①

- $J^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$

  $J_z |jm\rangle = m\hbar |jm\rangle \qquad m = -j, -j+1, \ldots 0, \ldots j-1, j$

- We want to solve $\boxed{-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi}$

  $V(r,\theta,\varphi) = V(r) \Rightarrow$ rotationally invariant problem

- Due to rotational invariance, do the problem in (r,θ,φ) coordinates.

  We need ∇^2 in (r,θ,φ) coordinates

- $$\nabla^2 \to \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Hence, Schrodinger eqn becomes

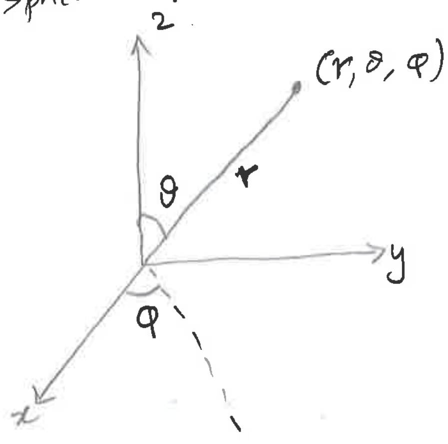
$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi)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

- Let $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

- Substitute this into Schrodinger Eqn

$$-\frac{\hbar^2}{2\mu}\left[Y(\theta,\varphi)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) + \frac{R(r)}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\varphi) + \frac{R(r)}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}Y(\theta,\varphi)\right] + V\cdot R(r)\,Y(\theta,\varphi)$$
$$= E\,R(r)\,Y(\theta,\varphi)$$

- Spherical-polar coordinates



$r \geq 0$

$0 \leq \theta \leq \pi$ — polar angle

$0 \leq \varphi \leq 2\pi$ — azimuth angle

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

- multiply by $-\frac{2\mu r^2}{\hbar^2}$ and divide throughout by $R(r)\,Y(\theta,\varphi)$

We get

$$\frac{1}{R(r)} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) R(r) + \frac{1}{Y(\theta,\varphi)\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) Y(\theta,\varphi)$$

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

- Rewrite it as :

$$\left\{ \frac{1}{R(r)} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) R(r) - \frac{2\mu r^2}{\hbar^2}\left[V(r) - E\right]\right\} +$$

$$\left\{ \frac{1}{Y(\theta,\varphi)} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) Y(\theta,\varphi) + \frac{1}{Y(\theta,\varphi)} \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} Y(\theta,\varphi)\right\} = 0$$

- There are two terms in this eqn. First one depends only on r, second term depends only on (θ,φ). Let each term be equal to same constant but opposite sign :

$$\{c\} - \{c\} = 0$$

- $\therefore$ We have two equations:

$$\frac{1}{R(r)} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) R(r) - \frac{2\mu r^2}{\hbar^2}\left[V(r) - E\right] = c$$

AND $$\frac{1}{Y(\theta,\varphi)} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) Y(\theta,\varphi) + \frac{1}{Y(\theta,\varphi)} \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} Y(\theta,\varphi) = -c$$

- $$\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) R(r) - \frac{2\mu r^2}{\hbar^2}\left[V(r) - E\right] R(r) = c\, R(r) \quad ---- (1)$$

- $$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) Y(\theta,\varphi) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} Y(\theta,\varphi) = -c\, Y(\theta,\varphi) \quad ---- (2)$$

- Now, let's examine L_x, L_y, L_z and L^2 in (r,θ,φ) representation

$$L_x = i\hbar\left(\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \cos\varphi \frac{\partial}{\partial\varphi}\right)$$

$$L_y = i\hbar\left(-\cos\varphi \frac{\partial}{\partial\theta} + \cot\theta \sin\varphi \frac{\partial}{\partial\varphi}\right)$$

$$L_z = -i\hbar \frac{\partial}{\partial\varphi}$$

$L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$.

- $$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

- Now, rewrite Eq (2) as:

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) = -c\, Y(\theta,\varphi)$$

- $$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) = c\hbar^2\, Y(\theta,\varphi)$$

  - $L^2\, Y(\theta,\varphi) = c\hbar^2\, Y(\theta,\varphi)$ $\Rightarrow$ $c = \ell(\ell+1)$

- Now, put $Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$

$$-\frac{\hbar^2\,\Phi(\varphi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) - \frac{\hbar^2\,\Theta(\theta)}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = c\hbar^2\,\Theta(\theta)\,\Phi(\varphi)$$

Divide by $\Theta(\theta)\,\Phi(\varphi)$

$$\frac{-\hbar^2}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) - \frac{\hbar^2}{\sin^2\theta\,\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = c\hbar^2$$

multiply by $-\sin^2\theta$

$$\frac{\cancel{\hbar^2}\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) + \sin^2\theta\, c\cancel{\hbar^2} = \underbrace{-\cancel{\hbar^2}\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi)}_{\text{we know this result}} = m^2$$

- $$\frac{\partial^2}{\partial \varphi^2} \Phi(\varphi) = -m^2 \Phi(\varphi)$$

- $$\Phi(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}}$$

- Assemble LHS of this eqn:

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right)\Theta(\theta) + \ell(\ell+1)\sin^2\theta + m^2 = 0$$

$$\left\{ \sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \left[\ell(\ell+1)\sin^2\theta - m^2\right] \right\} \Theta(\theta) = 0$$

- Divide throughout by $\sin^2\theta$

$$\left(\frac{1}{\sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right) + \left[\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right] \right) \Theta(\theta) = 0$$

- This equation is not easy to solve.

~~to~~ get put $\mu = \cos\theta$

- $$\frac{d}{d\mu}\left[(1-\mu^2)\frac{d\Theta}{d\mu}\right] + \left[\ell(\ell+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0$$

$$-1 \le \mu \le 1$$

- Solution is $\Theta(\theta) = A\, P_\ell^m(\cos\theta)$

associated Legendre function

where $$P_\ell^m(\cos\theta) = \frac{(-1)^\ell}{2^\ell\, \ell!} \sin^m\theta \frac{d^{\ell+m}(\sin^{2\ell}\theta)}{d(\cos^{\ell+m}\theta)}$$

- $$Y_\ell^m(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi) = A \frac{e^{im\varphi}}{\sqrt{2\pi}} P_\ell^m(\cos\theta)$$

- Normalisation $$\int_0^{2\pi}\int_0^{\pi} \left[Y_\ell^m(\theta,\varphi)\right]^* \left[Y_{\ell'}^{m'}(\theta,\varphi)\right] \sin\theta \, d\theta \, d\varphi = \delta_{\ell\ell'}\,\delta_{mm'}$$

$$Y_0^0(\theta,\varphi) = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^{\pm1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$$

$$Y_2^0(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}\,(3\cos^2\theta - 1)$$

$$Y_2^{\pm1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\varphi}$$

$$Y_2^{\pm2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\varphi}$$

- Some properties:

$$Y_\ell^{-m} = (-1)^m \left(Y_\ell^m\right)^* \quad \text{(Prove this!)}$$

- $$Y_\ell^m(\theta,\varphi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; e^{im\varphi}\, P_\ell^m(\cos\theta) \qquad (m \geq 0)$$

- $$Y_\ell^m(\theta,\varphi) = \sqrt{\frac{(2\ell+1)}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}} \quad \text{"} \quad \text{"} \qquad (m \leq 0)$$

Remember $\ell = 0, 1, 2, \ldots$

$m = -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell-1, \ell.$

- Radial equation:

  - $$\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) R(r) - \frac{2\mu r^2}{\hbar^2}\left[V(r) - E\right] R(r) = \ell(\ell+1)\, R(r)$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2}\right] R_{E\ell}(r) + V(r)\, R_{E\ell}(r) = E\, R_{E\ell}(r) \quad \text{----(3)}$$

Note: This is radial Schrodinger equation. Depends on ℓ.
Does not depend on m.
So, H will display $(2\ell+1)$-fold degeneracy.

- Put $R_{E\ell}(r) = \dfrac{U_{E\ell}(r)}{r}$

- Now, Eq (3) becomes

$$\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right] U_{E\ell} = 0$$

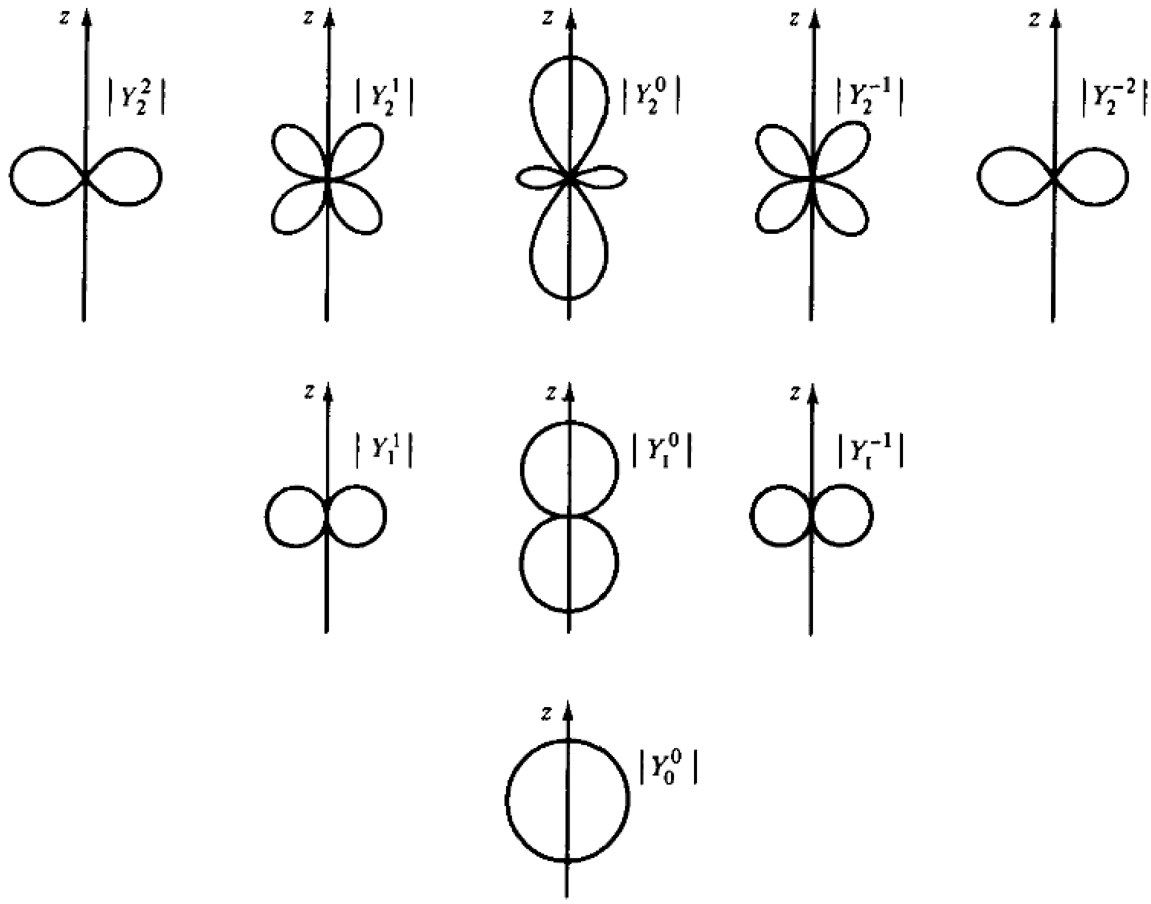


FIGURE 9.10 Polar plots of $|Y_l^m|$ versus θ in any plane through the z axis for $l = 0, 1, 2$. The equality $|Y_l^m| = |Y_l^{-m}|$ is exhibited.

From *Introduction to Quantum Mechanics* by Richard Liboff