

CHAPTER 4 :

QUANTUM MECHANICS IN 3D

⇒ 4.1 SCHRÖDINGER EQ. IN SPHERICAL COORDINATE

• GENERALIZATION TO 3D

$$\hookrightarrow \hat{H} \Psi = i \hbar \frac{\partial \Psi}{\partial t}$$

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} = \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2)$$

$$\hat{p}_x \rightarrow -i \hbar \frac{\partial}{\partial x}$$

$$\hat{p}_y \rightarrow -i \hbar \frac{\partial}{\partial y}$$

$$\hat{p}_z \rightarrow -i \hbar \frac{\partial}{\partial z}$$

$$\therefore \hat{p} \rightarrow -i \hbar \bar{\nabla}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi = i \hbar \frac{\partial \Psi}{\partial t}$$

WITH
 $V(\vec{r}, t)$
 $\vec{r} (x, y, z)$

$$\text{LAPLACIAN} \quad \nabla^2 \equiv \bar{\nabla} \cdot \bar{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

↓
CARTESIAN
COORDINATES

↳ NORMALIZATION

$|\Psi(\vec{r}, t)|^2 d^3\vec{r}$ PROBABILITY TO FIND PARTICLE
IN THE (INFINITESIMAL) VOLUME
 $d^3\vec{r}$ AT TIME t

$$\int d^3\vec{r} |\Psi(\vec{r}, t)|^2 = 1$$

↳ IF $V(\vec{r}, t) = V(\vec{r})$ TIME INDEPENDENT

⇓

COMPLETE SET OF STATIONARY STATES

$$\Psi_m(\vec{r}, t) = \psi_m(\vec{r}) e^{-\frac{i}{\hbar} E_m t}$$

$\psi_m(\vec{r})$ SATISFIES TIME INDEPENDENT SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_m + V \psi_m = E_m \psi_m$$

↳ IN GENERAL

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi}$$

↓

GENERAL SOLUTION

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}) e^{-\frac{i}{\hbar} E_n t}$$

• SEPARATION OF VARIABLES

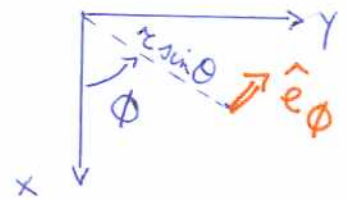
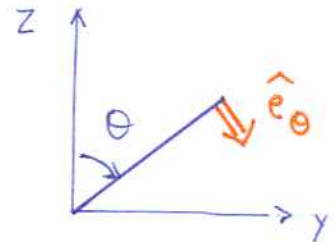
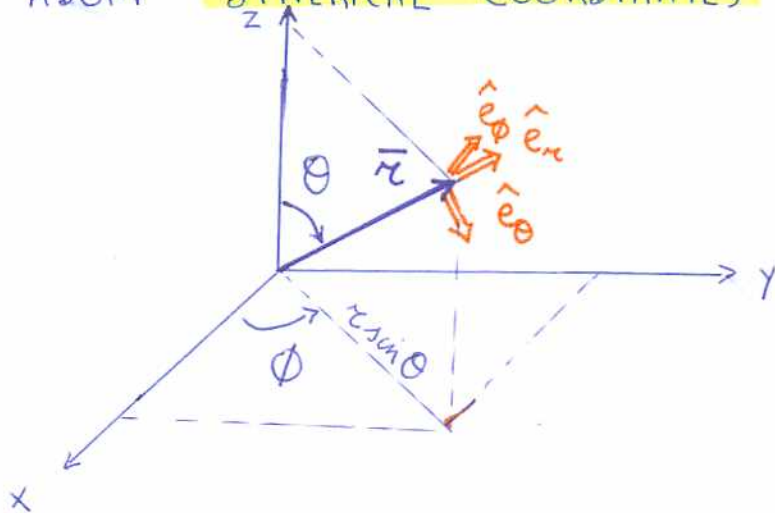
↳ FOR CENTRAL POTENTIAL $V(\vec{r}) = V(r)$

$$r = |\vec{r}|$$

V : DEPENDS ONLY ON DISTANCE FROM ORIGIN



ADOPT SPHERICAL COORDINATES



$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\hat{e}_r = \sin \theta \cos \phi \hat{i} + \sin \theta \sin \phi \hat{j} + \cos \theta \hat{k}$$

$$\hat{e}_\theta = \cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k}$$

$$\hat{e}_\phi = -\sin \phi \hat{i} + \cos \phi \hat{j}$$

4.4

$$\begin{aligned}\bar{\nabla} f &= \left(\frac{\partial f}{\partial x}\right) \hat{i} + \left(\frac{\partial f}{\partial y}\right) \hat{j} + \left(\frac{\partial f}{\partial z}\right) \hat{k} \\ &= (\bar{\nabla}_r f) \hat{e}_r + (\bar{\nabla}_\theta f) \hat{e}_\theta + (\bar{\nabla}_\phi f) \hat{e}_\phi\end{aligned}$$

$$\begin{aligned}\rightsquigarrow (\bar{\nabla}_r f) &= \hat{e}_r \cdot \bar{\nabla} f \\ &= \left(\frac{\partial f}{\partial x}\right) \underbrace{\sin \theta \cos \phi}_{\frac{\partial x}{\partial r}} + \left(\frac{\partial f}{\partial y}\right) \underbrace{\sin \theta \sin \phi}_{\frac{\partial y}{\partial r}} + \left(\frac{\partial f}{\partial z}\right) \underbrace{\cos \theta}_{\frac{\partial z}{\partial r}} \\ &= \frac{\partial f}{\partial r}\end{aligned}$$

$$\begin{aligned}\rightsquigarrow (\bar{\nabla}_\theta f) &= \hat{e}_\theta \cdot \bar{\nabla} f \\ &= \left(\frac{\partial f}{\partial x}\right) \underbrace{\cos \theta \cos \phi}_{\frac{1}{r} \frac{\partial x}{\partial \theta}} + \left(\frac{\partial f}{\partial y}\right) \underbrace{\cos \theta \sin \phi}_{\frac{1}{r} \frac{\partial y}{\partial \theta}} + \left(\frac{\partial f}{\partial z}\right) \underbrace{(-\sin \theta)}_{\frac{\partial z}{\partial \theta}} \\ &= \frac{1}{r} \frac{\partial f}{\partial \theta}\end{aligned}$$

$$\begin{aligned}\rightsquigarrow (\bar{\nabla}_\phi f) &= \hat{e}_\phi \cdot \bar{\nabla} f \\ &= \left(\frac{\partial f}{\partial x}\right) \underbrace{(-\sin \phi)}_{\frac{1}{r \sin \theta} \frac{\partial x}{\partial \phi}} + \left(\frac{\partial f}{\partial y}\right) \underbrace{(\cos \phi)}_{\frac{1}{r \sin \theta} \frac{\partial y}{\partial \phi}} \\ &= \frac{1}{r \sin \theta} \frac{\partial f}{\partial \phi}\end{aligned}$$

$$\bar{\nabla} = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

$$\bar{\nabla} = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$$

↓
 EXPRESS LAPLACIAN $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
 IN POLAR COORDINATES. (HOMEWORK!)

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

TIME-INDEP
 ↳ SCHRÖDINGER EQ.

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

SEPARATION OF VARIABLES

$$\underline{\underline{\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)}}$$

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + V(r) R Y = E R Y$$

⇓ DIVIDE BY RY
 × $\left(-\frac{2m r^2}{\hbar^2} \right)$

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m r^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0$$

FIRST { } DEPENDS ONLY ON r

SECOND { } DEPENDS ONLY ON θ, ϕ

\Downarrow

EACH { } IS CONSTANT

\downarrow
DENOTE BY $l(l+1)$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] = l(l+1)$$

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = -l(l+1)$$

1^o EQ: RADIAL EQ.

2^o EQ: ANGULAR EQ.

• ANGULAR EQUATION

$$\hookrightarrow \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \sin^2 \theta Y$$

↓

SOLUTION: TRY SEPARATION OF VARIABLES

$$\underline{\underline{Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)}}$$

$$\left\{ \frac{1}{\Theta} \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + l(l+1) \sin^2 \theta \right\} + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = 0$$

DEPENDS ONLY ON θ

DEPENDS ONLY ON ϕ

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

$$\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2$$

↳ **Φ EQUATION :**

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi$$

$$\Phi(\phi) = e^{im\phi}$$

m CAN BE BOTH POSITIVE & NEGATIVE

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

SAME PHYSICAL POINT IN SPACE

⇓

$$e^{im2\pi} = 1$$

⇓

$$m = 0, \pm 1, \pm 2, \pm 3, \dots$$

INTEGER

↳ **Θ EQUATION**

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

⇓

TURN THIS INTO EQ. FOR x = cos θ

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

ANGULAR EQ BECOMES

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

$$\Downarrow \quad \sin^2 \theta = 1 - x^2$$

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

⇓

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

⇓ DIVIDE BY (1-x^2)

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

↳ SOLUTIONS ARE ASSOCIATED LEGENDRE FUNCTIONS

$$\underline{\underline{\Theta(\theta) = A P_l^m(\cos \theta)}}$$

↳ ASSOCIATED LEGENDRE FUNCTIONS

$$P_l^m(x) \equiv (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x)$$

WITH $P_l(x)$: LEGENDRE FUNCTIONS (POLYNOMIAL)

NOTE $P_l^0(x) = P_l(x)$

LEGENDRE POLYNOMIALS ARE DEFINED BY RODRIGUES FORMULA

$$P_l(x) \equiv \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2-1)^l$$

l IS POSITIVE INTEGER
 $l = 0, 1, 2, \dots$

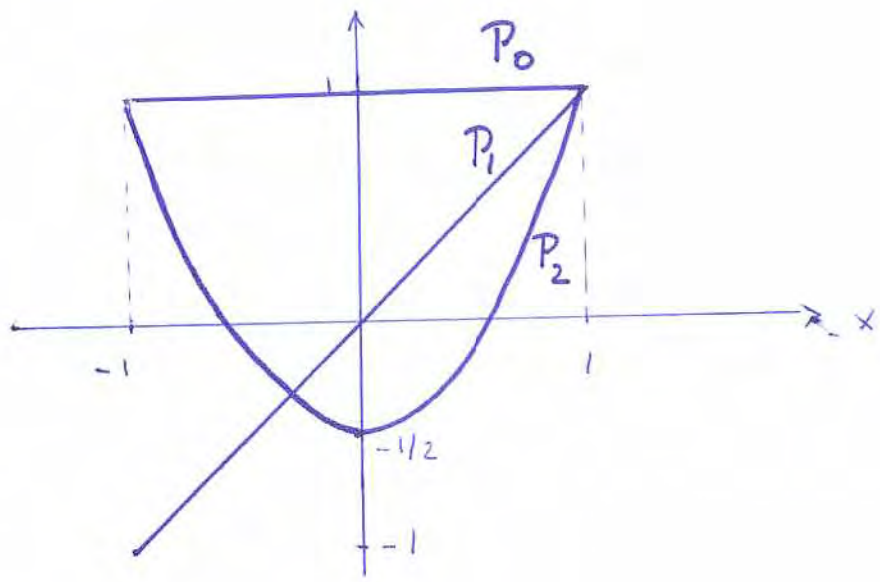
↳ SPECIAL CASES: P_l

$$\begin{aligned} P_0(x) &= 1 \\ P_1(x) &= \frac{1}{2} \frac{d}{dx} (x^2-1) = x \\ P_2(x) &= \frac{1}{4 \cdot 2} \frac{d^2}{dx^2} (x^2-1)^2 = \frac{1}{2} \frac{d}{dx} ((x^2-1)x) \\ &= \frac{1}{2} (3x^2-1) \end{aligned}$$

↳ IN GENERAL $P_l(x)$ IS POLYNOMIAL OF DEGREE l

↳ l EVEN $\rightarrow P_l$ IS EVEN FUNCTION IN x

l ODD $\rightarrow P_l$ IS ODD FUNCTION IN x



↳ SPECIAL CASES : P_l^m

FOR ANY $l \Rightarrow (2l+1)$ POSSIBLE VALUES OF m

$m = -l, -l+1, \dots, 0, 1, \dots, l-1, l$

• $P_0^0 = 1$

• $P_1^m = (\sqrt{1-x^2})^m \frac{d^m}{dx^m} P_1(x) = (\sqrt{1-x^2})^m \frac{d^m}{dx^m} x$

$\rightsquigarrow P_1^0 = x$

$\rightsquigarrow P_1^1 = \sqrt{1-x^2}$

• $P_2^0 = P_2 = \frac{1}{2} (3x^2 - 1)$

$m \neq 0 \quad P_2^m = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} \frac{1}{2} (3x^2 - 1)$

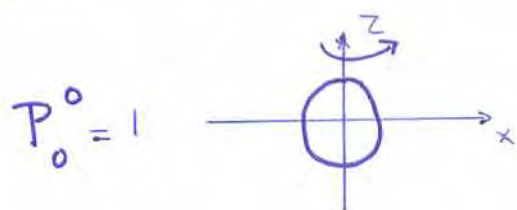
$$\rightsquigarrow P_2^1(x) = \sqrt{1-x^2} \cdot 3x$$

$$\rightsquigarrow P_2^2(x) = 3(1-x^2)$$

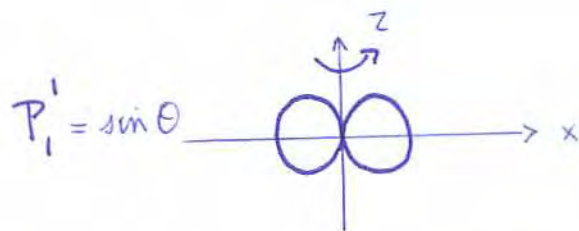
FOR m ODD P_e^m IS POLYNOMIAL MULTIPLIED BY $\sqrt{1-x^2}$

FOR m EVEN P_e^m IS POLYNOMIAL.

PLOT MAGNITUDE OF FUNCTION $P_e^m(\cos\theta)$ IN THE DIRECTION θ (ANGULAR PLOT)



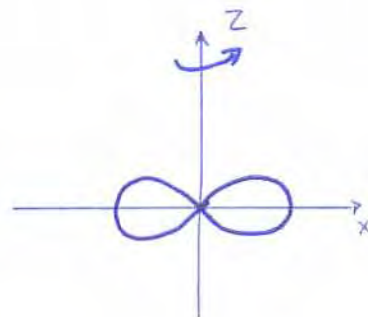
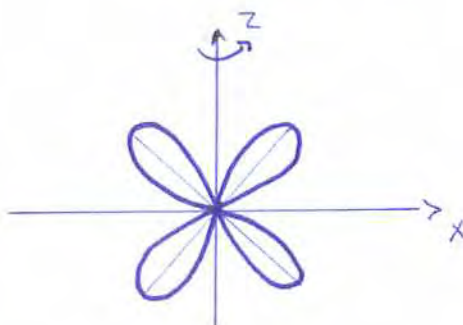
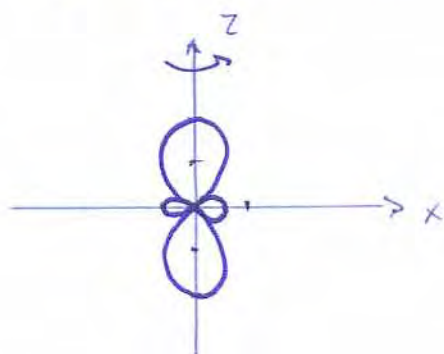
SPHERE



$$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^1 = 3\sin\theta\cos\theta$$

$$P_2^2 = 3\sin^2\theta$$



↳ NORMALIZATION

$$\rightsquigarrow \int d^3\vec{r} \quad |\Psi|^2 = 1$$

$$\rightsquigarrow d^3\vec{r} = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$\rightsquigarrow \Psi(\vec{r}) = R(r) Y(\theta, \phi)$$

$$\int dr \, r^2 |R(r)|^2 \int d\phi \, d\theta \, \sin\theta |Y(\theta, \phi)|^2 = 1$$

CONVENIENT CHOICE TO NORMALIZE R & Y SEPARATELY

$$\int_0^\infty dr \, r^2 |R(r)|^2 = 1$$

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \, \sin\theta |Y(\theta, \phi)|^2 = 1$$

$$Y(\theta, \phi) = Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(\cos\theta)$$

↳ $m \geq 0$

SPHERICAL HARMONICS

$$Y_{l-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi)$$

RADIAL EQUATION

↳

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m r^2}{\hbar^2} [V(r) - E] R = l(l+1) R$$

↳ CHANGE OF VARIABLES

$$U(r) \equiv r R(r)$$

$$R = \frac{U}{r}$$

$$\frac{dR}{dr} = \frac{1}{r^2} \left(r \frac{dU}{dr} - U \right)$$

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = \cancel{\frac{dU}{dr}} + r \frac{d^2 U}{dr^2} - \cancel{\frac{dU}{dr}}$$

$$-\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] U = E U$$

V_{eff} EFFECTIVE POT.

$$\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

REPULSIVE CENTRIFUGAL POT.

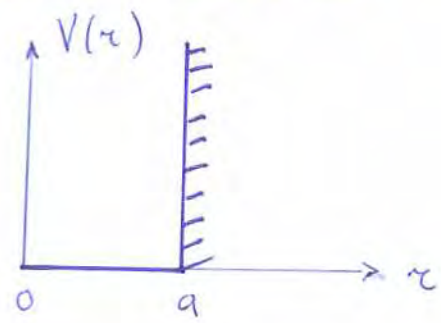
GROWS FOR LARGER l

↳

NORMALIZATION :

$$\int_0^\infty dr |U(r)|^2 = 1$$

INFINITE SPHERICAL WELL



PARTICLE CONFINED IN SPHERE OF RADIUS a

∞ SOLVE SCHRÖDINGER EQ. FOR W.F. & EIGENVALUES

$r > a : U(r) = 0$

$r < a : -\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} U = E U$

$E = \frac{\hbar^2 k^2}{2m}$

$\frac{d^2 U}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] U$

• $l=0$

$\frac{d^2 U}{dr^2} = -k^2 U$

$U(r) = A \sin(kr) + B \cos(kr)$

$R = \frac{1}{r} U$

$R(r=0)$ FINITE $\Rightarrow B=0$

$R(r=a)=0 \Rightarrow k = \frac{n\pi}{a}$

$R(r) = \frac{A}{r} \sin\left(\frac{n\pi}{a} r\right)$

$E_{n0} = \frac{\hbar^2 n^2 \pi^2}{2m a^2}$

$l=0$
 $n = 1, 2, 3, \dots$

NORMALIZE

$$\int_0^{\infty} dr \ r^2 |R(r)|^2 = 1$$

$$\int_0^{\infty} dr \ |U(r)|^2 = 1$$

↓

$$\underline{\underline{A = \sqrt{\frac{2}{a}}}}$$

∴ ANGULAR PART $l = 0, m = 0$

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

(INDEED $\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \frac{1}{4\pi} = 1$)

$$Y_{nlm} \rightarrow Y_{n00}(\bar{r}) = \sqrt{\frac{1}{2\pi a}} \frac{1}{r} \sin\left(\frac{n\pi}{a} r\right)$$

• SOLUTION FOR ARBITRARY l .

$$\Rightarrow \underline{\underline{U(r) = A r j_l(kr) + B r n_l(kr)}}$$

$j_l(x)$: SPHERICAL BESSEL FUNCTION
OF ORDER l

$n_l(x)$: SPHERICAL NEUMANN FUNCTION
OF ORDER l

$$\Rightarrow j_l(x) = (-1)^l x^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x}$$

$$\Rightarrow n_l(x) = -(-1)^l x^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\cos x}{x}$$

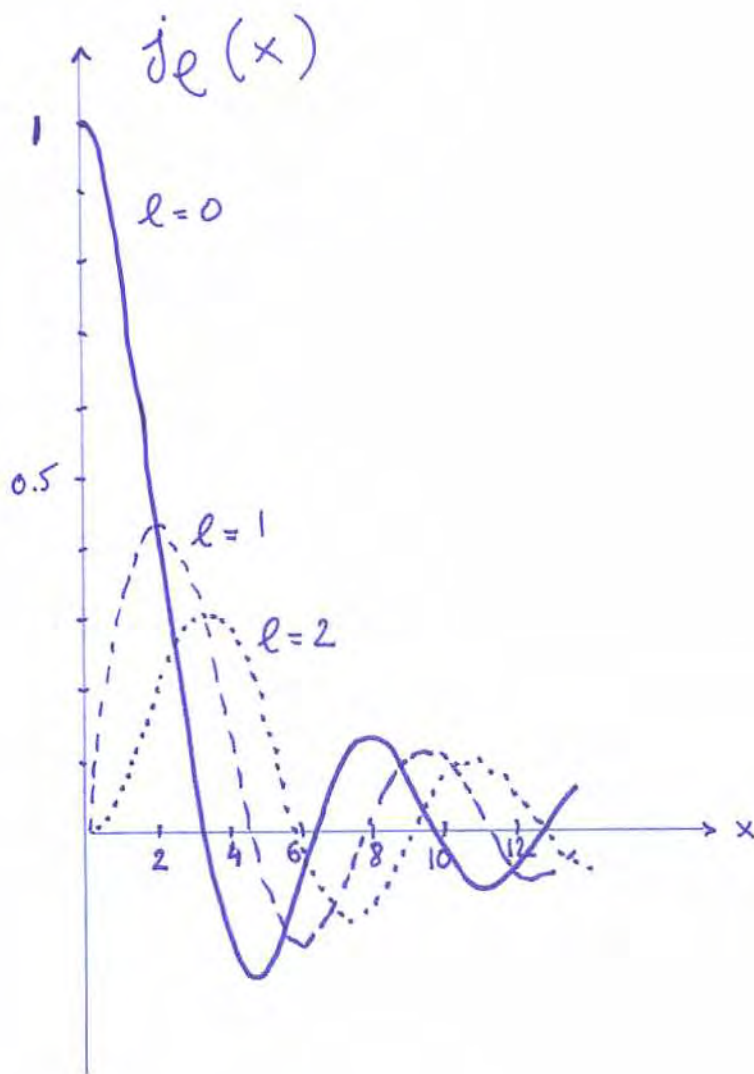
$$\Rightarrow j_0(x) = \frac{\sin x}{x}$$

$$j_1(x) = -x \left(\frac{1}{x} \frac{d}{dx} \right) \frac{\sin x}{x}$$

$$= \frac{\sin x}{x^2} - \frac{\cos x}{x}$$

$$j_2(x) = x^2 \left(\frac{1}{x} \frac{d}{dx} \right)^2 \frac{\sin x}{x}$$

$$= x^2 \left(\frac{1}{x} \frac{d}{dx} \right) \left(-\frac{\sin x}{x^3} + \frac{\cos x}{x^2} \right) = \frac{3 \sin x - 3x \cos x - x^2 \sin x}{x^3}$$



$$\rightsquigarrow \left. \begin{aligned} n_0(x) &= -\frac{\cos x}{x} \end{aligned} \right\}$$

$$n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$$

$$n_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x}\right) \cos x - \frac{3}{x^2} \sin x$$

NOTE $n_l(x) \xrightarrow{x \rightarrow 0} \infty$

$$\Rightarrow \underline{\underline{B = 0}}$$

CHOOSE k SUCH THAT

$$\underline{j_l(ka) = 0}$$



ZEROES OF BESSEL FUNCTIONS.

$$k = \frac{1}{a} \beta_{nl}$$



n -th ZERO OF BESSEL FUNCTION l .

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2$$

EACH LEVEL nl
IS $(2l+1)$ FOLD DEGENERATE
 $\forall l \Rightarrow m = -l, \dots, 0, \dots, l$

$$\psi_{nlm}(\vec{r}) = A_{nl} j_l\left(\beta_{nl} \frac{r}{a}\right) Y_{lm}(\theta, \phi)$$

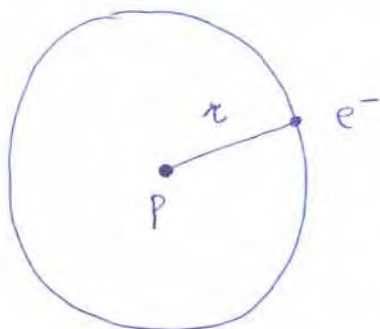
NORMALIZATION.

$$\int_0^\infty dr r^2 |R|^2 = 1$$

⇒ HYDROGEN ATOM

• COULOMB POTENTIAL

↳



POTENTIAL
ENERGY :

$$V(r) = - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$



ϵ_0 : PERMITTIVITY OF SPACE

$$\epsilon_0 \approx 8.854 \cdot 10^{-12} \frac{C^2}{Jm}$$

↳

RADIAL EQ.

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = E u$$

• RADIAL WAVE FUNCTION (FOR BOUND STATES) 4.22

$$\hookrightarrow \boxed{K \equiv \frac{\sqrt{-2mE}}{\hbar}} \quad E = -\frac{\hbar^2 K^2}{2m}$$

$$\frac{1}{K^2} \frac{d^2 U}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2} \frac{1}{K^2 r} + \frac{l(l+1)}{K^2 r^2} \right] U$$

$$\Downarrow \text{ USE } \boxed{\rho \equiv Kr}$$

$$\boxed{\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 K}}$$

$$\circ \circ \circ \quad \boxed{\frac{d^2 U}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] U}$$

\hookrightarrow ASYMPTOTIC BEHAVIOR $r \rightarrow \infty$, $\rho \rightarrow \infty$

$$\frac{d^2 U}{d\rho^2} = U$$

\Downarrow

$$U(\rho) = Ae^{-\rho} + \cancel{Be^{\rho}}$$

\uparrow
BLOWS UP FOR $\rho \rightarrow \infty$

↳ BEHAVIOR FOR $\kappa \rightarrow 0$

$\frac{1}{\rho^2}$ TERM DOMINATES

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$$

⇓

$$u(\rho) = C \rho^{l+1} + D \cancel{\rho^{-l}}$$

BLOWS UP FOR $\rho \rightarrow 0$

∴ CONVENIENT TO TAKE OUT BEHAVIORS OF SOLUTION FOR $\rho \rightarrow \infty$ & $\rho \rightarrow 0$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$$

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l+1 - \rho) v + \rho \frac{dv}{d\rho} \right]$$

$$\frac{d^2 u}{d\rho^2} = \rho^l e^{-\rho} \left\{ \left[-2l - 2 + \rho + \frac{l(l+1)}{\rho} \right] v + 2(l+1 - \rho) \frac{dv}{d\rho} + \rho \frac{d^2 v}{d\rho^2} \right\}$$

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1 - \rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)] v = 0$$

↳ WRITE SOLUTION AS POWER SERIES IN ρ

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

⇓
DETERMINE COEFFICIENTS

$$\frac{dv}{d\rho} = \sum_{j=1}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$\frac{d^2v}{d\rho^2} = \sum_{j=1}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

$$\begin{aligned} \rightsquigarrow & \rho \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1} \\ & + 2(\ell+1-\rho) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \\ & + [\rho_0 - 2(\ell+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0 \end{aligned}$$

⇓
EQUATING COEFFICIENT OF POWER ρ^j

$$j(j+1) c_{j+1} + 2(\ell+1)(j+1) c_{j+1} - 2j c_j + [p_0 - 2(\ell+1)] c_j = 0$$

⇓

$$c_{j+1} = \frac{[2(j+\ell+1) - p_0]}{(j+1)(j+2\ell+2)} c_j$$

↳ SOLVE RECURSIVELY STARTING FROM c_0

↳ FOR $j \gg$ (i.e. SOLUTION FOR LARGE p)

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$$

↓

$$\left\| c_j = \frac{2^j}{j!} c_0 \right.$$

$$v(p) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} p^j = c_0 e^{2p}$$

↓

$$u(p) = c_0 p^{\ell+1} e^p$$

BLOWS UP!

4.26

↳ PHYSICAL SOLUTIONS ONLY CORRESPOND WITH A SERIES WHICH TERMINATES!

SUPPOSE MAX VALUE OF j IS j_{\max}

$$\underline{C_{j_{\max}+1} = 0}$$

$$2(j_{\max} + l + 1) - \rho_0 = 0$$

DEFINE $n \equiv j_{\max} + l + 1$

↳ PRINCIPAL QUANTUM NUMBER
(INTEGER)

$$\rho_0 = 2n$$

⇓

$$E = -\frac{\hbar^2}{2m} k^2 = -\frac{\hbar^2}{2m} \frac{m^2 e^4}{(2\pi\epsilon_0)^2 \hbar^4 \rho_0^2}$$

$$= -\frac{m e^4}{8\pi^2 \epsilon_0^2 \hbar^2 4n^2}$$

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \equiv \frac{E_1}{n^2}$$

BOHR'S FORMULA
 $n = 1, 2, 3, \dots$

↳

$$E_1 = - \left[\frac{m}{2} \frac{1}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right]$$

$$= - 13.6 \text{ eV}$$

↳ BINDING ENERGY OF GROUND STATE LEVEL OF HYDROGEN ATOM

$$\rho_0 = \frac{m e^2}{2\pi\epsilon_0 \hbar^2 K}$$

$$\rho_0 = 2n$$

$$K = \left(\frac{m e^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} \equiv \frac{1}{a n}$$

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \cdot 10^{-10} \text{ m}$$

↑
BOHR RADIUS

$$e = K r = \frac{r}{a} \frac{1}{n}$$

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j$$



GROUND STATE

 $n = 1$

$$n = j_{\max} + l + 1$$

$$\Downarrow$$

$$n = 1 \Leftrightarrow j_{\max} = 0, l = 0$$

$$U_{nl}(r) = U_{10}(r) = c_0 \left(\frac{r}{a}\right) e^{-r/a}$$

$$R_{10}(r) = \frac{U_{10}(r)}{r} = \frac{c_0}{a} e^{-r/a}$$

$$\int_0^{\infty} dr r^2 |R_{10}(r)|^2 = 1$$

NORMALIZATION

$$\Downarrow$$

$$1 = \frac{|c_0|^2}{a^2} \int_0^{\infty} dr r^2 e^{-2r/a} = |c_0|^2 \frac{a}{8} \underbrace{\int_0^{\infty} dx x^2 e^{-x}}_2$$

$$\Downarrow$$

$$c_0 = \frac{2}{\sqrt{a}}$$

$$\circ \circ$$

$$\Psi_{nlm}(r) \Rightarrow \Psi_{100}(r) = \frac{1}{\sqrt{4\pi}} \cdot \frac{2}{\sqrt{a}} \cdot \frac{1}{a} e^{-r/a}$$

↳ FIRST EXCITED STATE n = 2

$$E_2 = - \frac{13.6 \text{ eV}}{4} = - 3.4 \text{ eV}$$

$$n = j_{\text{max}} + l + 1$$

$$n = 2 \iff j_{\text{max}} + l = 1$$

2 POSSIBLE VALUES OF l

- || l = 0 → j_{max} = 1
- || l = 1 → j_{max} = 0

- l = 0 $R_{20}(r) = \frac{1}{r} \left(\frac{r}{2a} \right) \cdot e^{-r/2a} \cdot c_0 \left(1 - \frac{r}{2a} \right)$

c₁ = -c₀

$R_{20}(r) = \frac{c_0}{2a} \left(1 - \frac{r}{2a} \right) e^{-r/2a}$

- l = 1 $R_{21}(r) = \frac{1}{r} \left(\frac{r}{2a} \right)^2 e^{-r/2a} \cdot c_0$

$R_{21}(r) = \frac{c_0}{4a^2} r e^{-r/2a}$

↳ ARBITRARY m

$$m = j_{\max} + l + 1$$

↓

$$l = m - 1 - j_{\max}$$

POSSIBLE VALUES OF $l = 0, 1, \dots, m-1$

FOR EACH l : $(2l+1)$ VALUES OF m

- DEGENERACY OF EACH LEVEL m

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

- POLYNOMIAL $v(\rho)$

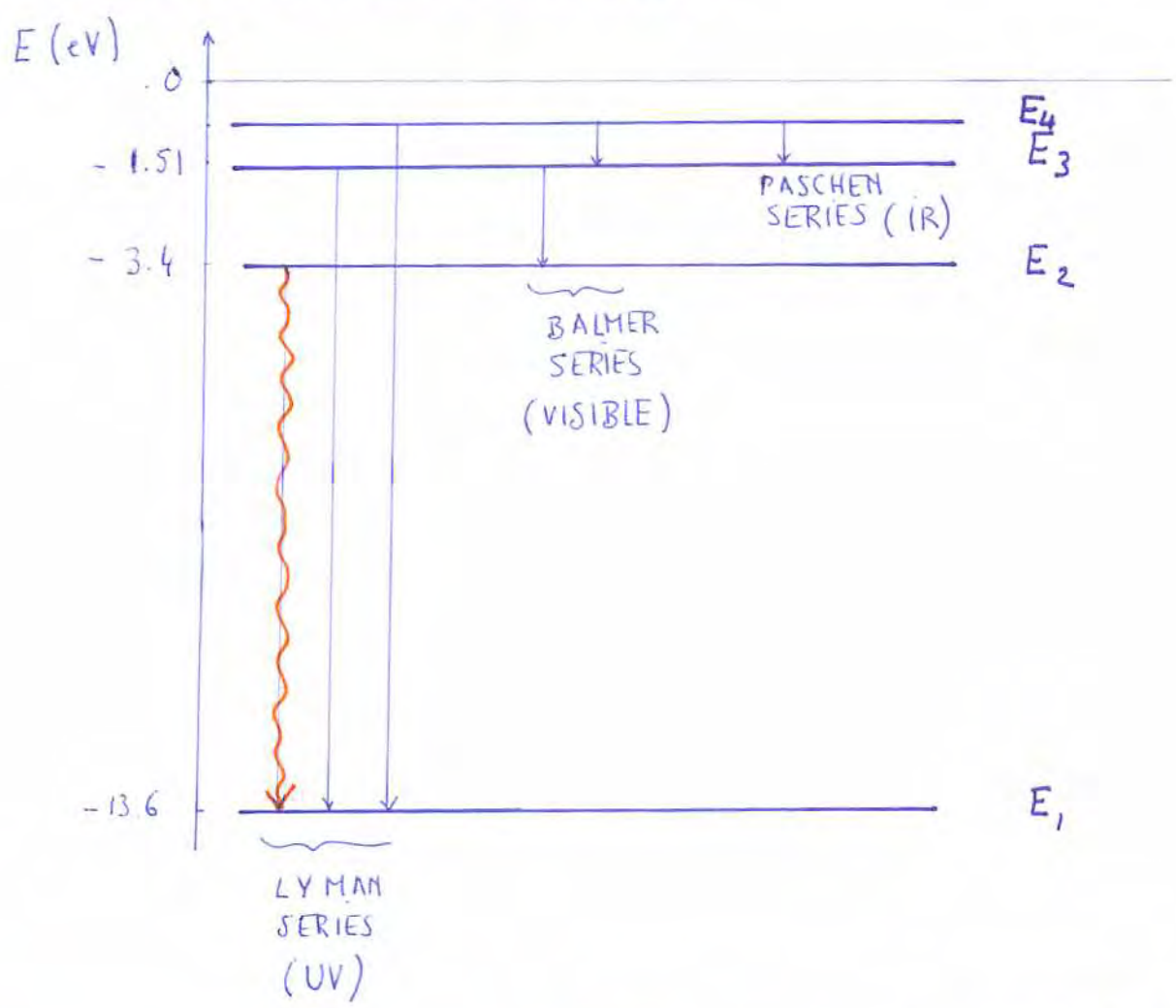
IS A SO-CALLED ASSOCIATED LAGUERRE POLYNOMIAL

$$v(\rho) \equiv L_{m-l-1}^{2l+1}(2\rho)$$

LAGUERRE →

$$\left\{ \begin{aligned} L_{q-p}^p(x) &\equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x) \\ L_q(x) &\equiv e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q) \end{aligned} \right.$$

SPECTRUM OF HYDROGEN



~~~~~ → **PHOTON IS EMITTED** WHEN  $e^-$  FALLS INTO DEEPER BOUND STATE

PHOTON IS ABSORBED WHEN  $e^-$  IS EXCITED

↳ ENERGY IS CONSERVED

∴ PHOTON HAS TO TAKE THE DIFFERENCE IN ENERGY

TRANSITION FROM  $E_i > E_f$



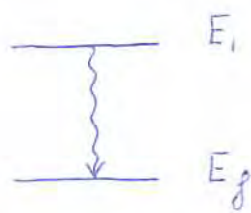
$$E_\gamma = E_i - E_f$$

$$= (-13.6 \text{ eV}) \cdot \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

↳ PLANCK'S FORMULA

$$\begin{cases} E_\gamma = h\nu \\ \frac{1}{\lambda} = \frac{\nu}{c} \end{cases} \quad (\lambda\nu = c)$$

$$\frac{1}{\lambda} = \frac{1}{hc} E_\gamma$$



$$= \frac{(-E_i)}{hc} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\downarrow \quad -E_i = \frac{m}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{h^2}$$

$$\frac{1}{\lambda} = \left[ \frac{m}{4\pi c h^3} \cdot \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$R$ : RYDBERG CONSTANT

$$R = 1.097 \cdot 10^7 \text{ m}^{-1}$$



## ⇒ 4.3 ANGULAR MOMENTUM

### DEFINITIONS

↳ CLASSICAL

$$\vec{L} = \vec{r} \times \vec{p}$$

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

↳ QUANTUM

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$$

$$p_y \rightarrow -i\hbar \frac{\partial}{\partial y}$$

$$p_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

### EIGENVALUES OF ANGULAR MOMENTUM OPERATOR

$$\begin{aligned} \hookrightarrow [L_x, L_y] &= [y p_z - z p_y, z p_x - x p_z] \\ &= [y p_z, z p_x] - [y p_z, x p_z] - [z p_y, z p_x] \\ &\quad + [z p_y, x p_z] \\ &= y p_x \underbrace{[p_z, z]}_{-i\hbar} - 0 - 0 + x p_y \underbrace{[z, p_z]}_{i\hbar} \\ &= i\hbar (x p_y - y p_x) = i\hbar L_z \end{aligned}$$

$$\begin{aligned} \left\{ \begin{aligned} [L_x, L_y] &= i\hbar L_z \\ [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y \end{aligned} \right. \end{aligned}$$

↳  $L_x, L_y, L_z$  ARE INCOMPATIBLE OBSERVABLES

GEN. UNCERTAINTY RELATION

$$\sigma_A^2 \sigma_B^2 \geq \left( \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

$$\left\| \sigma_{L_x}^2 \sigma_{L_y}^2 \geq \frac{\hbar^2}{4} \langle L_z \rangle^2 \right.$$

NO EIGENSTATES OF BOTH  $L_x$  &  $L_y$

$$\hookrightarrow L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\begin{aligned} [L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y \\ &\quad + L_z [L_z, L_x] + [L_z, L_x] L_z \end{aligned}$$

$$\begin{aligned}
 [L^2, L_x] &= L_y (-i\hbar L_z) - i\hbar L_z L_y \\
 &\quad + L_z (i\hbar L_y) + i\hbar L_y L_z \\
 &= 0
 \end{aligned}$$

$$\therefore \left\{ \begin{aligned}
 [L^2, L_x] &= 0 \\
 [L^2, L_y] &= 0 \\
 [L^2, L_z] &= 0
 \end{aligned} \right.$$

$\therefore$  SIMULTANEOUS EIGENSTATES OF  
 e.g.  $L^2$  AND  $L_z$  DO EXIST

$\hookrightarrow$  LADDER OPERATORS

$$L_{\pm} = L_x \pm i L_y$$

$$\begin{aligned}
 [L_z, L_{\pm}] &= \underbrace{[L_z, L_x]}_{i\hbar L_y} \pm i \underbrace{[L_z, L_y]}_{(-i\hbar)L_x} \\
 &= \pm \hbar (L_x \pm i L_y)
 \end{aligned}$$

$$\underline{\underline{[L_z, L_{\pm}] = \pm \hbar L_{\pm}}}$$

$$[L^2, L_{\pm}] = 0$$

→ IF  $f$  IS EIGENFUNCTION OF  $L^2, L_z$



$L_{\pm} f$  IS ALSO EIGENFUNCTION OF  $L^2, L_z$

$$\begin{cases} L^2 f = \lambda f \\ L_z f = \mu f \end{cases}$$

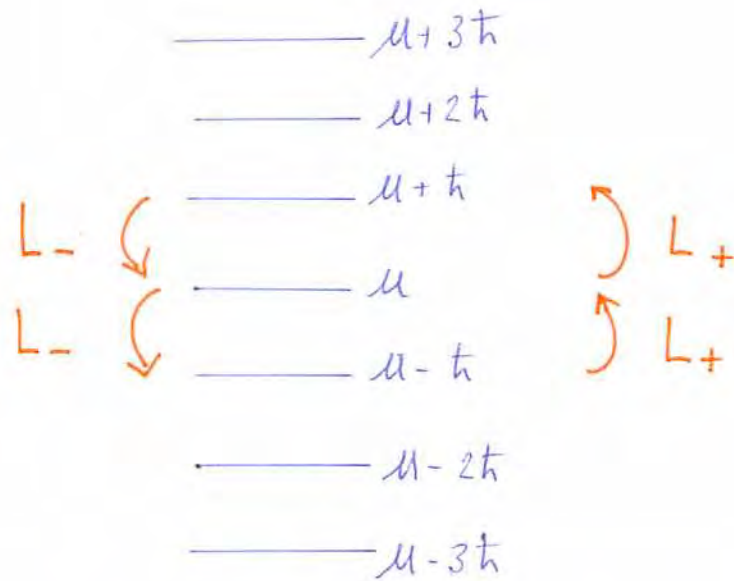
$\lambda, \mu$  : EIGENVALUES

$$\hookrightarrow L^2 (L_{\pm} f) = L_{\pm} (L^2 f) = \lambda (L_{\pm} f)$$

SAME EIGENVALUE

$$\begin{aligned} \hookrightarrow L_z (L_{\pm} f) &= L_{\pm} \underbrace{L_z f}_{\mu f} \pm \hbar L_{\pm} f \\ &= (\mu \pm \hbar) (L_{\pm} f) \end{aligned}$$

$L_{\pm} f$  IS EIGENFUNCTION OF  $L_z$   
WITH EIGENVALUE  $\mu \pm \hbar$



MAX. VALUE OF  $L_z$  (GIVEN BY TOTAL ANG. MOMENTUM)

$$L_+ \psi_{\text{top}} = 0$$

MIN VALUE OF  $L_z$

$$L_- \psi_{\text{bottom}} = 0$$

DEFINE

$$L_z \psi_{\text{top}} = (\hbar l) \psi_{\text{top}}$$

↳ EIGENVALUE OF TOP STATE

$$L_z \psi_{\text{bottom}} = (\hbar \bar{l}) \psi_{\text{bottom}}$$

$$\begin{aligned}
 L_{\pm} L_{\mp} &= (L_x \pm iL_y)(L_x \mp iL_y) \\
 &= L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) \\
 &\qquad\qquad\qquad \underbrace{\hspace{10em}}_{i\hbar L_z} \\
 &= L^2 - L_z^2 \mp i(i\hbar L_z)
 \end{aligned}$$

$$\underline{\underline{L^2 = L_{\pm} L_{\mp} + L_z^2 \mp \hbar L_z}}$$

$$\rightsquigarrow L^2 \psi_{\text{top}} = \lambda \psi_{\text{top}}$$

$$= (L_- L_+ + L_z^2 + \hbar L_z) \psi_{\text{top}}$$

$$= (0 + \hbar^2 l^2 + \hbar^2 l) \psi_{\text{top}}$$

$$= \hbar^2 l(l+1) \psi_{\text{top}}$$

$$\boxed{\lambda = \hbar^2 l(l+1)}$$

$\uparrow$   
 EIGENVALUE OF  $L^2$

$$\begin{aligned} \Rightarrow L^2 \psi_{\text{bottom}} &= \lambda \psi_{\text{bottom}} \\ &= (L_+ L_- + L_z^2 - \hbar L_z) \psi_{\text{bottom}} \\ &= \hbar^2 \bar{l} (\bar{l} - 1) \psi_{\text{bottom}} \end{aligned}$$

$$\lambda = \hbar^2 \bar{l} (\bar{l} - 1)$$

$$l(l+1) = \bar{l}(\bar{l}-1)$$

$$\Downarrow$$

$$\bar{l} = \cancel{l+1}$$

NOT POSSIBLE  $\bar{l} < l$

$$\bar{l} = -l$$

$2l$  is INTEGER

$$\hookrightarrow l = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$$

DENOTE EIGENVALUE OF  $L_z$  :  $\mu = \hbar m$

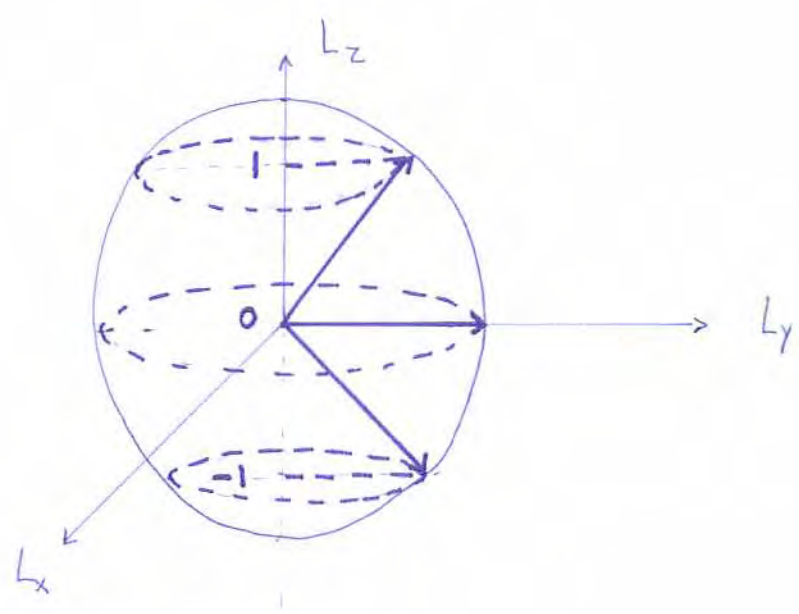
$$m = -l, \dots, +l \quad (\text{LADDER})$$

$$\begin{aligned} L^2 \psi_l^m &= \hbar^2 l(l+1) \psi_l^m \\ L_z \psi_l^m &= \hbar m \psi_l^m \end{aligned}$$

$$l = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \quad ; \quad m = -l, \dots, l$$

EXAMPLE  $l=1$

MAGNITUDE OF ANGULAR MOM:  $\sqrt{l(l+1)} = \sqrt{2} \approx 1.4$



• EIGENFUNCTIONS OF  $L^2, L_z$

$$\bar{L} = -i\hbar \bar{r} \times \bar{\nabla}$$

$$\bar{r} = r \hat{e}_r$$

$$\bar{\nabla} = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

$$\hat{e}_r \times \hat{e}_\theta = \hat{e}_\phi$$

$$\hat{e}_r \times \hat{e}_\phi = -\hat{e}_\theta$$

$$\hookrightarrow \bar{L} = -i\hbar \left( \hat{e}_\phi \frac{\partial}{\partial \theta} - \hat{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$



EXPRESS  $\hat{e}_\phi, \hat{e}_\theta$  IN  $\hat{i}, \hat{j}, \hat{k}$



→ READ OFF  $L_x, L_y, L_z$

→ CONSTRUCT  $L^2, L^2 = L_x^2 + L_y^2 + L_z^2$

→ VERIFY

$$\left\{ \begin{aligned} L_z \psi_l^m &= \hbar m \psi_l^m \\ L^2 \psi_l^m &= \hbar^2 l(l+1) \psi_l^m \end{aligned} \right.$$



$$\psi_l^m(\theta, \phi) = Y_{lm}(\theta, \phi)$$