CHAPTER 4 : QUANTUM MECHANICS IN 3D

⇒ 4.1 SCHRÖDINGER EQ. IN SPHERICAL COORDINATES

- GENERALIZATION TO 3D

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

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

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

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

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

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

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

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

WITH
$V(\bar{r}, t)$
$\bar{r}\ (x, y, z)$
↓
CARTESIAN COORDINATES

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

↳ NORMALIZATION

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

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

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

⇓

COMPLETE SET OF STATIONARY STATES

$$\Psi_n(\bar{r},t) = \psi_n(\bar{r}) \, e^{-\frac{i}{\hbar}E_n t}$$

$\psi_n(\bar{r})$ SATISFIES TIME INDEPENDENT SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n = E_n\psi_n$$

IN GENERAL

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

↓ GENERAL SOLUTION

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

- **SEPARATION OF VARIABLES**

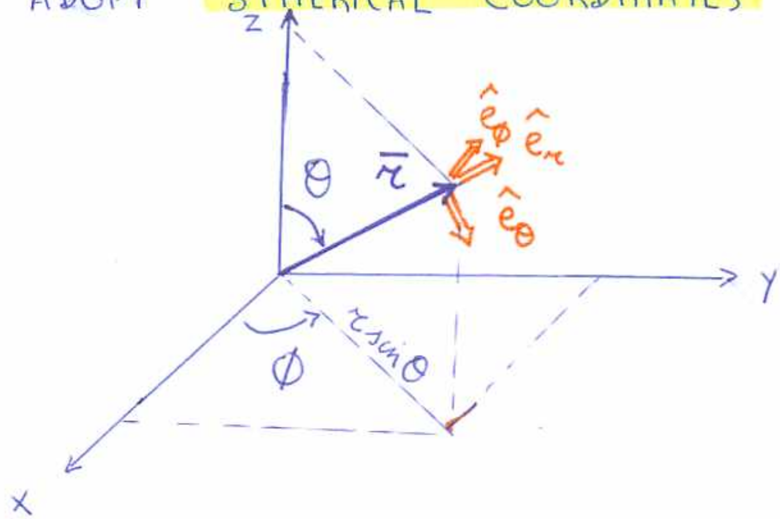
↳ FOR CENTRAL POTENTIAL $V(\bar{r}) = V(r)$

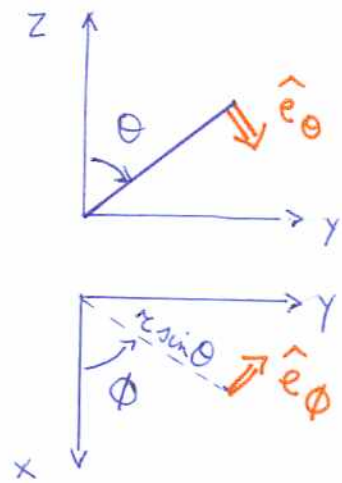
$r = |\bar{r}|$

V : DEPENDS ONLY ON DISTANCE FROM ORIGIN

$\Downarrow$

ADOPT SPHERICAL COORDINATES





$$
\begin{aligned}
x &= r \sin\theta \cos\phi \\
y &= r \sin\theta \sin\phi \\
z &= r \cos\theta
\end{aligned}
$$

$$
\begin{aligned}
\hat{e}_r &= \sin\theta\cos\phi\,\hat{i} + \sin\theta\sin\phi\,\hat{j} + \cos\theta\,\hat{k} \\
\hat{e}_\theta &= \cos\theta\cos\phi\,\hat{i} + \cos\theta\sin\phi\,\hat{j} - \sin\theta\,\hat{k} \\
\hat{e}_\phi &= -\sin\phi\,\hat{i} + \cos\phi\,\hat{j}
\end{aligned}
$$

$$\bar{\nabla} f = \left(\frac{\partial f}{\partial x}\right)\hat{i} + \left(\frac{\partial f}{\partial y}\right)\hat{j} + \left(\frac{\partial f}{\partial z}\right)\hat{k}$$

$$= (\bar{\nabla}_r f)\,\hat{e}_r + (\bar{\nabla}_\theta f)\,\hat{e}_\theta + (\bar{\nabla}_\phi f)\,\hat{e}_\phi$$

$$\rightsquigarrow (\bar{\nabla}_r f) = \hat{e}_r \cdot \bar{\nabla} f$$

$$= \left(\frac{\partial f}{\partial x}\right) \underbrace{\sin\theta\cos\phi}_{\frac{\partial x}{\partial r}} + \left(\frac{\partial f}{\partial y}\right) \underbrace{\sin\theta\sin\phi}_{\frac{\partial y}{\partial r}} + \left(\frac{\partial f}{\partial z}\right)\underbrace{\cos\theta}_{\frac{\partial z}{\partial r}}$$

$$= \frac{\partial f}{\partial r}$$

$$\rightsquigarrow (\bar{\nabla}_\theta f) = \hat{e}_\theta \cdot \bar{\nabla} f$$

$$= \left(\frac{\partial f}{\partial x}\right) \underbrace{\cos\theta\cos\phi}_{\frac{1}{r}\frac{\partial x}{\partial \theta}} + \left(\frac{\partial f}{\partial y}\right) \underbrace{\cos\theta\sin\phi}_{\frac{1}{r}\frac{\partial y}{\partial \theta}} + \left(\frac{\partial f}{\partial z}\right)\underbrace{(-\sin\theta)}_{\frac{\partial z}{\partial \theta}}$$

$$= \frac{1}{r}\frac{\partial f}{\partial \theta}$$

$$\rightsquigarrow (\bar{\nabla}_\phi f) = \hat{e}_\phi \cdot \bar{\nabla} f$$

$$= \left(\frac{\partial f}{\partial x}\right) \underbrace{(-\sin\phi)}_{\frac{1}{r\sin\theta}\frac{\partial x}{\partial \phi}} + \left(\frac{\partial f}{\partial y}\right) \underbrace{(\cos\phi)}_{\frac{1}{r\sin\theta}\frac{\partial y}{\partial \phi}} \quad \frac{\partial z}{\partial \phi}$$

$$= \frac{1}{r\sin\theta}\frac{\partial f}{\partial \phi}$$

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

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

EXPRESS LAPLACIAN $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

IN POLAR COORDINATES. (HOMEWORK !)

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

↳ TIME - INDEP
SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)\right.$$

$$\left.+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V(r)\psi=E\psi$$

SEPARATION OF VARIABLES

$$\psi(r,\theta,\phi)=R(r)\,Y(\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)\right.$$

$$\left.+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]+V(r)RY=ERY$$

$\Downarrow$ DIVIDE BY RY

$\times\left(-\frac{2mr^2}{\hbar^2}\right)$

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

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

FIRST { } DEPENDS ONLY ON r

SECOND { } DEPENDS ONLY ON θ, ϕ

$\Downarrow$

EACH { } IS CONSTANT

$\downarrow$

DENOTE BY $\ell(\ell+1)$

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

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

1° EQ: RADIAL EQ.

2° EQ: ANGULAR EQ.

- ANGULAR EQUATION

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

SOLUTION: TRY SEPARATION OF VARIABLES.

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

$$\underbrace{\left\{\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \ell(\ell+1)\sin^2\theta\right\}}_{\text{DEPENDS ONLY ON } \theta} + \underbrace{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}}_{\text{DEPENDS ONLY ON } \phi} = 0$$

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

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

↳ ϕ EQUATION :

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

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

m CAN BE BOTH POSITIVE & NEGATIVE

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

SAME PHYSICAL POINT IN SPACE

$$\Downarrow$$

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

$$\Downarrow$$

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

INTEGER

↳ Θ EQUATION

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

$$\Downarrow$$

TURN THIS INTO EQ. FOR $x = \cos\theta$

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

ANGULAR EQ. BECOMES

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

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

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

$$\Downarrow$$

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

$\Downarrow$ DIVIDE BY $(1-x^2)$

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

↳ SOLUTIONS ARE ASSOCIATED LEGENDRE FUNCTIONS

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

↳ ASSOCIATED LEGENDRE FUNCTIONS

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

WITH $P_\ell(x)$: LEGENDRE FUNCTIONS (POLYNOMIAL)

NOTE $P_\ell^0(x) = P_\ell(x)$

LEGENDRE POLYNOMIALS ARE DEFINED BY RODRIGUES FORMULA

$$\boxed{P_\ell(x) \equiv \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2-1)^\ell}$$

ℓ IS POSITIVE INTEGER
$\ell = 0, 1, 2, \ldots$

↳ SPECIAL CASES : P_ℓ

$$P_0(x) = 1$$

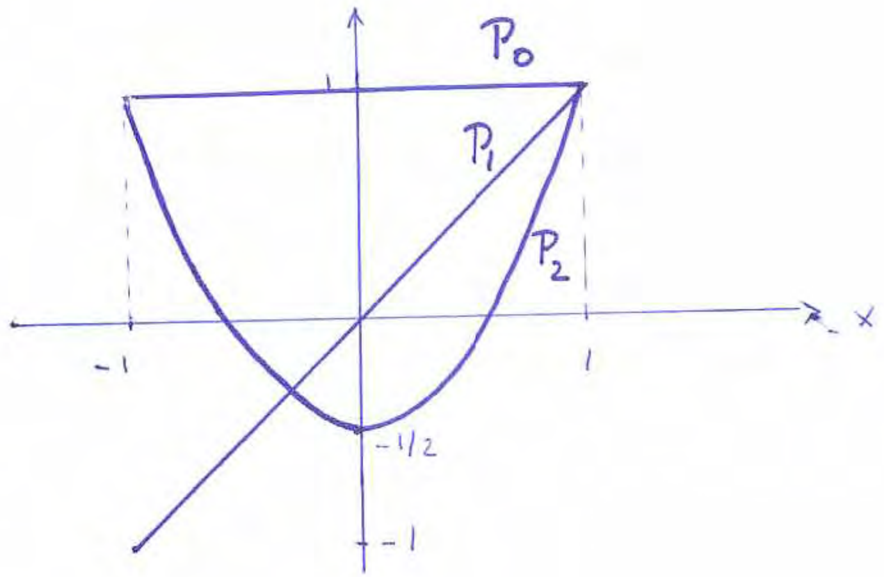
$$P_1(x) = \frac{1}{2} \frac{d}{dx}(x^2-1) = x$$

$$P_2(x) = \frac{1}{4.2} \frac{d^2}{dx^2}(x^2-1)^2 = \frac{1}{2} \frac{d}{dx}\left((x^2-1)\, x\right)$$

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

⇝ IN GENERAL $P_\ell(x)$ IS POLYNOMIAL OF DEGREE ℓ IN x

⇝ ℓ EVEN → P_ℓ IS EVEN FUNCTION IN x
ℓ ODD → P_ℓ IS ODD FUNCTION IN x



↳ SPECIAL CASES : P_ℓ^m

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

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

- $P_0^0 = 1$
- $P_1^m = \left(\sqrt{1-x^2}\right)^m \frac{d^m}{dx^m} P_1(x) = \left(\sqrt{1-x^2}\right)^m \frac{d^m}{dx^m}\, x$

$\rightsquigarrow \; P_1^0 = x$

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

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

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

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

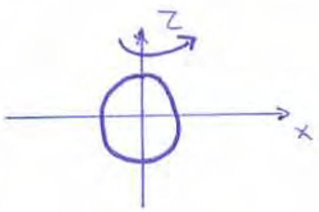
$\rightsquigarrow P_2^2(x) = 3(1-x^2)$

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

FOR m EVEN P_ℓ^m IS POLYNOMIAL.

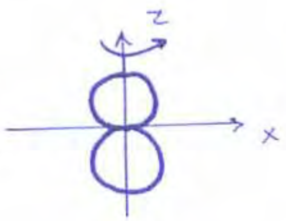
PLOT MAGNITUDE OF FUNCTION $P_\ell^m(\cos\theta)$ IN THE DIRECTION θ (ANGULAR PLOT)

$P_0^0 = 1$

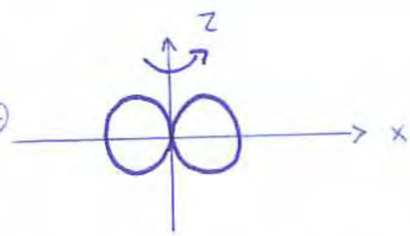


SPHERE

$P_1^0 = \cos\theta$



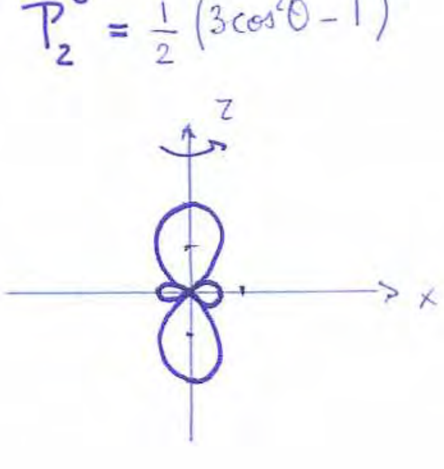
$P_1^1 = \sin\theta$

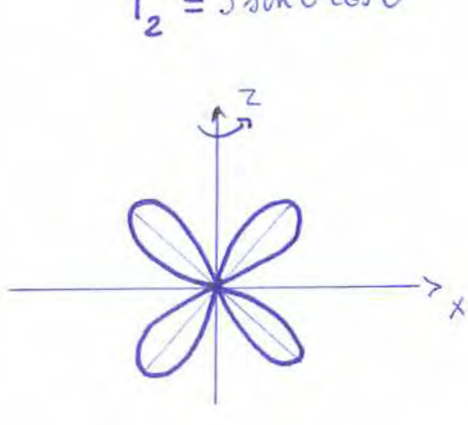


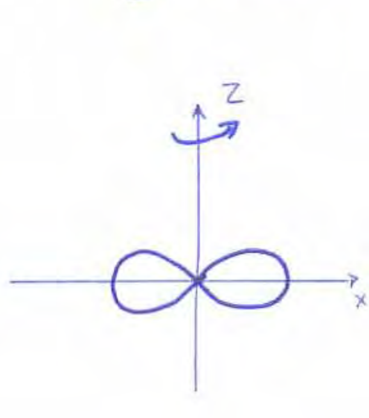
$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$

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

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







↳ NORMALIZATION

$\rightsquigarrow \int d^3\bar{r} \; |\psi|^2 = 1$

$\rightsquigarrow d^3\bar{r} = r^2 \sin\theta \; dr \; d\theta \; d\phi$

$\rightsquigarrow \psi(\bar{r}) = R(r)\, Y(\theta, \phi)$

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

CONVENIENT CHOICE TO NORMALIZE R & Y SEPARATELY

$$\boxed{\begin{gathered}\int_0^\infty dr \; r^2 \; |R(r)|^2 = 1 \\ \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \; |Y(\theta,\phi)|^2 = 1\end{gathered}}$$

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

↳ $m \geq 0$

SPHERICAL HARMONICS

$$Y_{\ell\,-m}(\theta,\phi) = (-1)^m \, Y^*_{\ell m}(\theta, \phi)$$

RADIAL EQUATION

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

↳ CHANGE OF VARIABLES

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

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

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

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

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2 U}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]}_{V_{eff}} U = E\, U}$$

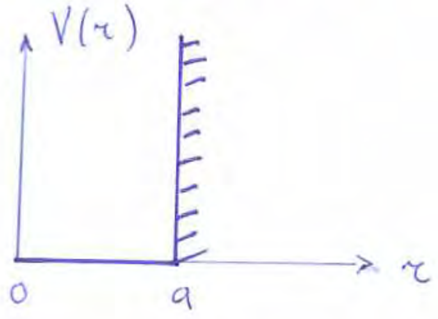
V_{eff} EFFECTIVE POT.

$\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ REPULSIVE CENTRIFUGAL POT.

GROWS FOR LARGER ℓ

↳ NORMALIZATION : $\boxed{\int_0^\infty dr\, |U(r)|^2 = 1}$

↳ INFINITE SPHERICAL WELL



PARTICLE CONFINED IN SPHERE OF RADIUS a

$\therefore$ SOLVE SCHRÖDINGER EQ. FOR W.F. & EIGENVALUES

$r \geq a$: $\quad u(r) = 0$

$r < a$: $\quad -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\,u = E\,u$

$$\boxed{E \equiv \frac{\hbar^2 k^2}{2m}} \qquad \boxed{\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right] u}$$

- $\ell = 0$ $\qquad \frac{d^2u}{dr^2} = -k^2 u$

$$\Downarrow$$

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

$R = \frac{1}{r} u$! $\qquad R(r=0)$ FINITE $\Rightarrow B = 0$

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

$$\therefore \quad \boxed{R(r) = \frac{A}{r} \sin\left(\frac{n\pi}{a} r\right)} \qquad \boxed{E_{n0} = \frac{\hbar^2 n^2 \pi^2}{2m\,a^2}}$$

$\ell = 0$

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

NORMALIZE

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

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

$$\Downarrow$$

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

$\therefore$ ANGULAR PART $\quad \ell = 0, \quad m = 0$

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \qquad \left(\text{INDEED } \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, \frac{1}{4\pi} = 1 \right)$$

$$\psi_{n\ell m} \rightsquigarrow \boxed{\psi_{n00}(\bar{r}) = \sqrt{\frac{1}{2\pi a}} \, \frac{1}{r} \sin\left(\frac{n\pi}{a} r\right)}$$

- SOLUTION FOR ARBITRARY ℓ.

$$\rightsquigarrow \quad \underline{\underline{U(r) = A r\, j_\ell(kr) + B r\, n_\ell(kr)}}$$

$j_\ell(x)$: SPHERICAL BESSEL FUNCTION OF ORDER ℓ

$n_\ell(x)$: SPHERICAL NEUMANN FUNCTION OF ORDER ℓ

$$\rightsquigarrow \quad \boxed{j_\ell(x) = (-1)^\ell x^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x}}$$

$$\rightsquigarrow \quad \boxed{n_\ell(x) = -(-1)^\ell x^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x}}$$

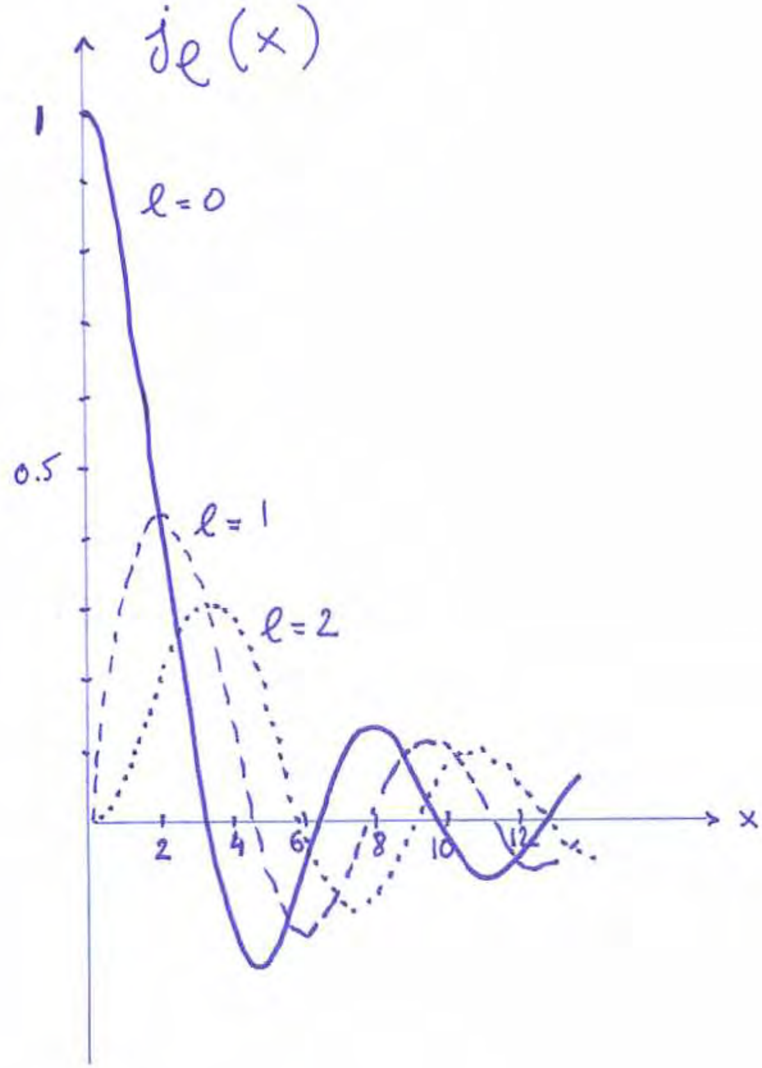
$$\rightsquigarrow \quad j_0(x) = \frac{\sin x}{x}$$

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

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

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

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



$$n_0(x) = -\frac{\cos x}{x}$$

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

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

NOTE $n_\ell(x) \underset{x \to 0}{\longrightarrow} \infty \quad \Longrightarrow \quad B = 0$

$\rightsquigarrow$ CHOOSE k SUCH THAT

$$\underline{\underline{j_\ell(ka) = 0}}$$

$$\Downarrow$$

ZEROES OF BESSEL FUNCTIONS.

$$\boxed{k = \frac{1}{a}\beta_{n\ell}}$$

n-th ZERO OF BESSEL FUNCTION ℓ.

$$\boxed{E_{n\ell} = \frac{\hbar^2}{2ma^2}\beta_{n\ell}^2}$$

EACH LEVEL $n\ell$
IS $(2\ell+1)$ FOLD DEGENERATE
$\forall \ell \Rightarrow m = -\ell, \ldots, 0, \ldots, \ell$

$$\therefore \boxed{\psi_{n\ell m}(\bar{r}) = A_{n\ell}\, j_\ell\left(\beta_{n\ell}\frac{r}{a}\right) Y_{\ell m}(\theta, \phi)}$$

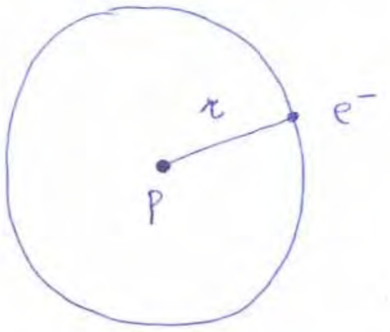
NORMALIZATION.

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

⇒ HYDROGEN ATOM

- COULOMB POTENTIAL

↳



POTENTIAL ENERGY :

$$\boxed{V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}}$$

ε_0 : PERMITTIVITY OF SPACE

$$\varepsilon_0 \simeq 8.854 \; 10^{-12} \; \frac{C^2}{J\,m}$$

↳ RADIAL EQ.

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = E\,u}$$

- **RADIAL WAVE FUNCTION** (FOR BOUND STATES)

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

$$\frac{1}{K^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\varepsilon_0\hbar^2}\frac{1}{K^2 r} + \frac{\ell(\ell+1)}{K^2 r^2}\right]u$$

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

$$\boxed{\rho_0 \equiv \frac{me^2}{2\pi\varepsilon_0\hbar^2 K}}$$

$$\therefore \quad \boxed{\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u}$$

↳ ASYMPTOTIC BEHAVIOR $r \to \infty$, $\rho \to \infty$

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

$$\Downarrow$$

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

BLOWS UP FOR $\rho \to \infty$

↳ BEHAVIOR FOR $r \to 0$

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

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

$$\Downarrow$$

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

BLOWS UP FOR $\rho \to 0$

$\therefore$ CONVENIENT TO TAKE OUT BEHAVIORS OF SOLUTION FOR $\rho \to \infty$ & $\rho \to 0$

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

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

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

$$\therefore \quad \boxed{\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + \left[\rho_0 - 2(\ell+1)\right] v = 0}$$

↳ WRITE SOLUTION AS POWER SERIES IN ρ

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

⇓

DETERMINE COEFFICIENTS

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

$$\frac{d^2 v}{d\rho^2} = \sum_{j=\cancel{1}\,0}^{\infty} j(j+1)\, c_{j+1}\, \rho^{j-1}$$

$$\rightsquigarrow \quad \rho \sum_{j=0}^{\infty} j(j+1)\, c_{j+1}\, \rho^{j-1}$$

$$+ \; 2(\ell+1-\rho) \sum_{j=0}^{\infty} (j+1)\, c_{j+1}\, \rho^j$$

$$+ \; \left[\rho_0 - 2(\ell+1)\right] \sum_{j=0}^{\infty} c_j\, \rho^j \; = \; 0$$

⇓

EQUATING COEFFICIENT OF POWER ρ^j

$$\boxed{\begin{aligned} & j(j+1)\, c_{j+1} + 2(\ell+1)(j+1)\, c_{j+1} \\ & - 2j\, c_j + \left[\rho_0 - 2(\ell+1)\right] c_j = 0 \end{aligned}}$$

$$\Downarrow$$

$$\boxed{c_{j+1} = \frac{\left[2(j+\ell+1) - \rho_0\right]}{(j+1)(j+2\ell+2)}\, c_j}$$

↳ SOLVE RECURSIVELY STARTING FROM C_0

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

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

$$\downarrow$$

$$c_j = \frac{2^j}{j!}\, c_0$$

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

$$\downarrow$$

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

BLOWS UP !

↳ PHYSICAL SOLUTIONS ONLY CORRESPOND WITH A SERIES WHICH <u>TERMINATES</u> !

SUPPOSE MAX VALUE OF j IS j_{max}

$$c_{j_{max}+1} = 0$$

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

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

↳ PRINCIPAL QUANTUM NUMBER (INTEGER)

$$\boxed{\rho_0 = 2n}$$

$$\Downarrow$$

$$E = -\frac{\hbar^2}{2m} \kappa^2 = -\frac{\hbar^2}{2m} \frac{m^2 e^4}{(2\pi\varepsilon_0)^2 \hbar^4 \rho_0^2}$$

$$= -\frac{m e^4}{8\pi^2 \varepsilon_0^2 \hbar^2 4n^2}$$

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \equiv \frac{E_1}{n^2}}$$

BOHR'S FORMULA

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

$$\boxed{E_1 = -\left[\frac{m}{2}\frac{1}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right] = -13.6 \ eV}$$

BINDING ENERGY OF GROUND STATE LEVEL OF HYDROGEN ATOM

$$\begin{cases} \rho_0 = \dfrac{m e^2}{2\pi\varepsilon_0 \hbar^2 K} \\ \rho_0 = 2n \end{cases}$$

$$\boxed{K = \left(\frac{m e^2}{4\pi\varepsilon_0 \hbar^2}\right)\frac{1}{n} \equiv \frac{1}{an}}$$

$$\boxed{a \equiv \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} = 0.529 \ 10^{-10} \ m}$$

BOHR RADIUS

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

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

$\hookrightarrow$ GROUND STATE $n = 1$

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

$$\Downarrow$$

$$n = 1 \iff j_{max} = 0 \ , \ \ell = 0$$

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

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

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

$$\Downarrow$$

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

$$\Downarrow$$

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

$$\therefore \ \boxed{\psi_{n\ell m}(\bar{r}) \Rightarrow \psi_{100}(\bar{r}) = \frac{1}{\sqrt{4\pi}} \cdot \frac{2}{\sqrt{a}} \ \frac{1}{a} \ e^{-r/a}}$$

$\hookrightarrow$ FIRST EXCITED STATE $\quad n = 2$

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

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

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

2 POSSIBLE VALUES OF ℓ

$$\ell = 0 \rightarrow j_{max} = 1$$

$$\ell = 1 \rightarrow j_{max} = 0$$

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

$$c_1 = -c_0$$

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

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

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

↳ ARBITRARY n

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

↓

$$\ell = n - 1 - j_{max}$$

POSSIBLE VALUES OF $\underline{\underline{\ell = 0, 1, \dots, n-1}}$

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

- DEGENERACY OF EACH LEVEL n

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

- POLYNOMIAL $v(\rho)$

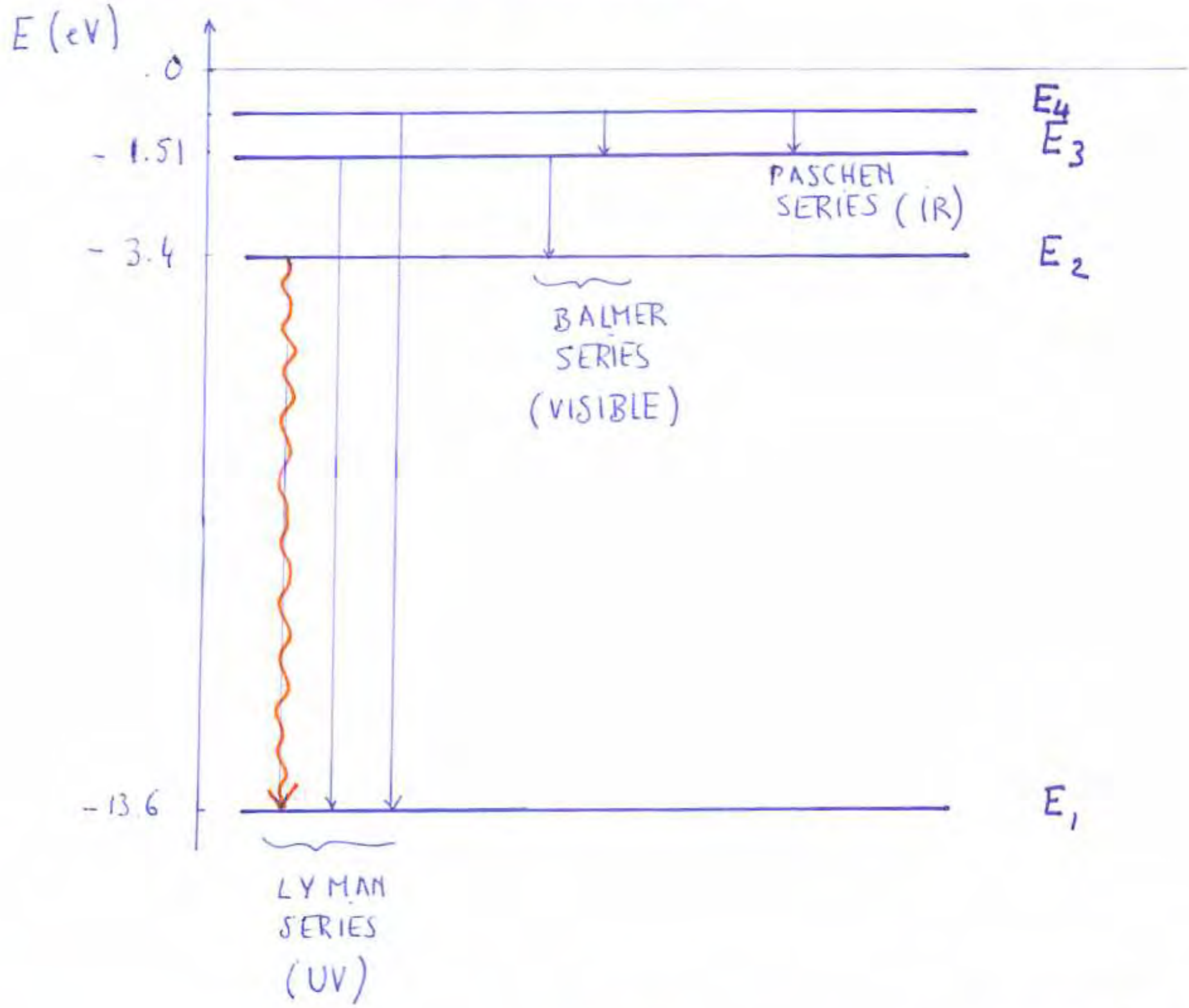
IS A SO-CALLED ASSOCIATED LAGUERRE POLYNOMIAL

$$v(\rho) \equiv L^{2\ell+1}_{n-\ell-1}(2\rho)$$

$$L^{p}_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

LAGUERRE → $$L_q(x) \equiv e^{x} \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

- SPECTRUM OF HYDROGEN



PHOTON IS EMITTED WHEN e^- FALLS INTO DEEPER BOUND STATE

PHOTON IS ABSORBED WHEN e^- IS EXCITED

↳ ENERGY IS CONSERVED

$\therefore$ PHOTON HAS TO TAKE THE DIFFERENCE IN ENERGY

TRANSITION FROM $E_i > E_f$

$\Downarrow$

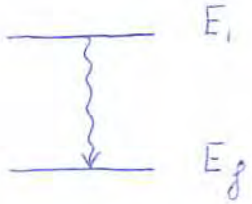
$$E_\gamma = E_i - E_f$$

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

↳ PLANCK's FORMULA

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

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



$$= \frac{(-E_1)}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$-E_1 = \frac{m}{2} \left(\frac{e^2}{4\pi \varepsilon_0} \right)^2 \frac{1}{\hbar^2}$$

$$\boxed{\frac{1}{\lambda} = \underbrace{\left[\frac{m}{4\pi c \hbar^3} \cdot \left(\frac{e^2}{4\pi \varepsilon_0} \right)^2 \right]}_{R\text{ : RYDBERG CONSTANT}} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)}$$

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

⇒ 4.3 ANGULAR MOMENTUM

- **DEFINITIONS**

↳ CLASSICAL

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

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

↳ QUANTUM

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

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

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

- **EIGENVALUES OF ANGULAR MOMENTUM OPERATOR**

↳ $[L_x, L_y] = [y p_z - z p_y,\ z p_x - x p_z]$

$$= [y p_z, z p_x] - [y p_z, x p_z] - [z p_y, z p_x] + [z p_y, x p_z]$$

$$= y p_x \underbrace{[p_z, z]}_{-i\hbar} - 0 - 0 + x p_y \underbrace{[z, p_z]}_{i\hbar}$$

$$= i\hbar (x p_y - y p_x) = i\hbar L_z$$

$$\therefore \quad [L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

$\hookrightarrow$ L_x, L_y, L_z ARE INCOMPATIBLE OBSERVABLES

GEN. UNCERTAINTY RELATION

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

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

NO EIGENSTATES OF BOTH L_x & L_y

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

$$[L^2, L_x] = [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x]$$

$$= L_y [L_y, L_x] + [L_y, L_x] L_y$$

$$+ L_z [L_z, L_x] + [L_z, L_x] L_z$$

$$[L^2, L_x] = L_y(-i\hbar L_z) - i\hbar L_z L_y$$
$$+ L_z(i\hbar L_y) + i\hbar L_y L_z$$

$$= 0$$

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

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

$\hookrightarrow$ LADDER OPERATORS

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

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

$$= \pm \hbar (L_x \pm i L_y)$$

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

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

$\rightsquigarrow$ IF f IS EIGENFUNCTION OF L^2, L_z

$$\Downarrow$$

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

$$\left\| \begin{aligned} L^2 f &\equiv \lambda f \\ L_z f &\equiv \mu f \end{aligned} \right.$$

λ, μ : EIGENVALUES

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

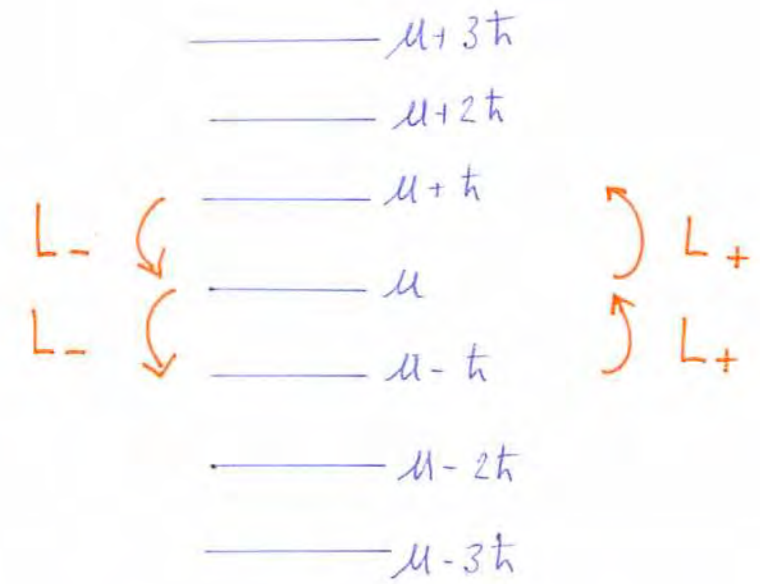
SAME EIGENVALUE

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

$$= (\mu \pm \hbar)(L_\pm f)$$

$L_\pm f$ IS EIGENFUNCTION OF L_z

WITH EIGENVALUE $\mu \pm \hbar$



<u>MAX.</u> VALUE OF L_z (GIVEN BY TOTAL ANG. MOMENTUM)

$$L_+ \, f_{top} = 0$$

<u>MIN</u> VALUE OF L_z

$$L_- \, f_{bottom} = 0$$

DEFINE $L_z \, f_{top} = (\hbar \ell) \, f_{top}$

↳ EIGENVALUE OF TOP STATE

$$L_z \, f_{bottom} = (\hbar \bar{\ell}) \, f_{bottom}$$

$$L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y)$$

$$= L_x^2 + L_y^2 \mp i \underbrace{(L_x L_y - L_y L_x)}_{i\hbar L_z}$$

$$= L^2 - L_z^2 \mp i\,(i\hbar L_z)$$

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

$$\rightsquigarrow \quad L^2 f_{top} = \lambda f_{top}$$

$$= (L_- L_+ + L_z^2 + \hbar L_z)\, f_{top}$$

$$= (0 + \hbar^2 \ell^2 + \hbar^2 \ell)\, f_{top}$$

$$= \hbar^2 \ell(\ell+1)\, f_{top}$$

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

$\uparrow$

EIGENVALUE OF L^2

$$\rightsquigarrow \quad L^2 f_{bottom} = \lambda f_{bottom}$$

$$= \left(L_+ L_- + L_z^2 - \hbar L_z \right) f_{bottom}$$

$$= \hbar^2 \bar{\ell} (\bar{\ell} - 1) f_{bottom}$$

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

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

$$\Downarrow$$

$\cancel{\bar{\ell} = \ell + 1}$ NOT POSSIBLE $\bar{\ell} < \ell$

$\bar{\ell} = -\ell$ 2ℓ is INTEGER

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

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

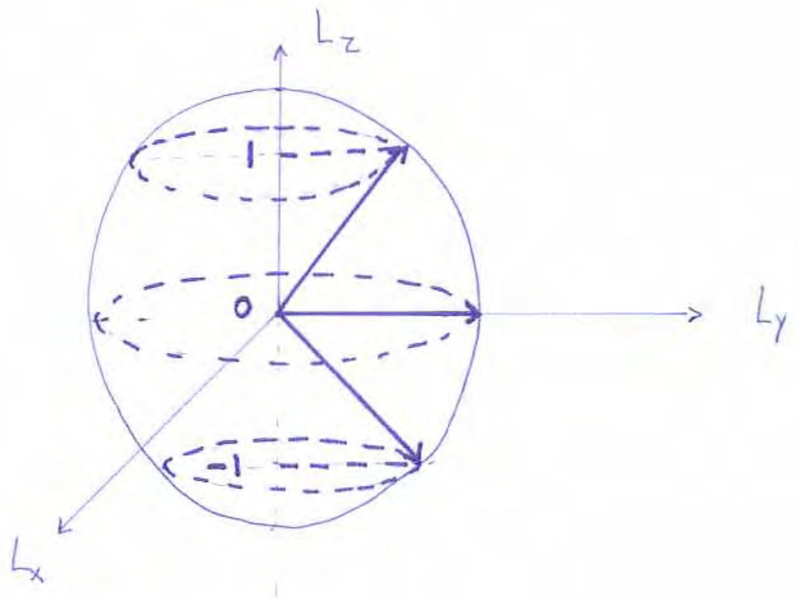
$m = -\ell, \dots, +\ell$ (LADDER)

$$\boxed{\begin{aligned} L^2 f_\ell^m &= \hbar^2 \ell(\ell+1) f_\ell^m \\ L_z f_\ell^m &= \hbar m f_\ell^m \end{aligned}}$$

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

EXAMPLE $\ell = 1$

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



- EIGENFUNCTIONS OF L^2, L_z

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

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

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

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

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

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

EXPRESS $\hat{e}_\phi$, $\hat{e}_\theta$ IN $\hat{\imath}, \hat{\jmath}, \hat{k}$

$\downarrow$

$\rightsquigarrow$ READ OFF L_x, L_y, L_z

$\rightsquigarrow$ CONSTRUCT L_z, $L^2 = L_x^2 + L_y^2 + L_z^2$

$\rightsquigarrow$ VERIFY

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

$\Downarrow$

$$\boxed{f_\ell^m(\theta,\phi) = Y_{\ell m}(\theta,\phi)}$$