The Schrödinger equation $\hat{H}\psi = \hat{E}\psi$ may thus be written as

$$\frac{1}{2I}\left[-\hbar^2\left\{\frac{1}{\sin\theta}\frac{1}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}\right]=E\psi \quad ...(4)$$

The above equation may be written as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2 I}{h^2}E\psi=0 \quad ...(5)$$

Equation (5) contains two angular variables θ and ϕ. It can be solved by the method of separation of variable, i.e., we look for a solution of the form

$$\psi(\theta,\phi)=\Theta(\theta)\Phi(\phi) \quad ...(6)$$

Substituting Equation (6) into equation (5) we obtain

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 IE}{h^2}\sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \quad ...(7)$$

We can set both sides of equation equal to a constant, say m^2, thereby obtaining two differential equations each in one variable. These equations are :

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi=0 \ \ and \quad ...(8)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0; \quad ...(9)$$

where $\beta=8\pi^2\frac{IE}{h^2}$

Equation (8) has the solution

$$\Phi(\phi)=N\exp(\pm im\phi) \qquad \left[where, i=\sqrt{-1}\right] \quad ...(10)$$

where N is the normalization constant.

This wave function is acceptable provided m is an integer. This condition arises because Φ must be single valued. Thus,

$$\Phi(\phi)=\Phi(\phi+2\pi) \quad ...(11)$$

If follows, therefore, that exp $(2\pi mi)=1$ ...(12)

Since $e^{ix}=\cos x+i\sin x \quad (Euler's\ relation)$ ...(13)

$$\therefore \cos 2\pi m+i\sin 2\pi m=1 \quad ...(14)$$

This can be true only if m= 0, $\pm$ 1, $\pm$ 2, $\pm$ 3,...........etc. Let us now normalize the wavefunction $\Phi(\phi)$ to determine the normalization constant N.

$$\int_0^{2\pi}\Phi^*\Phi\, d\phi=1 \ (0\le\phi\le 2\pi) \quad ...(15)$$

$$or \quad N^2\int_0^{2\pi}e^{im\phi}\, e^{-im\phi}d\phi=1 \quad ...(16)$$

$$or \quad N^2\int_0^{2\pi}d\phi=1 \Rightarrow N^2(2\pi)=1$$

So that $N = (2\pi)^{-1/2}$ ...(17)

Hence, the normalized wave function become

$$\Phi_{\pm m}(\phi) = (2\pi)^{-1/2} \exp(\pm im\phi); \; m = 0, 1, 2, 3, ... \quad ...(18)$$

We shall not attempt to give a complete solution of equation (9) but will merely state that if $\beta = \ell(\ell+1)$ where ℓ is the rotational quantum number, then this equation becomes a standard mathematical equation whose solutions are known to be associated legendre polynomials $P_\ell^{|m|}(\cos\theta)$ where, ℓ is either zero or a positive integer and $\ell \geq |m|$.

The normalized solutions are given by :

$$\Theta(\theta) = \Theta_{\ell,\pm m}(\theta) = \left[\frac{2\ell+1}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}\cos\theta \quad ...(19)$$

The energy eigenvalues of the rigid rotor are obtained as follows :

$$\beta = 8\pi^2 IE/h^2 = \ell(\ell+1) \quad ...(20)$$

Thus, $$E = \frac{\ell(\ell+1)h^2}{8\pi^2 I}; \; \ell = 0, 1, 2, 3 \quad ...(21)$$

In spectroscopy it is customary to use the symbol J rather than *l* for the rotational quantum number so that the rotational energy levels are given by the expression.

$$E_J = \frac{J(J+1)}{8\pi^2 I}; \; J = 0, 1, 2, 3.... \quad ...(22)$$

SOLVED PROBLEMS

1. The wave function (ψ) for hydrogen atom in terms of polar coordinates, is given by $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\theta)$. Which of the functions determines the shape of atomic orbitals ?

(a) R(r) (b) $\Theta(\theta)$ (c) $\Phi(\theta)$ (d) Both (b) & (c)

Soln. $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

$R(r) \rightarrow$ Radial dependence of wavefunction (size of atomic orbital determined by radial part of wave function). $\Theta(\theta)\Phi(\phi) \rightarrow$ Angular dependence of wavefunction (shape of atomic orbital determined by angular part of wave function)

Correct option is (d)

2. Which of the following sets of quantum numbers is correct for an electron of $4f$ orbital ?

(a) n = 4, *l* = 3, m = +4, s = $+\frac{1}{2}$ (b) n = 4, *l* = 4, m = -4, s = $-\frac{1}{2}$

(c) n = 4, *l* = 3, m = +1, s = $+\frac{1}{2}$ (d) n = 3, *l* = 2, m = -2, s = $+\frac{1}{2}$

Soln. For $4f$-orbital $n = 4$, $l = 3$

For $n = 4$, possible l-values are $l = 0, 1, ... (n-1) = 0, 1, 2, 3$

For $l = 3$, possible m_l values are $m_l = -3, -2, -1, 0, 1, 2, 3$

Correct option is (c)