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" The first and most important step towards success is to believe that we can succeed. "

Quantum Chemistry

* Einstein's equation : $E = mc^2$.

Planck's equation : $E = h\nu$

De-broglie equation : $h\nu = mc^2$

$$\Rightarrow \frac{hc}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} \Rightarrow \boxed{\lambda = \frac{h}{p}} \quad \text{—(*)}$$

→ With the help of * de-broglie showed that microscopic particles show wave nature as well as particle nature.

→ When wave nature is shown by a particle, then to describe it, we have a wave equation known as schrödinger wave equation.

→ The solution of this wave equation is also known as wave function denoted by the symbol ψ.

→ For every observable in classical mechanics, there is an operator corresponding to it in quantum mechanics.

* Some operators corresponding to every observable in quantum chemistry.

(i) Observable ⇒ Position	Operator	Function
x, y, z	$\hat{x}\ \hat{y}\ \hat{z}$	Multiply.

Ex:- $\psi = e^x$

$\hat{A}\psi = \hat{x}e^x$

$\boxed{\hat{A}\psi = xe^x}$

→ eigen value.

Remember, operator is meaningless without function. operator always operates from the left side.

* Observable — Operator

Linear Momentum

P_x

P_y

P_z

$$\boxed{\hat{P}_x = -i\hbar \frac{d}{dx} = -i\frac{h}{2\pi}\frac{\partial}{\partial x} = \frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{h}{2\pi i}\frac{\partial}{\partial x}}$$

Similarily,

$$\boxed{\hat{P}_y = -i\hbar \frac{\partial}{\partial y} = -i\frac{h}{2\pi}\frac{\partial}{\partial y} = \frac{\hbar}{i}\frac{\partial}{\partial y} = \frac{h}{2\pi i}\frac{\partial}{\partial y}}$$

<u>Function</u>: Differentiate w.r.t. 'x' or 'y' or 'z' in x, y, z direction respectively and multiply by $-i\hbar$ / $-\frac{ih}{2\pi}$

<u>Ex</u>:- <u>Gate</u>; $\psi = e^{ikx}$ and $P_x = -i\hbar\frac{\partial}{\partial x}$

we know that $\boxed{\hat{A}\psi = a\psi}$

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

$$= -i\hbar\frac{\partial}{\partial x}e^{ikx}$$

$$= -i\hbar . ik\, e^{ikx}$$

$$= -i^2\hbar k e^{ikx}$$

$$= \hbar k e^{ikx}$$

$$\boxed{\hat{P}_x\psi = \hbar k\psi}$$

Hence value of linear momentum for wave function $= \hbar k$

* Observable = Kinetic energy $\{K_x, K_y, K_z\}$

Operator = $\hat{K}_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} = -\left(\frac{h}{2\pi}\right)^2\frac{1}{2m}\frac{d^2}{dx^2} = \frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$

$$\hat{K}_y = \frac{-\hbar^2}{2m}\cdot\frac{d^2}{dy^2} = -\left(\frac{h}{2\pi}\right)^2\cdot\frac{1}{2m}\frac{d^2}{dy^2} = \frac{-h^2}{8\pi^2 m}\cdot\frac{d^2}{dy^2}$$

$$\hat{K}_z = \frac{-\hbar^2}{2m}\frac{d^2}{dz^2} = -\left(\frac{h}{2\pi}\right)^2\frac{1}{2m}\frac{d^2}{dz^2} = \frac{-h^2}{8\pi^2 m}\frac{d}{dz^2}$$

* Relation between Kinetic Energy Operator and Linear Momentum Operator.

We know that;

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

$$\hat{K}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$\because$ $KE = \frac{1}{2}mv^2$

$$KE = \frac{m^2v^2}{2m}$$

$$\boxed{KE = P^2/2m}$$ and $$\boxed{\hat{K}_x = \frac{\hat{P}_x^2}{2m}}$$

Proof:

$$K_x = \frac{\left(-i\hbar\frac{\partial}{\partial x}\right)^2}{2m}$$

$$\hat{K}_x = \frac{i^2\hbar^2\frac{\partial^2}{\partial x^2}}{2m}$$

$$\hat{K}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$= \boxed{\hat{K}_x = \frac{-\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}}$$

* Observable :- Potential $\{V_x, V_y, V_z\}$

Operator :- $\hat{V}_x$, $\hat{V}_y$, $\hat{V}_z$

Function :- Multiply.

* Total Energy Operator. Total energy operator is also known as Hamiltonian operator. It is represented by $\hat{H}$.

We know that,

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

$$\hat{H}_x = \hat{K}_x + \hat{V}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}_x$$

$$\hat{H}_y = \hat{K}_y + \hat{V}_y = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial^2 y} + \hat{V}_y$$

$$\hat{H}_z = \hat{K}_z + \hat{V}_z = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial^2 z} + \hat{V}_z$$

and we know that;

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}_x + \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial^2 y} + \hat{V}_y - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 z} + \hat{V}_z$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} + (\hat{V}_x + \hat{V}_y + \hat{V}_z)$$

and we know that

Laplacian operator $(\nabla^2) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V}$$

* Angular Momentum Operator :-

$$\boxed{\vec{L} = \vec{r} \times \vec{P}}$$

$\vec{L}$ = Angular Momentum

$\vec{r}$ = Position

$\vec{P}$ = Linear Momentum.

and we know that ;

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$\vec{P} = P_x\hat{i} + P_y\hat{j} + P_z\hat{k}$$

Now;

$$\vec{L} = \vec{r} \times \vec{P} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

$$= \hat{i}\{yP_z - zP_y\} - \hat{j}\{xP_z - zP_x\} + \hat{k}\{xP_y - yP_x\}$$

$$= \hat{i}\{yP_z - zP_y\} + \hat{j}\{zP_x - xP_z\} + \hat{k}\{xP_y - yP_x\}$$

$$= L_x\hat{i} + L_y\hat{j} + L_z\hat{k}$$

$$\boxed{\vec{L} = L_x\hat{i} + L_y\hat{i} + L_z\hat{k}}$$

where,

$$\boxed{\begin{aligned} \hat{L}_x &= yP_z - zP_y \\ \hat{L}_y &= zP_x - xP_z \\ \hat{L}_z &= xP_y - yP_x \end{aligned}}$$

$$L_x = yP_z - zP_y$$

$$= y\left\{-i\hbar\frac{\partial}{\partial z}\right\} - z\left\{-i\hbar\frac{\partial}{\partial y}\right\}$$

$$\boxed{L_x = -i\hbar\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}}$$

or

$$\boxed{L_x = \frac{\hbar}{i}\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}}$$

$$\boxed{L_x = \frac{h}{2\pi i}\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}}$$

* Let suppose we have,

operator = A^2
Function = ψ $\Rightarrow$ $\boxed{\hat{A}^2\psi = \hat{A}\hat{A}\psi}$

GATE:- $\hat{A} = \left[x + \frac{d}{dx}\right]$ find $\hat{A}^2$.

∵ We know that an operator is meaningless without a function. Hence let us consider a function, $\psi(x)$.

$$\boxed{\hat{A}^2\psi(x) = \left(x + \frac{d}{dx}\right)^2 = x^2 + \frac{d^2}{dx^2} + 2x\frac{d}{dx}}$$ —XX ये काम गलती से भी न करना.

Now,

$$\hat{A}^2 f(x) = \hat{A}\hat{A}f(x) = \hat{A}\left\{x + \frac{d}{dx}\right\}\psi(x)$$

$$= \hat{A}\left\{x\psi(x) + \frac{d}{dx}\psi(x)\right\}$$

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

$$\hat{A}^2\psi(x) = x^2\psi(x) + x\frac{d}{dx}\psi(x) + \frac{d}{dx}\overset{\mathrm{I}}{\psi(x)}\cdot\overset{\mathrm{II}}{x} + \frac{d^2}{dx^2}\psi(x).$$

$$= x^2\psi(x) + x\frac{d}{dx}\psi(x) + \psi(x) + x\frac{d}{dx}\psi(x) + \frac{d^2}{dx^2}\psi(x)$$

$$= x^2\psi(x) + 2x\frac{d}{dx}\psi(x) + \psi(x) + \frac{d^2}{dx^2}\psi(x)$$

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

Compairing with

$$\hat{A}^2\psi(x) = A^2\psi$$

$$\Rightarrow \boxed{A^2 = \left\{x^2 + 2x\frac{d}{dx} + \frac{d^2}{dx^2} + 1\right\}}$$

* Properties of Operators.

(i) Linearity :- Operators used in quantum chemistry are generally linear. i.e. they can be applied to a complete func as well as if a function is divided into two or more parts. If the result given by the operator in both the cases is same then the operator is said to be linear.

Ex :- Differentiation operator, Integration operator.

→ Differentiation operator.

Let $\psi = 5x^2$

and $\hat{A} = \frac{d}{dx}$

$\Rightarrow \hat{A}\psi = \frac{d}{dx} 5x^2 = 10x. \Rightarrow \boxed{\hat{A}\psi = 10x}$

Let $\psi = 3x^2 + 2x^2$

$\hat{A}\psi = \frac{d}{dx} 3x^2 + \frac{d}{dx} 2x^2 \Rightarrow 6x + 4x = 10x$ $\boxed{\hat{A}\psi = 10x}$

Hence diff. operator shows linear property.

⊛ COMMUTATOR :

Commutator is a mathematical operation b/w two operators.

Representation = $[\hat{A}, \hat{B}]$

Operation = $[AB - BA]$

If $AB - BA = 0 \Rightarrow$ Given two operation commutes with each other.

$AB - BA \neq 0 \Rightarrow$ Given two operators do not commute with each other.

→ Properties of Commutator :-

(i) Additional

(i) Antisymmetric :

$\psi(x) = x^2$

$\psi(-x) = x^2 \Rightarrow \boxed{\psi(x) = \psi(-x)}$

Given func^n is symmetric.

and if ;

$\psi(x) = x$

$\psi(-x) = -x$

$\Rightarrow \boxed{\psi(x) = -\psi(-x)}$

Given func^n is antisymmetric

Hence, $\boxed{[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]}$ If position of operators inside the commutator brackets are changed, then the commutator shows antisymmetric property.

iii) Linearity :- $[\hat{A}, \hat{B}+\hat{C}] = [\hat{A},\hat{B}] + [\hat{A},\hat{C}]$

$$[\hat{A}+\hat{B}, \hat{C}+\hat{D}] = [\hat{A},\hat{C}] + [\hat{A},\hat{D}] + [\hat{B},\hat{C}] + [\hat{C},\hat{D}]$$

Example:-

$$[x+P_x, P_x] = [\hat{x},\hat{P}_x] + [\hat{P}_x,\hat{P}_x]$$

iiii) Distributivity :-

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A},\hat{B}]\hat{C} + \hat{B}[\hat{A},\hat{C}]$$

Example,

$$[x\hat{P}_x, \hat{x}] = [\hat{x},\hat{x}]P_x + x[\hat{P}_x,\hat{x}]$$

(iv) Constant Quantity comes out of commutator bracket.

$$[a\hat{A},\hat{B}] = a[\hat{A},\hat{B}]$$

$$[a\hat{A}, b\hat{B}] = ab[\hat{A},\hat{B}]$$

Example:- $[P_x, x] = \left[-i\hbar\frac{\partial}{\partial x}, x\right] = -i\hbar\left[\frac{\partial}{\partial x}, x\right]$

(v) Self Commutation is zero.

$$[\hat{A},\hat{A}] = 0 \quad \text{and} \quad [\hat{A}\,\hat{A}^n] = 0$$

i.e. any operator always commutes with itself.

Ex:- GATE : Find Value of $\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right]$

we know that,

$$A = \frac{d}{dx} \quad \text{and} \quad [\hat{A},\hat{A}^2] = 0$$

$$A^2 = \frac{d^2}{dx^2}$$

$$\Rightarrow \left[\frac{d}{dx}, \frac{d^2}{dx^2}\right] = 0$$

Ex:- $[K_x, P_x]$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, -i\hbar\frac{d}{dx}\right] \Rightarrow \frac{-i\hbar^3}{2m}\left[\frac{d^2}{dx^2}, \frac{d}{dx}\right] \quad \text{and} \quad \left[\frac{d^2}{dx^2}, \frac{d}{dx}\right] = 0$$

$$\Rightarrow [K_x, P_x] = 0$$

VI :- Two operators with multiplication operation commutes with each-other.

Eg. Position → Multiplication
P.E. → Multiplication.

$\Rightarrow$ ~~for~~ $[x, V_x] = 0$

x → Position, V_x → Multiplication.

Ex:- Whether $\hat{A}, \hat{B}$ commutes or not when, $A = \frac{d}{dx}$ $B = x$.

First, Let us consider a func^n $\psi(x)$.

$$\left[\frac{d}{dx}, x\right]\psi \Rightarrow \left\{\frac{d}{dx}x - x\frac{d}{dx}\right\}\psi$$

$\because$ $[\hat{A}, \hat{B}]$ $\Downarrow$ $[AB - BA]$

$$= \left\{\frac{d}{dx}\underset{\text{I}}{x}\underset{\text{II}}{\psi} - x\frac{d}{dx}\psi\right\}$$

$$= x\frac{d}{dx}\psi + \psi\frac{d}{dx}x - x\frac{d}{dx}\psi$$

$$= 1.\psi$$

$$\left[\frac{d}{dx}, x\right]\psi = 1\cdot\psi.$$

$\Rightarrow \left[\frac{d}{dx}, x\right] = 1$ Hence $\left[\frac{d}{dx}, x\right]$ do not commute with each other.

Similarily, $\boxed{\left[\frac{d}{dx}, x^n\right] = nx^{n-1}}$ Results are similar to that of diff^n but this is not the diff^n. This is commutative operation.

$\Rightarrow$ First derivative operator commutes with position operator shows similar results to differentiation.

$\because$ Commutator shows antisymmetric property,

$$\Rightarrow \left[x, \frac{d}{dx}\right] = -1.$$

Similarily, $\left[x^n, \frac{d}{dx}\right] = -nx^{n-1}$.

Example:- $[P_x, x^n] = \left[-i\hbar\frac{d}{dx}, x^n\right]$

$$= -i\hbar\left[\frac{d}{dx}, x^n\right]$$

$$= -i\hbar nx^{n-1}$$

$[\hat{A}, a] = 0$ i.e. any operator commutates with constant quantity.

i.e.

$[\hat{A}, i\hbar] = 0.$

<u>Example</u>: Solve $[x, P_x^2]$

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

$$= i\hbar P_x + i\hbar P_x$$

$$= 2i\hbar P_x$$

$$\boxed{[x, P_x^n] = i\hbar n P_x^{n-1}}$$

$\Rightarrow$ $[x, P_x^2] = 2i\hbar P_x$ $\qquad$ $[P_x^2, x] = -2i\hbar P_x$

$[x, P_x^3] = 3i\hbar P_x^2$ $\qquad$ $[P_x^3, x] = -3i\hbar P_x^2$

$[x, P_x^4] = 4i\hbar P_x^3$ $\qquad$ $[P_x^4, x] = -4i\hbar P_x^3$

* Revision of Some Formulaes:

i. $\left[\frac{d}{dx}, x^n\right] = nx^{n-1}$ $\qquad$ ii. $\left[x^n, \frac{d}{dx}\right] = -nx^{n-1}$

iii. $[P_x, x^n] = -i\hbar n x^{n-1}$ $\qquad$ iv. $[x^n, P_x] = i\hbar(nx^{n-1})$

v. $[x, P_x^n] = ni\hbar P_x^{n-1}$ $\qquad$ vi. $[P_x^n, x] = -ni\hbar P_x^{n-1}$

* Commutator of Linear Momentum:-

$$\left.\begin{array}{ll} [P_x, P_x] = 0 & [P_x, P_y] = 0 \\ [P_y, P_y] = 0 & [P_y, P_z] = 0 \\ [P_z, P_z] = 0 & [P_z, P_x] = 0 \end{array}\right\} [\hat{P}, \hat{P}] = 0$$

* Linear Momentum and Position Operator.

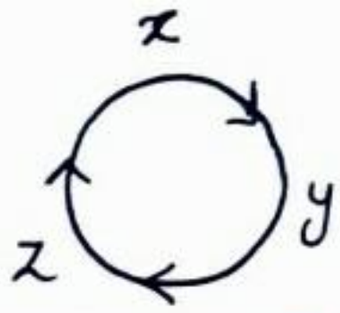
$[\hat{P}, \text{Position}] \Rightarrow$ value {some value will definitely come}

same direction

<u>Ex</u>: $[P_x, x] = -i\hbar.$

But $[P_x, y] = 0$, $[P_y, z] = 0$ } Different direction will give 0.

⊛ Commutator of Angular Momentum :-



$x \to y \to z$ {clockwise} (positive value)

$z \to y \to x$ {Anticlockwise} (negative value)

① [Angular Momentum, Position]

same direction → Always Commute.
Value = 0.

$[L_x, x] = 0$
$[L_y, y] = 0$
$[L_z, z] = 0$

Proof:- $[L_x, x] = [yP_z - zP_y, x]$

$= [yP_z, x] + [zP_y, x]$

$= y[P_z, x] - z[P_y, x]$ → Last page.

$= y(0) - z(0)$

$= 0.$

② [Angular Momentum, Position]

Different direction, never commutes, always give some value.

Ex:- $[L_x, y] = + i\hbar z$ $(x \to y \to z)$ $\quad [L_y, z] = i\hbar x$ $(y \to z \to x)$ $\quad [L_z, x] = i\hbar y$ $(z \to x \to y)$

③ [Angular Momentum, Linear Momentum]

$[L_x, P_x] = 0$
$[L_y, P_y] = 0$
$[L_z, P_z] = 0$

$[L_x, P_y] = i\hbar P_z$
$[L_y, P_z] = i\hbar P_x$
$[L_z, P_x] = i\hbar P_y.$
$[P_z, L_y] = -i\hbar P_x$

④ [Angular Momentum, Angular Momentum]

$[L_x, L_x] = 0$
$[L_y, L_y] = 0$
$[L_z, L_z] = 0$

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

* If two operator commutes i.e. $[\hat{A}, \hat{B}] = 0$ then observable corresponding to these operator can be measured simultaneously and they will violate Heisenberg's Uncertainity Rule.

Ex:- $[K.E, P.E] = 0$

Hence K.E. and P.E. can be calculated simultaneously.

* Ladder Operator :-

$$L_+ = L_x + iL_y$$

$$L_- = L_x - iL_y$$

Similarily;

Spin raising $S_+ = S_x + iS_y$

Spin lowering $S_- = S_x - iS_y$.

Example :- $[L_+, L_z] = [L_x + iL_y, L_z]$

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

$$= -i\hbar L_y + i^2\hbar L_x$$

$$[L_+, L_z] = -\hbar[iL_y + L_x]$$

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

* Note :-

$[A, B] = 0$ i.e. $AB - BA = 0 \Rightarrow \boxed{AB = BA}$

$[A, B] \neq 0$ Non-commutator.

and if $AB + BA = 0$ Anticommutator.

* Hermitian Operator :-

* Condition of Hermitian -

$\hat{A}$ = operator

ψ = wave func^n

ψ^* = complex Conjugate

$$\boxed{\int \psi^* \hat{A} \psi \, d\tau = \int \hat{\psi} \hat{A}^* \psi^* d\tau}$$

∵ Its very complex to evaluate above integral hence we use other conditions to check whether an operator is hermitian or not.

i.e. If,

Hermitian adjoint of operator A = Operator A

$$\boxed{(\hat{A})^\dagger = \hat{A}}$$

where,

$(\hat{A})^\dagger$ = Hermitian adjoint.

$\dagger$ (dragger) = transpose + complex conjugate = Hermitian adjoint.

* Properties of Hermitian Adjoint :-

(i) $(AB)^\dagger = B^\dagger A^\dagger$

(ii) $(A+B)^\dagger = A^\dagger + B^\dagger$

(iii) $(A-B)^\dagger = A^\dagger - B^\dagger$

(iv) $(A^n)^\dagger = (A^\dagger)^n$

(v) $(aA)^\dagger = a^*(A)^\dagger$

↳ complex conjugate of constant.

(vi) $(A^\dagger)^\dagger = A$

(vii) $\left(\frac{d}{dx}\right)^\dagger = -\frac{d}{dx}$

(viii) $(\text{Position})^\dagger = \text{Position}$

$(\hat{x})^\dagger = x$

$(\hat{y})^\dagger = y$

$(\hat{z})^\dagger = z$

*Note :- If $(A)^\dagger = A$ Hermitian

$(A)^\dagger = -A$ Non-Hermitian

$(A)^\dagger = B$ Anti Hermitian

* The sum of two Hermitian operator and difference of two Hermitian operator is also Hermitian.

Proof:- Let A and B be two hermitian operator such that;

$$(\hat{A})^\dagger = \hat{A} \quad \text{and} \quad (\hat{B})^\dagger = \hat{B}$$

$$(A \pm B)^\dagger = A^\dagger \pm B^\dagger$$
$$= A \pm B \Rightarrow (A \pm B)$$

$$\Rightarrow \boxed{(A \pm B)^\dagger = (A \pm B)}$$

* The product of two hermitian operator is not hermitian. It will be hermitian only when both the operator commute.

Let, A and B be two Hermitian operator,

$$(A^\dagger) = A \quad \text{and} \quad (B^\dagger) = B$$

Now;
$$(AB)^\dagger = B^\dagger A^\dagger$$
$$= BA$$ {hence product of two hermitian operator is not hermitian}

It will be hermitian

if, $AB = BA \Rightarrow AB - BA = 0$

$$[\hat{A}, \hat{B}] = 0$$

Hence if two hermitian operators commute with each other then their product is also hermitian otherwise it won't be hermitian.

(i) Prove that P_x is a Hermitian operator.

$$(P_x)^\dagger = \left(-i\hbar \frac{d}{dx}\right)^\dagger = (-i\hbar)^* \left(\frac{d}{dx}\right)^\dagger$$

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

$$= -i\hbar \frac{d}{dx} = P_x$$

$\because (P_x)^\dagger = P_x$

Hence P_x is a hermitian operator.

(ii) Prove that K_x is a Hermitian operator:

$$(K_x)^\dagger = \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right) = \left(\frac{-\hbar^2}{2m}\right)^* \left(\frac{d^2}{dx^2}\right)^\dagger$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left(\left[\frac{d}{dx}\right]^\dagger\right)^2$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left(\frac{-d}{dx}\right)^2$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$= K_x.$$

$\because (K_x)^\dagger = K_x$

$\Rightarrow K_x$ is a hermitian operator

(iii) The commutator of two hermitian operator is anti-hermitian :-

Given, $(A)^\dagger = A$ and $(B)^\dagger = B$

$[\hat{A},\hat{B}] = ??$

But,

$$[\hat{A},\hat{B}]^\dagger = [AB - BA]^\dagger$$

$$= (AB)^\dagger - (BA)^\dagger$$

$$= B^\dagger A^\dagger - A^\dagger B^\dagger$$

$$= -\{A^\dagger B^\dagger - B^\dagger A^\dagger\}.$$

$$= -\{AB - BA\}$$

$$= -[\hat{A},\hat{B}]$$

$\because [\hat{A},\hat{B}] = -[\hat{A},\hat{B}]$

Hence commutator of two Hermitian operator is antihermitian.

* If 'i' is attached to a Hermitian operator, then it becomes antihermitian.

* If 'i' is attached to a antihermitian operator, then it becomes hermitian.

* The product of operator $\hat{A}$ and it's Hermitian adjoint is always Hermitian.

i.e. $[AA^\dagger]^\dagger = (A^\dagger)^\dagger (A)^\dagger$

$= AA^\dagger$

* We know that, If $(A)^\dagger = A$ and $(B)^\dagger = B$

$[A,B]^\dagger =$ AntiHermitian

$i[A,B]^\dagger =$ Hermitian.

* Given operators $\hat{A}$ and $\hat{A}^\dagger$

find $(AA^\dagger)^\dagger$

$(AA^\dagger)^\dagger = (A^\dagger)^\dagger A^\dagger$

$= AA^\dagger$

find $[AA^\dagger + A^\dagger A]^\dagger$

$[AA^\dagger + A^\dagger A] = (AA^\dagger)^\dagger + (A^\dagger A)^\dagger$

$= (A^\dagger)^\dagger A^\dagger + (A^\dagger)(A^\dagger)^\dagger$

$= AA^\dagger + A^\dagger A$

} Both are Hermitian.

* Eigen Value Equation :-

$$\boxed{\hat{A}\,\psi = a\,\psi}$$

ψ → Eigen Function

$\hat{A}$ → Eigen Operator

a → Eigen Value = Value of observable.

Ex:- $\hat{A} = \frac{d}{dx}$ and $\psi = e^{ax}$

$$\hat{A}\psi = \frac{d}{dx} e^{ax}$$

$$\hat{A}\psi = a e^{ax}$$

$$\boxed{\hat{A}\psi = a\psi}$$

a → eigen value.

Gate $\psi = e^{ikx}$ $P_x = ?$

$$P_x\psi = -\frac{i\hbar\, d}{dx} e^{ikx}$$

$$= (-i\hbar)(ik)e^{ikx}$$

$$= \hbar e^{ikx}.k$$

$$P_x\psi = \hbar k.e^{ikx}$$

$\boxed{P_x\psi = \hbar k\psi}$ hence $\boxed{P_x = \hbar k}$ for $\psi = e^{ikx}$.

Note:- If we attach a constant with any function then the eigen value ~~changes~~, do not changes.

But if we attach constant with the operator then eigen value do ~~not~~ changes

Ex:- $\psi = e^{ax}$ $\hat{A} = \frac{d}{dx}$

$$\frac{d}{dx}\psi = a e^{ax}$$

$\boxed{\text{eigen value} = a}$

$\psi = e^{ax}$ $\hat{n} = 100\frac{d}{dx}$

$$100\frac{d}{dx}\psi = 100\frac{d}{dx}e^{ax}$$

$$= 100 a e^{ax}$$

$\boxed{\text{Eigen Value} = 100a}$

$\psi = 100\, e^{ax}$ $\hat{A} = \frac{d}{dx}$

$$\frac{d}{dx}\psi = 100 a e^{ax}$$

$$= a.100 e^{ax}$$

$\boxed{\text{Eigen value} = a}$

* Eigen value corresponding to Hermitian operator is always real.
* The sum of any two degenerate eigen function is also a eigen function.

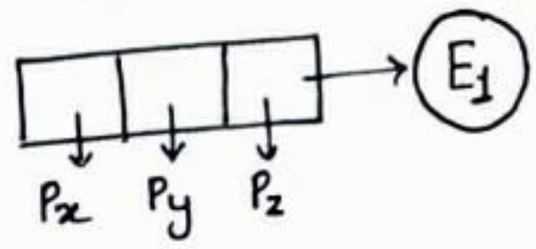
Let ψ_m and ψ_n be two eigen functions such that,

$$\boxed{\begin{aligned}\hat{A}\psi_m &= a\psi_m \\ \hat{A}\psi_n &= a\psi_n\end{aligned}}$$

Hence ψ_m and ψ_n are degenerate Eigen function.

if we operate the same operator over two different functions and they give the same eigen value then the functions are known as degenerate eigen functions.

Example :-



On Applying Hamiltonian operator.

$$\boxed{\hat{H}P_x = E_1 P_x} \quad \boxed{\hat{H}P_y = E_1 P_y} \quad \text{and} \quad \boxed{\hat{H}P_z = E_1 P_z}$$

Now,

$$\begin{aligned}\hat{A}(\psi_m + \psi_n) &= \hat{A}\psi_m + \hat{A}\psi_n \\ &= a\psi_m + a\psi_n \\ &= a(\psi_m + \psi_n)\end{aligned}$$

$$\Rightarrow \boxed{\hat{A}(\psi_m + \psi_n) = a(\psi_m + \psi_n)}$$

⇒ The sum and difference of any two degenerate eigen function is also a eigen function corresponding to the same operator.

⇒ The sum and difference of any two ~~degene~~ non-degenerate eigen function is not a eigen function corresponding to the same operator.

* Non-degenerate eigen function corresponding to Hermitian operator are orthogonal.

$$\hat{A}\psi_m = a\psi_m$$
$$\hat{A}\psi_n = b\psi_n$$

then $\boxed{\int \psi_m \cdot \psi_n \, d\tau = 0}$

∵ ∠ b/w ψ_m and $\psi_n = 90°$

and wave funcn (ψ) behaves as vector.

$$\Rightarrow \vec{\psi_m} \cdot \vec{\psi_n} = |\vec{\psi_m}||\vec{\psi_n}| \cos\theta.$$

$$\boxed{\vec{\psi_m} \cdot \vec{\psi_n} = 0}$$

* Angle b/w two wavefunctions is given by.

$$\cos\theta = \frac{\vec{\psi_m}\cdot\vec{\psi_n}}{|\psi_m||\psi_n|}$$

and

$$\boxed{\int \psi_m \cdot \psi_n \, d\tau = 0} \rightarrow \text{Condition of orthogonality.}$$

Example :- Calculate Kinetic Energy for particle in 1-D Box $[0-l]$ and $\psi_x = \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l}$

∵ We know that,

$$K_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$K_x \psi_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(\sqrt{\frac{2}{L}}\right)\sin\frac{n\pi x}{l}.$$

$$= \frac{-\hbar^2}{2m}\frac{d}{dx}\left\{\frac{d}{dx}\left(\sqrt{\frac{2}{L}}\right)\sin\frac{n\pi x}{l}\right\}$$

$$= \frac{-\hbar^2}{2m}\sqrt{\frac{2}{L}}\left(\frac{n\pi}{l}\right)\frac{d}{dx}\cos\frac{n\pi x}{l}$$

$$= \frac{-\hbar^2}{2m}\sqrt{\frac{2}{L}}\left(\frac{n\pi}{l}\right)^2\left(-\sin\frac{n\pi x}{l}\right)$$

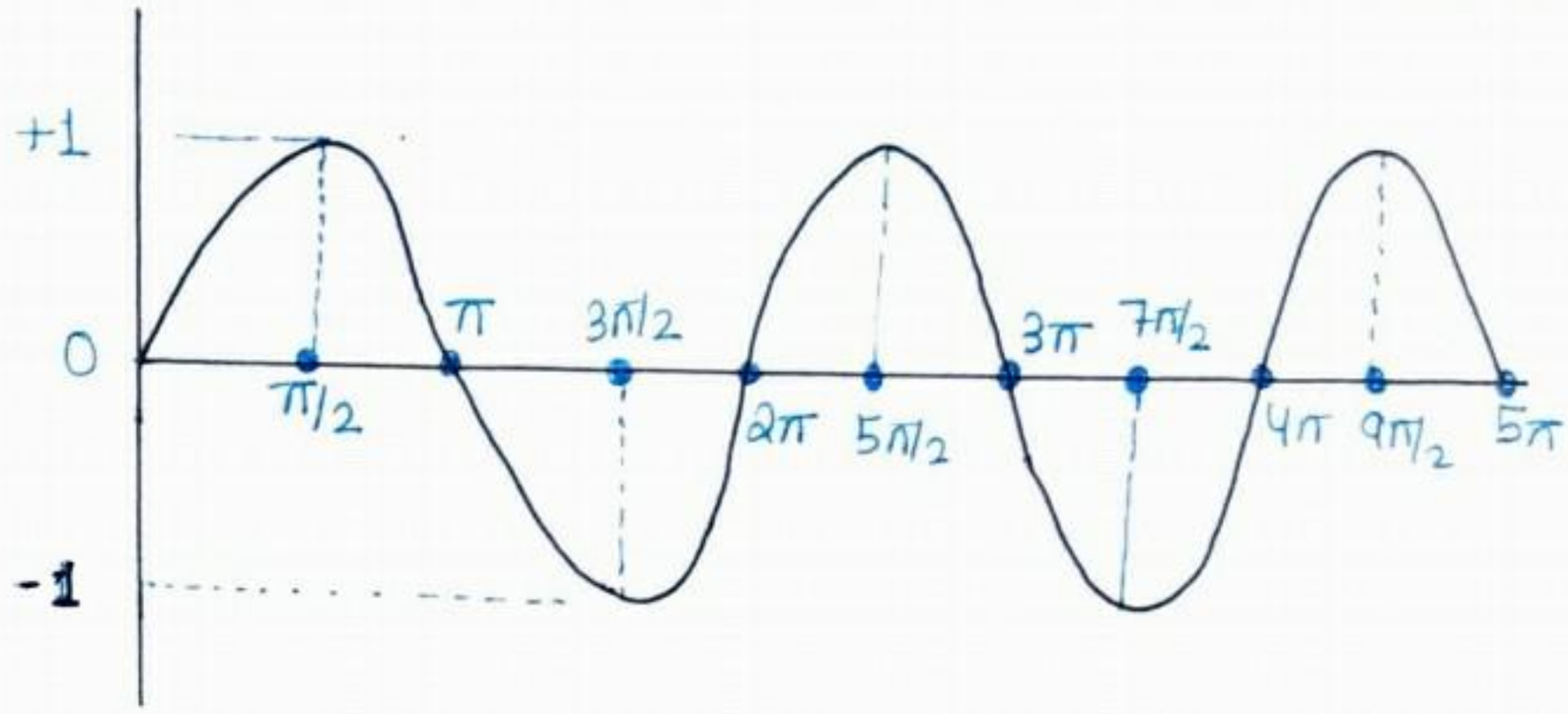
$$= \frac{\hbar^2}{2m}\sqrt{\frac{2}{L}}\left(\frac{n^2\pi^2}{l^2}\right)\sin\frac{n\pi x}{l}$$

$$= \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{l^2}\right)\psi$$

$$\boxed{K_x \psi = a\psi}$$

Hence, $K_x = \frac{\hbar^2}{2m}\cdot\frac{n^2\pi^2}{l^2}$

⊛ Sine Wave :-



$\sin n\pi = 0 \quad [n = 0, 1, 2, 3, 4, \ldots]$

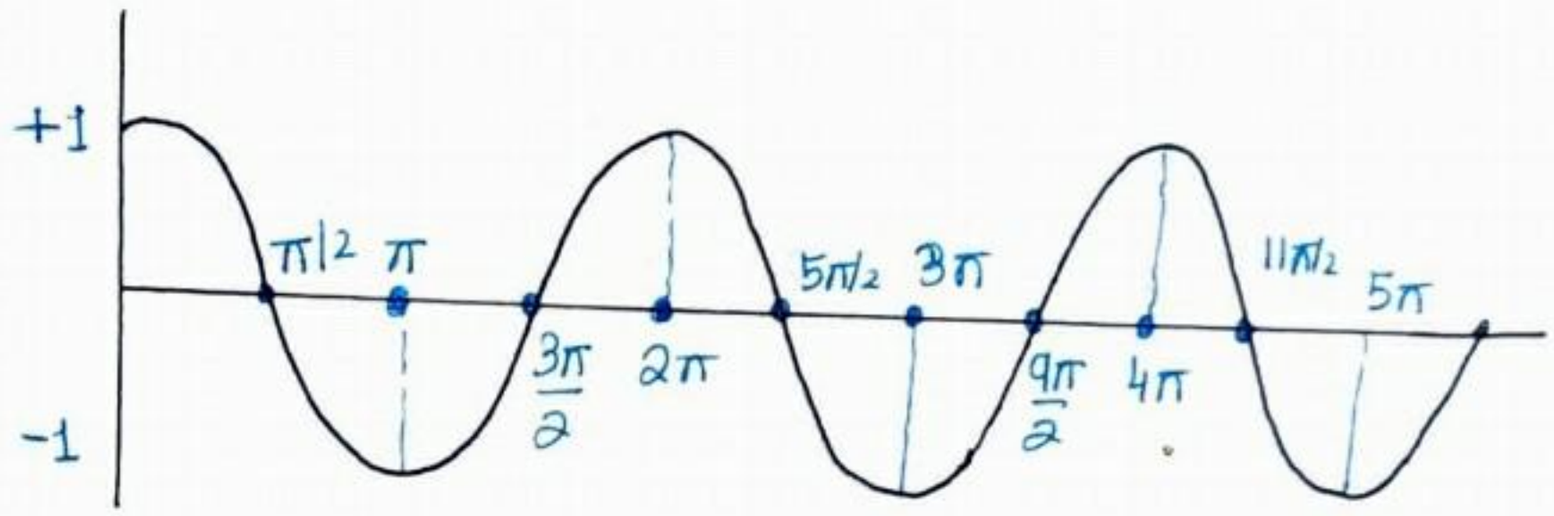
$\sin \frac{(2n+1)}{2}\pi = \pm 1$

+1 when n = even $[0, 2, 4, 6 \ldots]$

Ex:- $\sin \frac{\pi}{2}$, $\sin \frac{5\pi}{2}$, $\sin \frac{9\pi}{2}$.

-1 when n = odd $[1, 2, 3, 5, \ldots]$ Ex:- $\sin \frac{3\pi}{2}$, $\sin \frac{7\pi}{2}$, $\sin \frac{11\pi}{2}$

⊛ Cosine Wave :-



$\cos\left(\frac{2n+1}{2}\right)\pi = 0 \quad \{n = 0, 1, 2, 3 \ldots\}$

$\cos n\pi = \pm 1 \quad \{n = 0, 1, 2, 3, \ldots\}$

+1 when n = even

-1 when n = odd.

⊛ Some Important Integrations :-

① $\int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin 2dx.$

② $\int \cos^2 bx \, dx =$

⊛ Probability And Normalisation :-

According to Einstein, Intensity is directly proportional to square of amplitude. i.e,

$$I \propto (A)^2$$

Similarily, Probable density $\propto |\psi|^2$; ψ = wave func^n.

$$P.D. = \frac{P}{\text{Volume Element}}.$$

$$\boxed{\text{Probability} = \text{Probable density} \times \text{Volume Element.}}$$

$$\boxed{P = \psi^2 \, d\tau}$$

$$\boxed{P = \int_a^b \psi^* \psi \, d\tau}$$

If $\psi = A + iB$

$\psi^* = A - iB$

For 1-D Box :- $d\tau = dx$

For 2-D Box :- $d\tau = dx\,dy$

For 3-D Box :- $d\tau = dx\,dy\,dz$

For H-atom :- $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$. = TIFR

For 1-D Box with limit $[0-l]$, wave function is given by,

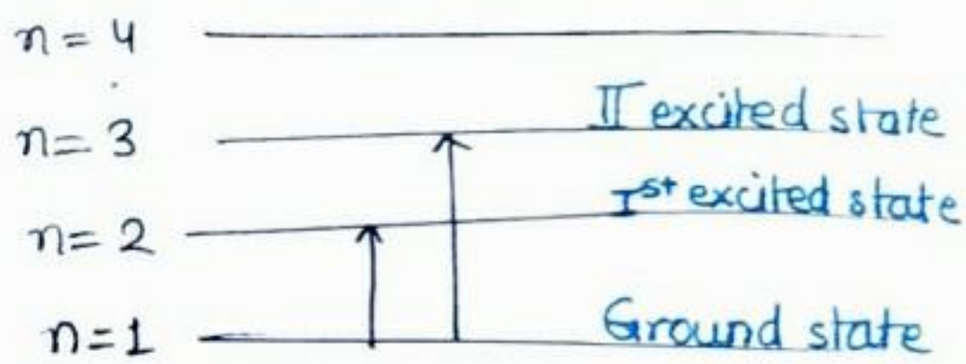
$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

n = Translational Quantum Number.

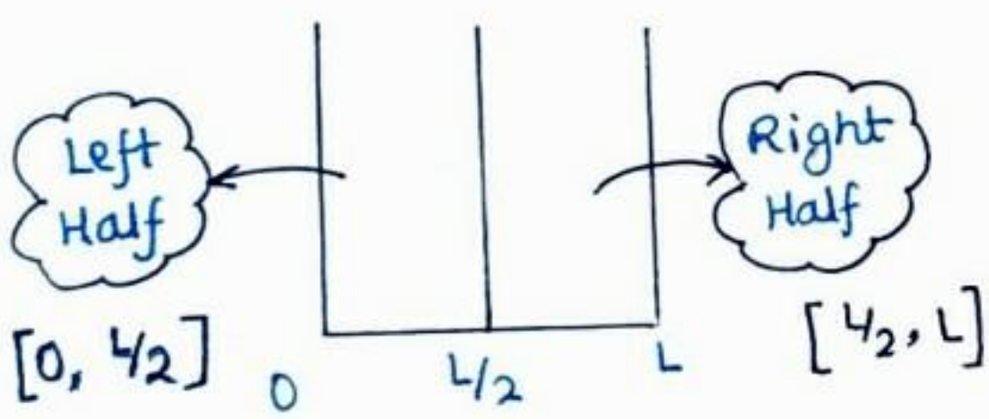
$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{l}$ $n=1$

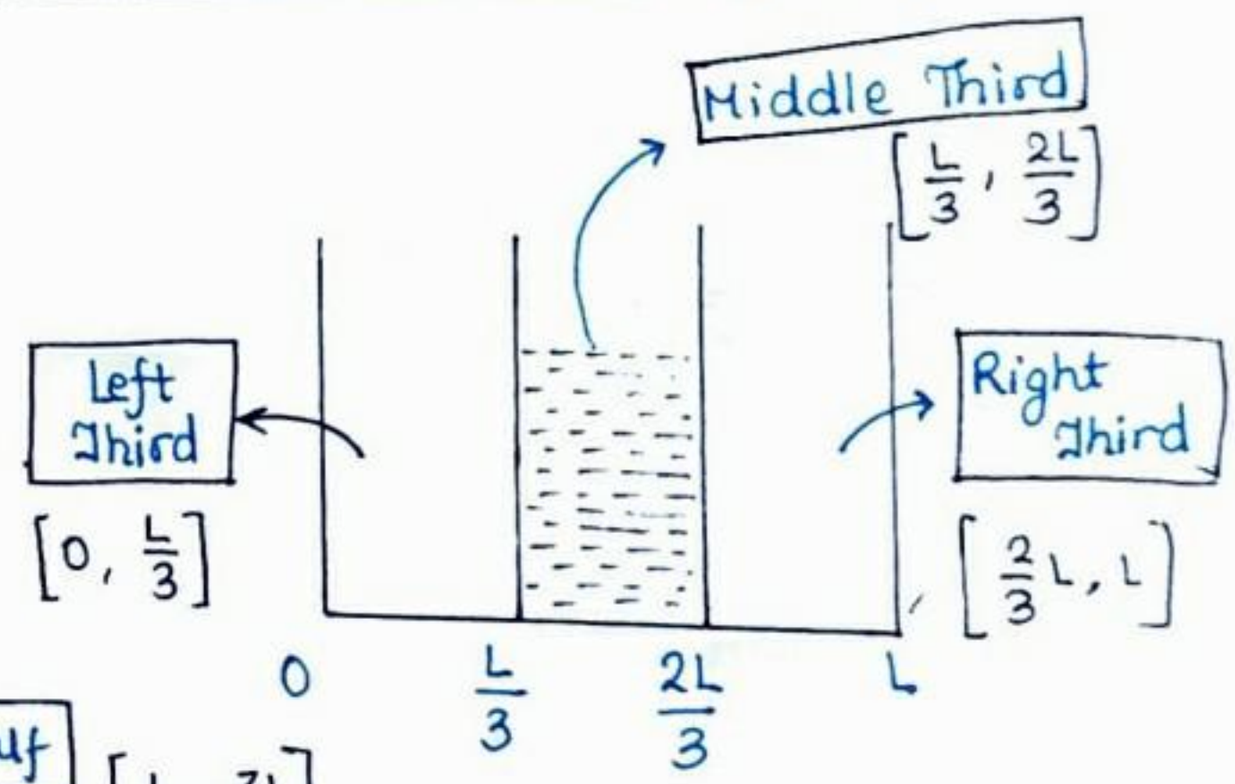
$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{l}$ $n=2$

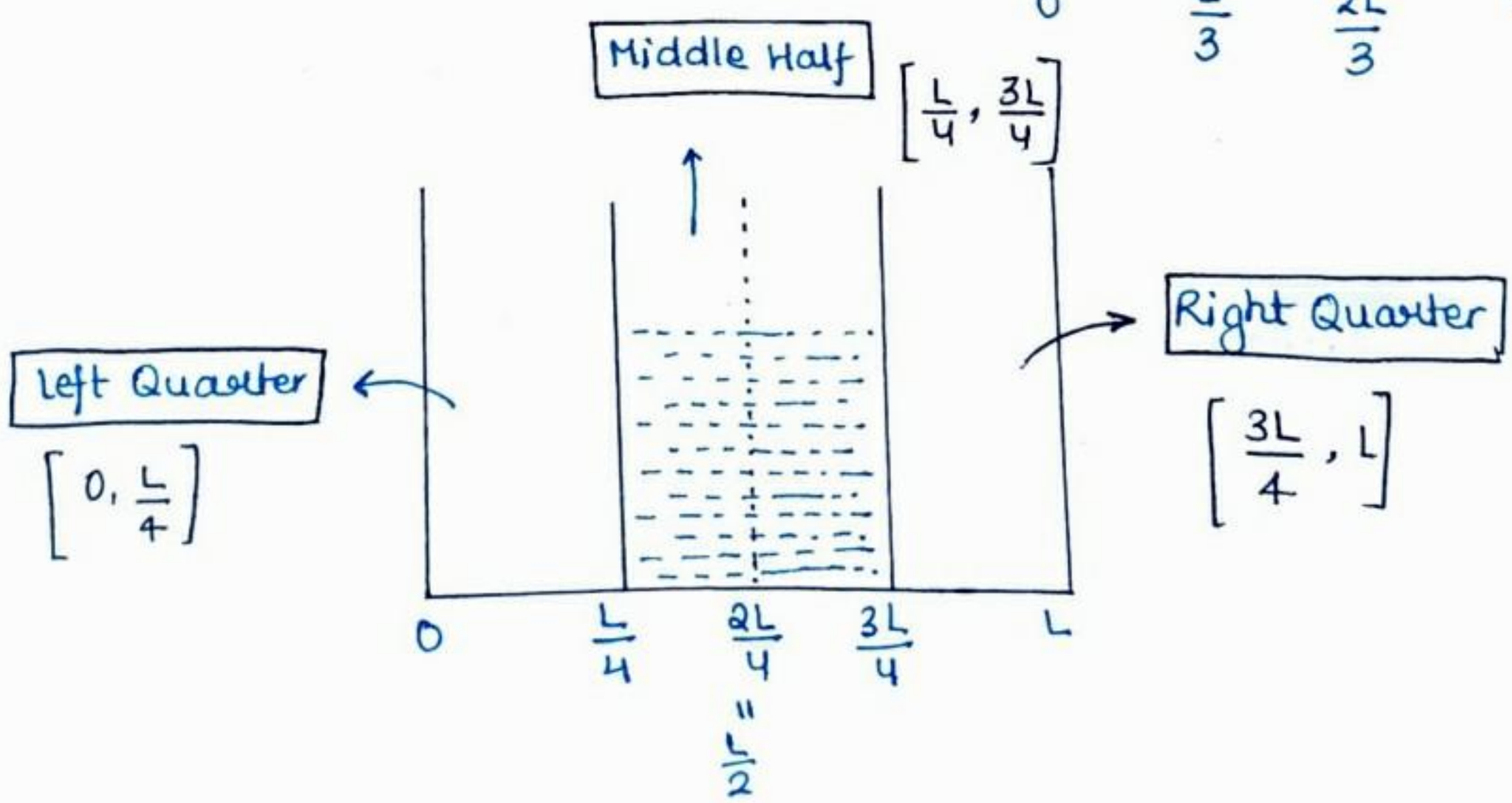
$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{l}$ $n=3$



* Distribution of 1-D Box into Various Limits :- {0, L}







⊛ Calculation of Probability for 1-D Box having limit [0, l]

We know that for 1-D Box [0, l]

$$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

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

$$\psi^* = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

1D-box ; $d\tau = dx$

$$P = \int_a^b \psi^* \psi \, d\tau = \int_a^b \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \cdot \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \, dx$$

$$\boxed{\because \int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin 2bx}$$

$$P = \frac{2}{l} \int_a^b \sin^2 \frac{n\pi x}{l} \, dx$$

$$\boxed{P = \frac{2}{l} \left[\frac{x}{2} - \frac{l}{4n\pi} \sin \frac{2n\pi x}{l} \right]_a^b}$$

or

It can be written as,

$$\boxed{P = \left[\frac{x}{l} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{l} \right]_a^b}$$

General expression to calculate probability for 1-D box with limit [0, l].

⊛ Normalisation:-

Condition of Normalisation,

$$\boxed{\int \psi^* \psi \, d\tau = 1}$$

Difference b/w probability and Normalisation.

$$\boxed{P = \int_a^b \psi^* \psi \, d\tau}$$

and if ψ is a normalised wave function, then probability of finding the particle is 100% i.e. 1.

$$\int_{\text{entire space/entire limit}} \psi^* \psi = 1$$

* How to normalise a given func^n (ψ) if,

$$\int \psi^* \psi \neq 1 \quad \text{and} \quad \int \psi^* \psi = N.$$

If on applying condition of Normalisation we get a value say 'N' other than '1' then the given func^n 'ψ' is not normalised. In such cases:

1.) Find the reciprocal of 'N' & its root $= \sqrt{\frac{1}{N}}$ (known as Normalisation Constant) N.C.

2.) Attach this N.C. to the given function ψ.

3.) Our new wave func^n is normalised.

Ex: $\int \psi^* \psi \, d\tau = N.$

$$\Rightarrow \quad N.C = \sqrt{\frac{1}{N}}$$

New wave func^n $= \sqrt{\frac{1}{N}} \psi$

Hence $\psi = \sqrt{\frac{1}{N}} \psi$ is our new normalised wave function.

Ex:- Check whether $\psi(x) = x$ is normalised or not.

$\psi = x$ in $[0,1]$

For a wave function to be normalised we have,

$$\int \psi^* \psi \, d\tau = 1$$

$$= \int_0^1 x \cdot x \, dx = \int_0^1 x^2 \, dx = \left[\frac{x^3}{3}\right]_0^1 = \frac{1}{3}.$$

$\because$ Given wave function is not normalised.

$$NC = \sqrt{\frac{1}{N}} = \sqrt{3}$$

$$\boxed{\psi_{new} = \sqrt{3}x}$$

Above wave function is our normalised wave function.

Ex:- Check whether $\psi = \sin\frac{\pi x}{l}$ in $[0, l]$ is normalised or not.

$$\int \psi^* \psi = \int_0^l \sin\frac{\pi x}{l} \times \sin\frac{\pi x}{l} \, dx$$

$$= \int_0^l \sin^2\frac{\pi x}{l} \, dx$$

$$= \left[\frac{x}{2} - \frac{l}{4\pi}\sin\frac{2\pi x}{l}\right]_0^l = \left[\frac{x}{2} - \frac{l}{4\pi}\sin\frac{2\pi x}{l}\right]_0^l$$

$$= \left[\frac{l}{2} - \frac{l}{4\pi}\right] = \left[\frac{x}{2} - \frac{l}{4\pi}\sin\frac{2\pi x}{l}\right]_0^l$$

$$= \left[\frac{l}{2} - \frac{l}{4\pi}\sin\frac{2\pi l}{l}\right] - \left[0 - \frac{l}{4\pi}\sin\frac{2\pi 0}{l}\right]$$

$$\int \psi^* \psi \, dx = \frac{l}{2}$$

$$\because \int \psi^* \psi \, dx \neq 1.$$

$$N.C. = \sqrt{\frac{2}{l}}$$

$\boxed{\psi = \sqrt{\frac{2}{l}}\sin\frac{\pi x}{l}}$ is our normalised wave function.

* Average Value Method / Expectation Value:-

In Quantum mechanics there are two ways to calculate the value of observable :

(i) Eigen Value Equation :- If the operator and the function follows eigen value eq^n then we can easily find the value of observable. i.e.

$$\boxed{\hat{A}\psi = a\psi}$$

a → value of observable.

Ex:- $\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$

$\hat{A} = K.E.$

$$K.E.\,\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l}$$

$$= \frac{n^2\hbar^2\pi}{2ml^2}\sqrt{\frac{2}{l}}\sin n\pi x$$

$$\boxed{K.E. = \frac{n^2\hbar^2\pi}{2ml^2}}$$

But it is not necessary that every operator in quantum mechanics follow eigen value equation with a given func^n.

Ex:- $\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$ $\quad \hat{A} = P_x$

$$P_x\psi = -i\hbar\frac{d}{dx}\sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l}$$

$$= \left[(-i\hbar)\sqrt{\frac{2}{l}}\frac{n\pi}{l}\right]\cos\frac{n\pi x}{l}$$

Hence momentum operator does not follow eigen value equation with the func^n ψ.

→ Hence for such cases we use expectation value method.

Expectation Value :-

$$\boxed{\underset{\text{observable}}{\langle M\rangle} = \frac{\int \psi^* M \psi \, d\tau}{\int \psi^* \psi \, d\tau}}$$

If function is normalised, $\int \psi^*\psi \, d\tau = 1$

$$\boxed{\langle M\rangle = \int \psi^* M \psi \, d\tau}$$

Note:- The value of observable calculated by the eigen value method and expectation value method are same.

Ex:- Calculate average value for the function $\psi = (x)$ and $\hat{A} = \hat{x}$. in $[0,1]$

We know that $(\hat{x})$ is a position operator.

$$\langle x \rangle = \frac{\int_0^1 \psi^* x \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$= \frac{\int_0^1 x \cdot x \cdot x \, dx}{\int_0^1 x \cdot x \, dx}$$

$$\langle x \rangle = \frac{\int_0^1 x^3 dx}{\int_0^1 x^2 dx} = \frac{\left[\frac{x^4}{4}\right]_0^1}{\left[\frac{x^3}{3}\right]_0^1} = \frac{\left[\frac{1}{4} - 0\right]}{\left[\frac{1}{3} - 0\right]}$$

$$\boxed{\langle x \rangle = \frac{3}{4}}$$

⊛ Schrodinger Wave Equation :-

Schrodinger wave equation is the Eigen value equation of Energy.

We know that for Energy being observable we use Hamiltonian operator in quantum mechanics.

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

$\hat{H}$ → Hamiltonian Operator

E → Energy.

and we know that,

$$H = P.E. + K.E.$$

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V$$

where $\boxed{\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}}$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi} \quad \text{—— (i)}$$

Multiply eq^{n}-1 by $-\frac{2m}{\hbar^2}$.

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

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[E\psi - V\psi\right] = 0$$

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0} \quad \text{—— (ii)}$$

Equation-(ii) is the required Schrodinger Wave equation.

$$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h}(E-V)\psi = 0} \quad \text{modified form } \left\{\hbar = \frac{h}{2\pi}\right\}$$

Hence Schrodinger Wave equa^{n} is an eigen value equation where operator is hamiltonian and eigen value is Energy.

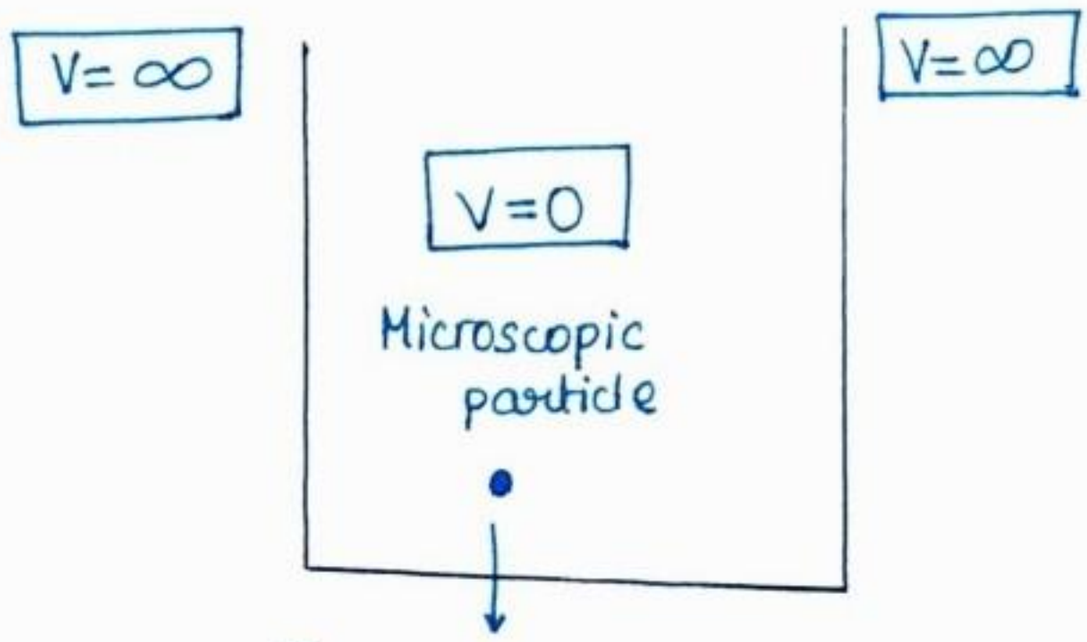
⊛ Application Of Schrodinger Wave Equation:-

1) Translational Motion ⇒ PIB Model
2) Electronic Motion ⇒ Hydrogen Atom.
3) Vibrational Motion ⇒ SHO
4) Rotational Motion ⇒ Rigid Rotor.

(I) PIB Model :- It is studied under translational Motion.

Three parts are studied in it.

- 2-D Box
- 1D-Box
- 3-D Box.



Particle is moving freely

$\boxed{V = \text{Constant} = 0}$

Microscopic particle shows tunneling effect, given by,

$$\boxed{T = e^{-2\beta L}} \quad \text{where} \quad \boxed{\beta = \frac{\sqrt{2M(V-E)}}{\hbar}}$$

$$\boxed{T = e^{-2\frac{\sqrt{2M(V-E)}}{\hbar}\cdot L}}$$

when $V = \infty$

$$T = e^{-\infty} = 0$$

Hence at infinite potential Microscopic particle can-not show tunneling effect.

<u>Applying Schrodinger Wave Equation to find wave function for the particle in 1-D Box. [0, L]</u>

for 1D Box; $\nabla^2 = \frac{d^2}{dx^2}$.

Applying Schrodinger Wave Equation,

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

<u>For 1-D Box</u>:-

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}[E-0]\psi = 0 \qquad \because V_{inside} = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

Let, $\boxed{\frac{2mE}{\hbar^2} = k^2}$

$$\boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0} \quad \text{—(i)}$$

On solving (i) we get,

$\boxed{\psi = A\sin kx + B\cos kx}$ → using this wave func^n and neglecting other we have,

$$\psi = Ae^{ikx} + Be^{-ikx}$$

$$\psi = A\sin Kx + B\cos kx \quad \text{——} (*)$$

Applying Boundary Conditions:-

(i) $x=0 \quad \psi=0$

$$0 = A\sin 0^\circ + B\cos 0^\circ$$

$$0 = B\cos 0^\circ \qquad [\because \cos 0^\circ = 1]$$

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

Putting in $*$ we have,

$$\boxed{\psi = A\sin Kx} \text{——} \{*^2\}$$

(ii) $x=l \quad \psi=0$

$$0 = A\sin kl$$

$$\because A \neq 0 \Rightarrow \sin kl = 0$$

$$\sin kl = \sin n\pi$$

$$\boxed{k = \frac{n\pi}{l}}$$

Hence our wave function comes out as,

$$\boxed{\psi = A\sin \frac{n\pi}{l}x}$$

here, $n = 1, 2, 3, 4, \ldots\ldots$

$\downarrow$

Translational Quantum Number.

Value of n can never be zero otherwise func^n will vanish.

$\because$ Our wave func^n $\psi = A\sin \frac{n\pi x}{l}$ is not normalised. Therefore by using condition of normalisation we will normalise the given wave function.

$$\psi = A\sin \frac{n\pi x}{l}.$$

$$\boxed{\int \psi^* \psi \, d\tau = 1} \rightarrow \text{Condition of Normalisation.}$$

$$= \int_0^L A\sin \frac{n\pi x}{l} . A\sin \frac{n\pi x}{l} \, dx = 1$$

$$= A^2 \int_0^L \sin^2 \frac{n\pi x}{l} \, dx = 1$$

$$= A^2 \left[\frac{x}{2} - \frac{l}{4n\pi} \sin \frac{2n\pi x}{l} \right]_0^l = 1$$

On applying limit we have,

$$A^2\left[\frac{l}{2} - \frac{l}{4n\pi}\sin\frac{n\pi l}{l}\right] - A^2[0] = 1$$

$$A^2 \cdot \frac{l}{2} = 1$$

$$\boxed{A = \sqrt{\frac{2}{l}}}$$

Hence our normalised wave function is,

$$\boxed{\psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{l}}$$

Now, we have assumed,

$$K^2 = \frac{2mE}{\hbar^2} \quad \text{—(i)}$$

and

$$K = \frac{n\pi}{l} \quad \text{—(ii)}$$

Equating (i) and (ii) we have,

$$\frac{n^2\pi^2}{l^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{\hbar^2}{2m}\cdot\frac{n^2\pi^2}{l^2}$$

$$\boxed{E = \frac{n^2\pi^2\hbar^2}{2ml^2}}$$

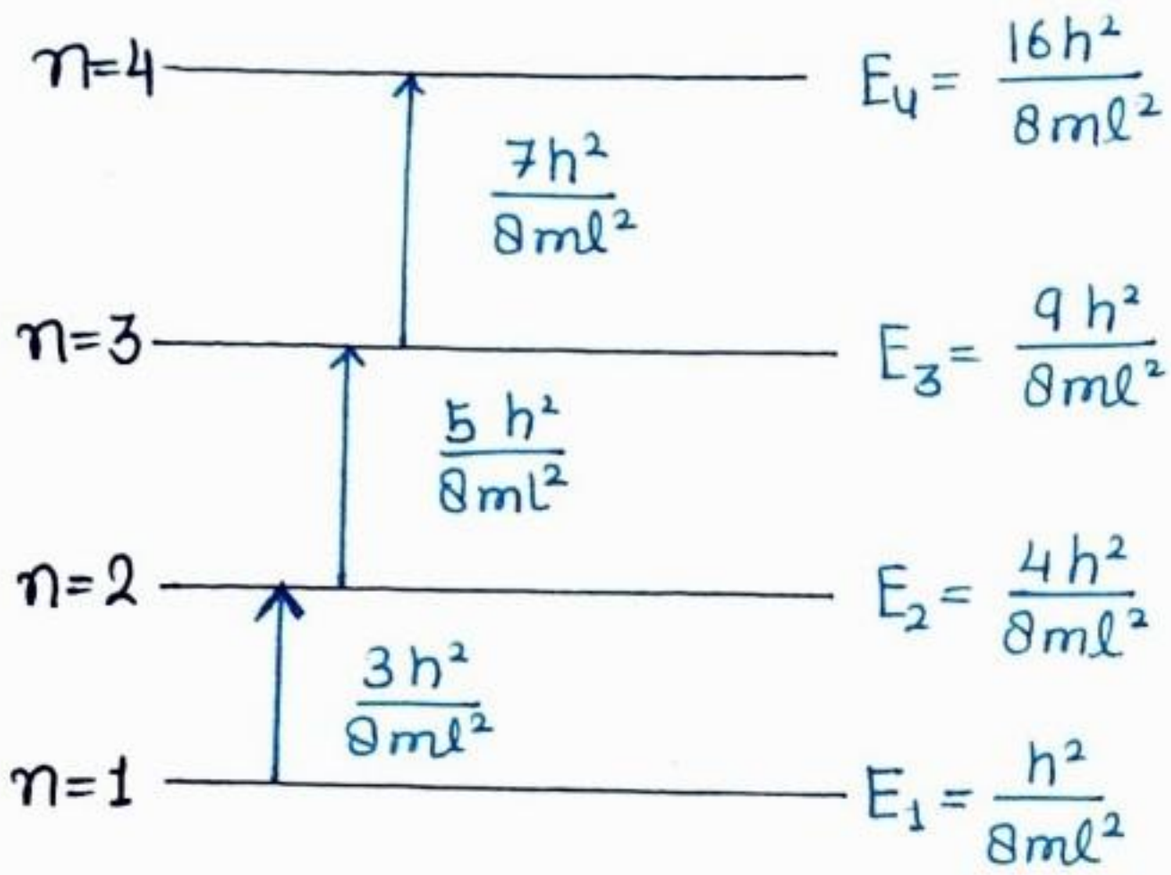
This is the expression for total energy and the result is same as that of K.E. operator over the same func^n

$\Rightarrow$ $\boxed{\text{Kinetic Energy of Particle in 1-D Box} = \text{Total Energy of the particle}}$

Now; $$E_n = \frac{n^2\pi\hbar^2}{2ml^2}$$

$\because \left[\hbar = \frac{h}{2\pi}\right]$

$$\boxed{E_n = \frac{n^2h^2}{8ml^2}}$$



Hence in 1-D Box, the energy spacing ↑ses as the value of Translational Quantum Number increases.

* Plot of ψ and ψ^2:-

For ground state, $n=1$

$$\psi_1 = \sqrt{\frac{2}{l}} \sin \frac{\pi x}{l}$$

Compairing we have,

$$\frac{\pi x}{l} = \frac{\pi}{2}$$

$\boxed{x = l/2}$, Hence we will have maxima at $x = \frac{l}{2}$.

when,

$$\frac{\pi x}{l} = \frac{5\pi}{2}$$

$\boxed{x = 2.5l}$ This is not possible at value of 'x' exceeds boundary condition.

~~Hence boun~~

Hence there will be only one maxima at ground state.

For maximum value,

$$\boxed{\sin \frac{\pi x}{l} = 1}$$

possible only when,

$$\frac{\pi x}{l} = \frac{\pi}{2}, \frac{5\pi}{2}, \frac{9\pi}{2}.$$

* For minimum value;

$$\sin \frac{\pi x}{l} = -1$$

possible only when, $\frac{\pi x}{l} = \frac{3\pi}{2}, \frac{7\pi}{2}, \frac{11\pi}{2}, \ldots$

$\frac{\pi x}{l} = \frac{3\pi}{2} \Rightarrow$ $\boxed{x = 1.5l}$ It also exceeds boundary cond^n hence, minima not possible in ground state

Node :- Value or points on the graph where wave function vanishes, except boundary points.

i.e. $\boxed{\psi=0}$ $\boxed{\sin\frac{\pi x}{l}=0}$

possible only when $\frac{\pi x}{l} = 0, \pi, 2\pi, 3\pi, 4\pi, \ldots\ldots$

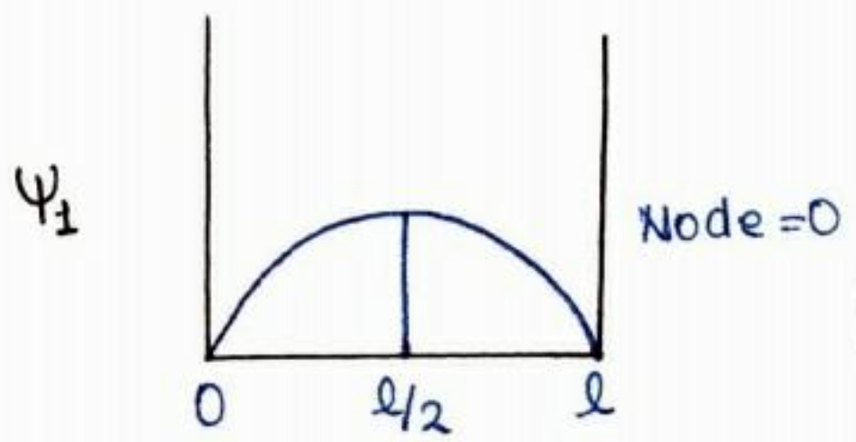
when, $\frac{\pi x}{l}=0$ $\qquad$ $\frac{\pi x}{l}=\pi$

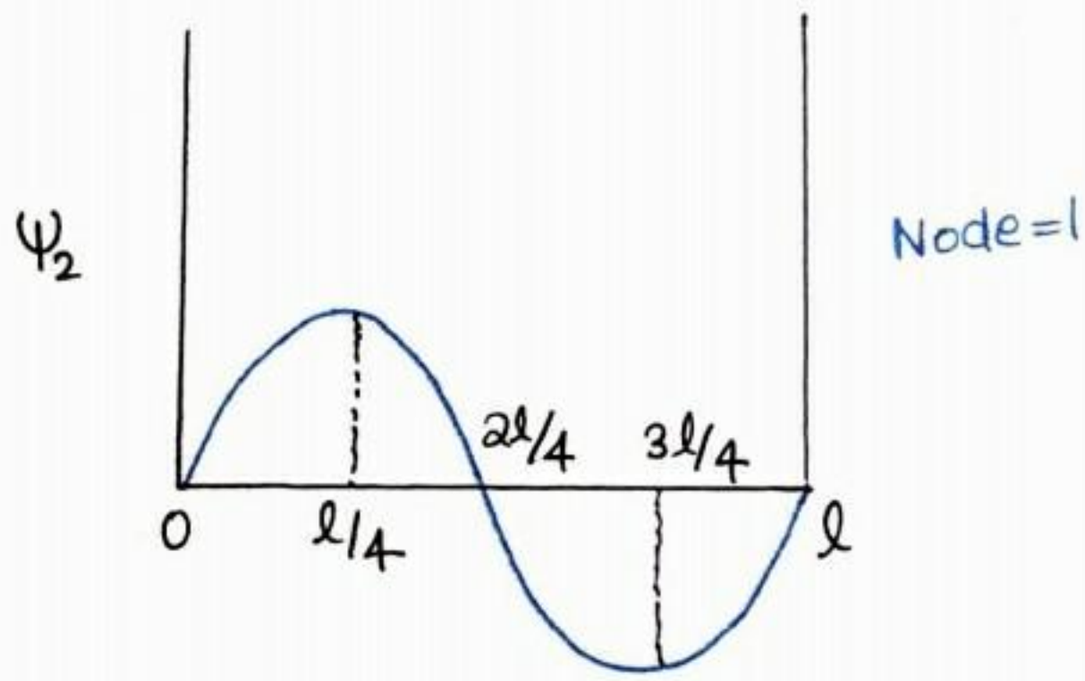
$\boxed{x=0}$ $\qquad$ $\boxed{x=l}$

Both are boundary condition.

Hence no node is present in ground state.

*** Graph for Ground State :-**





Trick to Remember

Order of Graph-Polation; Maxima → Node → Minima → Node → Maxima → Node → Minima

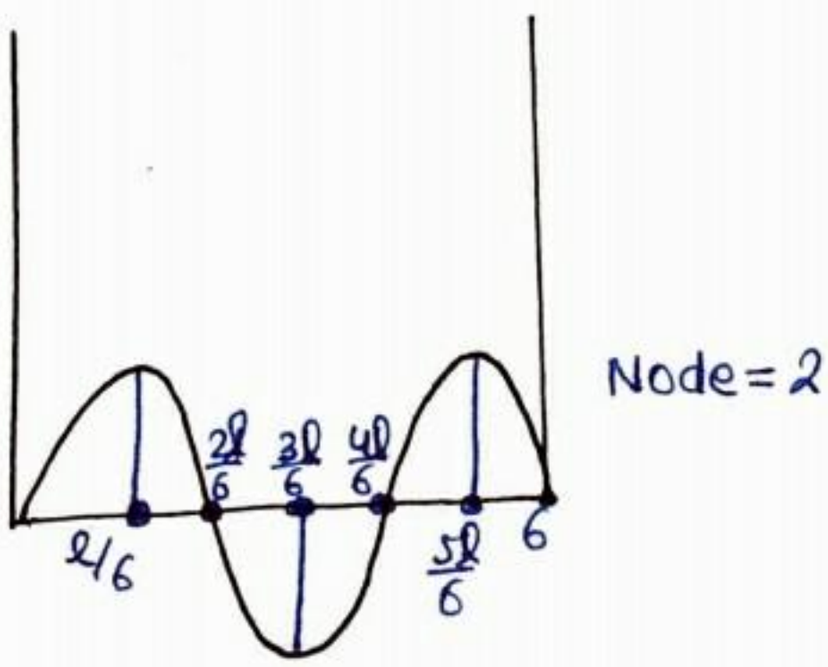
Value of maxima and nodes, $= \frac{l}{2n}$.

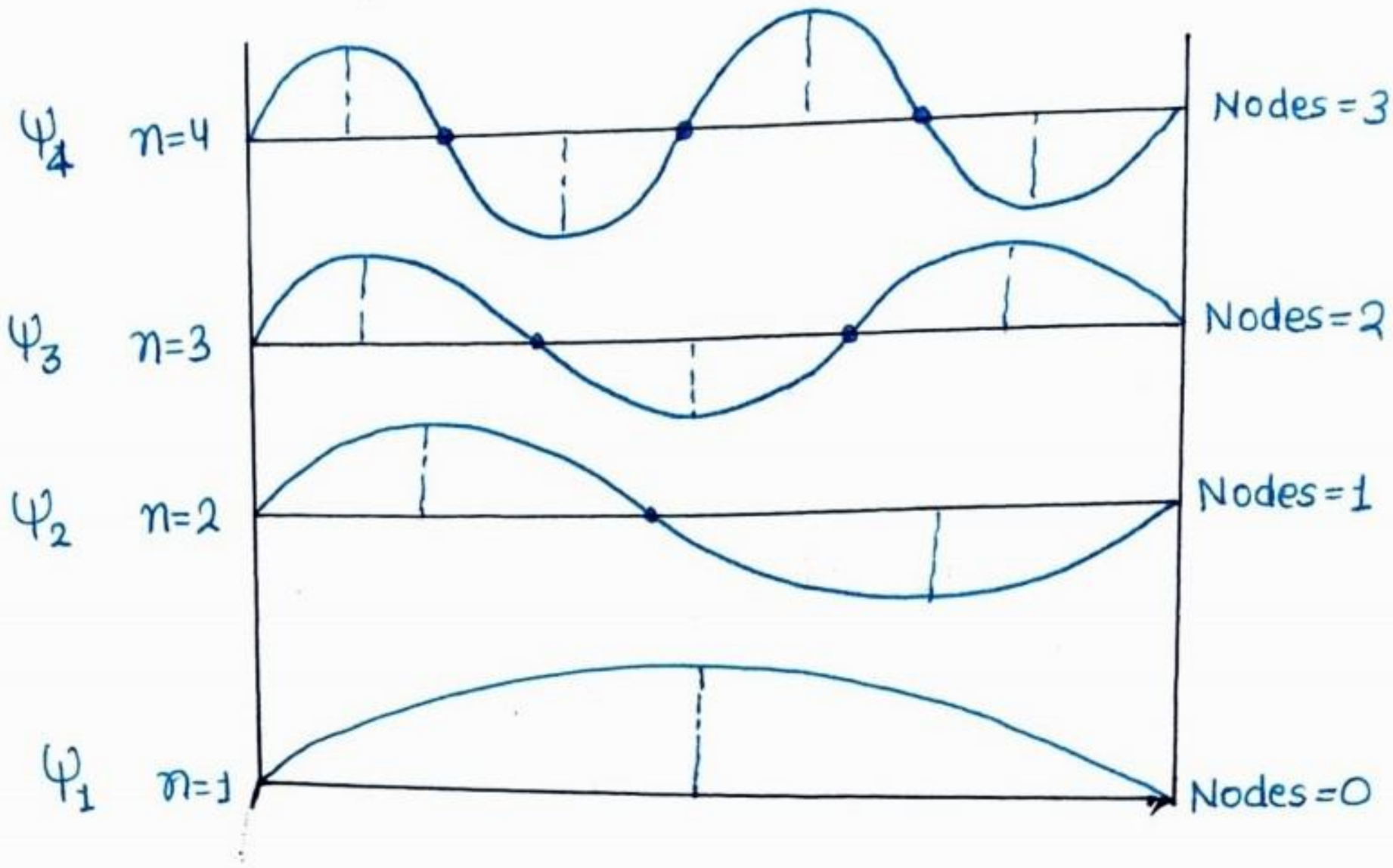
Ex for ψ_2, $n=2$

Maxima $= \frac{l}{4}$ $\quad$ Node $= \frac{l}{4}+\frac{l}{4} = \frac{2l}{4}$ $\quad$ Minima $= \frac{2l}{4}+\frac{l}{4} = \frac{3l}{4}$ $\quad$ Node $= \frac{3l}{4}+\frac{l}{4} = l$ boundary.

Ex :- for ψ_3, $n=3$

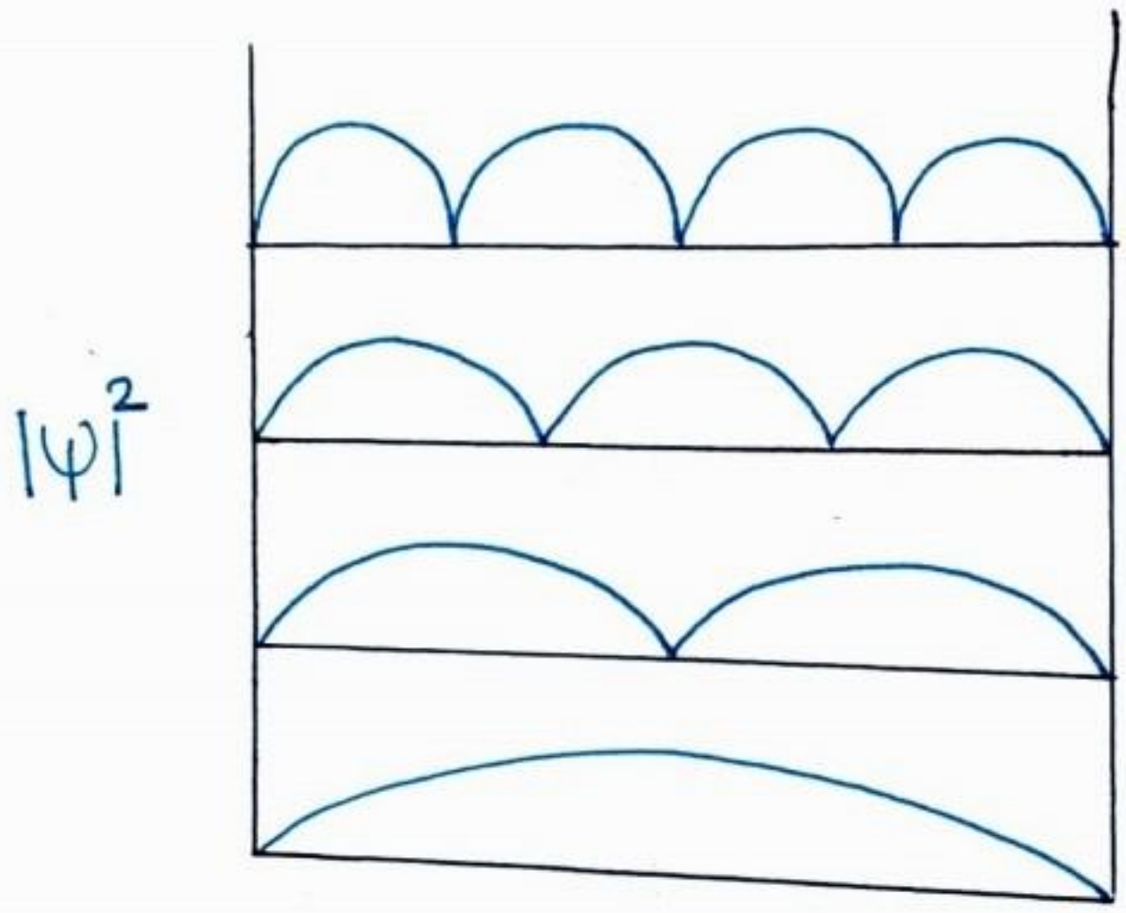
Maxima $= \frac{l}{6}$ $\quad$ Node $= \frac{2l}{6}$ $\quad$ Minima $= \frac{3l}{6}$ $\quad$ Node $= \frac{4l}{6}$ $\quad$ Maxima $= \frac{5l}{6}$ $\quad$ Boundary $= l$.





and odd ψ → symmetric $\{\psi_1, \psi_3, \psi_5, \psi_7\}$

even ψ → antisymmetric $\{\psi_2, \psi_4, \psi_6\}$



* Calculation of length of the box :-

We know that,

$$E = \frac{n^2h^2}{8ml^2} \longrightarrow (K.E) \quad (i)$$

and

$$K.E. = \frac{p^2}{2m} \quad \text{and} \quad p = \frac{h}{\lambda}$$

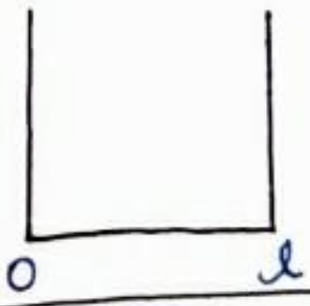
$$\boxed{K.E. = \frac{h^2}{2m\lambda^2}} \quad \text{—(ii)}$$

Equating (i) and (ii)

$$\frac{n^2h^2}{8ml^2} = \frac{h^2}{2m\lambda^2} \Rightarrow \boxed{l = \frac{n\lambda}{2}}$$

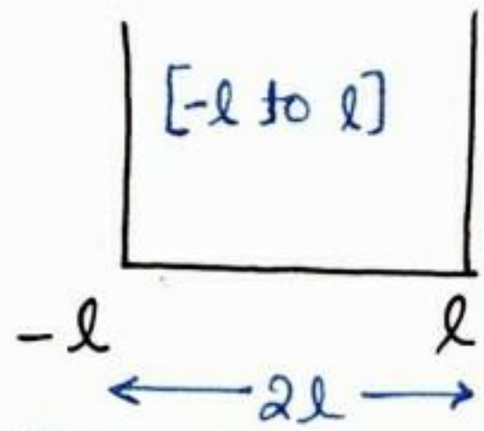
Hence length of the box is half of the wavelength or integral multiple of half of the wavelength.

* Variation in limits of 1-D Box :-



$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

$$\boxed{E_n = \frac{n^2 h^2}{8ml^2}}$$



Hence 'l' will be replaced by '2l'

ψ_n — n=even (2, 4, 6, 8...) →

$$\psi_n = \sqrt{\frac{2}{2l}} \sin \frac{n\pi x}{2l}$$

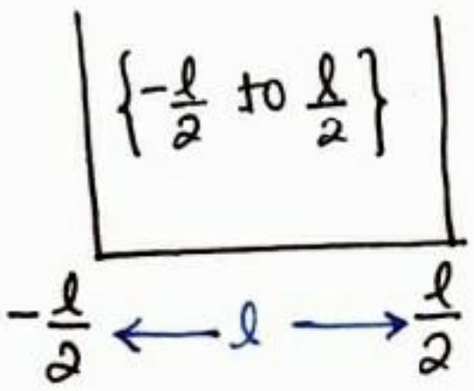
$$\boxed{\psi_n = \sqrt{\frac{1}{l}} \sin \frac{n\pi x}{2l}}$$

ψ_n — n=odd (1, 3, 5, 7...) →

$$\psi_n = \sqrt{\frac{2}{2l}} \cos \frac{n\pi x}{2l}$$

$$\boxed{\psi_n = \sqrt{\frac{1}{l}} \cos \frac{n\pi x}{2l}}$$

$$E_n = \frac{n^2 h^2}{8m(2l)^2} \Rightarrow \boxed{E = \frac{n^2 h^2}{32\, ml^2}}$$



ψ_n — n=even →

$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

ψ_n — n=odd →

$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \cos \frac{n\pi x}{l}}$$

$$\boxed{E_n = \frac{n^2 h^2}{8ml^2}}$$

Note :- Functions are multiplicative in nature and energy is additive in nature.

⊛ 2-D Box :- There can be two types of 2-D Box.

1.) Rectangular Box

$0 < x < a$
and $0 < y < b$ {Variations along x & y axis}

2.) Square Box

$0 < x < a$
$0 < y < a$ {∵ a=b}

∵ Functions are multiplicative in nature and energy is additive in nature.

$$\psi_{n_x n_y} = \psi_{n_x} . \psi_{n_y}$$

$$\psi_{n_x \cdot n_y} = \psi_{n_x} \cdot \psi_{n_y}$$

$$\boxed{\psi_{n_x n_y} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} . \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}}$$

$$\boxed{\psi_{n_x n_y} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} . \sqrt{\frac{2}{a}} \sin \frac{n_y \pi y}{a}}$$

$$E_{n_x n_y} = E_{n_x} + E_{n_y}$$

$$\boxed{E_{n_x n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2}}$$

$$E_{n_x \cdot n_y} = E_{n_x} + E_{n_y}$$

$$\boxed{E_{n_x n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8ma^2}}$$

⊛ n_x and n_y are two quantum numbers.

⊛ Concept of degeneracy will be involved in 2-D square box.

Degeneracy :- Availibity or presence of more than one state at one energy level is known as degeneracy.

Quantum Numbers :- When restrictions are imposed on a number during the solution of schrodinger wave equations the numbers are known as quantum numbers.

In Quantum, Value of quantum number can not be zero.

* Degeneracy in 2-D Box :- {Square}

$$E_{n_x n_y} = \frac{h^2}{8ma^2}[n_x^2 + n_y^2] = \frac{\hbar^2 \pi^2}{2ma^2}[n_x^2 + n_y^2]$$

(1,3) (3,1) ψ_{13} and ψ_{31} ; $E = \frac{10h^2}{8ma^2}$; $g=2$

(2,2) (n_x n_y) ψ_{22} ; $E = \frac{8h^2}{8ml^2}$; $g=1$

(1,2) (n_x n_y) (2,1) (n_x n_y) ψ_{12} and ψ_{21} {wavefunc^{n}s} ; $E = \frac{5h^2}{8ma^2}$ ∵ 2 states at same energy level = degeneracy.

(1,1) (n_x n_y) ψ_{11} and $E = \frac{2h^2}{8ma^2}$; $g=1$

Hence, $\boxed{g=2}$

* Trick to solve degeneracy :-

Examples :- $E_{2D} = \frac{10 h^2}{8ma^2}$

∵ We know that,

$$E = \frac{h^2}{8ma^2}[n_x^2 + n_y^2]$$

$$\Rightarrow \frac{h^2}{8ma^2}[n_x^2 + n_y^2] = \frac{10 h^2}{8ma^2}$$

$$\Rightarrow \boxed{n_x^2 + n_y^2 = 10}$$

Only two combinations n_x and n_y are possible for above equation.

$n_x = 1 \quad n_y = 3$ and $n_x = 3 \quad n_y = 1$

i.e. (1, 3) and (3, 1) , Hence degeneracy = $\boxed{g = 2}$

Example :- $E_{2D} = \frac{25 h^2}{8ma^2}$. Again on compairing we have,

$$\boxed{n_x^2 + n_y^2 = 25}$$

Possible Combination :- (4, 3) and (3, 4) Hence degeneracy = $g = 2$.

Example :- $E_{2D} = \frac{50 \hbar^2 \pi^2}{2ma^2}$

On compairing with , $E = \frac{\hbar^2 \pi^2}{2ma^2}[n_x^2 + n_y^2]$

$$\Rightarrow \boxed{n_x^2 + n_y^2 = 50}$$

Possible Combinations :- (7, 1) and (1, 7) and (5, 5) Hence degeneracy = $g = 3$

Value of quantum numbers are entirely different hence called accidental degeneracy.

* 3-D Box :-

We will consider cubic box only. $\left\{ \begin{array}{l} 0<x<a \\ 0<y<a \\ 0<z<a \end{array} \right\}$

Wave function $= \psi_{(n_x, n_y, n_z)} = \psi_{n_x} \cdot \psi_{n_y} \cdot \psi_{n_z}$

$$\boxed{\psi_{n_x,n_y,n_z} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \sqrt{\frac{2}{a}} \sin \frac{n_y \pi y}{a} \sqrt{\frac{2}{a}} \sin \frac{n_z \pi z}{a}}$$

Energy, $\boxed{E = E_{n_x} + E_{n_y} + E_{n_z}}$

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8ma^2} + \frac{n_z^2 h^2}{8ma^2}$$

$$\boxed{E_{3D} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

$$\boxed{E_{3D} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{\hbar^2 \pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

* Concept of Degeneracy :-

(2,2,2)			ψ_{222} and $E = \frac{12h^2}{8ma^2}$; $g=1$
(3,1,1)	(1,3,1)	(1,1,3)	$\psi_{311}, \psi_{131}, \psi_{113}$ and $E = \frac{11h^2}{8ma^2}$; $g=3$
(2,2,1)	(2,1,2)	(1,2,2)	$\psi_{221}, \psi_{212}, \psi_{122}$ and $E = \frac{9h^2}{8ma^2}$; $g=3$
(1,2,1)	(1,1,2)	(2,1,1)	$\psi_{121}, \psi_{112}, \psi_{211}$ and $E = \frac{6h^2}{8ma^2}$; $g=3$
	(1,1,1)		ψ_{111} and $E = \frac{3h^2}{8ma^2}$; $g=1$

*** Exampe** $E_{3D} = \frac{9h^2}{8ma^2}$ On compairing with $E_n = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]$

we have; $n_x^2 + n_y^2 + n_z^2 = 9$

Possible Combinations = (2, 2, 1) (2, 1, 2) (1, 2, 2) Hence $g=3$.

Example : $E_{3D} = \frac{27\hbar^2\pi^2}{2ma^2}$; On compairing we get,

$n_x^2 + n_y^2 + n_z^2 = 27$

Possible Combinations = (5, 1, 1) (1, 1, 5) $\underbrace{(1, 5, 1) \text{ and } (3, 3, 3)}_{\text{accidental degeneracy}}$.

HYDROGEN ATOM

* Some Important terms :-

Volume Element ($d\tau$) → For 1-D Box = dx

For 2-D Box = $dx\,dy$

For 3-D Box = $dx\,dy\,dz$

For Hydrogen Atom = $r^2 dr \sin\theta\, d\theta\, d\phi$.

Cartesian Co-ordinates = $[x, y, z]$

Polar Co-ordinates = $[r, \theta, \phi]$

$r \rightarrow [0-\infty]$, $\theta \rightarrow [0-\pi]$, $\phi \rightarrow [0-2\pi]$

Lapalacian operator $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$.

For H-atom ; $\boxed{\nabla^2 = \frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} + \frac{1}{r^2 \sin\theta}\frac{d}{d\theta}\sin\theta \frac{d}{d\theta} + \frac{1}{r^2 \sin^2\theta}\frac{d^2}{d\phi^2}}$

→ H-atom model was proposed for Hydrogenic species i.e. Li^{++}, He^{+}, Be^{3+} and so on i.e. single $e^{\ominus}$ system.

→ It is studied under electronic motion.

* In case of PIB model, potential energy inside the box is zero but in case of Hydrogen atom it is not so. i.e. potential energy is not zero.

* The solution of schrodinger wave equation gives wave func^n for H-atom which consists of two different parts → Radial Part, Angular Post.

Wave function for H-atom,

$$\boxed{\psi_{(r,\theta,\phi)} = R(r)\, Y(\theta,\phi)}$$

$\psi_{(r,\theta,\phi)}$ → Three different parts ↓ Three quantum numbers, $\psi(n, l, m)$

$R(r)$ → Radial Part ⇓ depends upon two quantum numbers $R(n, l)$

$Y(\theta,\phi)$ → Angular Part ⇓ depends upon two quantum numbers $Y(l, m)$

$$\boxed{\begin{aligned} n &= 1, 2, 3, 4, \ldots\ldots \\ l &= 0, 1, 2, 3, \ldots \\ m &= 0, \pm1, \pm2, \pm3 \ldots \end{aligned}}$$

⊛ Identification Of Radial Part :-

General Expression for Radial Part is given by.

$$\boxed{R_{(n,l)} = \left(\frac{2Zr}{na}\right)^{l} e^{-\frac{Zr}{na_0}}}$$

gives value of quantum number (n).

a_0 = Bohr radius.

gives value of quantum number (l).

Example :-

$$\psi = N e^{-\frac{r}{a_0}}$$

There is no free 'r' term,

i.e. $r^0 \Rightarrow \boxed{l=0}$ $\Rightarrow$ 1s orbital

and $\frac{r}{a_0} = \frac{r}{na_0} \Rightarrow \boxed{n=1}$

Hence given wave function is for 1s-orbital.

Example :- $\psi = r e^{-\frac{r}{2a_0}}$

We have free 'r', On compairing we get,

$r^1 = r^l$ and $\frac{r}{2a_0} = \frac{r}{na_0}$

$\Rightarrow \boxed{l=1}$ $\Rightarrow \boxed{n=2}$

→ 2p orbital.

Example :- $\psi = N(r^2 - 2r + 1)\, e^{-\frac{r}{3a_0}}$

In above wave func^n we will not consider 'r' in given polynomial.

For the value of 'l' we require free 'r'.

Hence again we have,

$r^0 = r^l \Rightarrow \boxed{l=0}$

and $\frac{r}{3a_0} = \frac{r}{na_0} \Rightarrow \boxed{n=3}$

3s orbital

Example :- $\psi = N\left[2 - \frac{r}{a^0}\right] e^{-\frac{r}{2a_0}}$

Again we do not have any free (r) hence

$l=0$, $n=2$ — 2s orbital.

⊛ Identification of Angular Part :

General Expression for Angular Part is given by;

$$\boxed{\underset{(m,l)}{Y(\theta,\phi)} = \sin^{|m|}\theta \cos^{l-|m|}\theta \, e^{im\phi}}$$

$e^{im\phi}$ → Gives value of (m)

$\cos^{l-|m|}\theta$ → Gives value of (l).

Example :-

$$Y(\theta,\phi) = N\cos\theta$$

On Compairing we get, $e^{im\phi} = e^{0}$

$$\Rightarrow \boxed{m=0}$$

and, $\cos\theta = \cos^{l-|m|}\theta$

$$\Rightarrow l-|m|=1$$

$$\boxed{l=1}$$

Hence $l=1$, $m=0$.

Example :-

$$Y(\theta,\phi) = N\sin\theta\cos\theta\, e^{-i\phi}$$

On compairing we get,

$e^{-i\phi} = e^{im\phi}$

$$\Rightarrow \boxed{m=-1}$$

and $\cos\theta = \cos^{l-|m|}\theta$

$\Rightarrow$ ~~$l-|m|=0$~~

$\Rightarrow l-|m|=1 \Rightarrow l-|-1|=1$ $\quad |-1|=1$

$l-1=1$

$$\boxed{l=2}$$

Hence $\boxed{m=-1}$ $\boxed{l=2}$

⊛ Radial Nodes and Angular Nodes :-

$$\boxed{\text{Radial Nodes} = n-l-1}$$

$$\boxed{\text{Angular Nodes} = l}$$

$$\boxed{\text{Total Nodes} = n-1}$$

For 1s orbital :-

$\boxed{1s}$ $n=1$, $l=0$

Radial Node = 0

$\boxed{2s}$ $n=2$, $l=0$ Radial Node = 1.

Example :- $\psi = N e^{-r/a_0}$

There are two ways to calculate the radial node for the above wave functions.

(I) Equate the radial part $=0$ and find the value of r.

No. of values of 'r' give no. of nodes present and value of 'r' gives the position of node.

$$\Rightarrow \boxed{e^{-r/a_0} = 0} \text{ —(i)}$$

equation (i) will be zero only if $r = \infty$ as $e^{-\infty} = 0$

$\Rightarrow r = \infty$ but $r \rightarrow [0, \infty]$

Hence this is boundary condition and nodes are not present at boundary.

(II) Compare the equa^n with general eq^n and find values of n and l.

→ On compairing we get that there is no free 'r'.

$\Rightarrow \boxed{l=0}$ and $\frac{r}{a_0} = \frac{r}{na_0} \Rightarrow \boxed{n=1}$

Radial Nodes $= n-l-1$

$= 1-0-1 = 0.$

Hence we get to know that no radial nodes are present for the above wave function.

Example :- $\psi = N\left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$

Again we have two methods.

(I) $\left(2 - \frac{r}{a_0}\right)\left(e^{-\frac{r}{2a_0}}\right) = 0$

$\Rightarrow 2 - \frac{r}{a_0} = 0$ and $e^{-r/2a_0} = 0$

$\boxed{r = 2a_0}$ $\boxed{r = \infty}$

Hence 1 node is present and the position of node is $2a_0$

~~Example~~ (II) On compairing we get,

$\boxed{l=0}$ and $\boxed{n=2}$

Radial Node $= 2-0-1$

$= 1$ Ans.

* Finding Wave Function for 1-s orbital for H-atom :-

We know that for H-atom ψ {wave func^n} consists of two parts, i.e. Radial Part and Angular part.

Hence,

$$\psi_{1s} = R(r) \cdot Y(\theta, \phi)$$

$$\psi_{1s} = R(n, l)\, Y(m, l)$$

For 1s orbital :-

$m = 0 \qquad l = 0 \qquad$ and $\qquad n = 1$

$$\boxed{\psi_{1s} = R(1,0)\, Y(0,0)}$$

Radial Part for 1s

We know that Radial part is given by,

$$\boxed{R_{nl} \propto \left(\frac{2Zr}{na_0}\right)^{l} e^{-\frac{Zr}{na_0}}}$$

For H-atom and 1-s orbital,

$n = 1, \quad l = 0 \quad Z = 1.$

$$R_{n,l} \propto \left(\frac{2 \times 1 \times r}{1 \times a_0}\right)^{0} e^{-\frac{1r}{na_0}}$$

$$\boxed{R_{n,l} = N e^{-r/a_0}}$$

Proportionality Constant.

We will find the value of 'N' by using condition of Normalisation.

We know that,

Condition of Normalisation $= \int \psi^* \psi \, d\tau = 1$

For H-atom,

$d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$

But we will use only,

$\boxed{d\tau = r^2 dr}$ because we are considering radial part only.

Hence on applying condition of Normalisation, we have,

$$\int R^*_{1,0} \cdot R_{10} \, d\tau = 1$$

Now; $R_{10} = Ne^{-r/a_0}$ $\quad R_{10}^* = Ne^{-r/a_0}$

$$\int_0^\infty R_{10}^* R_{10} r^2 dr = 1$$

$$\int_0^\infty Ne^{-r/a} \cdot Ne^{-r/a} r^2 dr = 1$$

$$\boxed{N^2 \int_0^\infty r^2 e^{-2r/a} dr = 1} \quad \text{—(i)}$$

Using integral formulae;

$$\boxed{\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{(\alpha)^{n+1}}}$$

In above integral we have, $n=2$ $\alpha = \frac{2}{a}$

$$N^2 \left[\frac{2!}{\left(\frac{2}{a}\right)^3} \right] = 1$$

$$N^2 \left[\frac{a^3}{4} \right] = 1$$

$$N^2 = \frac{4}{a^3}$$

$$\boxed{N = \frac{2}{(a)^{3/2}}} \doteq \text{Normalisation Constant.}$$

Hence Radial Part for 1-s orbital is given by;

$$\boxed{R_{10} = \frac{2}{a^{3/2}} e^{-r/a_0}}$$

⊛ Angular Part for 1-s orbital:-

For 1s orbital ; $l=0$ and $m=0$.

$$Y(0,0) \propto \sin^0\theta \cos^{0-|0|}\theta \, e^{-i0\phi}$$

$$Y \propto 1$$

$$\boxed{Y(0,0) = N}$$

Note :- For any s-orbital whether 1s, 2s, 3s, 4s value of angular part will be constant.

Again Normalising angular part,

$$d\tau = r^2 dr \sin\theta d\theta d\phi$$

But for angular part,

$$\boxed{d\tau = \sin\theta d\theta d\phi} \quad \text{where} \quad \boxed{\begin{matrix} 0 < \theta < \pi \\ 0 < \phi < 2\pi \end{matrix}}$$

On normalisation we have,

$$\int Y^*_{(l,m)} Y_{(l,m)} d\tau = 1$$

$$\int_0^{2\pi} \int_0^{\pi} Y^*_{(0,0)} Y_{(0,0)} \sin\theta \, d\theta \, d\phi = 1$$

$\boxed{\because \; Y = N}$ — we have finded it earlier.

$$\int_0^{2\pi} \int_0^{\pi} N \cdot N \sin\theta \, d\theta \, d\phi = 1$$

$$N^2 \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi = 1$$

$$N^2 \left[-\cos\theta\right]_0^{\pi} \left[\phi\right]_0^{2\pi} = 1$$

$$N^2 \left[-\cos\pi + \cos 0^\circ\right]\left[2\pi - 0\right] = 1$$

$$N^2 \left[1 + 1\right]\left[2\pi\right] = 1$$

$$N^2 4\pi = 1$$

$$\boxed{N = \sqrt{\frac{1}{4\pi}}} = \text{Normalisation Constant for Angular Part.}$$

Hence,

$$\psi_{(r,\theta,\phi)} = R(n,l)\, Y(l,m)$$

$$\psi_{1s} = R(1,0)\, Y(0,0)$$

$$\psi_{1s} = \frac{2}{(a)^{3/2}} e^{-r/a} \times \frac{1}{2\sqrt{\pi}}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \times \frac{1}{a^{3/2}} \times e^{-r/a} \quad \Rightarrow \quad \boxed{\psi_{1s} = \frac{e^{-r/a}}{\sqrt{\pi}\,(a)^{3/2}}}$$

⊛ Significance of n, l, m :-

→ In calculation of Energy of nth orbit of Hydrogen and Hydrogen like atom.

$$\boxed{E_n = \frac{-13.6\, z^2}{n^2}} \text{ eV}$$

$$\boxed{E_n = \frac{-0.5\, z^2}{n^2}} \text{ a.m/Heatree}$$

$$\boxed{E_n = \frac{-R_H\, z^2}{n^2}} \text{ cm}^{-1} \qquad R_H = \text{Rydberg Constant.}$$

$$\boxed{E_n = \frac{-R_H\, h \cdot c \cdot z^2}{n^2}} \text{ Joule}$$

∵ In all the above forms of energy representation it is clear that energy for Hydrogenic species depends upon value of principal quantum number (n)

For H-atom

$$E_n = \frac{-13.6}{n^2} \text{ eV}$$

Hence for all the hydrogenic atoms / species, energy level spacing ↓ses on ↑ing value of n.

In PIB model energy level spacing used to ↑se with ↑ing 'n'.

$n=5$ ——— $E_5 = \frac{-13.6}{25} = -0.53$ eV

$n=4$ ——— $E_4 = \frac{-13.6}{16} = -0.81$ eV

$n=3$ ——— $E_3 = \frac{-13.6}{9} = -1.51$ eV

$n=2$ ——— $E_1 = \frac{-13.6}{4} = -3.4$ eV

$n=1$ ——— $E_1 = \frac{-13.6}{1} = -13.6$ eV

* Concept of Degeneracy :-

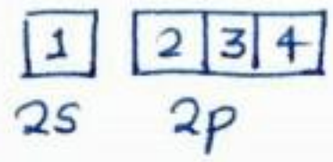
$$\boxed{\text{Degeneracy} = n^2}$$

as from above expressions energy depends only on 'n' for Hydrogenic species.

$$\boxed{\text{Spin including degeneracy} = 2n^2}$$

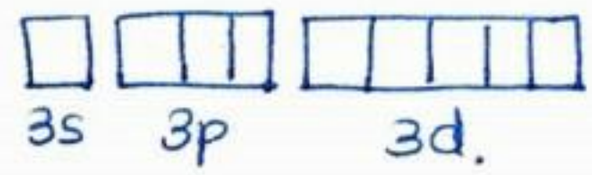
Example:- $n=1$ degeneracy $= 1$ Verification $=$ 1s

$n=2$ degeneracy $= 2^2 = 4$ Verification $=$ 2s , 2p



$n=3$ degeneracy $= 3^2 = 9$ Verification

3s, 3p, 3d ⇒



Example:- Calculate degeneracy for H-atom having energy,

$$E = \frac{-R_H}{25}$$

Compairing with,

$$E_n = \frac{-R_H Z^2}{n^2} \quad ; \text{ for H-atom } Z=1$$

$$\frac{-R_H}{n^2} = \frac{-R_H}{25} \Rightarrow \boxed{n^2 = 25}$$ Hence degeneracy is 25.

Example:- Calculate degeneracy for H-atom having energy,

$$E = -3.4\,eV$$

On Compairing we have,

$$E_n = \frac{-13.6 Z^2}{n^2} eV \; ; \text{ for H-atom } Z=1$$

$$\frac{-13.6}{n^2} = -3.4 \Rightarrow \boxed{n^2 = 4}$$ Hence degeneracy is 4.

Example:- $E_n = \dfrac{-e^2}{72\pi\varepsilon_0 a_0}$ for H-atom, calculate degeneracy.

Compairing with,

$$E = \frac{-e^2}{8\pi\varepsilon_0 a_0} \cdot \frac{Z^2}{n^2} \quad ; \text{ H-atom } Z=1$$

$$\frac{1}{n^2} \times \frac{-e^2}{8\pi\varepsilon_0 a_0} = \frac{-e^2}{72\pi\varepsilon_0 a_0}$$

$$\boxed{n^2 = 9}$$ Hence degeneracy is 9.

* Calculation of Total Orbital Angular Momentum :-

Orbital Angular Momentum,

$$\boxed{L_z = m\hbar}$$

Total Orbital Angular Momentum,

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

and we know that,

$$\boxed{L^2 = L_x^2 + L_y^2 + L_z^2}$$

GATE :- Calculate value of $L_x^2 + L_y^2 = ?$

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

$$L_x^2 + L_y^2 = L^2 - L_z^2$$

$$= l(l+1)\hbar^2 - m^2\hbar^2$$

$$\boxed{L_x^2 + L_y^2 = \hbar^2[l(l+1) - m^2]}$$

* Plotting graphs for different Probability :-

We know that,

$$\boxed{P = \int_a^b \psi^* \psi \, d\tau}$$

Since we are considering radial part only and for s-orbitals i.e. $m=0$, $l=0$ and $n=1, 2, 3 \ldots\ldots$

$$P = \int R_{nl} R^*_{nl} \, r^2 dr$$

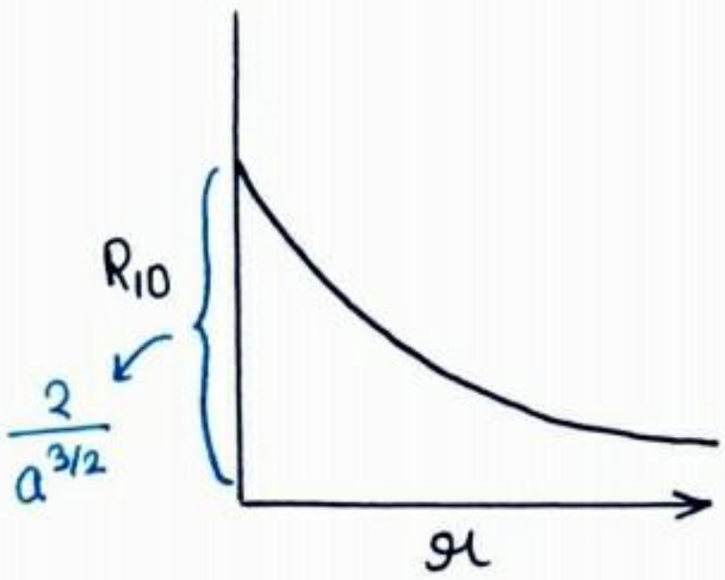
$$\boxed{P = \int R_{nl}^2 \, r^2 \, dr}$$

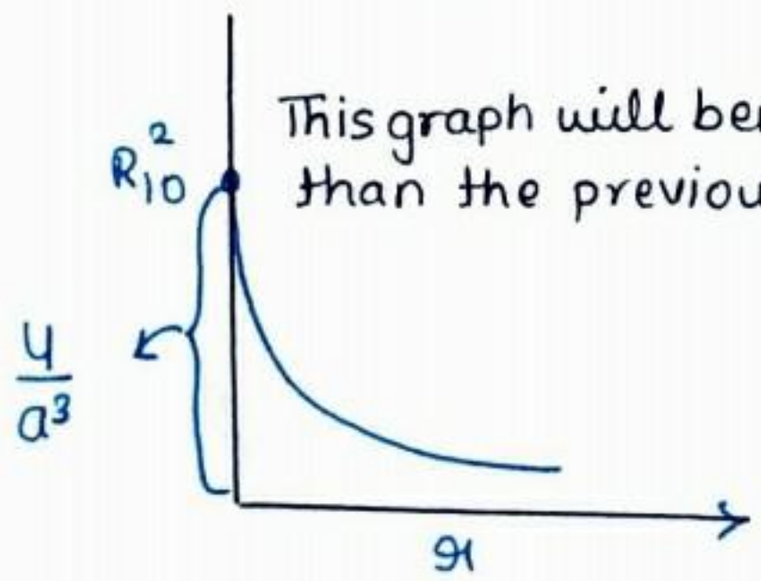
where $\boxed{R_{nl}^2 r^2 = \text{RDF (Radial Distributive function)}}$

For 1s :-

$$R_{10} = \frac{2}{(a)^{3/2}} e^{-r/a}$$

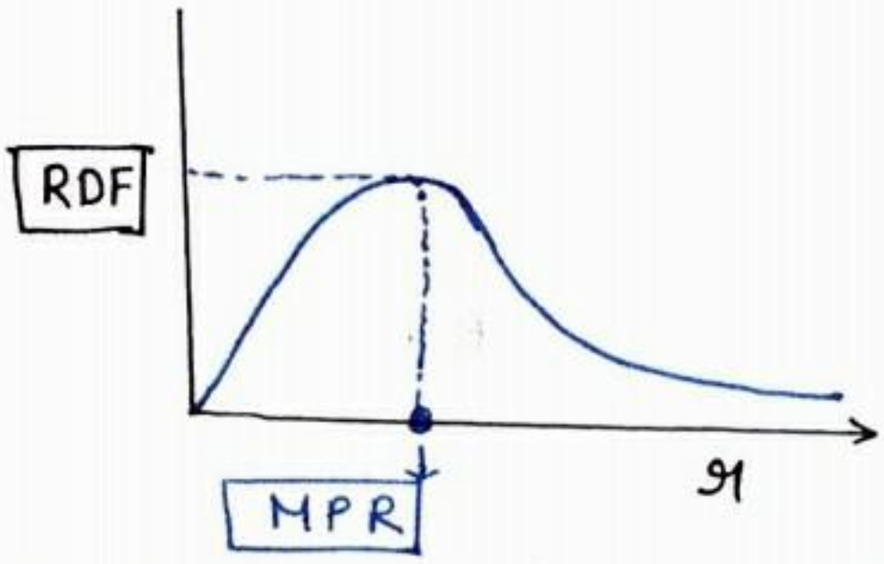
$$R_{10}^2 = \frac{4}{a^3} e^{-2r/a}$$





This graph will bend more than the previous one.

* R.D.F. for 1s = $r^2 R_{10}^2 = \frac{4}{3} e^{-2r/a} r^2$.



Most probable Radius = a_0

How to calculate MPR :-

By applying maxima-minima condition, we can find MPR.

$$\frac{d}{dr} RDF = 0 \quad \text{where} \quad RDF = \frac{4}{a^3} r^2 e^{-2r/a_0}$$

$$\Rightarrow \quad \frac{d}{dr}\left(\frac{4}{a^3} r^2 e^{-2r/a_0}\right) = 0$$

$$\frac{4}{a^3} \frac{d}{dr} r^2 e^{-2r/a_0} = 0$$

$$\frac{4}{a^3}\left\{ r^2\left(\frac{-2}{a}\right) e^{-2r/a} + e^{-2r/a} \cdot 2r \right\} = 0$$

$$\frac{4}{a^3} r e^{-2r/a} \left\{ -\frac{2r}{a} + 2 \right\} = 0$$

Now we have,

(i) $r = 0$ (boundary) → Not possible for MPR

(ii) $e^{-2r/a} = 0$, $r = \infty$ (boundary)

(iii) $-\frac{2r}{a} + 2 = 0$

$\boxed{r = a_0}$

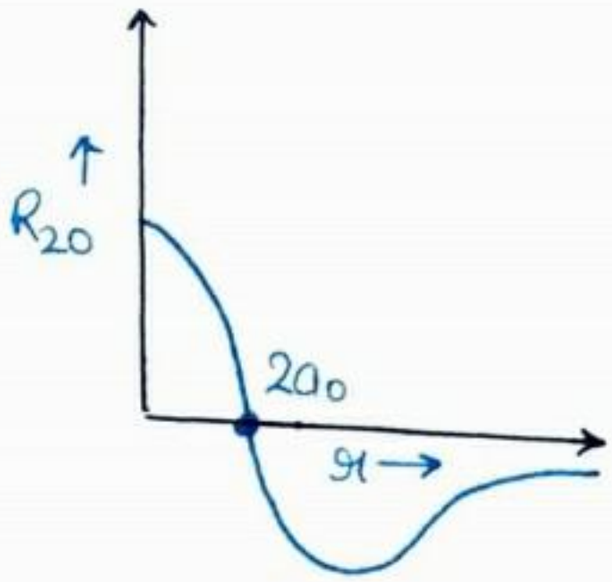
Hence MPR for 1s = a_0. → Bohr Radius.

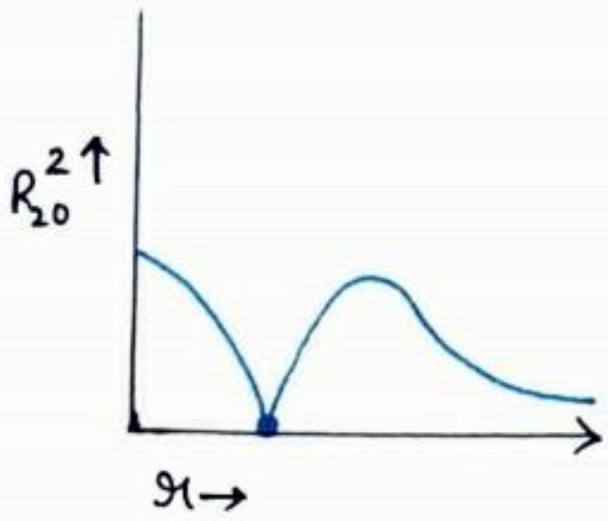
iii) For 2-s orbital :-

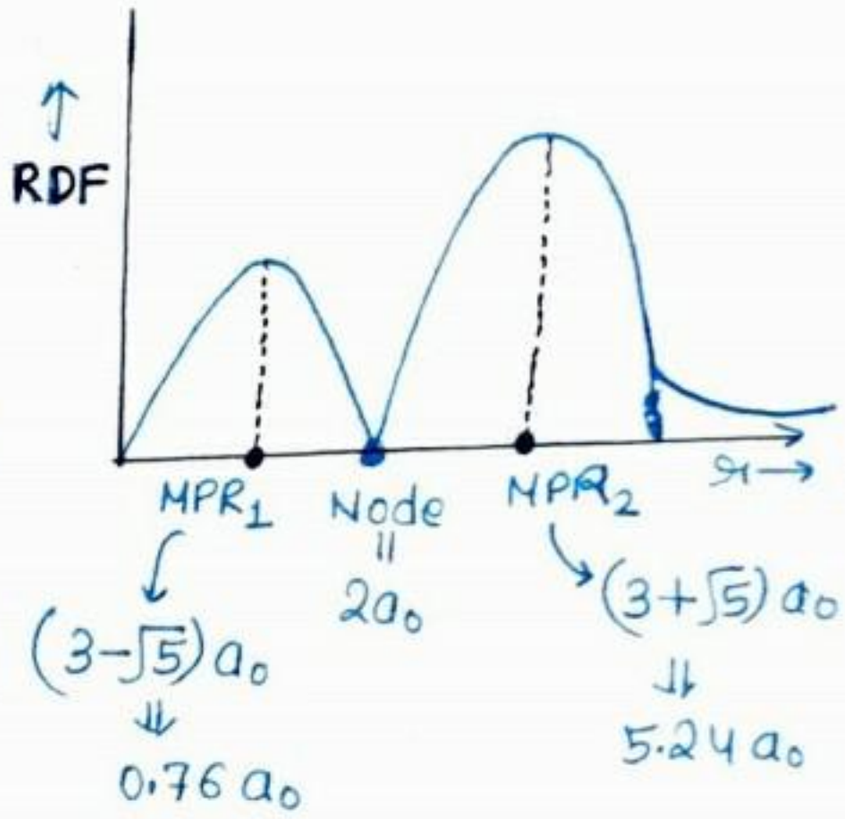
Radial Part ; $R_{20} = N\left\{2 - \frac{r}{a^0}\right\} e^{-r/2a_0}$

∵ Remember 1 radial node is also present at $r = 2a_0$. We have calculated it earlier.

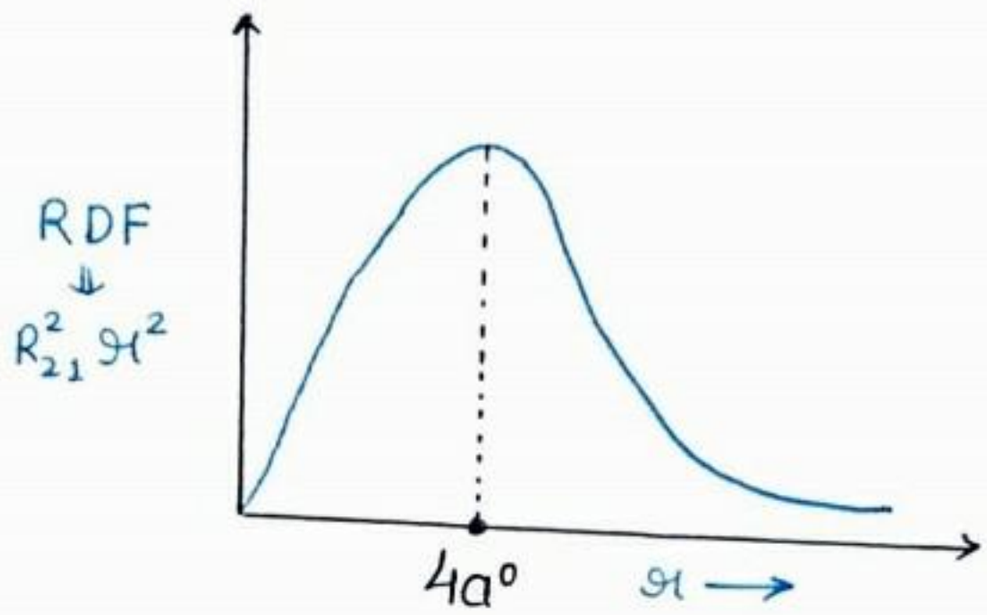
$RDF = R_{20}^2 r^2$







iii) For 2p orbital :-



Note : If on finding the wave function for a given orbital, our radial part comes out nodeless, then we have a direct formulae for the calculation of MPR.

$$\boxed{MPR = \frac{n^2 a_0}{Z}}$$

For H-atom ; $Z = 1$

- 1s $n-l-1 = 1-1 = 0$ Node $MPR = a_0$
- 2p $n-l-1 = 2-1-1 = 0$ Node $MPR = (2)^2 a_0 = 4a_0$
- 3d $n-l-1 = 3-2-1 = 0$ Node $MPR = (3)^2 a_0 = 9a_0$
- 4f $n-l-1 = 4-3-1 = 0$ Node $MPR = (4)^2 a_0 = 16\,a_0$

⊛ Average Value Results for H-atom :-

$\langle x \rangle = 0$ $\quad$ $\langle y \rangle = 0$ $\quad$ $\langle z \rangle = 0$

$$\langle r \rangle = \frac{a_0}{Z}\left[\frac{3}{2}n^2 - \frac{l(l+1)}{2}\right] \qquad \langle r^2 \rangle = \frac{n^2 a_0^2}{2Z^2}\left[5n^2 - 3l(l+1) + 1\right]$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0 n^2} \qquad \left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^3 n^3 \left(\frac{l+1}{2}\right)}$$

$$\langle K.E. \rangle = \frac{-\hbar^2}{2ma^2} \qquad \langle P.E. \rangle = \frac{-Ze^2}{4\pi\varepsilon_0 a^0}$$

Example :- Calculate $\langle r \rangle$ for 1s-orbital. H atom,

$Z = 1 \quad n = 1 \quad l = 0$

$$\langle r \rangle = \frac{a_0}{Z}\left[\frac{3}{2}n^2 - \frac{l(l+1)}{2}\right] = \frac{a_0}{1}\left[\frac{3}{2} \times 1 - 0\right]$$

$$\boxed{\langle r \rangle = 1.5\, a_0} \qquad \boxed{\langle r^2 \rangle = 3a_0^2} \qquad \boxed{\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0}}$$

* Uncertainity Concept

$$\boxed{\text{Uncertainity } (\Delta m) = \sqrt{\langle m^2 \rangle - \langle m \rangle^2}}$$

Example :- Find uncertainity in 'r' for 1s-orbital in H-atom.

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

We have already calculated $\langle r \rangle$ and $\langle r^2 \rangle$

$$\Delta r = \sqrt{3a_0^2 - \left(\frac{3}{2}a_0\right)^2}$$

$$\Delta r = \sqrt{3a_0^2 - \frac{9}{4}a_0^2} = \sqrt{\left(\frac{12-9}{4}\right)a_0}$$

$$\Delta r = \sqrt{\frac{3a_0^2}{4}}$$

$$\boxed{\Delta r = \frac{\sqrt{3}}{2}a_0}$$

For H-atom :-

$$\langle P_r \rangle = 0$$

$$\langle P_r^2 \rangle = \frac{\hbar^2}{a^2}.$$

$\because$ $\langle K.E. \rangle = \frac{\hbar^2}{2ma^2}$ —(i)

and $K.E. = \frac{P_r^2}{2m}$ —(ii)

from (i) and (ii) $\frac{P_r^2}{2m} = \frac{\hbar^2}{2ma^2}$

$$\boxed{P_r^2 = \frac{\hbar^2}{a^2}}$$

Uncertainity in Momentum,

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

$$\Delta P_r = \sqrt{\frac{\hbar^2}{a^2} - 0} = \frac{\hbar}{a}$$

$$\boxed{\Delta P_r = \frac{\hbar}{a}}$$

* Some Important Integrations:-

(i) $\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{(\alpha)^{n+1}} = \frac{n!}{(\alpha)^{n+1}}$

(ii) $\int_0^\pi \sin^3\theta \, d\theta = \frac{4}{3}$

(iii) $\int_0^\pi \cos^2\theta \sin\theta \, d\theta = \frac{2}{3}$

(iv) $\int_0^\pi \sin\theta \cos\theta \, d\theta = 0$

These integrations will be required during normalisation of wave func^n.

Example :- Find whether the wave function,

$$\psi = e^{-r} \cos\theta \quad \text{is normalised?}$$

Sol^n:- We know that for Normalisation;

$$\int \psi^* \psi \, d\tau = 1$$

$\Rightarrow$ $\int e^{-r} \cos\theta \cdot e^{-r} \cos\theta \, d\tau$

for H-atom ; $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$.

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-2r}\cos^2\theta\, r^2 dr\, d\theta \sin\theta\, d\phi$$

$$= \int_0^{\infty} e^{-2r}\cdot r^2 dr \int_0^{\pi} \sin\theta \cos^2\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{2!}{(2)^3} \times \frac{2}{3} \times 2\pi$$

$$= \frac{\pi}{3} \qquad \because \int \psi^*\psi\, d\tau \neq 1$$

Hence given wave func^n is not Normalised.

Normalisation Constant $= \sqrt{\frac{3}{\pi}}$

Hence,

Normalised Wave Function $= \sqrt{\frac{3}{\pi}}\, e^{-r}\cos\theta$.

Example :- Find whether wave function,

$\psi = e^{-r}\sin\theta$ is normalised ?

Sol^n, Again we will have.

$$\int_0^{\infty} e^{-2r} r^2 dr \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{2!}{2^3} \times \frac{4}{3} \times 2\pi$$

$$= \frac{2\pi}{3}$$; Again wave function is not normalised.

$N.C. = \sqrt{\frac{3}{2\pi}}$

$$\boxed{\psi_{new} = \sqrt{\frac{3}{2\pi}}\, e^{-r}\sin\theta}$$

⊛ Average Values in case of PIB Model :-

We know that in PIB model average values are calculated by,

$$\langle x \rangle = \int \psi^* x \psi \, dx.$$

Some Results :- $\langle x \rangle = \frac{l}{2}$ and $\langle x^2 \rangle = \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}$

Uncertainity in Position :-

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

$$= \sqrt{\frac{l^2}{3} - \frac{l^2}{2n^2\pi^2} - \frac{l^2}{4}} = \sqrt{\frac{l^2}{3} - \frac{l^2}{4} - \frac{l^2}{2n^2\pi^2}}$$

$$\Delta x = \sqrt{\frac{l^2}{12} - \frac{l^2}{2n^2\pi^2}}$$

$$\boxed{\Delta x = l\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}}$$

for ground state i.e $n=1$

$$\boxed{\Delta x = l\sqrt{\frac{1}{12} - \frac{1}{2\pi^2}}}$$

Results on Momentum :-

$$\langle P_x \rangle = 0 \quad \text{and} \quad \langle P_x^2 \rangle = \frac{n^2h^2}{4l^2}$$

In PIB model,

$$\langle K.E. \rangle = \frac{n^2h^2}{8ml^2}$$

and

$$\langle K.E. \rangle = \frac{P_x^2}{2m}$$

$$\Rightarrow P_x^2 = 2m \times \frac{n^2h^2}{8ml^2} = \frac{n^2h^2}{4l^2}$$

$$\boxed{P_x^2 = \frac{n^2h^2}{4l^2}}$$

Uncertainity in Momentum :-

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

$$= \sqrt{\frac{n^2h^2}{4l^2} - (0)^2}$$

$$\boxed{\Delta P_x = \frac{nh}{2l}}$$

SIMPLE HARMONIC OSCILLATOR

We have to study SHO in 3-parts,

1-D SHO 2-DSHO 3-DSHO

1-D SHO :-

We know that Schrodinger equation is given by:

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}[E-V]\psi = 0} \quad \text{and} \quad \boxed{V = \frac{1}{2}Kx^2}$$

$$\Rightarrow \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}Kx^2\right]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \left\{\frac{2mE}{\hbar^2} - \frac{mKx^2}{\hbar^2}\right\}\psi = 0$$

Let $\boxed{\alpha = \frac{2mE}{\hbar^2}}$ and $\boxed{\beta = \frac{mK}{\hbar^2}}$

$$\frac{d^2\psi}{dx^2} + \left\{\alpha - \beta^2x^2\right\}\psi = 0 \quad \text{——— (i)}$$

On solving equation (i), we have our final expression.

$$\boxed{\psi_n(\xi) = \left(\frac{1}{2^n n!}\right)^{1/2}\left(\frac{\beta}{\pi}\right)^{1/4} H_n(\xi)\, e^{-\frac{\xi^2}{2}}}$$

In SHO, $n = 0, 1, 2, 3, \ldots\ldots$

and $\boxed{(\xi) = \sqrt{\beta}\,x}$

when,

$n=0$ $H_0(\xi) = 1$

$n=1$ $H_1(\xi) = 2\xi_1 = 2\sqrt{\beta}\,x$

$n=2$ $H_2(\xi) = 4\xi_1^2 - 2 = 4\beta x^2 - 2.$

Note:-

When, $H_{n\,even} = (x)^{even}$

$H_{n\,odd} = (x)^{odd}$

* Now for ground state, $n=0$.

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

$$\boxed{\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}}$$

Hence we can reduce eq^n for wave func^n as,

$$\boxed{\psi_n = N H_n(\xi) e^{-\frac{\xi^2}{2}}}$$

In terms of 'x'

$$\boxed{\psi_n = N H_n(x) e^{-\frac{\beta x^2}{2}}}$$

n=even $\quad$ n=odd

x^{even} $\quad$ x^{odd}

N= Normalisation constant.

<u>Now,</u>

SHO in ground state i.e. $n=0$.

$$\boxed{\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}}$$

when <u>$n=1$</u>;

$$\boxed{\psi_1 = N \cdot x\, e^{-\frac{\beta x^2}{2}}}$$

* Energy Calculation:-

In order to evaluate the energy expression in SHO, we will use the relation,

$$\boxed{\frac{\alpha}{\beta} = (2n+1)}$$

where $\alpha = \dfrac{2mE}{\hbar^2}$

$$\beta = \frac{\sqrt{mK}}{\hbar^2}$$

$$\frac{\frac{2mE}{\hbar^2}}{\frac{\sqrt{mK}}{\hbar}} = (2n+1) \Rightarrow \frac{2\sqrt{m}E}{\hbar\sqrt{K}} = 2n+1.$$

$$E = \frac{(2n+1)}{\sqrt{m}\cdot 2} \times \hbar\sqrt{K} \Rightarrow E = \frac{(n+1/2)}{\sqrt{m}} \hbar\sqrt{K}$$

$$\boxed{E = \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{K}{m}}}$$ and $\hbar = \frac{h}{2\pi}$

$$\boxed{E = \left(n+\frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{K}{m}}}$$ and from spectroscopy,

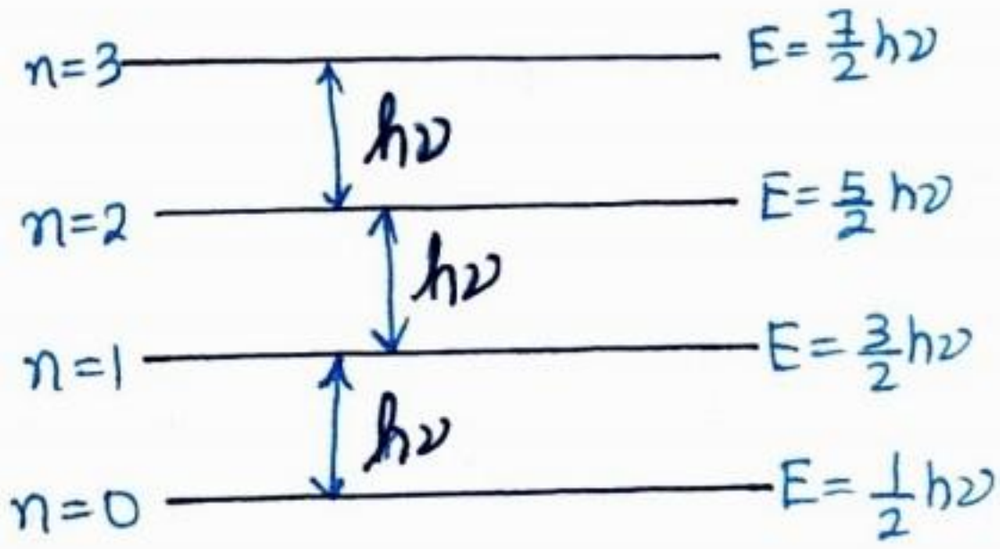
$$\nu(\text{frequency}) = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$$

$$\boxed{E = \left(n+\frac{1}{2}\right)h\nu} \longrightarrow \star$$

$\star$ is the required expression for the energy in 1-D SHO.

* Energy Levels:

In vibrational SHO, spacing b/w energy level is constant.



* Normalising the wave function:-

Limits used during integration $[-\infty, \infty]$

We will use integration of the type,

$$\int_{-\infty}^{\infty} x^n e^{-\beta x^2}\, dx \begin{cases} \xrightarrow{n=\text{even}} \dfrac{\Gamma\left(\frac{n+1}{2}\right)}{\beta^{\frac{n+1}{2}}} \\ \xrightarrow{n=\text{odd}} 0 \end{cases}$$

Note: $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$

$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\times\frac{1}{2}\sqrt{\pi}$

$\Gamma\left(\frac{7}{2}\right) = \frac{5}{2}\times\frac{3}{2}\times\frac{1}{2}\sqrt{\pi}$

Now; Wave function for SHO is given by,

$$\psi = Ne^{-\frac{\beta x^2}{2}}$$

We know that condition of normalisation is given by;

$$\int \psi^* \psi \, d\tau = 1$$

$$\int_{-\infty}^{\infty} Ne^{-\beta\frac{x^2}{2}} \cdot Ne^{-\beta\frac{x^2}{2}} \, dx = 1$$

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

$$N^2 \int_{-\infty}^{\infty} (x)^0 e^{-\beta x^2} dx = 1$$

Comparing above integration with

$$\int_{-\infty}^{\infty} x^n e^{-\beta x^2} dx = \frac{\Gamma\frac{n+1}{2}}{\beta^{\frac{n+1}{2}}}$$

We have, $n=0$ (even)

$$N^2 \int_{-\infty}^{\infty} (x)^0 e^{-\beta x^2} = 1$$

$$N^2 \frac{\Gamma\frac{0+1}{2}}{\beta^{0+1/2}} = 1$$

$$N^2 \frac{\Gamma\frac{1}{2}}{\beta^{1/2}} = 1$$

$$N^2 \sqrt{\frac{\pi}{\beta}} = 1$$

$$N^2 = \sqrt{\frac{\beta}{\pi}}$$

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

Hence our new wave func^n becomes.

$$\boxed{\psi(x) = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta\frac{x^2}{2}}}$$

* Plotting Graph :-

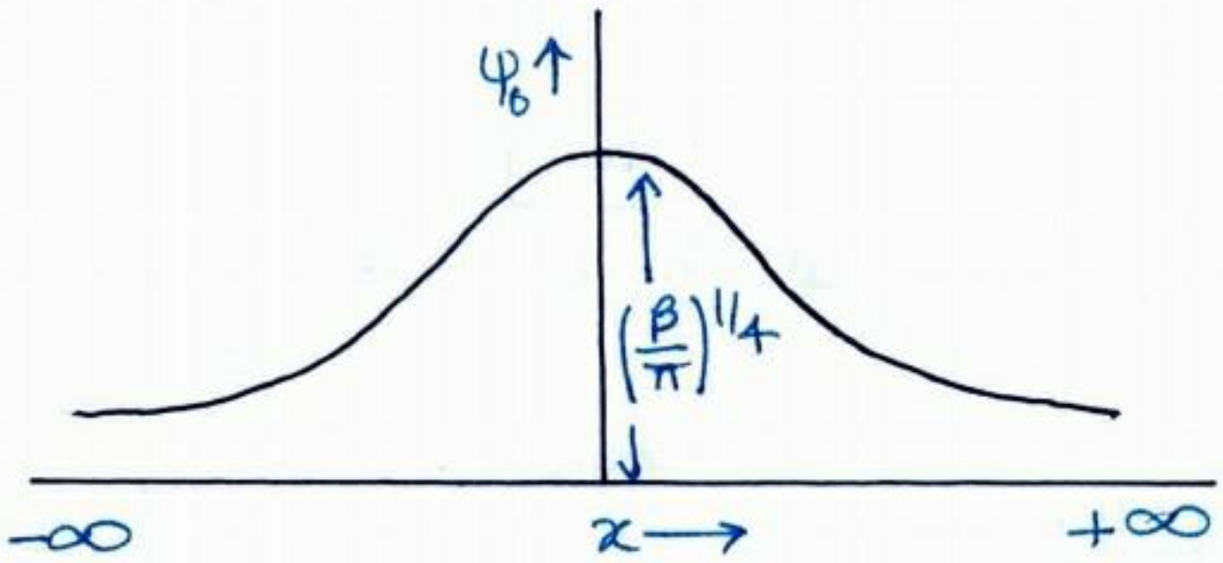
Boundary Conditions = $(-\infty, \infty)$

$$\boxed{\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}}$$

$\left.\begin{array}{l} x = -\infty \\ \text{and} \\ x = \infty \end{array}\right\} \rightarrow \psi_0 = 0$ as $e^{-\infty} = 0$

and

at $x=0$ $\quad \psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4}$



Hence,

max value of $\psi(x)$ is at $x=0$.

<u>Now,</u>

$$\psi(x) = N e^{-\beta\frac{x^2}{2}} \quad \text{and} \quad \psi(-x) = N e^{-\beta\frac{x^2}{2}}$$

$$\Rightarrow \boxed{\psi(x) = \psi(-x)}$$

Hence wave function $\psi_0(x)$ for SHO at $n=0$ (ground state) is a "Symmetric Wave Function".

<u>Now;</u> $\psi_1(x)$ for SHO ie. $n=1$

$$\psi_1 = \underbrace{\left(\frac{\beta}{\pi}\right)^{1/4}\sqrt{2\beta}}_{=N}\, x\, e^{-\beta\frac{x^2}{2}}$$

$$\boxed{\psi_1 = N x e^{-\beta\frac{x^2}{2}}}$$

at Boundary $[-\infty, \infty]$

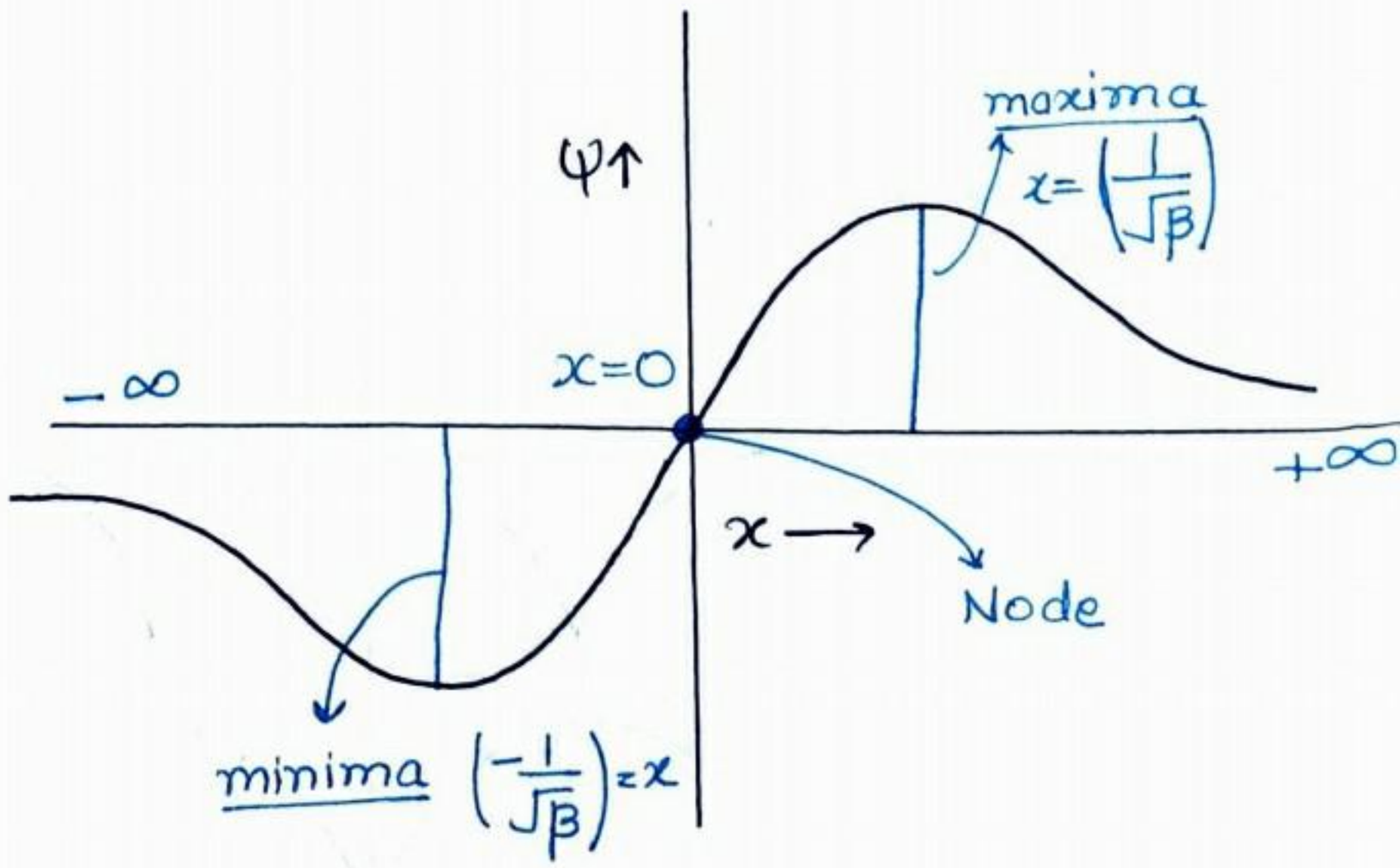
$x = \infty$ or $-\infty$

$e^{-\infty} = 0$

$$\Rightarrow \boxed{\psi_1(x) = 0}$$

at $x=0$

$$\boxed{\psi_1(x) = 0}$$



$\because$ $x=0$ is not boundary condition hence we will have 1 node.

Now,

$$\psi_1(x) = N x e^{-\frac{\beta x^2}{2}} \quad \text{and} \quad \psi_1(-x) = -N x e^{-\beta \frac{x^2}{2}}$$

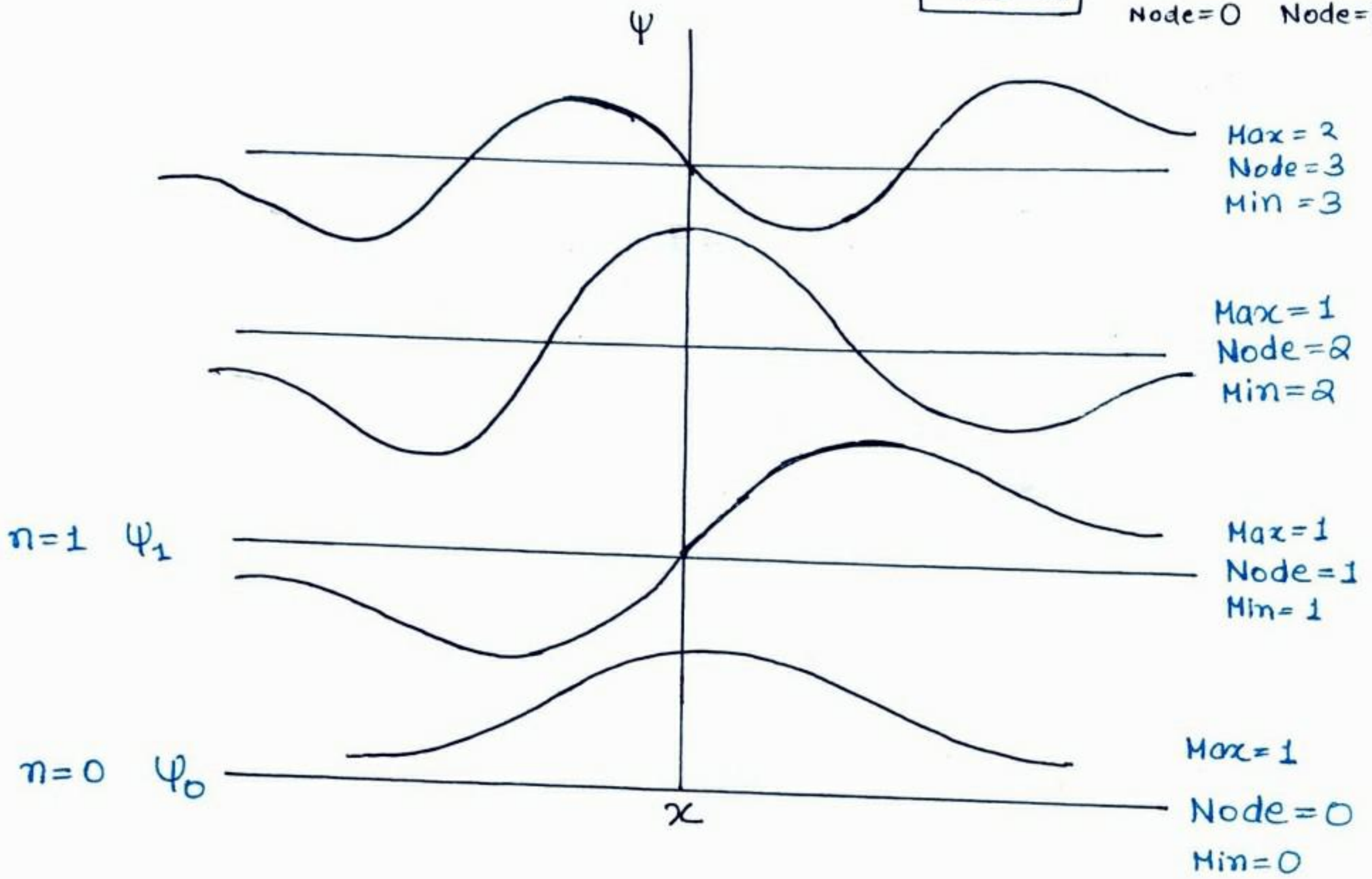
Hence, $\boxed{\psi_1(x) = -\psi_1(x)}$

Hence for $n=1$, SHO will have Antisymmetric function.

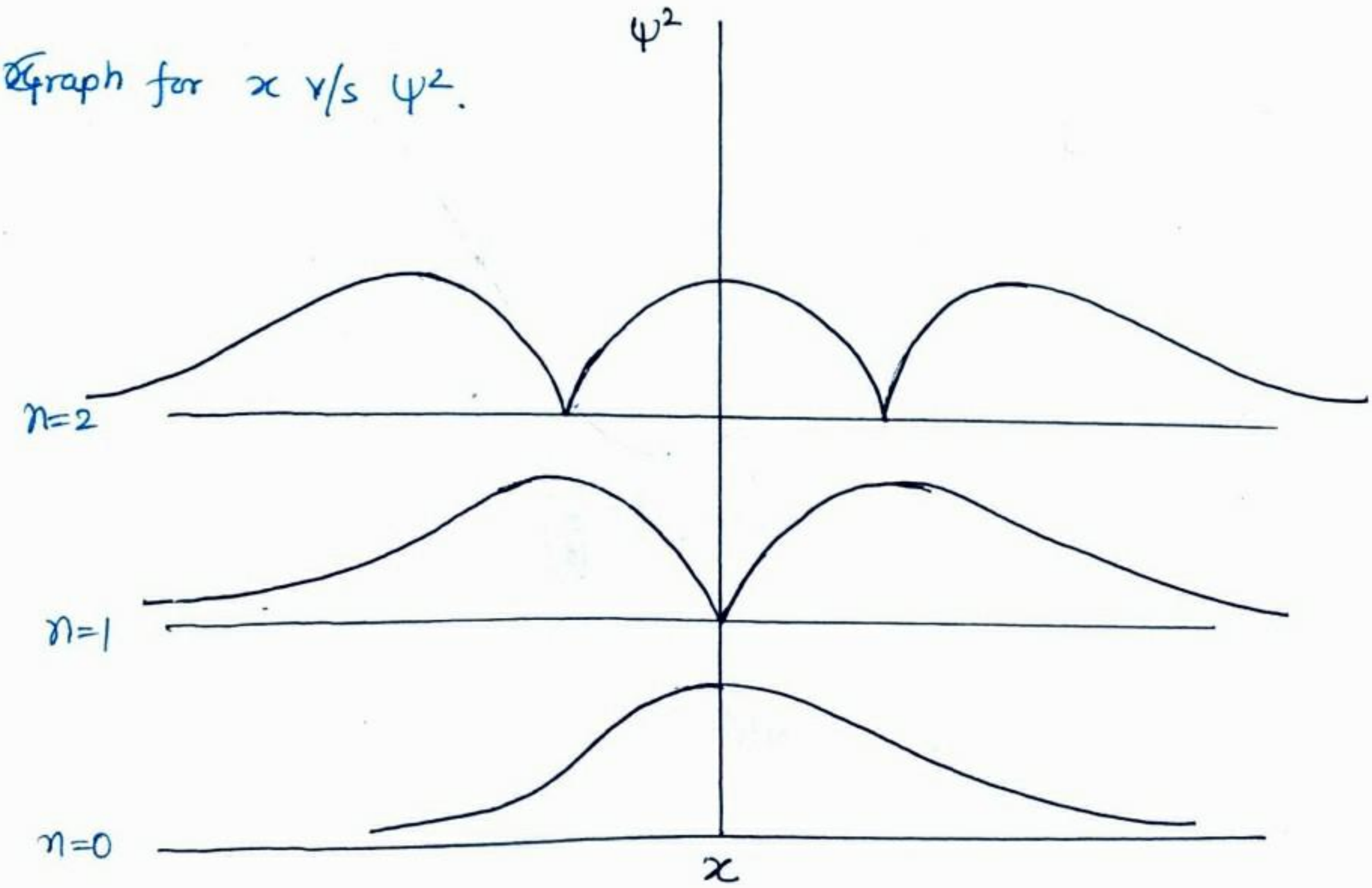
* Combining All Graphs :-

Hence, General formulae for Node,

$\boxed{\text{Node} = n}$ $n=0$ Node $=0$ $n=1$ Node $=1$.



Graph for x v/s ψ^2.



* Average Value Result :-

(i) $\langle x \rangle = 0$ (ii) $\langle P_x \rangle = 0$ (iii) $\langle x^2 \rangle = \left(n+\frac{1}{2}\right)\frac{1}{\beta}$

(iv) $\langle P_x^2 \rangle = \left(n+\frac{1}{2}\right)\beta\hbar^2$

{ Note $\underbrace{\langle x \rangle = 0 \text{ and } \langle P_x \rangle = 0}_{\text{for all values of } (n) \text{ is SHO}}$ }

Example :- Find $\langle x \rangle$ for $n=0$ in SHO.

Sol^n $\langle x \rangle = 0$ $\langle P_x \rangle = 0$ $\langle x^2 \rangle = \frac{1}{2\beta}$ $\langle P_x^2 \rangle = \frac{1}{2}\beta\hbar^2$

Example :- Calculate uncertainity in position in ground state for SHO.

Sol^n: Ground state $\Rightarrow n=0$.

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

$$\Delta x = \sqrt{\frac{1}{\beta} - 0} \Rightarrow \boxed{\Delta x = \frac{1}{\sqrt{\beta}}} \text{ and } \boxed{\beta = \frac{\sqrt{mk}}{\hbar}}$$

Example :- Calculate uncertainity in momentum.

$$\Delta P_x = \sqrt{\langle P_x^2 \rangle - \langle P_x \rangle^2} = \sqrt{\frac{1}{2}\beta\hbar^2 - 0} = \sqrt{\frac{\beta}{2}}\hbar$$

$$\boxed{\Delta P_x = \sqrt{\frac{\beta}{2}}\hbar}$$

* Comparison between classical and quantum mechanical SHO.

→ From the Graph for ψ v/s x and $|\psi^2|$ v/s x, it is clear that particle spend more time at eqb ($x=0$) in the ground state because function is maximum at ($x=0$).

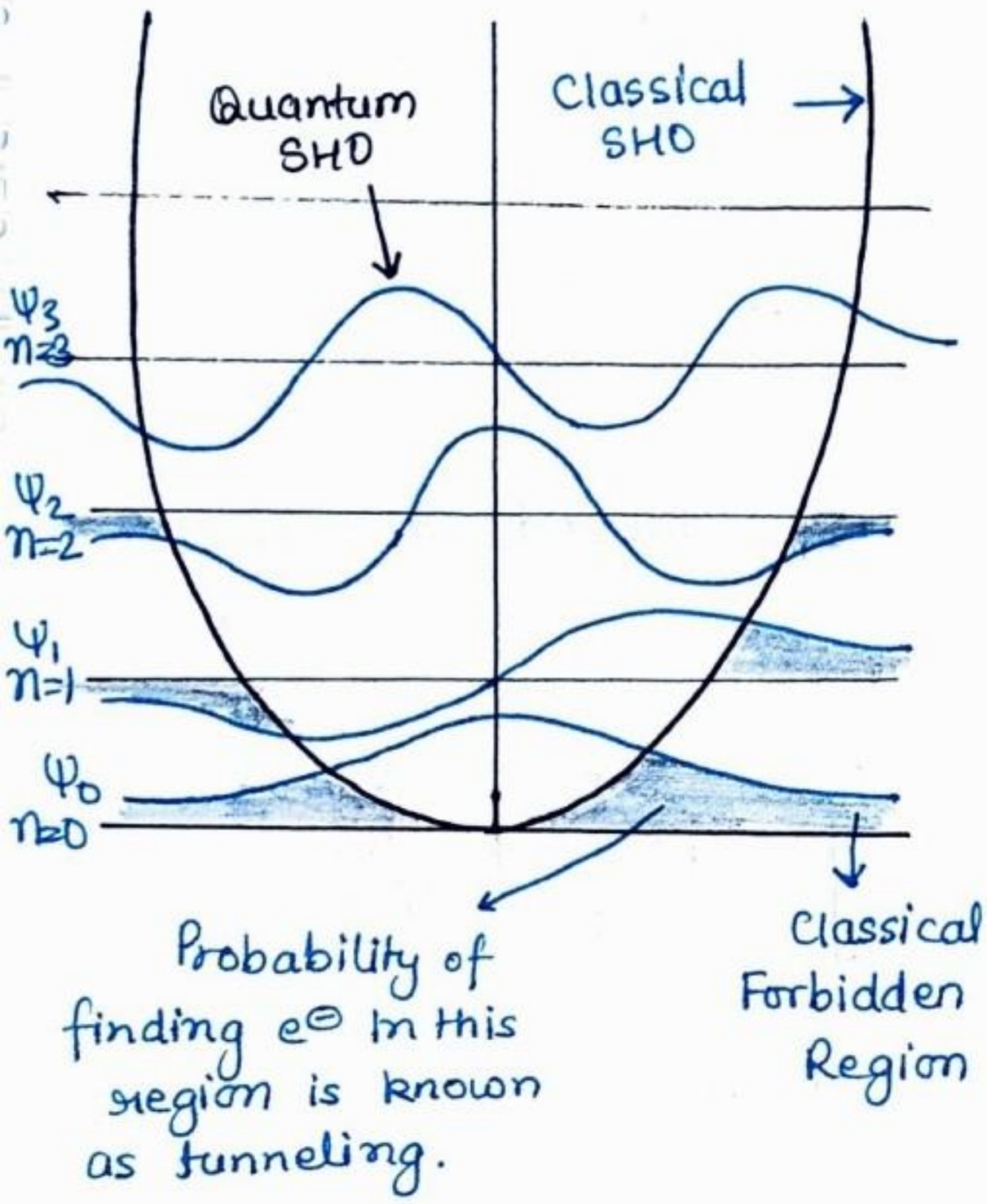
→ But in classical SHO, particle spend minimum time at eqb, $x=0$.

→ In classical, K.E. or P.E. can be zero but in quantum neither K.E. can be zero nor P.E.

→ In classical SHO particle have finite amplitude vibration but in quantum the particle can be found anywhere from $-\infty$ to $+\infty$. Therefore particle can also be found in classical forbidden region and this phenomenae is known as tunneling.

→ Tunneling decreases as value of (n) increases.

Bohr's Correspondance Principle :- At higher value of 'n', quantum mechanics approaches to classical mechanics.



⊛ 2-D SHO :-

It is classified into two categories;

(1) Isotropic $\Rightarrow \nu_x = \nu_y = \nu$ i.e. ν_x = frequency along 'x' axis.
ν_y = frequency along 'y' axis.

(2) Anisotropic $\Rightarrow \nu_x \neq \nu_y$.

∵ Wave functions are multiplicative in nature.

$$\boxed{\psi = \psi_x \cdot \psi_y}$$

For Anisotropic

and $$\psi_{(x,y)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta y^2}{2}}$$

also for isotropic

∵ Energy is additive in nature.

$$\boxed{E_{2D} = \left(n_x + \frac{1}{2}\right) h\nu_x + \left(n_y + \frac{1}{2}\right) h\nu_y}$$ = For Anisotropic.

<u>For isotropic</u>; $\nu_x = \nu_y = \nu$.

$$E_{2D} = \left(n_x + \frac{1}{2}\right) h\nu + \left(n_y + \frac{1}{2}\right) h\nu$$

$$E_{2D} = \left(n_x + n_y + \frac{1}{2} + \frac{1}{2}\right) h\nu$$

$$\boxed{E_{2D} = (n_x + n_y + 1) h\nu}$$

* Concept of degeneracy :-

We know that,

$$\boxed{E_{2D} = (n_x + n_y + 1) h\nu.}$$

(1,2)	(2,1)	(3,0)	(0,3)	$E = 4h\nu$	$g=4$
(1,1)	(2,0)	(0,2)		$E = 3h\nu$	$g=3$
(1,0)	(0,1)			$E = 2h\nu$	$g=2$
(0,0)				$E = h\nu$	$g=1$

* <u>Trick</u>;

If we have Energy in form of, $E = nh\nu$

Then, $\boxed{g = n}$ → degeneracy.

⊛ 3-D SHO :-

These are also classified into two categories;

(1) Anisotropic (2) Isotropic.

∵ Functions are multiplicative in nature.

$$\boxed{\psi_{(x,y,z)} = \psi_{(x)} \cdot \psi_{(y)} \cdot \psi_{(z)}}$$

$$\boxed{\psi_{(x,y,z)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta y^2}{2}} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta z^2}{2}}}$$

For isotropic 3-D SHO :-

$$E_{3D} = E_{(n_x, n_y, n_z)} = \left(n_x + \frac{1}{2}\right)h\nu + \left(n_y + \frac{1}{2}\right)h\nu + \left(n_z + \frac{1}{2}\right)h\nu$$

$$\boxed{E_{3D} = \left(n_x + n_y + n_z + \frac{3}{2}\right)h\nu}$$

* Concept of Degeneracy :-

$$E_{3D} = \left(n_x + n_y + n_z + \frac{3}{2}\right)h\nu$$

(1,0,1)	(1,1,0)	(0,1,1)	(2,0,0)	(0,2,0)	(0,0,2)	$E = \frac{7}{2}h\nu$ $g=6$
	(1,0,0)	(0,1,0)	(0,0,1)			$E = \frac{5}{2}h\nu$ $g=3$
		(0,0,0)				$E = \frac{3}{2}h\nu$ $g=1$

General formulae for Degeneracy :-

$$\boxed{g = \frac{(n+1)(n+2)}{2}} \quad \text{where} \quad \boxed{n = n_x + n_y + n_z}$$

Ex :) Calculate 'g' for $E = \frac{7}{2}h\nu$

$$E = \frac{7}{2}h\nu \quad \text{and} \quad E = \left(\underbrace{n_x + n_y + n_z}_{} + \frac{3}{2}\right)h\nu$$

$$E = \left(n + \frac{3}{2}\right)h\nu$$

$$\Rightarrow \quad \frac{7}{2}h\nu = \left(n + \frac{3}{2}\right)h\nu$$

$$n = \frac{7}{2} - \frac{3}{2} = 2$$

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

$$g = \frac{12}{2}$$

$$\boxed{g = 6} \text{ Ans.}$$

Ex :- Calculate 'g' for $E = \frac{13}{2}h\nu$

$$E = \frac{13}{2}h\nu \quad \text{and} \quad E = \left(n + \frac{3}{2}\right)h\nu$$

$$n = \frac{13}{2} - \frac{3}{2}$$

$$\boxed{n = 5}$$

$$g = \frac{(5+1)(5+2)}{2}$$

$$g = \frac{42}{2} = 21 \text{ Ans}$$

:- Rigid Rotor :-

Rigid rotor is proposed corresponding to study of rotational motion of microscopic particle.

$$\text{Rigid Rotor} = \{ \overset{\text{fixed}}{r}, \theta, \underset{[0, 2\pi]}{\phi} \}$$

and Hamiltonian operator (Energy operator in Quantum) $\hat{H}$ is given by,

$$\boxed{\hat{H} = \frac{L^2}{2I}}$$

<u>Now</u>;

$$\hat{H}\psi = \frac{L^2}{2I}\psi$$

$$\hat{H}\psi = \frac{L(L+1)}{2I}\hbar^2\psi \quad \Rightarrow \quad \boxed{E = \frac{L(L+1)\hbar^2}{2I}}$$

Here we replace 'L' with 'J'

$$\boxed{E = \frac{J(J+1)\hbar^2}{2I}}$$ where $J = 0, 1, 2, 3, \ldots\ldots$

Rotational Quantum Number.

$$E_J = \frac{J(J+1)}{2I}\left(\frac{h}{2\pi}\right)^2$$

$$E_J = J(J+1)\frac{h^2}{8\pi I^2}$$

$$\boxed{E_J = BJ(J+1)}$$ where $$\boxed{B = \frac{h^2}{8\pi I^2}}$$

* Concept of degeneracy :-

$$\boxed{g_n = 2J+1}$$

Now, $E = \frac{10\hbar^2}{I}$

Compairing with $E = \frac{J(J+1)\hbar^2}{2I}$ we have.

$$\frac{10\hbar^2}{I} = \frac{J(J+1)\hbar^2}{2I}$$

$$\Rightarrow \quad J^2 + J - 20 = 0$$

$$\Rightarrow \quad J^2 + 5J - 4J - 20 = 0$$

$$J(J+5) - 4(J+5) = 0$$

$$(J-4)(J+5) = 0$$

$$\boxed{J = 4 \text{ and } -5}$$

$\because$ J starts forom 0, 1, 2, 3.

$\Rightarrow \boxed{J \neq -5}$

Hence, $J = 4$.

degeneracy,

$$g_n = 2J + 1$$

$$g_n = 2 \times 4 + 1$$

$$\boxed{g_n = 9}$$

* Normalisation of Wave Function.

$$\psi = N e^{im\phi}$$

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

or

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

On applying condⁿ of normalisation we have,

$$\int \psi^* \psi \, d\tau = 1$$

$$\int_0^{2\pi} N e^{im\phi} \cdot N e^{-im\phi} \, d\phi = 1$$

$$\int_0^{2\pi} N^2 \, d\phi = 1$$

$$N^2 \int_0^{2\pi} d\phi = 1$$

$$N^2 \left[\phi\right]_0^{2\pi} = 1$$

$$2\pi N^2 = 1$$

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

Hence normalised wave function will be given by,

$$\boxed{\psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}}$$

* Comparison of Energy in different systems.

For Box; $E_n = \frac{n^2 h^2}{8ml^2}$ and $n = 1, 2, 3, 4, \ldots\ldots$

H-atom; $E_n = \frac{-13.6 Z^2}{n^2}$ and $n = 1, 2, 3, 4, \ldots\ldots$

SHO; $E = \left(n + \frac{1}{2}\right) h\nu$ and $n = 0, 1, 2, 3, \ldots\ldots$

Rigid Rotor; $E = \frac{J(J+1)\hbar^2}{2J}$ and $J = 0, 1, 2, 3, \ldots$

Only rigid rotor is the system having energy $(E) = 0$ in its ground state.

For Rigid Rotors and PIB Model $\Big\}$ $V = 0$ inside

For H-atom and SHO $\Big\}$ $V \neq 0$.

* Virial Theorem :-

$$\boxed{2T = BV}$$

where,

T = Kinetic Energy

V = Potential Energy

B = Fixed Value (Depends upon type of system).

(1) For SHO

$B = 2$.

$2T = 2V$

$T = V$

$\Rightarrow$ Kinetic Energy = Potential energy.

Energy of a SHO is given by,

$$E = \left(n + \frac{1}{2}\right) h\nu$$

Now,

Total Energy = Kinetic Energy + Potential Energy

and for SHO, $\boxed{KE = PE}$

$$T.E. = K.E. + K.E$$

$$KE = PE = \frac{T.E.}{2}$$

$$\Rightarrow \boxed{K.E. = \frac{\left(n+\frac{1}{2}\right)h\nu}{2}} \quad \text{and} \quad \boxed{P.E. = \frac{\left(n+\frac{1}{2}\right)h\nu}{2}}$$

<u>In case of H-atom :-</u>

For H-atom, $B = -1$.

$$2T = BV$$

$$\boxed{2T = -V} \Rightarrow \quad 2\,K.E. = -PE.$$

<u>Now;</u>

$$E = KE + PE$$

$$\boxed{E = -KE} \quad \text{and} \quad \boxed{E = \frac{PE}{2}}$$

Wave function:- A function satisfies a wave equation, and describe the properties of wave.

Heisenberg's Uncertinity Principle:-

According to this principal, "It is impossible to make simultaneously, the exact determination of the velocity of a particle and also its position."

The uncertainties in the determination of these two quantities very inversly so that, if one is determined fairly accurately, the other must be correspondingly less accurate.

If p and x represent two conjugate variables, such as momentum and position of any particle the product of the uncertainties Δp and Δx in the determination of their respective values is approximately equal to the plonck's constant. Thus,

$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$$

The Schrodinger Wave Equation :- full notes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

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The Schrodinger Wave Equation :-

According to the wave equation,

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{1}{u^2} \cdot \frac{\partial^2 \omega}{\partial t^2} \quad \text{--- (1)}$$

Where u is the velocity of propagation of the waves, sometimes called the phase velocity. The value of ω is depends upon the two variables x and t.

Thus ω may be expressed in the form.

$$\omega = f(x) \cdot g(t) \quad \text{--- (2)}$$

Where $f(x)$ is a function of co-ordinates x only, while $g(t)$ is a function of time t only.

$$g(t) = A \sin(2\pi \nu t) \quad \text{--- (3)}$$

Where ν is the vibrational frequency and A is constant which is known as the maximum amplitude. The equation for ω may then be written as.

$$\omega = f(x)\, A \sin(2\pi \nu t) \quad \text{--- (4)}$$

Diff. eq^n (4) w. r. to 't'

$$\frac{d\omega}{\partial t} = f(x)\, A \cos(2\pi \nu t) \cdot 2\pi \nu$$

diff. Again

$$\frac{\partial^2 \omega}{\partial t^2} = 2\pi \nu f(x) \left[- A \sin(2\pi \nu t)\right] 2\pi \nu$$

$$= -4\pi \nu^2 f(x)\, g(t) \quad \text{--- (5)}$$

from eq^n (3).

diff. eqn (2) w.r.to 'x' --

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial f(x)}{\partial x} \cdot g(t)$$

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} \cdot g(t) \quad \text{(Diff. Again)} \qquad \text{—— (6)}$$

Put the value of $\frac{d^2\omega}{\partial t^2}$ and $\frac{\partial^2 \omega}{\partial x^2}$ in eqn (1)

$$\cancel{g(t)} \cdot \frac{\partial^2 f(x)}{\partial x^2} = \frac{1}{u^2}(-4\pi v^2) f(x) \cancel{g(t)}$$

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi v^2}{u^2} f(x) \qquad \text{—— (7)}$$

We know that $v = u/\lambda \Rightarrow u = \lambda v$, Hence from Eqn (7)

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi \cancel{v^2}}{\lambda^2 \cancel{v^2}} f(x)$$

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi}{\lambda^2} f(x) \qquad \text{—— (8)}$$

Introducing the function $f(x) = \psi$ and extending the eqn to 3-dimensional.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda} \psi \qquad \text{—— (9)}$$

By De-broglie relationship ($\lambda = h/mu$)

So,
$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-4\pi^2 m^2 u^2}{h^2} \psi$$

Replacing the symbol ∇^2 for the differential operator, i.e,
$$\nabla^2 = \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$$

$$\nabla^2 \psi = \frac{-4\pi^2 m^2 u^2}{h^2} \psi \quad \text{--- (10)}$$

Where m is mass & u is the velocity of the particle
The total energy of the particle is

$$E = K + V$$

$$E - V = \frac{1}{2} m u^2$$

$$u^2 = \frac{2(E-V)}{m}$$

Hence from eqn (10),

$$\nabla^2 \psi = -\frac{4\pi m^{\cancel{2}}}{h^2} \times \frac{2(E-V)}{\cancel{m}} \psi$$

$$\nabla^2 \psi = -\frac{8\pi m (E-V)}{h^2} \psi$$

$$\nabla^2 \psi + \frac{8\pi m (E-V)}{h^2} \psi = 0 \quad \text{--- (11)}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi m (E-V)}{h^2} \psi = 0$$

This equation is known as Schrodinger time-independent Equation.

Hamiltonian operator

From the S.W. Equation -

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

Multiplying by $\frac{-h^2}{8\pi^2 m}$ on both sides

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2} \times \left(\frac{-h^2}{8\pi^2 m}\right)(E-V)\psi = 0$$

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi - E\psi + V\psi = 0$$

$$\left[-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right]\psi = E\psi$$

The expression $\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)$ is called Hamiltonion operator and is written as $\hat{H}$, Thus equation become

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

The Hamiltonion operator ($\hat{H}$) consists of two parts $\left(-\frac{h^2}{8\pi^2 m}\nabla^2\right)$ and the potential energy Part (V).

Posulates of Quantum Mechanics:-

Postulate 1:- The function f is continuous, Thus the function ψ can be subjected to differentiate.

Postulate 2:- The probability of finding the particle in the space with in x and $x+dx$ given by $\psi^* \psi \, dx$,

$$\boxed{\text{Probability} = \int_{x_1}^{x_2} \psi^* \psi \, dx}$$

Where $\psi(x)$ is the function & $\psi^*(x)$ is its complex conjugate.

Postulates 3:- The only possible values which a measurement of the observables whose operotor P can give, are eigenvalues p_n of the equation.

$$\boxed{P\psi = P_n \psi_n}$$

To find total momentum the equation is,

$$\boxed{i \frac{\hbar}{2\pi} \nabla \psi_n = P_n \psi_n}$$

Posulate 4:- Every physical observable is associated with a linear hermition operator i.e, a ~~momentum~~ measureable quantity can be represented as mathematical operator.

$$\boxed{\hat{A}\psi = d\psi}$$

↳ eigenvalue is real hermition operator so we use here Hemition oper.

Posulate 5:- The average value of an observable "a" corresponding to the operator $\hat{A}$, for a system described by wave function ψ is given by:-

$$\langle a \rangle = \frac{\int_{-\infty}^{+\infty} \psi^* A \psi \, d\tau}{\int_{-\infty}^{+\infty} \psi^* \psi \, d\tau}$$

Posulate 6:- As all the function are time dependent i.e, $\psi(x, y, z, t)$ then its subsequent behaviour should be decribed by time dependent schrodinger equation

$$-\frac{\hbar}{2\pi} \cdot \frac{d\psi[x, y, z, t]}{dt} = \hat{H}\psi[x, y, z, t]$$

Where $\hat{H}$ is known as hamiltonion operator of the system.

Postulate 7:- If ψ_i and ψ_j represent 2 different eigenfunction both of which are satisfying solution of the wave equation for a given system, then these function will be normalized.

$$\boxed{\int \psi_i \psi_j^* \, d\tau = 1 \ \& \ \int \psi_j^* \psi_i \, d\tau = 1}$$

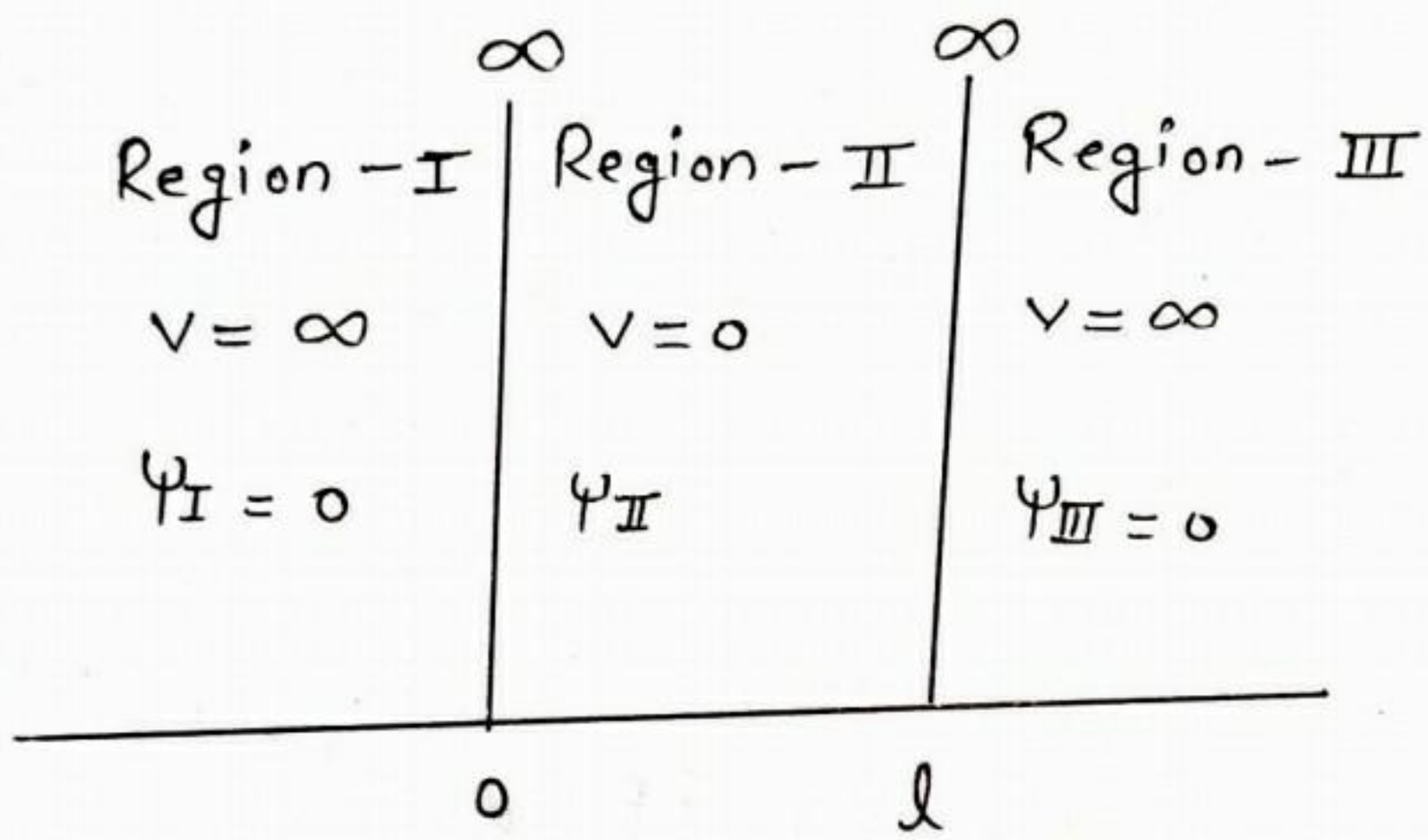
given third region is also $\psi_{III} = 0$.

Particle in 1-D Box :-

This is the simplest quantum mechanical problem which represent translation motion.

A particle of mass m is confined to move in a one-dimensional box of width l, having infintely high walls.

Let us assume that the potential energy of particle be zero i.e, $V = 0$ in the second region.



In the first region, $V = \infty$

$$\therefore \text{ S.W.E.} \Rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - \infty)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \infty \cdot \psi = 0$$

$$\psi = -\frac{1}{\infty}\frac{d^2\psi}{dx^2}$$

$$\boxed{\psi_I = 0}$$

Similar, to the first region third region is also $\psi_{III} = 0$.

In the second region, $V=0$

$\therefore$ S.W.E written as,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-0)\,\psi_{III} = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\,\psi_{III} = 0$$

Let $k^2 = \frac{8\pi^2 mE}{h^2}$, k is positive intergral intenger coff.

$$\frac{d^2\psi}{dx^2} + k^2\psi_{III} = 0 \quad \text{—— (I)}$$

Solution of Equation I,

$$\psi_{II} = A\sin kx + B\cos kx$$

Applying boundry condition in L.H.S, $x=0$

$$0 = A\sin k\times 0 + B\cos k\times 0$$

$$0 = B\cos 0$$

$$\boxed{B=0}$$

Putting the value of B in above equation,

$$\psi_{II} = A\sin kx \quad \text{—— (II)}$$

Applying boundary condition in R.H.S, $x=l$, $\psi_{II}=0$

$$\therefore A\sin kl = 0 \qquad (A\neq 0)$$

$$\sin kl = \sin n\pi$$

$$kl = n\pi$$

$$\boxed{k = \frac{n\pi}{l}}$$

$$\boxed{\psi_{II} = A \sin\left(\frac{n\pi x}{l}\right)} \quad \text{—— (3)}$$

From Eq^n(III) value of k putting in eq(ii) on normalisation, We get, $A = \sqrt{\frac{2}{l}}$

$$\boxed{\psi_{II} = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

Energy of 1-D Box :-

$$k^2 = \frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{l^2}$$

$$8\cancel{\pi^2} mE l^2 = n^2 \cancel{\pi^2} h^2$$

$$\boxed{E = \frac{n^2 h^2}{8ml^2}}$$

Normalisation of ψ :-

$$\psi = A \sin\left(\frac{n\pi x}{a}\right)$$ and normalisation condition

is $$\int_{-\infty}^{\infty} \psi \psi^* \, d\tau = 1.$$

For 1-D Box $d\tau = dx$ and $x = (0$ to $a)$. and ψ is real. $\psi^* = \psi$

So,
$$\int_0^a \psi^2 \, dx = 1$$

$$\int_0^a A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$\frac{A^2}{2}\int_0^a 2\sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$\frac{A^2}{2}\int_0^a \left(1 - \cos\frac{2n\pi x}{a}\right) dx = 1$$

$$\frac{A^2}{2}\left[\int_0^a dx - \int_0^a \frac{\cos 2n\pi x}{a} dx\right] = 1$$

$$\frac{A^2}{2}[1]_0^a - 0 = 1 \qquad = 1$$

As $\sin n\pi x = 0$, hence equation becomes,

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

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

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

Normalised wave function for particle is

$$\boxed{\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)}$$

The mathematical method described above is known as normalization and value of constant A is known as normalization factor $= \sqrt{\frac{2}{a}}$.

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

$$E = \frac{n^2 h^2}{8ml^2}$$

So,

$$E_1 = \frac{h^2}{8ml^2}, \quad E_2 = \frac{4h^2}{8ml^2}, \quad E_3 = \frac{9h^2}{8ml^2}$$

$$E_2 - E_1 = \frac{3h^2}{8ml^2}$$

$$E_3 - E_2 = \frac{5h^2}{8ml^2}$$

$$E_4 - E_3 = \frac{7h^2}{8ml^2}, \quad E_{(n+1)} - E_n = \frac{(2n+1)h^2}{8ml^2}$$

Plot for ψ :-

1. For ground state, $n = 1$

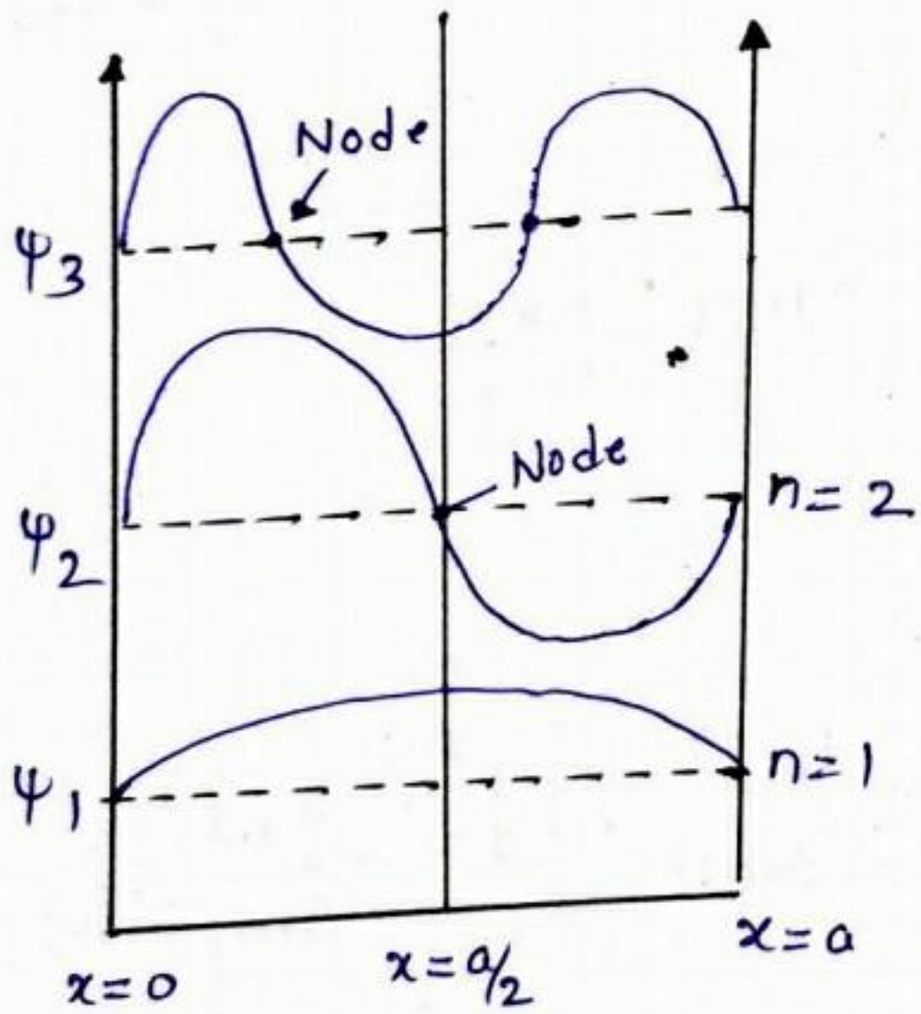
$$\psi_1 = \sqrt{\frac{2}{l}} \sin\left(\frac{\pi x}{l}\right)$$

ψ_1 is maximum when

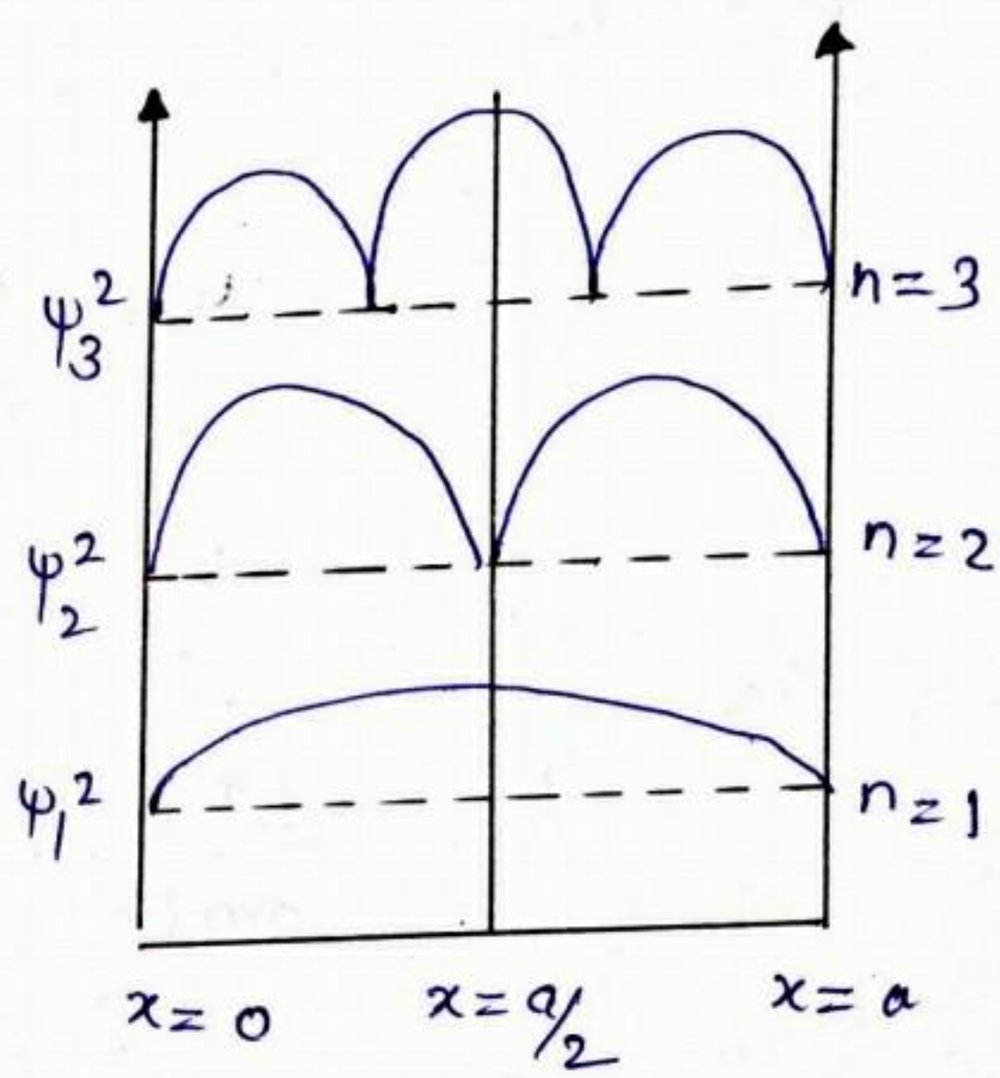
$$\sin\frac{\pi x}{l} = 1$$

$$\sin\frac{\pi x}{l} = \sin(\pi/2)$$

$$\boxed{x = \frac{l}{2}}$$



(Plot of ψ_n against x)



(Plot of ψ_n^2 against x)

Wave Function And Energy For a Free particle in a 2-D Box

The S.W.E. in 2-D Box written as,-

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{8\pi^2 m}{h^2}\left[(E_x + E_y) - V(x,y)\right]\psi = 0 \quad \text{--- (1)}$$

In the box potential will be zero, $V = 0$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{8\pi^2 m}{h^2}\left[(E_x + E_y)\right]\psi = 0 \quad \text{--- (2)}$$

The solution of this eq^n (2) can be assumed as the product of a function of x and a function of y

$$\text{Let } \psi(x,y) = X(x) \cdot Y(y) \quad \text{--- (3)}$$

$$\frac{\partial^2 X(x) \cdot Y(y)}{\partial x^2} + \frac{\partial^2 X(x) \cdot Y(y)}{\partial y^2} + \frac{8\pi^2 m}{h^2}\left[E_x + E_y\right] X(x) Y(y) = 0$$

$$\frac{\partial^2}{\partial x^2}\left(X(x) \cdot Y(y)\right) + \frac{\partial^2}{\partial y^2}\left(X(x) \cdot Y(y)\right) + \left[\frac{8\pi^2 m E_x}{h^2} + \frac{8\pi^2 m E_y}{h^2}\right] X(x) Y(y) = 0 \quad \text{--- (4)}$$

$$\text{Let } \frac{8\pi^2 m E_x}{h^2} = K_x^2 \quad \text{--- (5)}$$

$$\frac{8\pi^2 m E_y}{h^2} = K_y^2 \quad \text{--- (6)}$$

$$Y(y) \cdot \frac{\partial^2 X(x)}{\partial x^2} + X(x) \frac{\partial^2 Y(y)}{dy^2} + [K_x^2 + K_y^2] X(x) Y(y) = 0 \quad \text{— (7)}$$

Divide the eqn by $X(x)\, Y(y)$

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + [K_x^2 + K_y^2] = 0$$

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -[K_x^2 + K_y^2] \quad \text{— (8)}$$

Compairing L.H.S. to R.H.S, We get

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} = -K_x^2 \quad \text{— (9)}$$

$$\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -K_y^2 \quad \text{— (10)}$$

$$\boxed{\frac{\partial^2 X(x)}{\partial x^2} + K_x^2 X(x) = 0} \quad \text{— (11)}$$

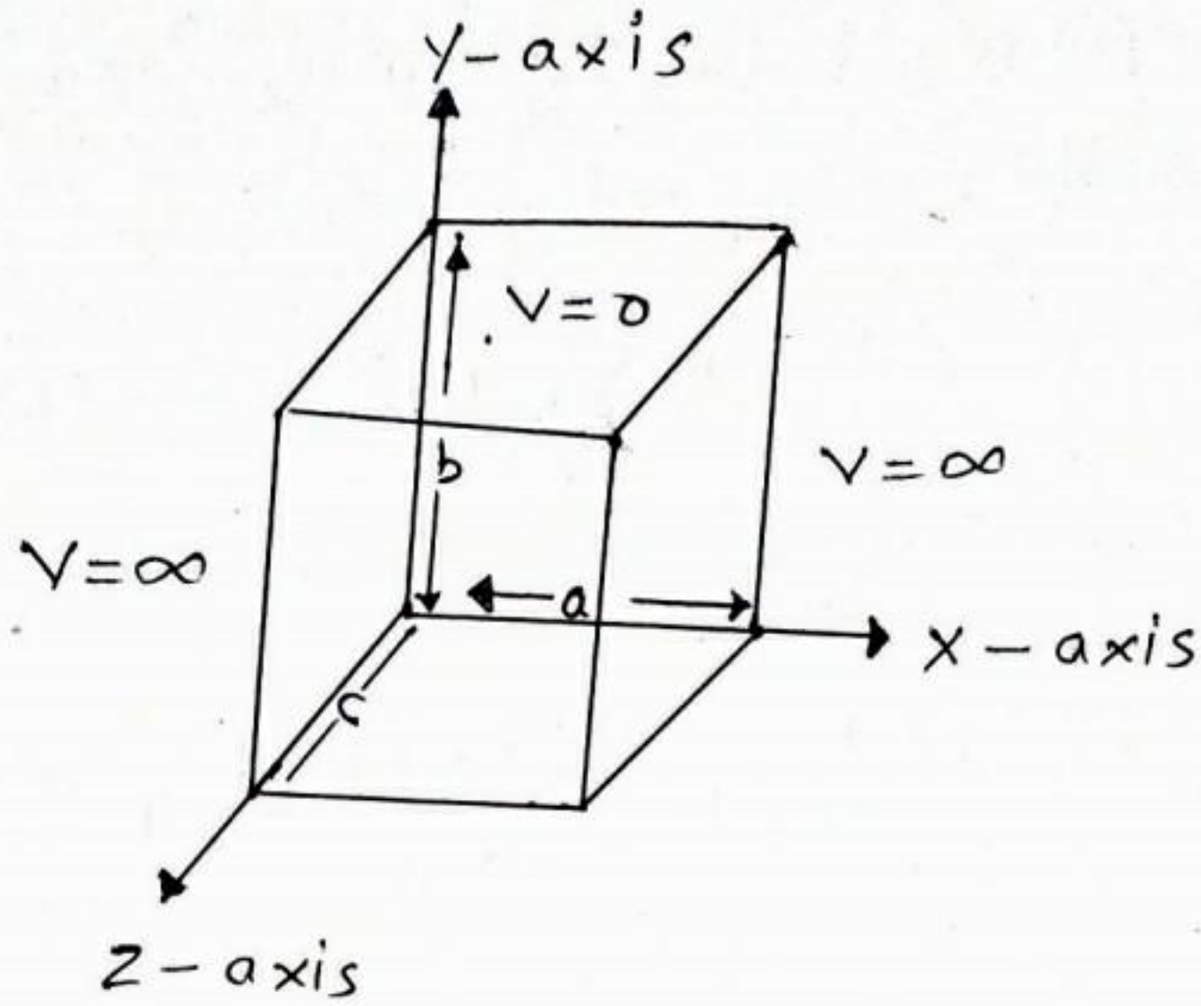
$$\boxed{\frac{\partial^2 Y(y)}{\partial y^2} + K_y^2 Y(y) = 0} \quad \text{— (12)}$$

Solution of (11) and (12)

$$X(x) = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi x}{l_x} \quad \text{— (13)}$$

$$Y(y) = \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi y}{l_y} \quad \text{— (14)}$$

A particle in a 3-D Box :-



A particle of mass m moving in 3-D rectangular potential box having sides a, b and c in length x, y and z-axes respectively. The potential energy of the particle is zero with in the box (V=0) but is infinite everywhere outside the box. (V=∞)

The Schrodinger's wave equation for the particle inside the box will be given by-

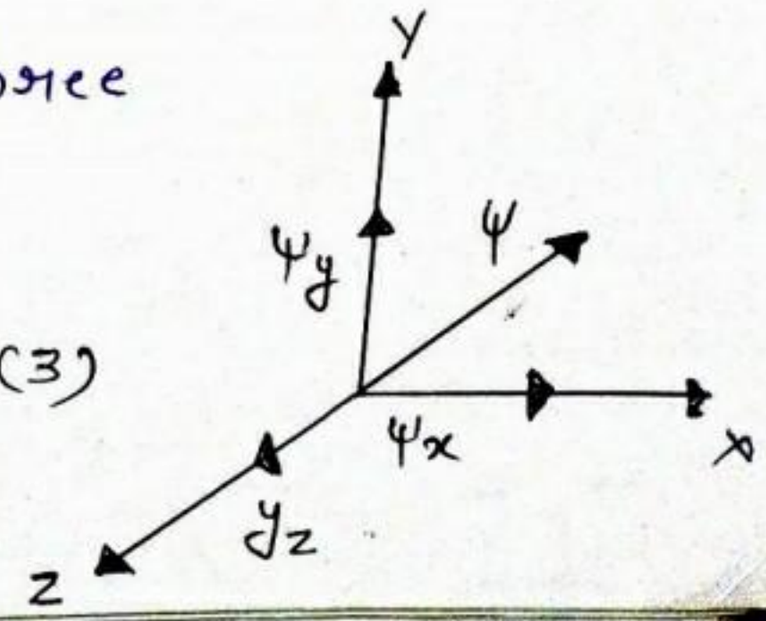
$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m E}{h^2}\psi = 0 \quad \text{—— (1)}$$

Dividing by ψ.

$$\frac{1}{\psi}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + \frac{8\pi^2 m E}{h^2} = 0 \quad \text{—— (2)}$$

The wavefunction ψ depends upon three co-ordinates x, y and z.

$$\psi = \psi_x \cdot \psi_y \cdot \psi_z \quad \text{—— (3)}$$



The total Energy (E) of the particle may be taken to three components E_x, E_y and E_z along the three axes, x, y and z respectively so-

$$E = E_x + E_y + E_z \quad \text{--- (4)}$$

combining these above equations-

$$\frac{1}{\psi_x \psi_y \psi_z}\left[\frac{\partial^2(\psi_x \psi_y \psi_z)}{\partial x^2} + \frac{\partial^2(\psi_x \psi_y \psi_z)}{\partial y^2} + \frac{\partial^2(\psi_x \psi_y \psi_z)}{\partial z^2}\right] + \frac{8\pi^2 m}{h^2}(E_x + E_y + E_z) = 0 \quad \text{--- (5)}$$

On simplification we get,

$$\left(\frac{1}{\psi_x}\cdot\frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{\psi_y}\cdot\frac{\partial^2 \psi_y}{\partial y^2} + \frac{1}{\psi_z}\cdot\frac{\partial^2 \psi_z}{\partial x^2}\right) + \frac{8\pi^2 m}{h^2}(E_x + E_y + E_z) = 0$$

$$\left(\frac{1}{\psi_x}\cdot\frac{\partial^2 \psi_x}{\partial x^2} + \frac{8\pi^2 m E_x}{h^2}\right) + \left(\frac{1}{\psi_y}\cdot\frac{\partial^2 \psi_y}{\partial y^2} + \frac{8\pi^2 m E_y}{h^2}\right) + \left(\frac{1}{\psi_z}\cdot\frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m E_z}{h^2}\right) = 0 \quad \text{--- (6)}$$

Equation (6) consists 3-independent terms, each other is the function of one variable only. Thus,

$$\frac{1}{\psi_x}\cdot\frac{\partial^2 \psi_x}{\partial x^2} + \frac{8\pi^2 m E_x}{h^2} = 0 \quad \text{--- (7)}$$

$$\frac{1}{\psi_y}\cdot\frac{\partial^2 \psi_y}{\partial y^2} + \frac{8\pi^2 m E_y}{h^2} = 0 \quad \text{--- (8)}$$

$$\frac{1}{\psi_y}\cdot\frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m E_z}{h^2} = 0 \quad \text{--- (9)}$$

The above equations (7), (8), (9) are similar to S.W.E. for the particle moving in a one-dimensional box only

$$E_x = \frac{n_x^2 h^2}{8ma^2} \quad \text{—— (10)}$$

$$E_y = \frac{n_x^2 h^2}{8mb^2} \quad \text{—— (11)}$$

$$E_z = \frac{n_x^2 h^2}{8mc^2} \quad \text{—— (12)}$$

The solutions of the wave functions are, thus

$$\psi_x = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \quad \text{—— (13)}$$

$$\psi_y = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi \cdot y}{b}\right) \quad \text{—— (14)}$$

$$\psi_z = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad \text{—— (15)}$$

Normalized Wave function:-

The total wavefunction ψ is given by

$$\psi = \psi_x \cdot \psi_y \cdot \psi_z$$

$$= \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

Volume of rectangular Box, $V = abc$

$$\psi = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

The above equation gives the value of Normalised wave function. The factor $\sqrt{\frac{8}{V}}$ is known as the normalization factor

Energy Levels:-

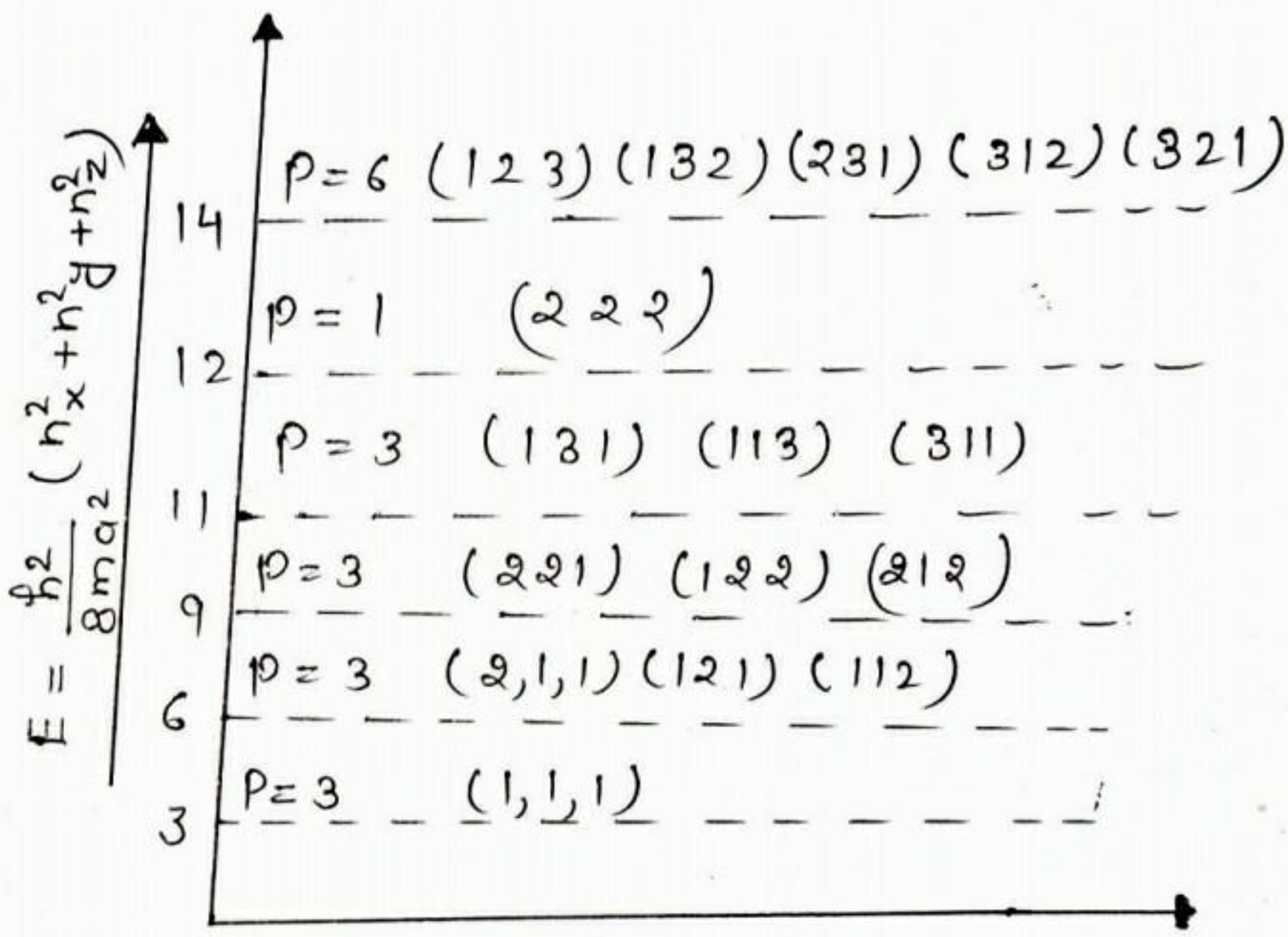
$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

if $a = b = c$

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$E_{111} = \frac{3h^2}{8ma^2}$$

$$E_{121} = \frac{6h^2}{8ma^2}$$



Linear Harmonic Oscillator:-

The quantum mechanical treatment of a simple harmonic oscillator is required for the proper understanding of molecular vibrations.

A point mass undergoing simple harmonic oscillator in one dimensional, due to the attraction by a force proportional to the displacement from the equilibrium position, constitutes a linear harmonic oscillator.

To provide a background, the classical treatment of the linear harmonic oscillator is attempted before the quantem mechanical treatment is considered.

In a SHO, the force tending to restore the particle to its equilibrium position is always directed towards the equilibrium position and is directly proportional to the displacement (x) from it, Thus

$$\boxed{F = -kx} \quad \text{—— (1)}$$

Where k = Force constant & x = displacement

The negative sign shows that restoring force is working in the direction opposite to the displacement

If m is the mass of then particle,

$$F = m \times a$$

$$F = m\left(\frac{d^2x}{dt^2}\right) \quad \text{—— (2)}$$

From eq^n ① and eq^n (2)

$$m\frac{d^2x}{dt^2} = -kx \quad \text{—} \quad ③$$

As the displacement is harmonic, x can be written as–

$$x = A\sin 2\pi\nu t \quad \text{—} \quad ④$$

A = Amplitude of vibration

ν = frequency of oscillator

double differentiating eq^n(4), w.r.t. 't':

$$\frac{d^2x}{dt^2} = -4\pi^2\nu^2 A\sin 2\pi\nu t \quad \text{—} \quad ⑤$$

Now, combining eq^n (3) and eq^n (5)

$$m(-4\pi^2\nu^2 A\sin 2\pi\nu t) = -kx \quad \text{—} \quad ⑥$$

Putting the value of 'x' in the above equation from eq^n ④

$$m(-4\pi^2\nu^2 \cancel{A\sin 2\pi\nu t}) = -k\cancel{A\sin 2\pi\nu t}$$

$$\cancel{-}m4\pi^2\nu^2 = \cancel{-}k \quad \text{—} \quad ⑦ \quad (k = 4\pi^2\nu^2 m)$$

$$\nu^2 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}} \quad \text{—} \quad ⑧$$

Eq^n (8) gives frequency of the linear harmonic oscillator.

Wave Equation for a Harmonic oscillator :-

The schrodinger wave equation in 1-D is given by-

$$\frac{d^2\psi}{dx^2} + 8\pi^2 m (E-V)\psi = 0 \quad \text{— (9)}$$

The potential energy of linear harmonic oscillator

$$V = \frac{1}{2} k x^2 \qquad (k = \text{Force Constant})$$

Putting the value of V in eq^n (9)

$$\frac{d^2\psi}{dx^2} + 8\pi^2 m \left(E - \frac{1}{2} k x^2\right)\psi = 0 \quad \text{— (10)}$$

If we change over to two new independent variable η and α are defined as,

$$\eta = \left(\frac{2\pi}{h}\sqrt{km}\right)^{1/2} \cdot x$$

But $k = 4\pi^2 \nu^2 m$

$$\eta = \left(\frac{2\pi}{h}\sqrt{4\pi^2 m \nu^2 m}\right)^{1/2} \cdot x$$

$$\eta = \left(\frac{4\pi^2 m\nu}{h}\right)^{1/2} \cdot x \quad \text{— (11)}$$

and

$$\alpha = \frac{4E\pi}{h}\sqrt{\frac{m}{k}}$$

$$\alpha = \frac{4E\pi}{h}\sqrt{\frac{1 \times m}{4\pi^2 \nu^2 m}} \qquad (k = 4\pi^2\nu^2 m)$$

$$\alpha = \frac{4\cancel{\pi} E}{h} \times \frac{1}{2\cancel{\pi}\nu}$$

$$\boxed{\alpha = \frac{2E}{h\nu}} \quad \text{—— (12)}$$

From eq^n (11)

$$\eta = \left(\frac{4\pi^2 m\nu}{h}\right)^{1/2} \cdot x$$

$$\eta^2 = \left(\frac{4\pi^2 m\nu}{h}\right) \cdot x^2$$

$$\boxed{x^2 = \frac{\eta^2 h}{4\pi^2 m\nu}} \quad \text{—— (13)}$$

From eq (12)

$$\boxed{E = \frac{h\nu\alpha}{2}} \quad \text{—— (14)}$$

Now,

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(\frac{d\psi}{dx}\right)$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(\frac{d\psi}{d\eta} \cdot \frac{d\eta}{dx}\right)$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{d\eta}\left(\frac{d\psi}{dx} \cdot \frac{d\eta}{dx}\right)$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{d\eta}\left(\frac{d\psi}{dx} \cdot \frac{d\eta}{dx}\right) \frac{d\eta}{dx}$$

$$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{d\eta^2} \cdot \left(\frac{d\eta}{dx}\right)^2 \quad \text{—— (15)}$$

Putting the value of $\frac{d^2\psi}{dx^2}$, x^2 and E in eq^n (10)

$$\left(\frac{4\pi^2 m\nu}{h}\right)\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\left[\frac{h\nu\alpha}{2} - \left(\frac{1}{2}\cancel{4\pi^2 m}\nu^2\right)\left(\frac{\eta^2 h}{\cancel{4\pi^2 m\nu}}\right)\right]\psi = 0$$

$$\frac{4\pi^2 m\nu}{h}\left[\frac{d^2\psi}{dx^2} + \frac{2}{h\nu}\left[\frac{h\nu\alpha}{2} - \frac{1}{2}\eta^2 h\nu\right]\right]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{\cancel{2\times h\nu}}{\cancel{h\nu\times 2}}\left[\alpha - \eta^2\right]\psi = 0$$

$$\frac{d^2\psi}{dx^2} = (\eta^2 - \alpha)\psi = 0$$

$$\boxed{\frac{d^2\psi}{dx^2} - (\eta^2 - \alpha)\psi = 1} \quad \text{—— (16)}$$

Equation (16) represent the wave equation of SHO.

<u>Energy</u>:- Since, We ~~hve~~ have

$$E = \frac{h\nu\alpha}{2}$$

and α an being solved comes out to be

$$\alpha = 2n+1$$

Now, $$E = \frac{h\nu}{2}(2n+1)$$

Where, $n = 0, 1, 2, 3$ — — —

The ground state $(n=0)$

$\boxed{E_0 = \frac{1}{2}h\nu}$ (called zero point energy)

From eqn (76),

$$\frac{d^2\psi}{dx^2} + (\alpha - \eta^2)\,\psi = 0$$

ψ should be finite, continuous and single valued the proper solution of equation above is-

$\alpha = 1$, $\psi = 1\, e^{-\eta^2/2}$

$\alpha = 3$, $\psi = 2\eta \cdot e^{-\eta^2/2}$

$\alpha = 5$, $\psi = (4\eta^2 - 2)\, e^{-\eta^2/2}$

$\alpha = 7$, $\psi = (8\eta^2 - 12\eta)\, e^{-\eta^2/2}$ and so on

and the value of α are given by $2n+1$; where, $n = 0, 1, 2, 3, 4$ --- and the values of ψ corresponding to these are termed as eigen function where as, the constant values are called eigen values.

The Rigid Rotor (or Rotator):-

A diatomic molecule rotating about an axis perpendicular to the internuclear axis and passing through the centre of gravity of the molecule, constituents an example of a rigid rotor it being assumed that the internuclear distance does not change during rotation.

This system represents rotational molecule The K.E. of the molecule is given by-

$$K.E. = T = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} \qquad \left[\because \omega = \frac{L}{I}\right]$$

Where ω is the angular velocity and I is the moment of inertia of the rotating molecule. The angular moment $L = I\omega$. If no force acts on the rotor, we can set the potential energy $V=0$. Hence the Hamiltonian is expressed as-

$$\hat{H} = T + V = \frac{L^2}{2I}$$

The expansion for L^2 in spherical polar coordinates (r, θ, ϕ) is given by-

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

The schrodinger eq^n $\hat{H}\psi = E\psi$ may be written as,

$$\frac{1}{2I}\left[-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}\right] = E\psi$$

on multiplying by $2I$ and rearranging,

The above equation may be written as,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2 I}{h^2}E\psi=0$$

Since, the above equation contain two angular variable θ and ϕ, can be solved by method of seperation variables i.e,

$$\psi(\theta,\phi) = \Theta(\theta)\cdot\phi(\phi)$$

on substituting the values and solving,

$$\frac{\sin\theta}{\Theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 IE}{h^2}\sin^2\theta = -\frac{1}{\phi}\frac{\partial^2\phi}{\partial\phi^2}$$

By putting both sides equal to a constant, we get

$$\frac{\partial^2\phi}{\partial\phi^2}+m^2\phi=0 \text{ and } \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0$$

Where, $\beta = \frac{8\pi^2 IE}{h^2}$

The above eqn has the solution,

$$\phi(\phi) = Ne^{(\pm im\phi)}, \quad \text{Where, } i=\sqrt{-1}$$

Where N is the normalization constant.

The wave equation to be acceptable,

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

$$e^{2\pi mi}=1$$

$$e^{x}=\cos x+i\sin x$$

$$\cos 2\pi m + i\sin 2\pi m = 1$$

for $m = 0, \pm1, \pm2, \pm3$ ----

Normalisation :-

$$\int_0^{2\pi} \phi^* \phi \, d\phi = 1 \qquad (0 \le \phi \le 2\pi)$$

$$N^2 \int_0^{2\pi} e^{im\phi} \times e^{-im\phi} \, d\phi = 1$$

$$N^2 (2\pi) = 1 = \boxed{N = \frac{1}{\sqrt{2\pi}}}$$

The energy eigen values obtained for rigid rotor are-

$$\beta = \frac{8\pi^2 I E}{h^2} = l(l+1)$$

Where l is the rotational quantum number, Thus

$$E = \frac{l(l+1)h^2}{8\pi^2 I}, \quad \text{Where, } l = 0, 1, 2, 3 \ldots$$

The spectroscopy we generally use the symbol J, rather than l for the rotational quantum number so that the rotational energy levels are given by the Eqn

$$\boxed{E_J = \frac{J(J+1)}{8\pi^2 I}}, \quad \text{where } J = 0, 1, 2, 3$$

The Hydrogen Atom :-

Hydrogen atom is the simplest of all the atoms. It is 3-D system and the schrodinger equation for this system is -

$$\hat{H}\psi = E\psi \quad \text{——} \quad (1)$$

Where,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_{(x,y,z)}$$

and where the Laplacian operator is

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

The potential energy of intraction b/w the e- and the nucleus is given by -

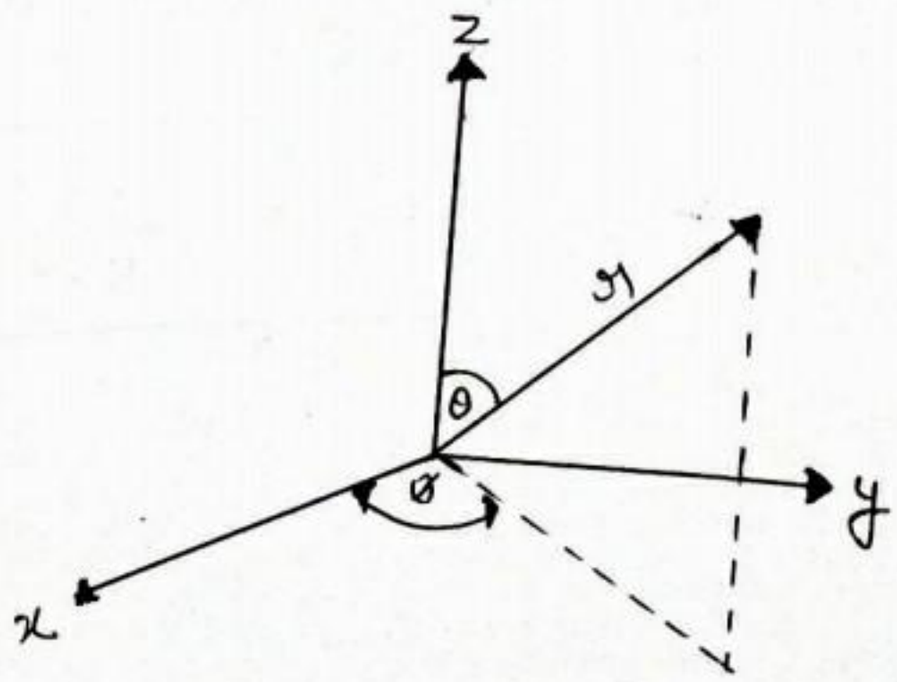
$$V_{(r)} = \frac{-Ze^2}{4\pi\varepsilon_0 r} \quad \text{—} \quad (2)$$

Since this attractive potential has spherical symmetry depending only upon r. it is convenient to express the S.E. in terms of polar cordinates (r, θ, ϕ) rather than cartesion (x, y, z)

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

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

$$z = r\cos\theta$$



We know the The S.E. in polar form –

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial^2\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{d\phi^2}+\frac{2\mu}{\hbar^2}(E-V(r))\psi=0 \quad \text{— (3)}$$

Where μ is the reduceed mass of the e- and the nucleus. Assuming that $V_{(r)}$ is a function of r only, the above wave equation can be solved by sepearating the variables.

$$\psi_{(r,\theta,\phi)} = R_{(r)}.\,\Theta_{(\theta)}.\,\Phi_{(\phi)} \quad \text{— (4)}$$

Where $R(r)$ is the Radial function which is a function of r only, and $\Theta(\theta)$, $\Phi(\phi)$ are angular functions.

$$\frac{\partial\psi}{dr} = \Theta_{(\theta)}\Phi_{(\phi)}\frac{dR}{dr}$$
$$\frac{d\psi}{d\theta} = R_{(r)}.\Phi_{(\phi)}\frac{d\Theta}{d\theta}$$
$$\frac{d^2\psi}{d\phi^2} = R_{(r)}\Theta_{(\theta)}\frac{d^2\phi}{d\phi^2}$$

Now using eq^n (3), eq^n (4) and multiplying by $\frac{r^2\sin^2\theta}{R\Theta\phi}$, we have

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2\mu}{\hbar^2}\left[E-V_{(r)}\right]r^2\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \quad \text{— (5)}$$

This left hand side of eq^n (5) is a function of r and θ and the right side is a function ϕ alone. This is Possible only when each side

is a constant say m^2

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

$$\frac{d^2\phi}{d\phi^2} = -m^2\Phi_{(\phi)}$$

and, $\frac{\sin^2\theta}{R}\cdot\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2\mu}{\hbar^2}[E-V_r]\times$

$r^2\sin^2\theta = m^2$

Divide the above equation by $\sin^2\theta$ ... — (6)

$$\frac{1}{R^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2\mu}{\hbar^2}[E-V_r]\times r^2 = \frac{m^2}{\sin^2\theta}$$

$$\frac{1}{R^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}(E-V_{(r)})r^2 = -\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\theta}{d\theta}\right) + \frac{m^2}{\sin^2\theta} \quad \text{— (7)}$$

This is possible when both sides are equal to λ

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \quad \text{— (8)}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}[E-V_{(r)}]R - \frac{\lambda}{r^2}R = 0 \quad \text{— (9)}$$

The 3-D S.E. wave equation in spherical polar cordinates has been sepearted into three 1-D equations (eqn 8, eqn 9). There are called respectively. The ϕ equation, the θ equation and R-equation.

Huckel Molecular Orbital Theory:-

The conjugated linear polyenes such as 1,3-butadien and 1, 3, 5- hexatriene and cyclic polyenes such as benzene, napthalene etc. were investigated by E. Huckel in 1931. His treatment was also extended further.

In a conjugated unsaturated hydrocarbon with alternate single & double bonds, the molecule is generally planner shape. In an n-carbon system, each carbon is sp^2 hybridized and has a $2p_z$ orbital centred on its.

The electrons in the sp^2 hybrid orbitals are called σ - electrons are containing in molecular plane. Each $2p_z$ orbital which is $\perp$ to the molecular plane contain one π - electron. Acc. to the LCAO-MO aproximation, the molecule orbital is written as-

$$\psi_i = \sum_{j=1}^{n} C_{ij} \phi_j \qquad (i = 1, 2, 3 ----)$$

Where ϕ_j is the $2p_z$ orbital centered on carbon atom j. The $n\pi$ MO's are formed by the overlapping of n $2p_z$ orbital. The HMOT is similar to the MOT of homonuclear diatomics.

Proceed ahead Huckel make the followings assumptions about the three kind of integrals:- coulomb integral, exchange integrals and overlap integrals to solve the secular system.

Eigenvalues For Angular Momentum :-

1. All overlap integral are zero, i.e, $S_{ij} = 0$

2. Coulmb integral which refer to the energy of on e- in the $2p_z$ orbital on the ith carbon atom is denoted by α.

3. The exchange integrals $H_{ij} = H_{ji} = 0$ unless the ith & jth orbitals are on adjacent carbon atom in which case, they are designated as β.

The HMOT gives a good description of bonding & qualative agreement b/w theorey and experiment

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & --- & 0 --- \\ \beta & \alpha - E & \beta & 0 & --- & 0 --- \\ 0 & \beta & \alpha - E & \beta & --- & 0 --- \\ 0 & 0 & \beta & \alpha - E & --- & \beta --- \\ --- & --- & --- & --- & --- & --- \\ --- & --- & --- & --- & --- & --- \end{vmatrix} = 0$$

Defining a dimensionless parameter $x = \frac{\alpha - E}{\beta}$

$$\begin{vmatrix} x & 1 & 0 & 0 & --- & 0 -- \\ 1 & x & 1 & 0 & --- & 0 -- \\ 0 & 1 & x & 1 & --- & 0 -- \\ 0 & 0 & 1 & x & --- & 1 -- \\ --- & --- & --- & --- & --- & --- \\ --- & --- & --- & --- & --- & --- \end{vmatrix} = 0$$

Expanison of $n \times n$ determinaht yields the polynomial equation which has the n real roots. Thus, The conjugated polymer has n energy levels and n MO's. The energy of the kth MO is given by

$$E_k = \alpha + x_k \beta$$

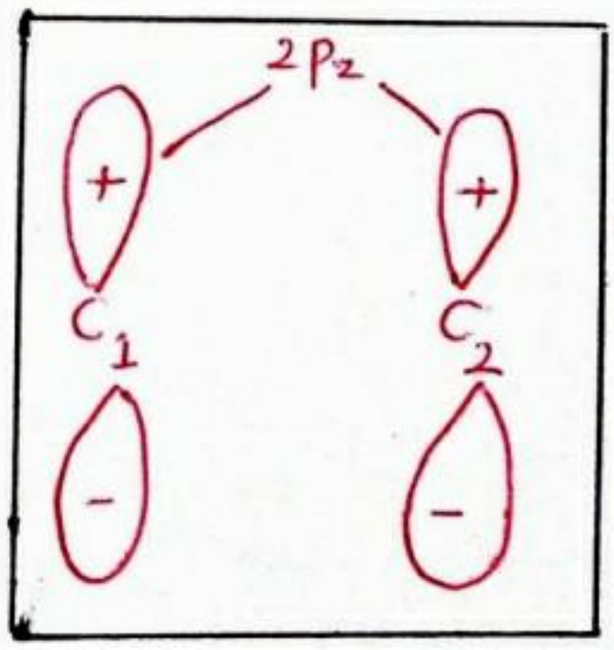
Where x_k is the kth root of the polynomial. Since the columb integral (α) and exchange integral (β) are both negative. The positive value of x_k represents an energy level (a) which is more negative and hence a more stable then the energy of an e- in a carbon $2p_z$ orbital.

This energy level is called a BMO and a negative value of x_k corresponds to an ABMO.

Application of HMOT :-

1. **Ethylene:-** The Huckel secular equation is given by

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad \left(\text{Where } x = \frac{(\alpha - E)}{h}\right)$$



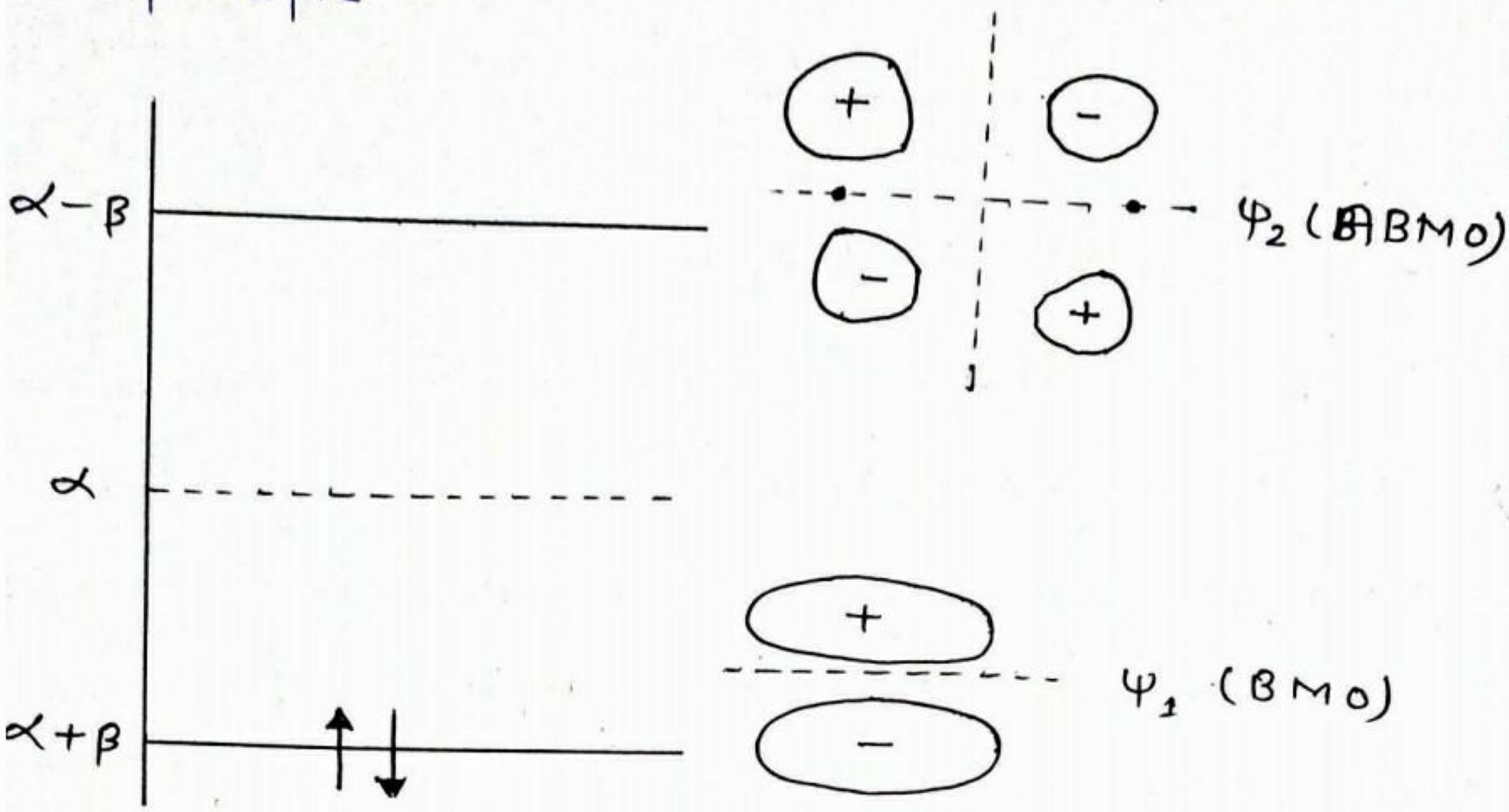
Which on expansion gives

$$x^2 - 1 = 0 \quad x = \pm 1$$

For $x = -1$, $E_1 = \alpha + \beta$ (BMO)

For $x = +1$, $E_2 = \alpha - \beta$ (AMBO)

The two π electron of ethylene occupy the BMO in the ground state in accordance with pauli exclusion principle



The total $\pi - e^-$ energy E_π, is equal to $2(\alpha+\beta)$. Since the energy of the two electrons in the isolated carbon $2p_z$ orbital is equal to the 2α, The π-bond energy in ethylene is equal $[2(\alpha+\beta)-2\alpha]$, i.e 2β.

To Determine the BMO ψ_1 and ABMO ψ_2 :-

The Secular equation corresponds to the simultaneous linear equations viz,

$$c_1 x + c_2 = 0 \text{ and } c_1 + c_2 x = 0 \quad \text{—— (1)}$$

For the BMO ψ_1, $x = -1$

$$-c_1 x + c_2 = 0 \text{ and } c_1 - c_2 = 0 \text{ i.e, } c_1 = c_2$$

Since ψ_1 must be normalised, i.e, $\int \psi_1 \psi_1 \, d\tau = 1$

$$\int (c_1 \phi_1 + c_2 \phi_2)(c_1 \phi_1 + c_2 \phi_2) \, d\tau = 1 \quad \text{—— (2)}$$

$$c_1^2 \int \phi_1 \phi_1 \, d\tau + c_2^2 \int \phi_2 \phi_2 \, d\tau + 2 c_1 c_2 \int \phi_1 \phi_2 \, d\tau = 1 \quad (3)$$

Again, ϕ_is form an orthonomal set, i.e,

$$\int \phi_i \phi_j \, d\tau = \delta_{ij} = \begin{cases} 1, & i = j \\ 0, & i = 1 \end{cases} \quad \text{— (4)}$$

Where $\delta_{ij} \rightarrow$ kroneker delta

In this case, it means that

$$\int \phi_1 \phi_1 \, d\tau = \int \phi_2 \phi_2 \, d\tau = 1 \text{ and } \int \phi_1 \phi_2 \, d\tau = 0 \quad \text{— (5)}$$

on substituting with the eqn (3), We get

$$c_1^2 + c_2^2 = 1 \text{ or } c_1 = \frac{1}{\sqrt{2}} \quad (\because c_1 = c_2) \quad \text{— (6)}$$

$$\therefore \boxed{\psi_1 = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2)}$$

Similarly, for $x = 1$, proceeding as above, we can show that,

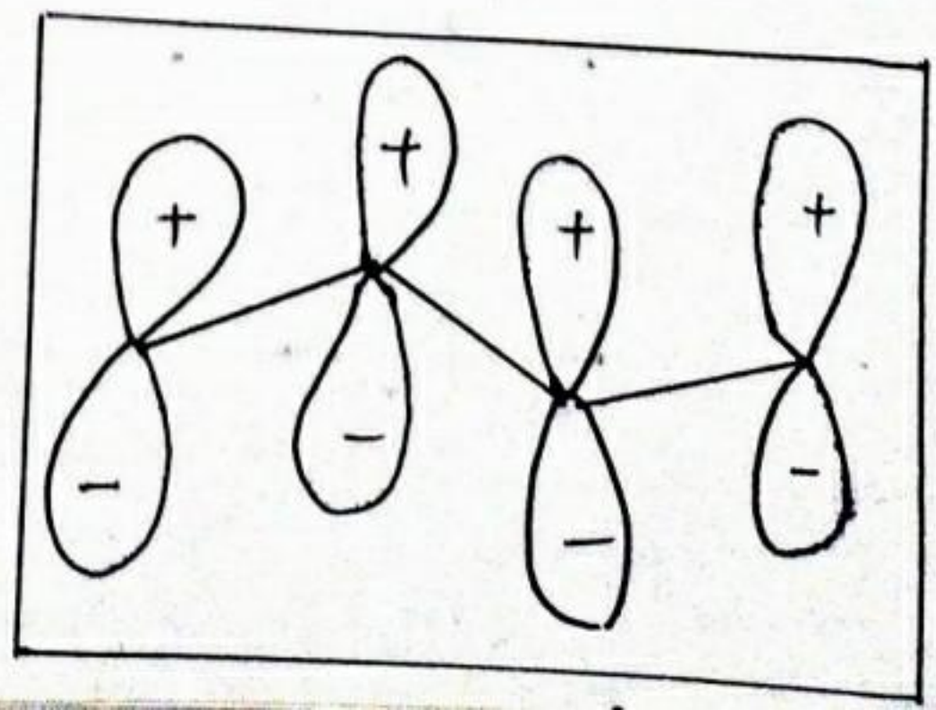
$$\boxed{\psi_2 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_2)}$$

Note that nodes (and the nodal planes) are the region in which the probabilality of finding the π-e^- is zero.

1,3- Butadiene :-

This system consists of four carbon $2p_z$ orbitals and four π electrons. The Huckel Secular equation is given by

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$



(Where $x = \frac{(\alpha - E)}{\beta}$)

which upon the expansion gives the polynomial

$$x^4 - 3x^2 + 1 = 0$$

Which has the roots, $x = \pm 1.618, \pm 0.618$

We obtain the four energy levels :-

$$E_1 = \alpha + 1.618\beta \text{ (BMO)}$$

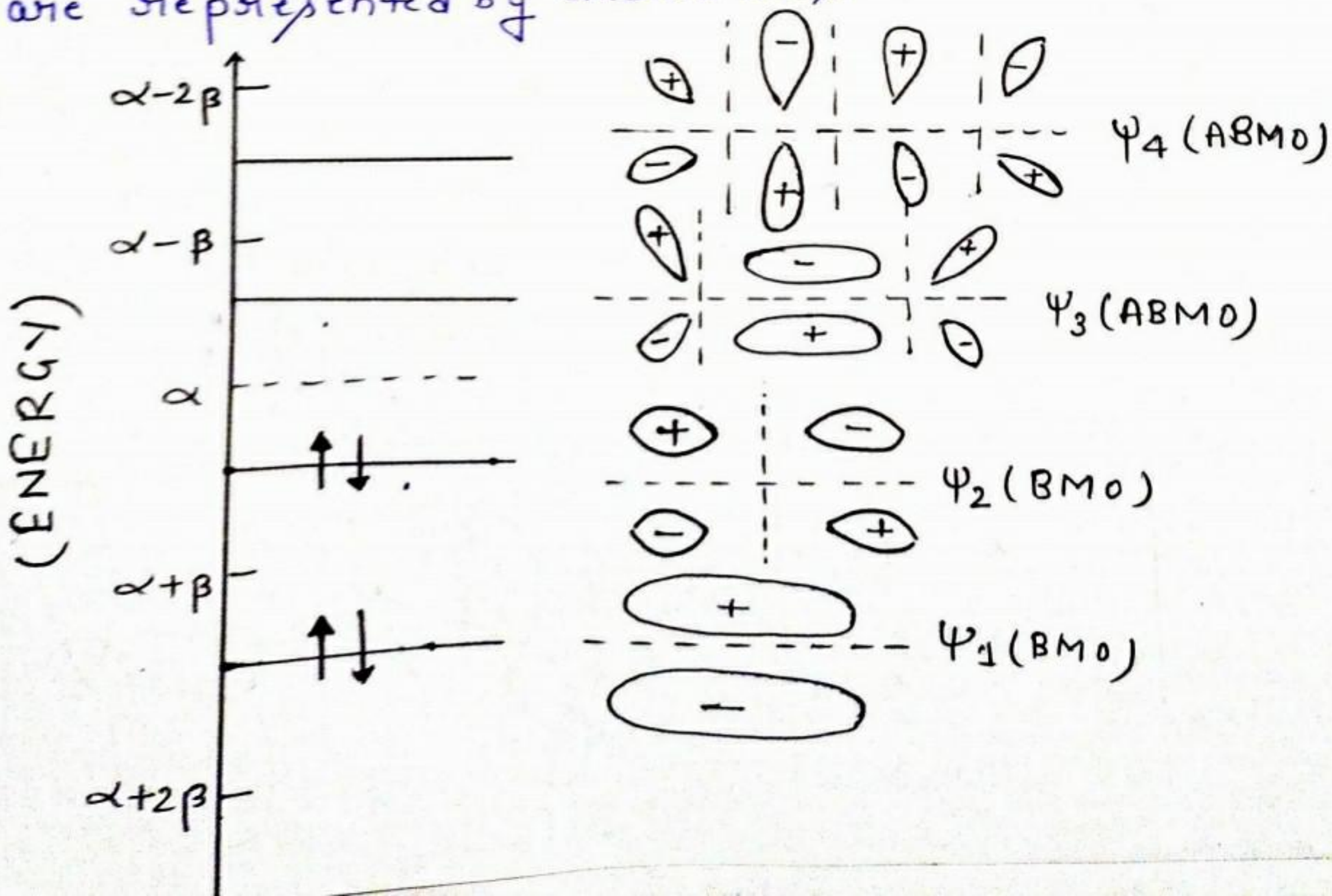
$$E_2 = \alpha + 0.618 \text{ (BMO)}$$

$$E_3 = \alpha - 1.618 \text{ (ABMO)}$$

$$E_4 = \alpha - 0.618 \text{ (ABMO)}$$

The four π electrons of 1,3 butadiene occupy the two BMO's ψ_1 and ψ_2 in the ground state of the molecule in accodance with Pauli Exclusion Principle.

HMO Diagram for 1,3 – butadiene. The carbon atoms are represented by dots and the nodal planes for the MO's are represented by dashed lines.



Nodes and Nodal plane are the region where probability of finding the electrons is zero. ground state has no node. The number of nodes in a MO increase with increase in energy. Thus, ψ_2 has one node, ψ_3 has two nodes and ψ_4 has three nodes.

The total π electron energy is equal to -

$$[2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)] \text{ i.e } 4\alpha + 4.472\beta$$

The energy of two electrons in ethylene is $2(\alpha + \beta)$

The delocalization energy (DE), also called the resonance energy (RE), is defined as the difference in energy of π electrons in a molecule and the sum of the energies of isolated double bonds present in the classical structure of same moleccule.

Thus, for 1,3-butadiene, DE (or RE).

$$= (4\alpha + 4.472\beta) - 2(2\alpha + 2\beta)$$

$$= 0.472\beta$$