

Matter → Bio
Matter → Non-Bio
(Building blocks are atoms)

Energy

Nature

1. Stability

2. Symmetry → Diversity

3. Quantization → Fixation

4. Homogeneity → Uniform manner.

Force applied on matter then it exhibits mechanical properties

Macroscopic → Pressure, Temp. (Bulk Property)
Volume.

Microscopic → Can't see, measure easily/directly,
e.g:- Size of an atom, bond strength
b/w atoms

Model → Simple Repres. of complex phenomena.

Hypothesis Theory → Law

If fits to
existing
facts then

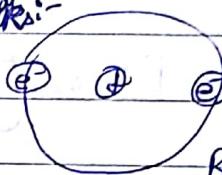
Atomic Models

Ruled Out bcoz
of emission
spectrum not
coming acc. to the
model / theory proposed.

Plum Pudding Model (Dressing the & -ve charge balance with other hence resultant force is zero.)

Rutherford Model

Draw Backs:-



Nucleus, which is present at centre, revolving.

But Electromagnetic Theory proved it wrong as no stability.

Bohr (some fixed orbits are allowed for one...)

$$mv_r = \frac{n(\hbar)}{2\pi} \quad \begin{array}{l} \text{Stationary orbits} \\ \text{No loss of energy} \end{array}$$

$1, 2, 3, \dots$

\rightarrow Stationary wave exists only when $mA = 2\pi r$

$$\text{DeBroglie} \rightarrow \lambda = \frac{\hbar}{mv}$$

Hence Stability &

Quantization both are related

$$\frac{m \ h}{mv} = 2\pi r$$

Explained '5' spectral lines for Hydrogen.

$$(\text{Wave Number}) \bar{v} = R \left[\frac{1}{m_1^2} - \frac{1}{m_2^2} \right]$$

$\bar{v} \leftarrow$
 $\lambda \leftarrow$
Rydberg's Constant.

Lyman's Series (UV region)

Balmer : (Visible region)

Pachmann : (IF)

Brackett : (IF)

Pfund : (IF)

Disadv. :-

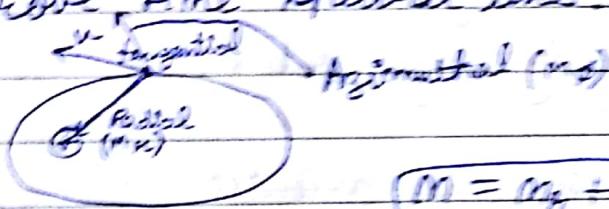
When spectral lines placed in magnetic & electric field, splitting of spectral lines.

(Fine Spectral Lines). This couldn't be explained

Sommerfeld

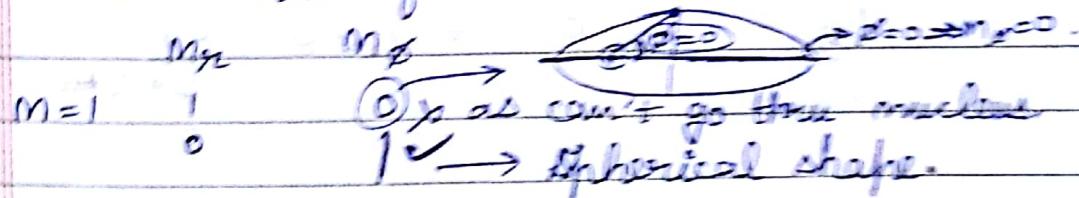
(proposed) E may have elliptical orbits.

to prove fine spectral lines.



$$m = m_z + m_r$$

Allowed Values for $m = 1$



$$m = 2 \quad 2 \quad [0] \times$$

1 1 \rightarrow elliptical. (2, 1, 0 orbit)

0 2 \rightarrow spherical (0 orbit)

couldn't explain fine spectral lines.

RelativisticRelativistic Correction

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

Using Bohr, calculate velocity of e^- . (as to c)

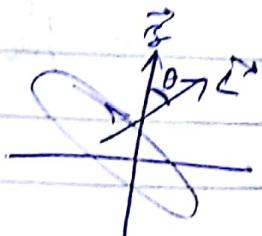
& calculated mass of e^- using $m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$

- Vector Atom Model (Special Quantization of Atoms) Explained Fine Spectral lines

In Bohr theory, 1 degree of freedom

In Sommerfeld, 2 \rightarrow α \rightarrow α

Quantizing α of orbital.



α specifies orientation of orbital

$$l_z = L \cos \alpha \Rightarrow \boxed{\cos \alpha = \frac{l_z}{L \rightarrow \text{Total}}}$$

$$(m_w) = \frac{m \cdot h}{2\pi} \quad (\text{m} = m_\alpha + m_\beta)$$

\downarrow

L

$$L = \textcircled{D} \cdot h$$

Principal Quantum No.	$l = 0$
$m=1$	$l=0, 0$
$m=2$	$l=0, 1$
$m=3$	$l=0, 1, 2$

$$m=1, m_\alpha = 0, m_\beta = 1,$$

$$m=2, m_\alpha = 1, m_\beta = 1 \\ m_\alpha = 0, m_\beta = 2$$

$$m=3, m_\alpha = 0 \\ m_\alpha = 1 \\ m_\alpha = 2$$

Fivefold Modified

$$\cos\theta = \frac{l_z}{l} = \frac{m_l \hbar}{\sqrt{l(l+1)} \hbar} = \frac{m_l}{\sqrt{l(l+1)}}$$

$$l \rightarrow \sqrt{l(l+1)}$$

$$l_z = (m_l) \left(\frac{\hbar}{2\pi}\right)$$

magnetic
quantum
no.

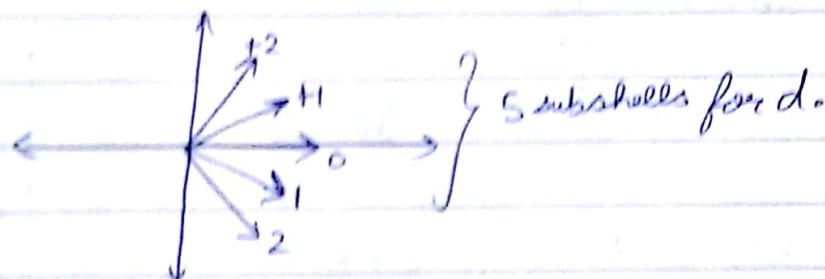
$$\cos\theta \in [-1, 1] \Rightarrow m_l = (\cos\theta) (\sqrt{l(l+1)})$$

$$= [-1, 1] l$$

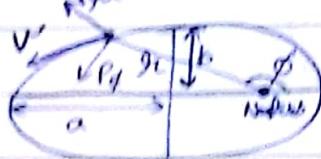
$$= [-l, l].$$

for $l=2$

$$\cos\theta = \frac{m_l}{\sqrt{l(l+1)}} = \frac{-2, -1, 0, +1, +2}{\sqrt{6}} = \frac{-\sqrt{2}}{\sqrt{6}}, \frac{-1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, \frac{\sqrt{2}}{\sqrt{6}}$$



- Using Bohr Theory \rightarrow Find freq. all spectral lines
- Allowed/Possible orientations of f-orbital using vector atom model, identify 7 (ℓ values)
- Sommerfeld.



P_ϕ (Azimuthal component of Momentum)

ϕ is Azimuthal Angle

$$P_\phi = m r^2 \dot{\phi} = m r^2 \frac{d\phi}{dt}$$

$$= m r^2 (\sin 90^\circ)$$

$$\vec{v} = \vec{r} \times \vec{\omega}$$

$$l = \vec{r} \times \vec{v}$$

$$= m (\vec{r} \times \vec{v})$$

$$= m r v (\sin 90^\circ)$$

$$= m r^2 v$$

$$= m r^2 \frac{d\phi}{dt}$$

$$\oint P_r dr = \ell h, \quad r = 1, 2, 3, \dots$$

$$\oint P_\phi d\phi = m h, \quad m = 1, 2, 3, \dots$$

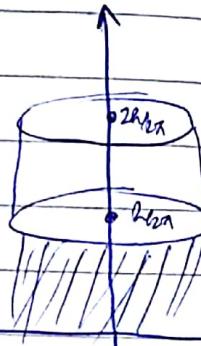
Acc. to Kepler's Laws, Angular momentum remains conserved So, P_ϕ is constant.

$$P_\phi \oint d\phi = P_\phi (2\pi) = \frac{m}{2\pi} h$$

$$\Rightarrow P_\phi = \frac{m}{2\pi} \left(\frac{h}{2\pi} \right)$$

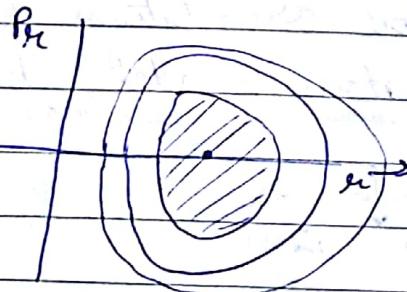
$$m = 1, \quad \frac{h}{2\pi}$$

$$m = 2, \quad \frac{2h}{2\pi}, \dots, \frac{3h}{2\pi}, \frac{4h}{2\pi}$$



$$\frac{m}{r_1 + m} = \frac{b}{a}, \quad m + r_1 = m \Rightarrow \frac{m}{m} = b/a$$

$m \neq 0$, else if $m=0$ then e^- collides with nucleus.



$R \uparrow$ ses, semi-min
 $b \uparrow$ ses & ellipticity
 $a \uparrow$ ses.

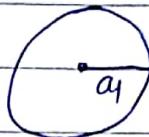
$$a = a_1 \frac{m^2}{2}$$

Bohr's
Radius

$$b = a_1 \frac{m}{2}$$

$Z = 1, m = 1, m = 1, g_z = 0.$ (Hydrogen)

$$a = a_1, b = a_1$$



(Allowed Orbit)

$Z = 2, m = 1, m = 1, g_z = 0.$

$$a = \frac{a_1}{2}, b = \frac{a_1}{2}$$



(Allowed Orbit)



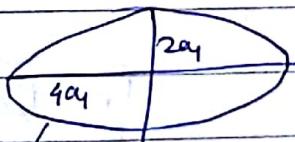
As $Z \uparrow$ ses, radius $\propto \frac{1}{\text{Atomic No.}}$

$Z = 1, m = 2, m = 2, 1, g_z = 0, 1$

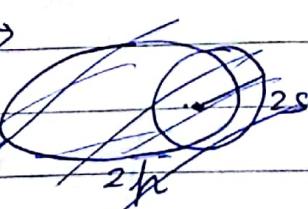
$$g_z = 0, a = \frac{a_1}{4}, b = \frac{a_1}{4}$$



$$m = 2, m = 1 \\ g_z = 1, a = \frac{a_1}{4}, b = \frac{a_1}{2}$$



$g_z \uparrow$ ses, $b \downarrow$ ses.



$$m = 3 \quad m = 2$$

$$g_1 = 0 \quad g_2 = 1$$

$$m = 1 \quad m = 2$$

$$\begin{matrix} Z=1 & 9a_1 & 9a_1 & 9a_1 \\ m=3 & 9a_1 & 6a_1 & 3a_1 \end{matrix}$$

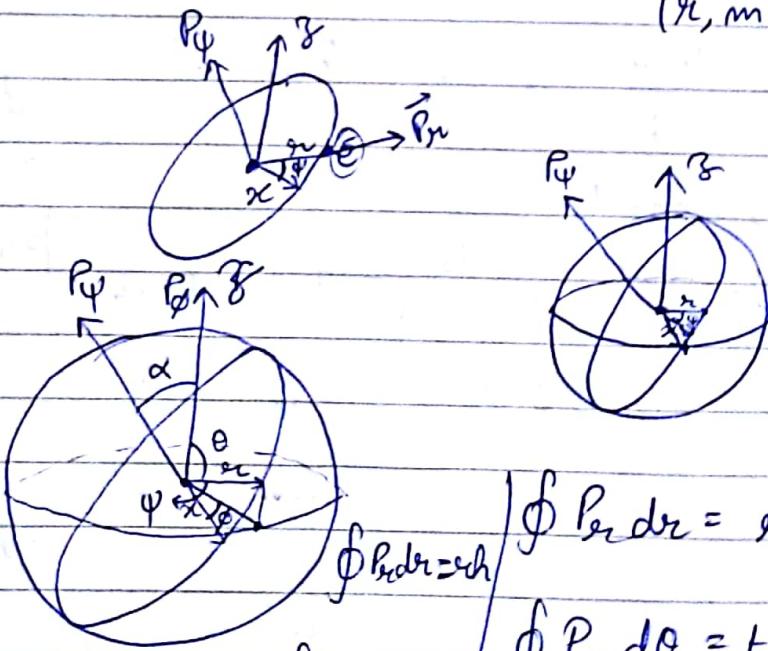
$d \quad p \quad s$

$\left\{ \begin{array}{l} m=2 \\ m=1 \end{array} \right. \rightarrow \text{Both have same energy}$

\rightarrow Two different λ only when different energy of each $m=2$ orbital but Sommerfeld theory failed on fine spectrum.

All orientations are not allowed only particular $n = n$ allowed.

(g_l, m are existing quantum Nos.)



$$\int P_r dr = g_l h$$

$$\int P_\phi d\psi = k h$$

$$\int P_\theta d\theta = t h$$

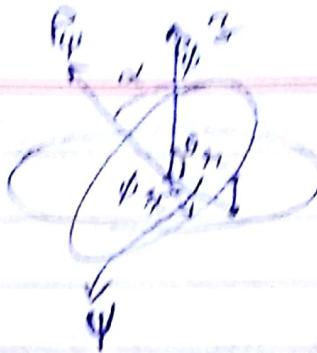
$$g_l + k = g_l + t + l_m \Rightarrow k = t + m$$

(Total Momentum Constant)

Sommerfeld model
 $m \neq 0$

$m=0$ allowed discrete

Date
Page



$$(\cos\alpha) P_{ip} = P_{ix}$$

$$\Rightarrow \left[\cos\alpha \frac{P_{ix}}{P_{ip}} \right] = \frac{m}{l}$$

l_1

$m = \pm 1$

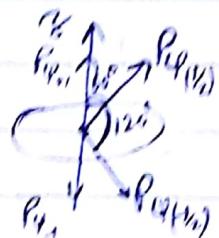


$l_2 = 2$

$m = \pm 2, \pm 1$

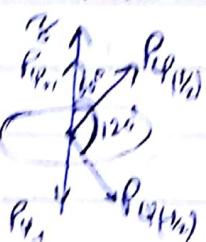
$$\cos\alpha = \pm \frac{1}{2}, \pm 1$$

$\alpha = 60^\circ, 120^\circ, 0^\circ, 180^\circ$



$l_3 = 3$

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

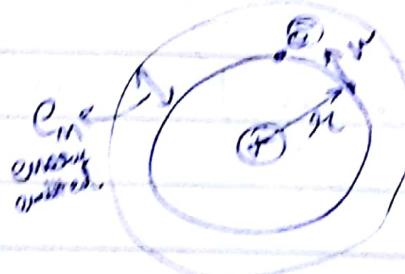


→ De Broglie's Hypothesis, Heisenberg's Uncertainty Principle

Classical Mechanical & Wave Mechanics become somewhat large in value quantum mechanics

Modern Physics by Arthur Beiser.

Bohr Correspondence principle



if it revolves 100 times
the freq. emitted
will be 100 Hz.

$$V = \frac{2\pi r}{T} \Rightarrow \frac{1}{T} = \frac{V}{2\pi r}$$

$$\Rightarrow f = V = \frac{V}{2\pi r}$$

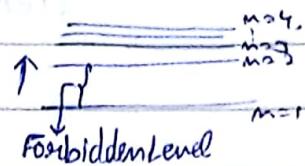
$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$mv^2 = \frac{mr}{2\pi}$$

Can find v, ϵ_m
then
if we can get $\nu = \frac{v}{2\pi R}$

Energy emitted $\leftarrow \epsilon_m = R \left(\frac{1}{m_1^2} - \frac{1}{m_2^2} \right) = h\nu$

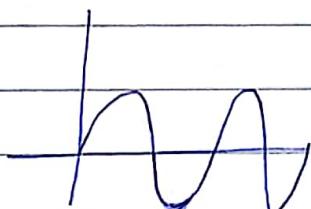
$$\Rightarrow \nu = \frac{R}{h} \left(\frac{1}{m_1^2} - \frac{1}{m_2^2} \right)$$



Wave Mechanical Model (Wave Mechanics)

$$\lambda = \frac{h}{mv} = 6.62 \times 10^{-34} \text{ J-sec.}$$

$$y = A \sin(\omega t - kx) \text{ or } A \cos(\omega t - kx).$$



$2\pi/k$ (Phase variation)
 x (Distance travelled)

Matter Wave :- Periodic ^{variation of} wave function. Not constituted of single wave.

Composed of Multiple Waves with superimposing wavelengths.

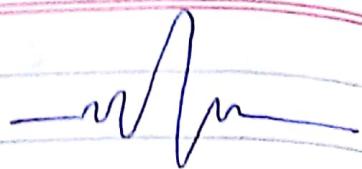
$$y_1 = A_1 \cos(\omega t - kx)$$

$$y_2 = A_2 \cos((\omega + dw)t - (k + dk)x)$$

Superimposition
Motion of Matter wave

Phase Velocity & Group Velocity

$$Y_{\text{total}} = Y_1 + Y_2$$



Wave Packet.

Wave Funct^m

ψ , ψ^2
Probability of Actual Significance

finding one (0 or 1) but ψ gets -ve values at some time.

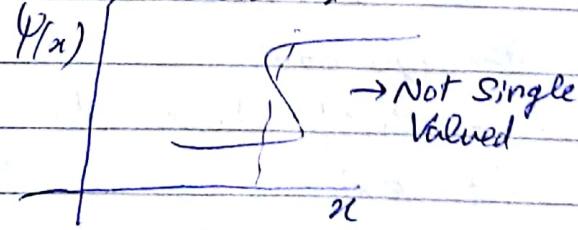
So, ψ^2 to avoid -ve values.

ψ^2 = Probability Density = Prob. of finding in a volume dV in unit volume

$$\int \psi^2 dV = \iiint_{x=0, y=0, z=0}^{\infty \infty \infty} \psi^2 dx dy dz = 1 \quad (\text{Can find any where in universe})$$

$$\psi^2 = \psi \psi^*$$

- Wave Funct^m (ψ) must be single valued at given point / location.

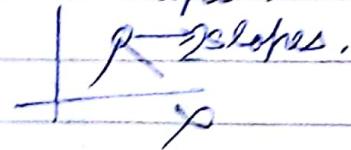


Wrong Graph

curvature

- Ψ should not be ∞ .

- Ψ should be continuous & its 1st Derivative must be continuous.



Normalization $\rightarrow 1 = N \int_{-\infty}^{\infty} |\Psi|^2 dV$
or that Probability
is 1 (Valid)

$$\Psi = A e^{-i(\omega t - kx)} \quad \frac{\partial^2 \Psi}{\partial t^2} = \frac{1}{m} \frac{\partial^2 \Psi}{\partial x^2}$$

$$\Psi(x, t) = A e^{-i(\omega t - kx)}$$

$$= A e^{-i(2\pi\nu t - \frac{2\pi}{\lambda}x)} = A e^{-2\pi i(\nu t - \frac{x}{\lambda})} \quad \textcircled{1}$$

$E = h\nu$ (Energy Frequency Relationship)

$$= \frac{h}{2\pi} (2\pi\nu) = \frac{h}{\lambda} (\nu)$$

$$\Rightarrow \boxed{\nu = \frac{c}{\lambda(2\pi)}} \quad \textcircled{2}$$

$$\lambda = \frac{h}{\nu} = \frac{2\pi h}{h(2\pi)} = \boxed{\frac{2\pi h}{h}} \quad \textcircled{3}$$

Using $\textcircled{2}$ & $\textcircled{3}$ in $\textcircled{1}$:-

$$\Psi(x, t) = A e^{-2\pi i \left(\frac{E}{\hbar} t - \frac{x}{\lambda} \right)} = \boxed{A e^{\frac{-i}{\hbar} (Et - x\lambda)}}$$

$$E = \frac{p^2}{2m} + U(x). \Rightarrow E \Psi(x, t) = \frac{p^2}{2m} \Psi(x, t) + U(x) \Psi(x, t).$$

$$-i\hbar(Et - Px)$$

$$\frac{\partial \Psi(x,t)}{\partial t} = A e^{-i\hbar(Et - Px)}$$

$$X\left(\frac{-iE}{\hbar}\right)$$

$$\Rightarrow E\Psi(x,t) = \Psi(x,t) \times \left(\frac{-i}{\hbar}\right) E.$$

$$\Rightarrow [E\Psi(x,t) = \frac{\partial \Psi(x,t)}{\partial t} \times \left(\frac{-i}{\hbar}\right) E]$$

$$\frac{\partial \Psi(x,t)}{\partial x} = A e^{-i\hbar(Et - Px)} \times iP \frac{d}{dt}$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = A e^{-i\hbar(Et - Px)} \times \left(\frac{iP}{\hbar}\right)^2$$

$$= \Psi(x,t) \times \left(-\frac{P^2}{\hbar^2}\right)$$

$$\Rightarrow \boxed{P^2\Psi(x,t) = -\hbar^2 \frac{\partial^2 \Psi(x,t)}{\partial x^2}}$$

$$E\Psi(x,t) = \left(\frac{P^2}{2m}\right) \Psi''(x,t) + V(x)\cdot \Psi(x,t)$$

$$\Rightarrow \boxed{\frac{\partial \Psi(x,t)}{\partial t} \times \left(\frac{-i}{\hbar}\right) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\cdot \Psi(x,t)}$$

(Schrodinger Time ^{dependent} Eqn)

W/o excitation, i.e. no change w.r.t time, only $V(x)$ is important.

$$\begin{aligned} \Psi(x,t) &= A e^{-i\frac{Et}{\hbar}} \cdot e^{\frac{iPx}{\hbar}} \\ &= \Psi(x) \cdot e^{-i\frac{Et}{\hbar}} \end{aligned}$$

$$\frac{\partial \Psi(x,t)}{\partial t} = \Psi(x) \cdot e^{-i\frac{Et}{\hbar}} \times \left(-\frac{iE}{\hbar}\right)$$

$$\Rightarrow \boxed{\frac{\partial^2 \psi(x,t)}{\partial t^2} = \frac{\partial^2 \psi(x)}{\partial x^2} \cdot e^{-\frac{iEt}{\hbar}} \times \cancel{X} \left(\frac{-iE}{\hbar} \right) - \cancel{e^{-\frac{iEt}{\hbar}}} \downarrow \text{put in } (4)}$$

$$\cancel{\frac{iE}{\hbar} X \cancel{e^{-\frac{iEt}{\hbar}}} \times \psi(x)} \cdot \cancel{e^{-\frac{iEt}{\hbar}}} = \frac{-\hbar^2}{2m} \times \frac{\partial^2 \psi(x)}{\partial x^2} \cdot \cancel{e^{-\frac{iEt}{\hbar}}} + U(x) \cdot \psi(x) \cdot \cancel{e^{-\frac{iEt}{\hbar}}}$$

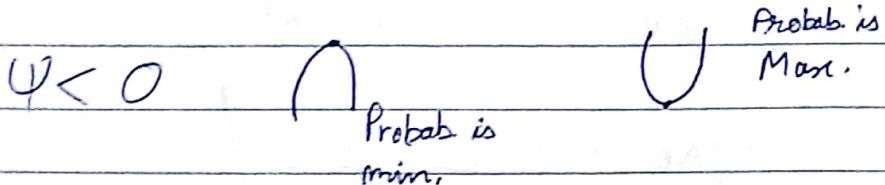
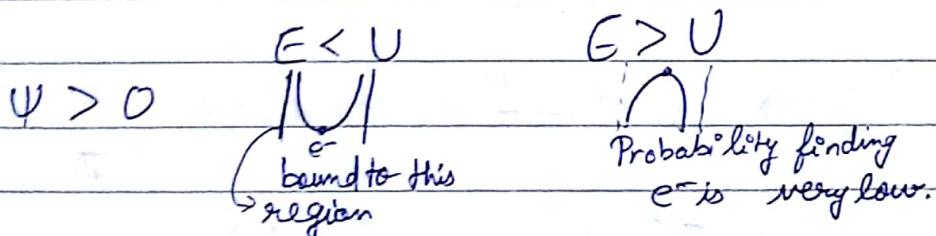
$$\Rightarrow E \times \psi(x) = -\frac{\hbar^2}{2m} \times \frac{\partial^2 \psi(x)}{\partial x^2} + U(x) \psi(x)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x)}{\partial x^2} \right) = \psi(x) [E - U(x)]$$

$$\Rightarrow \boxed{\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} [E - U(x)] \psi(x) = 0}$$

↓ ↓
Sum of Only
K.E & P.E. P.E.

If $E > U(x)$ then e^- becomes free whereas $U(x) > E$ then e^- bounded to system & don't participate in bond formation.



$$\frac{\partial \Psi(x,t)}{\partial t} = A e^{\frac{i\hbar}{\hbar}(Et - \frac{p}{\hbar}x)} (-\frac{i}{\hbar}) \epsilon$$

$$= \Psi(x,t) \left(\frac{-1}{\hbar} \right) \epsilon$$

Eigenvalue

$$\epsilon \Psi(x,t) = (i\hbar) \frac{\partial \Psi(x,t)}{\partial t}$$

Energy operator: $\rightarrow \hat{E} = i\hbar \frac{\partial}{\partial t}$

$$\frac{\partial \Psi(x,t)}{\partial x} = \Psi(x,t) \left(\frac{iP}{\hbar} \right)$$

$$\Rightarrow P \Psi(x,t) = \frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x}$$

$$\hat{P} = -i\hbar \frac{\partial}{\partial x}$$

$$k = E = P^2 / 2m$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \Psi(x,t) \left(\frac{-P^2}{\hbar^2} \right)$$

$$\Rightarrow -\frac{P^2}{2m} \Psi(x,t) = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2}$$

$$\Rightarrow \hat{k}^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

$$\begin{aligned} E \Psi(x) &= U_0 \Psi(x) - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} \\ &= \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \Psi(x). \end{aligned}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{U} \rightarrow \text{Hamiltonian Operator}$$

Expectation Value

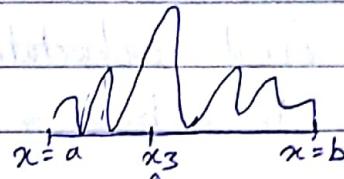
$$N_1 \rightarrow x_1$$

$$N_2 \rightarrow x_2$$

$$N_3 \rightarrow x_3$$

:

$$N_n \rightarrow x_m$$



$$x = \frac{N_1 x_1 + N_2 x_2 + \dots + N_m x_m}{N_1 + N_2 + \dots + N_m} \quad (\text{Avg. Position of particle.})$$

Probability of finding ^{ith} particle at $x_i \rightarrow |\Psi_i|^2$

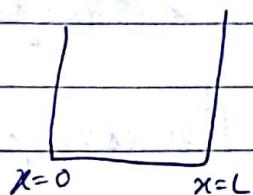
$$x_2 \rightarrow |\Psi_2|^2$$

$$x_3 \rightarrow |\Psi_3|^2$$

$$\langle x \rangle = \frac{x_1 |\Psi_1|^2 + x_2 |\Psi_2|^2 + \dots}{|\Psi_1|^2 + |\Psi_2|^2 + \dots}$$

Most probable position of *i*th particle.

$$\langle x_i \rangle = \frac{\int_{x=0}^L x_i |\Psi_i|^2 dx}{\int |\Psi_i|^2 dx}$$



$$\langle P \rangle = \int_{-\infty}^{\infty} \psi^* \hat{P} \psi dx$$

(Expectation
momentum)

$$= \int_{-\infty}^{\infty} (\hat{P}) \psi^* \psi dx = (\psi^* \psi) \Big|_{-\infty}^{\infty}$$

Normalizing factor

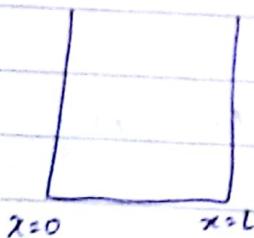
$$\langle \theta \rangle = \int_{-\infty}^{\infty} \psi^* \hat{\theta} \psi dz$$

$\int dx dy dz$

Q: Find expectation value of pos. of particle trapped in a box of length L.

$$\Psi_m(x) = \left(\sqrt{\frac{2}{L}} \right) \sin \left(\frac{m\pi x}{L} \right)$$

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



Def.

$$\langle x \rangle = \int_0^L \left(\sqrt{\frac{2}{L}} \sin \left(\frac{m\pi x}{L} \right) \right)^2 x dx$$

$$= \frac{2}{L} \int_0^L x \sin^2 \left(\frac{m\pi x}{L} \right) dx$$

$$= \frac{1}{L} \int_0^L x \left(1 - \cos \left(\frac{2m\pi x}{L} \right) \right) dx$$

$$= \frac{1}{L} \int_0^L (2x - x \cos \left(\frac{2m\pi x}{L} \right)) dx$$

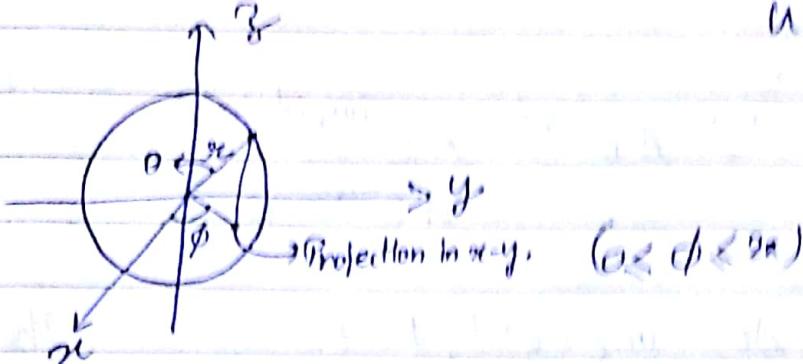
$$= \frac{L}{2} - \int_0^L x \cos \left(\frac{2m\pi x}{L} \right) dx$$

$$= \boxed{\frac{L}{2}}$$

Quantum Theory of H atom.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} [E - U] \cdot \psi(r, \theta, \phi) = 0,$$

$$U = \frac{-e^2}{4\pi\epsilon_0 r}$$



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

$$\frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi = 0$$

$$\psi(r, \theta, \phi) \equiv R(r) \Theta(\theta) \Phi(\phi)$$

$$\frac{\partial^2 \Phi}{\partial \phi^2} + m_p^2 \Phi = 0$$

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

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2m}{\hbar^2} r_i^2 \left[\frac{e^2}{4\pi\epsilon_0 r} + C \right] = \rho(\theta)$$

$$\frac{\partial^2 \psi}{\partial \theta^2} + m^2 \psi = 0$$

(SHM like
equation)

$$\psi = A e^{im\theta}$$

$$\psi(\theta) = \psi(\theta + 2\pi)$$

$$\therefore A e^{im\theta} = A e^{im(\theta + 2\pi)} \\ = A e^{im\theta} \cdot e^{im2\pi}$$

So, $m = g \pm 1, \pm 2, \dots$ Then only
(Discrete Values)

Principal Quantum No. related to g .

g varies, θ varies

Given value θ , many values of g .

Quantum No. associated with $\theta > \phi(l)$
 g with that of $\theta > \theta$.
(n)

Types of Wave Functions

Symmetric (Ψ_S) & Antisymmetric (Ψ_A)

$\Psi_1 \rightarrow$ Wave functⁿ of particle 1.

$\Psi_m \rightarrow$ _____
m,

No interactⁿ b/w them

$\Psi = \Psi_1 \cdot \Psi_2 \dots \cdot \Psi_m$ if

$$\Psi(\psi \downarrow \psi \downarrow)$$

$m \quad l \quad m_e$

classmate

Date _____

Page _____

Particle 1 \rightarrow be in state 'a' (Fixed m, l, m_e for it)
 - - - 2 \rightarrow n n n 'b' (- n - - -)

$$\Psi_I = \Psi_a(1) \cdot \Psi_b(2), \quad \Psi_{II} = \Psi_a(2) \cdot \Psi_b(1)$$

Symmetric $\Psi = \frac{1}{\sqrt{2}} (\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1))$
 For Bond Formation No. of particles Normalization.

Anti-sym. $\Psi_A = \frac{1}{\sqrt{2}} (\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1))$

If $a=b$, then $\Psi_A = 0$ (So, By Pauli's Exclusion Principle no 2 e-i-s can have same states)

"Wave funct" can be used to determine energy.

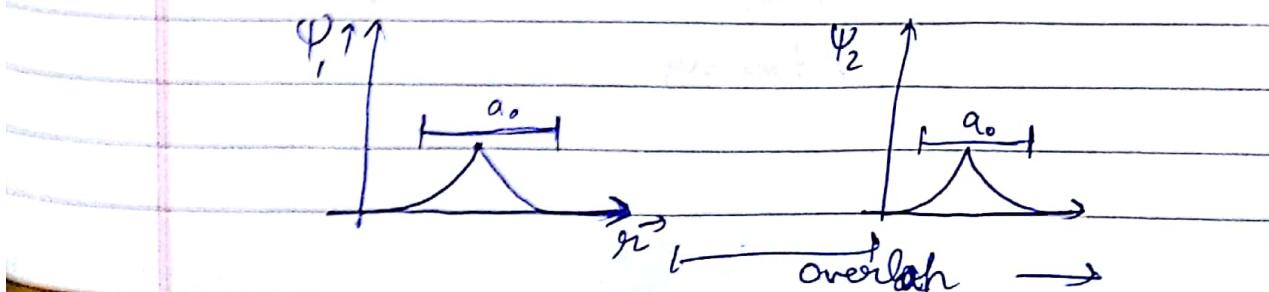
1, a	2, b	(Different m, l, m_e)
$\Psi_a(1)$	$\Psi_b(2)$	

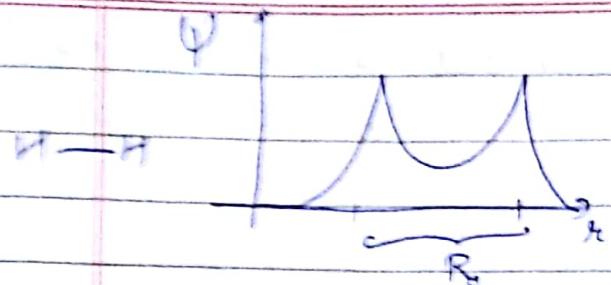
$\Psi_I = \Psi_a(1) \Psi_b(2)$ (If non-interacting).
 both are

$$\Psi_{II} = \Psi_a(2) \Psi_b(1)$$

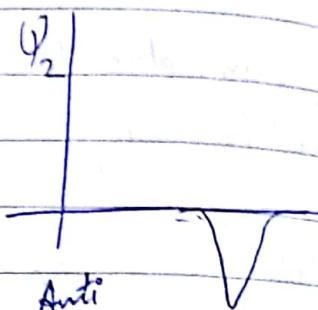
$$\Psi_{\text{symmetric}} = \frac{(\Psi_I + \Psi_{II})}{\sqrt{2}} \quad \& \quad \Psi_{\text{anti}} = \frac{(\Psi_I - \Psi_{II})}{\sqrt{2}}$$

$a \neq b$ from Pauli's Exclusion principle.

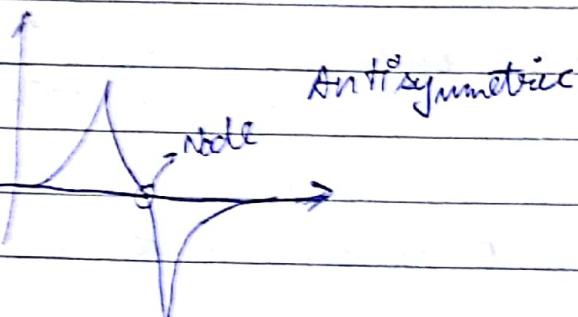




Symmetric Overlap
gives ~~symmetry~~
stability.



Anti



Antisymmetric

For formation of stable bond b/w 2 atoms,
wave funct's. should be symmetric

$$\Psi(x)$$

exchange changes sign.

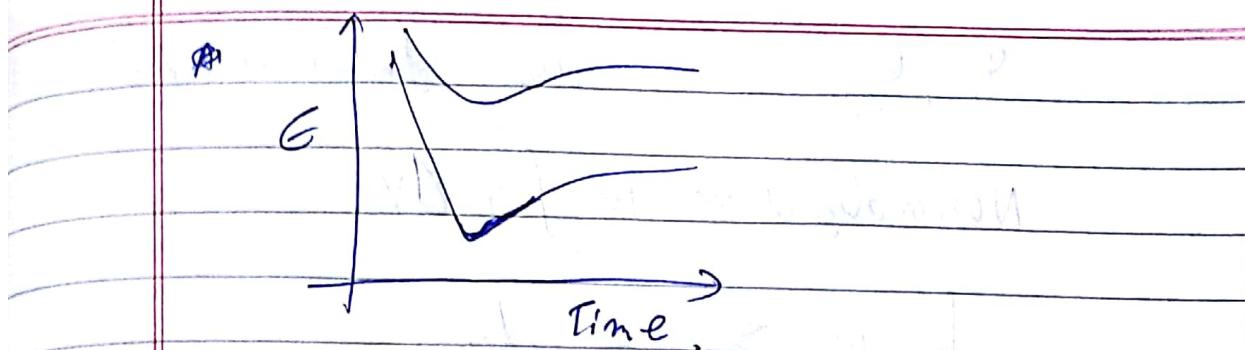
$$\Psi_A = \Psi_S S_A$$

Actual

$$\Psi_A = \Psi_A S_S$$

Symmetric

Antisymmetry



Symmetry over ~~shift~~ coordinates

Exchange of e^- over ~~shift~~ or anti-symmetric is more stable.

Molecular Orbital Theory (MOT)

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{p=1}^N \nabla_p^2 - \frac{\alpha^2}{2m} \sum_{j=1}^m \nabla_j^2 - \sum_{p=1}^N \sum_{j=1}^m \frac{Z_j e^2}{r_{pj}}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

distance b/w i^{th} nuclei & j^{th}

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{j=1}^m \nabla_j^2 - \sum_{i=1}^N \sum_{j=1}^m \frac{Z_i e^2}{r_{ij}} + \sum_{j < k} \frac{e^2}{r_{jk}} + \sum_{l < L} \frac{Z_l Z_e}{r_{el}}$$

nucleus-nucleus ~~attraction~~ repulsion

$$\hat{H} \Psi_{m_0} = \sum \Psi_{m_0} \rightarrow \text{condition}$$

$$\text{Complete wave funct}^n = \Psi_{m_0} = C_1 \Psi_1 + C_2 \Psi_2 + C_3 \Psi_3 \dots$$

$\Psi_1, \Psi_2, \dots, \Psi_m$ should satisfy individually.

ψ_1, ψ_2 are ~~orthogonal~~ ^{->} ~~orthonormal~~

Normalized $\Rightarrow 1 = \int_{-a}^a \psi^2 dV$.

$$\int \psi_i \psi_j \sum_p g^p \psi_p dV$$

$$= \sum_p g_p \underbrace{\int \psi_i \psi_j dV}_{\text{Kronecker Delta}} = \sum_p g_p \delta_{ij}$$

$$= \sum_{p \neq j} g_p^2$$

$$= \boxed{0}$$

$$\int \sum_p g^p \psi_p \hat{H} \sum_j g^j \psi_j dV$$

$$\sum_p \sum_j g^p g^j \int \psi_i \hat{H} \psi_j dV = \sum_p \sum_j g^p g^j E_j \int \psi_i \psi_j dV$$

$$\sum_p g^p \psi_p = \sum_p \sum_j g^p g^j E_j \delta_{ij}$$

$$\Rightarrow \boxed{\sum_p g^p \psi_p}$$

Coefficients are not important
Variation Principle \rightarrow Every sys. there is a lowest energy.