$$-\frac{h^2}{8\pi^2 mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]=E\psi \quad ...(6.19)$$

or, on simplification,

$$\frac{\partial^2\psi}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\cdot\frac{\partial\psi}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{8\pi^2 mr^2}{h^2}E\psi=0 \quad ...(6.20)$$

where the wave function ψ is $\psi(\theta, \varphi)$.

6.2.1.2 Separation of Variables

The partial differential Schrodinger Equation (6.20) can be solved by separating the variables. For this, suppose that the function $\psi(\theta, \varphi)$ is a product of two functions $P(\theta)$ and $F(\varphi)$, each being a function of a single variable only, *i.e.*,

$$\psi(\theta, \varphi) = P(\theta)\,F(\varphi) \quad ...(6.21)$$

Differentiating partially with respect to θ, we get

$$\frac{\partial\psi}{\partial\theta}=F(\varphi)\frac{dP}{d\theta},\quad \frac{\partial^2\psi}{\partial\theta^2}=F(\varphi)\frac{d^2P}{d\theta^2}$$

and with respect to φ, we get

$$\frac{\partial\psi}{\partial\varphi}=P(\theta)\frac{dF}{d\varphi},\quad \frac{\partial^2\psi}{\partial\varphi^2}=P(\theta)\frac{\partial^2F}{\partial\varphi^2}$$

Substituting these relations into Equation (6.20)

$$F\cdot\frac{d^2P}{d\theta^2}+\frac{\cos\theta}{\sin\theta}\cdot F\cdot\frac{dP}{d\theta}+\frac{1}{\sin^2\theta}P\frac{d^2F}{d\varphi^2}+\frac{8\pi^2 mr^2}{h^2}EPF=0$$

Multiplying through by $\frac{\sin^2\theta}{PF}$,

$$\frac{\sin^2\theta}{P}\cdot\frac{d^2P}{d\theta^2}+\cos\theta\cdot\sin\theta\cdot\frac{1}{P}\cdot\frac{dP}{d\theta}+\frac{1}{F}\cdot\frac{d^2F}{d\varphi^2}+\frac{8\pi^2 mr^2}{h^2}\sin^2\theta\, E=0$$

where P and F stand for $P(\theta)$ and $F(\varphi)$ respectively.

or

$$\frac{\sin^2\theta}{P}\cdot\frac{d^2P}{d\theta^2}+\cos\theta\,.\,\sin\theta\cdot\frac{1}{P}\cdot\frac{dP}{d\theta}+\frac{8\pi^2 mr^2}{h^2}\sin^2\theta\, E=-\frac{1}{F}\cdot\frac{d^2F}{d\varphi^2} \quad ...(6.22)$$

Now the left hand side (l.h.s.) of Equation (6.22) depends on θ only while the right hand side (r.h.s.) depends on φ only. If φ is maintained constant while θ varies, the r.h.s. will remain constant. Since l.h.s. = r.h.s., the l.h.s. will also remain equal to the same constant even though θ varies. The same argument applies to the situation when θ is kept constant and φ varies. Both sides of Equation (6.22) are, therefore, equal to the same constant. Let the constant be denoted by M^2 for convenience. Thus, Equation (6.22) splits into the following two ordinary differential equations:

$$-\frac{1}{F}\cdot\frac{d^2 F}{d\varphi^2} = M^2 \quad \text{...(6.23)}$$

and, after multiplying Equation (6.22) by $P/\sin^2\theta$,

$$\frac{d^2 P}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\cdot\frac{dP}{d\theta} + \beta\cdot P = \frac{M^2 P}{\sin^2\theta} \quad \text{...(6.24)}$$

where

$$\beta = \frac{8\pi^2 mr^2}{h^2} E \quad \text{...(6.25)}$$

References:

1. Quantum Chemistry by R.K.Prasad, 3rd Edition, New Age International Publishers.
2. Engineering Physics by Senthil Kumar.