⇒ PRAKASH JOSHI

⇒ Quantum Chemistry

⇒ Date: 12 march 2016

QUANTUM

Eigen value and Eigen function:

$$\frac{d}{dx} e^{-iKx} = -iK\, e^{-iKx} \Rightarrow \text{eigen value equation}$$

$\frac{d}{dx}$ ⇓ operator

e^{-iKx} ⇒ eigenfunction

$-iK$ ⇓ eigen value

$$\hat{O} f(x) = c f(x) \Rightarrow \text{eigen value equation}$$

$\hat{O}$ → operator

$f(x)$ → eigen fun^n

c → eigen value

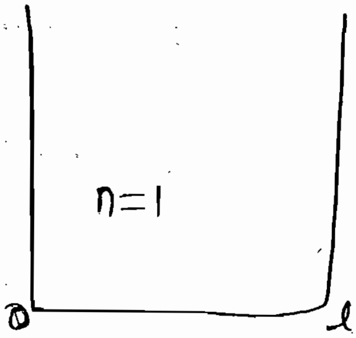
In this, Its not a property of operator or function any ~~per~~ operator or funtion may or may not be eigen valuecable
⇒ It depends on both function and operator.

$$\frac{d}{dx}(e^{ax}) = ae^{x} \checkmark$$

$$\frac{d}{dx} \sin(ax) = a\cos x(x)$$

eigenvalue for :

$$\psi_1 = \sqrt{\frac{2}{l}} \sin\left(\frac{\pi x}{l}\right)$$



momentum operator:

$$p_x \psi = ? \, \psi_1$$

$$\frac{d}{dx}\sqrt{\frac{2}{l}} \sin\left(\frac{\pi x}{l}\right) = \sqrt{\frac{2}{l}} \cos\left(\frac{\pi x}{l}\right) \cdot \frac{\pi}{l}$$

$$\frac{d}{dx}\sqrt{\frac{2}{l}} \sin\left(\frac{\pi x}{l}\right) = \frac{2\pi}{l^{3/2}} \cos\left(\frac{\pi x}{l}\right)$$

$$i\hbar \frac{\partial}{\partial x}\sqrt{\frac{2}{l}} \sin\left(\frac{\pi x}{l}\right) = i\hbar \frac{\times 2\pi}{l^{3/2}} \cos\left(\frac{\pi x}{l}\right)$$

$$p_x \sqrt{\frac{2}{l}} \sin\left(\frac{\pi x}{l}\right) = i\hbar \frac{\pi}{l^{3}} \sqrt{\frac{2}{l}} \cos\left(\frac{\pi x}{l}\right)$$

Bra-Ket Algebra: / Ket-Bra-algebra:

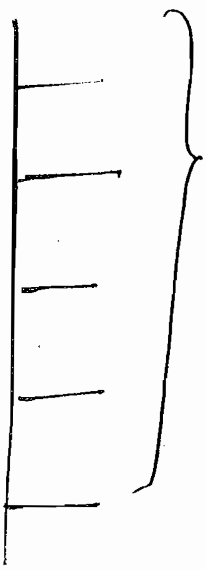
$\langle|$ ⇓ Bra

$|\rangle$ ⇓ Ket

$$(|\psi_3\rangle)^* = \langle\psi_3|$$

(Ket) = Bra- / Rawmatrices

State vector are column matrices. conjugation of column becomes Row.



basis = orthonormal set of state

$2p_x, 2p_y\ 2p_z$ $\quad \langle 2p_x|2p_x\rangle = 1$

$\{p_x, p_y, p_z\}$ $\quad \langle 2p_x|2p_y\rangle = 0$

H $(1s^1) \Rightarrow$ basis (no. of atomic orbital which will take part in a molecular orbitals.

$$\langle\phi_1|\phi_1\rangle = 1$$

$\langle\phi_1|\phi_2\rangle = 0$ one Electron cant be reach at two ~~step~~ state at one time so it shouldd be allways zero.

Suppose we took a basis

$\{\phi_1, \phi_2, \phi_3\}$

ψ (Ketvector) $\doteq 2i|\phi_1\rangle + 3i|\phi_2\rangle - i|\phi_3\rangle$

$\psi_N = ?$

$$\psi = \left(2i|\phi_1\rangle + 3i|\phi_2\rangle - i|\phi_3\rangle\right) N$$

Now $N^2 \langle\psi|\psi\rangle = 1$

$$N^2 c = 1$$

Normalised constant $= \boxed{N = \frac{1}{\sqrt{c}}}$

$\Rightarrow$ $\{\phi_1 \; \phi_3\}$

$\langle\,|$ = Bravector $\Downarrow$ Row

$|\,\rangle$ = Ketvector $\Downarrow$ Column

$$|\psi\rangle = 2i|\phi_1\rangle - 3|\phi_2\rangle$$

$$2|\phi_1\rangle \equiv |2\phi_1\rangle$$

$$3i|\phi_1\rangle = |3i\phi_1\rangle$$

$$\langle 2i\phi_1| = \langle\phi_1|(-2i)$$

$$\langle\phi_2|2i|\phi_1\rangle = \langle -2i\phi_2|\phi_1\rangle$$

$$= \langle\phi_2|2i\phi_1\rangle$$

$$\Rightarrow \quad \langle \phi_2 | -3i\,\phi_1\rangle \qquad (1) \qquad \langle \phi_2 | 2i | \phi_1\rangle$$

Bra : Ket

$$\langle +3i\,\phi_2 | \phi_1\rangle$$

$$\langle \phi_2 | -3i | \phi_1\rangle$$

$$\Rightarrow \quad \langle \phi_1 | \phi_2\rangle \ \times$$

$$\Rightarrow \quad \langle \phi_1 | \phi_2\rangle^* = \langle \phi_2 | \phi_1\rangle$$

$$\Rightarrow \quad \langle 2i\,\phi_1 | \phi_2\rangle^* = \langle \phi_2 | 2i\,\phi_1\rangle$$

Flip

$\Rightarrow$ Q $\quad |\psi\rangle = 2i|\phi_1\rangle - 3i|\phi_2\rangle + 5|\phi_3\rangle$

$$\langle \psi | = (|\psi\rangle)^*$$

$$= \left(2i|\phi_1\rangle - 3i|\phi_2\rangle + 5|\phi_3\rangle\right)^*$$

$$= \cancel{5 \neq 0} \ \cancel{\ldots} - 3i$$

$$= \langle \phi_3 | 5 + \langle \phi_2 | (-3i) + \langle \phi_1 | 2i$$

$\otimes$

$$|\psi\rangle = |2i\phi_1\rangle + |-3i\phi_2\rangle + 5|5\phi_3\rangle$$

$$\langle\psi| = (|\psi\rangle)^* = \left(|2i\phi_1\rangle + |-3i\phi_2\rangle + 5|5\phi_3\rangle\right]^*$$

$$|\psi| = \langle 2i\phi_1| + \langle -3i\phi_2| + \langle 5\phi_3|.$$

$$\underline{\langle\psi| = -2i\langle\phi_1| + 3i\langle\phi_2| + 5\langle\phi_3|}$$

Q $\Rightarrow$ Conversion ket to Bra:

$$|\psi\rangle = -i|\phi_1\rangle + 3i|\phi_2\rangle - i|\phi_3\rangle$$

$$\langle\psi| = (|\psi\rangle)^* = \left(|(-i)\phi_1\rangle + |3i\phi_2\rangle + |-i\phi_3\rangle\right)^*$$

$$\langle\psi| = \langle -i\phi_1| + \langle\phi_2 3i| + \langle\phi_3(-i)|$$

$$\langle\psi| = i\langle\phi_1| - 3i\langle\phi_2| + i\langle\phi_3|$$

$\Rightarrow$
$$\langle\psi| = 2i\langle\phi_1| - i\langle\phi_2|$$

$$\langle\psi| = \langle -2i\phi_1| + \langle i\phi_2|$$

$$|\psi\rangle = (\langle\psi|)^2 = \left((\langle -2i\phi_1| + \langle i\phi_2|\right)^*$$

$$= |-2i\phi_1\rangle + |i\phi_2\rangle$$

$$|\psi\rangle = -2i|\phi_1\rangle + i|\phi_2\rangle.$$

$\Rightarrow \quad |\psi\rangle = |\phi_1\rangle - 2|\phi_2\rangle$

$\langle\psi_1| = \langle\phi_1| - 2\langle\phi_2|$

$\langle\psi|\psi\rangle = (\langle\phi_1| - 2\langle\phi_2|)(|\phi_1\rangle - 2|\phi_2\rangle)$

$= 1 + 4\times 1$

$\underline{\underline{\langle\psi|\psi\rangle = 5}}$

$\Rightarrow \quad |\psi\rangle = 3i|\phi_1\rangle + 2i|\phi_2\rangle - 3i|\phi_3\rangle$

$\langle\psi| = -3i\langle\phi_1| - 2i\langle\phi_2| + 3i\langle\phi_3|$

$\langle\psi|\psi\rangle = (-3i\langle\phi_1| - 2i\langle\phi_2| + 3i\langle\phi_3|)\times(3i|\phi_1\rangle + 2i|\phi_2\rangle - 3i|\phi_3\rangle)$

$= +9 + 4 + 9$

$\langle\psi|\psi\rangle = \cancel{} = \underline{\underline{+22}}$

(B) $|\alpha\rangle = i|1\rangle - 2|2\rangle - i|3\rangle$, $\langle\alpha| = -i\langle 1| - \langle 2|2 + \langle 3|i$

$|\beta\rangle = i|1\rangle + 2|3\rangle$

$\langle\alpha|\beta\rangle = (-i\langle 1| - \langle 2|2 + \langle 3|i)\times(i|1\rangle + 2|3\rangle)$. 220

$= 1 + 0 + 2i = \underline{1+2i}$

$\langle\alpha|\beta\rangle^* = \langle\beta|\alpha\rangle = (1+2i)^* = \underline{(1-2i)}$

(16) $|\alpha\rangle = |1\rangle - i|2\rangle + i|3\rangle$

$|\beta\rangle = i|1\rangle - 2|3\rangle \Rightarrow \langle\beta| = -i\langle 1| - 2\langle 3|$

then

$$|\alpha\rangle\langle\beta| = (|1\rangle - i|2\rangle + i|3\rangle) \times (-i\langle 1| - \langle 3|)$$

$\Downarrow$

wait (It will give an operator) =

$$|\alpha\rangle\langle\beta| = \begin{array}{c|ccc} & |1\rangle & |2\rangle & |3\rangle \\ \hline \langle 1| & \langle 1|\alpha\rangle\langle\beta|1\rangle & \langle 1|\alpha\rangle\langle\beta|2\rangle & \langle 1|\alpha\rangle\langle\beta|3\rangle \\ \langle 2| & \langle 2|\alpha\rangle\langle\beta|1\rangle & \langle 2|\alpha\rangle\langle\beta|2\rangle & \langle 2|\alpha\rangle\langle\beta|3\rangle \\ \langle 3| & \langle 3|\alpha\rangle\langle\beta|1\rangle & \langle 3|\alpha\rangle\langle\beta|2\rangle & \langle 3|\alpha\rangle\langle\beta|3\rangle \end{array}$$

$\langle 1|\alpha\rangle = 1\,(|1\rangle - i|2\rangle + i|3\rangle) = 1$

$\langle 2|\alpha\rangle = -i$

$\langle 3|\alpha\rangle = +i$

$\langle\beta|1\rangle = -i$

$\langle\beta|2\rangle = 0$

$\langle\beta|3\rangle = -2$

$$\Rightarrow \begin{bmatrix} 1\times -i & 1\times 0 & 1\times -2 \\ -i\times -i & 0 & -i\times -2 \\ i\times -i & 0 & i\times -2 \end{bmatrix} = \begin{bmatrix} -i & 0 & -2 \\ -1 & 0 & 2i \\ \cancel{-i}\ 1 & 0 & -2i \end{bmatrix}$$

(B)

$\Rightarrow$ not Hermitian

$\Rightarrow \quad \{\phi_1, \phi_2, \phi_3\}$

$$|\psi\rangle \doteq 2i|\phi_1\rangle + 3|\phi_2\rangle$$

suppose

$$|\psi\rangle = N\left(2i|\phi_1\rangle + 3|\phi_2\rangle\right)$$

$$\langle\psi| = N\left(-2i\langle\phi_1| + 3\langle\phi_2|\right)$$

$$\langle\psi|\psi\rangle = N\left(-2i\langle\phi_1| + 3\langle\phi_2|\right) \times N\left(2i|\phi_1\rangle + 3|\phi_2\rangle\right)$$

$$= N^2(4+9) = \underline{13N^2}$$

$$\langle\psi|\psi\rangle = 13N^2$$

$$13N^2 = 1 \quad \Rightarrow \quad N = \frac{1}{\sqrt{13}}$$

Now $\quad |\psi_n\rangle = \frac{N}{\sqrt{13}}\left(2i|\phi_1\rangle + 3|\phi_2\rangle\right)$

$\Rightarrow \quad \phi_1 =$

$$|\psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle$$

$$\langle\psi| = +c_1^*\langle\phi_1| + c_2^*\langle\phi_2|$$

$$1 = \langle\psi|\psi\rangle = \left(c_1|\phi_1\rangle + c_2|\phi_2\rangle\right) \times \left(c_1^*\langle\phi_1| + c_2^*\langle\phi_2|\right)$$

$$|\psi_n\rangle = \frac{1}{\sqrt{c_1^2 + c_2^2}}\left[c_1|\phi_1\rangle + c_2|\phi_2\rangle\right]$$

$$|\psi_n\rangle = \frac{1}{\sqrt{c_1 c_1^* + c_2 c_2^*}}\left[c_1|\phi_1\rangle + c_2|\phi_2\rangle\right]$$

$$\Rightarrow |\psi\rangle \doteq 2i\,|\phi_1\rangle - 2|\phi_2\rangle$$

$$N = \frac{1}{\sqrt{2i \times -2i + 2\times 2}} \left(2i\,|\phi_1\rangle - 2|\phi_2\rangle\right)$$

$$\doteq \frac{1}{\sqrt{8}} \left(2i|\phi_1\rangle - 2|\phi_2\rangle\right)$$

$$|\psi_N\rangle = \frac{1}{2\sqrt{2}} \left(2i|\phi_1\rangle - 2|\phi_2\rangle\right)$$

$$\underline{|\psi_N\rangle = \frac{1}{\sqrt{2}} \left[i|\phi_1\rangle - |\phi_2\rangle \right]}$$

$$\langle \psi_1 | \hat{O} | \psi_2 \rangle = \langle \psi_1 \hat{O} | \psi_2 \rangle = \langle \hat{O}^{\dagger} \psi_1 | \psi_2 \rangle$$

$$\underline{\text{OR}} = \langle \psi_1 | \hat{O} \psi_2 \rangle$$

If $\hat{O}$ is ~~then~~ Then $\hat{O}$ is Hermitian

के form में जायेगा $\Leftarrow \dagger$

$$\langle \psi_1 | \hat{O} | \psi_2 \rangle$$

Bravector

$$= \langle \hat{O}^{\dagger} \psi_1 | \psi_2 \rangle = A$$

OR

$$\langle \psi_1 | \hat{O} \psi_2 \rangle = B$$

If $A = B$ then operator will said tobe Hermitian

$$\Rightarrow \quad \langle \psi_1 | \hat{O} | \psi_2 \rangle^* = ?$$

$$\langle \psi_1 | \hat{O} \psi_2 \rangle^* = \underline{\langle \hat{O} \psi_2 | \psi_1 \rangle}$$

$$= \underline{\langle \psi_2 | \hat{O}^{\dagger} | \psi_1 \rangle}$$

$$= \underline{\langle \psi_2 | \hat{O}^{\dagger} \psi_1 \rangle}$$

$$\Rightarrow \quad \langle \psi_1 | c | \psi_2 \rangle = \langle \psi_1 | c \psi_2 \rangle$$

$$\parallel$$

$$\langle c^* \psi_1 | \psi_2 \rangle$$

ψ'

$\Rightarrow \langle \psi_1 | c | \psi_2 \rangle^* = \langle \psi_1 | c\psi_2 \rangle^*$

$= \langle c\psi_2 | \psi_1 \rangle$

$= \langle \psi_2 | c^* | \psi_1 \rangle = \langle \psi_2 | c^* \psi_1 \rangle$

$\Rightarrow \langle \psi_1 | \hat{O} | \psi_2 \rangle^*$

$= \langle \psi_1 | \hat{O} \psi_2 \rangle^*$

$= \langle \hat{O} \psi_2 | \psi_1 \rangle = \langle \psi_2 | \hat{O}^\dagger | \psi_1 \rangle$

$= \langle \psi_2 | O^\dagger \psi_1 \rangle$

$\langle \hat{O}^\dagger \psi_1 | \psi_2 \rangle^*$

$= \langle \psi_2 | \hat{O}^\dagger \psi_1 \rangle$ every thin is possible rotate one side to another with proper way

Q$\Rightarrow$ $\hat{H} | \psi_{2\,1\,-1} \rangle = ?$ For Hydrogen - ψ_{21-1} (n, l, m)

$\hat{H} | \psi_{21-1} \rangle = E | \psi_{21-1} \rangle$ then $E = ?$

$n = 2$, $l = 1$ $m = 1$

2p $\Rightarrow$ $E_n = -13.6 \frac{Z^2}{n^2}$ eV

$E = -13.6 \times \frac{1}{4}$ eV =

One atomic unit Energy $\Rightarrow$ two times of I.E. of
(1 au) H-atom

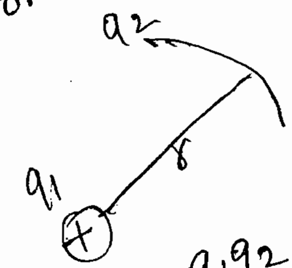
$2 \times 13.6 = \underline{27.2\ au}$

(special) (deviation)

imp

<u>Virial Theory</u> : when we need a rel^n b/w K.E., P.E and Total energy.

For Hydrogen atom



$V = \frac{q_1 q_2}{r} = r^{-1}$

Suppose $V \propto x^{+K}$

then by virial theory

$$\boxed{2\langle T\rangle = +K\langle V\rangle}$$

$T = K.E$

For Harmonic oscilator

$V = \frac{1}{2} K x^2$

then $\cancel{2}(\text{Kinetic energy}) = \cancel{2}(\overset{\text{potential}}{U})$

$$\boxed{K.E = P.E}$$

$V \propto (\text{position})^K$

$2\langle T\rangle = K\langle \hat{V}\rangle$

Relation b/w K.E, P.E. and T.E in hydrogen atom:

for Hydrogen atom

$$V \propto -\frac{1}{r}$$

$$V \propto -r^{-1}$$

from varial theorum

$$2\langle T\rangle = -1\langle U\rangle \Rightarrow \frac{U}{2} = -T$$

Total Energy $\langle E\rangle = \langle U\rangle + \langle T\rangle$

$$\langle E\rangle = \langle U\rangle - \frac{\langle U\rangle}{2}$$

$$\boxed{E = \frac{\langle U\rangle}{2}}$$

$$E = U + T$$

$$E = -2T + T$$

$$E = -T = -T$$

$$\Rightarrow \boxed{\langle E\rangle = \frac{\langle U\rangle}{2} = -\langle T\rangle}$$

If $E = -13.6$

$$-13.6 = \frac{U}{2} \Rightarrow \underline{U = -27.2}$$

$$E = -T$$

$$\boxed{13.6 = U}$$

(18) $f_1(x) = \sin kx + \cos kx$

$$\hat{P}_x f_1(x) = -i\hbar \frac{\partial}{\partial x}(\sin kx + \cos kx)$$

$$= i\hbar\,(k\cos kx - k\sin kx)$$

$$= k i\hbar\,(\cos kx - k\sin kx)$$

$f_1(x)$ is not a eigen function. in the same away ans is (d).

(19) $$\left(\frac{d^2}{dx^2} - 16x^2\right) f(x)$$

$$= \frac{d^2}{dx^2} A e^{-Bx^2} - 16 A e^{-Bx^2} \cdot x^2$$

$$= A \frac{d}{dx} e^{-Bx^2} \cdot 2x(-B) - 16 A e^{-Bx^2} \cdot x^2$$

$$= -2AB \frac{d}{dx}\left(x \cdot e^{-Bx^2}\right) - 16 A e^{-Bx^2} \cdot x^2$$

$$= -2AB\left[x \cdot e^{-Bx^2}(-B \cdot 2x) + e^{-Bx^2}\right) - 16 A e^{-Bx^2} \cdot x^2$$

$$= -2AB\left[-2Bx^2 e^{-Bx^2} + e^{-Bx^2}\right) - 16 A e^{-Bx^2} x^2$$

$$= 4AB^2x^2 e^{-Bx^2} - 2AB e^{-Bx^2} - 16 A e^{-Bx^2} \cdot x^2$$

$$= (4B^2x^2 - 2B - 16x^2) A e^{-Bx^2}$$

$\therefore$ above function eigen ~~value~~ fun^n for above operator so the componant of x should be zero

$$4B^2x^2 - 16x^2 = 0$$

$$4B^2\cancel{x^2} = 16\cancel{x^2}$$

$$\cancel{4}B^2 = \cancel{16} \qquad \boxed{B = \pm 2}$$

$$B^2 = 4$$

Now we have two value of B = i.e $+2, -2$

i.e If $B = -2$ $\quad f(x) = Ae^{2x^2} = Ae^{2\infty} = \infty$ but should be finite.

If $\underline{\underline{B=2}}$ $\quad f(x) = Ae^{-2x^2}$ (Gaussian function)

$x = \infty \qquad f(x) = Ae^{-\infty} = 0$ finite

So the exact value of B will be 2.

eigen value $= -2B$

$= -2 \times 2 = \underline{\underline{-4}}$

e^{-x^2} = Gaussian function

$e^{\pm ikx}$ = oscillatory function

$e^{\pm x}$ = decaying function

acceptable function $\begin{cases} e^{-x^2} \\ e^{-x}\ (0 - \infty) \\ e^{\pm ikx} \end{cases}$

$\underline{e^{x}\ (0 \text{ to } -\infty)}$

(a). $\langle \psi | B | \psi \rangle^* = \langle \psi | B\psi \rangle^* \neq \langle \psi | \hat{B} | \psi \rangle$

$= \langle B\psi | \psi \rangle$

$= \langle \psi | \hat{B}^\dagger | \psi \rangle$

(b) $\langle \psi | \hat{B} | \psi \rangle^* = \langle \psi | B\psi \rangle^*$

$= \langle B\psi | \psi \rangle$

$= \langle \psi | B^\dagger | \psi \rangle$

$\neq -\langle B\psi | \psi \rangle$

(c) $\langle \psi | \hat{B} | \psi \rangle^* = \langle \psi | \hat{B}\psi \rangle^*$

$= \langle \hat{B}\psi | \psi \rangle$

$= \langle \psi | B^\dagger | \psi \rangle$

$= -\langle \psi | \hat{B} | \psi \rangle$ ✓

(21) $|\psi_{32-1}\rangle$

$\left.\begin{array}{l} n=3 \\ l=2 \\ m=-1 \end{array}\right\}$ Radial node $= 0$

$r_{mp} = \frac{n^2}{2} a_0$

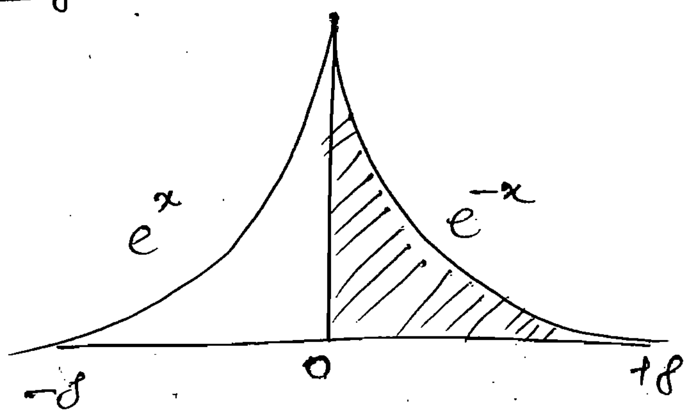
$= \frac{9}{3} a_0 = \underline{3a_0}$

(20)

$e^{x} \longrightarrow 0 - -\infty$ | $e^{-|x|}$ acceptable in all range

$\therefore$ $e^{-x} \longrightarrow 0 - \infty$

acceptability of wave function.



$\bar{e}^{x} = (\bar{e}^{x})^{*} = e^{-x}$.

$$2N^2 \int_0^{\infty} e^{-2x'} dx = 1$$

$$2N^2 \cdot \frac{\sqrt{\frac{1}{2}}}{\cancel{1} \times 2^{1/2}} = 1$$

$$\cancel{2}N^2 \cdot \frac{1}{\cancel{2}} = 1$$

$$N^2 \frac{\sqrt{\pi}}{\sqrt{2}} = 1 \quad \boxed{N = \pm 1}$$

$$2N^2 \int_0^{\infty} e^{-2x} dx = 1$$

$$2N^2 \left[\frac{e^{-2x}}{-2}\right]_0^{\infty} = 1$$

$$-N^2 \left[e^{-\infty} - e^{0}\right] = 1$$

$$-N^2 [0 - 1] = 1$$

$$N^2 = 1 \Rightarrow N = \pm 1$$

$$\underline{N = 1}$$

$\sin x$ and $\cos x$ function always acceptable which two are identical

(a) $(\phi_1 + 2\phi_2)$ — a and b

(b) $i(\phi_1 + 2\phi_2)$ — b & c

(c) $(\phi_1 - 2\phi_2)$ — a and d

(d) $(\phi_1 + 3\phi_2)$ — a & c

$\phi_1 + 2\phi_2 = \psi$

$2\phi_1 + 4\phi_2 = 2\psi$

$\Downarrow$

same Energy state.

$\hat{H}\psi = E\psi$

$\hat{H}2\psi = 2\hat{H}\psi = 2E\psi$
$= E(2\psi)$

State function are linearly independent

(24) $\psi(x) = \cos\theta\, e^{ikx} + \sin\theta\, e^{-ikx}$ $\cdot \dfrac{1}{\sqrt{\cos^2\theta + \sin^2\theta}}$

$\Downarrow$ $+\hbar K$ $\Downarrow$ $-\hbar K$

probability 25%
$= \frac{1}{4}$

$\Rightarrow$

$+\hbar K = \cos^2\theta = \frac{1}{4}$

$\cos\theta = \pm\frac{1}{2} = 0.5$

$\theta = 60 = \pi/3$

$-\hbar K = \frac{3}{4} = \sin^2\theta$

$\sin\theta = \pm\frac{\sqrt{3}}{2} = 0.87$

so $\theta = \underline{60}$

$\psi(x) = 0.5e^{ikx} \pm 0.87e^{-ikx}$

(26) $\psi = \frac{1}{2} f_1 - \left(\frac{3}{8}\right)^{1/2} f_2 + \left(\frac{3}{8} i\right)^{1/2} f_3$ normalised

$$\begin{array}{ccc} \Downarrow & \Downarrow & \Downarrow \\ a_1 & a_2 & a_3 \end{array}$$

$$\langle A \rangle = \frac{1}{4} a_1 + \frac{3}{8} a_2 + \frac{3}{8} a_3$$

given $a_3 = 4a_1$ $a_2 = 2a_1$

$$\langle A \rangle = \frac{1}{4} a_1 + \frac{3}{8} \times 2a_1 + \frac{3}{8} 4a_1$$

$$= \frac{2a_1 + 6a_1 + 12a_1}{8} = \frac{20 a_1}{8}$$

$$=$$

$$= 2.5 a_1$$

(27) $\hat{A}\psi_1 = \psi_2$ and $\hat{A}\psi_2 = \psi_1$

then $\psi = 3\psi_1 + 4\psi_2$

$$\langle A \rangle = \frac{\int (3\psi_1 + 4\psi_2)^* \hat{A} (3\psi_1 + 4\psi_2) d\tau}{\int (3\psi_1 + 4\psi_2)^* (3\psi_1 + 4\psi_2) d\tau}$$

$$= \frac{\int (3\psi_1 + 4\psi_2)^* (3\psi_2 + 4\psi_1) d\tau}{\int (3\psi_1 + 4\psi_2)^* (3\psi_1 + 4\psi_2) d\tau} = \frac{12 + 12}{9 + 16}$$

$$= 24/25$$

(28) If $\hat{A}\psi_1 = \psi_2$ and $A\psi_2 = \psi_1$ then

$$A^2\psi_1 = A(\hat{A}\psi_1) = A\psi_2 = \psi_1$$

$$A^2\psi_2 = A(\psi_1) = \psi_2$$

Note $\boxed{\langle P_x \rangle = 0 \text{ for real function always.}}$

(44)

$$[e^{\alpha \hat{P}_x}, \hat{x}] = \alpha e^{\alpha P_x}(-i\hbar)$$

$$[x, \sin P_x] = (\cos P_x)\cdot(i\hbar)$$

$$[P_x, \sin x] = \cos x(-i\hbar)$$

$$\left[\frac{d}{dx}, x\frac{d}{dx}\right] = x\left[\frac{d}{dx}, \frac{d}{dx}\right] + \left[\frac{d}{dx}, x\right]\frac{dx}{dx}$$

$$= 0 + \left(\frac{d}{dx}x + x\frac{d}{dx}\right)\frac{d}{dx}$$

$$= \left(x\frac{d}{dx} + 1 + x\frac{d}{dx}\right)\frac{d}{dx}$$

$$= \left(2x\frac{d}{dx} + 1\right)\frac{d}{dx} =$$

$$[P_x, xP_x] = x[P_x, P_x] + [P_x\ x]\ P_x$$

$$= 0 + -i\hbar P_x$$

$$= -i\hbar\ \frac{\hat{d}}{dx}(i\hbar)$$

$$= (-i\hbar)\ (+i\hbar)\ \frac{\hat{d}}{dx}$$

$$= 1 \times 1\ \frac{d}{dx} = \left(\frac{\hat{d}}{dx}\right).$$

⇒ Simple harmonic oscillator:

model system = vibration of particle / molecule

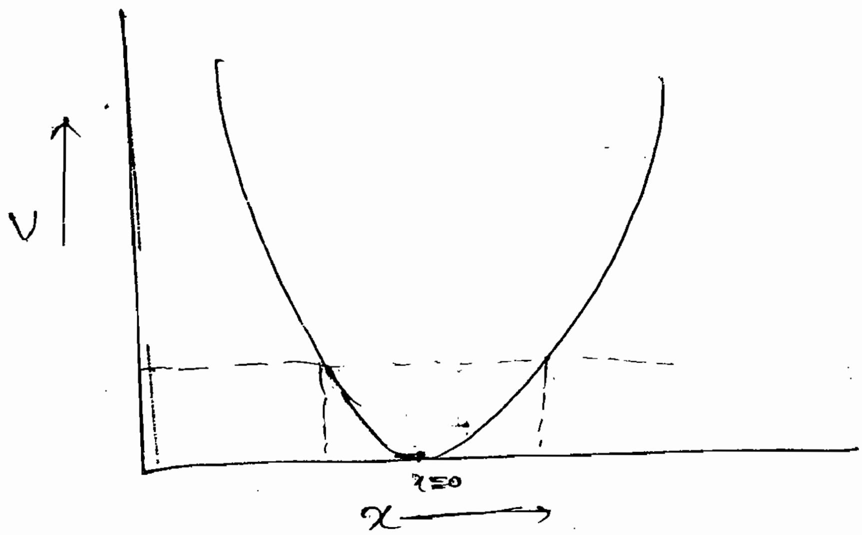
$$\text{Potential} = \frac{1}{2} m\omega^2 x^2$$
$$= \frac{1}{2} K x^2$$

$$\left[K = \frac{d^2 V}{dx^2} \right)_{x=0} \quad \underset{\text{force const.}}{\underset{\Downarrow}{K}} = V$$

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

Graphical Representation of potential:

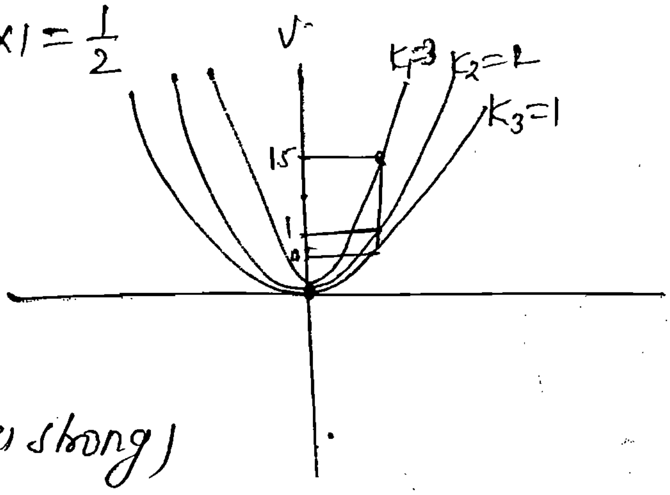
$$V = \frac{1}{2} K x^2$$



$$V = \frac{1}{2} K_1 x^2 = \frac{1}{2} \times 3 \times 1 = \frac{3}{2}$$

$$V = \frac{1}{2} K_2 x^2 = \frac{1}{2} \times 2 \times 1 = 1$$

$$V = \frac{1}{2} K_3 x^2 = \frac{1}{2} \times 1 \times 1 = \frac{1}{2}$$



$$K \propto \frac{1}{\text{bridth}}$$

(K ↑ Bond becomes strong)

<u>Energy operator for SHO</u> :

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

$$= \frac{P_x^2}{2m} + \frac{1}{2} K x^2$$

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} K x^2$$

Schrodinger wave equation:

$$\hat{H}\psi = \hat{E}\psi$$

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} K x^2\right) \psi = E\psi$$

$\downarrow$ sol^n

ψ_n (state) $\quad\quad$ E_n (Energy of state)

Content

1. $\psi_0 =$

   $\psi_1 =$

   $\psi_n =$

2. Node = ?

3. energy = ?

4. $\langle x \rangle = ?$

5. $\langle \hat{P}_x \rangle = ?$

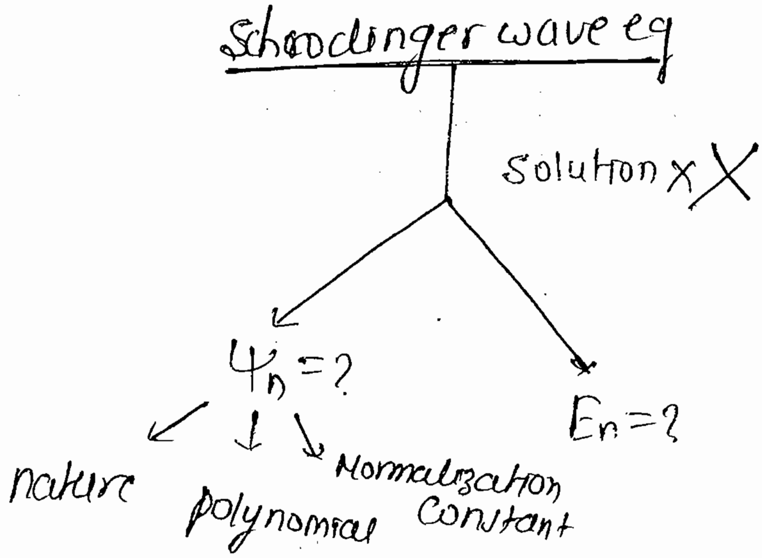
6. $\langle T \rangle = ?$

   $\langle V \rangle = ?$

7. $\Delta P_x = ?$

(6) $\Delta x = ?$

$\Delta x \cdot \Delta P_x = ?$



wave function of Harmonic oscillator:

$$\psi_n = \left(\frac{1}{2^n \lfloor n}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} H_n(\xi) \boxed{e^{-\frac{\alpha x^2}{2}}}$$

Hermit polynomial   Gaussian function

$$\alpha = \frac{\sqrt{km}}{\hbar}$$

$$H_n = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} \qquad \xi = \sqrt{\alpha}\, x$$

$$H_0 = (-1)^0 e^{\xi^2} \frac{d^0}{d\xi^0} e^{-\xi^2}$$

$$= 1\, e^{\xi^2} e^{-\xi^2} = 1 \times e^0 = 1$$

$$\boxed{\psi_0 = N_0 \cdot 1 \cdot e^{-\frac{\alpha x^2}{2}}} \quad \text{----- (1)}$$

$$H_1 = (-1)^1 e^{\xi^2} \frac{d}{d\xi} e^{-\xi^2}$$

$$= (-1)\, e^{\xi^2} (-2\xi)\, e^{-\xi^2}$$

$$= 2\xi$$

$$\boxed{\psi_1 = N_1\, 2\xi\, e^{-\frac{\alpha x^2}{2}}} \quad \text{----- (2)}$$

$$H_2 = (-1)^2 e^{\xi^2} \frac{d^2}{dx^2} e^{-\xi^2}$$

$$= e^{\xi^2} \cdot e^{-\xi^2}(-2\xi) \frac{d}{dx} e^{-\xi^2} \cdot \xi$$

$$= (-2) \left[e^{-\xi^2} - 2\xi^2 e^{-\xi^2} \right]$$

$$=$$

$$H_2 = 4\xi^2 - 2$$

<u>Trick</u> $H_0 = 1$

$H_1 = 2\xi$

$H_2 = 2\xi H_1 - 2 \times 1 H_0$

$H_2 = 2\xi \times 2\xi - 2 \times 1$

$H_2 = 4\xi^2 - 2$

$H_3 = 2\xi H_2 - 2 \times 2 H_1$

$= 2\xi(4\xi^2 - 2) - 4 \times 2\xi$

$= 8\xi^3 - 4\xi - 8\xi$

$$\boxed{H_3 = 8\xi^3 - 12\xi}$$

$H_4 = 2\xi H_3 - 3 \times 2 H_2$

$= 2\xi(8\xi^3 - 12\xi) - 6(4\xi^2 - 2)$

$= 16\xi^4 - 24\xi^2 - 24\xi^2 + 12$

$H_4 = 16\xi^4 - 48\xi^2 + 12$

$H_5 = 2\xi H_4 - 5 \times 2 H_3$

$= 2\xi(16\xi^4 - 48\xi^2 + 12) - 10(8\xi^3 - 12\xi)$

$= 32\xi^5 - 96\xi^3 + 24\xi - 80\xi^3 + 120\xi$

$= 32\xi^5 - 176\xi^3 + 144\xi$

even $H_0 = 1$

odd $H_1 = 2\xi$

even $H_2 = 4\xi^2 - 2$

odd $H_3 = 8\xi^3 - 12\xi$

$H_4 = 16\xi^4 - 48\xi^2 + 12$

$H_5 = 32\xi^5 - 160\xi^3 + 120\xi$

$H_1 = 2\sqrt{2}\,x$

$x = -x$

$H_1 = -2\sqrt{2}\,x$ (change)

(odd)

Nature of ψ

If $n =$ even, $\psi_n =$ even

If $n =$ odd $\psi_n =$ odd

$$\boxed{H_{n+1} = 2\xi H_n - 2n H_{n-1}}$$

Recursion Relation

Calculation of $\langle x \rangle$:

$$\langle \hat{O} \rangle = \frac{\int \psi^* \hat{O} \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\langle \hat{x} \rangle_3 = \frac{\int_{-\infty}^{\infty} \underset{\text{odd}}{\psi_3^*} \, \underset{\text{odd}}{x} \, \underset{\text{odd}}{\psi_3} \, d\tau}{\int_{-\infty}^{\infty} \psi_3^* \psi_3 \, d\tau} \Rightarrow \text{odd}$$

$$\int_{-2}^{2} x \, dx = \left[\frac{x^2}{2}\right]_{-2}^{+2} = \frac{4}{2} - \frac{4}{2} = 0$$

$$= 0$$

$x = \text{odd}$

$(-x)$ = change हो जाता.

$$\langle x \rangle_2 = \frac{\int_{-\infty}^{\infty} \underset{\text{even}}{\psi_2^*} \, \underset{\text{odd}}{x} \, \underset{\text{even}}{\psi_2} \, d\tau}{\int_{-\infty}^{\infty} \psi_2^* \psi_2 \, d\tau} \Rightarrow \text{odd} = 0$$

so $\boxed{\langle x \rangle_n = 0}$ always

avarage displace from mean position in case of n^{th} state of simple harmonic oscillator is zero.

$\langle P_x \rangle \Rightarrow$

$$\frac{\int_{-\infty}^{\infty} \psi_n^* \, p_x \, \psi_n \, dx}{\int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx} \Rightarrow e^{-\frac{x^2}{2}} \Rightarrow (x) \text{ odd आ देगा}$$

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

or

$P_x \Rightarrow$ के कारण Total value i के साथ आयेगी i.e. imagnory

$= 0 + i\cancel{0} = \underline{0} + i0$.

$$\Rightarrow \boxed{\langle P_x \rangle_n = 0}$$

Calculation for x^2 and P_x^2 $\Rightarrow$

ψ_n

$E_n = \left(n + \frac{1}{2}\right) \hbar \omega$

$n = 0, \; E_0 = \frac{1}{2} \hbar \omega$

$E_1 = \frac{3}{2} \hbar \omega$

$E_2 = \frac{5}{2} \hbar \omega$

$$V = \frac{1}{2} m\omega^2 x^2$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega$$

Virial Theorem = $V \propto x^2 \Rightarrow 2\langle T\rangle = n\langle V\rangle$

$$2\langle T\rangle = 2\langle V\rangle$$

$$\langle T\rangle = \langle V\rangle$$

$$E_n = \langle T\rangle + \langle V\rangle$$

$$E_n = \langle V\rangle + \langle V\rangle \Rightarrow E_n = 2\langle V\rangle$$

$$\langle V\rangle = \frac{E_n}{2} \qquad \boxed{\langle V\rangle = \frac{E_n}{2}} \text{ or } \langle T\rangle = \frac{E_n}{2} \quad \text{—(A)}$$

$$\left\langle \frac{1}{2} m\omega^2 x^2 \right\rangle = \left(n+\frac{1}{2}\right)\frac{\hbar\omega}{2}$$

$$\frac{1}{\cancel{2}} m\omega^{\cancel{2}}\langle x^2\rangle = \left(n+\frac{1}{2}\right)\frac{\hbar\cancel{\omega}}{\cancel{2}}$$

$$\boxed{\langle x^2\rangle_n = \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}}$$

we can calculate $\langle x^2\rangle$ for any state.

$\langle p_x^2\rangle$

$$\langle T\rangle = \left\langle \frac{p_x^2}{2m} \right\rangle$$

$$\langle T\rangle = \frac{1}{2m}\langle p_x^2\rangle \quad \text{—(B)}$$

from (A) and (B) $\quad \frac{1}{2m}\langle p_x^2\rangle = \frac{E_n}{2}$

$$\frac{1}{\cancel{2}m}\langle p_x^2\rangle = \left(n+\frac{1}{2}\right)\frac{\hbar\omega}{\cancel{2}}$$

$$\boxed{\langle p_x^2\rangle_n = \left(n+\frac{1}{2}\right) m\hbar\omega}$$

Formula $\quad \Delta\hat{O} = \sqrt{\langle \hat{O}^2\rangle - \langle \hat{O}\rangle^2}$

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

$$= \sqrt{\left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}}$$

$$\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2}$$

$$= \sqrt{\left(n+\frac{1}{2}\right)\hbar m\omega}$$

<u>Now</u>

$$\Delta x\,\Delta p_x = \sqrt{\left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}} \times \sqrt{\left(n+\frac{1}{2}\right)\hbar m\omega}$$

$$= \sqrt{\left(n+\frac{1}{2}\right)^2\hbar^2} = \left(n+\frac{1}{2}\right)\hbar$$

$$\boxed{\Delta x\,\Delta p_x = \left(n+\frac{1}{2}\right)\hbar}$$

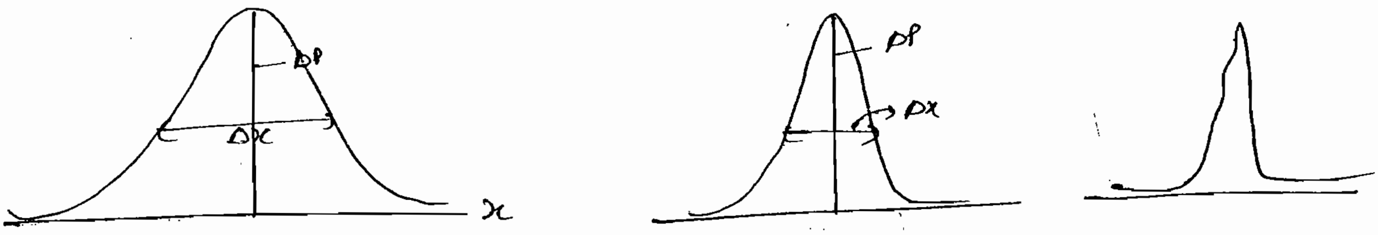
$n=0$

$$\Delta x\,\Delta p_x = \frac{1}{2}\hbar = \frac{h}{4\pi}$$

$$\Rightarrow \boxed{\Delta x\,\Delta p_x \geq \frac{h}{4\pi}}$$

note ⇒ The characteristic property of SHO in ground state uncertainity product of position and momentum is exactly equal to $\frac{h}{4\pi}$ ∴ $(\Delta x \Delta P_x)_{n=0} = \frac{h}{4\pi}$

Δx and ΔP_x



$\Delta x \downarrow \; \Delta P \uparrow$

streching frequancy $\gamma = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$

angular freq $\Leftarrow \omega = \frac{2\pi}{T} = 2\pi\gamma$

$\omega = \frac{\theta}{t}$

$\boxed{F = -kx}$ $\boxed{-\frac{dv}{dx} = f}$

$\Downarrow$

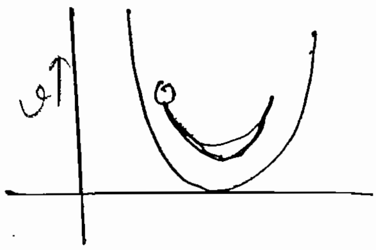
: Hooke's law

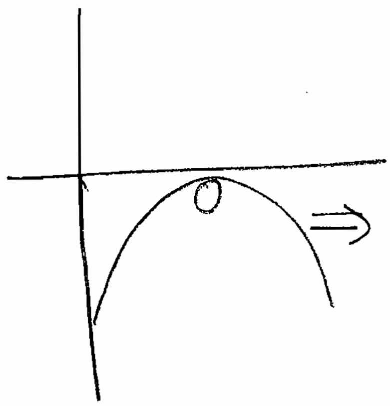
$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega = \left(n+\frac{1}{2}\right)\frac{h}{2\pi}\times 2\pi\gamma = \left(n+\frac{1}{2}\right)h\gamma$$

Q $U = \frac{1}{2}m\omega^2x^2$ and $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$, $E_0 = \frac{1}{2}\hbar\omega$

so what will be the value

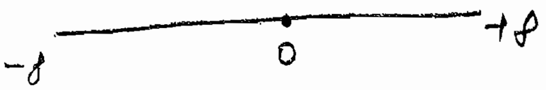
$U = -\frac{1}{2}m\omega^2x^2$, $E_0 = ?$ × There is no bound state exist.





$\Rightarrow$ not possible

Graphical Representation of wavefunction:



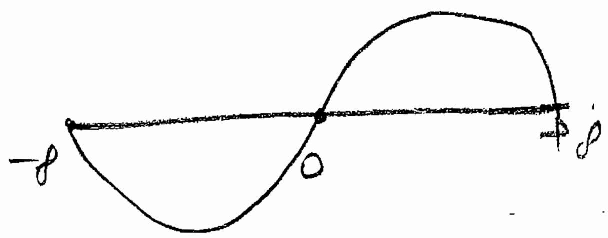
$$\psi_0 = c \cdot 1 \cdot e^{-\frac{\alpha x^2}{2}}$$

$$\psi_1 = c \cdot 2\xi \cdot e^{-\frac{\alpha x^2}{2}} = c \cdot 2\sqrt{\alpha}\, x\, e^{-\frac{\alpha x^2}{2}}$$

$$\psi_2 = c \cdot (4\alpha x^2 - 2)\, e^{-\frac{\alpha x^2}{2}}$$

$\cancel{\psi_1 = c \cdot 2\sqrt{\alpha}\, x}$

$$\psi_1 = c \cdot 2\sqrt{\alpha}\, x\, e^{-\frac{\alpha x^2}{2}}$$



$$\psi_2 = c\,(4\alpha x^2 - 2)\, e^{-\frac{\alpha x^2}{2}}$$

$4\alpha x^2 - 2 = 0$

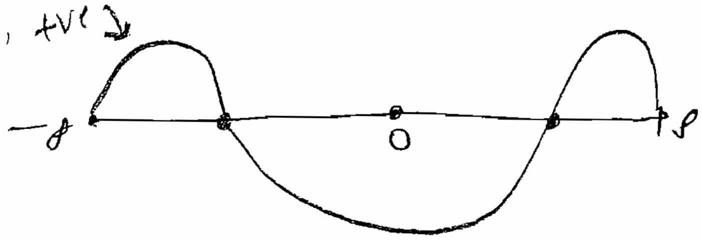
$4\alpha x^2 = 2$

$x^2 = \frac{1}{2\alpha}$

$x = \pm\sqrt{\frac{1}{2\alpha}}$

① $x = 0$ करने पर $\psi_2 \neq 0$ so it will not pass through 0

② $x = -ve$ " " $+ve$



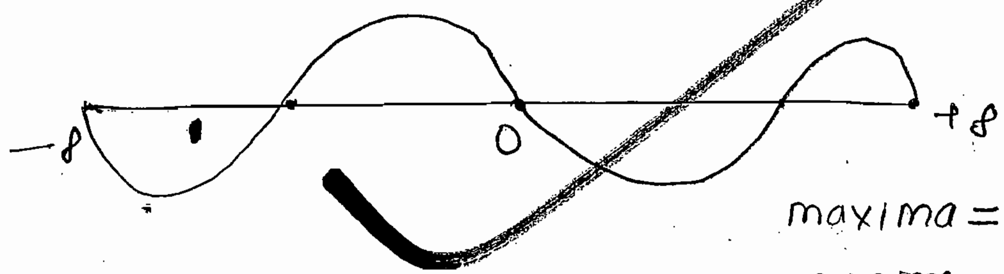
① ψ_n = n = odd then graph will pass from origen and strats from $-ve$

② ψ_n = n = node

③ If n = even it will not pass through origin but starts from +ve lobes.

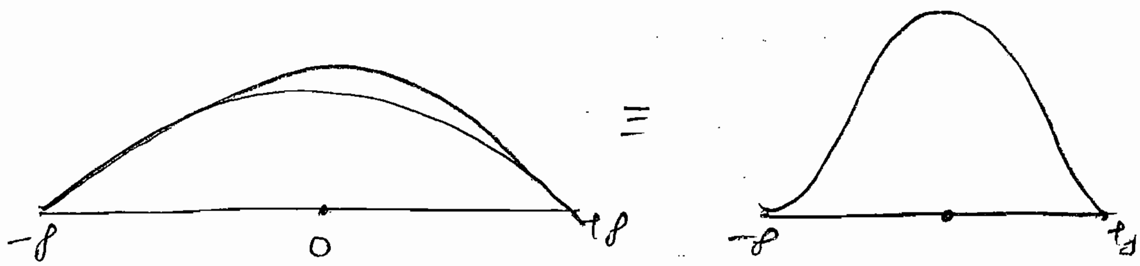
$\underline{\underline{\psi_3}}$ = odd = origin = −ve

odd = 0 = −



maxima = 2
minima = 2

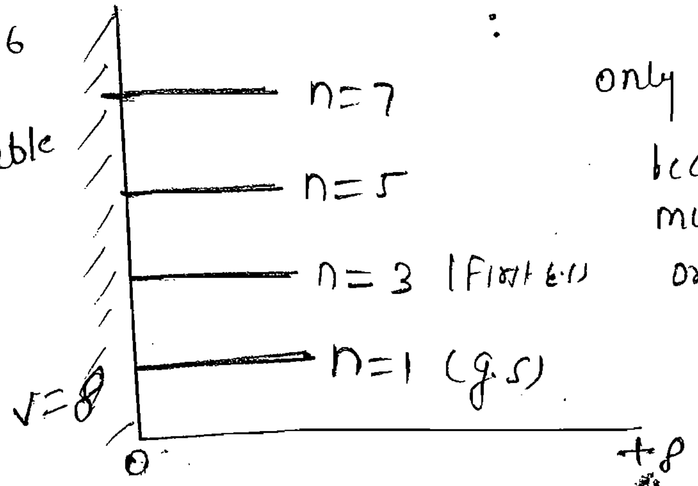
$\underline{\underline{\psi_0}}$ = even = +v



$V = \frac{1}{2} m\omega^2, \quad 0 \text{ to } \infty \Rightarrow$ Origin at boundry i.e $V = \infty$

otherwise (0 to $-\infty$)

$n=0, n=2, n=6$ X will not applicable



only $n =$ odd will exits because wave function must pass through the origin. ∴ ∞ potential barrier is at origin

(half range) 0 to ∞ or 0 to $-\infty$

(15) ✓

(16) $\psi(x) = \frac{1}{\sqrt{5}} i\psi_0 + \frac{2}{\sqrt{5}}\psi_1 \Rightarrow \psi_0 = \psi_1 = \frac{3}{2}\hbar\omega$

$\psi_1 = \psi_3 = \frac{7}{2}\hbar\omega$

$$\psi(x) = \frac{1}{\sqrt{5}} i\psi_0 + \frac{2}{\sqrt{5}}\psi_1 \left(\frac{1}{\sqrt{\frac{-i}{\sqrt{5}} \times \frac{i}{\sqrt{5}} + \frac{4}{5}}} \right)$$

$= \quad " \quad + \frac{2}{\sqrt{5}}\psi_1$ normalized

$$\psi \; E = \left(\frac{1}{\sqrt{5}}\right)^2 \times \frac{3}{2}\hbar\omega + \left(\frac{2}{\sqrt{5}}\right)^2 \times \frac{7}{2} \times \hbar\omega$$

$= \frac{1}{5} \times \frac{3}{2}\hbar\omega + \frac{4}{5} \times \frac{7}{2}\hbar\omega = \left(\frac{3}{2\sqrt{5}} + \frac{7}{\sqrt{5}}\right)\hbar\omega = \frac{3+14}{2\sqrt{5}}\hbar\omega$

$= \left(\frac{3}{10} + \frac{14}{5}\right)\hbar\omega = \left(\frac{3+28}{10}\right)\hbar\omega = \frac{31}{10}\hbar\omega$

$$\Rightarrow \quad \psi(x) = \frac{1}{\sqrt{5}} i \psi_0 + \frac{2}{\sqrt{5}} \psi_1$$

$$= \left(\frac{1}{\sqrt{5}} i\right)\left(\frac{-i}{\sqrt{5}}\right) \times E_{q.s} + \left(\frac{2}{\sqrt{5}}\right)\left(\frac{2}{\sqrt{5}}\right) \cdot E_{E.S.I}$$

$$= \left(\frac{1}{5}\right) \frac{3}{2} \hbar\omega + \frac{4}{5} \times \frac{7}{2} \hbar\omega$$

$$\left(\frac{3}{10} + \frac{28}{10}\right) \hbar\omega = \frac{31}{10} \hbar\omega \quad (a)$$

① $\psi = 2i\psi_a + \psi_b \left(\frac{1}{\sqrt{2ix - 2i + 1}}\right)$

$V = 2m\omega^2 x^2$ but

$$\psi = \frac{2i}{\sqrt{5}} \psi_a + \frac{1}{\sqrt{5}} \psi_b$$

$2\cancel{m}\omega^2 \cancel{x^2} = \frac{1}{2} \cancel{m}\omega'^2 \cancel{x^2}$

$$E = \frac{2i}{\sqrt{5}} \times \left(\frac{3}{2} \hbar\omega'\right) + \frac{1}{\sqrt{5}} \left(\frac{7}{2} \hbar\omega'\right)$$

$\omega'^2 = 2\omega^2$

$\omega' = 2\omega$

sq

$$= \frac{6i}{2\sqrt{5}} \hbar(2\omega) + \frac{7}{2\sqrt{5}} \hbar(2\omega)$$

$$= \left(\frac{12i}{2\sqrt{5}} + \frac{14}{2\sqrt{5}}\right) \hbar\omega$$

$$= \frac{(6i + 7)}{\sqrt{5}} \hbar\omega$$

$$= \frac{4}{5} \times 3\hbar\omega + \frac{1}{5} \times 7\hbar\omega$$

$$= \left(\frac{12}{5} + \frac{35}{5}\right) \hbar\omega$$

$$= \left(\frac{12}{5} + 7\right) \hbar\omega$$

$$= \frac{19}{5} \hbar\omega$$

(4) $\Delta x \Delta P = ?$

$$\Delta x \Delta P = \left(n+\frac{1}{2}\right)\hbar$$

$\underline{\Psi_3}$ $= \frac{7}{2}\hbar$ (b)

(5) $\psi(x,0) = 3\varphi_0 + 4\varphi_1 \frac{1}{\sqrt{3\times 3^* + 4\times 4^*}}$

$$\psi = (3\varphi_0 + 4\varphi_1)\frac{1}{\sqrt{9+16}}$$

$\psi = \frac{3}{5}\varphi_0 + \frac{4}{5}\varphi_1$ (now its normalised

Probability ψ $\Downarrow$ $\frac{9}{25}$ $\Downarrow$ $\frac{16}{25}$ (MPS) $= \varphi_1 = \frac{3}{2}\hbar\omega$

average ~~avar~~ $E = \left(\frac{4}{5}\right)\left(\frac{4}{5}\right)^2 \frac{3}{2}\hbar\omega$

$E = \frac{24}{25}\hbar\omega$ X

⑥ $K \longrightarrow 4K$

$m\omega^2 x^2 \quad 4m\omega^2 x^2$

$\frac{1}{2}m\omega^2 x^2 = \frac{1}{2}4m\omega^2 x^2$

$\omega' = 2\omega$

$E_n = (n+\frac{1}{2})\hbar\omega$

$E_n = (n+\frac{1}{2})\hbar(2\omega)$

$E_0 = \frac{1}{2}\hbar 2\omega$

$\boxed{E_0 = \hbar\omega}$

⑦ $\psi = \psi_0(x) + 2i\psi_1 + 2\psi_2(x)$

$\psi = (\psi_0 + 2i\psi_1 + 2\psi_2)\frac{1}{\sqrt{1+4+4}}$

$\Psi_{(x,0)} \frac{1}{3} \frac{\psi_0}{3}\psi_0 \frac{2i}{3}\psi_1 i\psi_1 \frac{2}{3}\psi_2\psi_2$

a.v $\langle E\rangle = \frac{1}{9}\times\frac{1}{2}\hbar\omega + \frac{4}{9}\times\frac{3}{2}\hbar\omega + \frac{4}{9}\times\frac{5}{2}\hbar\omega$

$= \frac{1}{18}\hbar\omega + \frac{12}{18}\hbar\omega + \frac{20}{18}\hbar\omega$

$\langle E\rangle = (\frac{33}{18})\hbar\omega$

$\langle T\rangle = \frac{\langle E\rangle}{2} = \frac{33}{36}\hbar\omega$

⑨

$\psi_1 = \phi_0 - 2\phi_1 + 3\phi_2$

$\psi_2 = \phi_0 - \phi_1 + a\phi_2 \quad \langle\psi_1\psi_2\rangle = 0$

$\langle\psi_1\psi_2\rangle = \quad |\psi_1\rangle = |\phi_0\rangle - 2|\phi_1\rangle + 3|\phi_2\rangle$

$|\psi_2\rangle = |\phi_0\rangle - |\phi_1\rangle + a|\phi_2\rangle$

$\langle\psi_1| = \langle\phi_0| - \langle\phi_1|2 + \langle\phi_2|3$

$\langle\psi_1\psi_2\rangle = (\langle\phi_0| - \langle\phi_1|2 + \langle\phi_2|3)(|\phi_1\rangle - |\phi_2\rangle + a|\phi\rangle$

$= 1+2+3\alpha = 0$

$3\alpha = -3$

$\alpha = -1$

$$\psi_2 = \phi_0 - \phi_1 + \phi_2$$

$$\therefore \psi_2 = \frac{1}{\sqrt{3}}\phi_0 - \frac{1}{\sqrt{3}}\phi_1 - \frac{1}{\sqrt{3}}\phi_2 \quad \text{(normalised)}$$

$$\langle E\rangle = \left(\frac{1}{3}\right)\frac{1}{2}\hbar\omega + \frac{1}{3}\frac{3}{2}\hbar\omega + \frac{1}{3}\frac{5}{2}\hbar\omega$$

$$= \left(\frac{1}{6} + \frac{3}{6} + \frac{5}{6}\right)\hbar\omega = \frac{9}{6}\hbar\omega$$

$$= \frac{3}{2}\hbar\omega$$

(17)

$$\langle O\rangle = \int$$

$$= \left(\frac{1}{2}\langle\psi_1| + \frac{1}{\sqrt{2}}\langle\psi_2| + \frac{1}{2}\langle\psi_3|\right)\hat{O}\left(\frac{1}{2}|\psi_1\rangle + \frac{1}{\sqrt{2}}|\psi_2\rangle + \frac{1}{2}|\psi_3\rangle\right)$$

$$= \left(\frac{1}{2}\langle\psi_1| + \frac{1}{\sqrt{2}}\langle\psi_2| + \frac{1}{2}\langle\psi_3|\right)\left(\frac{1}{2}|\psi_2\rangle + \frac{1}{\sqrt{2}}|\psi_3\rangle + \frac{1}{2}|\psi_1\rangle\right)$$

$$= \frac{1}{2} + \frac{1}{2\sqrt{2}} + \frac{1}{2\sqrt{2}} = \frac{\sqrt{2}+2}{2\sqrt{2}} = \frac{(2+\sqrt{2})}{2\sqrt{2}}$$

$$= \frac{\left(\frac{1+\sqrt{2}}{2}\right)}{\frac{1}{4}+\frac{1}{2}+\frac{1}{4}}$$

$$= \sqrt{}$$

$$= \frac{\frac{1+\sqrt{2}}{2}}{\cancel{\frac{4}{4}}} =$$

A5

(7) $[x^{-1}\ P_x^2] = [x x^{-1}\ P_x^2] = 0$

$$= x[x^{-1}\ P_x^2] + [x, P_x^2]x^{-1} = 0$$

$$x[R] + 2i\hbar P_x x^{-1} = 0$$

$$x[R] = 2i\hbar P_x x^{-1}$$

$$x[R] = 2i\hbar x^{-1}$$

$$[R] = -2i\hbar\ \underline{x^{-1} P_x x^{-1}}$$

$[P_x\ x^{-1}] = -x^{-2}(-i\hbar)$

$P_x x^{-1} - x^{-1}P_x = i\hbar x^{-2}$

$P_x x^{-1} = \underline{i\hbar x^{-2} + x^{-1}P_x}$

$$[R] = -2i\hbar x^{-1}[i\hbar x^{-2} + x^{-1}P_x]$$

$$= -2i\hbar x^{-2}[i\hbar x^{-1} + P_x]$$

$$= \frac{-x}{x} 2i\hbar x^{-2}[i\hbar x^{-1} + P_x]$$

$$[R] = \frac{-2i\hbar}{x^3}[i\hbar + xP_x]$$

$$= \frac{-2\hbar}{x^3}(-\hbar + xP_x)$$

$$= \frac{2\hbar}{x^3}[\hbar - xP_x]$$

$$\left\{\begin{array}{l}[\hat{H}, P_x] \neq 0 \\ H = \underline{T + V(x)}\end{array}\right\}$$

(45) $[x^2, \sin P_x] = 2$

$[x.x, \sin P_x] = x[x, \sin P_x) + [x, \sin P_x]x$

$= x(i\hbar)\cos P_x + (i\hbar)\underline{\cos P_x . x}$

$= i\hbar x\cos P_x + i\hbar(i\hbar \sin x + x\cos P_x)$

$= i\hbar x\cos P_x - \hbar^2 \sin x + i\hbar x\cos P_x$

$= -\underline{\hbar^2 \sin x} + 2i\hbar x\cos P_x$

$[\cos P_x\ x]$

$\cos P_x x - x\cos P_x = +i\hbar \sin x$

$\cos P_x . x = i\hbar \sin x + x\cos P_x$

$$\psi_n = C_n \, H_n(\xi) \, e^{-\frac{\alpha x^2}{2}}$$

$$\Downarrow$$

$$\left(\frac{1}{2^n \lfloor n}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\psi_0 = \left(\frac{1}{2^0 \lfloor 0}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} H_0(\xi) \, e^{-\frac{\alpha x^2}{2}}$$

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} 1 \, e^{-\frac{\alpha x^2}{2}} \quad \text{---} \quad ①$$

$$\psi_1 = \left(\frac{1}{2}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} 2\xi \, e^{-\frac{\alpha x^2}{2}} \quad \text{---} \quad ②$$

$$\psi_2 = \left(\frac{1}{8}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} H_2(\xi) \, e^{-\frac{\alpha x^2}{2}} \quad \text{---} \quad ③$$

<u>Born-approximation</u>:

Probability at a point $= \psi^* \psi = |\psi|^2$

" with in a region $(dx) = |\psi|^2 dx$

" " within $(-\infty \text{ to } +\infty)$

$$= \int_{-\infty}^{\infty} |\psi|^2 dx$$

Total probability $= \int_{-\infty}^{\infty} |\psi|^2 dx > 0$

$|z|^2 = \sqrt{z^* z}$

Unit of ψ in SHO:

$\int \psi^2 dx = 1$

$|\psi^2| = \frac{1}{L} \Rightarrow \psi = \sqrt{\frac{1}{l}} = \underline{\underline{m^{-1/2}}}$

In case of Hydrogen atom:

$\int |\psi|^2 d\tau = \int \psi^2 dv = 1$

$\int |\psi|^2 m^3 = 1$

$\psi = \sqrt{\frac{1}{m^3}} = \underline{\underline{m^{-3/2}}}$

$$\psi_0 = C_n \cdot 1 \cdot e^{-\frac{\alpha x^2}{2}}$$

$$C_n^2 \int_{-\infty}^{\infty} e^{-\frac{\alpha x^2}{2}} \cdot e^{-\frac{\alpha x^2}{2}} dx = 1$$

$$C_n^2 \int_{-\infty}^{\infty} x^0 e^{-\alpha x^2} dx = 1$$

$$C_N^2 \cancel{\times 2} \left(\frac{\sqrt{\frac{0+1}{2}}}{\cancel{2} \times \alpha^{1/2}} \right) = 1$$

$$C_N^2 \left(\frac{\sqrt{\frac{1}{2}}}{\alpha^{1/2}} \right) = 1$$

$$C_N^2 = \left(\frac{\alpha}{\pi} \right)^{1/2}$$

$$\boxed{C_n = \left(\frac{\alpha}{\pi} \right)^{1/4}}$$

$$\psi_1 = C_n \, 2 \xi_1 e^{-\frac{\alpha x^2}{2}} \qquad \xi_1 = \sqrt{\alpha} x$$

$$2 \times 2 C_n^2 \int_{-\infty}^{\infty} (\sqrt{\alpha} x)^2 e^{-\alpha x^2} dx = 1$$

$$2 \times 4 \alpha C_n^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = 1$$

$$1 = 2 \times 4 \alpha \cdot C_n^2 \left(\frac{\sqrt{\frac{2+1}{2}}}{2 \times \alpha^{3/2}} \right) = 2 \times 4 \alpha C_n^2 \frac{\frac{1}{2} \cdot \sqrt{\pi}}{\cancel{2} \times \alpha^{3/2}}$$

$$C_n^2 \, 3 \sqrt{\frac{\pi}{2}} = 1$$

$$C_n = \left(\frac{\alpha}{\pi} \right)^{1/4} \cdot \frac{1}{\sqrt{6}}$$

$$= C_n = \left(\frac{1}{2^n \Gamma n}\right)^{1/2} \left(\frac{2}{\pi}\right)^{1/4}$$

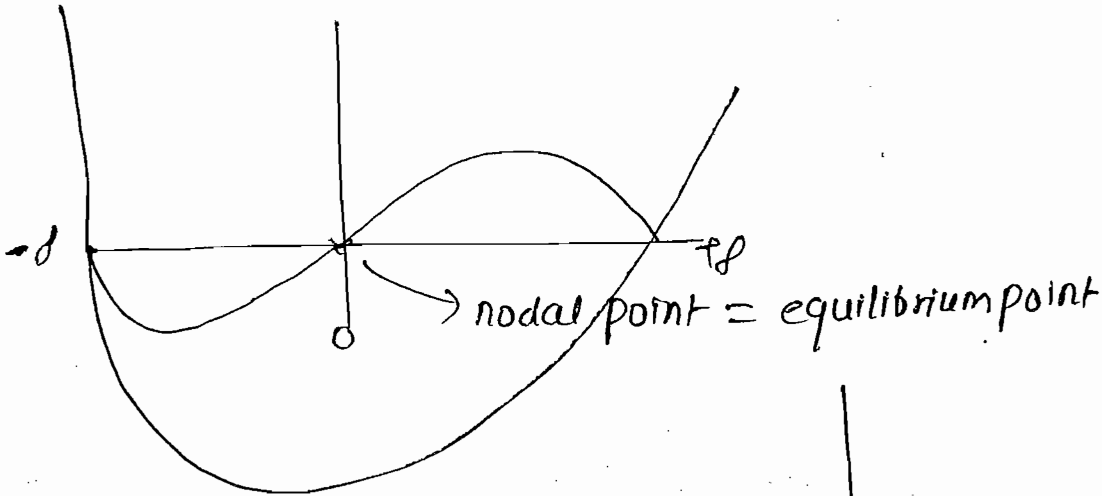
Classical Turning point / position for maximum probability / position of node:

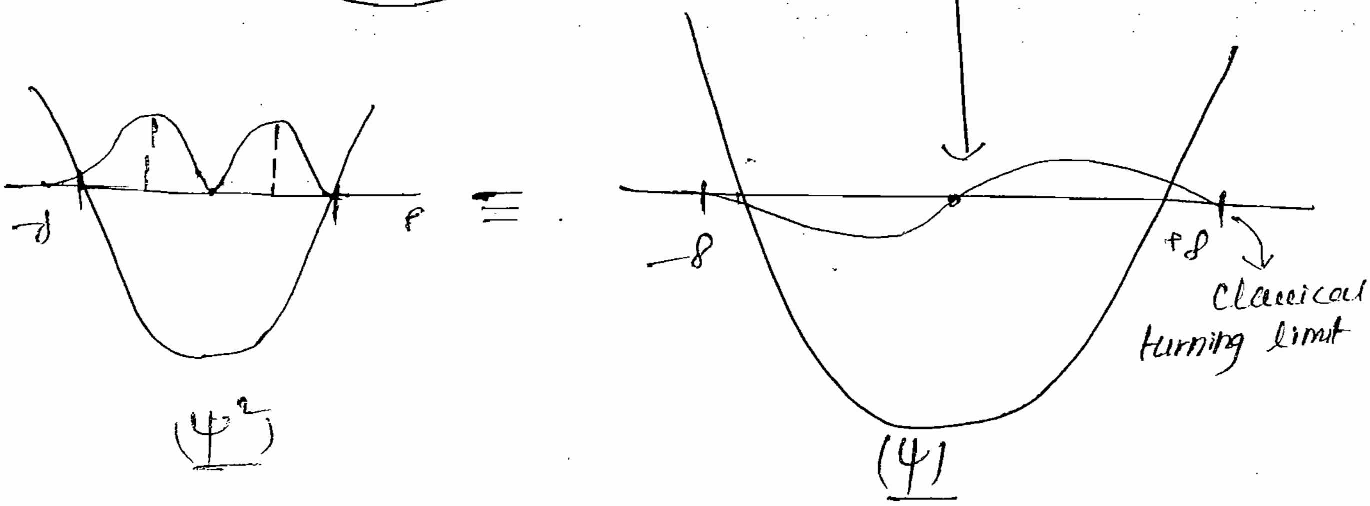
Position of Node: (ψ_n):

$H_n = 0$ roots of equation give nodal point.

for 1st excited state:

$$\psi_1 = C_1 H_1(\xi) e^{-\frac{\alpha x^2}{2}}$$





$$\psi_1 = C_1 \cdot \underline{2\sqrt{\alpha}\, x}\; e^{-\frac{\alpha x^2}{2}} =$$

$$H_1 = 0$$

$$2\sqrt{\alpha}\, x = 0$$

$\boxed{x = 0}$ at origin node ξ_1

<u>for ψ_2:</u> $\psi_2 = C_2 H_2 e^{-\frac{\alpha x^2}{2}}$

$$H_2 = 0$$

$$4\xi^2 - 2 = 0$$

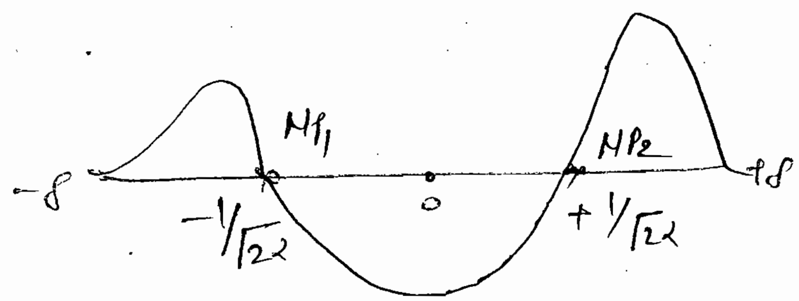
$$4(\sqrt{\alpha})^2 x^2 - 2 = 0$$

$$4\alpha x^2 = 2$$

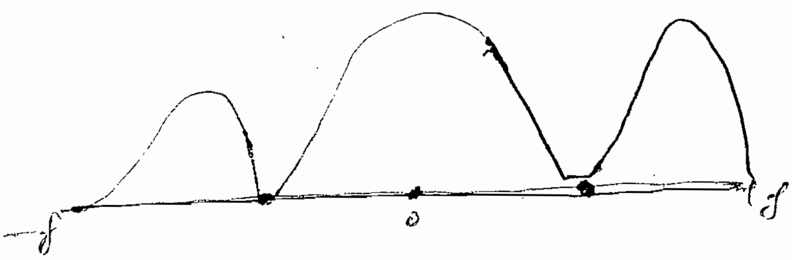
$x = \pm \frac{1}{\sqrt{2\alpha}}$ two node.

$$\alpha = \frac{\sqrt{Km}}{\hbar}$$

$\underline{\psi}$



ψ^2



$\psi_3 = \quad H_3 = 0$

$8\xi^3 - 12\xi = 0$

$\xi(8\xi^2 - 12) = 0 \quad 8\xi^3 = 12\xi$

$2\xi^{\cancel{3}} = 3\cancel{\xi}$

$\xi = 0$

$\xi^2 = \frac{3}{2}$

$\sqrt{\alpha}\, x = 0$

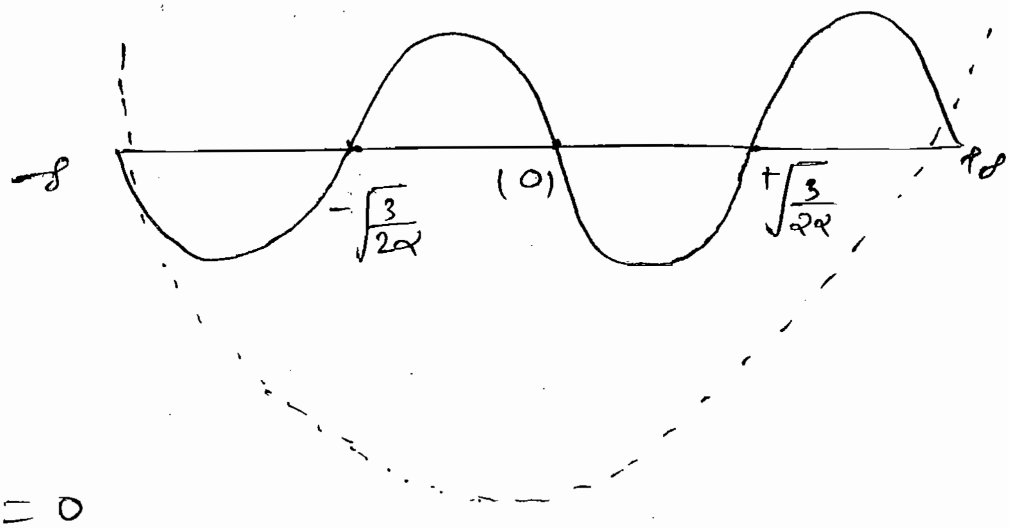
$x = 0$

$\xi = \sqrt{\frac{3}{2}}$

$\sqrt{\alpha}\, x = \sqrt{\frac{3}{2}}$

$x = \pm\sqrt{\frac{3}{2\alpha}}$

$x = 0, +\sqrt{\frac{3}{2\alpha}}, -\sqrt{\frac{3}{2\alpha}}$



$\underline{\underline{\psi_4}}$:

$H_4 = 0$

$16\xi^4 - 48\xi^2 + 12 = 0 \qquad 4\eta^2 - 12\eta + 3 = 0$

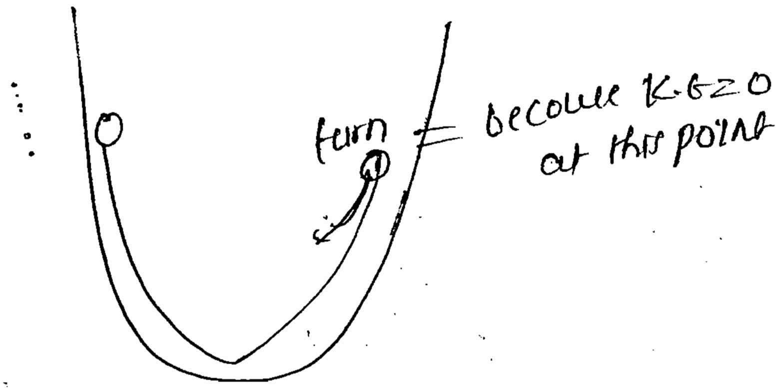
$4\xi^4 - 12\xi^2 + 3 = 0 \qquad \eta = \frac{+12 \pm \sqrt{144 - 48}}{8}$

$4\xi^2(\xi^2 - 3) + 3 = 0 \qquad \xi^2 = \frac{12 \pm \sqrt{96}}{8}$

$\xi^2 = \frac{12 \pm 4\sqrt{6}}{8}$

$\xi = \pm\left(\frac{3 \pm \sqrt{6}}{2}\right)^{1/2} \Leftarrow \xi^2 = \frac{3 \pm \sqrt{6}}{2}$

Turning point:



at classical turning point K.E = 0

$$E = K.E + P.E = \left(n+\frac{1}{2}\right)\hbar\omega.$$

$$\frac{1}{2}Kx^2 = \left(n+\frac{1}{2}\right)\hbar\omega$$

$$x^2 = \left(n+\frac{1}{2}\right)\frac{2\hbar\omega}{K}$$

$$x_{tl} = \pm\left[(2n+1)\frac{\hbar}{m\omega}\right]^{1/2}$$

or $x = \pm\sqrt{\left(n+\frac{1}{2}\right)\frac{2\hbar\omega}{K}}$

for ground state

$\psi_0 =$ $n = 0$ $\quad x = \pm\sqrt{\frac{1}{\cancel{2}}\times\frac{\cancel{2}\hbar\omega}{K}}$

$$= \pm\sqrt{\frac{\hbar\omega}{K}}$$

$$x = +\sqrt{\frac{\hbar\omega}{K}}, \; -\sqrt{\frac{\hbar\omega}{K}}$$

2D - Harmonic oscillator:

$$P.E = V = \frac{1}{2} m\omega_x^2 x^2 + \frac{1}{2} m\omega_y^2 y^2$$

$$\Downarrow$$

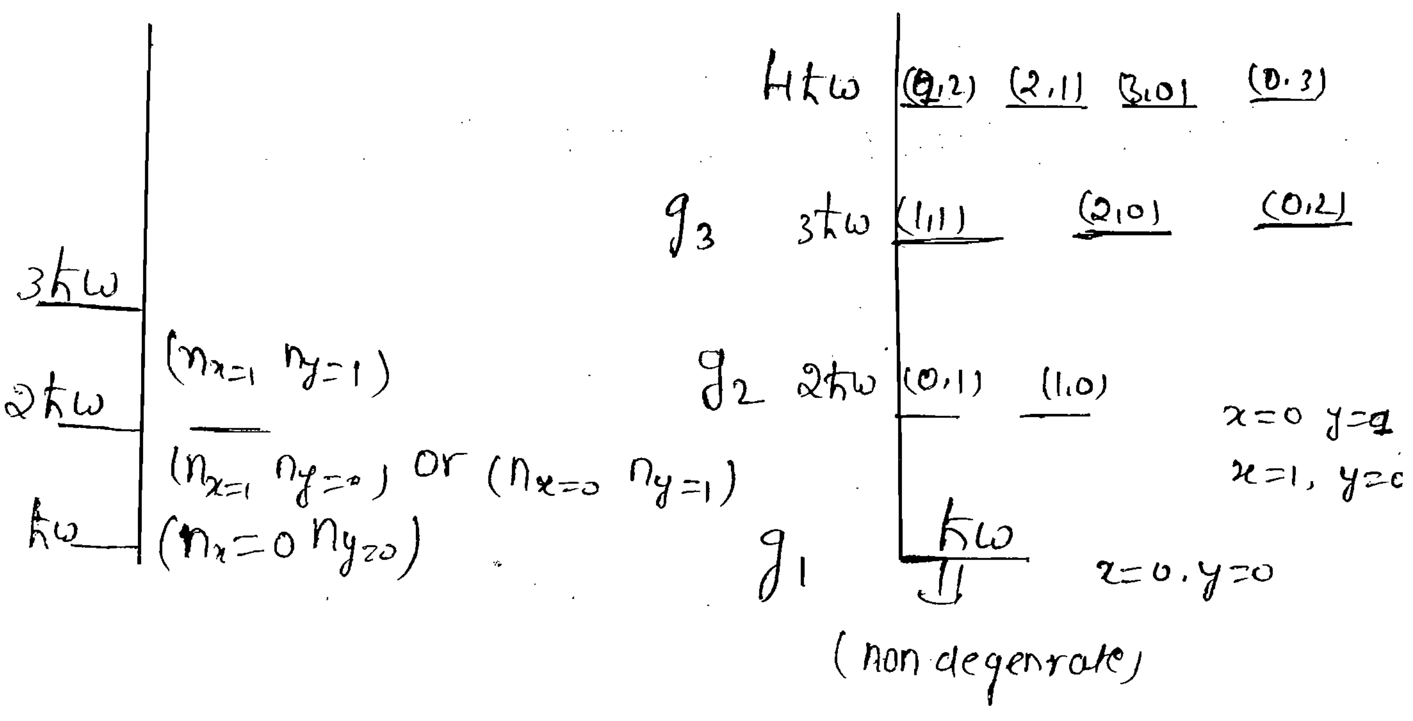
$$E = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y$$

$$\Downarrow \text{ if } \omega_x = \omega_y = \omega$$

$$E = \left(n_x + \frac{1}{2}\right) + n_y + \frac{1}{2}\Big)\hbar\omega$$

$$\boxed{E = (n_x + n_y + 1)\hbar\omega}$$

Energy level upto n=5:



(degenracy)

no. of state in same energy level. called degenracy.

If $\omega_x = 2\omega_y$

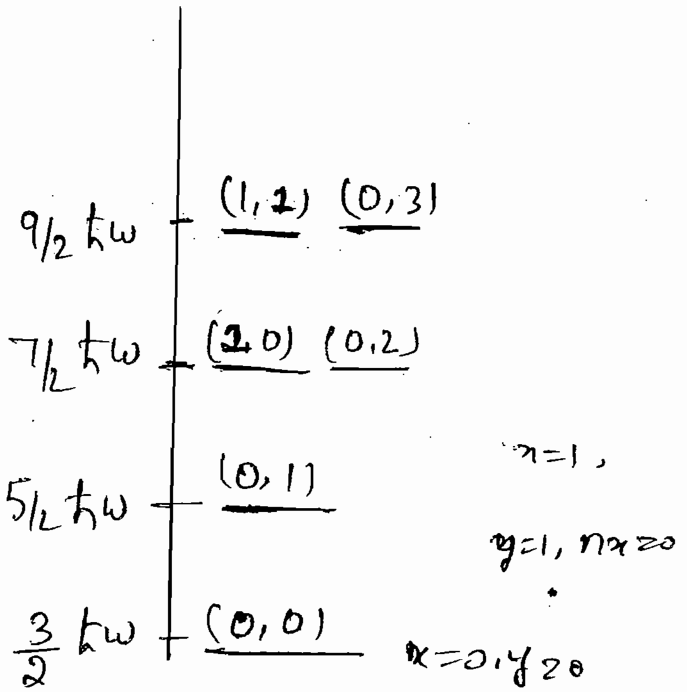
$$E = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y$$

$$= \left(n_x + \frac{1}{2}\right) 2\omega_y + \left(n_y + \frac{1}{2}\right)\hbar\omega_y$$

$$= \left(2n_x + 1 + n_y + \frac{1}{2}\right)\hbar\omega_y$$

$$E_n = \left(2n_x + n_y + \frac{3}{2}\right)\hbar\omega_y$$

<u>upto three energy level:</u>



Suppose

$V = 2m\omega^2x^2 + \frac{1}{2}m\omega^2y^2$ then what will the second E.S.

$$2\cancel{m}\omega^2\cancel{x^2} = \frac{1}{2}\cancel{m}\omega'^2\cancel{x^2}$$

$$\omega'^2 = \underline{2\omega^2}$$

$$E = \left(n_x + \frac{1}{2}\right)2\hbar\omega + \left(n_y + \frac{1}{2}\right)\hbar\omega$$

$$E = \left(2n_x + 1 + n_y + \frac{1}{2}\right)\hbar\omega$$

$$\boxed{E_n = \left(2n_x + n_y + \frac{3}{2}\right)\hbar\omega}$$

$\frac{7}{2}\hbar\omega$ — (1,0) (0,2)

$1^{st} \Rightarrow \frac{5}{2}\hbar\omega$ — (0,1)

Ground energy state $\Rightarrow \frac{3}{2}\hbar\omega$ — (0,0)

$$\hbar\omega = \frac{h}{2\pi}\cdot 2\pi\nu$$

$$\boxed{\hbar\omega = h\nu}$$

$\Rightarrow$ **3D- Harmonic oscillator:**

$$V = \frac{1}{2} m\omega_x^2 x^2 + \frac{1}{2} m\omega_y^2 y^2 + \frac{1}{2} m\omega_z^2 z^2$$

$$E_{n_x,n_y,n_z} = \left(\frac{1}{2}+n_x\right)\hbar\omega_x + \left(n_y+\frac{1}{2}\right)\hbar\omega_y + \left(n_z+\frac{1}{2}\right)\hbar\omega_z$$

Lett $\omega_x = \omega_y = \omega_z = \omega$ isotropic Harmonic oscillator.

$$\boxed{E = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega}$$

$9/2\,\hbar\omega$ — (1,1,1) (2,1,0) (0 2 1) 2 0 1 (3,0,0) 0,3,0) (0,0 3)

$7/2\,\hbar\omega$ — (1,1,0) (1,0,1) (0,0,1) (2,0,0) (0,2,0) (0,0,2)

$5/2\,\hbar\omega$ — (1,0,0) (0,1,0) (0,0,1)

$3/2\,\hbar\omega$ — (0,0,0) $\Rightarrow$ zeroth excited state

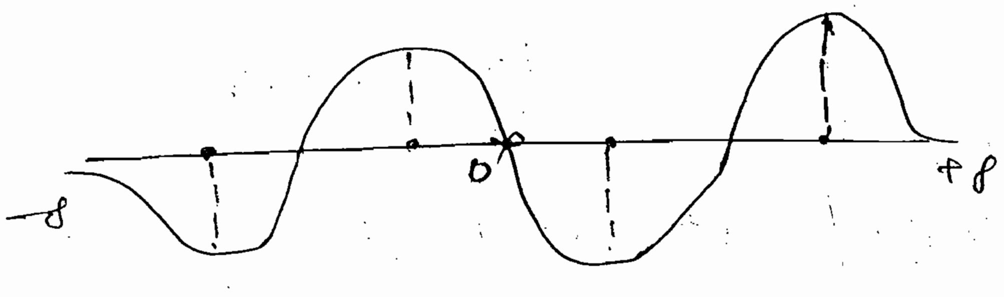
no of degenrate state for n^{th} excited state

$$= \quad g_n = \frac{1}{2}(n+1)(n+2)$$

for ground level $n=0$

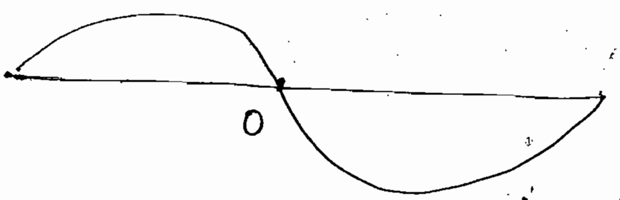
* Position of probability density maxima:

$n=3$



The maxima and minima of ψ are corresponding to the maximax of ψ^2.

position of maxima or minima of ψ is calculated by as $\frac{d\psi}{dx} = 0$ will give x (maxima and minima)



ie $\psi_n = C_n \cdot H_n \cdot e^{-\frac{\alpha x^2}{2}}$

$$\frac{d\psi_n}{dx} = C_n \frac{d}{dx}\left(H_n \cdot e^{-\frac{\alpha x^2}{2}}\right)$$

$$= C_n \left[H_n \frac{d}{dx} e^{-\frac{\alpha x^2}{2}} + e^{-\frac{\alpha x^2}{2}} \frac{d}{dx} H_n\right] = 0$$

$$\left(-\alpha x H_n e^{-\frac{\alpha x^2}{2}} + e^{-\frac{\alpha x^2}{2}} \frac{dH_n}{dx}\right) = 0$$

$$e^{-\frac{\alpha x^2}{2}}\left[-\alpha x H_n + \frac{\partial H_n}{dx}\right]=0$$

$$\boxed{-\alpha x H_n + \frac{dH_n}{dx} = 0} \quad \text{-----} \; (1)$$

$$\frac{dH_n}{dx} = \alpha x H_n$$

<u>Position of ψ^2</u>

For first excited state having $V = \frac{1}{2} m\omega^2 x^2$

$$-\alpha x \cdot 2\sqrt{\alpha}\, x + \frac{d}{dx}\sqrt{\alpha}\, x = 0$$

$$\frac{d}{dx} 2\sqrt{\alpha}\, x = \alpha x \cdot 2\sqrt{\alpha}\, x$$

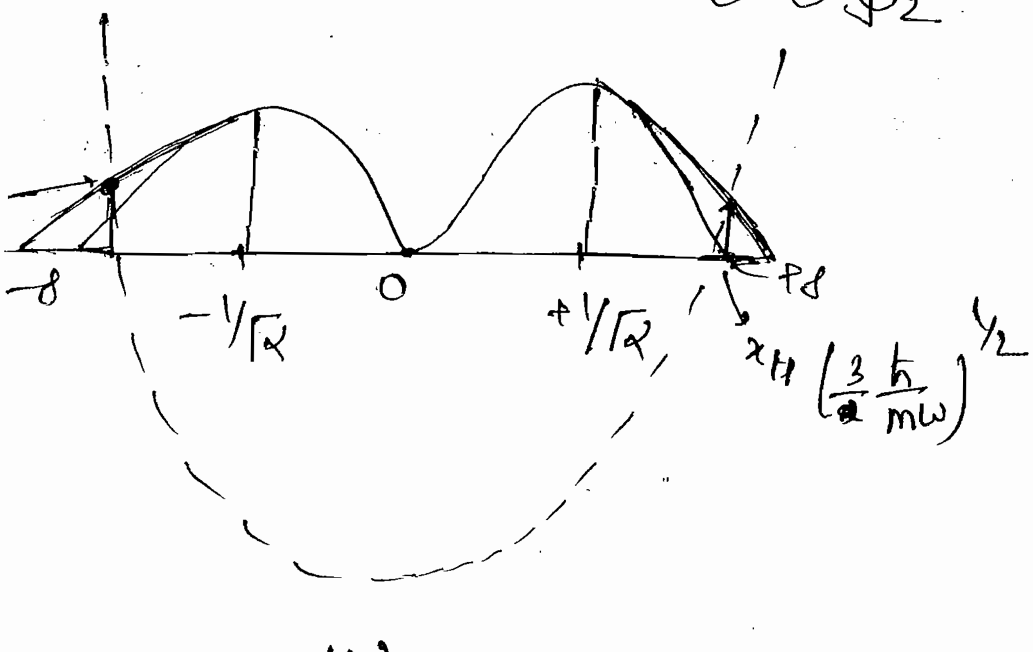
$$\cancel{2}\cancel{\sqrt{\alpha}} = \alpha x^2 \cancel{2}\cancel{\sqrt{\alpha}}$$

$$\cancel{\sqrt{\alpha} = +\alpha x \sqrt{\alpha}\, x}$$

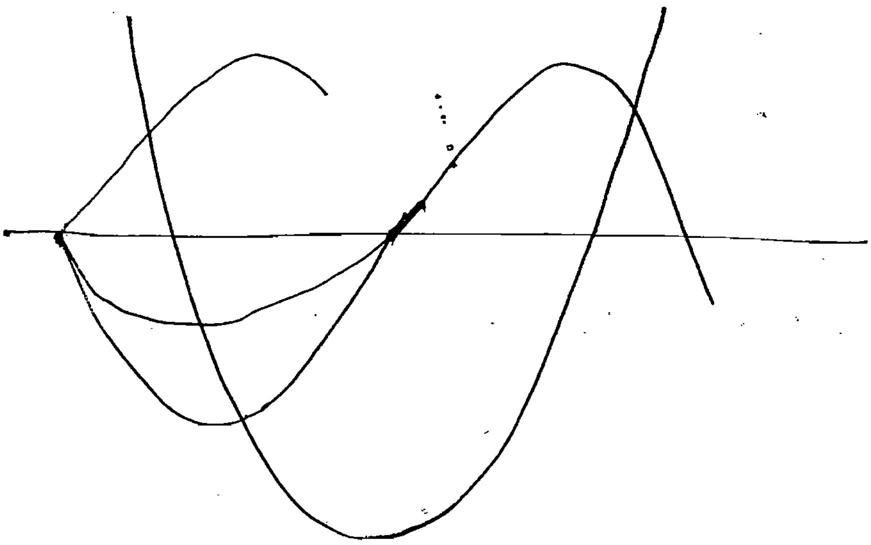
$$x = \pm\sqrt{\frac{1}{\alpha}}$$

$$\cancel{x^2 = \frac{1}{2}}$$

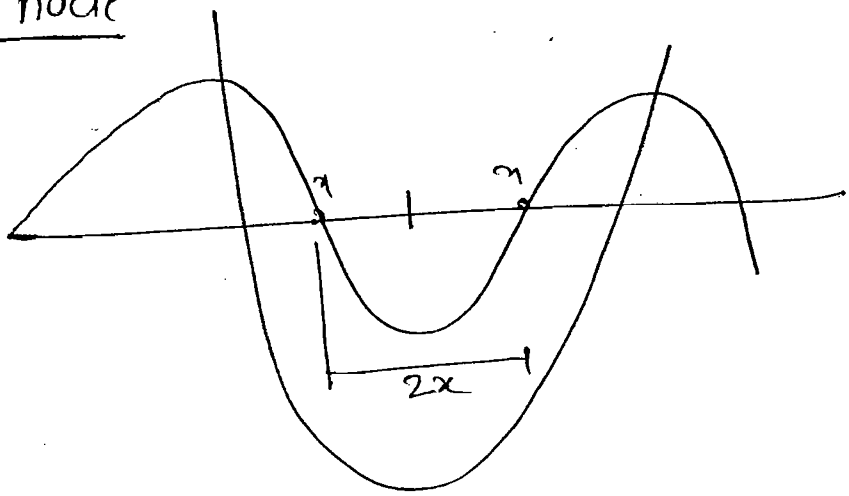
$$\cancel{x = \pm\sqrt{\frac{1}{2}}}$$

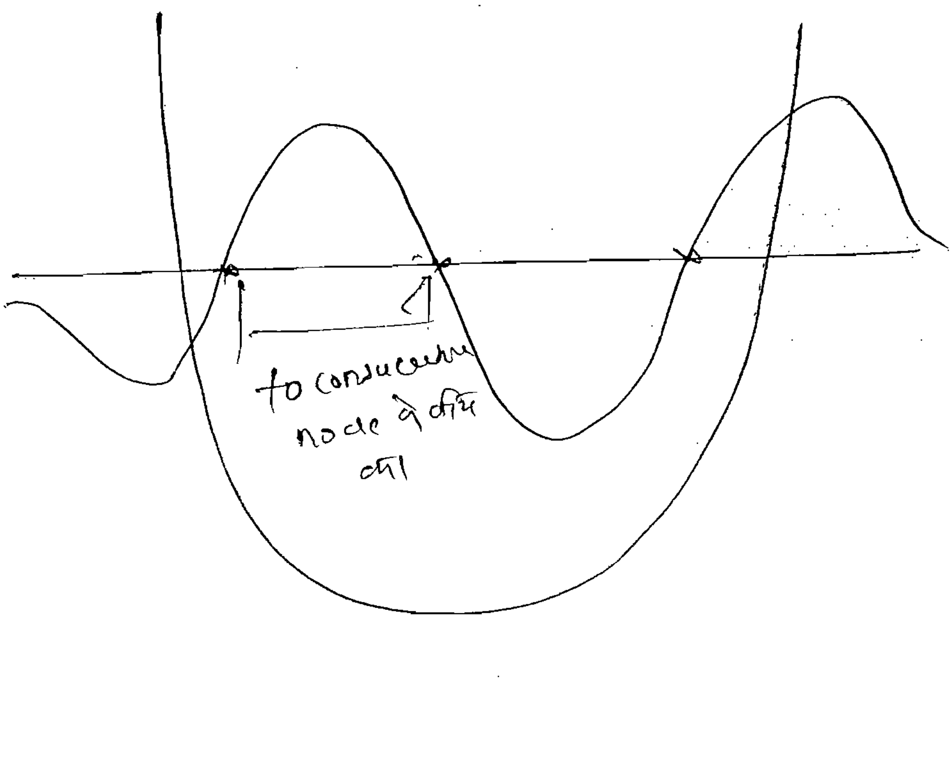


ψ^2



<u>distance b/w two node</u>

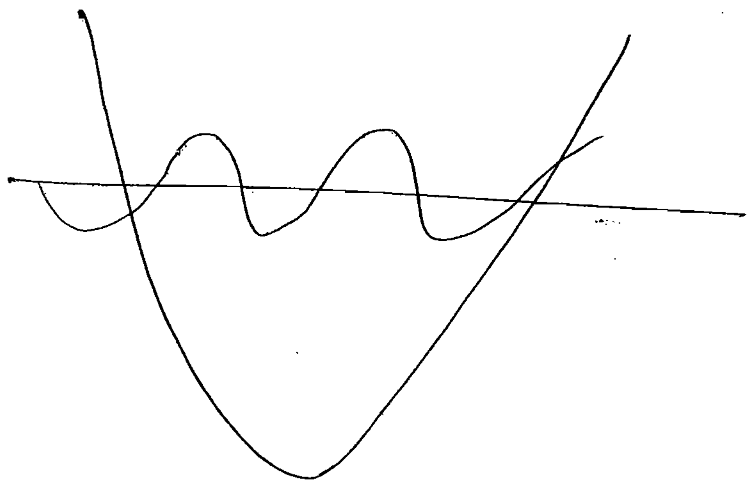


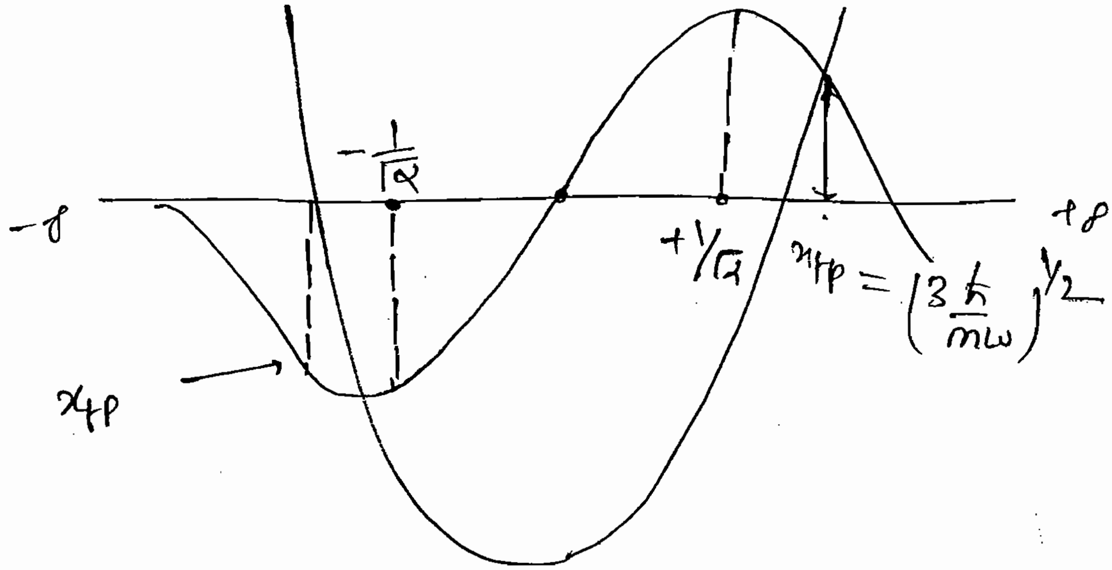


$$\psi = \begin{array}{cc} \text{minima} & \text{maxima} \\ \left[\begin{matrix} (-x_1, +x_1) & (-x_2 \ \ x_2) \end{matrix}\right] \end{array}$$

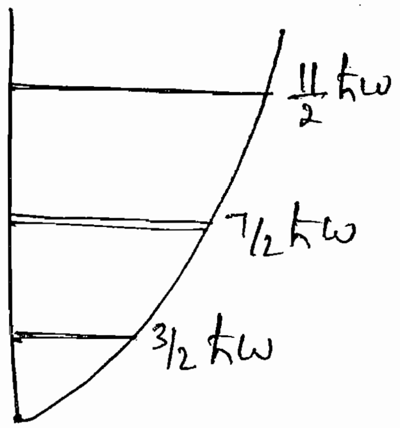
$$\psi^2 = \left[(-x+x_1),\ (x_1+x_2)\right]$$

$$\left[-x_1, x_1, -x_2, x_2\right]$$





Q1B



(1b) C ~~$=$~~ $n = 0, 1, 2, 3, \ldots$

$= \left(2n + \frac{3}{2}\right)\hbar\omega$

(2i)

$$\psi(x) = N\left[3\psi_0'(x) - 2\psi_1'(x) + \psi_2'(x)\right]\frac{1}{\sqrt{9+4+1}}$$

$$V = 4m\omega^2 x^2$$

$$\frac{1}{\cancel{2}}\cancel{m}\omega'^2 \cancel{x^2} = 4\cancel{m}\omega^2 \cancel{x^2}$$

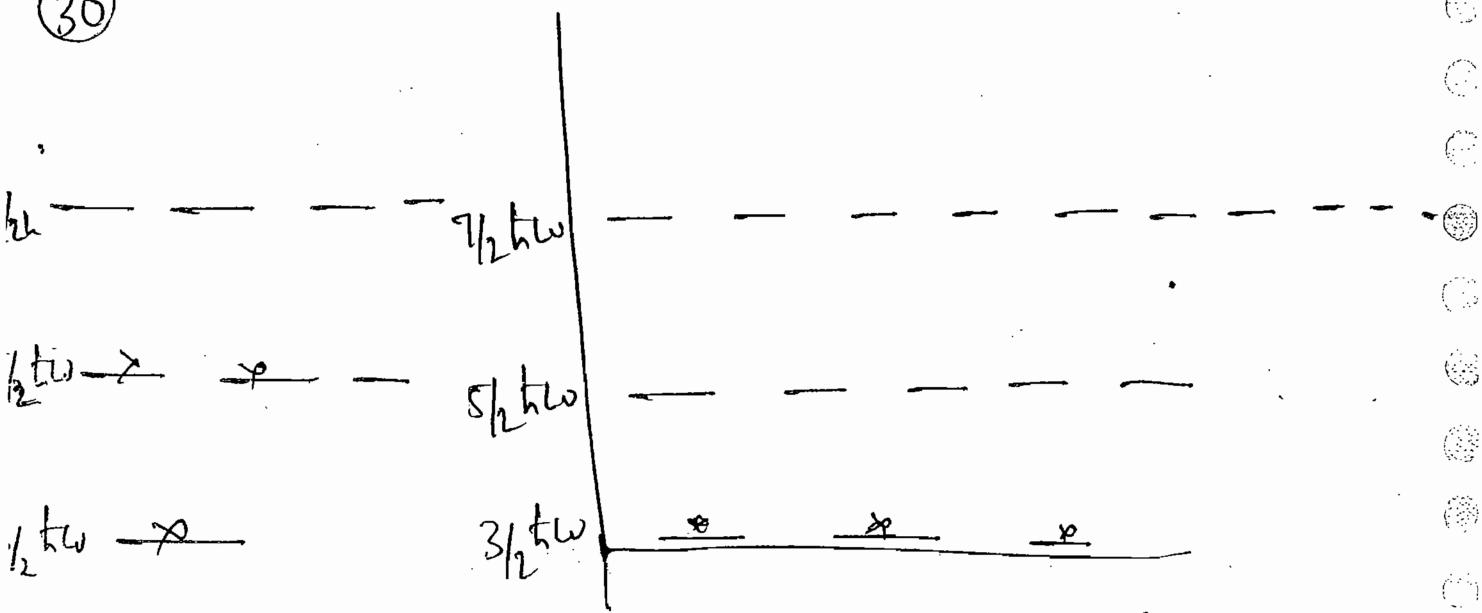
$$\omega' = \sqrt{8}\,\omega \qquad E = \left(n + \frac{1}{2}\right)\hbar\omega'$$

$$E = \left(n + \frac{1}{2}\right)\hbar\sqrt{8}\,\omega$$

$$E = \frac{1}{14} \times \frac{1}{\cancel{2}}\hbar\cancel{2}\sqrt{2}\,\omega + \frac{1}{14}\cdot\frac{3}{\cancel{2}}\hbar\cdot\cancel{2}\sqrt{2}\,\omega + \frac{1}{14}\cdot\frac{5}{\cancel{2}}\hbar\cancel{2}\sqrt{2}\,\omega$$

$E = \frac{1}{14}$

(30)



$\frac{3}{2}\hbar\omega + 5/2\,\hbar\omega + \frac{5}{2}\hbar\omega$ $\left(\frac{3}{2}\hbar\omega + \frac{3}{2}\hbar\omega + \frac{3}{2}\hbar\omega\right)$

$= \frac{13}{2}\hbar\omega$

(12) $\Delta x = \sqrt{\left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}}$

$\Delta x = \sqrt{(n+1/2)\frac{\hbar}{m\sqrt{\frac{K}{m}}}} = \boxed{\Delta x \propto K^{-1/4}}$

and $\boxed{p_x \propto K^{+1/4}}$

(13)

$\frac{\Delta x}{2} = \sqrt{\frac{1}{2}\frac{\hbar}{m\omega}}$ or $\left(\frac{d_1}{d_2}\right) = \left(\frac{K_1}{K_2}\right)^{-1/4}$

$d_2 = \frac{d_1}{2}$

$2 = \frac{K_1^{-1/4}}{K_2^{-1/4}} \Rightarrow 16 = \frac{K_1^{-1}}{K_2^{-1}}$

$16 = \frac{K_2}{K_1}$

$\boxed{K_2 = 16 K_1}$

(14) $\Delta x \Delta P = \text{const}$

$\frac{1}{2}\Delta P = \text{const}$

$\Delta P = 2 \text{ times} \times C \uparrow$

$$\int_0^{\infty} x^n e^{-\alpha x}\, dx = \frac{\Gamma(n+1)}{\alpha^{n+1}}$$

$$\int_0^{\infty} x^n e^{-\alpha x^2}\, dx = \frac{\Gamma\left(\frac{n+1}{2}\right)}{2\alpha^{n+1}}$$

HMO Huckel molecular orbital Theory:

$$\psi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \cdots$$

→ (I) Basis ⇒ $\{2P_z\}$

(II) doesn't differentiating conformational isomer, (cis, trans)

→ (II) System ⇒ (1) conjugated linear chain.

(2) conjugated monocyclic chain

→ (III) For Exam: content:

1. Total π electron Energy: = E_π = ?
2. π bonding energy = ?
3. Delocalisation energy = ?
4. No. of delocalised bond.
5. Energy level in a system.
6. π bond order b/w two centres.
7. Electron density at centres (orbital coefficient জানা)
8. Charge density at centre.
9. free valence (F) i.e about valency কি কোথায় থাকছে.
10. no. of non bonding molecular orbital in a system
11. Huckel determinant.

⇒ This theory only depends on <u>connectivity</u>.

$C_1 - C_2 - C_3 - C_4 - C_5$ (different)

$C_1 - C_2(-C_5) - C_3 - C_4$,,

<u>Note</u> connectivity will different then it will give different result.

basis = no. of centre = no. of P_z e^- = no. of π e^-

⇒ form of MO may be

$$\psi_a = C_{1a}\phi_1 + C_{2a}\phi_2 + C_{3a}\phi_3$$

$$\Rightarrow \psi_1 = C_{11}\phi_1 + C_{21}\phi_2 + C_{31}\phi_3$$

$$\psi_2 = C_{12}\phi_1 + C_{22}\phi_2 + C_{23}\phi_3$$

$$\psi_3 = C_{13}\phi_1 + C_{32}\phi_2 + C_{33}\phi_3$$

$$\begin{array}{c|ccc|} & \phi_1 & \phi_2 & \phi_3 \\ \hline \phi_1 & H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ \phi_2 & H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ \phi_3 & H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{array}$$

$\langle \phi_1 | H | \phi_1 \rangle = H_{11}$

① Culamb ontegral:

$\langle \phi_i | \hat{H} | \phi_i \rangle = \alpha,$

② Resonance ontegral:

$\langle \phi_i | \hat{H} | \phi_j \rangle = \beta$ 9f = $i - j$ σ bond से connect हो

$= 0$ 9f = $i \not- j$ are not conected by σ

$C_1 - C_2 - C_3$

$C_{12} = \beta, \quad C_{13} = 0$

③ Overlap integral: 9ts a constant (S) it will be a no.

$$S_{11} = \int \phi_1^* \phi_1 \, d\tau = 1, \quad \int \phi_1^* \phi_2^* \, d\tau = 0$$

$$S_{12} = \langle \phi_i | \phi_i \rangle = 1 \qquad \langle \phi_i | \phi_j \rangle = 0$$

eg $C^1 - C^2 - C^3 - C^4$

$$
\begin{array}{c|cccc|}
 & 1 & 2 & 3 & 4 \\
1 & H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\
2 & H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{23} \\
3 & H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & H_{34} - ES_{34} \\
4 & H_{41} - ES_{41} & H_{41} - & & \\
\end{array} = 0
$$

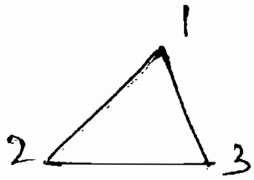
$$\Big\downarrow \text{By appling HMO}$$

$$
\begin{array}{c|cccc|}
 & 1 & 2 & 3 & 4 \\
1 & \frac{\alpha - E}{\beta} & \beta/\beta & & \\
2 & & & & \\
3 & & & & \\
4 & & & & \\
\end{array}
$$

$x =$ $\frac{\alpha - E}{\beta}$

2

(1)



$$\begin{array}{c|ccc|}
 & 1 & 2 & 3 \\
1 & x & 1 & 1 \\
2 & 1 & x & 1 \\
3 & 1 & 1 & x
\end{array} = 0$$

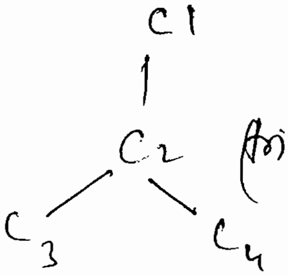
where = $x = \frac{\alpha - E}{\beta}$

(2) $C_1 - C_2 - C_3$

$$\begin{array}{c|ccc|}
 & 1 & 2 & 3 \\
1 & x & 1 & 0 \\
2 & 1 & x & 1 \\
3 & 0 & 1 & x
\end{array} = 0$$

$x = \frac{\alpha - E}{\beta}$

(3)



(trimethylene methane)

$$\begin{array}{c|cccc|}
 & 1 & 2 & 3 & 4 \\
1 & x & 1 & 0 & 0 \\
2 & 1 & x & 1 & 1 \\
3 & 0 & 1 & x & 0 \\
4 & 0 & 1 & 0 & x
\end{array} = 0$$

Energy levels in linear chain molecules:

$$\boxed{E = \alpha + 2\beta\cos\left(\frac{k\pi}{n+1}\right)}$$

$k = 1, 2, 3, 4, 5 \ldots$ translational quantum no.

n = no. of centre.

e.g. C − C − C

$n = 3$, , k की $(1, 2, 3)$

$$E = \alpha + 2\beta\cos\left(\frac{\pi}{3+1}\right) = \alpha + 2\beta\cos\left(\frac{\pi}{4}\right)$$

$$= \alpha + \cancel{2}\beta \times \frac{1}{\sqrt{\cancel{2}}}$$

$$E_1 = (\alpha + \sqrt{2}\beta) = \alpha + 1.41\beta$$

K = 2

$$E = \alpha + 2\beta\cos\left(\frac{2\pi}{4}\right)$$

$$E_1 = \alpha$$

K = 3

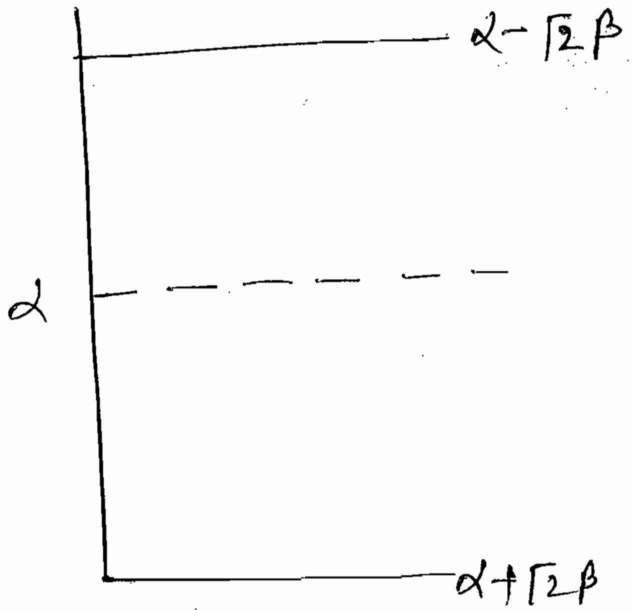
$$E = \alpha + 2\beta\cos\frac{3\pi}{4}$$

$$E = \alpha + 2\beta \times \left(-\frac{1}{\sqrt{2}}\right)$$

$$(E_1 = \alpha - 1.141\beta)$$

$\beta = -75$ kJ/mol

$\alpha = 0$



$\Rightarrow \quad \overset{1}{C} - \overset{2}{C}$

$$\begin{array}{c|cc} & 1 & 2 \\ \hline 1 & & \\ 2 & & \end{array} \quad \begin{array}{c} \\ 1 \\ 2 \end{array}\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$x = \frac{\alpha - E}{\beta}$

$x^2 - 1 = 0$

$x = +1, -1$

$+1 = \frac{\alpha - E}{\beta}$

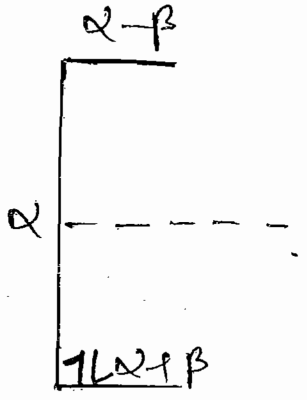
$\boxed{E = \alpha + \beta}$

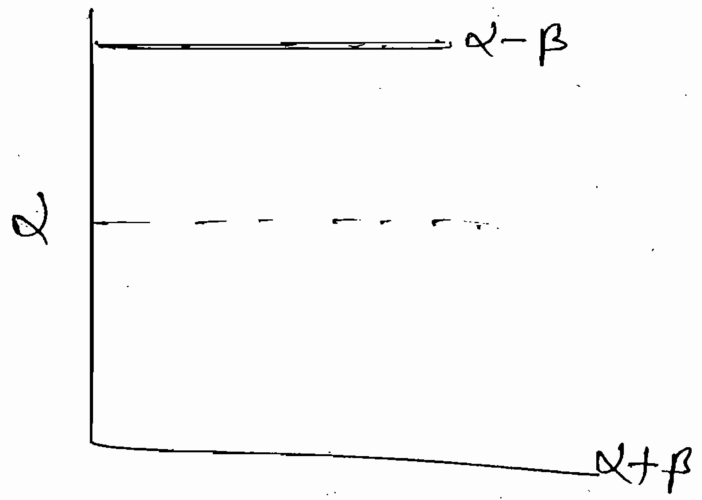
$x = -1$

$-1 = \frac{\alpha - E}{\beta}$

$-\beta = \alpha - E$

$\boxed{E = \alpha + \beta}$

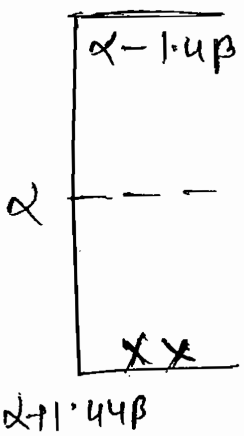


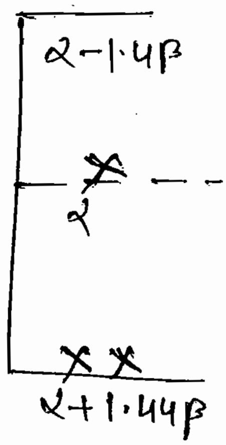


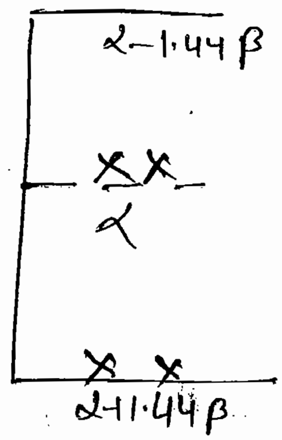
$E_\pi = 2(\alpha + \beta)$

$E_\pi = 2\alpha + 2\beta$

$C-C-C^{+}$ (1) $>$ $C-C=C^{\circ}$ (2) $>$ $C-C=C^{-}$ (3)







$E_{\pi} = 2(\alpha + 1.44\beta)$

$\underline{E_{\pi} = 2\alpha + 2.88\beta}$

$E_{\pi} = 2(\alpha + 1.44\beta) + 1\alpha$

$\underline{E_{\pi} = 3\alpha + 2.88\beta}$

$E_{\pi} = 2(\alpha + 1.44\beta) + 2\alpha$

$\underline{E_{\pi} = 4\alpha + 2.88\beta}$

$\underline{\pi \text{ Bonding Energy}}$: we will not consider α because β α isolated from π energy eq

$\underline{E_{\pi} = 2.88\beta}$ $\underline{E_{\pi} = 2.88\beta}$ $\underline{E_{\pi} = 2.88\beta}$

π bonding energy / electron

$E_{\pi}/e = \frac{2.88\beta}{2} = 1.44\beta$ $E_{\pi}/e = \frac{2.88\beta}{3} = 0.96\beta$ $E_{\pi}/e = \frac{2.88\beta}{4} = 0.72$

(1) $>$ (2) $>$ (3)

$$\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$$

$$\begin{array}{c c}
 & \begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \end{array} \\
\begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array} & \begin{vmatrix} x & 1 & 0 & 0 & 0 \\ & & & & \\ & & & & \\ & & & & \\ & & & & \end{vmatrix}
\end{array}$$

$$\overset{1}{C} - \overset{2}{C} - \overset{3}{C} - \overset{4}{C} - \overset{5}{C}$$ Pentadienyl system

$$\begin{array}{c|ccccc|}
 & 1 & 2 & 3 & 4 & 5 \\
1 & x & 1 & 0 & 0 & 0 \\
2 & 1 & x & 1 & 0 & 0 \\
3 & & & & & \\
4 & & & & & \\
5 & & & & &
\end{array} = 0$$

$$\frac{\alpha - E}{\beta} = x \quad , \quad E = \alpha + 2\beta \cos\left(\frac{k\pi}{n+1}\right)$$

$n = 5$

$k=1 \quad E = \alpha + 2\beta \cos\left(\frac{\pi}{6}\right)$

$= \alpha + \cancel{2}\beta \times \frac{\sqrt{3}}{\cancel{2}} = \alpha + \sqrt{3}\beta = \underline{\alpha + 1.73\beta}$

$k=2 \quad E = \alpha + 2\beta \cos\left(\frac{\cancel{2}\pi}{\cancel{6}\,3}\right) = \underline{\alpha + \beta}$

$k=3 \quad E = \alpha + 2\beta \cos\left(\frac{\cancel{3}\pi}{\cancel{6}\,2}\right) = \underline{\alpha}$

$= \alpha + 2\beta \times 0 = \cancel{\alpha + 2\beta}$

180

6

$k=4 \quad E = \alpha + 2\beta \cos\left(\frac{4\pi}{6}\right) = \alpha + 2\beta \times \cos\left(\frac{2\pi}{3}\right)$

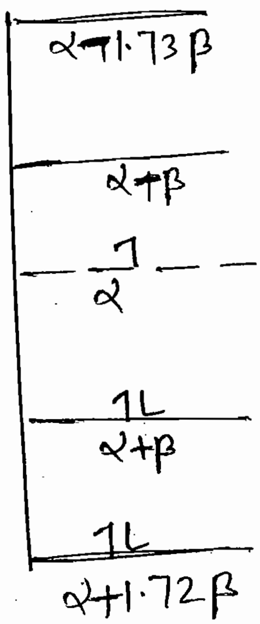
$= \underline{\alpha - \beta}$

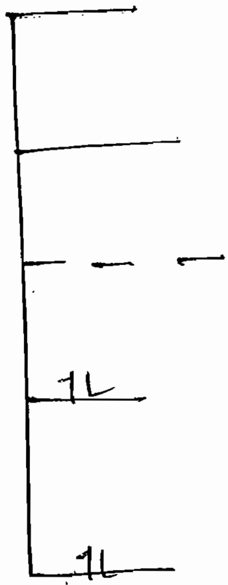
30

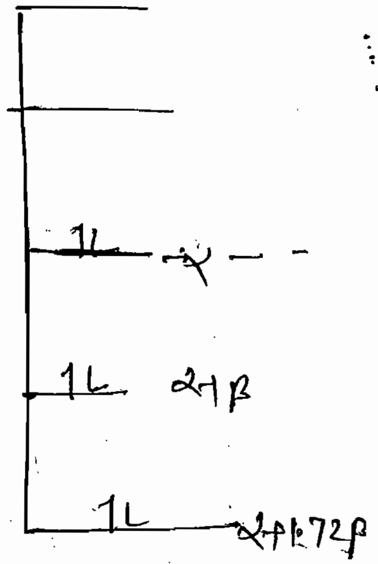
180

$k=5 \quad E = \alpha + 2\beta \cos\left(\frac{5\pi}{6}\right)$

$= \alpha + 2\beta \times (-0.86) = \underline{\alpha - 1.72\beta}$







(C)

$$E_\pi^{\cdot} = 2(\alpha+1.72\beta) + 2\alpha + 2\beta + \alpha$$

$$= 5\alpha + 3.44\beta + 2\beta$$

$$E_\pi^{\cdot} = 5\alpha + 5.44\beta$$

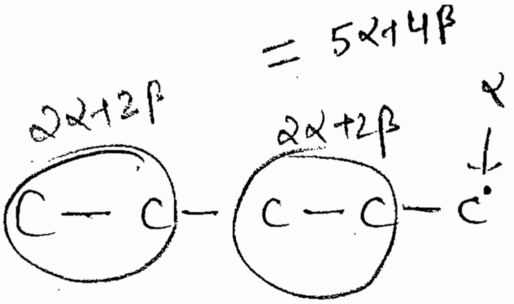
$$E_\pi^{\ominus} = 2\alpha + 3.44\beta + 2\alpha + 2\beta$$

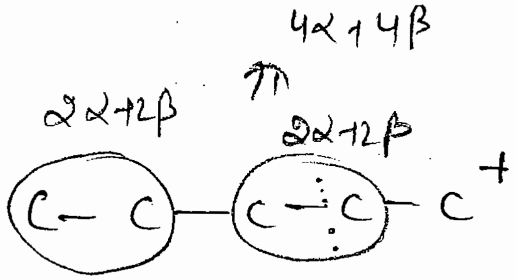
$$= 4\alpha + 5.44\beta + 2\alpha$$

$$= 6\alpha + 5.44\beta$$

(C) $$E_\pi^{\oplus} = 2\alpha + 3.44\beta + 2\alpha + 2\beta$$

$$= 4\alpha + 5.44\beta$$





$E_\pi = 5\alpha + 5.464\beta$

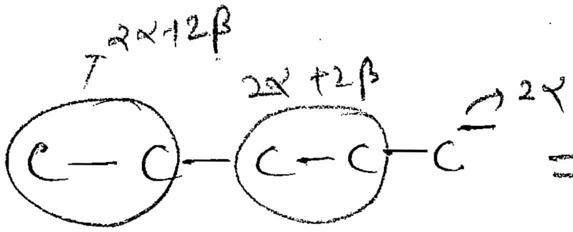
$DE = (5\alpha + 5.464\beta) - (5\alpha + 4\beta)$

$= 1.464\beta$

$E_\pi = 4\alpha + 5.464\beta$

$DE = (4\alpha + 5.464\beta) - (4\alpha + 4\beta)$

$= 1.464\beta$



$\Rightarrow E = 6\alpha + 4\beta$

$E_\pi = 6\alpha + 5.464\beta$

$DE = (6\alpha + 5.464\beta) - (6\alpha + 4\beta)$

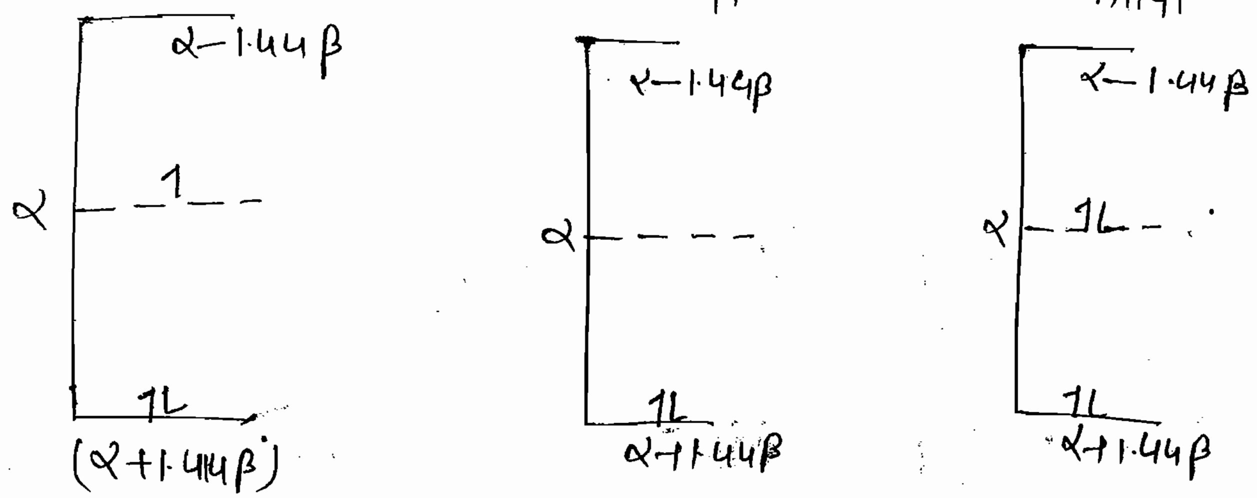
$= \underline{1.464\beta}$

Delocalisation Energy $= E_\pi -$ (Energy of ethylene unit) $\times$ no. of ethylene + no. of isolated $e^- \times \alpha$

$= E_\pi - (2\alpha + 2\beta) \times$ no. of $(C{=}C)$ + no of isolated $e^- \times \alpha$

allyle system:

allyl° allyl$^{\oplus}$ Allyl^{-}



$E_\pi = 2\alpha + 2.828\beta + \alpha$ $\quad E_\pi = 2\alpha + 2.828\beta + \cdot$ $\quad E_\pi = 4\alpha + 2.828\beta$

$= 3\alpha + 2.828\beta$

C — C — C

$D.E = 2.828\beta - 2\alpha - 2\beta - \alpha + 3\alpha$

$=$ ⇓

$= 0.828\beta$ $\quad DE = 0.828\beta$ $\quad DE = 0.828\beta$

$D.E/e = \frac{0.828\beta}{3}$ $\quad DE/e = \frac{0.828\beta}{2}$ $\quad DE/e = \frac{0.828\beta}{4}$

$=$

Butadien:

$$C = C - C = C$$

$$E = \alpha + 2\beta \cos\left(\frac{K\pi}{n+1}\right) \qquad n=4$$

$$E_1 = \alpha + 2\beta \cos\left(\frac{\pi}{5}\right)^{36} = \alpha + 2\beta(0.8090) = \alpha + 1.6180$$

$$E_1 = \alpha + 2\beta \cos\left(\frac{2\pi}{5}\right)^{72} = \alpha + 2\beta(0.3090) = \alpha + 0.618\beta$$

$$E_2 = \alpha + 2\beta \cos\left(\frac{3\pi}{5}\right)^{144} = \alpha + 2\beta \cos 108$$

$$= \alpha - 0.6180\beta$$

$$E_3 = \alpha + 2\beta \cos\left(\frac{4\pi}{5}\right) = \alpha + 2\beta \cos\frac{4\pi}{5}$$

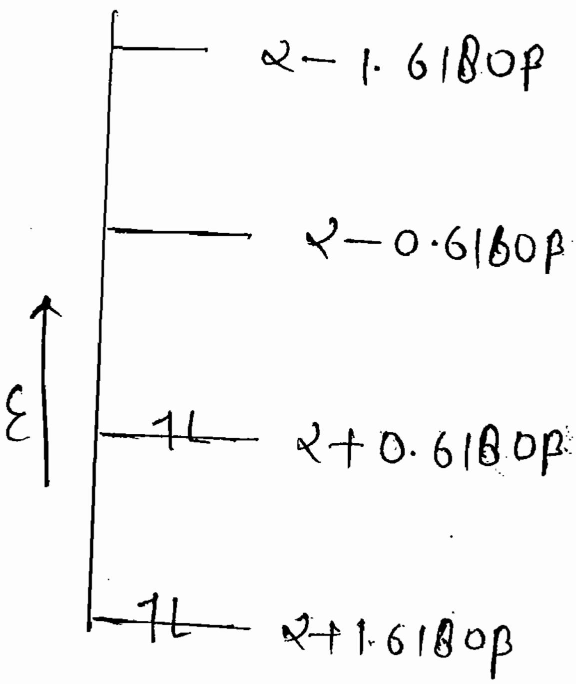
$$= \alpha - 1.6180$$

$$\cancel{E_4 = \alpha + 2\beta \cos(\pi)}$$

$$\cancel{\boxed{E_4 = \alpha - 2\beta}}$$

~~1.95 82 52~~

0	18	36	54	72	90°	108	126	144	
1	.95	.82	.52	.32	0	−.32	−.52	−.80	



$E_\pi = 2(\alpha + 1.6180\beta) + 2(\alpha + 0.6180\beta$

$= 4\alpha + 2.$[illegible]$\beta + 1.$[illegible]β

$E_\pi = 4\alpha + 4.472\beta$

π · bonding energy $= 4.472\beta$

$D \cdot E = 4.472\beta - 4\beta$

$\boxed{D \cdot E = 0.472\beta}$

HMO for monocyclic system :

⋮

$$E = \alpha + 2\beta \cos\left(\frac{2\pi J}{N}\right)$$

J = Rotational quantum no.

$0, \pm 1, \pm 2, \pm 3, \pm 4 \ldots$

$J = 0 . \quad N = 3$

$$E = \alpha + 2\beta \cos 0$$

$$\boxed{E = \alpha + 2\beta}$$

$J = +1 \quad N = 3$

or

$J = -1$

$$E = \alpha + 2\beta \cos\left(\frac{2\pi}{3}\right)$$

$$= \alpha + 2\beta \cdot \frac{-1}{2} =$$

$$\boxed{E = \alpha - \beta}$$

$J = 2 \quad N = 3$

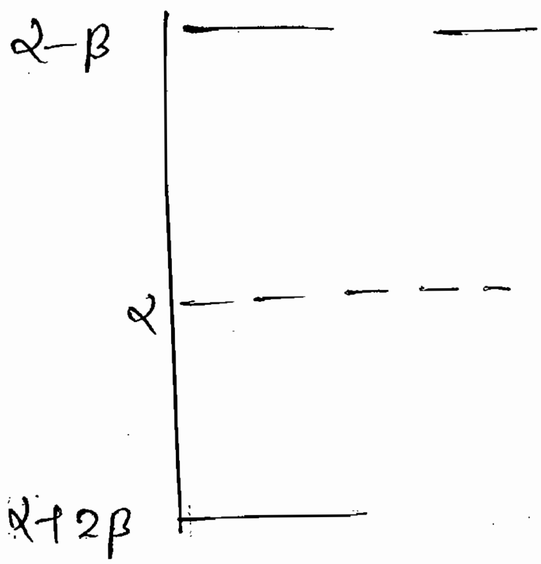
$$E = \alpha + 2\beta \cos\left(\frac{4\pi}{3}\right)$$

$$E = \alpha + 2\beta \cos 240$$

$$= \alpha + 2\beta$$

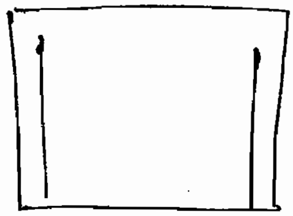
$J = (+1) \Rightarrow E = \alpha - \beta$

$J = (-1) \Rightarrow E = \alpha - \beta$



α−β
α
α+2β

Cyclo buta diene:



$$E = \alpha + 2\beta \cos\left(\frac{2\pi J}{N}\right)$$

$J = 0$

$$\boxed{E = \alpha + 2\beta}$$

$J = +1$ $\quad = \alpha + 2\beta \cos \frac{2\pi 1}{4}$

$E = \cancel{\alpha + 2\beta \times \left(\frac{-1}{2}\right)} = \alpha + 2\beta \times 0$

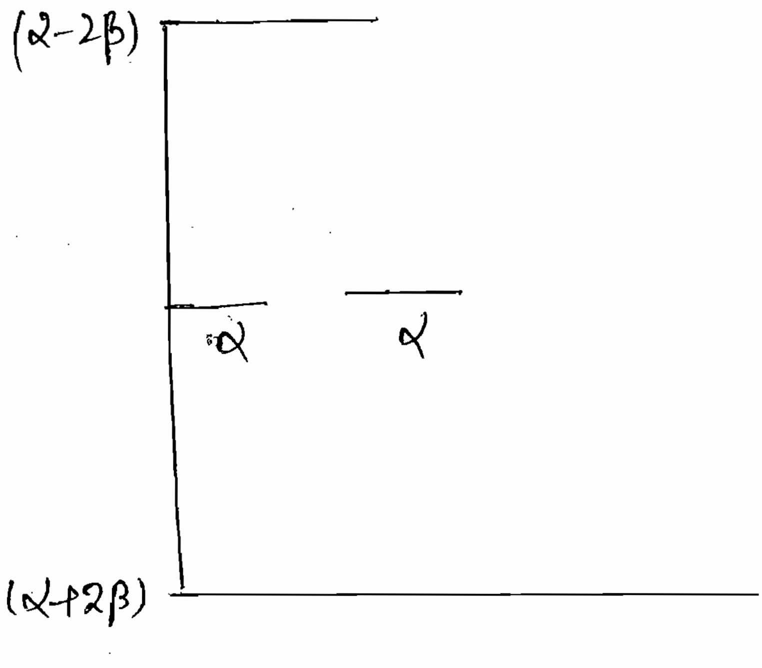
$\cancel{E = \alpha\beta}$ $\quad = \alpha$

$J = +1$ $\quad \alpha = 0,$ $\quad J = -1$ $\quad = \alpha = 0$

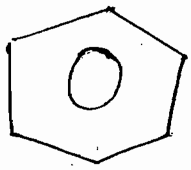
$J = +2$

$$E = \alpha + 2\beta \cos\left(\frac{2\pi \times 2}{4}\right)$$

$$\boxed{E = \alpha - 2\beta}$$



For Benzene:



$$E = \alpha + 2\beta \cos\left(\frac{2\pi J}{n}\right)$$

$n = 6 \quad J = 0$

$E = \alpha + 2\beta$

$n = 6, \; J = \pm 1$

$E = \alpha + 2\beta \cos\left(\frac{2\pi}{6}\right)$

$E = \alpha + \beta \; (2)$

$n = 6, \; J = \pm 2$

$E = \alpha + 2\beta \cos\left(\frac{4\pi}{6}\right)$

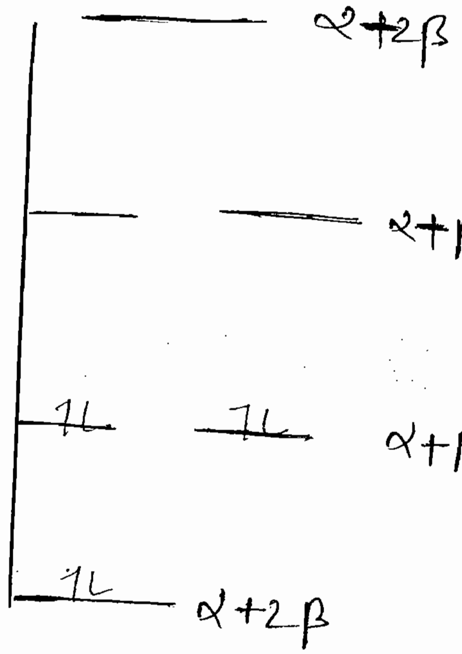
$= \alpha + 2\beta \cos\left(\frac{2\pi}{3}\right)$

$\underline{E = \alpha - \beta} \; (2)$

$n = 6, \; J = 3$

$E = \alpha + 2\beta \cos\left(\frac{2\pi \times 3}{6}\right)$

$E = \alpha - 2\beta$



$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta)$$

$$= 2\alpha + 4\beta + 4\alpha + 4\beta$$

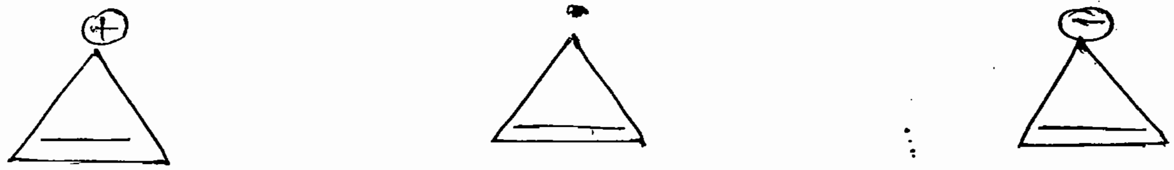
$$= 6\alpha + 8\beta$$

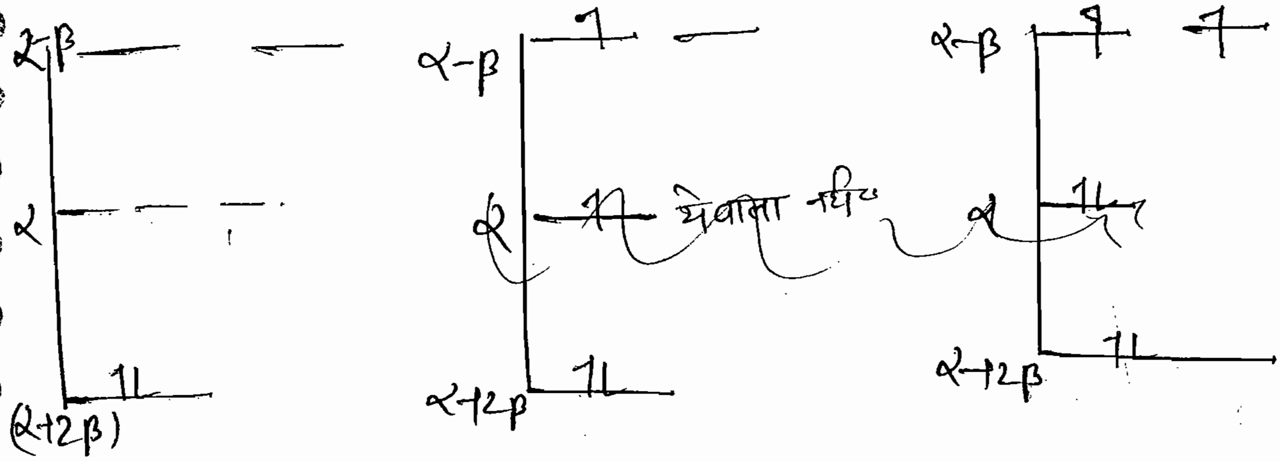
π bonding energy $= 8\beta$

Delocalisation energy $= 8\beta - 3\text{ bond} \times 2\beta$

$= 8\beta - 6\beta$

$= \underline{\underline{2\beta}}$





$E_\pi = 2(\alpha+2\beta)$

$= 2\alpha + 4\beta$

$\pi BE = 4\beta$

$DE = 2\beta$

Delocalisation energy/e^-

$= \frac{2\beta}{2}$

$= \beta$

(A)

$E_\pi = 2\alpha+4\beta+\cancel{\alpha}$

$E_\pi = 3\alpha+4\beta$

$\pi BE = 4\beta$

$DE = 2\beta$

Delocalisation energy/e^- =

$= \frac{2\beta}{3}$

$= 0.6\beta$

(B)

$E_\pi = 2\alpha+4\beta+2\alpha$

$= 4\alpha+4\beta$

$\pi BE = 4\beta$

$DE = 2\beta$

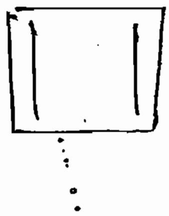
$DE/e^- = \frac{2\beta}{4}$

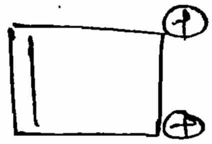
$= 0.5\beta$

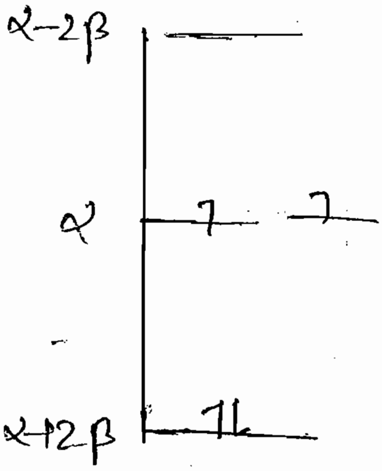
(C)

$\boxed{A > B > C}$ Stability

Cyclobutadiene:





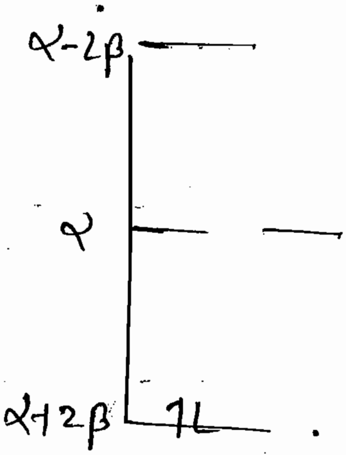


$E_\pi = 2(\alpha+2\beta)+2\alpha$

$= 2\alpha+2\beta+2\alpha$

$= 4\alpha+2\beta$

D.E $= 0$



$E_\pi = 2(\alpha+2\beta)$

$= 2\alpha+4\beta$

D.E $= 2\beta$

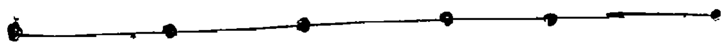
Electron density

C — C
x
↓
(π-bond order)

(y) Free valency y = const. no.

Assi. 8

(6)



0.8711 0.8711

E_π = πBO = 3.498

(localised) Expected π bond order = 3

Excess πBO = 3.498 − 3

= 0.498

according to HMO energy of a π bond is 2β

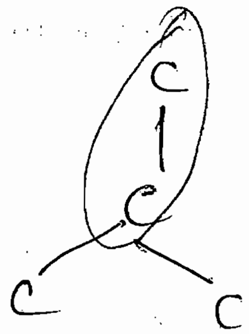
= 0.498 × 2β

= 0.987β

① π bonding order $= 3 \times 0.5777$

$= 1.7331$

localised $= 1$



$E\pi BO = 1.7331 - 1$

$= 0.7331$

delocalisation energy $= 0.7331 \times 2\beta$

$= \underline{1.4662}\,\beta$

$\underline{C_6H_6}$ 0.6667×6

$=$

5 april:

(3) $\psi = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$

$$\langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\psi = \frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 + \frac{1}{2}\phi_5 - \frac{1}{2}\phi_6$$

$$= \left(\frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 + \frac{1}{2}\phi_5 - \frac{1}{2}\phi_6\right)\frac{1}{\sqrt{\frac{1}{4}+\frac{1}{4}+\frac{1}{4}+\frac{1}{4}}}$$

Normalised.

$$\langle E \rangle = \langle \psi | H | \psi \rangle$$

$$= \left(\frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 + \frac{1}{2}\phi_5 - \frac{1}{2}\phi_6\right)\hat{H}\left(\frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 + \frac{1}{2}\phi_5 - \frac{1}{2}\phi_6\right)$$

$$= \frac{1}{2}\frac{1}{2}\langle(\phi_2 - \phi_3 + \phi_5 - \phi_6)|\hat{H}|\phi_2 - \phi_3 + \phi_5 - \phi_6\rangle$$

$$= \cancel{\frac{1}{4}(\alpha+\alpha+\alpha+\alpha)}$$

$$= \frac{1}{4}(\alpha - \beta - \beta + \alpha + \alpha - \beta - \beta + \alpha)$$

$$= \frac{1}{4}(4\alpha - 4\beta)$$

$$= \underline{\alpha - \beta}$$

(B) $\psi_{HMO} = \frac{1}{2}\phi_2 + \frac{1}{2}\phi_3 - \frac{1}{2}\phi_5 - \frac{1}{2}\phi_6 \quad \frac{1}{\sqrt{\frac{1}{4}+\frac{1}{4}+\frac{1}{4}+\frac{1}{4}}}$

$\langle E\rangle = \frac{1}{4}\langle \phi_2+\phi_3-\phi_5-\phi_6 | H | \phi_2+\phi_3-\phi_5-\phi_6\rangle$

$= \frac{1}{4}(\alpha+\beta+\beta+\alpha+\alpha+\beta+\beta+\alpha)$

$= \cancel{3\alpha} \quad \frac{4\alpha+4\beta}{4} = \underline{\underline{\alpha+\beta}}$

$\frac{\cancel{4}(\alpha+\beta)}{\cancel{4}} = \underline{(\alpha+\beta)}$

P19
(2)
(41) $\psi = -a\phi_2 - a_2\phi_3 + a\phi_5 - a\phi_7 - a\phi_8 + a\phi_{10}$

again $\psi = -a\phi_2 - a\phi_3 + a\phi_5 - a\phi_7 - a\phi_8 + a\phi_{10} \quad \frac{1}{\sqrt{6a^2}}$

$= -\frac{1}{\sqrt{6}}\phi_2 - \frac{1}{\sqrt{6}}\phi_3 + \frac{1}{\sqrt{6}}\phi_5 - \frac{1}{\sqrt{6}}\phi_7 - \frac{1}{\sqrt{6}}\phi_8 + \frac{1}{\sqrt{6}}\phi_{10}$

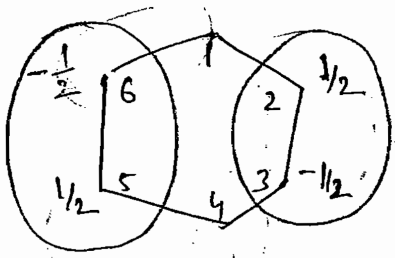
$\langle E\rangle = \frac{1}{6}\langle(-\phi_2-\phi_3+\phi_5-\phi_7-\phi_8+\phi_{10})|H|(-\phi_2-\phi_3+\phi_5-\phi_7-\phi_8+\phi_{10})\rangle$

$= \frac{1}{6}(\underline{\alpha}+\underline{\beta}+\underline{\beta}+\underline{\alpha}+\underline{\alpha}+\beta+\beta+\beta+\beta+\underline{\alpha})$

$=$

trick

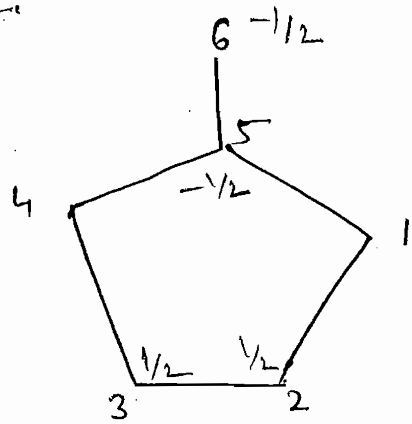
for (3), (41) etc



$\Rightarrow \cancel{\alpha + 3(}$

$$\alpha + \left(-\frac{1}{4} \times 2\beta - \frac{1}{4}\, 2\beta\right) = \underline{\underline{\alpha - \beta}}$$

using:
(B)

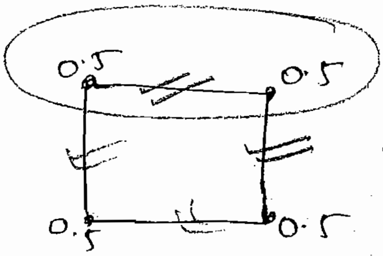


$$= \alpha + \left(\frac{1}{4} \times 2\beta + \frac{1}{4}\, 2\beta\right)$$

$$= \alpha + \left(\frac{\beta}{2} + \frac{\beta}{2}\right)$$

$$= \alpha + \beta$$

appendix
(B)



$$= \alpha + \cancel{0.025}\ 0.25$$

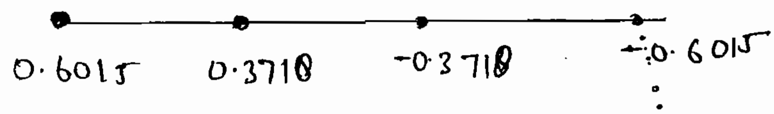
$$= \alpha + (2\beta \times 0.25 + 2\beta \times 0.25 + 2\beta \times 0.25 + 2\beta \times 0.25)$$

$$= \alpha + 4 \times (2\beta \times 0.25)$$

$$= \underline{\underline{\alpha + 2\beta}}$$

ans $\alpha - \frac{E}{\beta} = -0.6180$

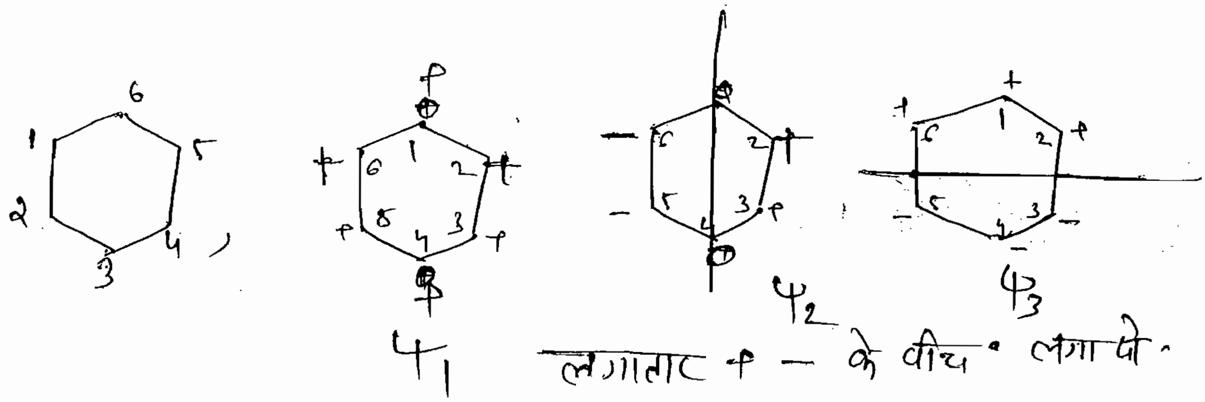
(3) 0.3618



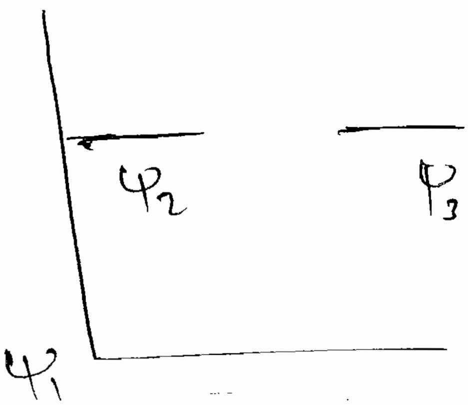
$$= \alpha + 2\beta \times (0.6015)^2 + 2\beta$$

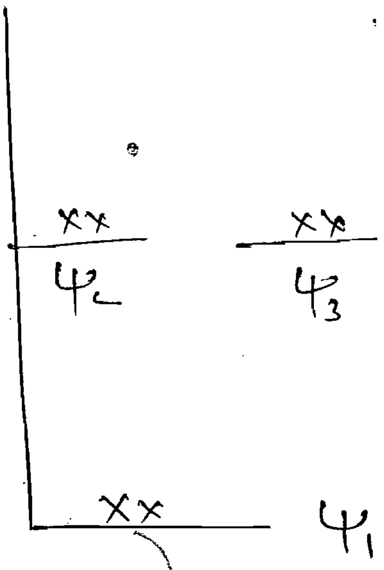
Calculation of π-bond order b/w two directly attached centre:

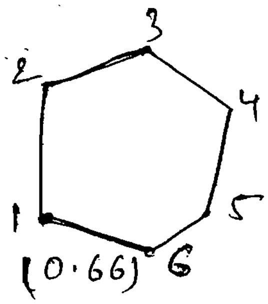
610



लगातार + − के बीच • लगा दो.







$$\pi_{16} = \underbrace{2 \times 0.4082 \times 0.4082}_{\psi_1} + \underbrace{2 \times 0 \times -0.5}_{\psi_2} + \underbrace{2 \times 0.5774 \times 0.2887}_{\psi_3}$$

$$= 0.66$$

$$\pi_{54} = 2 \times 0.4082 \times 0.4082 + 2 \times 0 \times (-0.50) + 2 \times (-0.5774)(0.2887)$$

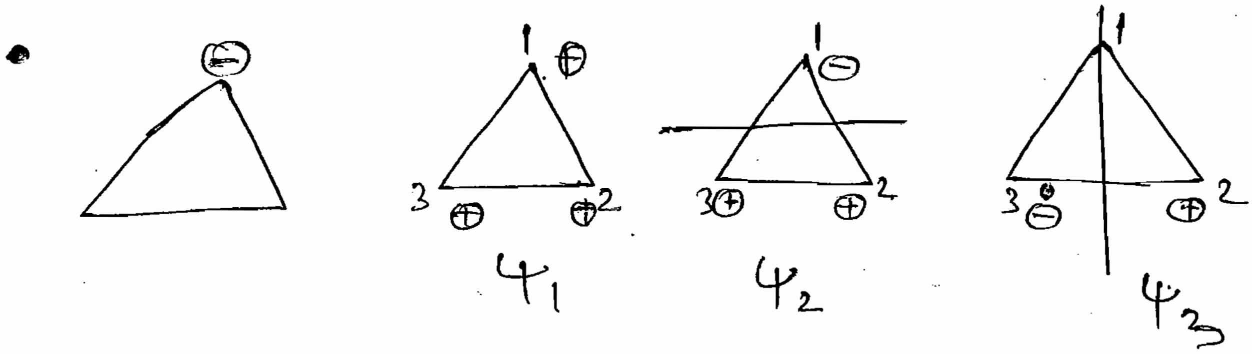
$$= \underline{0.66}$$

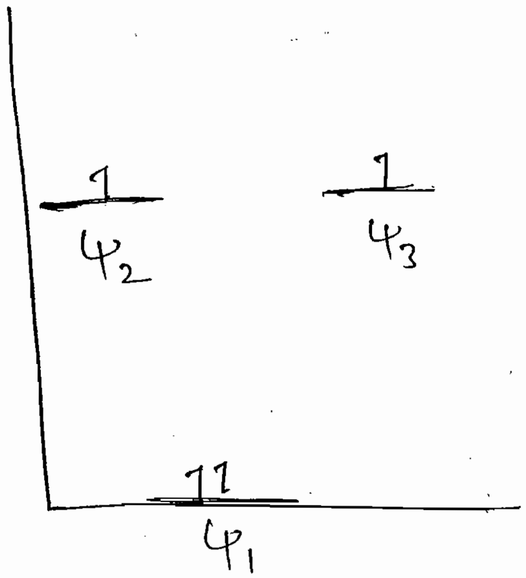
π bond order b/w two centre (r, s)

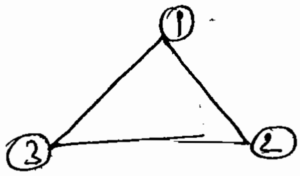
$$\boxed{\pi_{rs} = \sum_{i} n_i C_{ir} C_{is}}$$ (i = molecular orbital)

n_i = no. of π electron in i^{th} molecular orbital

C_{ir} and C_{is} = cofficient of i^{th} molecular orbital

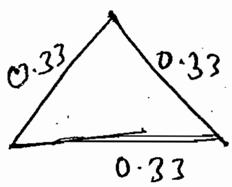




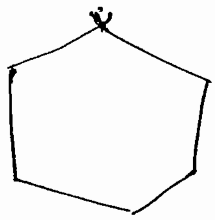


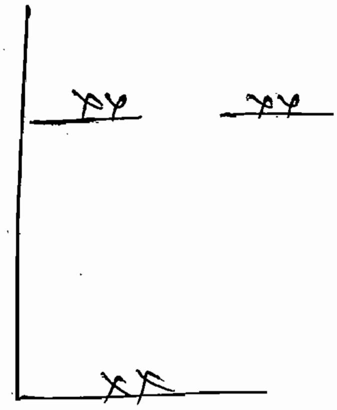
$$\psi_\pi(1,2) = 2\times 0.5774\,(\overset{0.5774}{\cancel{0.8165}}) + 1\times -0.8165\times 0.4082$$
$$+ 1\times 0\times 0.7071$$

$$= \underline{0.3335}$$



π Electron density :

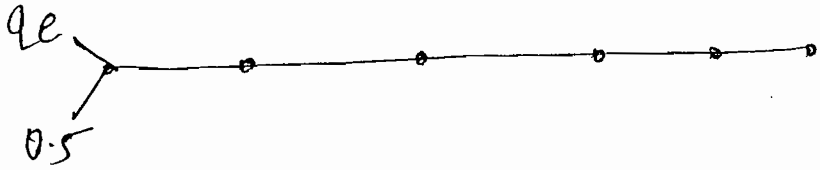


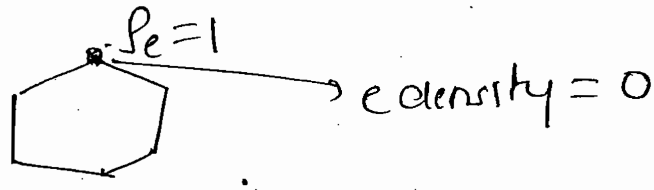


$$\rho_1 = 2\times(0.4082)^2 + 2\times(0.4082)^2 + 2\times(0.5774)^2$$

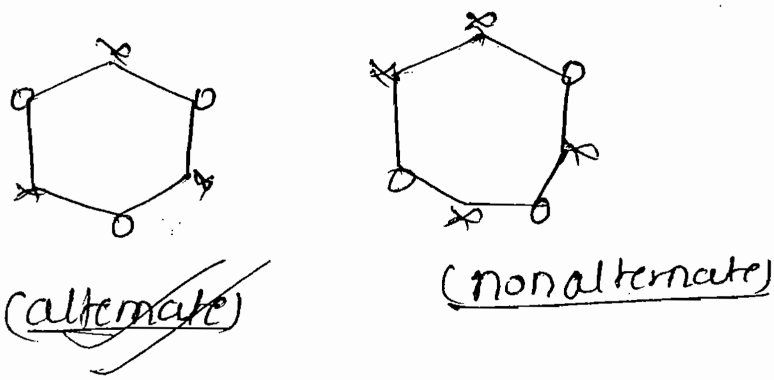
$$\boxed{\rho_1 = 1}$$

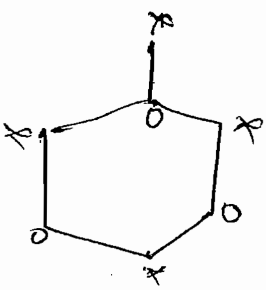
Charge density : $\rho_e + q_e = 1$





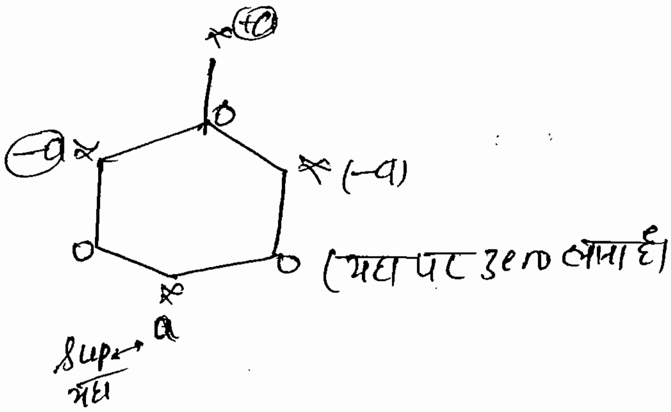
Pairing Theorem :

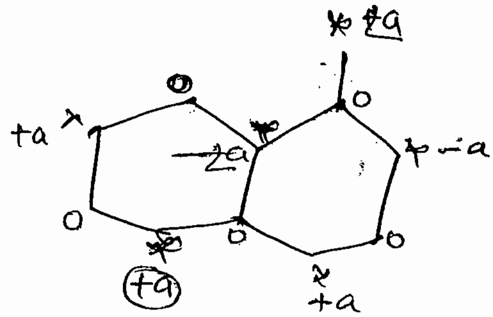


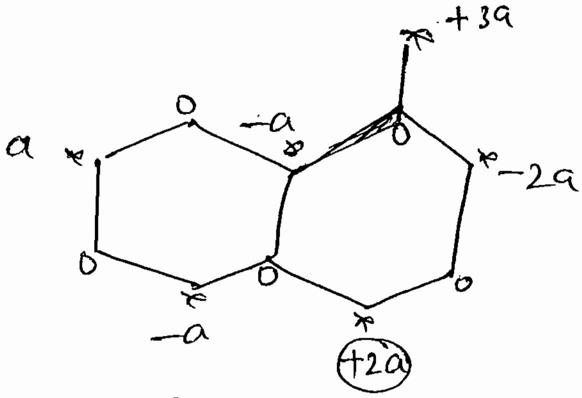


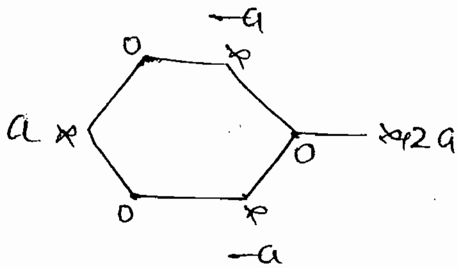
$\Rightarrow$ Odd alternant (diff b/w * and 0) and those alternate compound in which * and 0 is even (2, 4, 6 ..) then pairing theorem can be applied.

$\overset{*}{C} — \overset{0}{C} — \overset{*}{C}$ ✓ $\overset{*}{C} — \overset{0}{C} — \overset{*}{C} — \overset{0}{C} — \overset{*}{C}$ ✓







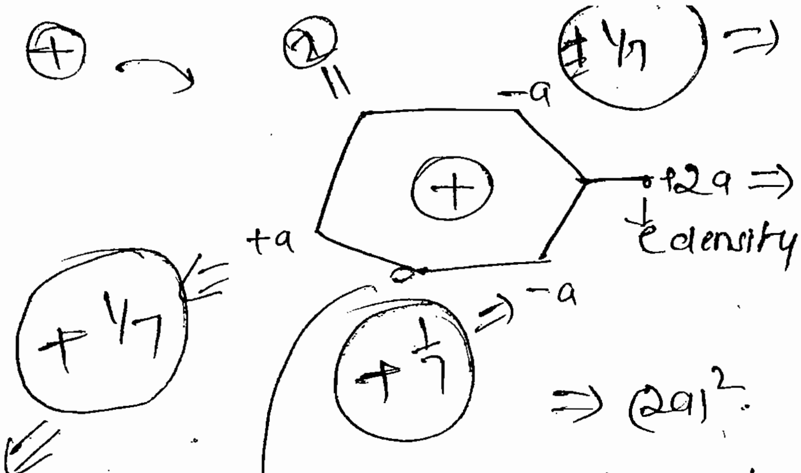


$$= (a)^2 + (-a)^2 + (-a)^2 + (2a)^2$$

$$= a^2 + a^2 + a^2 + 4a^2 = 1$$

$$7a^2 = 1$$

$$a^2 = \frac{1}{7} \qquad a^2 = \pm\sqrt{\frac{1}{7}}$$



$\Rightarrow \frac{0}{7}$

$+2a \Rightarrow \frac{4}{7} \Rightarrow \frac{3}{7}$ ⋮

$\rho_e = \frac{6}{7}$

$\Rightarrow (2a)^2$

$\Rightarrow 4 \times \frac{1}{7} \times (+1) \Rightarrow +\frac{4}{7}$

$\Downarrow$

$\rho_c + \rho_e = 1$

$\rho_c = 1$

$\rho_e + \rho_e = 1$

$\rho_e + \frac{4}{7} = 1 \Rightarrow \rho_e = \frac{6}{7}$

Electron density Charge density

$$\overset{}{\underset{*}{C}} - \underset{o}{C} - \underset{*}{C} - \underset{o}{C} - \overset{-}{\underset{*}{C}}$$

$+a \qquad\qquad -a \qquad\qquad +a$

$3a^2 = 1$

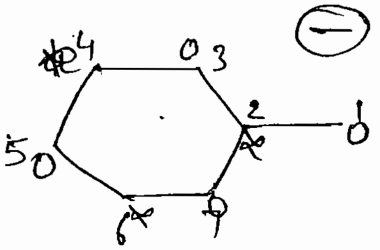
$a^2 = \frac{1}{3}$

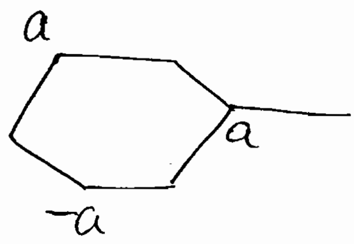
$$\overset{+a}{\underset{*}{C}} - \overset{o}{\underset{o}{C}} - \overset{-a}{\underset{*}{C}} - \overset{o}{\underset{o}{C}} - \overset{+a}{\underset{*}{C}}$$

~~Elect~~ Prob	$a^2 = \frac{1}{3}$	0	$a^2 = \frac{1}{3}$	0	$a^2 = \frac{1}{3}$
Charge ρ	$-\frac{1}{3}$	0	$-\frac{1}{3}$	0	$-\frac{1}{3}$
$C\rho$	$\frac{4}{3}$	1	$4/3$	1	$4/3$

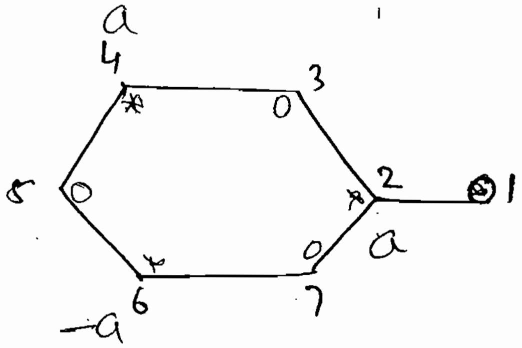
(एक -ve हो तो सब को उस -ve Charge से multiply कर दो।

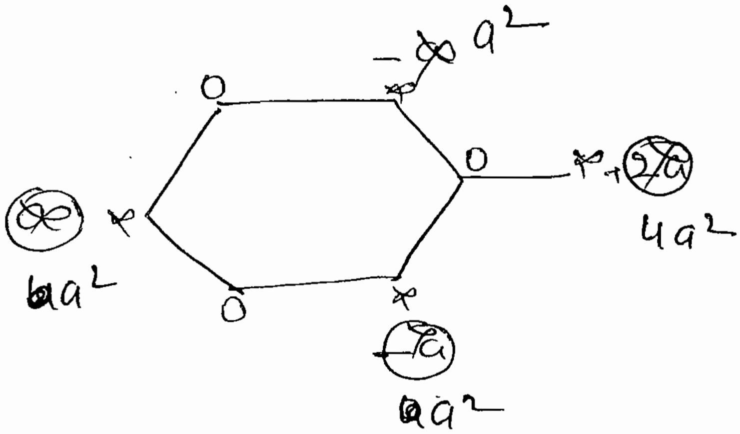
②





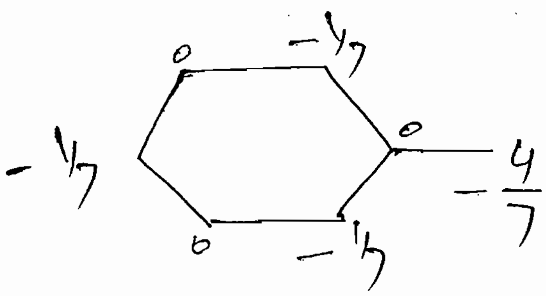
Electron density





$7a^2 = 1$

$a^2 = \frac{1}{7}$



⟸ Charge density

electronda

Q

$\oplus$

$$\overset{*}{C}-\overset{0}{C}-\overset{*}{C}-\overset{0}{C}-\overset{*}{C}-\overset{0}{C}-\overset{*}{C}$$

$a \qquad -a \qquad +a \qquad -a$

$a^2 \qquad a^2 \qquad a^2 \qquad a^2$

$4a^2 = 1$

$a^2 = \frac{1}{4}$

$1-\frac{1}{4}$

$+\frac{1}{4} \quad 0 \quad +\frac{1}{4} \quad 0 \quad +\frac{1}{4} \quad 0 \quad +\frac{1}{4} \quad \rho_c$

$\frac{3}{4} \quad 1 \quad \frac{3}{4} \quad 1 \quad \frac{3}{4} \quad 1 \quad \frac{3}{4} \quad \rho_e$

allyl cation: $C - C - C^{\oplus}$

$$\begin{array}{ccc} \overset{*}{C} & - \overset{o}{C} - & \overset{*}{C}^{+} \\ a & 0 & -a \\ a^2 & & a^2 \end{array}$$

$2a^2 = 1$

$a^2 = \frac{1}{2}$

$+\frac{1}{2} \quad 0 \quad +\frac{1}{2} = \rho_c$

$\frac{1}{2} \quad 1 \quad \frac{1}{2} = \rho_e$

② allyl anion: $C - C - C^{\ominus}$

$C - C - C^{\ominus}$

$-\frac{1}{2} \quad 0 \quad -\frac{1}{2} = \rho_c$

$\frac{1}{2} \quad 1 \quad \frac{1}{2} = \rho_e$

Radical

$$\dot{C} - \dot{C} - \dot{C}$$

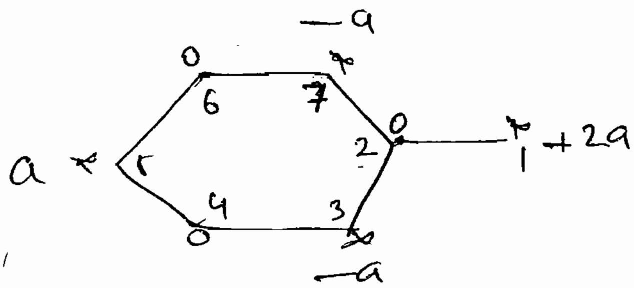
$$\tfrac{1}{2}\times 0 \quad 0\times 0 \quad \tfrac{1}{2}\times 0 = \rho_c$$

$$\begin{array}{ccc} \| & \| & \| \\ 0 & 0 & 0 \end{array}$$

$$1 \quad 1 \quad 1 \quad = \rho_c$$

L

non bonding molecular orbital:



$$a^2 = \frac{1}{7}$$

$$a = \pm\frac{1}{\sqrt{7}}$$

NBMO same:

$$\psi = \frac{1}{\sqrt{7}}\phi_5 - \frac{1}{\sqrt{7}}\phi_7 - \frac{1}{\sqrt{7}}\phi_3 + \frac{2}{\sqrt{7}}\phi_1$$

(2)

$$\overset{*}{\underset{a}{C^1}} - \overset{0}{C^2} - \overset{*}{\underset{-a}{C^3}}$$

$$\begin{cases} 2a^2 = 1 \\ a^2 = \frac{1}{2} \\ a = \pm \frac{1}{\sqrt{2}} \end{cases}$$

$$\boxed{\psi_{NBM} = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3}$$

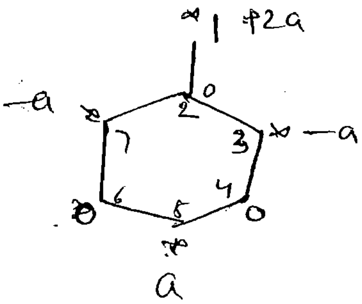
(3)

$$\overset{*}{\underset{a}{C_1}} - \overset{0}{C_2} - \overset{*}{\underset{-a}{C_3}} - \overset{0}{C_4} - \overset{*}{\underset{+a}{C_5}}$$

$$3a^2 = 1$$
$$a^2 = \frac{1}{3}$$
$$a = \pm\frac{1}{\sqrt{3}}$$

$$\psi_{NB} = \frac{1}{\sqrt{3}}\phi_1 - \frac{1}{\sqrt{3}}\phi_3 + \frac{1}{\sqrt{3}}\phi_5$$

(4)

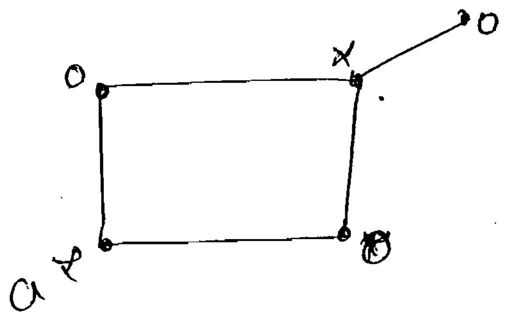


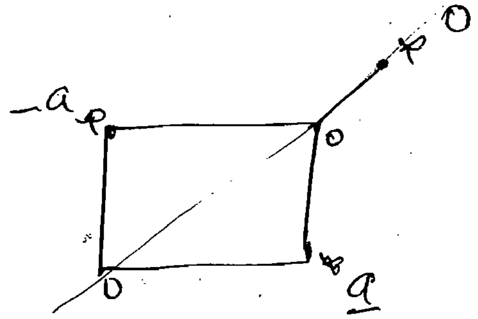
$$\begin{cases} a^2 = \frac{1}{7} \\ a = \pm\frac{1}{\sqrt{7}} \end{cases}$$

$$\psi_{NB} = \frac{2}{\sqrt{7}}\phi_1 - \frac{1}{\sqrt{7}}\phi_3 + \frac{1}{\sqrt{7}}\phi_5 - \frac{1}{\sqrt{7}}\phi_7$$

$$C_2 = C_4 = C_6 = 0$$

(21)



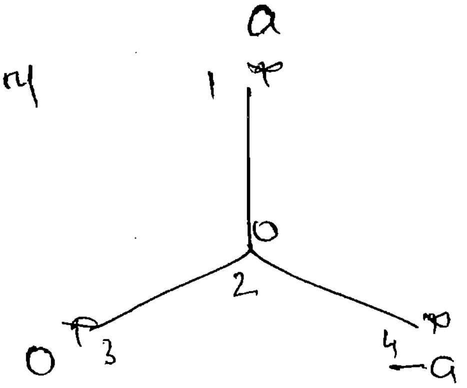


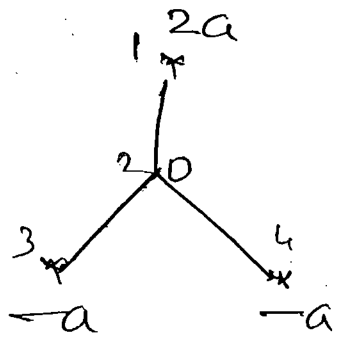
$$2a^2 = 1$$

$$a = \frac{1}{\sqrt{2}}$$

$$a = \pm 0.707.$$

(22) two nonbonding





$$2a^2 = 1$$

$$a = \pm\frac{1}{\sqrt{2}}$$

$$\psi_{nB} = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_4$$

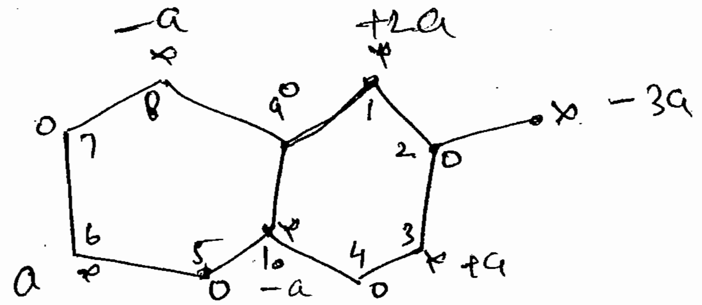
$$4a^2 + a^2 + a^2 = 1$$

$$6a^2 = 1$$

$$a = \pm\frac{1}{\sqrt{6}}$$

$$\psi_{nB} = \frac{2}{\sqrt{6}}\phi_1 - \frac{1}{\sqrt{6}}\phi_3 - \frac{1}{\sqrt{6}}\phi_4$$

(23)



$a^2+a^2+a^2+a^2+4a^2+9a^2=1$

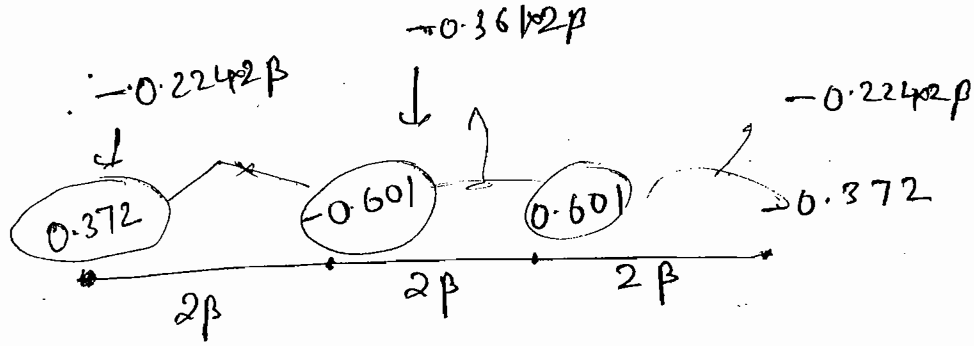
$17a^2 = 1$

$a^2 = +\frac{1}{\sqrt{17}}$

$$\boxed{\psi_{NBMO} = \frac{2}{\sqrt{17}}\phi_1 + \frac{1}{\sqrt{17}}\phi_3 + \frac{1}{\sqrt{17}}\phi_6 - \frac{1}{\sqrt{17}}\phi_8 - \frac{1}{\sqrt{17}}\phi_{10} - \frac{3}{\sqrt{17}}\phi_{11}}$$

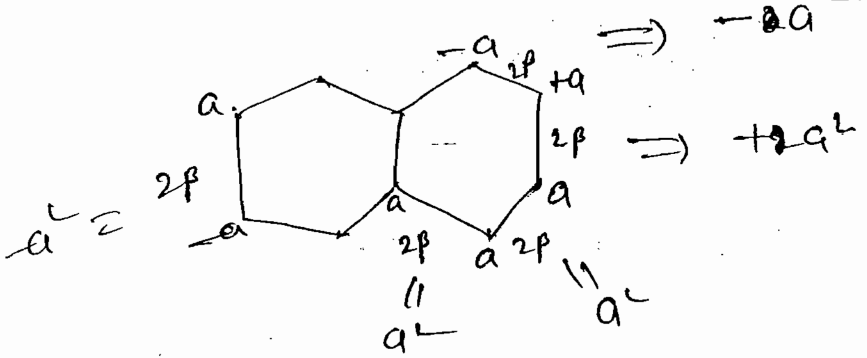
(4b)

ψ_4



$E = \alpha + 2\beta(-0.224 - 0.361 - 0.224)$

$\underline{E = \alpha - 1.6\beta}$



$$= \alpha + 2\beta(\cancel{-a^2} \cancel{+a^2} + a^2 \cancel{+a^2} \cancel{-a^2})$$

$$= \alpha + 2\beta(3a^2) = \alpha + 2\beta(a^2)$$

$$= \alpha + 6a^2\beta \qquad = \alpha + 2\beta a^2$$

$$7a^2 = 1$$

$$a^2 = \frac{1}{7} \Rightarrow \alpha + \frac{2}{7}\beta$$

---

(41) $\alpha + 2\beta(a^2 + a^2 + a^2) \qquad a^2 = \frac{1}{6}$

$\alpha + 2\beta \times 3a^2$

$\alpha + \beta$

(42) ψ को भी निकालने बाद
$\langle \psi | H\psi \rangle$ करते है
भी निकाला
जा सकता

(14) $\left\langle \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3 \middle| H \middle| \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3 \right\rangle$

$$= \frac{1}{4}\alpha + \frac{1}{2\sqrt{2}}\beta + \frac{1}{2\sqrt{2}}\beta + \frac{1}{2}\alpha + \frac{1}{2\sqrt{2}}\beta + \frac{1}{2\sqrt{2}}\beta + \frac{1}{4}\alpha)$$

$$= \frac{\alpha}{4} + \frac{\alpha}{2} + \frac{\alpha}{4} + \frac{\beta}{2\sqrt{2}} + \frac{\beta}{2\sqrt{2}} + \frac{\beta}{2\sqrt{2}} + \frac{\beta}{2\sqrt{2}}$$

$$= \frac{\alpha + 2\alpha + \alpha}{4} + \frac{\cancel{4}\beta}{\cancel{2}\sqrt{2}}$$

$$= \alpha + \frac{2\beta}{\sqrt{2}}$$

$$= \alpha + \sqrt{2}\beta$$

(b) $\left(\frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3\right)\left(\frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3\right)$

$$= \frac{1}{2}\alpha + \frac{1}{2}\alpha$$

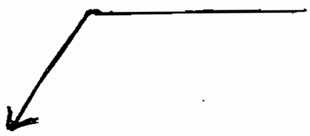
$$= \alpha$$

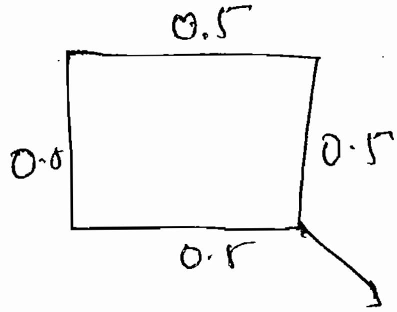
(a) $\langle \cancel{\psi_2|H|\psi_2} \rangle$ $\langle \psi_1|H|\psi_2 \rangle$

$$\left(\frac{1}{2}\phi_1+\frac{1}{\sqrt{2}}\phi_2+\frac{1}{2}\phi_3\right)\cdot\left(\frac{1}{\sqrt{2}}\phi_1-\frac{1}{\sqrt{2}}\phi_3\right)$$

$$\cancel{\frac{1}{2\sqrt{2}}\alpha}+\cancel{\frac{1}{2}\beta}-\cancel{\frac{1}{2}\beta}-\cancel{\frac{1}{2\sqrt{2}}\alpha}=0$$

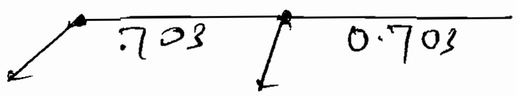
free valenc :





$F = \sqrt{3}-1 \Rightarrow \underline{0.732}$

$\dot{C}H_3 \longrightarrow F = 1.732$



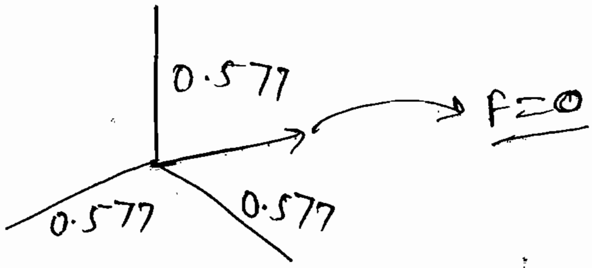
$1-0.703$
$= \underline{1.028}$

$1-(0.703+0.703)$

$\|$

$\underline{0.318}$

maxi. π delocalisation.

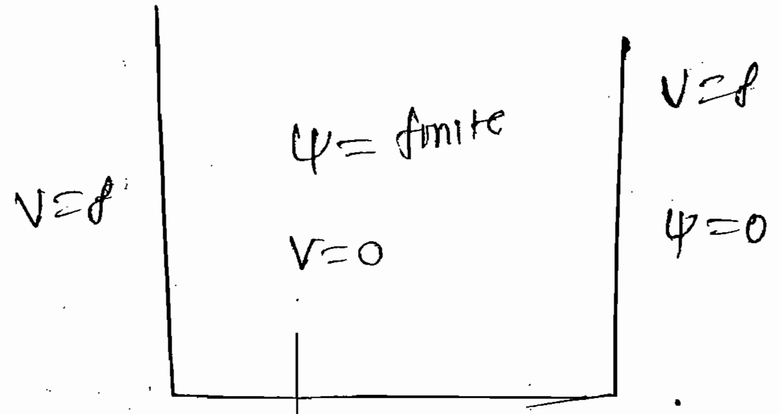


$$q_{ij} = \sum_{a} n_a C_{ia} C_{ja}$$

$$\rho_i = \sum_{a,b,\ldots} n_a C_{ia}^{*} C_{ia}$$

$$\rho_e + q_e = 1$$

Particle in Box : particle never be in rest in 1D box.



→ free particle (π Electron in 1,3, butadiene.
no interaction gas molecule in a container

$$\left\{ \begin{array}{l} V=0 \\ \\ K.E = ? \end{array} \right. \qquad \left\{ T = \frac{P_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \right.$$

$$\boxed{\hat{T}\psi(x) = E\psi(x)} \text{ - - - - } \psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

eigenvalue eq^n for T for 1D

$$\hat{T}\psi(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(\sqrt{\frac{2}{L}}\right)\sin\left(\frac{n\pi x}{L}\right)$$

$$= \boxed{\frac{\hbar^2}{2m}\cdot\left(\frac{n\pi}{L}\right)^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = E\psi$$

$E=$

i.e $\boxed{E = \frac{n^2\pi^2}{l^2}\frac{\hbar^2}{2m}}$ eigenvalue of T

$$\langle T\rangle = \frac{\langle\psi_n|\hat{T}|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle} = \frac{\langle\psi_n|c_n|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle}$$

$$= c_n\frac{\langle\psi_n|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle}$$

$$= c_n$$

accepetation value of KE

$$\langle T\rangle = E = \frac{n^2\cancel{\pi^2}}{l^2}\frac{h^2}{8m^2\cancel{\pi^2}}$$

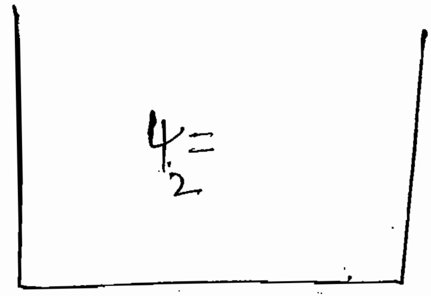
$$\boxed{E = \frac{n^2h^2}{8ml^2}}$$

अगर generally always Hermitian operator give real value but if an time we get only imagary part like is then the value will be → $0 + is$

0

$$E_n = \frac{n^2h^2}{8ml^2}$$

for ground state $E_1 = \frac{h^2}{8ml^2}$



$\psi_2 = \sin\left(\frac{3\pi x}{a}\right)$

State function ψ_2 is proportion to $\sin\left(\frac{3\pi x}{a}\right)$ then Energy of particle in this state is

$\frac{n\pi x}{l} = \frac{3\pi x}{a}$ $\qquad$ $\frac{\pi x}{a} = \frac{3\pi x}{l}$

$\frac{2\pi x}{a} = \frac{3\pi x}{l}$ $\qquad$ $l = 3a$

$l = \frac{a}{2}$

ψ_2 $\quad E_2 = \frac{h^2}{8ml^2}$ $\qquad E_2 = \frac{h^2}{8m \cdot 9 \cdot a^2}$

$\psi_3 \propto \sin\left(\frac{2\pi x}{a}\right)$

$n = \cancel{2}3$, $\frac{n\pi x}{l} = \frac{2\pi x}{a}$

$$\frac{3\cancel{\pi x}}{l} = \frac{2\cancel{\pi x}}{a}$$

$$l = \frac{3a}{2}$$

$\cancel{E = \frac{4h^2}{8ma^2}}$

$\cancel{E = \frac{h^2}{2ma^2}}$

$$E = \frac{\overset{3}{\cancel{9}}h^2 \times 4}{\cancel{8}m\,\cancel{9}a^2}$$

$$E = \frac{\overset{2}{\cancel{3}}h^2}{2ma^2}$$

$\psi_1 \propto \sin\frac{2\pi x}{a}$

$n = 1$ $\frac{n\pi x}{l} = \frac{2\pi x}{a}$

$$\frac{\cancel{\pi x}}{l} = \frac{2\cancel{\pi x}}{a} \qquad l = \frac{a}{2}$$

$$E_1 = \frac{h^2 \times 4}{8ma^2}$$

$$E_1 = \frac{h^2}{2ma^2}$$

$$\psi_3 \propto \sin\left(\frac{\pi x}{l}\right)$$

$$\frac{n\pi x}{a} = \frac{\pi x}{l}$$

$$\frac{3\cancel{\pi x}}{a} = \frac{\cancel{\pi x}}{l}$$

$$\boxed{a = 3l}$$

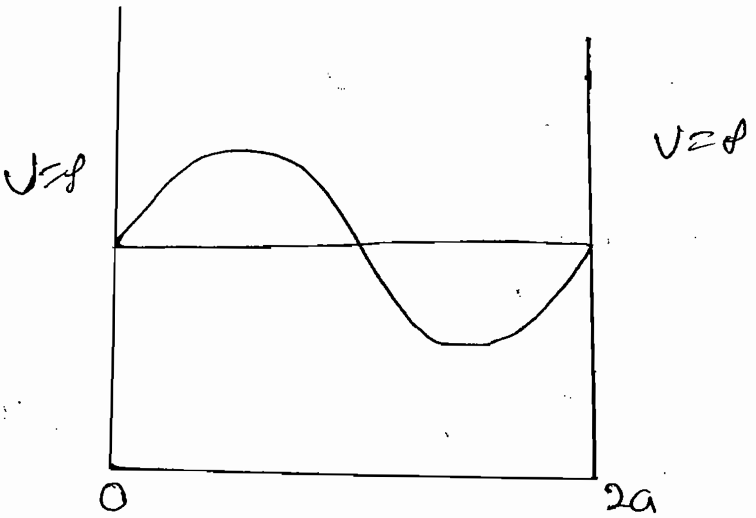
$$\psi_3 = \sqrt{\frac{2}{3l}} \sin\left(\frac{3\pi x}{3l}\right) = \underline{\sqrt{\frac{2}{3l}} \sin\left(\frac{\pi x}{l}\right)}$$

$$E_3 = \frac{n^2 h^2}{8ml^2} = \frac{\cancel{9} h^2}{8m.\cancel{9}l^2} = \boxed{\frac{h^2}{8ml^2}}$$

ground state energy $E_1 = \frac{h^2}{8m\,9l^2}$

$$\boxed{E_1 = \frac{h^2}{72ml^2}}$$

* for given state function of a particle in box Calculate the Kinetic Energy.



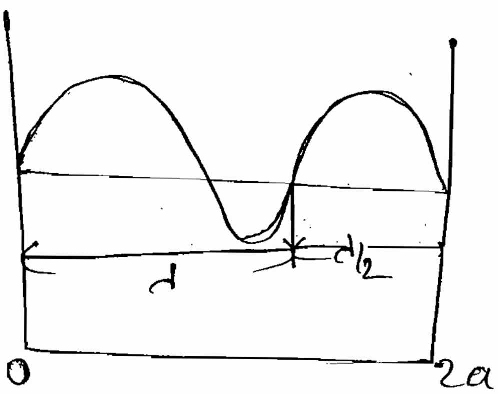
$l = 2a \,;\; \psi_1$

$n = 2$

$$E = \frac{4 \times h^2}{8m(2a)^2} = \frac{4 \times h^2}{32ma^2}$$

$$= \frac{h^2}{8ma^2}$$

(2)



$d + d/2 = 2a$

$\frac{3d}{2} = 2a$

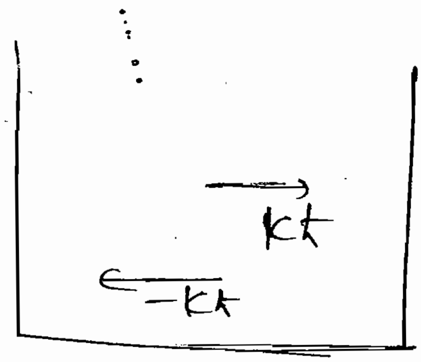
$d = \frac{4a}{3}$

$$p = \frac{h}{d} = \frac{h \times 3}{4a}$$

$$\langle T \rangle = \frac{p^2}{2m} = \frac{\frac{h^2 \times 9}{16a^2}}{2m}$$

$$\boxed{\langle T \rangle = \frac{9h^2}{32ma^2}}$$

IIIrd methods;



cos kx + i sin kx $\qquad e^{-ikx}$ — $k\hbar$

cos kx − i sin kx $\qquad e^{-ikx}$ — $k\hbar$

$\psi_3 \propto \sin\left(\frac{2\pi}{l}\right)x \longrightarrow k$

$$\boxed{T = \frac{(k\hbar)^2}{2m}}$$

sin kx

cos kx

ultimate

$$T = \frac{\left(\frac{\cancel{2\pi}}{l}\cdot\frac{h}{\cancel{2\pi}}\right)^2}{2m} = \frac{h^2}{2ml^2}$$

Calculation of Energy in 2D box:

$$\psi = \sqrt{\frac{2 \times 2}{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \cdot \sin\left(\frac{n_y \pi y}{L_y}\right)$$

$$T\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right] \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \cdot \sin\left(\frac{n_y \pi y}{L_y}\right)$$

$$= \frac{-\hbar^2}{2m} \sqrt{\frac{4}{L_x L_y}} \left\{ -\sin\frac{n_y \pi y}{L_y} \cdot \sin\frac{n_x \pi x}{L_x} \cdot \left(\frac{n_x \pi}{L_x}\right)^2 \right.$$

$$\left. + \sin\left(\frac{n_x \pi x}{L_x}\right) \cdot \sin\left(\frac{n_y \pi y}{L_y}\right) \cdot \left(\frac{n_y \pi}{L_y}\right)^2 \right.$$

$$= \frac{\hbar^2}{2m}\left[\left(\frac{n_x \pi}{L_x}\right)^2 + \left(\frac{n_y \pi}{L_y}\right)^2\right] \sqrt{\frac{4}{L_x L_y}} \sin\frac{n_x \pi x}{L_x} \cdot \sin\frac{n_y \pi y}{L_y}$$

$$= \underbrace{\frac{\hbar^2}{2m}\left[\left(\frac{n_x \pi}{L_x}\right)^2 + \left(\frac{n_y \pi}{L_y}\right)^2\right]}_{\substack{\parallel \\ E}} \psi$$

$$E = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x} + \frac{n_y^2}{L_y}\right)$$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

(II) Excited state

$$E = \frac{h^2}{8m}\left(\frac{1}{L_x^2} + \frac{1}{L_y^2}\right), \quad (n_x = 1, n_y = 1)$$

$$E = \frac{h^2}{8m}\left(\frac{1}{l^2} + \frac{1}{4l^2}\right)$$

$$= \frac{h^2}{8m}\left(\frac{4+1}{4l^2}\right)$$

$$E = \frac{5h^2}{32ml^2}$$

Rough

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y}\right)$$

$n_x = 0, \; n_y = 1$

$(1,0) \; (0,1) \; \frac{h^2}{8m}$

l, and $2l$

$$E = \frac{\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) = \frac{\hbar^2}{2m}\left(\frac{n_x^2}{l^2} + \frac{n_y^2}{4l^2}\right)$$

$$= \frac{\hbar^2}{2ml^2}\left(n_x^2 + \frac{n_y^2}{4}\right)$$

$(n_x=1,\ n_y=3) = \frac{\hbar^2}{2ml^2}\left(1+\frac{9}{4}\right)$

$= \cancel{4.25\,\varepsilon_1}\ 3.25\,\varepsilon_1$

$(n_x=1,\ n_y=2)$ $\cancel{3.25}$ $2.5\,\varepsilon_1$

$(n_x=1,\ n_y=1)$ $1.25\,\varepsilon_1$.

In square Box

$l_x = l = l_y$

$$E_n = \frac{h^2}{2m}\left(\frac{n_x^2}{l} + \frac{n_y^2}{l}\right)$$

$$= \frac{h^2}{2ml^2}(n_x^2 + n_y^2)$$

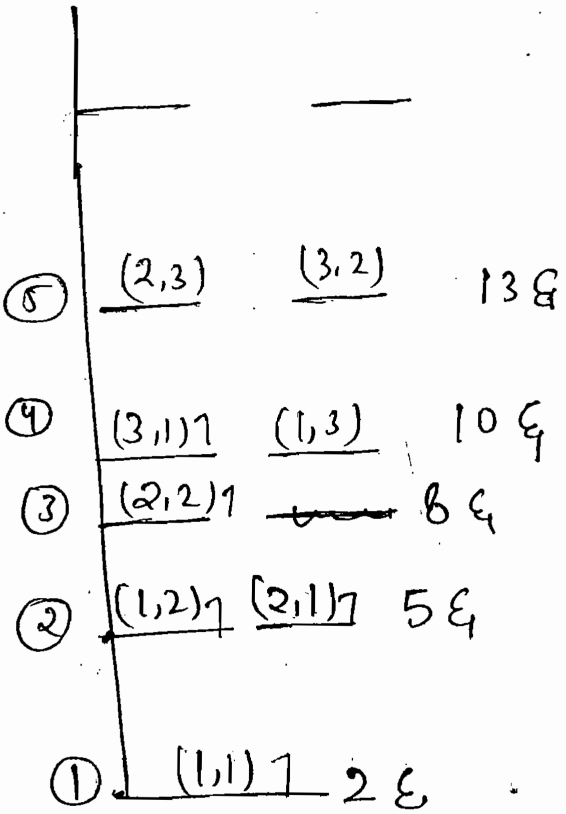
① $(n_x = 1,\ n_y = 1)$

② (1,2) (2,1)

③ (2,2) ϵ_2

③ (1,3) (3,1)

④ (2,3) (3,2)



$$\boxed{\epsilon_1 = \frac{h^2}{2ml^2}}$$

9, 4

Q. Five non interacting classical particle are in 2D. box having length L_x and L_y $L_x = L_y = l$ If one particle consist only one state the lowest value of energy for this system is.

$\boxed{\cancel{E_n = \frac{h^2}{ml^2}}}$ + ① + ②

$E = 2\epsilon_1 + 5\epsilon_1 \times 2 + 8\epsilon_1 + 10\epsilon_1$

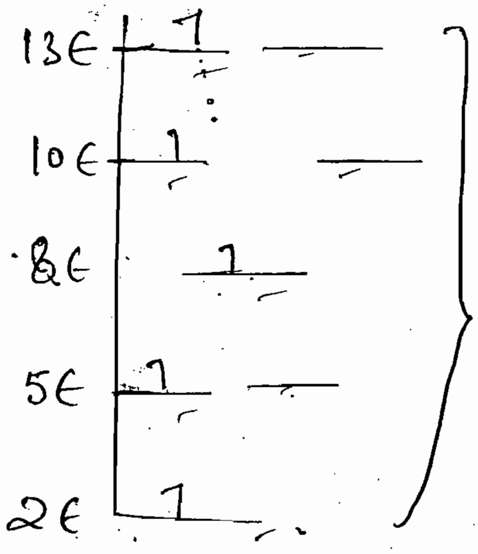
$= 2\epsilon_1 + 10\epsilon_1 + 8\epsilon_1 + 10\epsilon_1$

$= \underline{30\epsilon_1}$

If in above, each level consist one particle

$E = 36\epsilon$

$E = \frac{36\,h^2}{8ml^2}$



In a square no. of state up to $\frac{14\,h^2}{8ml^2}$ energy are? $= 6$

3D BOX : $\psi_{n_x n_y n_z} = \psi_{n_x} \cdot \psi_{n_y} \cdot \psi_{n_z}$

$$\psi_{3D} = \psi_{n_x} \cdot \psi_{n_y} \cdot \psi_{n_z}$$

$$\hat{T}\psi_{3D} = E\psi_{3D}$$

$$\downarrow$$

$$\boxed{E_{3D} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z}{L_z^2}\right)}$$

$l_x = L$, $L_y = 2L$ $L_z = l$

$$E_{3D} = \frac{h^2}{8ml^2}\left(\frac{n_x^2}{} + \frac{n_y^2}{4} + \frac{n_z^2}{}\right)$$ $\frac{4}{4} = 1$ $1+1+1$ $1, 0.25+1$

$n_x = 1$, $n_y = 1$, $n_z = 1$ $n_x = 1$, $n_y = 2$, $n_z = 1$

$E_{3D} = \underline{E \times 2.5}$ $\underline{3E}$ $4 + 0.5 + \frac{9}{2}$, 4.8

$4 + 0.5 + 1$

$n_x = (\underline{2, 1, 1})$ $(\underline{1, 1, 2})$ $3, 1, 1$

$3.5E$, $(1, 3, 1)$ $9, +1, -$ 1.8

$(1 + 1.5 + 1)$

$= 4.5E$

10.E (3,1,1) (1,1,3) = 10.25 E

2,2,2 — 9.

~~1,2,2~~ ~~2,2,1~~ ~~(4,1,1)~~

4.5E (1,3,1) E = 6.25E

3.5E (2,1,1) (1,1,2) E = 5.25E

3E (1,2,1) E = 3E

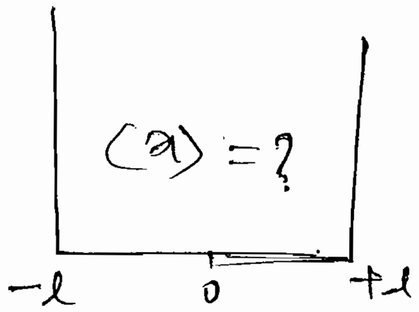
2.5E (1,1,1) E = 2.25

(1,4,1), 1,

(131)

$$\psi = \sqrt{\frac{2}{l}\,\frac{2}{2l}\,\frac{2}{l}}\;\sin\frac{\pi x}{l}\;\sin\frac{3\pi y}{2l}\;\sin\frac{\pi z}{l}$$

Expectation value for position in state of 1D box :

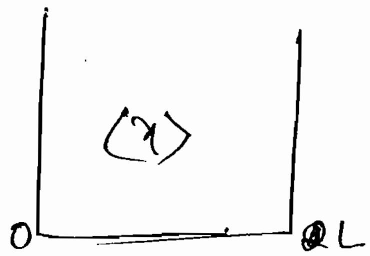


$\cos\frac{n\pi x}{L}$

$\sin\frac{n\pi x}{l}$

$$\langle \hat{x} \rangle = \frac{\int_{-l}^{+l} \psi_n^* \, x \, \psi_n \, dx}{\int \psi_n^* \psi_n \, dx} = 0$$

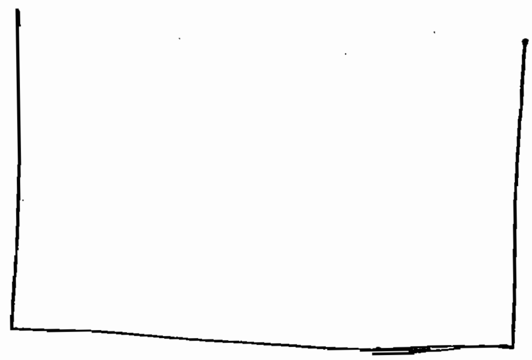
odd $\Rightarrow$ mid point



$\langle x \rangle = \frac{L}{2}$

average position of particle inside the box is the mid point of the box.

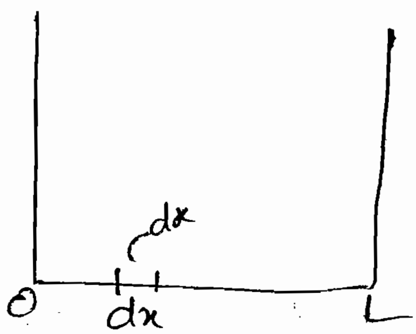
$\langle x^2 \rangle = ?$



when given $n \to \infty$ (classical limit)

expectation value of

$\langle x^n \rangle =$



$L \longrightarrow 1$

$1 \longrightarrow \frac{1}{L}$

$dx \longrightarrow \frac{1}{L} dx$

Probability distribution function for particle in box, If length of the box is l then probability for finding the particle in dx length is $\frac{1}{L} dx$ this function equivalent to (is called) probability distribution function

If we want to calculate average of $\langle x^n \rangle$ the

$$\langle x^n \rangle = \int_{x_i}^{x_f} x^n \frac{1}{L} dx$$

(l = length)

(0) $$\int_{-a}^{a} \frac{x^3}{a}\,dx = \frac{1}{a}\left[\frac{x^4}{4}\right]_{-a}^{a}$$
$$= \frac{1}{4a}\left[a^4 - a^4\right] = 0$$

Q 0 to $2a$

$$\int_{0}^{2a} \frac{1}{a} x^3\,dx = \frac{1}{a}\left[\frac{x^4}{4}\right]_{0}^{2a}$$
$$= \frac{1}{4a}\left[16a^4\right]$$
$$= \underline{4a^3}$$

Q $$\int_{-a}^{a} \frac{x^4}{a}\,dx = \frac{1}{a}\left[\frac{x^5}{5}\right]_{-a}^{a}$$
$$= \frac{1}{5a} \cdot a^5 + a^5 = \frac{2a^5}{5a} = \frac{2}{5}a^4$$

(24)

$$\frac{1}{2a}\int_{-a}^{a} x^4\,dx = \frac{1}{2a}\left[\frac{x^5}{5}\right]_{-a}^{a}$$
$$= \frac{1}{2a\times 5}\left[a^5 + a^5\right]$$
$$= \frac{2a^5}{2a\times 5} = \frac{a^4}{5}$$

① $\langle x^3 \rangle$ $\quad 0 \to 2a$

$$= \frac{1}{2a}\int_0^{2a} x^3 dx = \frac{1}{2a}\left(\frac{x^4}{4}\right)_0^{2a}$$

$$= \frac{1}{\cancel{8a}} \cancel{16a^4} = \underline{2a^3}$$

② $-\frac{a}{2}$ to $\frac{a}{2}$

ⓐ $$= \frac{1}{a}\int_{-a/2}^{a/2} x^4 dx = \frac{1}{a}\left[\frac{x^5}{5}\right]_{-a/2}^{a/2}$$

$$= \frac{1}{5a}\left[\frac{a^5}{32} + \frac{a^5}{32}\right]$$

$$= \frac{1}{5 \times \cancel{32}_{16} \times \cancel{a}} \cancel{2}a^5 = \frac{a^4}{80}$$

ⓑ $$\frac{1}{2a}\int_{-a}^{a} x^3 dx = \frac{1}{2a}\left(\frac{x^4}{4}\right)_{-a}^{a}$$

$$= \frac{1}{8a}(a^4 - a^4) = \underline{0}$$

$$\langle \Delta x^2 \rangle^{a} = \sqrt{\langle x^2 \rangle - \langle x \rangle}$$

Q -a to a

$$x = \frac{1}{2a}\int_{-a}^{a} x\,dx = \frac{1}{2a}\left[\frac{x^2}{2}\right]_{-a}^{a} = \frac{1}{4a}(a^2 - a^2)$$

$$= \frac{1a}{2}$$

$$x^2 = \frac{1}{2a}\int_{-a}^{+a} x^2\,dx = \frac{1}{2a}\left[\frac{x^3}{3}\right]_{-a}^{a} = \frac{\cancel{2}a^3}{\cancel{6}a} =$$

$$= \frac{1}{6a}\left[a^3 + a^3\right] = \frac{\cancel{2}a^3}{\cancel{6}a} = \frac{a^2}{3}$$

$$(\Delta x)^2 = \sqrt{\frac{a^2}{3}} = \frac{a}{\sqrt{3}}$$

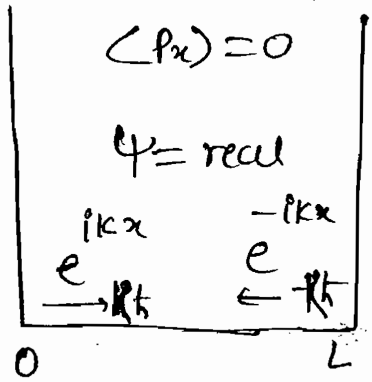
Q $(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2$

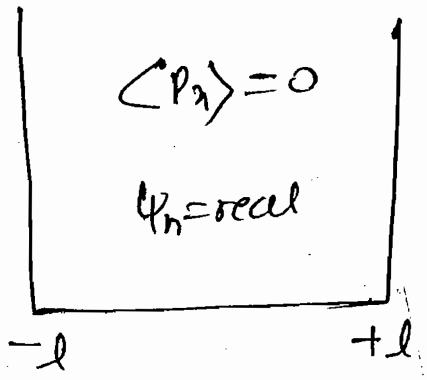
$$x^2 = \frac{1}{a}\int_0^a x^2 dx = \frac{1}{\cancel{a}} \frac{a^{\cancel{3}}}{3} = \frac{a^2}{3}$$

$$\langle x \rangle = \frac{a}{2}$$

$$(\Delta x)^2 = \frac{a^2}{3} - \frac{a^2}{4} = \frac{4a^2 - 3a^2}{12} = a^2/12$$

$\langle P_x \rangle = ?$ $\quad\quad$ $\langle P_x^2 \rangle = ?$





$\langle P_x \rangle = 0$, $\langle p_x \rangle = \hbar k$

$$\langle \cancel{KE} \rangle = \frac{n^2 h^2}{8mL^2}$$

$$\left\langle \frac{P_x^2}{2m} \right\rangle = \frac{n^2 h^2}{8mL^2}$$

$$\langle P_x^2 \rangle = \frac{n^2 h^2}{8mL^2} \times 2m = \frac{n^2 h^2}{4l^2}$$

$$\langle P_x^2 \rangle = \frac{n^2 h^2}{4l^2}$$

$$\langle \Delta P_x \rangle = \sqrt{\langle P_x^2 \rangle - \langle P_x \rangle^2}$$

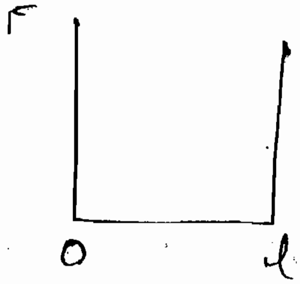
$$= \sqrt{\frac{n^2 h^2}{4l^2} - 0}$$

$$\boxed{\langle \Delta P_x \rangle = \frac{nh}{2l}}$$

0 to l $\quad \Delta x = \frac{al}{\sqrt{12}}$

$$\Delta x \Delta P_x = \frac{\cancel{l}}{\sqrt{12}} \times \frac{nh}{2\cancel{l}}$$

$$\boxed{\Delta x \Delta P_x = \frac{nh}{4\sqrt{3}}} \text{ — (1)}$$



$$\Delta x \Delta P_x = \frac{l}{\sqrt{12}} \cdot \frac{nh}{2l}$$

$-l$ to l $\quad \Delta x = \frac{a}{\sqrt{3}} = \frac{l}{\sqrt{3}}$

$$\cancel{\Delta x \Delta P_x = \frac{l}{\sqrt{3}} \frac{nh}{2l}}$$

$$\cancel{\boxed{\Delta x \Delta P_x = \frac{nh}{\sqrt{3}}}}$$

$l = 2l$

$$\Delta x P_x = \frac{\cancel{l}}{\sqrt{3}} \times \frac{nh}{4\cancel{l}}$$

$$\boxed{\Delta x P_x = \frac{nh}{4\sqrt{3}}} \text{ — (2)}$$

$$\boxed{\Delta x P_x = \frac{nh}{4\sqrt{3}}}$$

$\Rightarrow \Delta x \Delta P_x \neq 0$

$\Delta x \neq 0$

$P_x \neq 0$

(9)

$$\boxed{n = 0}$$

$\psi = 0$

$E = 0$

$\langle P_x^2 \rangle = 0$

$\Delta P_x = 0$ ✗ not possible

$\Delta x = \infty$

(13) (c) $\langle xy\rangle^2 = \langle x\rangle^2 \langle y\rangle^2$

$$\langle xy\rangle = \int \psi^*_{n_x} \psi^*_{n_y} (xy)\, \psi_{n_x} \psi_{n_y} \, dx\, dy$$

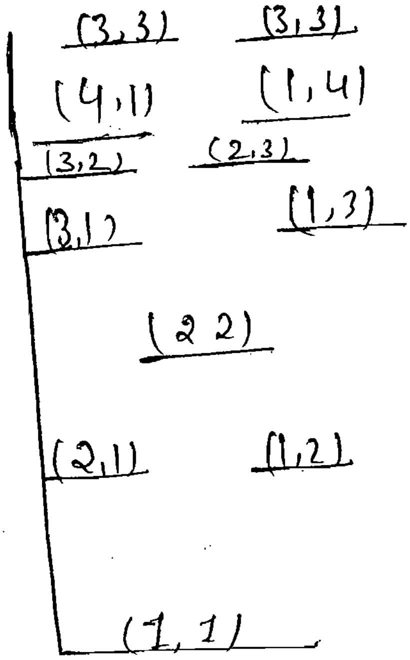
$$= \underbrace{\int \psi^*_{n_x} x\, \psi_{n_x}\, dx}_{\langle x\rangle} \; \underbrace{\int \psi^*_{n_y} (y)\, dy}_{\langle y\rangle}$$

$=$

$\langle xy\rangle = \langle x\rangle \langle y\rangle$

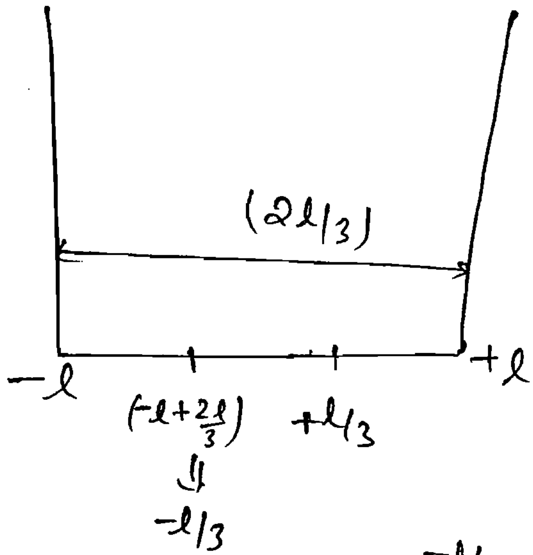
$\langle xy\rangle^2 = \langle x\rangle^2 \langle y\rangle^2$ (✓)

(2)



$$= \frac{h^2}{8ml^2}(n_x^2 + n_y^2)$$

Probability b/w the range:



$$\left(\sqrt{\frac{2}{l}}\right)^2 \int_{-l}^{-l/3} \sin^2\left(\frac{n\pi x}{l}\right) dx \quad \text{or} \quad \left(\sqrt{\frac{2}{l}}\right)^2 \int_{-l}^{-l/3} \cos^2\left(\frac{n\pi x}{l}\right) dx$$

$$\int_{x_i}^{x_f} \sin^2 ax\, dx = \frac{(x_f - x_i)}{2} - \frac{1}{4\,\text{Const}}\left(\sin 2ax_f - \sin 2ax_i\right)$$

$$\int_{x_i}^{x_f} \cos^2 ax\, dx = \frac{(x_f - x_i)}{2} + \frac{1}{4\,\text{Const}}\left(\sin 2ax_f - \sin 2ax_i\right)$$

Tunneling

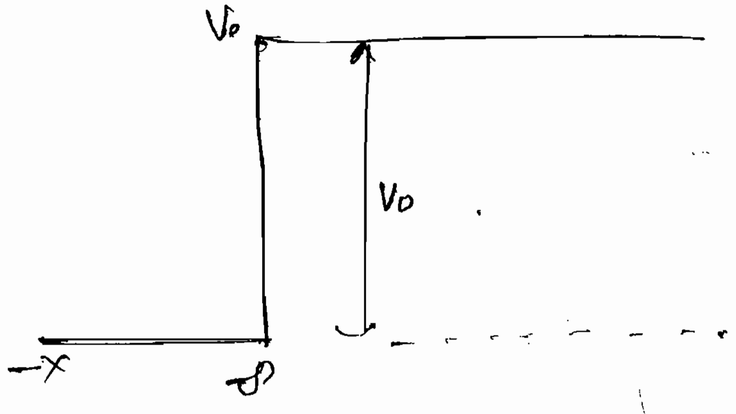
Terminology:

Barrier hight

Boundary

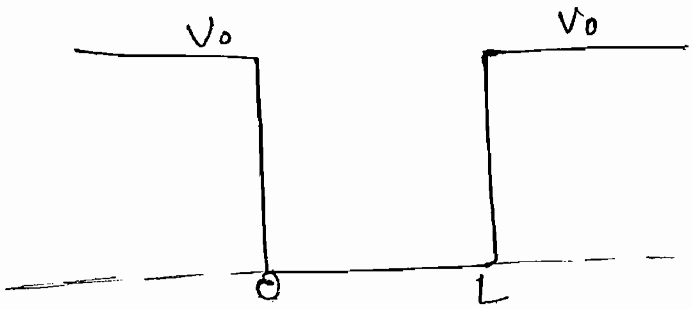
Barrier width

Tunneling probability



$V = 0 \quad x < 0$

$V = V_0 \quad x \geq 0$



$V = 0$ at 0 to L

$V = V_0$ at $x < 0$

$V = V_0$ at $x > 0$

$V = V_0 \quad x < 0$

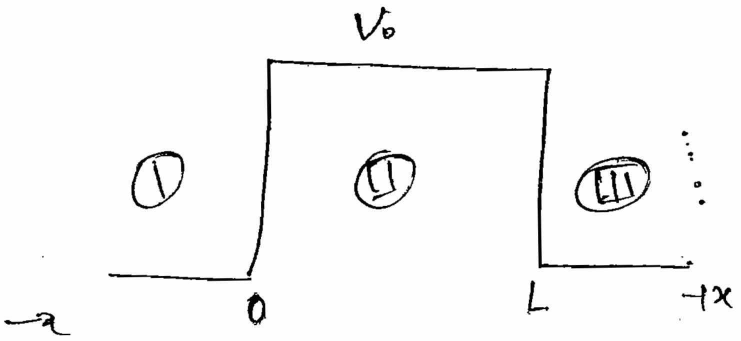
~~$V = V_0 \quad x > 0$~~

~~$V = 0 \quad 0 < x < L$~~

$V = 0, \quad 0 \leq x \leq L$

$V = V_0, \quad x \leq 0$

$V = V_0, \quad x > L$

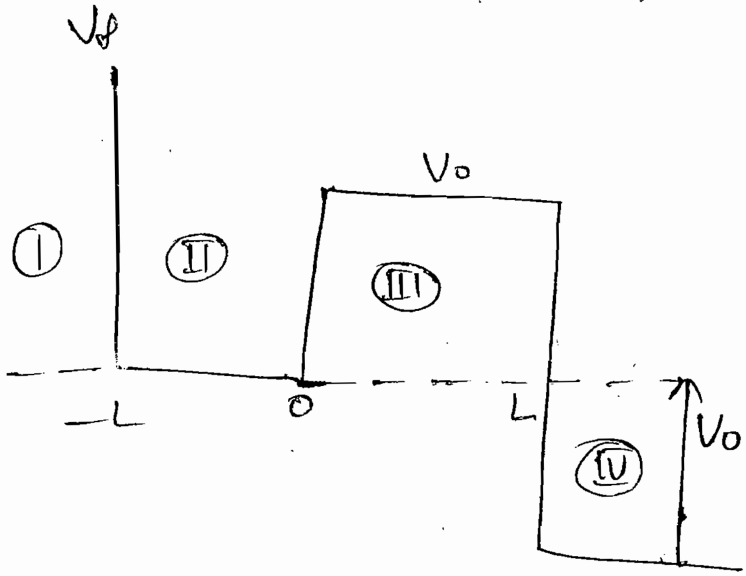


$$V(x) = \begin{cases} = 0 & x < 0 \\ = V_0 & 0 \le x \le L \\ = 0 & 0 < x \end{cases}$$

~~V=V0 at 0 to L~~

~~V=0 at x<0~~

~~V=0 at x>L~~



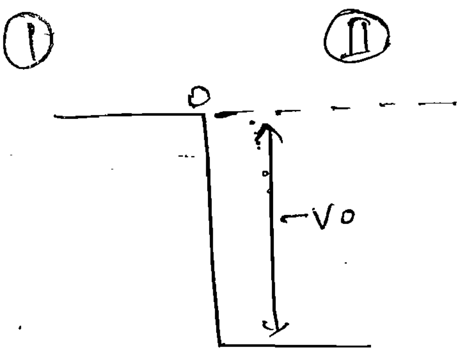
$V = V_0, \quad 0 \le x \le L$

$= 0, \quad -L < x < 0$

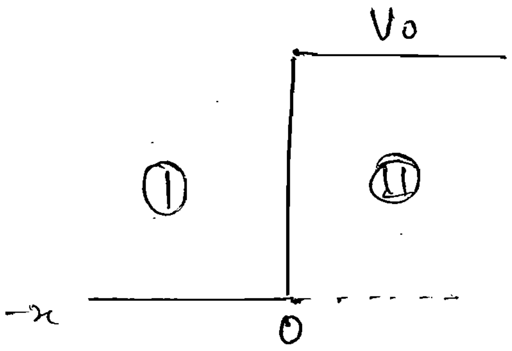
$= -V_0, \quad x > L$

$= \infty \quad x \le -L$

$$V(x) = \begin{cases} = V_\infty & x > -L \\ = 0 & -L \le x \le 0 \\ = V_0 & 0 < x < L \\ = V_0 & L \le x \end{cases}$$

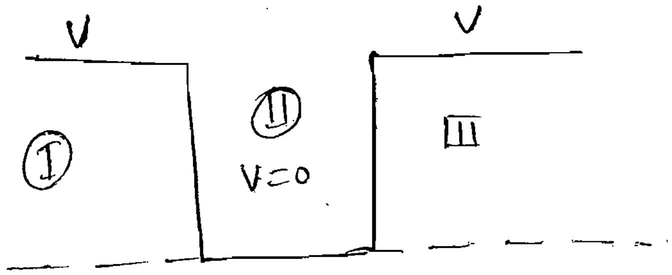


$$V(x) = \begin{cases} V = 0 & x \le 0 \\ V = -V_0 & x > 0 \end{cases}$$



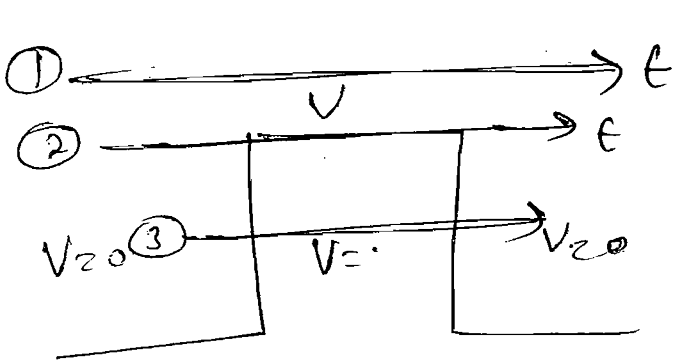
$$V(x) = \begin{cases} = 0 & x < 0 \\ = V_0 & 0 \leq x \leq \ell \end{cases}$$

$\Rightarrow$



gmp

$\Rightarrow$



$E > V$

$E = V$

$E < V$

$V = 0$

G.K

$$H\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V = \hat{H}$$

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi = (E-V)\psi$$

$$\frac{d^2}{dx^2}\psi = -\frac{2m}{\hbar^2}\underbrace{(E-V)}_{\text{always take +ve}}\psi$$

Case I $E > V$

$$\frac{d^2\psi}{dx^2} = \frac{-2m}{\hbar^2}(E-V)\psi$$

$$\frac{d^2\psi}{dx^2} = -K^2\psi \qquad K^2 = \frac{2m}{\hbar^2}(E-V)$$

$$\Downarrow$$

$$\psi = e^{\alpha x}$$

$$\alpha^2 e^{\alpha x} = -K^2 e^{\alpha x}$$

$$\alpha^2 = -K^2 \qquad \boxed{\psi = Ae^{iK} + Be^{-iK}} \text{ --- (1)}$$

$$\alpha = \sqrt{-K^2}$$

$$= \pm i\sqrt{K^2}$$

$$\alpha = \pm iK$$

Case 2 : $V > E$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}[E-V]\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V-E]\psi$$

$$\frac{d^2\psi}{dx^2} = K^2\psi \qquad K^2 = \frac{2m}{\hbar^2}(V-E)$$

$$\Downarrow$$

$$e^{\alpha x} \qquad K = \sqrt{\frac{2m}{\hbar^2}(V-E)}$$

$$\alpha^2 = K^2$$

$$\alpha = \pm K \quad \Rightarrow \underbrace{\psi = Ae^{Kx} + Be^{-Kx}}$$

Case ③ $V = 0$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}E\psi$$

$$\frac{d^2\psi}{dx^2} = -K^2\psi \qquad K^2 = \frac{2mE}{\hbar^2}$$

$$\Downarrow$$

$$\alpha^2 = -K^2 \qquad \psi = e^{\alpha} \quad iK \qquad \boxed{K = \sqrt{\frac{2mE}{\hbar^2}}}$$

$$\alpha = \pm iK \qquad \boxed{\psi = Ae^{iKx} + Be^{-iKx}}$$

$V = \delta$ $\quad \frac{d^2\psi}{dx^2} = \frac{-2m}{\hbar^2}[E - \delta]$

$$\frac{d^2\psi}{dx^2} = \delta\psi$$

$$\Downarrow e^{\alpha}$$

$\alpha^2 = \delta^2$ $\qquad \psi = Ae^{\delta x} + Be^{-\delta x}$

$\alpha = \pm\delta$ $\qquad \psi = 0$ $\quad \psi$ should be zero.

Case III : $\quad E = V$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E - E)$$

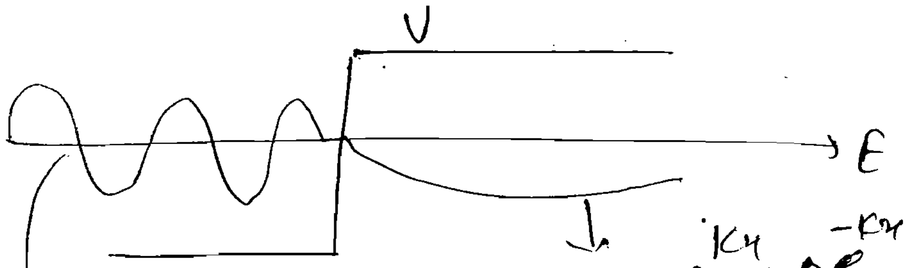
$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} \times 0$$

$\frac{d^2\psi}{dx^2} = 0 \quad \Rightarrow \psi \neq 0$ not possible.

$\cancel{\psi = Ae^0 + Be^0}$ $\qquad \psi = e^{\alpha x}$

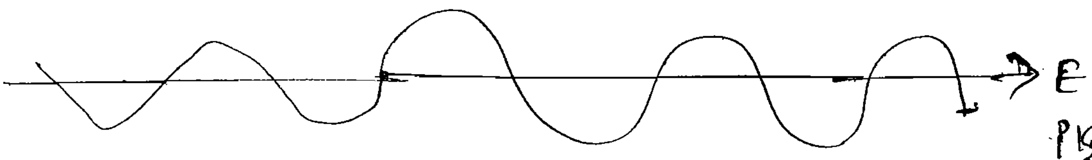
$\cancel{\psi = A + B}$ $\qquad \psi = e^0 = 1$ Constant

(1)



$\psi = Ce^{iKx} + De^{-Kx}$

$\psi = Ae^{+iKx} + Be^{-iKx}$



$\psi = Ae^{iK_2x} + \cancel{Be^{-iK_2x}}$

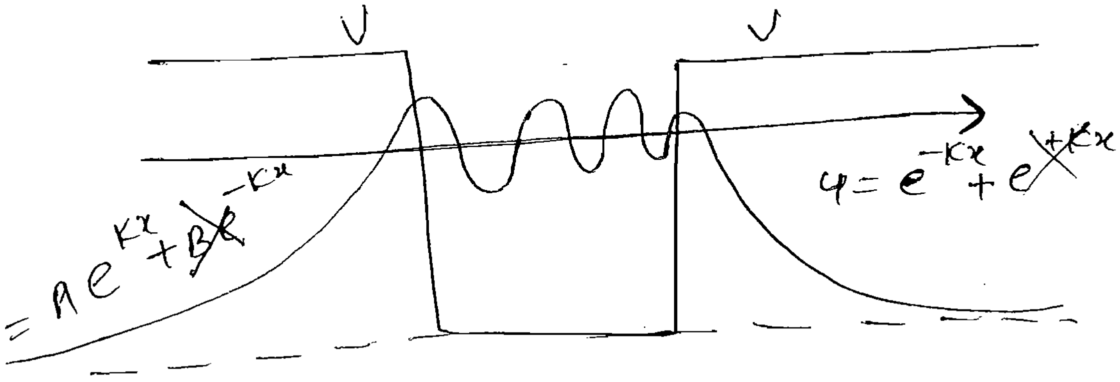
$\psi =$

(2) $\psi = Ae^{iK_1x} + Be^{-iK_1x}$

$\hbar K$

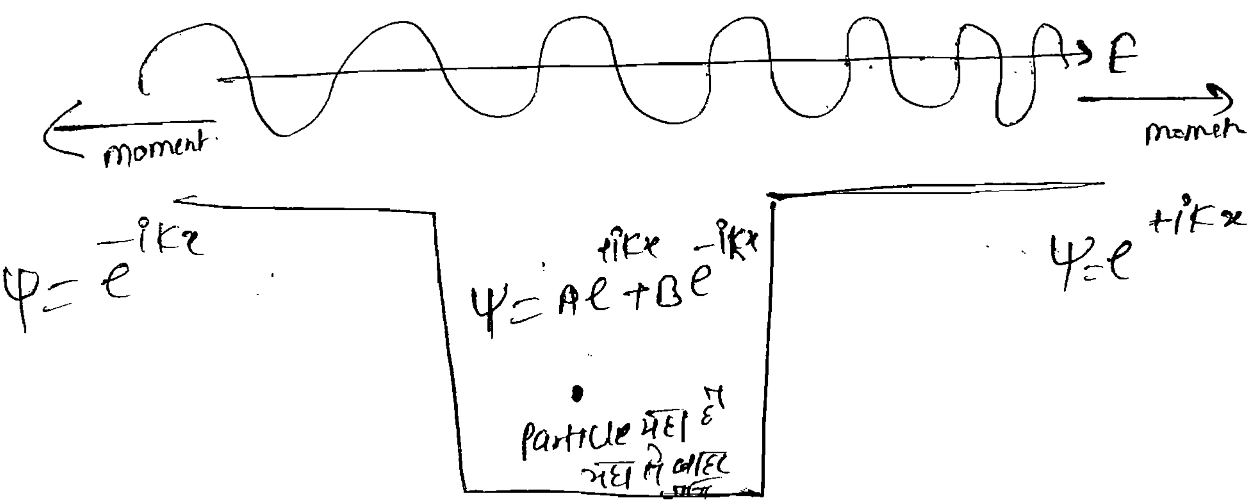
$-\hbar K$

(3)

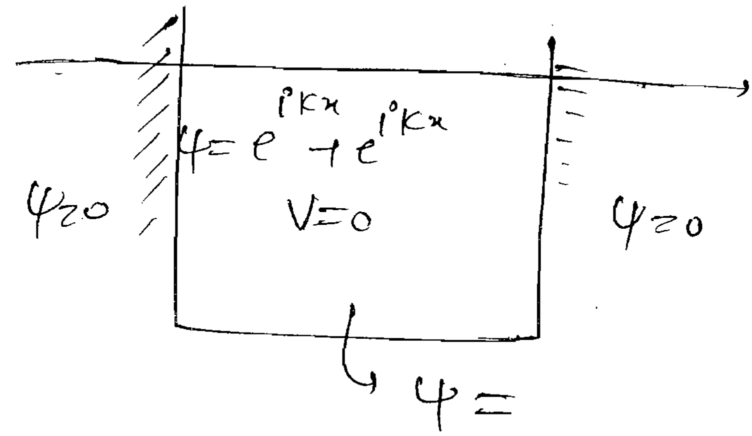


$\psi = Ae^{Kx} + \cancel{Be^{-Kx}}$

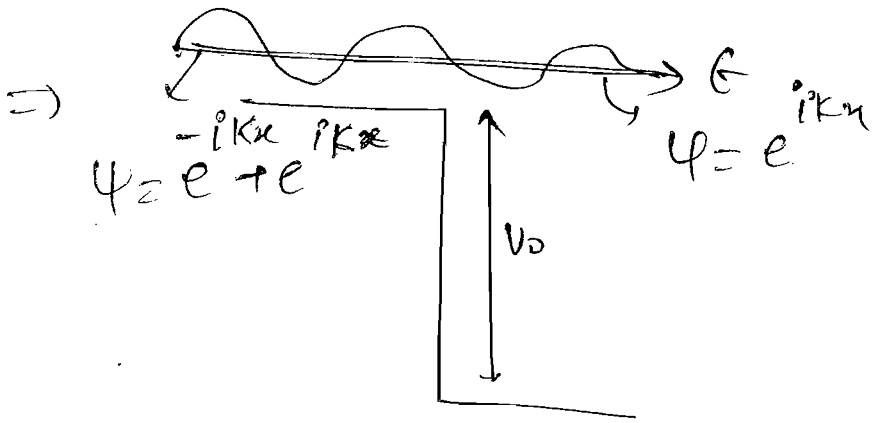
$\psi = e^{-Kx} + \cancel{e^{+Kx}}$



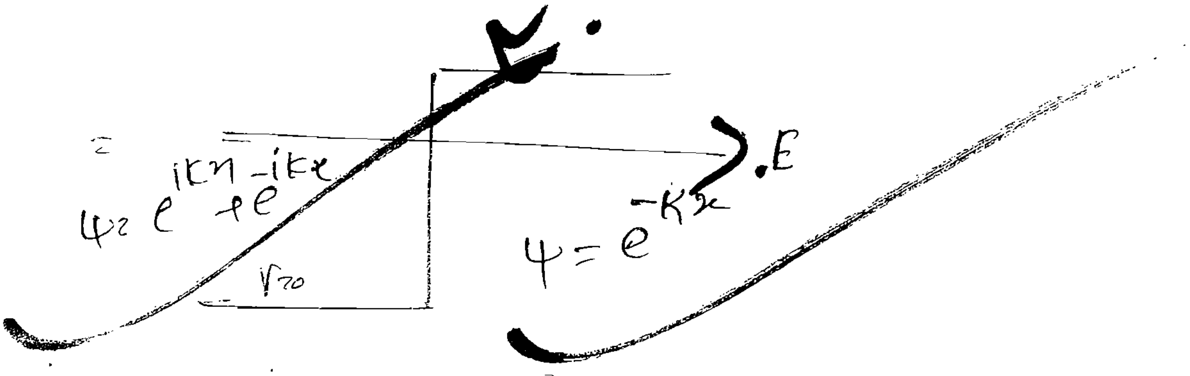
E
moment
momen
$\psi = e^{-ikx}$
$\psi = Ae^{ikx} + Be^{-ikx}$
$\psi = e^{+ikx}$
particle यहा है



$\psi = e^{ikx} + e^{ikx}$
$V = 0$
$\psi = 0$
$\psi = 0$
$\psi =$

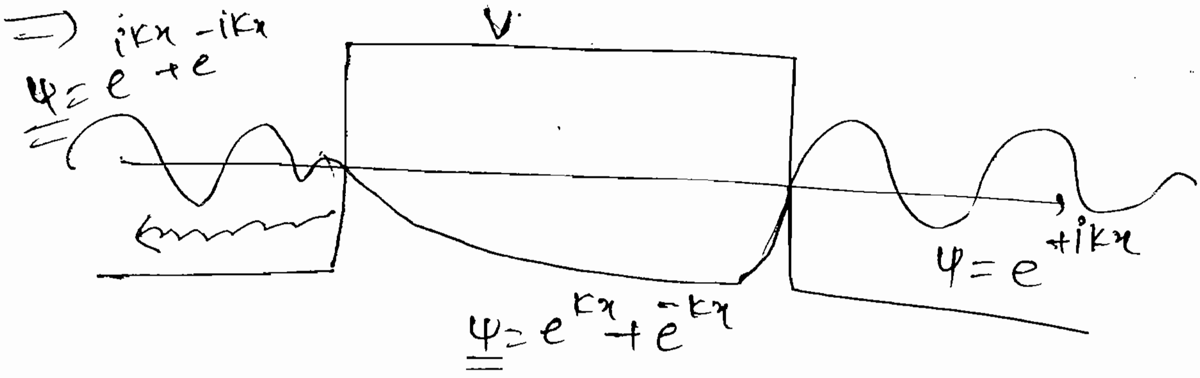


E
$\psi = e^{-ikx} + e^{ikx}$
$\psi = e^{ikx}$
V_0



=
E
$\psi = e^{ikx} + e^{-ikx}$
$\psi = e^{-kx}$
$V = 0$

$\Rightarrow$

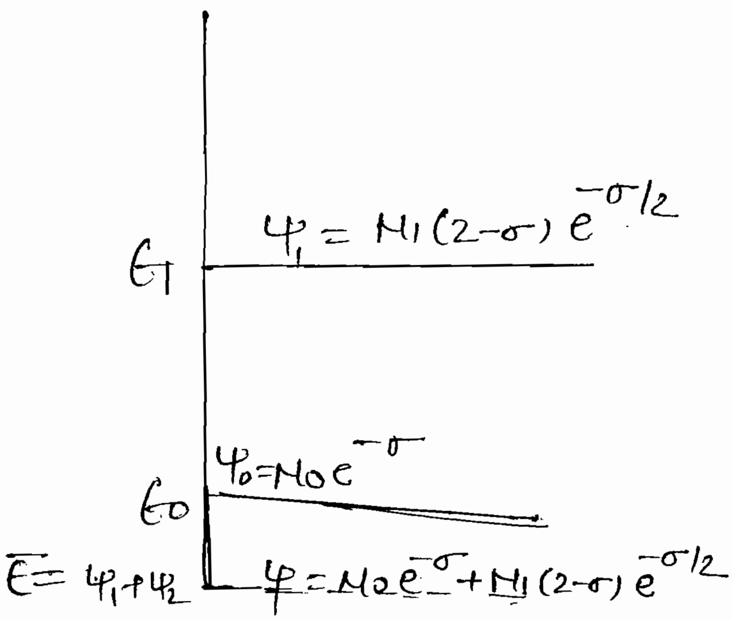


: 24 april 2016 :

① $E_0 = N_0 e^{-\sigma}$

$E_1 = N_1(2-\sigma) e^{-\sigma/2}$

$\boxed{\bar{E} < E_0 < E_1}$



② $\psi_1 = c_1\phi_1 + c_2\phi_2$

$H_{11} = 0, \quad H_{12} = 2.0, \quad H_{21} = 2.0, \quad H_{22} = 3$

$$E = \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

$$\begin{vmatrix} -E & 2 - E \times 0 \\ 2 - 0 & 3 - E \end{vmatrix} = 0 \Rightarrow \begin{bmatrix} -E & 2 \\ 2 & 3 - E \end{bmatrix} = 0$$

$-3E + E^2 - 4 = 0$

$E^2 - 3E - 4 = 0$

$$E = \frac{3 \pm \sqrt{9+16}}{2} = \frac{3 \pm 5}{2}, \frac{8}{2}, \frac{-2}{2} \Rightarrow 4, -1$$

$\boxed{E = -1}$

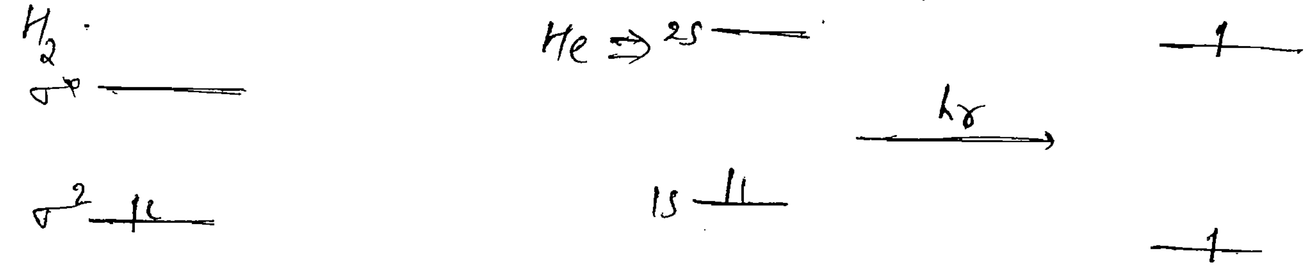
Variation के according ...

③ $H_{11} = 4\epsilon$ $H_{22} = 9\epsilon$ $\Rightarrow$ unperturbed

$H_{01} = 0.2\epsilon$ $H_{02} = 0.3\epsilon$ $H_{12} = 0.4\epsilon$, $H_{21} = 0.4\epsilon$

24 april

Slater determinant: way of writing the wave function of multi electron system.



Q Write down the Hamitonian of He.

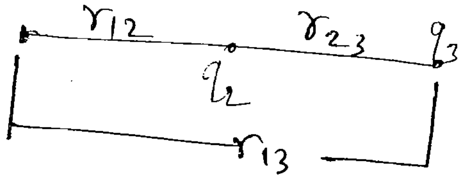
$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} \rightarrow \begin{cases} -\dfrac{\hbar^2}{2m_{NH}} \cdot \dfrac{\partial^2}{\partial r_1^2} \\ -\dfrac{\hbar^2}{2m_e} \dfrac{\partial^2}{\partial r^2} \end{cases}$$

$\Rightarrow$ $q_1 \xrightarrow{r_{12}} q_2$

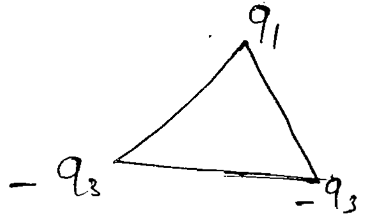
$$V = \frac{1}{4\pi\varepsilon}\left(\frac{q_1 q_2}{r_{12}}\right)$$

$\Rightarrow$

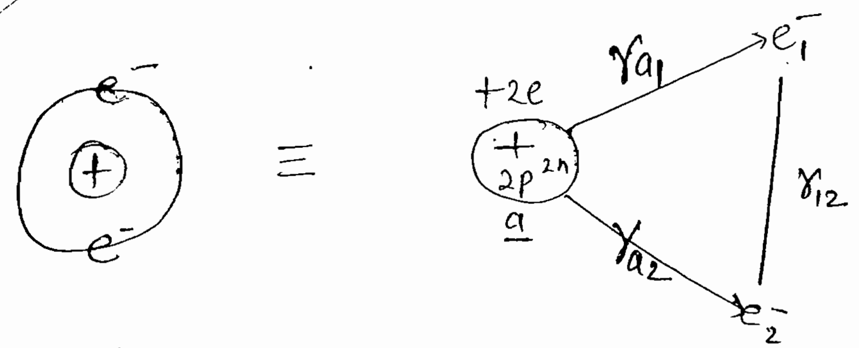


$$V = \frac{1}{4\pi\varepsilon_0}\left[\frac{q_1 q_2}{r_{12}} + \frac{q_2 q_3}{r_{23}} + \frac{q_1 q_3}{r_{13}}\right]$$

$\Rightarrow$



⇒ He

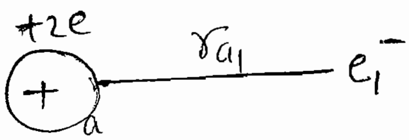


$$V = \frac{1}{4\pi\varepsilon_0}\left[-\frac{2e \times e_1}{r_{a_1}} - \frac{2e \times e_2}{r_{a_2}} + \frac{e_1 e_2}{r_{12}}\right]$$

$$\hat{V} = \frac{1}{4\pi\varepsilon_0}\left[-\frac{2e^2}{r_{a_1}} - \frac{2e^2}{r_{a_2}} + \frac{e^2}{r_{12}}\right]$$

$$\hat{T} = -\frac{\hbar^2}{2m_H}\nabla_H^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2$$

⇒ He^+



(you can take normally r)

$$V = \frac{1}{4\pi\varepsilon_0}\left(-\frac{2e^2}{r_{a_1}}\right)$$

$$T = -\frac{\hbar^2}{2m_H}\nabla_H^2 - \frac{\hbar^2}{2m_e}\nabla_e^2$$

$$H = T + V$$

$$\hat{H} = -\frac{\hbar^2}{2m_H}\nabla_H^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r}$$

applying Born-openheimer approximation. mass of neucleus is so high as compare to e⁻ thats why nucleus will not move ie K.E will so low, so it can be neglect

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r}$$

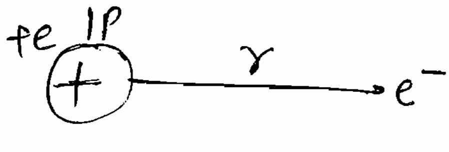
$(K.E)_{nucl} < (K.E)_{Electron}$

$(K.E)_{elect} + (K.E)_{nuc} \approx (K.E)_e$

In term of amu

$$\hat{H} = -\frac{1}{2}\nabla_e^2 - \frac{2}{r}$$

Hamiltonian for Hydrogen atom :



$$T = -\frac{\hbar^2}{2m_N}\nabla_n^2 - \frac{\hbar^2}{2m_e}\nabla_e^2$$

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

$$H = -\frac{\hbar^2}{2m_N}\nabla_n^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

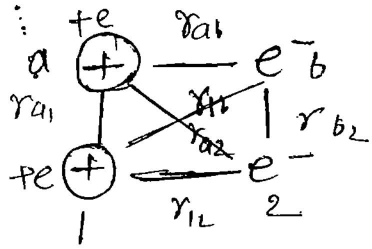
by applying Born approximation

$$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon}\frac{e^2}{r}$$

in term of amu

$$\boxed{H = -\frac{1}{2}\nabla_e^2 - \frac{1}{r}}$$

$\Rightarrow \hat{H}$ for H_2 molecule:



$$T = -\frac{\hbar^2}{2m_N}\nabla_a^2 - \frac{\hbar^2}{2m_N}\nabla_1^2 - \frac{\hbar^2}{2m_{e_b}}\nabla_b^2 - \frac{\hbar^2}{2m_{e_2}}\nabla_2^2$$

$$V = \frac{1}{4\pi\varepsilon_0}\left(\frac{-e^2}{r_{ab}} + \frac{e^2}{r_{b2}} - \frac{e^2}{r_{12}} + \frac{e^2}{r_{a1}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{a2}}\right)$$

afte applying BOnA:

$$T = -\frac{\hbar^2}{2m_{e_b}}\nabla_b^2 - \frac{\hbar^2}{2m_{e_2}}\nabla_2^2$$

$$\hat{H} = -\frac{\hbar^2}{2m_{e_b}}\nabla_b^2 - \frac{\hbar^2}{2m_{e_2}}\nabla_2^2 + \frac{1}{4\pi\varepsilon_0}\left(\frac{-e^2}{r_{ab}} + \frac{e^2}{r_{b2}} - \frac{e^2}{r_{12}} + \frac{e^2}{r_{a1}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{a2}}\right)$$

in term of amu

$$\hat{H} = \left(-\frac{\nabla_b^2}{2} - \frac{1}{2}\nabla_e^2 - \frac{1}{r_{ab}} + \frac{1}{r_{b2}} - \frac{1}{r_{12}} + \frac{1}{r_{a1}} - \frac{1}{r_{1b}} - \frac{1}{r_{a2}}\right)$$

(repulsive)

He

2s ——

spinorbital

1s —↑↓— → $1s(2)\,\alpha(2)$, $1s(1)\,\beta(1)$

2s —↑— $2s(\ )\,\alpha(\ )$

1s —↑— $1s(\ )\,\alpha(\ )$

2s —↑— $2s(\ )\,\alpha(\ )$

1s —↓— $1s(\ )\,\beta(\ )$

Li ⟹

2s —↑— $2s(\ )\,\alpha(\ )$

1s —↑↓— → $1s(\ )\,\beta(\ )$, $1s(\ )\,\alpha(\ )$

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1), & 1s(1)\beta(1), & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2), & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

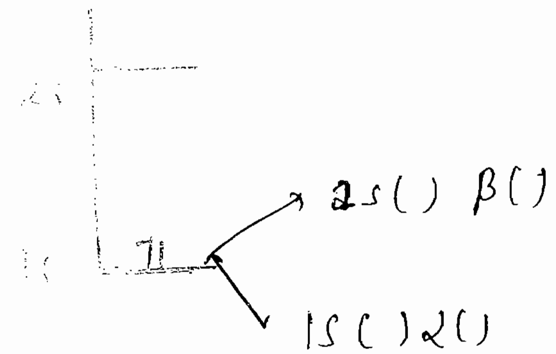
⟹ Sletterdetteminant.

→ no. of possible arrangment

If there are n no. of e^- in the system then normalization Cont for Slater determinat = $\frac{1}{\sqrt{n!}}$

→ no. of possible arrangment

He



$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\,\alpha(1) & 1s(1)\,\beta(1) \\ 1s(2)\,\alpha(2) & 1s(2)\,\beta(2) \end{vmatrix}$$

$\Rightarrow \quad \psi = a\phi_1 + b\phi_2 \cdot \frac{1}{\sqrt{a_1^2 + b_1^2}}$

$\psi = (\phi_1 + \phi_2)\frac{1}{\sqrt{2}}$

$\psi = [1s(1)\,\alpha(1)\,1s(2)\,\beta(2) - 1s(2)\,\alpha(2)\,1s(1)\,\beta(1)]\,\frac{1}{\sqrt{2}}$

like $\psi = (\phi_1 - \phi_2)\frac{1}{\sqrt{2}}$

$\Rightarrow$ gn cal of Li

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a\,|2\times2| - b\,|2\times2| + c\,|2\times2|$$

2 2 2 2

2 6

Slatter determinant for E.S of He

$2s \;\downarrow\; 2s(1)\beta(1)$ $\qquad$ $\uparrow\; 2s(1)(\alpha)$ $\qquad \uparrow \qquad \downarrow$

$1s \;\uparrow\; 1s(1)\alpha(1)$ $\qquad$ $\uparrow\; 1s(2)\alpha(1)$ $\qquad \downarrow \qquad \downarrow$

$$\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} \frac{1}{\sqrt{2}} = \psi_1 \; +$$

$$\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} \frac{1}{\sqrt{2}} = \psi_2 \; +$$

$$\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix} \frac{1}{\sqrt{2}} = \psi_3 \; +$$

$$\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix} \frac{1}{\sqrt{2}} = \psi_3 \; +$$

$$\psi = \left(\frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{2}}\psi_2 + \frac{1}{\sqrt{2}}\psi_3 + \frac{1}{\sqrt{2}}\psi_4\right)\frac{1}{\sqrt{\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}}}$$

$$\psi = \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2}}\left(\psi_1 + \psi_2 + \psi_3 + \psi_4\right)$$

$$\psi = \frac{1}{2}\left(\psi_1 + \psi_2 + \psi_3 + \psi_4\right)$$

Slatter dottermmant for H_2:

$2s$ ——

$\sigma 1s$ —$\uparrow\downarrow$— $\rightarrow$ $\sigma 1s(\,)\beta(\,)$, $\sigma 1s(\,)\alpha(\,)$

$$=\frac{1}{\sqrt{2}}\begin{vmatrix} \sigma 1s(1)\,\beta(1) & \sigma 1s(1)\,\alpha(1) \\ \sigma 1s(2)\,\beta(2) & \sigma 1s(2)\,\alpha(2) \end{vmatrix}$$

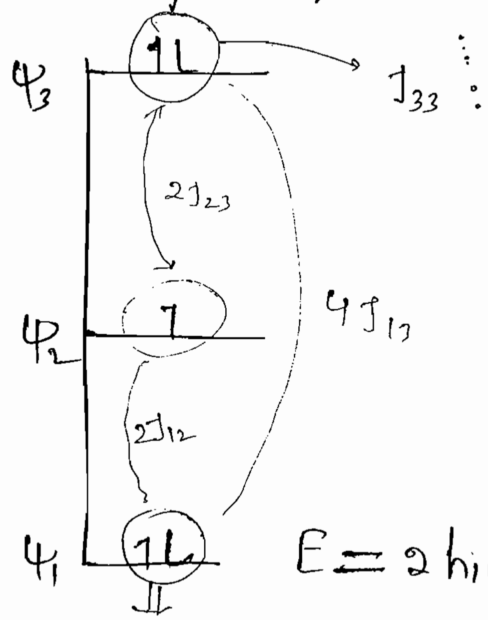
$\Rightarrow$

ψ_2 —$\uparrow$— $\psi_2(\,)\alpha(\,)$

ψ_1 —$\uparrow\downarrow$— $\rightarrow$ $\psi_1(\,)\beta(\,)$, $\psi_1(\,)\alpha(\,)$

$$=\frac{1}{\sqrt{6}}\begin{vmatrix} \psi_1(1)\,\alpha(1) & \psi_1(1)\,\beta(1) & \psi_2(1)\,\alpha(1) \\ \psi_1(2)\,\alpha(2) & \psi_1(2)\,\beta(2) & \psi_2(2)\,\alpha(2) \\ \psi_1(3)\,\alpha(3) & \psi_1(3)\,\beta(3) & \psi_2(3)\,\alpha(3) \end{vmatrix}$$

~~Sig~~ single electron atomic energy is represented by h



$$\langle \psi_1 | H | \psi_1 \rangle = H_{11} = h_{11}$$

$$E = 2h_{11} + h_{22} + 2h_{33} + J_{11} + 2J_{12} + 4J_{13} + 2: + J_{33}$$

repulsion is also there so term will be J

so ψ_1 के लिए J_{11}

$$E = 2h_{11} + h_{22} + 2h_{33} + J_{11} + 2J_{12} + 4J_{13} + 2J_{23} + J_{33}$$

$+$

(Exchange energy) $\Rightarrow K$

$$\Rightarrow 2K_{13} + K_{12} + K_{23}$$

<u>total energy</u>

$$\boxed{E = 2h_{11} + h_{22} + 2h_{33} + J_{11} + 2J_{12} + 4J_{13} + 2J_{23} + J_{33} + 2K_{13} + K_{12} + K_{23}}$$

He ⇅ $E = 2h_{11} + J_{11}$

2 ⇅

1 ⇅ $E = 2h_{11} + 2h_{22} + J_{11} + 4J_{12} + 2K_{12} + J_{22}$

h = single electron atomic energy

J = Coulomb energy / Repulsive energy

K = exchange energy

(20) H_2 — H_a — $1s_a$ (⇅) or H_b — $1s_b$ (⇅)

Ionic $\begin{vmatrix} 1s_a(1)\,\alpha(1) & 1s_a(1)\,\beta(1) \\ 1s_a(2)\,\alpha(2) & 1s_a(2)\,\beta(2) \end{vmatrix}$

Symmetric and antisymmetric wave function:

$$\hat{P}_{12}\ \overset{\psi_1}{1s(1)\,2s(2)} = a\,?\,\overset{\psi_{1x}}{\left(1s(2)\,2s(1)\right)}$$

$$\hat{P}_{21}\ 1s(2)\,2s(1) = a\ 1s(1)\,2s(2)$$

neither symmetric nor antisymm.

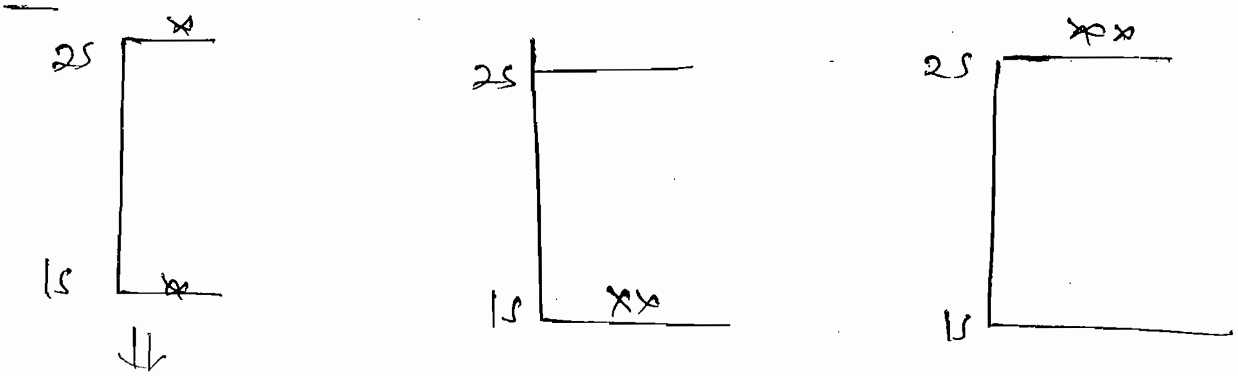
$$\hat{P}\left[1s(1)\,1s(2)\right] = +1\left(1s(2)\,1s(1)\right) \longrightarrow \text{sym.}$$

$$\hat{P}\left(2s(1)\,2s(2)\right) = +1\left(2s(2)\,2s(1)\right) \longrightarrow \text{symmetric}$$

$$\left\{\begin{array}{l} \hat{P}_p(\psi) = -1(\psi) = \text{antisymmetric} \\ \hat{P}(\psi) = +1(\psi) = \text{symmetric} \end{array}\right\}$$

- The wavefunctⁿ which give eigenvalue +1 by applying permutation operator called symmetric wavefunction.
- If it give (−1) then called antisymmetric

<u>He</u>



$$\hat{P}\left[1s(1)\,2s(2)\right] = 1s(2)\,2s(1)$$

$$\hat{P}\left[1s(2)\,2s(1)\right] = 1s(1)\,2s(2)$$

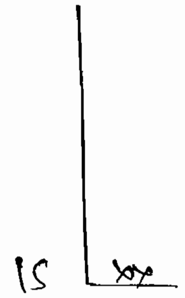
Combined both

$$\hat{P}\left[1s(1)\,2s(2) + 1s(2)\,2s(1)\right] = +1\left[1s(2)\,2s(1) + 1s(1)\,2s(2)\right] \quad \text{symmetric}$$

$$\hat{P}\left[1s(1)\,2s(2) - 1s(2)\,2s(1)\right] = \left[1s(2)\,2s(1) - 1s(1)\,2s(2)\right]$$

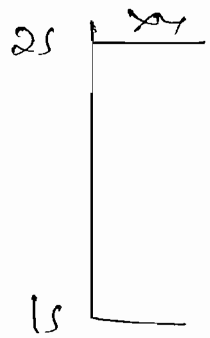
$$= (-1)\left[1s(1)\,2s(2) - 1s(2)\,2s(1)\right]$$

$\hookrightarrow$ ~~sc~~ -1 = antisymmetric



$\Rightarrow$ $1s(1)\,1s(2)$

$\hat{P}\,(1s(1)\,2s(2)) = (1s(2)\,1s(1)) =$ symm



$$\hat{P}\,[2s(1)\,2s(2)] = +1\,(2s(2)\,2s(1))$$

$\Downarrow$

symmetric

$\Rightarrow$ $\left.\phi_1 , \phi_2\right\}$ 2 electron

$\phi_1(1)\,\phi_1(2) \longrightarrow$ symmetric

$\phi_2(1)\,\phi_2(2) \longrightarrow$ symmetric

$$\left.\begin{array}{l}\phi_1(1)\,\phi_2(2)\\ \phi_1(2)\,\phi_2(1)\end{array}\right\} \Rightarrow \begin{array}{l}\phi_1(1)\,\phi_2(2) + \phi_1(2)\,\phi_2(1) \text{ — symmetric}\\ \phi_1(1)\,\phi_2(2) - \phi_1(2)\,\phi_2(1) \text{ — antisym}\end{array}$$

Spin part: $\quad \alpha(1)\ \beta(1)\ ]\ 2e^-$

$\overset{+\frac{1}{2}}{\alpha}(1)\ \overset{+\frac{1}{2}}{\alpha}(2) \longrightarrow$ symmetric $m_s = +1$

$\overset{-1/2}{\beta}(1)\ \overset{-1/2}{\beta}(2) \longrightarrow$ symmetric $m_s = -1$

$\left.\begin{array}{l}\alpha(1)\ \beta(2) \\ \alpha(2)\ \beta(1)\end{array}\right\}$ neither symmetric nor antisymmetric

Linear combination

$\Rightarrow \overset{+\frac{1}{2}}{\alpha}(1)\ \overset{-\frac{1}{2}}{\beta}(2) + \overset{+1/2}{\alpha}(2)\ \overset{-\frac{1}{2}}{\beta}(1) \Rightarrow$ symmetric $m_s = 0$

$\overset{+1/2}{\alpha}(1)\ \overset{-1/2}{\beta}(2) - \overset{+1/2}{\alpha}(2)\ \overset{-1/2}{\beta}(1) \Rightarrow$ antisymmetric $m_s =$

symmetric m_s $\quad +1 \quad 0 \quad -1 \Rightarrow S = 1$

$2S+1$

$2S+1 = 2\times1+1 = (3 \text{ triplet})$

Q For H_2 molecule in the E.S $\sigma g(1)\,\sigma u(1)$ the spin part is tripletet state with $m_s = -1$ then the space part is

spin part $\beta(1)\ \beta(2)$ — symmetric

$= \frac{1}{\sqrt{2}}(\sigma g(1)\,\sigma u(2) - \sigma g(2)\,\sigma u(1))$

$= \frac{1}{\sqrt{2}}[\sigma g(1)\,\sigma u(2) - \sigma g(2)\,\sigma u(1)]$

(10)

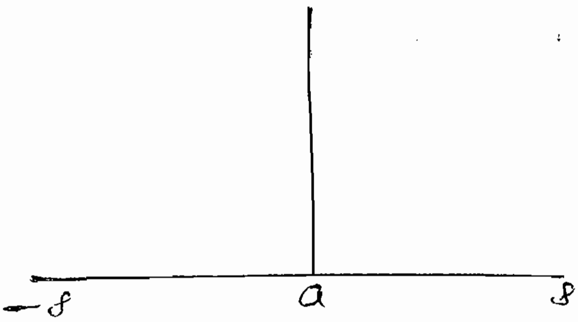
$$\begin{vmatrix} \sigma(1)\alpha(1) & \sigma(1)\beta(1) \\ \sigma(2)\alpha(2) & \sigma(2)\beta(2) \end{vmatrix}$$

$$= \sigma(1)\alpha(1)\sigma(2)\beta(2) - \sigma(2)\alpha(2)\sigma(1)\beta(1) = \phi.$$

$$= \sigma(2)\alpha(2)\sigma(1)\beta(1) - \sigma(1)\alpha(1)\sigma(2)\beta(2)$$

$$= -1\,[\quad \phi. \quad] \Rightarrow$$ antisymmetric

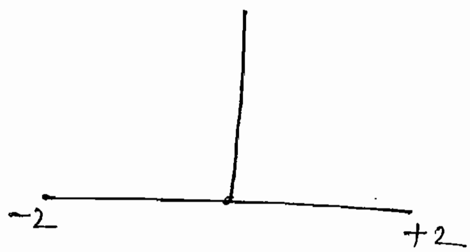
Dirac Delta function : function define on only one point in given range.



$\delta(x-a) = 1$
$= 0$ (otherwise)

$$\int_{-2}^{2} x^2 \delta(x-1)\, dx = (1)$$

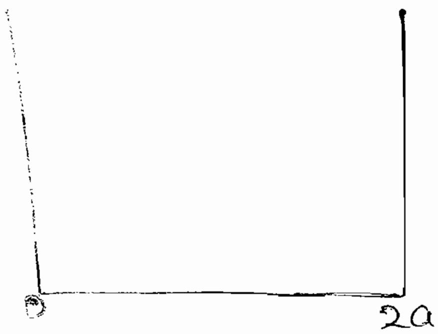
$(1)^2 \times 1 = 1$

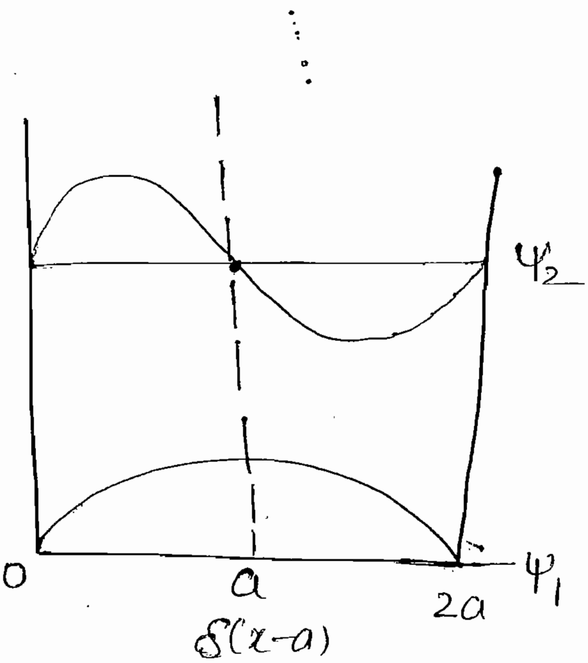


$$\int_{-2}^{5} (x^2+2)\, \delta(x-3)\, dx$$

$\Downarrow$

$(3^2+2) \times 1 = (9+2)$
$= 11$





$$\frac{2}{a}\int_0^{2a} \sin^2\left(\frac{\pi x}{a}\right)\, \delta(x-a)\, dx$$

ψ_2

$$\Downarrow$$

$$\sin^2\left(\frac{a\pi}{a}\right) \quad 1$$

$$= \sin^2 \pi \times 1 = 0$$

Q
$$\frac{1}{a}\int_0^{2a} \sin^2\left(\frac{\pi x}{2a}\right)\, \delta(x-a)\, dx$$

$$\Downarrow$$

$$\frac{1}{a} \times \sin^2(\pi/2) \times 1 = \frac{(1)}{a}$$

In general $\displaystyle\int_{-\delta}^{\delta} f(x)\, \delta(x-a)\, dx = \underline{f(a)}$

Q $\displaystyle\int_0^L \psi_1 (\text{Pert}^n)\, \psi_1\, dx =$

$$\int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \cdot \delta(x-a) \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx$$

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

$$= \frac{2}{L} \times \sin^2\left(\frac{\pi \times \cancel{L}}{\cancel{L}}\right) \times 1$$

$$= \frac{2}{L} \times \sin^2 \pi \Rightarrow \underline{\underline{0}}$$

Q $\displaystyle\int_0^{L/2} \left(\frac{2}{L}\right) \sin^2 \frac{\pi x}{L}\, \delta\left(x - \frac{L}{2}\right) dx$

$$= \left(\frac{2}{L}\right) \sin^2\left(\frac{\pi \times \cancel{L}}{\cancel{L} \times 2}\right) \times 1$$

$$= \left(\frac{2}{L}\right) \times 1 \times 1 = \underline{\underline{\left(\frac{2}{L}\right)}}$$

(7) First excited state $\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$

$$= \int \left(\frac{2}{a}\right) \sin^2\left(\frac{2\pi x}{a}\right) \cdot \delta\left(x - \frac{a}{2}\right) dx$$

$$= \left(\frac{2}{a}\right) \cdot \sin^2\left(\frac{2\pi \cancel{a}}{\cancel{2} \times \cancel{a}}\right)$$

$$= 0$$

(8) $$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad \int_0 \psi \, P_{ert}^n \psi^*$$

$$= \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{im\phi} \cdot H_1 \cdot \frac{1}{\sqrt{2\pi}} e^{-im\phi} d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{\cancel{2}im\phi} \cdot p\cos\phi \, d\phi$$

$$= \frac{\rho}{2\pi} \int_0^{2\pi} e^{2im\phi} \cdot \cos\phi \, d\phi$$

$$= \frac{\rho}{2\pi} \cdot \int_0^{2\pi} \cos\phi \, d\phi$$

$$= \frac{\rho}{2\pi} \left[\sin\phi\right]_0^{2\pi} = \frac{\rho}{2\pi} \left[\sin 2\pi - \sin 0\right]$$

$$= \frac{\rho}{2\pi} \times 0 = \underline{0}$$

(10) $\text{Pert}^n = \frac{Vx}{a}$

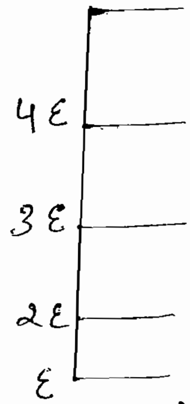
$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$\int_0^a \psi \, \text{Pert}^n \psi \, dx = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \cdot \frac{Vx}{a} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{V}{a} \cdot \frac{2}{a} \int_0^a$$

S

Second order perturbation :



$$E_2^{2} = \frac{|H'_{21}|^2}{E_2^{(0)} - E_1^{(0)}} + \frac{|H'_{23}|^2}{E_2^{(0)} - E_3^{(0)}} + \frac{|H'_{24}|^2}{E_2^{(0)} - E_4^{(0)}}$$

{ 2nd order perturbation for n=2 state }

$$E_1^{2} = \frac{|H_{12}|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{|H_{13}|^2}{E_1^{(0)} - E_3^{(0)}} + \frac{|H_{14}|^2}{E_1^{(0)} - E_4^{(0)}}$$

Characterstic property of 2nd order perturbation :

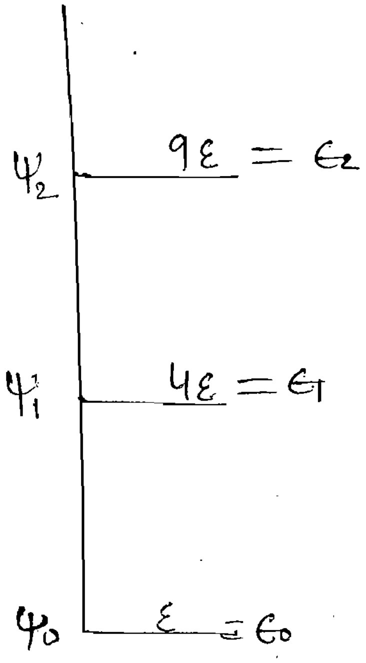
1. ⇒ Energy correction for ground state is always −ve
2. ⇒ Lowering of energy for ground state depends on perturbation (H') if perturbation is higher then lowering of energy will also be higher.
3. ⇒ If spacing b/w levels increases then lowering of energy decreases.

③

$H_{01} = 0.2\epsilon = H_{10}$

$H_{02} = 0.3\epsilon = H_{20}$

$H_{21} = 0.4\epsilon = H_{12}$



ⓐ $$E_0^2 = \frac{|H_{01}|^2}{E_0 - E_1} + \frac{|H_{02}|^2}{E_0 - E_2}$$

$$E_0^2 = \frac{(0.2\epsilon)^2}{\epsilon - 4\epsilon} + \frac{(0.3\epsilon)^2}{\epsilon - 9\epsilon} = -\frac{0.04\epsilon}{3} - \frac{0.09}{8\epsilon} =$$

$$= -\frac{0.2\cancel{\epsilon}}{3\cancel{\epsilon}} + \frac{0.3\cancel{\epsilon}}{8\cancel{\epsilon}} = -\left(\frac{0.2}{3} + \frac{0.3}{8}\right) = \frac{-1.6 - 0.9}{24} = \frac{-2.5}{24}$$

ⓐ

ⓑ

24/4/2016

spin matrices :

$$\langle \psi_{21-1} | \hat{L}_z | \psi_{21-1} \rangle = ? \quad \langle \psi_{21-1} | -\hbar | \psi_{21-1} \rangle = -\hbar \langle \psi_{21-1} | \psi_{21-1} \rangle$$
$$= -\hbar$$

$$\langle \psi_{210} | \hat{L}_z | \psi_{210} \rangle = 0$$

$$\langle \psi_{210} | \hat{L}_z | \psi_{21-1} \rangle = ? \langle \psi_{210} | -\hbar | \psi_{21-1} \rangle = -\hbar \times 0 = 0$$

$\langle$

$$\hat{L}_z | \psi_{31-1} \rangle = ? \; -i\hbar \frac{\partial}{\partial \phi} [R, \theta, e^{-i\phi}] = (-i\hbar)(-i) | \psi_{31-1} \rangle = -\hbar | \psi_{31-1} \rangle$$

$$\hat{L}_z | \psi_{21-1} \rangle = ? -\hbar | \psi_{21-1} \rangle$$

$$\hat{L}_z | \psi_{211} \rangle = +\hbar | \psi_{211} \rangle$$

$$\hat{L}_z | \psi_{100} \rangle = 0$$

$$\hat{L}_z | \psi_{322} \rangle = +2\hbar | \psi_{322} \rangle$$

$$\langle \psi_{21m} | L_z | \psi_{21m'} \rangle = \langle \psi_{21m} | m'\hbar | \psi_{21m'} \rangle$$

$\Downarrow$

$$= m'\hbar \langle \psi_{21m} | \psi_{21m'} \rangle$$

$l = 1 \quad m = +1, 0, -1, \; m' = +1, 0, -1$

$$= m'\hbar \times 0$$

$$= 0$$

$\Longrightarrow$

$\langle \psi_{21m} | L_z | \psi_{21m'} \rangle =$ $\quad l = 1$

$$\begin{array}{c|ccc} m' \backslash m & +1 & 0 & -1 \\ \hline 1 & \hbar & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & -\hbar \end{array}$$

$\langle \psi_{32m} | L_z | \psi_{32m'} \rangle$

$$\begin{array}{c|ccccc} m & +2 & +1 & 0 & -1 & -2 \\ \hline +2 & \hbar & 0 & 0 & 0 & 0 \\ +1 & 0 & \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & -\hbar & 0 \\ -2 & 0 & 0 & 0 & 0 & -2\hbar \end{array}$$

$\Rightarrow L_+ | \psi_{21-1} \rangle = \hbar \sqrt{l(l+1) - m(m+1)}$

$= \hbar \sqrt{1(1+1) - (-1)(-1+1)}\, | \psi_{210} \rangle$

$= \hbar \sqrt{2}\, | \psi_{210} \rangle$

$L_+ | \psi_{210} \rangle = \hbar \sqrt{1(1+1) - 0(0+1)}\, | \psi_{211} \rangle$

$$\hat{L}_+ |\psi_{nlm}\rangle = \hbar \sqrt{l(l+1) - m(m+1)}\, |\psi_{nl(m+1)}\rangle$$

$$L_+^{\dagger} = L_-$$

$$\langle \psi_{21+1} | L_+ | \psi_{21-1} \rangle = \langle L_- \psi_{21+1} | \psi_{21-1} \rangle$$

$$\langle \psi_{21+1} | L_+ | \psi_{21-1} \rangle = \langle \psi_{21+1} | \psi_{210} \rangle = 0$$

$$\langle L_- \psi_{21+1} | \psi_{21-1} \rangle = \langle \psi_{210} | \psi_{21-1} \rangle = 0$$

$\Longrightarrow$

$$\langle \psi_{nlm} | \hat{L}_+ | \psi_{nlm'} \rangle = \langle \psi_{nlm} | \psi_{nl(m'+1)} \rangle \;\; \cancel{=} \;\; 0$$

$$\langle \psi_{nlm} | \hat{L}_+ | \psi_{nlm'} \rangle = \langle L_- \psi_{nlm} | \psi_{nlm'} \rangle = \langle \psi_{nl(m-1)} | \psi_{nlm'} \rangle$$

$$\langle \psi_{32-1} | L_+ | \psi_{320} \rangle$$

$$= \langle \psi_{32-1} | \psi_{321} \rangle$$

$$= 0$$

$$\langle \psi_{320} | \hat{L}_+ | \psi_{320} \rangle = \langle \psi_{320} | \psi_{321} \rangle = 0$$

$$\langle \psi_{321} | \hat{L}_+ | \psi_{320} \rangle = \langle \psi_{321} | \psi_{321} \rangle = \sqrt{6}\,\hbar$$

$$\langle \psi_{32-1} | \hat{L}_+ | \psi_{32-2} \rangle = \langle \psi_{32-1} | \psi_{32-1} \rangle = +2\hbar$$

$$\langle \psi_{320} | \hat{L}_+ | \psi_{32\underbrace{-1}_{m}} \rangle = \langle \psi_{320} | \psi_{320} \rangle = \hbar\sqrt{6}$$

$$\hat{L}_+ = \hbar \sqrt{l(l+1) - m(m+1)}$$

$$= \hbar\sqrt{6}$$

$$L_+ = \hbar$$

$$\begin{array}{c|ccc}
l = 1 & +2 & 1 & 0 \\
m & +1 & 0 & -1 \\
\hline
+1 & 0 & \sqrt{2}\hbar & 0 \\
0 & 0 & 0 & \sqrt{2}\hbar \\
-1 & 0 & 0 & 0
\end{array}$$

$$\hat{L}_+ \equiv \begin{array}{c|ccc}
 & +1 & 0 & -1 \\
\hline
+1 & 0 & \sqrt{2}\hbar & 0 \\
0 & 0 & 0 & \sqrt{2}\hbar \\
-1 & 0 & 0 & 0
\end{array} \equiv$$

$$\hat{L}_+ = \begin{bmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & 0 & 0 \end{bmatrix}$$

$$\hat{L}_- |\psi_{310}\rangle = \hbar\sqrt{l(l+1) - m(m-1)}\, |\psi_{31-1}\rangle$$

$$= \hbar\sqrt{2}\, |\psi_{31-1}\rangle$$

$$= \hbar\sqrt{2}\, |\psi_{31-1}\rangle$$

$l = 1$

$$L \quad \begin{array}{c|ccc}
 & 0 & -1 & -2 \\
 & +1 & 0 & -1 \\
\hline
+1 & 0 & 0 & 0 \\
0 & \sqrt{2}\hbar & 0 & 0 \\
-1 & 0 & \sqrt{2}\hbar & 0
\end{array}$$

$$\hbar\sqrt{1(1+1)} = \sqrt{2}\hbar$$

$$\hbar\sqrt{1(1+1) - (-1)}$$

$$\hat{L}_+ = \begin{bmatrix} 0 & \sqrt{2}\hbar & 0 \\ 0 & 0 & \sqrt{2}\hbar \\ 0 & 0 & 0 \end{bmatrix} = \hat{L}_x + i\hat{L}_y$$

$$\hat{L}_- = \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2}\hbar & 0 & 0 \\ 0 & \sqrt{2}\hbar & 0 \end{bmatrix} = \hat{L}_x - i\hat{L}_y$$

$$L_+ + L_- = 2L_x = \begin{bmatrix} 0 & \sqrt{2}\hbar & 0 \\ \sqrt{2}\hbar & 0 & \sqrt{2}\hbar \\ 0 & \sqrt{2}\hbar & 0 \end{bmatrix}$$

$$L_x = \begin{bmatrix} 0 & \hbar/\sqrt{2} & 0 \\ \hbar/\sqrt{2} & 0 & \hbar/\sqrt{2} \\ 0 & \hbar/\sqrt{2} & 0 \end{bmatrix}$$

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$\hat{L}_+ + \hat{L}_-$$
$$\| \quad 2iL_y = \begin{bmatrix} 0 & \sqrt{2}\hbar & 0 \\ -\sqrt{2}\hbar & 0 & \sqrt{2}\hbar \\ 0 & -\sqrt{2}\hbar & 0 \end{bmatrix} =$$

$$L_y = \frac{1}{2i}\sqrt{2}\hbar\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$$

$$L_y = \frac{\hbar}{\sqrt{2}i}\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$$

$$L_y = \frac{i\hbar}{\sqrt{2}}\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$$

Spin matrices:

$$\left.\begin{array}{l} S_+ \\ S_- \\ S_x \\ S_y \\ S_z \end{array}\right\}$$

$s \Rightarrow \frac{1}{2}$

$m_s \quad +\frac{1}{2} \qquad -\frac{1}{2}$

$$\left|\frac{1}{2}, +\frac{1}{2}\right\rangle \equiv \hat{\alpha} \qquad \hat{\alpha} = \left|\hat{s}, m_s\right\rangle$$

$$\left|\frac{1}{2}, -\frac{1}{2}\right\rangle \equiv \hat{\beta}$$

$$S_z \left|\alpha\right\rangle = \hat{S}_z \left|\frac{1}{2}, +\frac{1}{2}\right\rangle = \underline{+\frac{1}{2}\hbar} \left|\alpha\right\rangle$$

$$S_z \left|\beta\right\rangle = -\frac{1}{2}\hbar \left|\beta\right\rangle$$

$s = 1/2$

$$\begin{array}{c|cc} & +\frac{1}{2} & -1/2 \\ \hline +1/2 & +1/2\,\hbar & 0 \\ -1/2 & 0 & -1/2\,\hbar \end{array} \Rightarrow \begin{bmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -1/2\,\hbar \end{bmatrix}$$

$$S_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\hat{S}_z = \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle = -\tfrac{1}{2}\hbar\,|\beta\rangle$$

$$\hat{S}_z = \left|\tfrac{1}{2}, +\tfrac{1}{2}\right\rangle = +\tfrac{1}{2}\hbar\,|\alpha\rangle$$

$$\hat{S}_+\left|\tfrac{1}{2}\ \tfrac{-1}{2}\right\rangle = \hbar\sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right) - \left(\tfrac{-1}{2}\right)\left(\tfrac{-1}{2}+1\right)}\,\left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle$$

$$= \hbar\sqrt{\tfrac{3}{4}+\tfrac{1}{4}} \qquad S_+ = \hbar\sqrt{s(s+1)-m_s(m_s+1)}$$

$$= \hbar\left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle$$

$$S_+\left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle = \hbar\sqrt{\tfrac{1}{2}\left(\tfrac{3}{2}\right) - \left(\tfrac{1}{2}\right)\left(\tfrac{3}{2}\right)}\ \left|\tfrac{1}{2}\ \tfrac{3}{2}\right\rangle$$

$$= 0$$

$$S_- = \hbar\sqrt{s(s+1)-m_s(m_s\ldots)}$$
$$\hbar\sqrt{\tfrac{1}{2}\times\tfrac{3}{2} - \left(-\tfrac{1}{2}\right)\left(\tfrac{1}{2}\right)}$$
$$\tfrac{3}{4}+\tfrac{1}{4}$$

$$S_+ = \tfrac{1}{2} \quad \begin{array}{c|cc} & 3/2 & 1/2 \\ & +\tfrac{1}{2} & -1/2 \\ \hline +\tfrac{1}{2} & 0 & \hbar \\ -1/2 & 0 & 0 \end{array} \qquad = \qquad S_- = 1/2 \quad \begin{array}{c|cc} & -1/2 & -3/2 \\ & +1/2 & -1/2 \\ \hline +1/2 & 0 & 0 \\ -1/2 & \hbar & 0 \end{array}$$

$$S_+ = \begin{bmatrix} 0 & \hbar \\ 0 & 0 \end{bmatrix} \qquad S_- = \begin{bmatrix} 0 & 0 \\ \hbar & 0 \end{bmatrix}$$

$$S_+ = \begin{bmatrix} 0 & \hbar \\ 0 & 0 \end{bmatrix} \quad S_- = \begin{bmatrix} 0 & 0 \\ \hbar & 0 \end{bmatrix}$$

$$S_+ + S_- = 2S_x = \begin{bmatrix} 0 & \hbar \\ \hbar & 0 \end{bmatrix} =$$

$$\underline{\underline{S_x}} = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$S_+ - S_- = 2iS_y = \begin{bmatrix} 0 & \hbar \\ -\hbar & 0 \end{bmatrix}$$

$$\underline{\underline{S_y}} = \frac{\hbar}{2i}\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} = \frac{i\hbar}{2}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

<u>Pauli spin matrices</u> : $\hbar = 2$

Pauli matrix

$$\hat{S}_x = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\hat{S}_y = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\sigma_+ = \begin{bmatrix} 0 & 2 \\ 0 & 0 \end{bmatrix}$$

$$\sigma_- = \begin{bmatrix} 0 & 0 \\ 2 & 0 \end{bmatrix}$$

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} e & f \\ g & h \end{bmatrix} = \begin{bmatrix} ae+bg & af+bh \\ ce+dg & cf+dh \end{bmatrix}$$

$$\sigma_x \cdot \sigma_z = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

$$\sigma_z \sigma_x = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$

$$\underline{\sigma_x \sigma_z} + \underline{\sigma_z \sigma_x} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

anti commutator

So pauli spin matrices $(\sigma_x, \sigma_y, \sigma_z)$ are anticommutator of each other.

$$\hat{\sigma}_x \hat{\sigma}_z + \hat{\sigma}_z \hat{\sigma}_x = 0$$

$$\hat{\sigma}_y \hat{\sigma}_z + \hat{\sigma}_z \hat{\sigma}_y = 0$$

$$\hat{\sigma}_z \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\vdots$$

$$\sigma_x \sigma_x = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \hat{\sigma}_z \hat{\sigma}_z$$

$$\boxed{\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1} = E$$

$$[\hat{L}_x \; \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{S}_x \; \hat{S}_y] = i\hbar \hat{S}_z$$

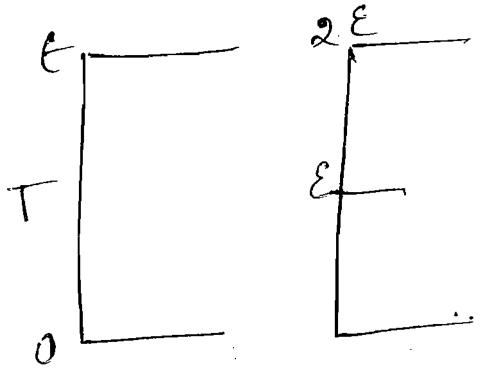
$$[\hat{\sigma}_x \; \hat{\sigma}_y] = 2i \hat{\sigma}_z$$

Statistical mechanics: This is a tool which is best on molecular level and define the same property i.e defined by thermodynamic.

Partition function: no. of possible states at given temp (thermodynamical condⁿ) is called partition function.

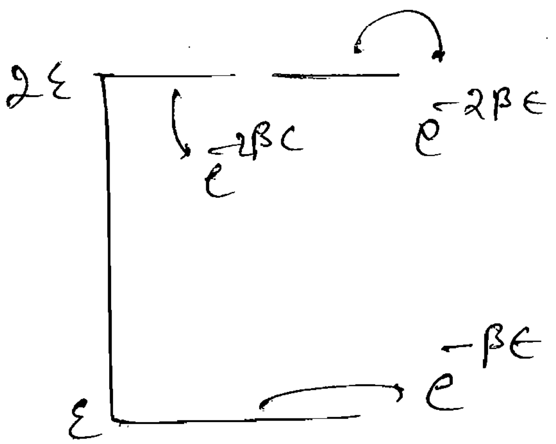
Calculation of partition function: (z) or (q or f):

Boltzmann factor: Two energy level system / three energy level system

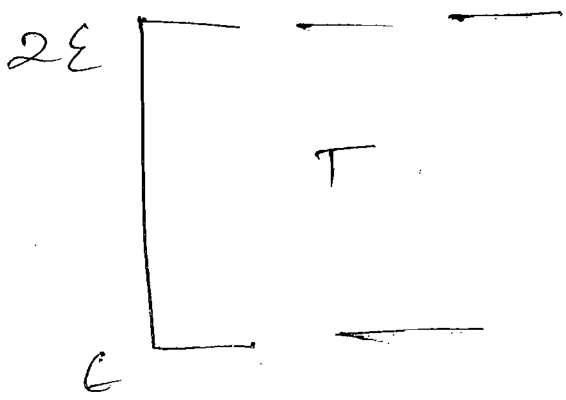


$e^{-\varepsilon\beta}$ $\beta = \frac{1}{k_b T}$

Partition function



$$\boxed{q = e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}$$



$$q = 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon}$$

$\rightarrow e^{-0} = 1$

$\beta = \frac{1}{K_b T}$

$T \rightarrow \infty = 0$

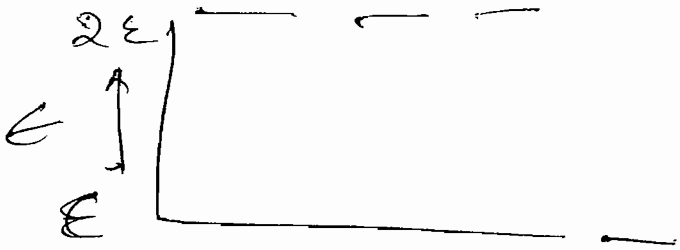
$e^{-\beta\epsilon} = e^{-\infty} = 0$

$\beta = \frac{1}{K_b T}$

$T = 0 \Rightarrow \infty$

$T=0$, Boltzmann factor $=0$ → $e^{-\beta\epsilon}$

$T\to\infty$, " $=1$



$$Z = 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon}$$

$T=0$ → 0

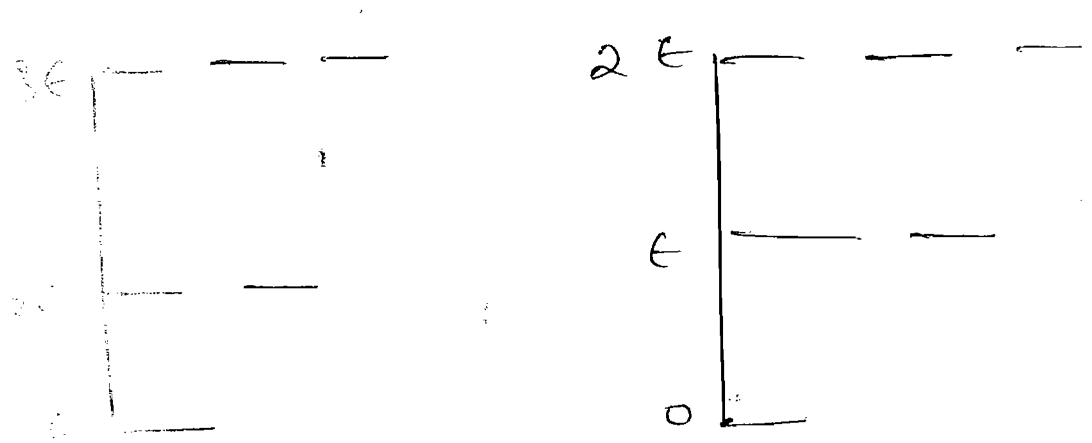
$Z=0$

valid physically acceptable

$$Z_T = 2 + 3e^{\cancel{-2\epsilon\beta}} \Rightarrow Z_1 = 2 + 3e^{-\epsilon\beta}$$

$T=0$ Boltz fact $=0$

$$Z_1 = 2$$



$+ 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} \quad {}^{-3\beta\epsilon}$

$q = 1 + 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon}$ $\cancel{ZPE}$

$e^{-\beta\epsilon}(1 + 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon})$

considering zero point energy

Valid

without considering zero point energy

Partition funct^n by cond^m zero PE = product of part^n fu^n without considering zero point energy and contribution of ground level in partition fu^n

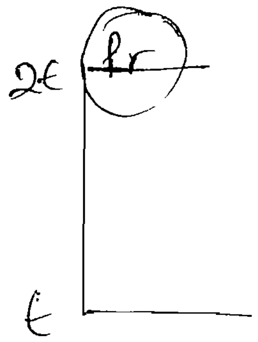
$$q_{PE} = e^{-\beta\epsilon}\, q_{\cancel{ZPE}}$$

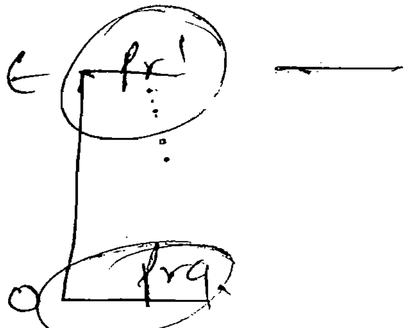
Q. Partition fu^n of a system by considering Z.P.E is , and en. of ground level is β^1 the partition fu $q_{\cancel{ZPE}}$

$$q = e^{-\beta \cdot \beta^1} q_{\cancel{ZPE}}$$

$$q_{\cancel{ZPE}} = q \times e^{1}$$

$\simeq \underline{2.79}$





$$q = e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}$$

$$q = 1 + e^{-\beta\epsilon}$$

$$q = e^{-\beta\epsilon}(1 + 2e^{-\beta\epsilon})$$

probability for finding the particle in a state or level is

$$P_r = \frac{e^{-2\beta\epsilon}}{q} , \qquad P_r' = \frac{e^{-\beta\epsilon}}{q}$$

$$= \frac{e^{-\cancel{2}\beta\epsilon}}{\cancel{e^{-\beta\epsilon}}(1+2e^{-\beta\epsilon})}$$

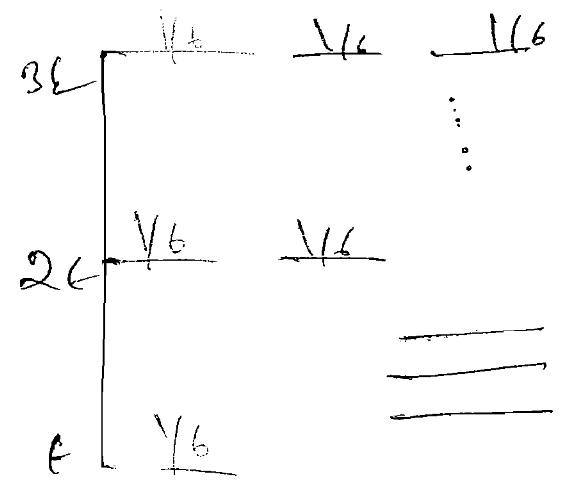
$$P_r' = \frac{e^{-\beta\epsilon}}{1+2e^{-\beta\epsilon}}$$

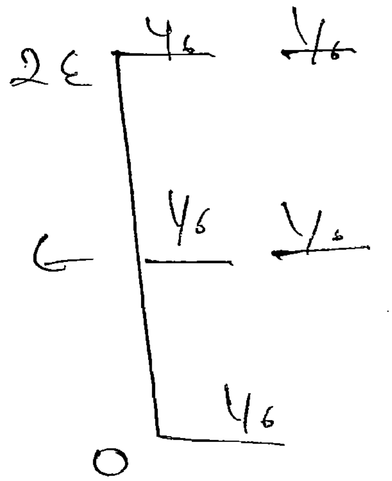
$$P_r' = \frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}$$

probability become same

in a state of 2st ε level

$$P_{rq} = \frac{1}{1+e^{-\beta\epsilon}}$$





$$\mathcal{f}_T = e^{-\beta\epsilon} + 2e^{-2\epsilon\beta} + 3e^{-\beta 3\epsilon}$$

$$\mathcal{f} = 1 + 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon}$$

$$\mathcal{f}_{T\to\infty} = 1 + 2 + 3 = 6$$

$T \to \infty$, $\beta\epsilon = 1$

$$\mathcal{f}_{T\to} = 1\times1 + 2\times1 + 3\times1$$

$= 6$ (all state are ~~them~~ equally probable at sufficient thermal energy.)

equiprobable

Q There are 100 level in a system all level are doubly degerate except ground level the probability for finding the particle in an Exited level at $T \to \infty$.

$$\frac{2}{199} \quad 99\times2.$$

In a system a there are 5 levels degeneracy remain 1, 2, 3, and so on then for sufficient thermal energy ($T \to \infty$) the probability of a state in a state of III level is $1/15$

4 marks

$$\boxed{q_{T\to\infty} = \sum_{level} g_{level}}$$

$$\boxed{q_{T\to 0} = g_{ground\ level}}$$

$$Pr \text{ in a state at } T \to \infty = \frac{1}{\sum_{level} g_{level}}$$

Pr. in a excited state at $T = 0 = 0$

$$= 2e^{-\varepsilon\beta} + 4e^{-2\varepsilon\beta}$$

$$= 2e^{-1} + 4e^{-2}$$

$$\frac{2}{e} + \frac{4}{e^2}$$

Translational energy level — quantum mechanical model

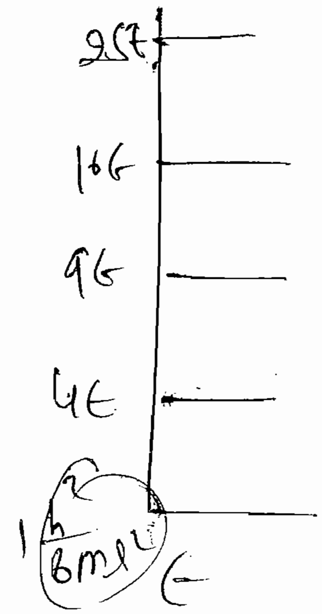
Particle in box: $E = \frac{n^2 h^2}{8ml^2}$

1D

Level for 2D: $E = \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right)\frac{h^2}{8m}$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)$$

One dimensional translational partition function for a molecule having mass m (~~under~~ upto 5 translation level)



$$f = e^{-\beta\epsilon} + e^{-4\beta\epsilon} + e^{-9\beta\epsilon} + e^{-16\beta\epsilon} + e^{-25\beta\epsilon}$$

In above eqn the probability for finding the particle in II excited state

$$Pr \text{ for } (II) = \frac{e^{-9\beta t}}{q_{1D}}$$

at $T \to \infty$

$$Pr(II) = \frac{1}{8}$$

$$T \to 0 \Rightarrow 0$$

2D translation

angle b/w two hydrid orbital:

$$sp^2 \Rightarrow as + bp_x + cp_y$$

$$sp^2 = a's + b'p_x + c'p_y$$

$$\psi_I = b\hat{i} + c\hat{j}$$

$$\psi_{II} = b'\hat{i} + c'\hat{j}$$

s

$$\psi_I \cdot \psi_{II} = |\psi_I||\psi_{II}|\cos\theta$$

$$\psi_I \cdot \psi_{II} = \sqrt{b^2+c^2}\,\sqrt{b'^2+c'^2}\cdot\cos\theta$$

$$bb' + cc' = \sqrt{b^2+c^2}\,\sqrt{b'^2+c'^2}\cdot\cos\theta$$

$$\frac{bb'+cc'}{\sqrt{b^2+c^2} + \sqrt{b'^2+c'^2}} = \cos\theta$$

JIIIS

Hydrogen atom: Rotational system

State-identification :

$$\psi = \left(\frac{Z}{a_0}\right)^{3/2} r\, e^{-\frac{Zr}{2a_0}} \underbrace{\sin\theta \cos\phi}_{x}$$

x अगर यहा ϕ clear नही होता यानी $e^{im\phi}$ के form मे होता तो हम P_x, P_y, P_z के बारे मे नही बता पाते बल्की m की दे देते!

$$\frac{Zr}{na_0} = \frac{Zr}{2a_0}$$

$$n = 2$$

$$\psi = e^{-\frac{3r}{3a_0}}$$

$$\frac{Zr}{na_0} = \frac{r}{3a_0}$$

$$\frac{3r}{na_0} = \frac{r}{3a_0}$$

$$n = 9$$

Value of l :

$$\psi = \left(\frac{Z}{a_0}\right)^{3/2} r^0 (2-r)\, e^{-\frac{Zr}{2a_0}} \quad 2s$$

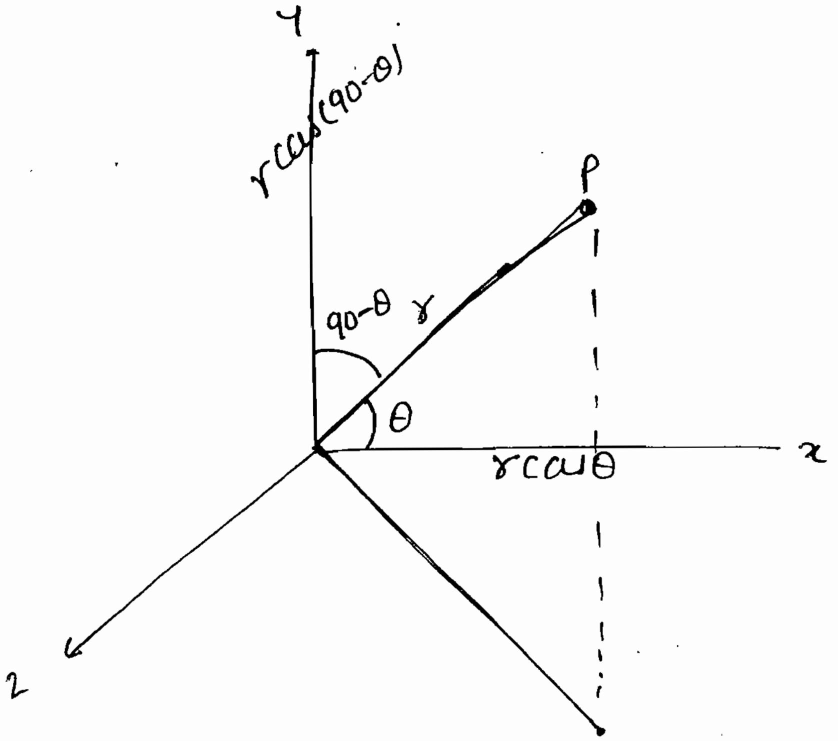
$$\psi = \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \quad 2p \checkmark \quad 2-1-1 = 0 \text{ nodes}$$

$$\psi = \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \underbrace{(2-r)}_{1 \text{ node}} e^{-\frac{Zr}{2a_0}} \quad 2p \times$$

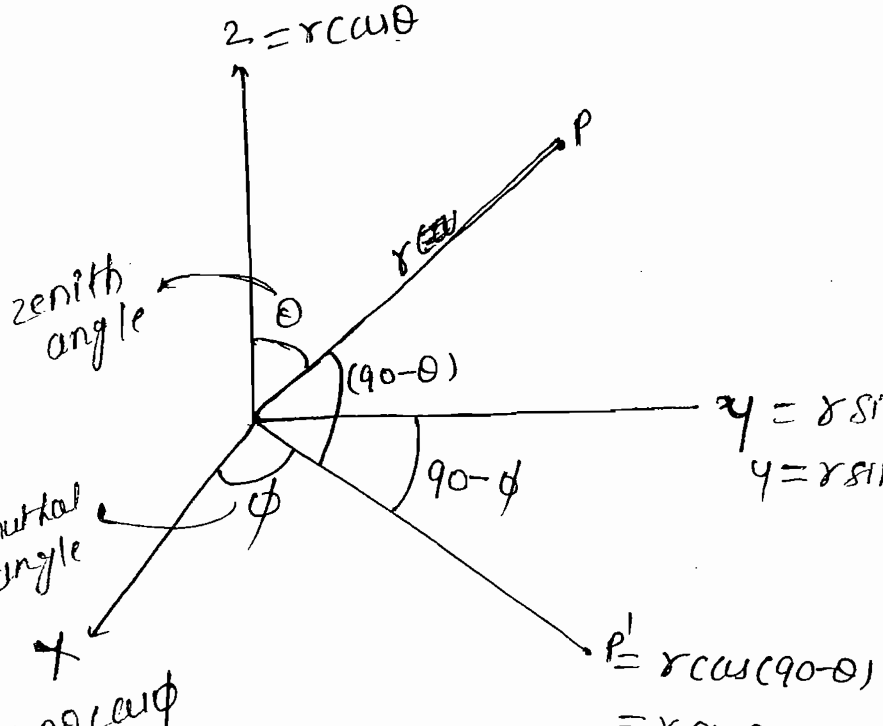
l की value के साथ-साथ node पर ध्यान देना जरूरी है।

Polynomial से बाहर r की power ही l की value होती है।

✱ Component of orbital:



$x = r\cos\theta$



$y = r\sin\theta\cos(90-\phi)$

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

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

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

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

$z = r\cos\theta$

Component of d-orbital:

$$d_{xy} = xy$$
$$= r\sin\theta\cos\phi \cdot r\sin\theta\sin\phi$$
$$= r^2\sin^2\theta\cos\phi\sin\phi$$
$$= r^2\sin^2\theta\,\frac{\sin 2\phi}{2} = \frac{r^2}{2}\underline{\sin^2\theta\sin 2\phi}$$

$$d_{x^2-y^2} = (r\sin\theta\cos\phi)^2 - (r\sin\theta\sin\phi)^2$$
$$= r^2\sin^2\theta(\cos^2\phi - \sin^2\phi)$$
$$= \underline{r^2\sin^2\theta\cos 2\phi}$$

$$d_{xz} = r\sin\theta\cos\phi\, r\cos\theta$$
$$= \underline{r^2\sin\theta\cos\theta\cos\phi}$$

$$d_{yz} = r\sin\theta\sin\phi \cdot r\cos\theta$$
$$= \underline{r^2\sin\theta\cos\theta\sin\phi}$$

$$d_{z^2} = d_{z^2-x^2} + d_{z^2-y^2}$$

$z^2-x^2+z^2-y^2+z^2-z^2$

$3z^2-r^2$

$$3z^2-r^2 = (3r^2\cos^2\theta - r^2)$$
$$= \underline{3r^2(\cos^2\theta - 1)}$$

$\Rightarrow$ Value of m : $= e^{mi\phi}$

It will give value of m

$$\psi_{2p_x} \propto r \, e^{\frac{-2r}{2a_0}} \sin\theta\cos\phi$$

$$\psi_{2p_y} \propto r^1 e^{\frac{-2r}{2a}} \sin\theta \sin\phi$$

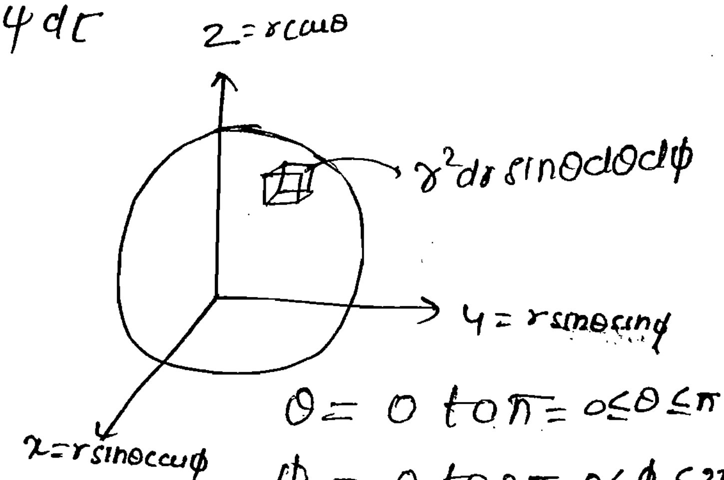
$$\psi_{3p_y} \propto r \left(\cancel{\alpha} - \cancel{\frac{2r}{a}}\right) e^{\frac{-2r}{3a}} \sin\theta \sin\phi$$

Li^{++} $\psi_{3s} \propto (\alpha - r)(\beta - r)\, e^{-\frac{\cancel{3}r}{3a_0}}$

$Z=1$ for H $\psi_{1s} \propto e^{\frac{-r}{a_0}}$

average value of $\langle r \rangle_{1s}$:

$$\langle O \rangle = \frac{\int \psi^* \hat{O} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$ → volume element



$\theta = 0$ to $\pi = 0 \le \theta \le \pi$

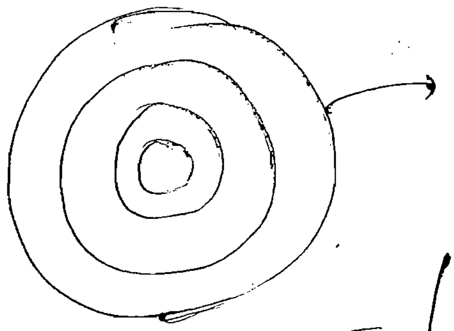
$\phi = 0$ to 2π $0 \le \phi \le 2\pi$

$r = 0$ to ∞

$$= \int_0^r r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= \frac{r^3}{3} \times 2 \times 2\pi = \frac{4}{3}\pi r^3$$

If Hydrogen atom is conciderd as planar –



$d\tau = r\,dr\,d\theta$, $\theta = 0$ to 2π

$$= \int_0^r r\,dr \int_0^{2\pi} d\theta$$

$$= \pi r^2$$

Q If $\bar{e}$ moves on a sphere with fixed radius the it is called spherical harmonic also called Rigid rotor in diatomic molecule

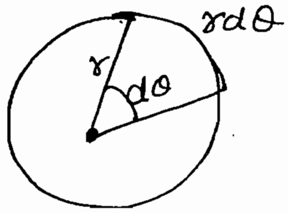
$$d\tau = \sin\theta \, d\theta \, d\phi$$

$d\tau = \cancel{r^2 \sin\theta d\theta}$

Q If Electron moves on a circle of radius r then

Elemental length of ring $d\tau = r d\theta$, angle $= d\theta$

$\underline{0 \text{ to } 2\pi}$



$\langle r \rangle$ $\psi_{1s} \propto e^{-r}$

$$\langle r \rangle = \frac{\int_0^\infty e^{-r} \cdot r\, e^{-r} r^2 dr \cancel{\int_0^\pi \sin\theta d\theta} \cancel{\int_0^{2\pi} d\phi}}{\int_0^\infty e^{-r} \cdot e^{-r} r^2 dr \cancel{\int_0^\pi \sin\theta d\theta} \cancel{\int_0^{2\pi} d\theta}}$$

$$\langle r \rangle = \frac{\int_0^\infty r^3 e^{-2r} dr}{\int_0^\infty r^2 e^{-2r} dr}$$

$$= \frac{\frac{\lfloor 4}{(2)^4}}{\frac{\lfloor 3}{2^3}} = \frac{3}{2}$$

$$\boxed{\langle r \rangle = \frac{a_0}{2Z}\left[3n^2 - l(l+1)\right]}$$

Li, 2p, $n=2$

$l=1$

$Z=3$

$$\langle r \rangle = \frac{a_0}{6}[12-2] = \frac{10a_0}{6} = \frac{5}{3}a_0$$

$$\langle \tfrac{1}{r} \rangle = \frac{\int_0^\infty e^{-r}\left(\frac{1}{\cancel{r}}\right) e^{-r} r^{\cancel{2}} dr}{\int_0^\infty e^{-r} e^{-r} r^2 dr}$$

$$= \frac{\int_0^\infty r e^{-2r}}{\int_0^\infty r^2 e^{2r} dr} = \frac{\frac{\Gamma 2}{(2)^2}}{\frac{\Gamma 3}{2^3}} = \frac{1}{\cancel{4}} \times \frac{\cancel{8}\,4}{\cancel{2}} =$$

$$= \frac{1}{4} \times \frac{8}{2} = a^0 \; 1 \quad \text{or} \left(\frac{1}{a_0}\right)$$

$$\frac{1}{2} \times \frac{8}{2} = 2$$

$$\boxed{\langle \tfrac{1}{r} \rangle = \frac{Z}{n^2 a}}$$

$$r^2 = \frac{\Gamma 5}{\cancel{(2)^5}} \times \frac{\cancel{2^3}}{(2)^2} = \frac{4 \times 3 \times \cancel{2}}{\cancel{2} \times \cancel{2} \times \cancel{2}}$$

3

$$(r_{mpv}) = \frac{n^2 a_0}{Z}$$

for

1s 2d 3p 4f

$$\langle r^2 \rangle = \frac{n^2 a_0^2}{2Z}\left[5n^2 - 3l(l+1) + 1\right]$$

$$\boxed{\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^2 n^3 \left(l + \frac{1}{2}\right)}}$$

For H_{2s} $$\frac{\left\langle \frac{1}{r} \right\rangle}{\frac{1}{\langle r \rangle}}$$

$$\left\langle \frac{1}{r} \right\rangle_{2s} = \frac{1}{4}$$

$$\langle \cancel{r} \rangle_{2s} = \frac{1}{2}\left[12\right] = 6 = \frac{1}{6}$$

$$= \frac{1}{4} \times 6 = 3/2$$

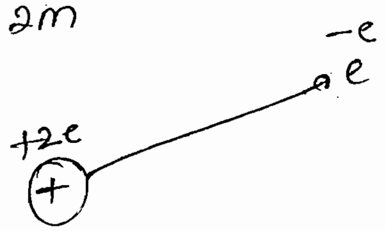
Energy of hydrogen and hydrogen like atom:

$\hat{H} =$ (K.E) operator + (P.E) operator

$=$

$$(K.E) = -\frac{\hbar^2}{2m}\nabla^2$$

(P.E)



$$V = +\frac{1}{4\pi\varepsilon_0}\,\frac{-Ze^2}{r}$$

$$V = \left(-\frac{1}{r}\right)$$

in a.u.

$4\pi\varepsilon_0 = 1$ unit, $m = 1$ unit

$a_0 = 1$ au, $\hbar = 1$ unit

$e = 1$ unit

1 au energy = 1 hartree

$= 27.2$ eV

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\,\frac{Ze^2}{r}$$

$$\hat{H} = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right) \text{------} (1)$$

$$\langle A \rangle = \frac{\int \psi_{nlm}^{*}\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\psi_{nlm}\, r^2 dr \sin\theta d\theta d\phi}{\int \psi_{nlm}^{*}\psi_{nlm}\, r^2 dr \sin\theta d\theta d\phi}$$

or

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

$\langle V \rangle = \langle -\frac{1}{r} \rangle = \left(-\frac{Z}{n^2 a_0}\right)$ $\underline{\text{auit}}$ $\underline{\text{au}}$

$\langle \hat{H} \rangle =$ or SI

$$\left(-\frac{1}{4\pi\varepsilon}\frac{Ze^2}{r}\right) = \frac{-1}{4\pi\varepsilon} Ze^2 \times \frac{Z}{n^2 a_0}$$

or

$$\langle V \rangle = \frac{-Z^2}{n^2} \cdot \text{au}$$

$$\langle V \rangle = -\frac{27.2\, Z^2}{n^2} \text{eV}$$

<u>Virial Theorem</u>:

$$V \propto q^{K} \rightarrow \text{position}$$

$$2\langle T \rangle = K\langle V \rangle$$

$$V \propto r^{-1}$$

$E =$ K.T + P.E

$= \langle T \rangle -$

$$\boxed{2\langle T \rangle = -\langle V \rangle}$$

$$\cancel{2}\langle T \rangle = +\frac{\cancel{27.2}\, Z^2}{n^2} \text{eV}$$

$$\langle T \rangle = \frac{13.6\, Z^2}{n^2}$$

Total energy

$$\langle E\rangle = +13.6\,\frac{Z^2}{n^2}\,eV - 27.2\,\frac{Z^2}{n^2}\,eV$$

$$\boxed{\langle E\rangle = -13.6\,\frac{Z^2}{n^2}\,eV}$$

$$\Rightarrow \quad \langle V\rangle = -27.2\,\frac{Z^2}{n^2}\,eV$$

$$\langle T\rangle = 13.6\,\frac{Z^2}{n^2}\,eV$$

$$\langle E\rangle = -13.6\,\frac{Z^2}{n^2}\,eV$$

$$-\langle V\rangle = 2\langle T\rangle = -2\langle E\rangle$$

Q

$E = ?$ for 2s e^- of carbon

$$C = 1s^2\,2s^2\,2p^2$$

$\downarrow$

$$n = 2,\quad Z = 6$$

$$\langle E\rangle = -13.6 \times \frac{\overset{9}{\cancel{36}}}{\cancel{4}}\,eV$$

$= -122.4\,eV$ ✗

$$C = 1s^2\, 2s^2\, 2p^2 \qquad Z^* = (2-\sigma)$$

Z^* , σ screening const.

$$E = -13.6 \frac{Z^{*2}}{n^2} eV$$

Q 65 $\quad E = \frac{-13.6}{27.6} \frac{Z^2}{n^2} = -0.5 \frac{Z^2}{n^2} = 0.5$ au.

$$= -0.5 \times \frac{1}{1} = -0.5$$

$$Z^* = \xi = 1.32$$

$$E = -0.5 \times \frac{(1.3)^2}{1} = -0.8$$

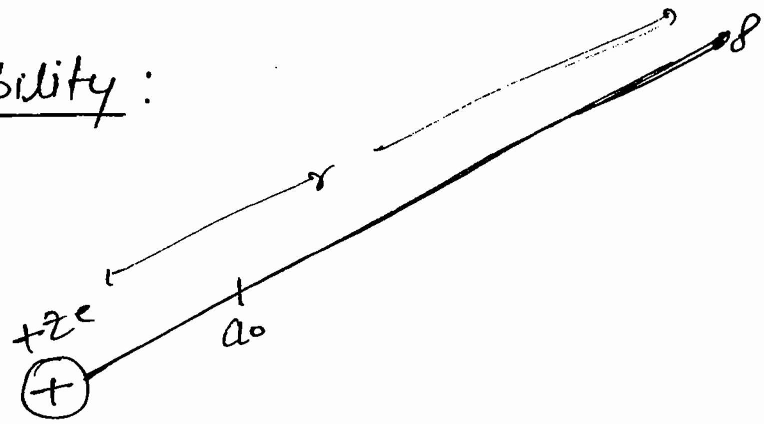
(c) less then 0.5au.

Q gonisation energy of He^+, Li^{++}, Be^{+3} in au

He^+ $\quad E = -\frac{0.5 \times 4}{1} = -13.6 \times 4 = -54.4$ eV

$I.E = E = +13.6 \times 4$ eV

Probability :



ψ_s

Q Find the probability of electron with in a_0 distance from Nucleus in ground state of H atom.

$$\int_0^{a_0} \psi \psi^* d\tau = ? \qquad \psi_{1s} = \left(\frac{Z}{a_0}\right)^{3/2} \cdot \frac{1}{\sqrt{\pi}} e^{-\frac{Zr}{a_0}}$$

$$\int_0^{a_0} e$$

$$\left(\frac{Z}{a_0}\right)^3 \frac{1}{\pi} \int_0^{a_0} e^{-2\frac{Zr}{a_0}} dr = \left(\frac{Z}{a_0}\right) \frac{1}{\pi} \left[e^{\frac{-2Zr}{a_0}} \left(-\frac{2Z}{a_0}\right) \right]_0^{a_0}$$

$$= -\left(\frac{Z}{a_0}\right)^3 \frac{1}{\pi} \cdot \frac{2Z}{a_0} \left[e^{-\frac{2Zr}{a_0}} \right]_0^{a_0}$$

$$= -\left(\frac{Z}{a_0}\right)^3 \frac{1}{\pi} \cdot \frac{2Z}{a_0} \left[e^{-2Z} \right]$$

$$= -\left(\frac{1}{a_0}\right)^3 \frac{1}{\pi} \cdot 2 \cdot (e^{-2})$$

$$= -\frac{2}{\pi a_0^3} e^{-2}$$

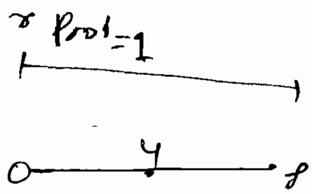
$$\int_0^{a_0} \text{Proba} =$$

$$\underline{\text{Prb}} = \frac{\cancel{e^2} \int_0^{a_0} e^{-\frac{2Zr}{a_0}} r^2 dr \cancel{\int_0^{\pi} \sin\theta d\theta} \cancel{\int_0^{2\pi} d\phi}}{\cancel{e^2} \int_0^{\infty} e^{-\frac{2Zr}{a_0}} r^2 dr \cancel{\int_0^{\pi} \sin\theta d\theta} \cancel{\int_0^{2\pi} d\phi}}$$

$$\underline{\text{Prob}} = \frac{\int_0^{a_0} r^2 e^{-\frac{2Zr}{a_0}} dr}{\int_0^{\infty} r^2 e^{-\frac{2Zr}{a_0}} dr}$$

if distan is y be 0-to y

$$\text{Prob} = \frac{\int_0^{y} r^2 e^{-\frac{2Zr}{a_0}} dr}{\int_0^{\infty} r^2 e^{-\frac{2Zr}{a_0}} dr}$$



or

$$\text{Prob} = 1 - \frac{\cancel{1} - \int_y^{\infty} r^2 e^{-\frac{2Zr}{a_0}}}{\int_0^{\infty} r^2 e^{-\frac{2Zr}{a_0}} dr}$$

$$\underline{Prob} = 1 - \frac{\frac{\cancel{\lceil 2+1}}{(2z)^3} \times e^{-(2zy)} \left(\frac{(2zy)^0}{\lfloor 0} + \frac{(2zy)^1}{\lfloor 1} + \frac{(2zy)}{\lfloor 2} \right.}{\frac{\cancel{\lceil 2+1}}{(2z)^3}}$$

$$\boxed{\int_0^4 Prob = 1 - e^{-(2zy)} \left[1 + (2zy) + 2z^2 y^2 \right]}$$

$\underline{e.g}$ Calculate 0 to a_0 0 to 1

$$Prob = 1 - \left[e^{-2.1.1} (1+2+2) \right]$$

$$= 1 - 5e^{-2}$$

$$= 1 - 5 \times 1.135$$

$$= 1 - 67.0$$

$$= 0.33\% , \underline{33\%}$$

He^{+}

$$= 1 - e^{-4} (1+4+8)$$

$$= \underline{0.77\%}$$

Li^{++}

$$= 1 - e^{-6} (1+6+18)$$

$$= 1 - e^{-6} \times 25$$

$$= \underline{0.93\%} \; \underline{93\%}$$

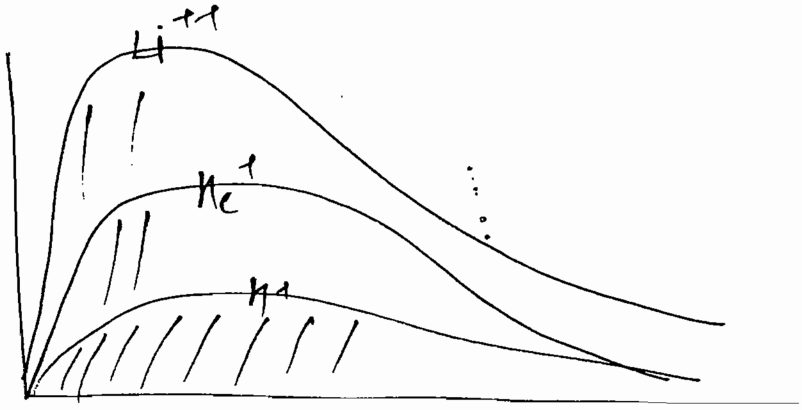
$\underline{Cal.}$ 0 to 2

$$= 1 - e^{-4} (1+4+8)$$

$$= 1 - e^{-4} \times 13$$

$$= 1 - 0.23$$

$$= 0.77\% \; 77\%$$



$$\langle x \rangle = \int \psi_{1s}^{*} \, (x) \, \psi_{1s} \, d\tau$$

$$\langle x \rangle = 0 \ , \ \langle y \rangle = 0 \ , \ \langle z \rangle = 0$$

$$\langle p_x \rangle = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \psi_{1s}^{*} \left(-i\hbar \frac{\partial}{\partial x}\right) \psi_{1s} \, d\tau$$

Rigid Rotator / spherical harmonics :

$\Downarrow$ molecular system $\Downarrow$ Y_J^m

$\Downarrow$ atomic $\Downarrow$ Y_l^m

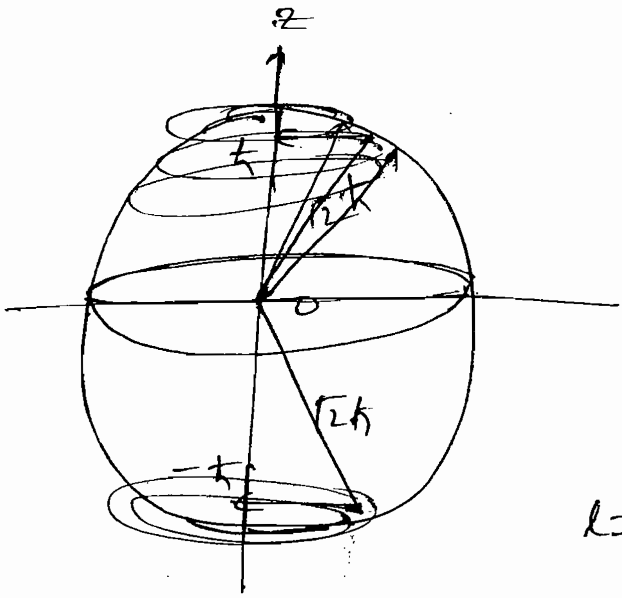
$$Y_l^m = P_l^{|m|}(\cos\theta)\, e^{im\phi}$$

$$\downarrow$$

$$P_l^{|m|} = \underline{C.\sin\theta\cos\theta}$$

ये पूरा $\cos\theta$ का term होना चाहिए

$$Y_J^m = P_J^{|m|}(\cos\theta)\, e^{im\phi}$$



$l = 1$

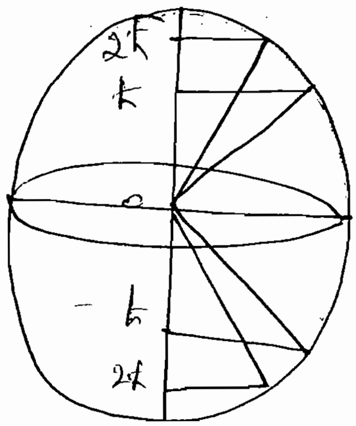
$L^2 = l(l+1)\hbar^2$

$|L| = \sqrt{l(l+1)}\,\hbar$

$l = 1 = |L| = \sqrt{2}\hbar \simeq 1.414\hbar$

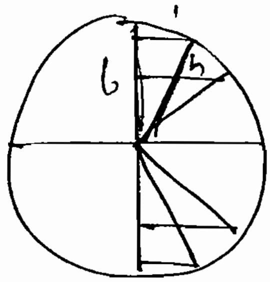
$l = 1,\ m = \underline{\hbar, 0, -\hbar}$

$l = 2,\ |L| = \sqrt{6}\hbar = 2.45\hbar$



Q If $m = 2$ $l = +2$

$\theta =$ with z axis



$$\cos\theta = \frac{b}{h}$$

$$\theta = \cos^{-1}\left(\frac{2\hbar}{\sqrt{6}\hbar}\right)$$

angular rotation for an e^- with z axis

$$\theta = \cos^{-1}\left(\frac{m\hbar}{\sqrt{l(l+1)}\,\hbar}\right)$$

$$\boxed{\theta = \cos^{-1}\left(\frac{m}{\sqrt{l(l+1)}}\right)}$$

<u>Energy</u>:

$$\hat{H} = \frac{L^2}{2I}$$

without Nucleus

$$\hat{H} = \frac{l(l+1)\hbar^2}{2I} = \frac{l(l+1)\hbar^2}{2\mu r^2}$$

atom

$$E = \frac{l(l+1)h^2}{2 \times 4\pi^2 \mu r^2}$$

$$\boxed{E = \frac{l(l+1)\,h^2}{8\pi^2 \mu r^2}}$$ Joule

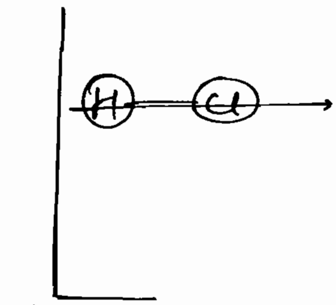
for rigid rotator

$$\boxed{E = \frac{J(J+1)h^2}{8\pi^2 \mu r^2}}$$

$\boxed{E = B\, J(J+1)}$ Joule

$B = \frac{h^2}{8\pi^2 \mu r^2}$ rotational cont

$J = 0, 1, 2, 3, \ldots$



J=0

degeneracy of the level : $(2J+1)$

rotational

Q If Energy of a molecule under rigid rotor consideration is 30 B then deg.

$2J+1 = 11$

$J = -1 \pm \sqrt{\quad}$

$30\cancel{B} = \cancel{B}\, J(J+1)$

$J^2 + J - 30 = 0$

Q $110B \longrightarrow 10 \times 11$, 21

$(2J+1) = 21$

Q $E = 20B$, ~~10×2~~ 4×5 then max value z compon

$J = \cancel{12}$, $4\hbar$

9

Q If Energy of rotational level is 3 times of ground level then ratio of ~~ge~~ degeneracy of level are

$$E = 3 \times 0 = 0 \quad , \quad deg = 1$$

degeneracy = 1

Q If enery of rotational is 30 Joule and its deg. is 5 then B?

$$2J+1 = 5$$

$$J = 2$$

$$E = BJ(J+1)$$

$$30 = B\, 2 \times 3 \qquad B = 5$$

$$B = \frac{30}{12}$$

Q Cal the M.I

$$B = \frac{h^2}{8\pi^2 I}$$

$$I = \frac{h^2}{5 \times 8 \times \pi^2}$$

$$\boxed{I = \frac{h^2}{40\pi^2}} =$$

Q If rotational const of a molecule is 3 unit then mini. energy require to rotate this molecu. und rigid rotor case.

$$B = 3 \quad , \quad B = 3$$

$$E = 3 \qquad = 2B = ,$$

$$E = BJ(J+1)$$

$$E = B \times 1(2) \qquad 3 \times 2 = 6\,u$$

$$= 2B = 3$$

$$B =$$

mini Energy req. to rotate an e- in sphe Lamy radia a.

$E = -\underline{13.6 eV}$