Quantum Chemistry.

Mathematical Formulae -

Trigonometric formulae -

	0°	30°	45°	60°	90°	180°
$\sin\theta$	0	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{\sqrt{3}}{2}$	1	0
$\cos\theta$	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0	-1
$\tan\theta$	0	$\frac{1}{\sqrt{3}}$	1	$\sqrt{3}$	∞	0

$\cos 2\theta = \cos^2\theta - \sin^2\theta$

$\cos 2\theta = 2\cos^2\theta - 1$

$\cos 2\theta = 1 - 2\sin^2\theta$

$\sin 2\theta = 2\sin\theta \cdot \cos\theta$.

Integration formulae -

$$\int_0^{\pi/2} \cos^2 x \, dx = \pi/4 \quad \ldots \quad \cos^2 x = \frac{\cos 2x + 1}{2}$$

$$\int_0^{\pi} \sin x \cdot x \, dx = \pi \quad \ldots \quad \int uv\,dx = u \int v\,dx - \int\left(\frac{du}{dx}\int v\,dx\right)dx$$

$$\left.\begin{array}{l} \int_0^{\infty} e^{-2x} \cdot x \, dx = 1/4 \\ \int_0^{\infty} x^2 e^{-2x} \, dx = 1/4 \\ \int_0^{\infty} x^3 e^{-2x} \, dx = 3/8 \\ \int_{-\infty}^{\infty} x^5 e^{-2x^2} \, dx = 0 \end{array}\right\} \ldots \text{Gamma function.}$$

First function -

I L A T E

Inverse, Log, Arithmetic, Trignometric, Exponential.

Gamma function -

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

a & n are constants.

$$\Gamma(n) = (n-1)!$$

Gamma function will not operate on zero and negative value

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

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

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

$$\Gamma\left(\frac{9}{2}\right) = \frac{7}{2} \cdot \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi}$$

$$\Gamma\left(\frac{17}{2}\right) = \frac{15}{2} \cdot \frac{13}{2} \cdot \frac{11}{2} \cdot \frac{9}{2} \cdot \frac{7}{2} \cdot \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi}$$

#

$$\int_{-\infty}^{\infty} x^n \cdot e^{-ax^2} \, dx = \begin{cases} \text{If } n = \text{odd}, & \text{ans} = 0 \\ \text{If } n = \text{even}, & \text{ans} = \dfrac{\Gamma\left(\frac{n+1}{2}\right)}{a^{\frac{n+1}{2}}} \end{cases}$$

Operators-

⇒ Operators are like the mathematical operations addition, subtraction, multiplication.

⇒ As mathematical operations (+ - ×) needs numbers to be operated.

Operator needs function / Operand

Some operators and their meanings-

① Position ($\hat{x}$) ⇒ Multiplication by x.

② Momentum ($\hat{P}_x$) ⇒ $-i\hbar \frac{d}{dx}$

$i = iota = \sqrt{-1}$ and $\hbar = \frac{h}{2\pi}$

③ Total momentum ($\hat{P}$) $= \hat{P}_x + \hat{P}_y + \hat{P}_z$

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

④ Kinetic energy ($\hat{K}_x$)

$K = \frac{1}{2}mv^2 = \frac{1}{2}mv^2 \times \frac{m}{m} = \frac{1}{2}\frac{m^2v^2}{m} = \frac{p^2}{2m}$

$\boxed{K = \frac{p^2}{2m}}$

$\Rightarrow \hat{K}_x = \frac{\hat{P}_x^2}{2m} = \frac{\left(-i\hbar \frac{d}{dx}\right)^2}{2m} = \frac{-\hbar^2 \cdot \frac{d^2}{dx^2}}{2m}$

⑤ Total kinetic energy ($\hat{K}$)

$\boxed{\hat{K} = \hat{K}_x + \hat{K}_y + \hat{K}_z}$

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

⑥ Hamiltonian operator ($\hat{H}_x$)

↳ Total energy operator = K.E + P.E.

$\boxed{\hat{H}_x = \hat{K}_x + \hat{V}_x}$

$\hat{H}_x = -\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} + \hat{V}_x$

⑦ Total Hamiltonian operator. ($\hat{H}$)

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

$\hat{H} = \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} + \hat{V}_x\right) + \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dy^2} + \hat{V}_y\right) + \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dz^2} + \hat{V}_z\right)$

$= (\hat{K}_x + \hat{V}_x) + (\hat{K}_y + \hat{V}_y) + (\hat{K}_z + \hat{V}_z)$

Angular momentum

Angular momentum = position × momentum
↳ linear momentum

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

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

↳ cross product (vectors)

Cross product -

$$(x\hat{i} + y\hat{j} + z\hat{k}) \times (m\hat{i} + n\hat{j} + l\hat{k})$$

$$= \begin{array}{ccc} + & - & + \end{array}$$
$$\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ m & n & l \end{vmatrix}$$

$$= i(yl - nz) - j(xl - zm) + k(xn - ym)$$

Now,
$$\hat{r} = \hat{x}\hat{i} + \hat{y}\hat{j} + \hat{z}\hat{k}$$
$$\hat{p} = \hat{P}_x\hat{i} + \hat{P}_y\hat{j} + \hat{P}_z\hat{k}$$

$$\hat{r} \times \hat{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{P}_x & \hat{P}_y & \hat{P}_z \end{vmatrix}$$

$$= (\hat{y}\cdot\hat{P}_z - \hat{z}\cdot\hat{P}_y)\hat{i} - (\hat{x}\cdot\hat{P}_z - \hat{z}\hat{P}_x)\hat{j} + (\hat{x}\hat{P}_y - \hat{y}\hat{P}_x)\hat{k}$$

Total angular momentum -

$$\boxed{\hat{L} = \hat{L}_x\cdot\hat{i} + \hat{L}_y\cdot\hat{j} + \hat{L}_z\cdot\hat{k}}$$

Comparing above two equations -

$$\hat{L}_x = \hat{y}\hat{P}_z - \hat{z}\hat{P}_y$$
$$\hat{L}_y = -x\hat{P}_z + z\cdot\hat{P}_x$$
$$\hat{L}_z = x\hat{P}_y + y\cdot\hat{P}_x$$

Remember as

x
y z

Expression of an operator -

Ex. ① $\left(\frac{\hat{d}}{dx} + \hat{x}\right)^2$.

Ans.- $\left(\frac{\hat{d}}{dx} + \hat{x}\right)^2 f(x) = \left(\frac{\hat{d}}{dx} + \hat{x}\right)\left(\frac{\hat{d}}{dx} + \hat{x}\right) f(x)$

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

$$= \frac{\hat{d}^2}{dx^2} f(x) + \underbrace{\frac{\hat{d}}{dx}(\hat{x}\cdot f(x))} + \hat{x}\cdot\frac{\hat{d}}{dx} f(x) + \hat{x}^2 f(x)$$

$$= \frac{\hat{d}}{dx^2}\cdot f(x) + \hat{x}\cdot\frac{\hat{d}}{dx} f(x) + f(x)\frac{\hat{d}}{dx}\hat{x}$$
$$+ \hat{x}\cdot\frac{\hat{d}}{dx} f(x) + \hat{x}^2 f(x).$$

$$\left(\frac{\hat{d}}{dx} + \hat{x}\right)^2 \cancel{f(x)} = \frac{\hat{d}}{dx^2}\cancel{f(x)} + 2\hat{x}\cdot\frac{\hat{d}}{dx}\cdot\cancel{f(x)} + \hat{x}^2\cancel{f(x)} + 1\cdot\cancel{f(x)}$$

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

Ex. 2 $\left(\frac{\hat{d}}{dx} - \hat{x}\right)\left(\frac{\hat{d}}{dx} + \hat{x}\right)$

Ans - $\left(\frac{\hat{d}}{dx} - \hat{x}\right)\left(\frac{\hat{d}}{dx} + \hat{x}\right) f(x) = \left(\frac{\hat{d}}{dx} - \hat{x}\right)\left(\frac{\hat{d}}{dx} \cdot f(x) + \hat{x} \cdot f(x)\right)$

$$= \frac{\hat{d}^2}{dx^2} f(x) + \frac{\hat{d}}{dx} \hat{x} f(x) - \hat{x} \cdot \frac{\hat{d}}{dx} f(x) - \hat{x}^2 \cdot f(x)$$

$$= \frac{\hat{d}^2}{dx^2} f(x) + \hat{x} \cdot \cancel{\frac{\hat{d}}{dx} f(x)} + f(x) \cdot \frac{\hat{d}}{dx} x - \hat{x} \cdot \cancel{\frac{\hat{d}}{dx} f(x)} - x^2 \cdot f(x)$$

$$= \frac{\hat{d}^2}{dx^2} f(x) - \hat{x}^2 f(x) + (1) f(x)$$

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

$$\left(\frac{\hat{d}}{dx} - \hat{x}\right)\left(\frac{\hat{d}}{dx} + \hat{x}\right) \cancel{f(x)} = \left(\frac{\hat{d}^2}{dx^2} - \hat{x}^2 + 1\right) \cancel{f(x)}$$

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

Commutation of an Operator -

⇒ If two operators commute each other then they can be calculated simultaneously.

⇒ Representation of commutation -

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

⇒ $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$ Commutator.

then $\hat{A}$ & $\hat{B}$ commute each other.

⇒ $\hat{A}\hat{B} - \hat{B}\hat{A} = 0$

$$\boxed{\hat{A}\hat{B} = \hat{B}\hat{A}}$$

Ex. 1. Find the commutator of $\left[\hat{x}, \frac{\hat{d}}{dx}\right]$.

$$\left[\hat{x}, \frac{\hat{d}}{dx}\right] = \left(\hat{x} \cdot \frac{\hat{d}}{dx}\right) - \left(\frac{\hat{d}}{dx} \cdot \hat{x}\right)$$

$$\left[\hat{x}, \frac{d}{dx}\right] \psi = \left(\hat{x} \frac{\hat{d}}{dx} - \frac{\hat{d}}{dx} \cdot \hat{x}\right) \cdot \psi$$

$$= \hat{x} \cdot \frac{\hat{d}}{dx} \psi - \frac{\hat{d}}{dx} \cdot \hat{x} \cdot \psi$$

$$= \hat{x} \cdot \cancel{\frac{\hat{d}}{dx} \psi} - \hat{x} \cancel{\frac{\hat{d}}{dx} \psi} - \psi \cdot \frac{\hat{d}}{dx} \hat{x}$$

$$= (-1) \psi$$

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

Ex. ② Find the commutator of $\left[\frac{\hat{d}}{dx}, \hat{x}^2\right]$

Ans. - $\left[\frac{\hat{d}}{dx}, \hat{x}^2\right] = \left(\frac{\hat{d}}{dx}\cdot\hat{x}^2 - \hat{x}^2\frac{\hat{d}}{dx}\right)$

$$\left[\frac{\hat{d}}{dx}, \hat{x}^2\right]\psi = \left(\frac{\hat{d}}{dx}\hat{x}^2 - \hat{x}^2\frac{\hat{d}}{dx}\right)\psi$$

$$= \frac{\hat{d}}{dx}\hat{x}^2\cdot\psi - \hat{x}^2\frac{\hat{d}}{dx}\cdot\psi$$

$$= \hat{x}^2\cdot\cancel{\frac{\hat{d}}{dx}}\cdot\psi + \psi\frac{\hat{d}}{dx}\hat{x}^2 - \hat{x}^2\cdot\cancel{\frac{\hat{d}}{dx}}\cdot\psi$$

$$= \psi\cdot(2x)$$

$$\left[\frac{\hat{d}}{dx}, \hat{x}^2\right]\cancel{\psi} = (2x)\cancel{\psi}$$

$$\boxed{\left[\frac{\hat{d}}{dx}, \hat{x}^2\right] = 2x} \rightarrow \text{commutator}$$

Que - Which of the following commute?

i) $\hat{x}$ and $\frac{\hat{d}}{dx}$

ii) $\hat{x}^2$ and $\frac{\hat{d}}{dx}$

iii) $\hat{x}^2\frac{\hat{d}}{dx}$ and $\frac{d^2}{dx^2}$

✓ iv) $\frac{\hat{d}}{dx}$ and $\frac{d^2}{dx^2} + 2\frac{\hat{d}}{dx}$

Ans. -

① $\left[\hat{x}, \frac{\hat{d}}{dx}\right]\psi = \left(\hat{x}\frac{\hat{d}}{dx} - \frac{\hat{d}}{dx}\cdot\hat{x}\right)\psi$

$$= \hat{x}\cdot\frac{\hat{d}}{dx}\psi - \frac{\hat{d}}{dx}\cdot\hat{x}\psi$$

$$= \hat{x}\cdot\cancel{\frac{\hat{d}}{dx}}\psi - \hat{x}\cdot\cancel{\frac{\hat{d}}{dx}}\psi - \psi\frac{\hat{d}}{dx}\hat{x}$$

$$= (-)\psi$$

$\Rightarrow$ Commutator $= -1$.

② $\left[\hat{x}^2, \frac{\hat{d}}{dx}\right]\psi = \left(\hat{x}^2\frac{\hat{d}}{dx} - \frac{\hat{d}}{dx}\cdot\hat{x}^2\right)\psi$

$$= \hat{x}^2\frac{\hat{d}}{dx}\psi - \frac{\hat{d}}{dx}\hat{x}^2\cdot\psi$$

$$= \hat{x}^2\cdot\cancel{\frac{\hat{d}}{dx}}\cdot\psi - \hat{x}^2\cdot\cancel{\frac{\hat{d}}{dx}}\psi - \psi\cdot\frac{\hat{d}}{dx}\cdot\hat{x}^2$$

$$= (-2x)\psi$$

$\Rightarrow$ Commutator $= -2x$

③ $\left[\hat{x}^2 \cdot \frac{\hat{d}}{dx}, \frac{d^2}{dx^2}\right]\psi = \left(\hat{x}^2 \cdot \frac{\hat{d}}{dx} \cdot \frac{\hat{d}^2}{dx^2} \cdot \psi - \frac{\hat{d}^2}{dx^2} \cdot \hat{x}^2 \frac{d}{dx}\psi\right)$

$= \hat{x}^2 \frac{\hat{d}^3}{dx^3}\psi - \hat{x}^2 \cdot \frac{\hat{d}}{dx} \cdot \frac{\hat{d}^2}{dx^2}\psi - \psi \cdot \frac{\hat{d}^2}{dx^2} \cdot \hat{x}^2 \cdot \frac{\hat{d}\psi}{dx}$

$= \hat{x}^2 \cdot \cancel{\frac{\hat{d}^3}{dx^3}\psi} - \hat{x}^2 \cancel{\frac{d^3}{dx^3}} \cdot \psi - \psi \frac{\hat{d}^2}{dx^2} \cdot \hat{x}^2 \cdot \frac{\hat{d}\psi}{dx}$

$= \left(-\frac{\hat{d}^2}{dx^2} \cdot \hat{x}^2 \cdot \frac{\hat{d}}{dx}\right)\psi$ $\quad -2 \cdot \frac{\hat{d}\psi}{dx}$ ← ans.

← Commutator.

$\Rightarrow$ commutator $= -\frac{\hat{d}^2}{dx^2} \cdot \hat{x}^2 \frac{\hat{d}}{dx}$

④ $\left[\frac{\hat{d}}{dx}, \frac{\hat{d}^2}{dx^2} + 2\frac{\hat{d}}{dx}\right]\psi = \left[\frac{\hat{d}}{dx}\left(\frac{\hat{d}^2}{dx^2} + 2\frac{\hat{d}}{dx}\right) - \left(\frac{\hat{d}^2}{dx^2} + 2\frac{\hat{d}}{dx}\right)\frac{\hat{d}}{dx}\right]\psi$

$= \cancel{\frac{\hat{d}^3}{dx^3}}\psi + 2\cancel{\frac{\hat{d}^2}{dx^2}}\psi - \cancel{\frac{\hat{d}^3}{dx^3}}\psi - 2\cancel{\frac{\hat{d}^2}{dx^2}}\psi.$

$= 0$

$\Rightarrow$ Commutator $= 0.$ ✓

$\Rightarrow$ These two operators commute each other.

Ans - Option (iv)

Tricks to solve Commutation.

$$\boxed{\left[\frac{\hat{d}}{dx}, \hat{x}^n\right] = n \cdot x^{n-1}}$$

$\frac{d}{dx}(x^n)$

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

$= -\hat{B}\hat{A} + \hat{A}\hat{B}$

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

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

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

$$\boxed{\left[\hat{x}^n, \frac{\hat{d}}{dx}\right] = -n \cdot x^{n-1}}$$

Position and momentum commutator-

$[\hat{x}, \hat{p}_x] = (\hat{x}\hat{p}_x - \hat{p}_x \cdot \hat{x})$

$$[\hat{p}_x \cdot \hat{p}_x]\psi = (\hat{x}\hat{p}_x - \hat{p}_x \cdot \hat{x})\psi$$

$$= \hat{x} \cdot \hat{p}_x \psi - \hat{p}_x \cdot \hat{x} \cdot \psi$$

$$= \hat{x} \cdot \left(-i\hbar \frac{d}{dx}\right) \cdot \psi - p\left(-i\hbar \frac{d}{dx}\right)\hat{x}\psi$$

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

$$= -i\hbar \cancel{\hat{x} \cdot \frac{d\psi}{dx}} + i\hbar \cancel{\hat{x} \cdot \frac{d}{dx}\psi} + i\hbar \psi \cdot \frac{d}{dx}\hat{x}$$

$$= i\hbar \psi (1)$$

$$[\hat{x}, \hat{p}_x]\cancel{\psi} = i\hbar \cancel{\psi}$$

$$\boxed{[\hat{x}, \hat{p}_x] = i\hbar}$$

$$\boxed{[\hat{x}, \hat{p}_x] = i\hbar}$$

$$\boxed{[\hat{p}_x, \hat{x}] = -i\hbar}$$

$[\hat{x}, [\hat{x}, \hat{p}_x]]$

Imp

Any Operator commutes with every constant.

$$[\hat{x}, i\hbar] \to \text{constant}$$

$$\Rightarrow [\hat{x}, i\hbar] = 0$$

$$\boxed{[\hat{x}, [\hat{x}, \hat{p}_x]] = 0}$$

$[\hat{x}^3, \hat{p}_x] = (\hat{x}^3 \hat{p}_x - \hat{p}_x \hat{x}^3)$

$$[\hat{x}^3, \hat{p}_x]\psi = (\hat{x}^3 \hat{p}_x - \hat{p}_x \hat{x}^3)\psi$$

$$= \hat{x}^3\left(-i\hbar \frac{d}{dx}\right)\psi + i\hbar \frac{d}{dx}\hat{x}^3\psi$$

$$= -\hat{x}^3 \cdot i\hbar \frac{d\psi}{dx} + i\hbar \frac{d}{dx}(\hat{x}^3 \cdot \psi)$$

$$= -\hat{x}^3 \cdot i\hbar \frac{d\psi}{dx} + i\hbar \left[\hat{x}^3 \cdot \frac{d\psi}{dx} + \psi \cdot \frac{d}{dx}\hat{x}^3\right]$$

$$= \cancel{-\hat{x}^3 \cdot i\hbar \frac{d\psi}{dx}} + \cancel{\hat{x}^3 \cdot i\hbar \frac{d\psi}{dx}} + i\hbar \psi (3x^2)$$

$$= i\hbar (3x^2)\psi$$

$$\boxed{[\hat{x}^3, \hat{p}_x] = i\hbar (3x^2)}$$

Trick to solve commutation-
(Only for position & momentum)

$$\boxed{[\hat{A}^n, \hat{B}] = n.A^{n-1}\,[\hat{A}, \hat{B}]}$$

(differentiate the operator which is given
with some power
and multiply by $[\hat{A}, \hat{B}]$)

$[\hat{x}, \hat{p}_x^3]$

By trick-

$$[\hat{x}, \hat{p}_x^3] = \frac{d}{dx}(\hat{p}_x^3) \times [\hat{x}, \hat{p}_x]$$

$$= 3\hat{p}_x^2 \times i\hbar$$

$$= 3\,i\hbar\,\hat{p}_x^2$$

$[\hat{x}, [\hat{x}, \hat{p}_x^2]]$ is equal to ?

$$[\hat{x}, \underbrace{[\hat{x}, \hat{p}_x^2]}_{(2\hat{p}_x\, i\hbar)}]$$

By trick

$$[\hat{x}, 2i\hbar\,\hat{p}_x] \Rightarrow 2i\hbar\,[\hat{x}, \hat{p}_x] \Rightarrow 2i\hbar\,(i\hbar) = -2\hbar^2$$

Options -
i) $[\hat{p}_x \hat{x}, [\hat{x}, \hat{p}_x]]$
ii) $[\hat{x}\hat{p}_x, [\hat{x}, \hat{p}_x]]$
iii) $-[\hat{p}_x, [\hat{x}^2, \hat{p}_x]]$
iv) $[\hat{x}, [\hat{x}^2, \hat{p}_x]]$

Ans.- (i) $[\hat{p}_x \hat{x}, \underbrace{[\hat{x}, \hat{p}_x]}_{i\hbar \to \text{constant.}}]$

$\Rightarrow 0.$

(ii) $[\hat{x}\hat{p}_x, \underbrace{[\hat{x}, \hat{p}_x]}_{i\hbar \to \text{constant}}]$

$\Rightarrow 0$

✓ (iii) $-[\hat{p}_x, \underbrace{[\hat{x}^2, \hat{p}_x]}_{2\hat{x}\, i\hbar}] \Rightarrow -2i\hbar\,[\hat{p}_x, \hat{x}]$

$-2i\hbar\,(-i\hbar)$

$2i^2\hbar^2$

$-2\hbar^2$

(iv) $[\hat{x}, \underbrace{[\hat{x}^2, \hat{p}_x]}_{2\hat{x}\, i\hbar}]$

$2i\hbar\,\underbrace{[\hat{x}, \hat{x}]}_{0}$

$\Rightarrow 0$

IMP
Any operator commutes with itself.

Trick -

(for position & momentum operator only).

$$\boxed{[\hat{x}, f(\hat{P}_x)] = f'(\hat{P}_x)\,[\hat{x}, \hat{P}_x]}$$

differentiation.

Que $[\hat{x}, \sin\hat{P}_x]$

By trick $\Rightarrow$ $\left(\frac{d}{dx}\sin\hat{P}_x\right).\,[\hat{x}, \hat{P}_x]$

Ans. $\Rightarrow$ $\boxed{\cos\hat{P}_x \; i\hbar}$

$$\boxed{[f(\hat{P}_x), \hat{x}] = -\,f'(\hat{P}_x)\,[\hat{x}, \hat{P}_x]}$$

Que $[\hat{x}, e^{\alpha\hat{P}_x}]$

By trick $\Rightarrow$ $\frac{d}{d\hat{P}_x}\left(e^{\alpha\hat{P}_x}\right).\,[\hat{x}, \hat{P}_x]$

$\frac{d}{d\hat{P}_x}(\alpha\hat{P}_x).\, e^{\alpha\hat{P}_x}\; i\hbar$

$\left[\alpha.\frac{d}{d\hat{P}_x}.\hat{P}_x + \hat{P}_x\,\frac{d}{d\hat{P}_x}\alpha\right] e^{\alpha\hat{P}_x}\; i\hbar$

$(\alpha + 0)\, e^{\alpha\hat{P}_x}\; i\hbar$

Ans $\Rightarrow$ $\boxed{\alpha.\, e^{\alpha.\hat{P}_x}.\; i\hbar}$

Que - $[e^{\alpha\hat{P}_x}, \hat{x}]$

$[\hat{x}, e^{\alpha\hat{P}_x}] = \alpha\, e^{\alpha.\hat{P}_x}\; i\hbar$

$$\boxed{[e^{\alpha.\hat{P}_x}, \hat{x}] = -\,\alpha.\, e^{\alpha.\hat{P}_x}\; i\hbar}$$

Normalisation -

If any wave function ψ satisfies following condition, then it is called as normalised wave function

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

→ volume element.

⇒ If $\psi = e^{im\phi}$

then $\psi^* = e^{-im\phi}$

⇒ If $\psi = e^{-x^2}$

then $\psi^* = \psi = e^{-x^2}$

(Change in case of sign of iota only)

⇒ Volume element

Particle in a box and SHO

$$\left.\begin{array}{l} \text{Particle in a box} \\ \text{and} \\ \text{SHO} \end{array}\right\} \begin{array}{lll} 1D & \Rightarrow & dx \\ 2D & \Rightarrow & dx.dy \\ 3D & \Rightarrow & dx.dy.dz \end{array}$$

Rigid Rotor } $\int_0^{2\pi} d\phi$

Hydrogen atom

$$\boxed{d\tau = \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} r^2 \, dr \, \sin\theta \, d\theta \, d\phi}$$

For $\underbrace{\text{radial}}_{r}$ + $\underbrace{\text{angular}}_{\theta + \phi}$ parts.

⇒ For radial part only -

$$d\tau = \int_{r=0}^{\infty} r^2 dr \int_{\theta=0}^{\pi} \sin\theta \, d\theta . \int_{\phi=0}^{2\pi} d\phi$$

$$= \int_{r=0}^{\infty} r^2 dr \, [-\cos\theta]_0^{\pi} . [\phi]_0^{2\pi}$$

$$= \int_{r=0}^{\infty} r^2 dr \, [-(\cos\pi - \cos 0)] . [(2\pi - 0)]$$

$$= \int_{r=0}^{\infty} r^2 dr \, \underbrace{[-(-1-1)] . [2\pi]}_{4\pi}$$

$$\boxed{d\tau = 4\pi . \int_{r=0}^{\infty} r^2 dr}$$

Normalisation constant -

Que Find normalisation constant of -

$\Rightarrow$ $\psi = e^{im\phi}$ $(0 < \phi < 2\pi)$ (rigid rotor)

Ans. = $1/\sqrt{2\pi}$

Ans $\Rightarrow$

$\psi = e^{im\phi}$

$\psi^* = e^{-im\phi}$

For rigid rotor $\Rightarrow$ $d\tau = d\phi$

$$\int \psi^* \psi \, d\tau = \int_0^{2\pi} e^{-im\phi} \, e^{+im\phi} \, d\phi$$

$$= \int_0^{2\pi} e^{-im\phi + im\phi} \, d\phi$$

$$= \int_0^{2\pi} e^0 \, d\phi$$

$$= \int_0^{2\pi} 1 \, d\phi$$

$$= [\phi]_0^{2\pi}$$

$$= [2\pi - 0]$$

$$= 2\pi$$

$\hookrightarrow$ Not equal to 1

Hence, given wave function is not normalised.

For normalisation -

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

$$\int (N\psi^*)(N\psi) \, d\tau = 1$$

$$N^2 \int \psi^* \psi \, d\tau = 1$$

$$N^2 = \frac{1}{\int \psi^* \psi \, d\tau}$$

$$\boxed{N = \sqrt{\frac{1}{\int \psi^* . \psi \, d\tau}}}$$

Same question 1 -

$\psi = e^{im\phi}$

$(0 < \phi < 2\pi) \Rightarrow$ (rigid rotor)

$$\int \psi^* \psi \, d\tau = 2\pi$$

$$\therefore N = \sqrt{\frac{1}{\int \psi^* . \psi \, d\tau}}$$

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

$\uparrow$

Normalisation constant.

Normalised wave function (ψ_N) -

$$\boxed{\psi_N = N . \psi}$$

$$\boxed{\psi_N = N.\psi}$$

$\psi = e^{im\phi}$

$\psi^* = e^{-im\phi}$

$N = \frac{1}{\sqrt{2\pi}}$

$$\boxed{\psi_N = \frac{1}{\sqrt{2\pi}} e^{im\phi}}$$

$$\int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{-im\phi} \frac{1}{\sqrt{2\pi}} e^{im\phi} \, d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{-im\phi} . e^{im\phi} \, d\phi$$

$$= \frac{1}{2\pi} \times 2\pi$$

$= 1 \rightarrow$ Normalised

$$\boxed{\begin{array}{l} e^{-\infty} = 0 \\ e^{0} = 1 \\ e^{\infty} = \infty \end{array}}$$

Que. $\psi = \sin\left(\frac{n\pi x}{l}\right)$ Ans. $= \sqrt{2/l}$

$(0 < x < l)$ (1D-box)

Ans - $\psi = \sin\left(\frac{n\pi x}{l}\right)$

$\psi^* = \sin\left(\frac{n\pi x}{l}\right)$

For 1D box $d\tau = dx$.

$$\therefore \int_0^l \psi^* \psi \, dx = \int_0^l \sin\left(\frac{n\pi x}{l}\right) . \sin\left(\frac{n\pi x}{l}\right) dx$$

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

$\cos 2\theta = 1 - 2\sin^2\theta$

$\sin^2\theta = \frac{1-\cos 2\theta}{2}$

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

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

$$= \left[\frac{1}{2}x\right]_0^l - \frac{1}{2} \times \frac{\left[\sin\left(\frac{2n\pi x}{l}\right)\right]_0^l}{(2n\pi/l)}$$

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

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

$$= l/2$$

$$\boxed{\Rightarrow N = \frac{1}{\sqrt{l/2}} = \sqrt{\frac{2}{l}}}$$

Que $\psi = e^{-\beta x^2/2}$ for 1D SHO $(-\infty$ to $\infty)$ Ans. $= (\beta/\pi)^{1/4}$

Ans - $\psi = e^{-\beta x^2/2}$

$\psi^* = e^{-\beta x^2/2}$

For 1D SHO $\Rightarrow d\tau = dx$

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = \int_{-\infty}^{\infty} e^{-\beta x^2/2} \cdot e^{-\beta x^2/2} \, dx$$

$$= \int_{-\infty}^{\infty} e^{-\cancel{2}\beta x^2/\cancel{2}} \, dx$$

$$= \int_{-\infty}^{\infty} e^{-\beta x^2} \, dx$$ ... Ans. By using Gamma Function.

$$\cancel{= \left[\frac{e^{-\beta x^2}}{-\beta}\right]_{-\infty}^{\infty}}$$

$$\int_{-\infty}^{\infty} x^n \cdot e^{-ax^2} dx = \frac{\Gamma(n+1/2)}{a^{(n+1/2)}}$$

$$\cancel{= -\frac{1}{\beta}\left\{e^{-\beta\infty} - e^{-\beta(-\infty)}\right\}}$$

$$\cancel{= +\frac{1}{\beta}\left\{e^{-\infty} - e^{\infty}\right\}}$$

$$= \int_{-\infty}^{\infty} x^0 \cdot e^{-\beta x^2} dx$$

$$= \frac{\Gamma(0+1/2)}{\beta^{(0+1/2)}} = \frac{\Gamma(1/2)}{\beta^{1/2}} = \frac{\sqrt{\pi}}{\sqrt{\beta}} = \sqrt{\frac{\pi}{\beta}}$$

$$\boxed{N = \sqrt{\frac{1}{\sqrt{\pi/\beta}}} = \sqrt{\sqrt{\beta/\pi}} = (\beta/\pi)^{1/4}}$$

Que. - $\psi = e^{-r/a_0}$ (0 to ∞) for H-atom Ans $= \frac{1}{\sqrt{\pi}\, a_0^{3/2}}$

Ans. $\Rightarrow$ For radial part only.

$$d\tau = 4\pi \int_0^{\infty} r^2 \, dr$$

Now,

$$4\pi \int_0^{\infty} \psi^* \psi \, r^2 dr = 4\pi \int_0^{\infty} r^2 \, e^{-r/a_0} \cdot e^{-r/a_0} \, dr$$

$$= 4\pi \int_0^{\infty} r^2 \cdot e^{-2r/a_0} \, dr$$

Gamma function

$$= 4\pi \frac{\Gamma(2+1)}{\left(\frac{2}{a_0}\right)^{2+1}}$$

$$= 4\pi \frac{\Gamma 3}{(2/a_0)^3} \qquad \Gamma 3 = 2!$$

$$= \frac{\cancel{4}\pi \times \cancel{2} \times 1}{\cancel{2} \times \cancel{2} \times \cancel{2}} \times a_0^3$$

$$= \pi a_0^3$$

$$\Rightarrow N = \frac{1}{\sqrt{\pi a_0^3}}$$

$$\boxed{N = \frac{1}{\sqrt{\pi}\, a_0^{3/2}}}$$

Que. - $\psi(x) = N(2x^2-1)e^{-x^2/2}$ ($-\infty$ to ∞)

1D SHO

Ans. = $\left(\frac{1}{2\sqrt{\pi}}\right)^{1/2}$

Ans - For 1D SHO -

$d\tau = dx$

$\boxed{\psi_N = N.\psi}$

Therefore given function is normalised.

$\psi_N = \int (N\psi^*).(N\psi)\,d\tau = 0$

Hence.

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

$\int_{-\infty}^{\infty} N(2x^2-1).e^{-x^2/2}.\,N(2x^2-1)e^{-x^2/2}\,dx = 1$

$N^2\int_{-\infty}^{\infty}(2x^2-1)^2\,e^{-x^2}\,dx = 1$

$N^2\int_{-\infty}^{\infty}(4x^4-4x^2+1)\,e^{-x^2}\,dx = 1$

$N^2\left\{\int_{-\infty}^{\infty} 4x^4 e^{-x^2}dx - \int_{-\infty}^{\infty} 4x^2 e^{-x^2}dx + \int_{-\infty}^{\infty} x^0 e^{-x^2}dx\right\} = 1$

Use gamma function

$N^2\left\{4\left[\frac{\Gamma\frac{4+1}{2}}{(1)^{\left(\frac{4+1}{2}\right)}}\right] - 4\left[\frac{\Gamma\frac{2+1}{2}}{1^{\left(\frac{2+1}{2}\right)}}\right] + \left[\frac{\Gamma\frac{0+1}{2}}{1^{\left(\frac{0+1}{2}\right)}}\right]\right\} = 1$

$N^2\left\{4\,\Gamma\tfrac{5}{2} - 4\,\Gamma\tfrac{3}{2} + \Gamma\tfrac{1}{2}\right\} = 1$

$N^2\left\{4\times\frac{3}{2}\times\frac{1}{2}\sqrt{\pi} - 4\times\frac{1}{2}\sqrt{\pi} + \sqrt{\pi}\right\} = 1$

$N^2\{\sqrt{\pi}\,(3 - 2 + 1)\} = 1$

$N^2(2\sqrt{\pi}) = 1$

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

$\boxed{N = \sqrt{\frac{1}{2\sqrt{\pi}}} = \left(\frac{1}{2\sqrt{\pi}}\right)^{1/2}}$

Eigen value and Eigen function -

Operator (Function) = constant (Function)

i.e. $\boxed{\hat{A}\psi = a\psi}$ ← Eigen equation

Eigen operator

Eigen function

Eigen value

Que. Find the eigen values :-

1) Operator - $\frac{\hat{d}^2}{dx^2} + 2\frac{\hat{d}}{dx} + 3$

Function - $e^{\alpha x}$

Ans - $\alpha^2 + 2\alpha + 3$

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

$\left(\frac{\hat{d}^2}{dx^2} + 2\frac{\hat{d}}{dx} + 3\right)e^{\alpha x} = \frac{\hat{d}^2}{dx^2}e^{\alpha x} + 2.\frac{\hat{d}}{dx}e^{\alpha x} + 3.e^{\alpha x}$

$= \frac{\hat{d}}{dx}\left(\frac{e^{\alpha x}}{\cancel{\alpha}}\times\alpha\right) + 2.\,e^{\alpha x}\times\alpha + 3e^{\alpha x}$

$= e^{\alpha x}.\alpha.\alpha + 2.e^{\alpha x}.\alpha + 3e^{\alpha x}$

$= (\alpha^2 + 2\alpha + 3).\,e^{\alpha x}$

$\Rightarrow$ $\boxed{\text{Eigen value} = \alpha^2 + 2\alpha + 3}$

* Laplacian Operator -

$$\left(\frac{\hat{d}^2}{dx^2}+\frac{\hat{d}^2}{dy^2}+\frac{\hat{d}^2}{dz^2}\right)$$

Que

2) Operator - Laplacian $\qquad$ Ans. = $-(a^2+b^2+c^2)$

Function - cos ax . cos by . cos cz

Ans - $\left(\frac{\hat{d}^2}{dx^2}+\frac{\hat{d}^2}{dy^2}+\frac{\hat{d}^2}{dz^2}\right)(\cos ax)\cos by \cdot \cos cz)$

$$= \frac{\hat{d}^2}{dx^2}(\cos ax.\cos by.\cos cz) + \frac{\hat{d}^2}{dy^2}(\cos ax.\cos by.\cos cz) + \frac{\hat{d}^2}{dz^2}(\cos ax.\cos by.\cos cz)$$

$$= (-a^2\cos ax.\cos by.\cos cz) + (-b^2.\cos by.\cos ax.\cos cz) + (-c^2.\cos ax.\cos by.\cos cz)$$

$$= -(a^2+b^2+c^2).(\cos ax\ \cos by\ \cos cz)$$

$$\boxed{\Rightarrow \text{Eigen value} = -(a^2+b^2+c^2)}$$

3) Operator - $\hat{P}_x$ $\qquad$ Ans. = $(\hbar k)$

Function - e^{ikx}

Ans. - $\hat{P}_x\,(e^{ikx}) = \left(-i\hbar\frac{\hat{d}}{dx}\right).e^{ikx}$

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

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

$$= \hbar k.e^{ikx} \quad \ldots \quad i^2=-1$$

$$\boxed{\Rightarrow \text{Eigen value} = \hbar k}$$

4) Operator - $\frac{\hat{d}^2}{dx^2} - 16x^2$ $\qquad$ Ans. = (-4)

Function - e^{-2x^2}

Ans. - $\left(\frac{\hat{d}^2}{dx^2} - 16x^2\right)e^{-2x^2} = \frac{\hat{d}^2}{dx^2}e^{-2x^2} - 16x^2.e^{-2x^2}$

$$= (-4x).\frac{\hat{d}}{dx}\,x e^{-2x^2} - 16x^2.e^{-2x^2}$$

$$\cancel{= (-4x)(-4x).e^{-2x^2} - 16x^2\,e^{-2x^2}}$$

$$= -4\left[x.(-4x).e^{-2x^2} + e^{-2x^2}\right] - 16x^2.e^{-2x^2}$$

$$= \cancel{16x^2.e^{-2x^2}} - 4.e^{-2x^2} - \cancel{16x^2.e^{-2x^2}}$$

$$= -4.e^{-2x^2}$$

$$\boxed{\Rightarrow \text{Eigen value} = -4}$$

Schrodinger Wave equation-

For Hamiltonian operator,
We have eigen equation as-

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

$$(\hat{K}_x + \hat{V}_x)\psi = E\psi$$

$$\left(\frac{\hat{P}_x^2}{2m} + \hat{V}_x\right)\psi = E\psi$$

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

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x\right]\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V_x\psi\right] = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi - V_x\psi$$

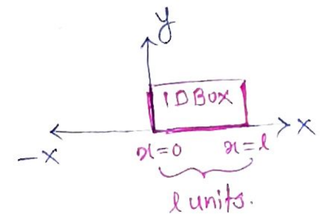
$$-\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}(E - V_x)\psi$$

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

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V_x)\psi = 0} \quad \ldots \hbar = \frac{h}{2\pi}$$

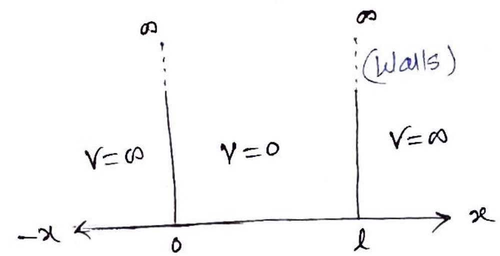
This is Schrodinger wave equation.

Particle in a 1-D Box-



Particle is a free particle.
That means - There is no othe[r] particle inside the box.
That means - There will be no any force on that free particl[e].

$$F = -\frac{dV}{dr}$$



⇒ No potential also inside in box.

⇒ Outside the box, there will be particles in environment
Hence $V = \infty$

⇒ ∞ walls means particle cannot go outside the box.

⇒ Wave function of a particle-

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

⇒ Particle will be present inside the box.
To check - wheather particle is present on walls or no[t]!

Boundary-

$x = 0 \Rightarrow \psi = \sqrt{\frac{2}{l}}.\sin 0° \Rightarrow \boxed{\psi = 0}$

particle does not exist

$x = l \Rightarrow \psi = \sqrt{\frac{2}{l}}.\sin(n\pi)$

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

⇒ Particle does not exist on walls.

For 1D Box - Remember -

$$\boxed{\psi(x) = \sqrt{\frac{2}{l}} \cdot \sin\left(\frac{n\pi x}{l}\right)}$$

$$\boxed{E = \frac{n^2h^2}{8ml^2}} \qquad n = 1, 2, 3, 4, \ldots, \infty \qquad \boxed{n \neq 0}$$

m → mass of particle

Wave function plots - 1D Box

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

Ground State (n=1)

$$\psi_1 = \sqrt{\frac{2}{l}} \cdot \sin\left(\frac{\cancel{1}\pi x}{l}\right)$$

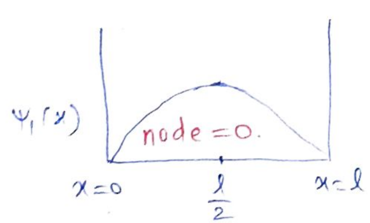
⇒ For ψ_1 to be maximum, term of sin must be max. Max. value of sin function is 1.

$$\sin\frac{\pi x}{l} = 1 \rightarrow \sin\frac{\pi}{2}$$

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

$$\frac{x}{l} = \frac{1}{2}$$

$$\boxed{x = l/2}$$



First Excited State (n=2)

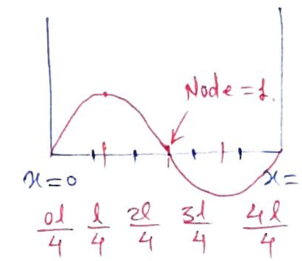
$$\psi_2 = \sqrt{\frac{2}{l}} \cdot \sin\left(\frac{2\pi x}{l}\right)$$

⇒ For ψ_2 to be maximum,

$$\sin\left(\frac{2\pi x}{l}\right) = 1 \rightarrow \sin\frac{\pi}{2}$$

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

$$\boxed{x = l/4}$$



⇒ For $x = 2l/4$

$$\psi_2 = \sqrt{\frac{2}{l}} \cdot \sin\frac{2\pi}{\cancel{l}} \cdot \frac{2\cancel{l}}{4}$$

$$= \sqrt{\frac{2}{l}} \cdot \sin\pi$$

$$= 0.$$

⇒ For $x = 3l/4$

$$\psi_2 = \sqrt{\frac{2}{l}} \cdot \sin\frac{2\pi}{\cancel{l}} \cdot \frac{3\cancel{l}}{4}$$

$$= \sqrt{\frac{2}{l}} \cdot \sin\frac{3}{2}\pi \rightarrow -1$$

$$= -\sqrt{\frac{2}{l}}.$$

$\psi_2 = 0 \leftarrow x = 0$

$\psi_2 = \sqrt{\frac{2}{l}} \leftarrow x = l/4$

$\psi_2 = 0 \leftarrow x = 2l/4$

$\psi_2 = -\sqrt{\frac{2}{l}} \leftarrow x = 3l/4$

$\psi_2 = 0 \leftarrow x = l.$

Second Excited State ($n=3$)

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

For ψ_3 to be max. $\sin\frac{3\pi x}{l} = 1 \hookrightarrow \sin\frac{\pi}{2}$

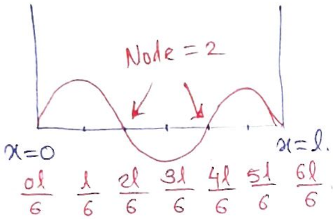
$$\frac{3\pi x}{l} = \frac{\pi}{2}$$

$$\boxed{x = \frac{l}{6}}$$

$\Rightarrow$ At $x = 2l/6 = l/3$

$$\psi_3 = \sqrt{\frac{2}{l}} \sin\frac{3\pi}{l}\cdot\frac{l}{3}$$

$$= 0$$



Trick

Conclusions - 1. $x=0 \Rightarrow \psi=0$

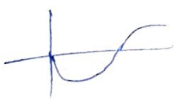
$x=l \Rightarrow \psi=0$

2. Nodes - where particle is not present.

$\boxed{\text{no. of nodes} = n-1}$

3. Increasing curve always.

Decreasing curve -

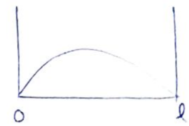


By trick

Wave function plots -

ψ_1

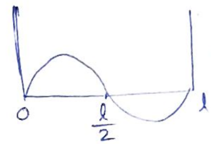
Nodes $= 1-1=0$.



← Ground state $n=1$ ψ_1

ψ_2

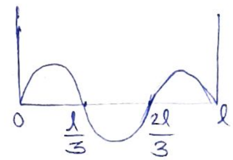
Nodes $= 2-1 = 1$.



← First excited state $n=2$ ψ_2

ψ_3

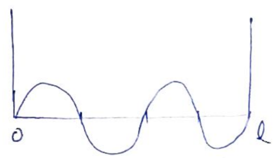
Nodes $= 3-1 = 2$



← Second excited sta[te] $n=3$ ψ_3

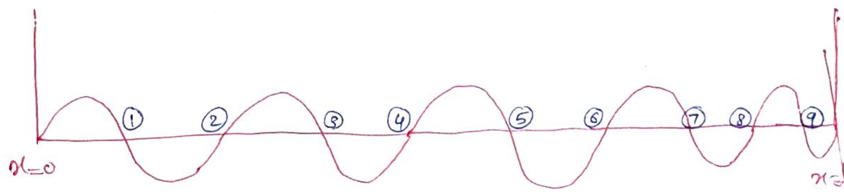
ψ_4

Nodes $= 4-1 = 3$

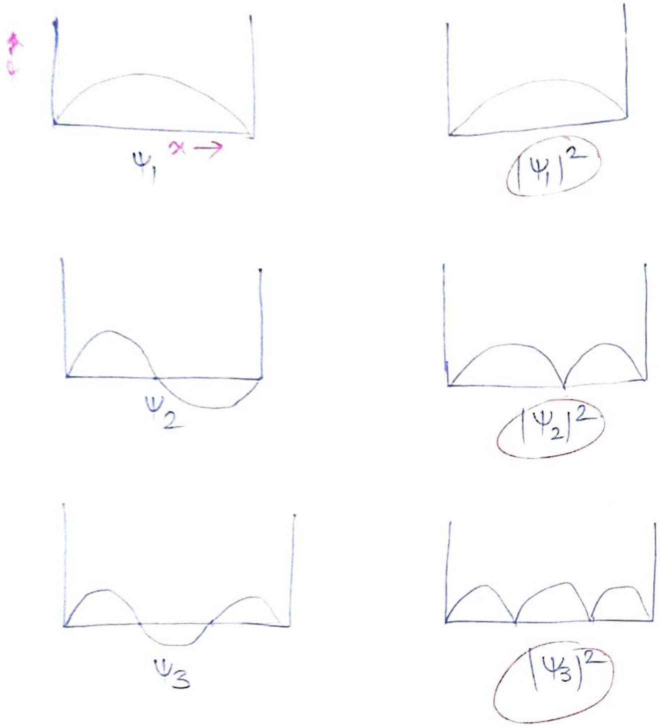


ψ_{10}

Nodes $= 10-1 = 9$



Probability plots -



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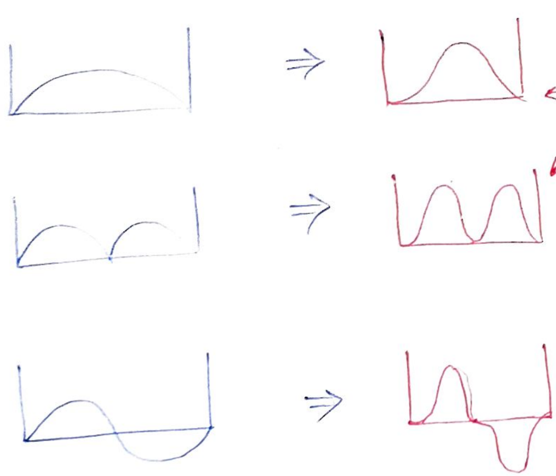
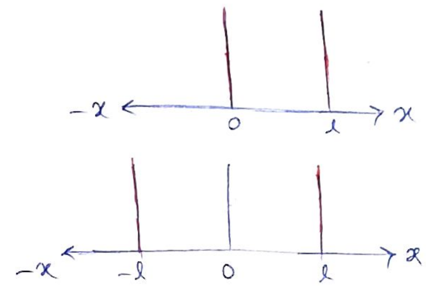


More correct representatn acc. to standard books.

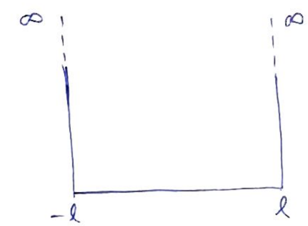
Particle in a 1D - Symmeteic Box -



← Unsymmeteic Box

{with respect to origin (0).

← Symmeteic Box.



Wave function of a particle in asymmeteic box -

$$\boxed{\psi_A = \sqrt{\frac{2}{l}} \cdot \sin\left(\frac{n\pi x}{l}\right)} \qquad \boxed{E_A = \frac{n^2 h^2}{8ml^2}}$$

For symmeteic box -

$$\boxed{\psi_S = \sqrt{\frac{1}{l}} \cdot \sin\left(\frac{n\pi x}{2l}\right)} \quad \ldots n = 2, 4, 6, 8, \ldots \text{ (even)}$$

$$\boxed{\psi_S = \sqrt{\frac{1}{l}} \cdot \cos\left(\frac{n\pi x}{2l}\right)} \quad \ldots n = 1, 3, 5, 7, \ldots \text{ (odd)}$$

$$\boxed{E_S = \frac{n^2 h^2}{32\, m l^2}}$$

Wave function plots for 1D-symmetric box.

For Ground State $(n=1)$ → odd → cos

$$\psi_1 = \sqrt{\frac{1}{l}} \cdot \cos \frac{\pi x}{2l}$$

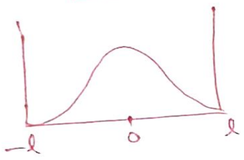
For ψ_1 to be maximum.

$$\cos \frac{\pi x}{2l} = 1 \leftarrow \cos 0^\circ$$

$$\frac{\pi x}{2l} = 0$$

$$\boxed{x = 0}$$

$\boxed{n=1}$ ψ_1



$\boxed{\frac{0l}{1} \quad \frac{l}{1}}$

For First excited state - $(n=2)$ → even → sin

$$\psi_2 = \sqrt{\frac{1}{l}} \cdot \sin \left(\frac{2\pi x}{2l}\right)$$

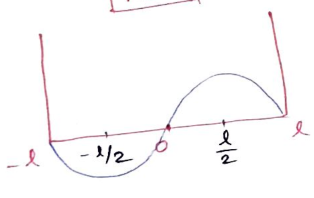
For ψ_2 to be maximum

$$\sin\left(\frac{\pi x}{l}\right) = 1 \leftarrow \sin \frac{\pi}{2}$$

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

$$\boxed{x = l/2}$$

$\boxed{n=2}$ ψ_2



$\boxed{\frac{0l}{2} \quad \frac{l}{2} \quad \frac{2l}{2}}$

For $x = 0 \Rightarrow \psi_2 = 0$

For second excited state $(n=3)$ → odd ← cos.

$$\psi_3 = \sqrt{\frac{1}{l}} \cdot \cos \frac{3\pi x}{2l}.$$

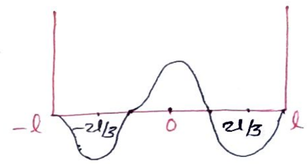
For ψ_3 to be maximum.

$$\cos \frac{3\pi x}{2l} = 1 \leftarrow \cos 0^\circ$$

$$\frac{3\pi x}{2l} = 0.$$

$$\boxed{x = 0}$$

$\boxed{n=3}$ ψ_3



$\boxed{\frac{0l}{3} \quad \frac{l}{3} \quad \frac{2l}{3} \quad \frac{3l}{3}}$

For all odd numbers of n. maximum lies at $\boxed{x=0}$

Trick

Conclusions -
1) $n = \text{odd} \Rightarrow x = 0$ gives maximum ψ
2) $n = \text{even} \Rightarrow x = 0 \Rightarrow \psi = 0$
3) No. of nodes $= n-1$

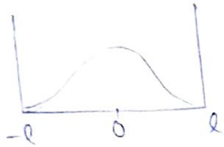
By trick

Wave function plots-

$n = 1$ ← odd ← $x = 0$ max.

ψ_1

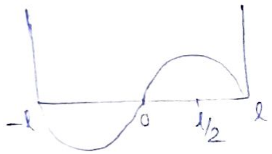
Nodes = 0



$n = 2$ ← $\psi = 0$ at $x = 0$.

ψ_2

Nodes = 1

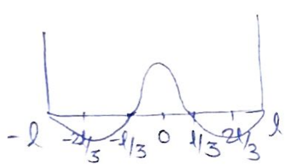


Maximum must be checked by putting $\boxed{x = l/2 \text{ or } -l/2}$

$n = 3$ ← odd ← $x = 0$ max.

ψ_3

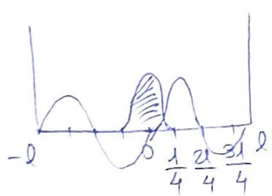
Nodes = 2



$n = 4$ ← $\psi = 0$ at $x = 0$

ψ_4

Nodes = 3



put $x = \frac{l}{4}$ ⇒ $\psi_4 = \sqrt{\frac{1}{l}} \cdot \sin \frac{4\pi l}{2l \times 4}$ ⇒ $\sin\frac{\pi}{2} = 1$ max.

⇒ $l/4$ gives maximum.

IMP

Wave functions are $\boxed{\text{multiplicative}}$ in nature.

Energy is $\boxed{\text{additive}}$ in nature.

1D Box

$$\boxed{\psi_{(x)} = \sqrt{\frac{2}{l}} \cdot \sin\left(\frac{n\pi x}{l}\right)}$$

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

2D Box

$$\psi_{(x,y)} = \psi_{(x)} \cdot \psi_{(y)}$$

$$\boxed{\psi_{(x,y)} = \sqrt{\frac{2}{l_x}} \cdot \sin\frac{n_x \pi x}{l_x} \cdot \sqrt{\frac{2}{l_y}} \cdot \sin\frac{n_y \pi y}{l_y}}$$

$$E_{(x,y)} = E_x + E_y.$$

$$\boxed{E_{(x,y)} = \frac{n_x^2 h^2}{8ml_x^2} + \frac{n_y^2 h^2}{8ml_y^2} = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right)}$$

3D Box

$$\psi_{(x,y,z)} = \psi_{(x)} \cdot \psi_{(y)} \cdot \psi_{(z)}$$

$$\boxed{\psi_{(x,y,z)} = \sqrt{\frac{2}{l_x}} \sqrt{\frac{2}{l_y}} \sqrt{\frac{2}{l_z}} \cdot \sin\frac{n_x \pi x}{l_x} \cdot \sin\frac{n_y \pi y}{l_y} \cdot \sin\frac{n_z \pi z}{l_z}}$$

$$E_{(x,y,z)} = E_{(x)} + E_{(y)} + E_{(z)}$$

$$\boxed{E_{(x,y,z)} = \frac{h^2}{8m^2}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)}$$

Degeneracy in 1D - 2D - 3D Box -

Zero point energy -

Ground state ene. ≡ Zero point energy.

$\boxed{n=1}$

1D-Box

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

For ground state / zero point ene. (ZPE) -

$\boxed{n=1}$

$$\boxed{E = \frac{1^2 h^2}{8ml^2}}$$

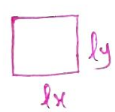
2D-Box

$$E_T = E_x + E_y.$$

$$\boxed{E_T = \frac{n_x^2h^2}{8ml_x^2} + \frac{n_y^2h^2}{8ml_y^2}}$$

For square box -

$l_x = l_y = l$



$$E_T = \frac{n_x^2h^2}{8ml^2} + \frac{n_y^2h^2}{8ml^2}$$

$$\boxed{E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2)}$$

For zero point energy -

$n_x = 1, \; n_y = 1$

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

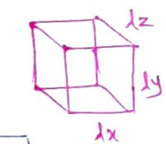
3D-Box

$$E_T = E_x + E_y + E_z$$

$$\boxed{E_T = \frac{n_x^2h^2}{8ml_x^2} + \frac{n_y^2h^2}{8ml_y^2} + \frac{n_z^2h^2}{8ml_z^2}}$$

For cubic Box -

$l_x = l_y = l_z = l$



$$\boxed{E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)}$$

For zero point energy,

$n_x = 1, \; n_y = 1, \; n_z = 1$

$$\boxed{E = \frac{3h^2}{8ml^2}}$$

Conclusion -

$E_{ZPE}(3D) = 3 \cdot E_{ZPE}(1D)$

$E_{ZPE}(2D) = 2 \cdot E_{ZPE}(1D)$

order -

Zero pt. ene -

$\boxed{3D > 2D > 1D}$

Degeneracy -

⇒ States having equal energy.

1D - Box

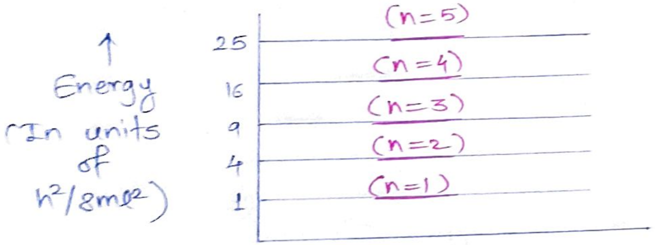
$$E = \frac{n^2h^2}{8ml^2}$$

For Ground state, $n=1$, $E = \frac{h^2}{8ml^2}$

For 1st excited state, $n=2$, $E = \frac{4h^2}{8ml^2}$

For 2nd excited state, $n=3$, $E = \frac{9h^2}{8ml^2}$

For 3rd excited state, $n=4$, $E = \frac{16h^2}{8ml^2}$



⇒ No degeneracy in 1D - Box

i.e. $\boxed{\text{Degeneracy} = 1}$

2D - Box

$$E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2)$$ ——— Square Box.

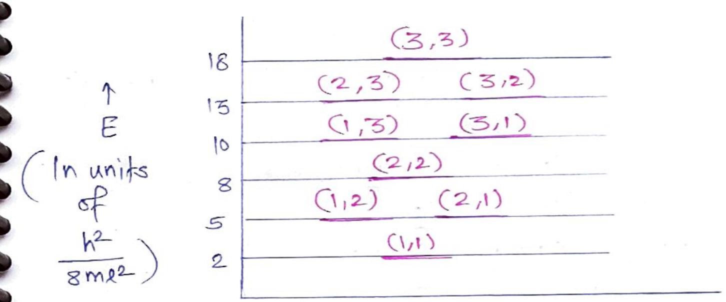
Possible values of (n_x, n_y) - $(n_x^2+n_y^2)$ value

2 (1,1)   8 (2,2)   18 (3,3)   32 (4,4) ....

5 (1,2)   13 (2,3)   25 (3,4)   41 (4,5) ...

10 (1,3)   20 (2,4)   34 (3,5)   (4,6) ....

And so on .....



Conclusion -

If $n_x = n_y$ ⇒ $\boxed{\text{Degeneracy} = 1}$

If $n_x \neq n_y$ ⇒ $\boxed{\text{Degeneracy} = 2}$

3D-Box

$$E = \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

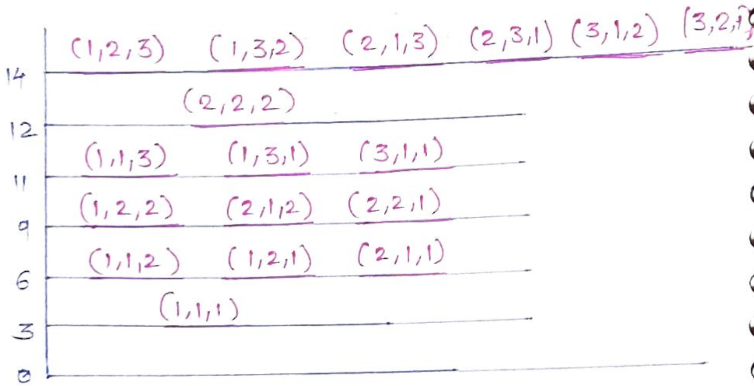
Possible values of (n_x, n_y, n_z)

3 (1,1,1) 6 (1,1,2) 9 (1,2,2) 14 (1,2,3)

12 (2,2,2) 11 (1,1,3) 19 (1,3,3)

27 (3,3,3) 18 (1,1,4) 33 (1,4,4)

..... and so on .....



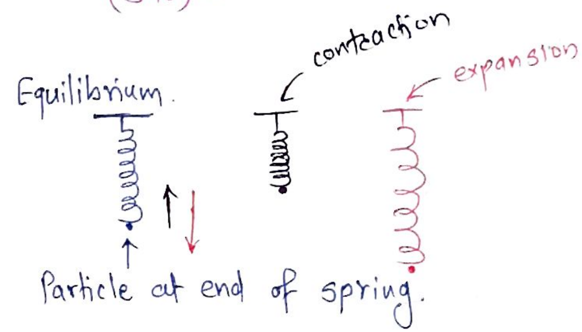
Conclusion -

If $n_x = n_y = n_z \Rightarrow$ Degenaracy = 1

$n_x = n_y \neq n_z \Rightarrow$ Degeneracy = 3

$n_x \neq n_y \neq n_z \Rightarrow$ Degeneracy = 6

Simple Harmonic Oscillator (SHO) -



Degeneracy -

$$\boxed{E = \left(n + \tfrac{1}{2}\right) h\nu} \quad \ldots \quad (n = 0, 1, 2, \ldots)$$

$\Rightarrow$ Zero point energy - $\boxed{n=0}$

$$\boxed{E_0 = \tfrac{1}{2} h\nu}$$

$\Rightarrow$ First excited state - $\boxed{n=1}$

$$\boxed{E_1 = \tfrac{3}{2} h\nu}$$

Energy (SHO) -

1D SHO $\boxed{E = (n+\frac{1}{2})h\nu}$ ...$(n = 0, 1, 2, \ldots)$

2D SHO $E_T = E_x + E_y$

$= (n_x+\frac{1}{2})h\nu + (n_y+\frac{1}{2})h\nu$

$\boxed{E_{2D} = (n_x+n_y+1)h\nu}$

3D SHO $E_T = E_x + E_y + E_z$

$= (n_x+\frac{1}{2})h\nu + (n_y+\frac{1}{2})h\nu + (n_z+\frac{1}{2})h\nu$

$\boxed{E_{3D} = (n_x+n_y+n_z+\frac{3}{2})h\nu}$

Degeneracy -

1D SHO $\boxed{E = (n+\frac{1}{2})h\nu}$

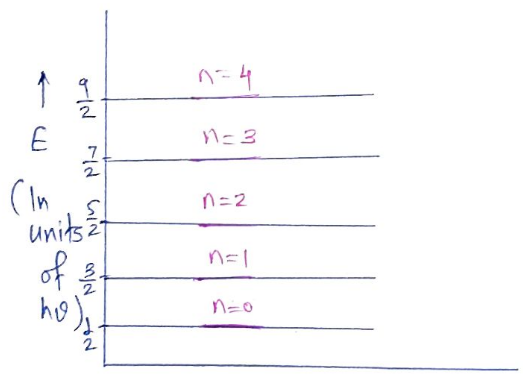
$n=0$, $E = \frac{1}{2}h\nu$

$n=1$, $E = \frac{3}{2}h\nu$

$n=2$, $E = \frac{5}{2}h\nu$

$n=3$, $E = \frac{7}{2}h\nu$

$n=4$, $E = \frac{9}{2}h\nu$



Degeneracy = 1

2D - SHO

$E = (n_x+n_y+1)h\nu$

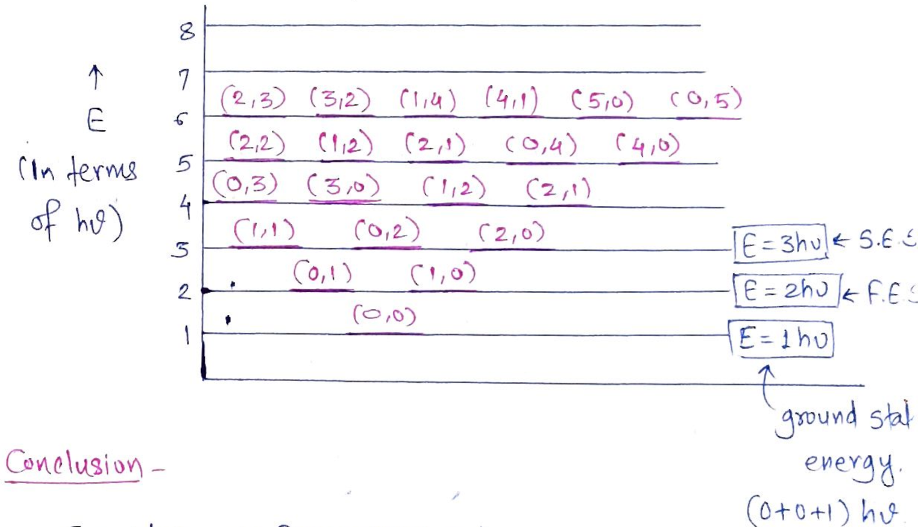
Possible values of (n_x, n_y) - (n_x+n_y+1)

① (0,0) ② (0,1) ③ (0,2) ④ (0,3) ⑤ (0,4)

③ (1,1) ④ (1,2) ⑤ (1,3) ⑥ (1,4) ⑦ (1,5)

⑤ (2,2) ⑥ (2,3) ⑦ (2,4) ⑧ (2,5)

⑦ (3,3)



Conclusion -

$E = 1h\nu \Rightarrow$ Degeneracy = 1

$E = 2h\nu \Rightarrow g = 2$

$E = 3h\nu \Rightarrow g = 3$

⋮

$E = nh\nu \Rightarrow g = n$.

Value of energy in case of SHO -

$\boxed{n h\nu}$ natural no.

$10 h\nu$ ✓

$42 h\nu$ ✓

$\frac{33}{2} h\nu$ ✗ Not natural no.

3D - SHO

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

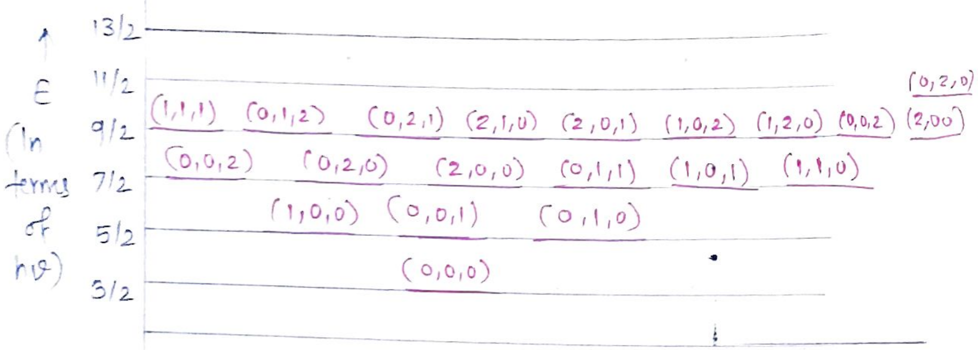
Possible values of (n_x, n_y, n_z) -

$\frac{3}{2}$ (0,0,0) $\quad$ $\frac{7}{2}$ (0,1,1) $\quad$ $\frac{9}{2}$ (0,1,2) $\quad$ $\frac{11}{2}$ (0,2,2) $\quad$ $\frac{5}{2}$ (0,0,1)

$\frac{9}{2}$ (1,1,1) $\quad$ $\frac{11}{2}$ (0,2,2) $\quad$ $\frac{11}{2}$ (0,1,3) $\quad$ $\frac{13}{2}$ (0,2,3) $\quad$ $\frac{7}{2}$ (0,0,2)

$\frac{15}{2}$ (2,2,2) $\quad$ $\frac{15}{2}$ (0,3,3) $\quad$ $\frac{13}{2}$ (0,1,4) $\quad$ $\frac{9}{2}$ (0,0,3)

$\frac{21}{2}$ (3,3,3)



Trick -

$E = (n_x + n_y + n_z + \frac{3}{2}) h\nu$

$\hookrightarrow E = (n + \frac{3}{2}) h\nu$

$(n_x + n_y + n_z) = n$

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

For ex. Given - $E = \frac{21}{2} h\nu$. Find degeneracy for 3D-SHO.

Ans - We have - $E = (n + \frac{3}{2}) h\nu$ Compare

$n = \frac{21}{2} - \frac{3}{2} = \frac{18}{2} = 9$

$\boxed{n_x + n_y + n_z = 9}$

(2, 3, 4) ⇐ possible (n_x, n_y, n_z) value

$$g = \frac{(n+1)(n+2)}{2} = \frac{(9+1)(9+2)}{2} = \frac{10 \times 11}{2} = 11 \times 5 = \cancel{90}\ 55$$

$\boxed{\text{degeneracy} = \cancel{90}\ 55}$

Que. Given - 3D-SHO energy of a level $= \boxed{\frac{91}{2} h\nu}$

Find degeneracy of that level.

Ans. -

$E = \frac{91}{2} h\nu$

For 3D-SHO We have, $E = (n + \frac{3}{2}) h\nu$

Comparing these eqⁿs -

$n + \frac{3}{2} = \frac{91}{2}$

$n = \frac{91}{2} - \frac{3}{2} = \frac{91-3}{2} = \frac{88}{2} = 44$

$\boxed{n = 44}$

$$g = \frac{(44+1)(44+2)}{2} = \frac{45 \times 46}{2} = 45 \times 23 = 1035$$

$\boxed{g = 1035}$

SHO -
(Basics)

We have Schrodinger wave equation -

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

In case of SHO,

potential ene. $(V) = \frac{1}{2}kx^2$

$\Rightarrow$ Equation becomes -

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\cdot\left(E - \frac{1}{2}kx^2\right)\psi = 0.$$

$$\frac{d^2\psi}{dx^2} + \underbrace{\frac{8\pi^2 m}{h^2}E}_{\alpha}\psi - \underbrace{\frac{8\pi^2 m}{h^2}\cdot\frac{1}{2}k}_{\beta^2}x^2\cdot\psi = 0.$$

$$\frac{d^2\psi}{dx^2} + \alpha\psi - \beta^2 x^2\psi = 0$$

$$\boxed{\frac{d^2\psi}{dx^2} + (\alpha - \beta^2x^2)\psi = 0}$$

~~Constant~~ Variable $\boxed{\xi^2 = \beta x^2}$ ← Comes in derivation.

Wave function of SHO -

Remember - Variable $\boxed{\xi^2 = \beta x^2}$

For 1D-Box wave function $\Rightarrow$ $\psi_{(x)} = \sqrt{\frac{2}{l}}\cdot\sin\left(\frac{n\pi x}{l}\right)$

For SHO Wave function $\Rightarrow$ (general expression) $\boxed{\psi_n(\xi) = H_n(\xi)\, e^{-\xi^2/2}}$

Hermite polynomial $\boxed{H_n(\xi)}$

Normalised wave function for SHO -

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

Normalisation constant.

Normalisation constant (N) -

$$\boxed{N = \sqrt{\frac{1}{2^n \cdot n!}}\cdot\left(\frac{\beta}{\pi}\right)^{1/4}}$$

$\boxed{n! \equiv \lfloor n}$

$\boxed{0! = 1}$

$\Rightarrow$ N for ground state of SHO ($n=0$).

$$N_0 = \sqrt{\frac{1}{2^0 \cdot 0!}}\cdot\left(\frac{\beta}{\pi}\right)^{1/4} = (\beta/\pi)^{1/4}$$

$$\boxed{N_0 = (\beta/\pi)^{1/4}}$$

$\Rightarrow \boxed{N_0 = (\beta/\pi)^{1/4}}$

$\Rightarrow$ N for first excited state $(n=1)$

$$N_1 = \sqrt{\frac{1}{2^1 \cdot 1!}} \cdot \left(\frac{\beta}{\pi}\right)^{1/4} = \sqrt{\frac{1}{2}} \left(\frac{\beta}{\pi}\right)^{1/4}$$

$$\boxed{N_1 = \frac{1}{\sqrt{2}} \cdot (\beta/\pi)^{1/4}}$$

$\Rightarrow$ N for second excited state $(n=2)$

$$N_2 = \sqrt{\frac{1}{2^2 \cdot 2!}} \left(\frac{\beta}{\pi}\right)^{1/4} = \sqrt{\frac{1}{8}} (\beta/\pi)^{1/4}$$

$$\boxed{N_2 = 1/\sqrt{8} \cdot (\beta/\pi)^{1/4}}$$

Hermite Polynomial ($H_n(\xi)$) -

$$\boxed{H_n(\xi) = (-1)^n \cdot e^{\xi^2} \cdot \frac{d^n}{d\xi^n} \cdot e^{-\xi^2}}$$

$x^1 = x$

$(-x)^1 = x$

$\Rightarrow$ For ground state $(n=0)$

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

$\frac{d^0}{dx^0} = 1$

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

$\therefore \boxed{H_0(\xi) = 1}$ ← Hermite polynomial of zero degree

$\Rightarrow$ For first excited state $(n=1)$

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

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

$$= 2\xi \cdot e^{\xi^2 - \xi^2}$$

$$\boxed{H_1(\xi) = 2\xi}$$

$\Rightarrow$ For second excited state $(n=2)$

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

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

$$= e^{\xi^2} (-2) \cdot \left[\xi (-2\xi e^{-\xi^2}) + e^{-\xi^2}(1)\right]$$

$$= 4\xi^2 \cdot e^{\xi^2 - \xi^2} - 2 \cdot e^{\xi^2 - \xi^2}$$

$$= 4 \cdot \xi^2 (1) - 2 \cdot (1)$$

$$\boxed{H_2(\xi) = 4\xi^2 - 2}$$

Trick

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

remember $\boxed{H_0(\xi) = 1}$

Hermite Polynomial By Trick-

$$H_{n+1}(\xi) = 2\xi\, H_n(\xi) - 2n.\, H_{n-1}(\xi)$$

$\Rightarrow n=0$

H_1

$$H_{0+1}(\xi) = 2\xi\, H_0(\xi) - 2(0)\, H_{0-1}(\xi)$$

$\to 1$ $\to H_{-1}$ cannot be calculated.

$$= 2\xi\,(1) - 0$$

$$\boxed{H_1(\xi) = 2\xi}$$

$\Rightarrow n=1$

H_2

$$H_{1+1}(\xi) = 2\xi\, H_1(\xi) - 2(1)\, H_{1-1}(\xi)$$

$$H_2(\xi) = 2\xi\,(2\xi) - 2.\, H_0(\xi)$$

$$\boxed{H_2(\xi) = 4\xi^2 - 2(1)}$$

$\Rightarrow n=2$

H_3

$$H_{2+1}(\xi) = 2\xi\, H_2(\xi) - 2(2).\, H_{2-1}(\xi)$$

$$H_3(\xi) = 2\xi\,(4\xi^2 - 2) - 4.\, H_1(\xi)$$

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

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

$$\boxed{H_3(\xi) = 8\xi^2 - 12\xi}$$

Normalised wave function.

$$\psi_n(\xi) = N.H_n(\xi).\, e^{-\xi^2/2}$$

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

Ground state

$$\psi_0(\xi) = N_0.\, H_0(\xi).\, e^{-\xi^2/2}$$

$$= (\beta/\pi)^{1/4} \times (1) \times e^{-\xi^2/2}$$

$$\boxed{\psi_0(\xi) = (\beta/\pi)^{1/4} \times e^{-\xi^2/2}}$$

$$\boxed{\psi_0(x) = (\beta/\pi)^{1/4}.\, e^{-\beta x^2/2}}$$

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

First excited state.

$$\psi_n(\xi) = N\, H_n(\xi).\, e^{-\xi^2/2}$$

$$\psi_1(\xi) = N_1.\, H_1(\xi).\, e^{-\xi^2/2}$$

$$= \frac{1}{\sqrt{2}}.\,(\beta/\pi)^{1/4} \times 2\xi.\, e^{-\xi^2/2}$$

*

$\xi^2 = \beta x^2$

$$\boxed{\psi_1(\xi) = \sqrt{2}.(\beta/\pi)^{1/4}.\, \xi.\, e^{-\xi^2/2}}$$

Same equation in terms of x.

$$\boxed{\psi_1(x) = \sqrt{2}.\,(\beta/\pi)^{1/4}.\, \sqrt{\beta}.x^2.\, e^{-\beta x^2/2}}$$

Simply substitute $\xi^2 = \beta x^2$.

Wave function plots for SHO.

$n=0$ Ground State

$\psi_0(x) = (\beta/\pi)^{1/4} \cdot e^{-\beta x^2/2}$

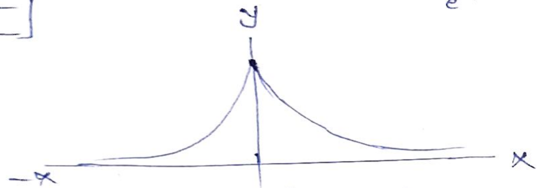
$\boxed{\psi_0(x) = e^{-x^2}}$

Neglect the constant terms as they are const. ← not varying.

Let $\boxed{y = e^{-x^2}}$

x	0	1	-1
y	1	0.36	0.36

e^{-0} $e^{-(1)^2} = e^{-1}$ $e^{-(-1)^2} = e^{-1}$



Symmetrical graph.

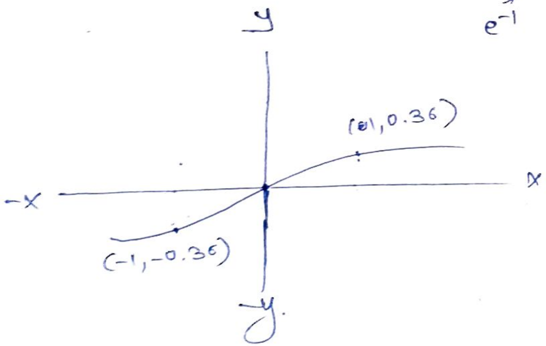
$n=01$ First excited state

$\psi_1(x) = \sqrt{2} \cdot (\beta/\pi)^{1/4} \cdot \sqrt{\beta} \cdot x \cdot e^{-\beta x^2/2}$

$\psi_1(x) = x \cdot e^{-x^2}$

x	0	1	-1	2	-2
y	0	0.36	-0.36		

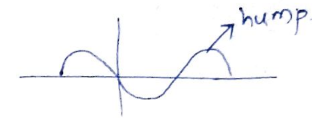
e^{-1} $-e^{-1}$



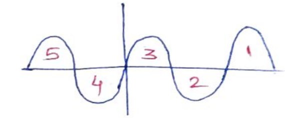
Tricks

①

Levels	No. of Humps
n	n+1
0	1
1	2
2	3



② Numbering of humps should be from right to left



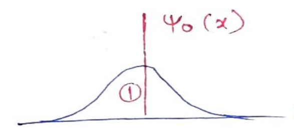
③ Odd numbers ⇒ always up
(1,3,5)
even no.s ⇒ always down.
(2,4)

By trick

⇒ For Y-axis Make the graph symmetric by line

$n=0$

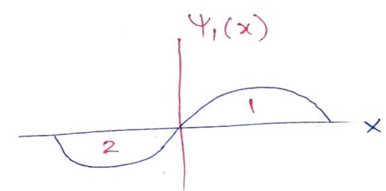
humps = 1
odd
↳ always up.



$n=1$

humps = 2

1 and 2
up   down.



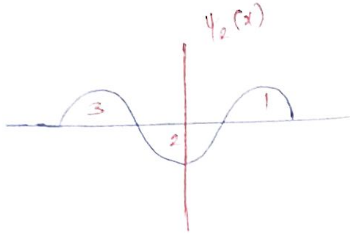
$n=2$

humps $= 3$

3   2   1

↑   ↑

up   up



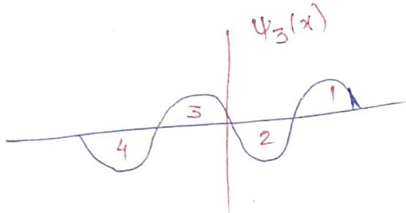
$n=3$

humps $= 4$

1   2   3   4

↑   ↑

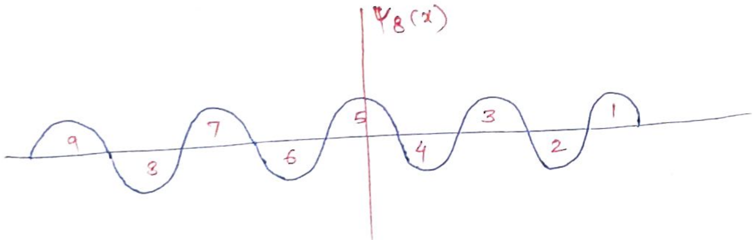
up   up



<u>Que</u> Draw wave function plot for 8^{th} excited state.

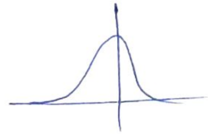
<u>Ans</u> - 8^{th} excited state $\Rightarrow \boxed{n=8}$

no. of humps $= 8+1 = 9$



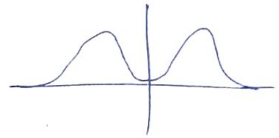
Probability plots for SHO. - $|\psi(x)|^2$ Vs x.

$n=0$



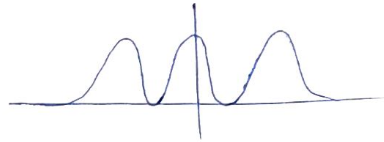
$|\psi_0(x)|^2$

$n=1$



$|\psi_1(x)|^2$

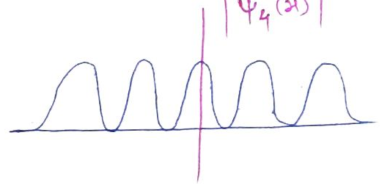
$n=2$



$|\psi_2(x)|^2$

$n=4$

$|\psi_4(x)|^2$



humps $= 5$

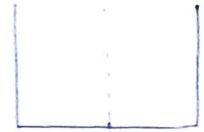
$\Rightarrow$ probability plot.

all humps up

Que- The probability of finding a free particle inside the left half of 1D box in between 0 to $l/2$ is?

Ans = (0.5)

Ans-



$0 \qquad \frac{l}{2} \qquad l$

Formula- $\int_0^{l/2} \psi^* \psi \, d\tau$ = Probability

$\boxed{\text{1D Box}} \Rightarrow \quad \psi = \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l}$

$d\tau = dx$ ← (volume element)

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

$$\therefore P = \int_0^{l/2} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \cdot \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \, dx$$

$$= \frac{2}{l} \int_0^{l/2} \sin^2 \frac{n\pi x}{l} \, dx \qquad \left(\sin^2 x = \frac{1-\cos 2x}{2}\right)$$

$$= \frac{2}{l} \cdot \frac{1}{2} \int_0^{l/2} \left(1 - \cos \frac{2xn\pi}{l}\right) dx$$

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

$$= \frac{1}{l} \left\{ \frac{l}{2} - 0 - \frac{l}{2} \cdot \frac{\sin \cancel{2} \frac{ln\pi}{\cancel{2}}}{2n\pi} - \sin 0 \right\}$$

$$= \frac{1}{2} - \frac{1}{2l} \cdot \frac{\sin l n\pi}{2n\pi} \quad \ldots (\sin n\pi = 0)$$

$$\boxed{P = \frac{1}{2}}$$

$\boxed{\text{For } \% = \frac{1}{2} \times 100 = 50\%}$

Que- The probability of finding a free particle inside the 1D box in between $l/4$ to $3l/4$ is ...?

Ans = $\left(\frac{1}{2} + \frac{1}{\pi}\right)$

Ans.-

$$P = \int \psi^* \cdot \psi \cdot d\tau$$

$$= \int_{l/4}^{3l/4} \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l} \cdot \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l} \, dx$$

$$= \frac{2}{l} \cdot \int_{l/4}^{3l/4} \sin^2 \frac{n\pi x}{l} \, dx$$

$$= \frac{\cancel{2}}{l} \times \frac{1}{\cancel{2}} \int_{l/4}^{3l/4} \left(1 - \cos \frac{2n\pi x}{l}\right) dx$$

$$= \frac{1}{l} \left\{ [x]_{l/4}^{3l/4} - \left[\frac{\sin \frac{2n\pi x}{l}}{2n\pi/l} \right]_{l/4}^{3l/4} \right\}$$

$$= \frac{1}{l} \left\{ \frac{3l}{4} - \frac{l}{4} - \left[\frac{l}{2n\pi} \left(\sin \frac{2n\pi \cdot 3\cancel{l}}{\cancel{4}_2 \cancel{l}} - \sin \frac{2n\pi \cancel{l}}{\cancel{4}_2 \cancel{l}} \right) \right] \right\}$$

$$= \frac{1}{l} \left\{ \left(\frac{3l - l}{4}\right) - \frac{l}{2n\pi} \left(\sin \frac{3n\pi}{2} - \sin \frac{n\pi}{2} \right) \right\}$$

$$= \frac{1}{l} \left[\frac{l}{2} + \frac{l}{2\pi} \left(-\sin \frac{3\pi}{2} + \sin \frac{\pi}{2} \right) \right] \quad \ldots \boxed{n=1}$$

$$= \frac{1}{l} \left[\frac{l}{2} + \frac{l}{2\pi} \right] \underbrace{(-(-1) + 1)}_{2}$$

$$= \frac{1}{l} \left[\frac{l}{2} + \frac{l}{2\pi} \times 2 \right]$$

$$= \frac{1}{\cancel{l}} \left[\frac{l\pi}{2} + \frac{2l}{\pi} \right] = \frac{\pi + 2}{2\pi} = \boxed{\frac{1}{2} + \frac{1}{\pi}}$$

Average Value -
(Expectation Value) -

Average value for any operator O - representation $\langle \hat{O} \rangle$.

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

Que - Find average value of position in 1D-Box.

Ans -

Ans. = $(l/2)$

$$\langle \hat{x} \rangle = \int_0^l \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l} \hat{x} \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l} \cdot dx$$

$$= \frac{2}{l} \int_0^l x \cdot \sin^2 \left(\frac{n\pi x}{l}\right) dx$$

$$= \frac{2}{l} \cdot \int_0^l x \frac{1}{2} \left[1 - \cos \frac{2n\pi x}{l}\right] dx$$

I L A T E

$$= \frac{2}{l} \cdot \int_0^l \left(\frac{x}{2} - \frac{1}{2} x \cdot \cos \frac{2n\pi x}{l}\right) dx$$

$$= \frac{1}{l} \left[\frac{x^2}{2} - \left(\int x \cdot \cos \frac{2n\pi x}{l} dx\right)\right]$$

$$= \frac{1}{l} \left\{\frac{l^2}{2} - \left[x \cdot \frac{\sin \frac{2n\pi x}{l}}{2n\pi/l} - \int (1) \frac{\sin \frac{2n\pi x}{l}}{2n\pi/l} dx\right]\right\}$$

$$= \frac{1}{l} \left\{\frac{l^2}{2} - \frac{l \cdot l}{2n\pi} \cdot \sin \frac{2n\pi l}{l} + \frac{l}{2n\pi} \times \frac{l}{2n\pi} \cos \frac{2n\pi l}{l} - \frac{\cos 0}{2n\pi/l}\right\}$$

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

$$\langle x \rangle = \int_0^l \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l} \cdot \hat{x} \cdot \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l} \, dx$$

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

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

$$= \frac{1}{l} \int_0^l \left(x - x \cdot \cos \frac{2n\pi x}{l}\right) dx$$

$$= \frac{1}{l} \left[\frac{x^2}{2}\right]_0^l - \frac{1}{l} \left\{x \cdot \frac{\sin 2n\pi x/l}{2n\pi/l} - \left(\int \frac{\sin 2n\pi x/l}{2n\pi/l} dx\right)\right\}$$

$$= \frac{1}{l} \left(\frac{l^2}{2} - 0\right) - \frac{1}{l} l^2 \frac{\sin 2n\pi}{2n\pi} - \frac{1}{l} \cdot \frac{l}{2n\pi} \left[\frac{\cos 2n\pi x/l}{2n\pi/l}\right]_0^l$$

$$= \frac{l}{2} - \frac{l}{2n\pi} \cdot \sin 2n\pi - \frac{l}{(2n\pi)^2} [\cos 2n\pi - \cos 0]$$

$$= \frac{l}{2} - \frac{l}{2n\pi} (0) - \frac{l}{(2n\pi)^2} [(1) - (1)]$$

$$= \frac{l}{2} - (0) - (0)$$

$$= l/2$$

$$\Rightarrow \boxed{\langle \hat{x} \rangle = l/2}$$

Que - Find average value of $\hat{x}^2$ in 1D Box.

Ans $= \left(\frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}\right)$

Ans -

$$\langle \hat{x}^2 \rangle = \int_0^l \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l} \cdot \hat{x}^2 \sqrt{\frac{2}{l}} \cdot \sin\frac{n\pi x}{l} \, dx$$

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

$$= \frac{2}{l} \cdot \frac{1}{2} \int_0^l x^2 \left(1 - \cos\frac{2n\pi x}{l}\right) dx$$

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

$$= \frac{1}{l}\left\{\left[\frac{x^3}{3}\right]_0^l - \left[x^2 \frac{\sin 2n\pi x/l}{2n\pi/l}\right]_0^l + \left(\int_0^l 2x \frac{\sin 2n\pi x/l}{2n\pi/l} dx\right)\right.$$

$$= \frac{1}{l}\left(\frac{l^3}{3} - 0\right) - \frac{1}{l}\left(\frac{l^2 \, l}{2n\pi} \sin 2n\pi - 0\right) + \frac{2}{l}\left[x \times \frac{-\cos 2n\pi x/l)}{(2n\pi/l)^2}\right]_0^l$$

$$- \frac{1}{l}\int \frac{-\cos 2n\pi x/l}{(2n\pi/l)^2} dx$$

$$= \frac{l^2}{3} - \frac{l^2}{2n\pi}(0) - \frac{2}{l} \cdot \frac{l^2}{(2n\pi)^2}\left[l \cos 2n\pi - 0\right]$$

$$+ \frac{1}{l} \cdot \frac{l^2}{2n\pi}\left(\sin\frac{2n\pi x/l}{(2n\pi/l)}\right)_0^l$$

$$= \frac{l^2}{3} - 0 - \frac{l^2}{2(n\pi)^2}(1) + \frac{l^2}{(2n\pi)^2}(\sin 2n\pi - \sin 0)$$

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

$$\boxed{\langle \hat{x}^2 \rangle = \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}}$$

Que - Find average value of $\hat{P}_x$ in 1D-Box.

Ans. $= (0)$

Ans -

$$\langle \hat{P}_x \rangle = \int_0^l \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l} \cdot \hat{P}_x \sqrt{\frac{2}{l}} \cdot \sin\frac{n\pi x}{l} \, dx$$

$$= \frac{2}{l}\int_0^l \left(\sin\frac{n\pi x}{l} \cdot (-)i\hbar \frac{d}{dx} \cdot \sin\frac{n\pi x}{l}\right) dx$$

$$= \frac{2}{l} \int_0^l \left(\sin\frac{n\pi x}{l} \times (-i\hbar) \cdot \cos\frac{n\pi x}{l} \times \frac{n\pi}{l}\right) dx$$

$$= \frac{2}{l} \times \frac{n\pi}{l} \times (-i\hbar) \int_0^l \sin\frac{n\pi x}{l} \cdot \cos\frac{n\pi x}{l} \, dx$$

$$= \frac{-2i\hbar n\pi}{l^2} \cdot \frac{1}{2} \int_0^l \sin\frac{2n\pi x}{l} \, dx$$

$$= -\frac{i\hbar n\pi}{l^2}\left[-\frac{\cos 2n\pi x}{l}\right]_0^l \times \frac{l}{2n\pi}$$

$$= -\frac{i\hbar n\pi}{l^2} \times \frac{l}{2n\pi}\left[-\cos 2n\pi + \cos 0\right]$$

$$= -\frac{i\hbar}{l}\left[-(1) + (1)\right]$$

$$= 0$$

$$\Rightarrow \boxed{\langle \hat{P}_x \rangle = 0}$$

Que Find average value of $\hat{p}_x^2$ in one D Box.

$\left(Ans = \frac{n^2h^2}{4l^2}\right)$

Ans – $\langle \hat{p}_x^2 \rangle = \int_0^l \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l} \, \hat{p}_x^2 \, \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l} \, dx$

$\langle \hat{p}_x^2 \rangle = \frac{2}{l} \int_0^l \sin\frac{n\pi x}{l} \left(-i\hbar \frac{d}{dx}\right)^2 \sin\frac{n\pi x}{l} \, dx$

$= -\frac{2\hbar^2}{l} \int_0^l \sin\frac{n\pi x}{l} \cdot \frac{d^2}{dx^2} \sin\frac{n\pi x}{l} \, dx$

$= -\frac{2\hbar^2}{l} \int_0^l \sin\frac{n\pi x}{l} \times \frac{n\pi}{l} \times \frac{n\pi}{l} \cdot \left(-\sin\frac{n\pi x}{l}\right) dx$

$= +\frac{2\hbar^2}{l} \frac{(n\pi)^2}{l^2} \int_0^l \sin\frac{n\pi x}{l} \cdot \sin\frac{n\pi x}{l} \, dx$

$= +\frac{2\hbar^2 (n\pi)^2}{l^3} \int_0^l \sin^2\frac{n\pi x}{l} \, dx$

$= +\frac{2\hbar^2 (n\pi)^2}{l^3} \cdot \frac{1}{2} \int_0^l \left(1 - \cos\frac{2n\pi x}{l}\right) dx$

$= +\frac{\hbar^2 (n\pi)^2}{l^3} \left[x - \frac{\sin 2n\pi x}{l} \times \left(\frac{l}{2n\pi}\right) \right]_0^l$

$= +\frac{\hbar^2 (n\pi)^2}{l^3} [l - 0] - \frac{\hbar (n\pi)^2}{l^3} \times \frac{l}{2n\pi} \left[\underbrace{\sin 2n\pi}_{0} - \underbrace{\sin 0}_{0}\right]$

$= +\frac{\hbar^2 n^2 \pi^2}{l^2} - 0$

$= +\frac{h^2 \cdot n^2 \cdot \pi^2}{4\pi^2 \, l^2} = \boxed{+\frac{n^2 h^2}{4 l^2}}$

Que.- Find average value of $(\hat{x})$ in 1D-SHO and $(\hat{x}^2)$ in ground state $(n = 0)$

Ans.- For 1D-SHO

$\psi = (\beta/\pi)^{1/4} \cdot e^{-\xi^2/2}$ $(\because n = 0)$

$\psi = (\beta/\pi)^{1/4} \cdot e^{-\beta x^2/2}$ .... $\boxed{\xi^2 = \beta x^2}$

limits $\Rightarrow -\infty$ to $+\infty$

$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} (\beta/\pi)^{1/4} \, e^{-\beta x^2/2} \cdot \hat{x} \, (\beta/\pi)^{1/4} \, e^{-\beta x^2/2} \, dx$

$= \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x \cdot e^{-2\beta x^2/2} \, dx$

$= \left(\frac{\beta}{\pi}\right)^{1/2} \underbrace{\int_{-\infty}^{\infty} x \cdot e^{-\beta x^2} \, dx}_{0}$ ....(Gamma function)

power of x is odd $= f$.

$\boxed{\langle \hat{x} \rangle = 0}$

Ans.- For $\langle \hat{x}^2 \rangle$

$\langle \hat{x}^2 \rangle = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \cdot \int_{-\infty}^{\infty} x^2 \cdot e^{-\beta x^2} \, dx$ $\qquad \boxed{\frac{\Gamma\frac{n+1}{2}}{a^{\frac{n+1}{2}}}}$

$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \frac{\Gamma\frac{2+1}{2}}{\beta^{\left(\frac{2+1}{2}\right)}} = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \cdot \frac{\Gamma 3/2}{\beta^{3/2}}$

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

$\boxed{\langle \hat{x}^2 \rangle = \frac{1}{2\beta}}$

Huckel Theory -

⇒ Used to determine the energy of π-bond for simple conjugated system.
ex. benzene, 1,3- butadiene, allylic system
(delocalisation energy).
← ene. of π-bond

Secular Determinant -

⇒ Order - $\boxed{\text{Rows} \times \text{Columns}}$

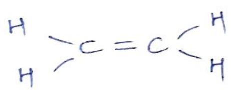
$\begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix}$ ↳ Order = 2×2

elements.

$\begin{vmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{vmatrix}$ ↳ Order = 2×3

⇒ Finding order of secular determinant.

ex. ethene



No. of π e⁻s (n) = 2
|||
No. of carbon atoms

Now, $\boxed{\text{order} = 2\times2}$

$\boxed{\text{Order} = n\times n}$

no. of carbon atoms.

Ex. Benzene

n = 6

$\boxed{\text{Order} = 6\times6}$

Ex. 1,3- butadiene

$H_2C = CH - CH = CH_2$

n = 4

$\boxed{\text{Order} = 4\times4}$

Ex.

n = 3

$\boxed{\text{Order} = 3\times3}$

⇒ Elements of determinant -

In quantum, $\boxed{\text{elements} \equiv \text{Integrals.}}$

Order = 2×2

general determinant = $\begin{vmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{vmatrix}$

$\boxed{C = H - ES}$

energy.

∴ general determinant = $\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix}$

⇒ Integrals -

- ↳ Coulomb Integral (α)
- ↳ Overlap Integral (S_{ij})
- ↳ Resonance Integral (H_{ij}) (Exchange)

Coulomb Integral (α) -

no. of rows = no. of colums

$$\boxed{\alpha = H_{ii}}$$

ex. $H_{11} - ES_{11} \equiv \alpha - E.S_{11}$

$H_{22} - ES_{22} \equiv \alpha - ES_{22}$

Overlap Integral (S_{ij})

no. of rows ≠ no. of columns.

Condition - S_{ij} → $= 1$ ..... if $i = j$; → $= 0$ ..... if $i \neq j$

ex. $H_{11} - ES_{11} \equiv H_{11} - E(1) = H_{11} - E$

$H_{12} - ES_{12} \equiv H_{12} - E(0) = H_{12}$

$H_{21} - E.S_{21} \equiv H_{21} - E(0) = H_{21}$

$H_{22} - E.S_{22} \equiv H_{22} - E(1) = H_{22} - E$

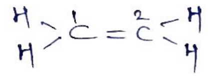
⇒ By using coulombic & overlap integrals - determinant becomes

$$\begin{vmatrix} H_{11} - E.S_{11} & H_{12} - E.S_{12} \\ H_{21} - E.S_{21} & H_{22} - E.S_{22} \end{vmatrix} \equiv \begin{vmatrix} \alpha - E & H_{12} \\ H_{21} & \alpha - E \end{vmatrix}$$

Resonance / Exchange Integral (H_{ij}) -

Condition

H_{ij} → β ..... (If bond is present between C_i and C_j) ; → 0 ..... (If no bond between C_i & C_j)

Ex. 

H_{12} ⇒ Bond is present betn C_1 & C_2 ⇒ β

H_{21} ⇒ β

Secular determinant for molecule ethene -

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix}$$

$H_2\overset{1}{C} = \overset{2}{C}H - \overset{3}{C}H = \overset{4}{C}H_2$

$\boxed{n = 4}$

→ no. of π-bonds ∝ no. of carbon atoms.

$\boxed{\text{order} = n \times n}$ → 4×4

$$\text{Secular Determinant} = \begin{vmatrix} C_{11} & C_{12} & C_{13} & C_{14} \\ C_{21} & C_{22} & C_{23} & C_{24} \\ C_{31} & C_{32} & C_{33} & C_{34} \\ C_{41} & C_{42} & C_{43} & C_{44} \end{vmatrix}$$

$$\boxed{C = H - ES}$$

$$= \begin{vmatrix} H_{11} - E.S_{11} & H_{12} - E.S_{12} & H_{13} - E.S_{13} & H_{14} - E.S_{14} \\ H_{21} - E.S_{21} & H_{22} - E.S_{22} & H_{23} - E.S_{23} & H_{24} - E.S_{24} \\ H_{31} - E.S_{31} & H_{32} - E.S_{32} & H_{33} - E.S_{33} & H_{34} - E.S_{34} \\ H_{41} - E.S_{41} & H_{42} - E.S_{42} & H_{43} - E.S_{43} & H_{44} - E.S_{44} \end{vmatrix}$$

Secular determinant for 1,3-butadiene =

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

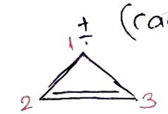
$\left[H_2\overset{1}{C} = \overset{2}{C}H - \overset{3}{C}H_2\right]^{\pm}$ (cation / anion / radical)

$\boxed{n = 3}$

$\boxed{\text{Order} = 3 \times 3}$ ← $n \times n$

$$\text{Secular determinant} = \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$$

(cation / anion / radical)

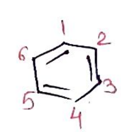


$n = 3$

Order $= 3 \times 3$

$$\text{Secular determinant} = \begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix}$$

#



$\boxed{n = 6}$ $\boxed{\text{order} = 6 \times 6}$

$$\text{Secular determinant} = \begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

Energy of π - bond :-

Ethene -

$H_2C = CH_2$

Secular determinant = $\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix}$

Secular determinant equation-

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & \frac{\beta}{\beta} \\ \frac{\beta}{\beta} & \frac{\alpha - E}{\beta} \end{vmatrix} = 0 \quad \ldots\ \text{Divide by } \beta$$

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad \ldots\ \text{Let } \frac{\alpha - E}{\beta} = x$$

$$\boxed{x^2 - 1 = 0}$$

$(x+1)(x-1) = 0$ ..... $a^2 - b^2 = (a+b)(a-b)$

$x + 1 = 0$ or $x - 1 = 0$

$\boxed{x = -1}$ $\boxed{x = 1}$

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

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

Remember -

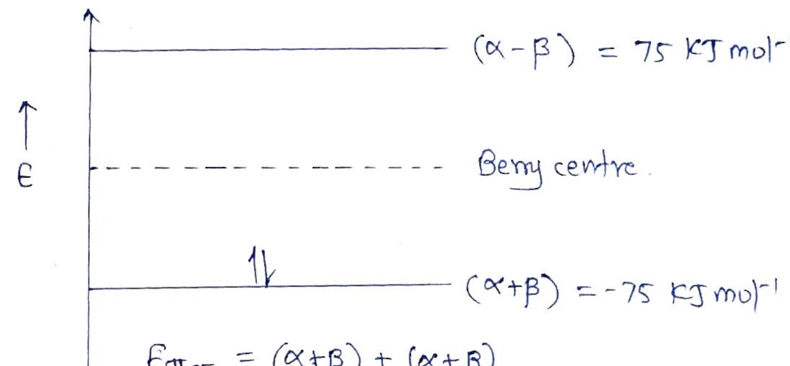
$\alpha = 0$ KJ/mol

$\beta = -75$ KJ/mol.

Now, $\alpha + \beta = 0 + (-75)$ $\alpha - \beta = 0 - (-75)$

$\boxed{E = -75 \text{ KJ/mol}}$ $\boxed{E = 75 \text{ KJ/mol}}$

⇒ Energy of π - electrons for ethene -



$E_{\pi e^-} = (\alpha+\beta) + (\alpha+\beta)$

$= 2(\alpha+\beta)$

Allylic System

$[H_2C=CH-CH_2]^{\pm}$

$\Rightarrow$ Secular determinant =
$$\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$$

$\Rightarrow$ Secular determinant equation-

$$\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix} = 0$$

$$\begin{vmatrix} \frac{\alpha-E}{\beta} & \frac{\beta}{\beta} & \frac{0}{\beta} \\ \frac{\beta}{\beta} & \frac{\alpha-E}{\beta} & \frac{\beta}{\beta} \\ \frac{0}{\beta} & \frac{\beta}{\beta} & \frac{\alpha-E}{\beta} \end{vmatrix} = 0 \quad \text{.... Divide by } \beta$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \quad \text{.... put } \frac{\alpha-E}{\beta} = x$$

$x(x^2-1)-1(x-0)+0(1-0)=0$

$x^3-x-x=0$

$\boxed{x^3-2x=0}$

$(x^3-2x)=0$

$x(x^2-2\cancel{x})=0$

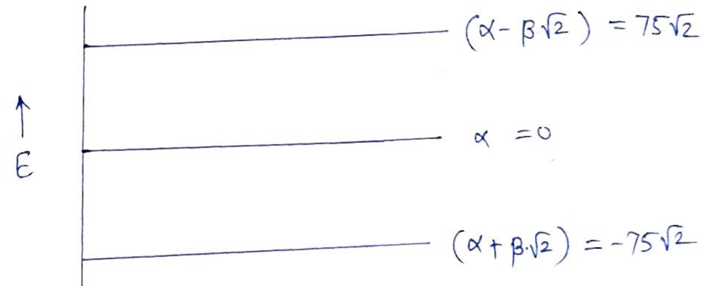
$\boxed{x=0}$ or $x^2-2=0$

$x^2=2$

$\boxed{x=\sqrt{2}}$ or $\boxed{x=-\sqrt{2}}$

$\frac{\alpha-E}{\beta}=0$	$\frac{\alpha-E}{\beta}=\sqrt{2}$	$\frac{\alpha-E}{\beta}=-\sqrt{2}$
$\alpha-E=0$	$\alpha-E=\sqrt{2}.\beta$	$\alpha-E=-\sqrt{2}.\beta$
$\boxed{E=\alpha}$	$\boxed{E=\alpha-\beta.\sqrt{2}}$	$\boxed{E=\alpha+\beta.\sqrt{2}}$
$\boxed{E=0}$	$E=0-(-75)\sqrt{2}$	$E=0+(-75)\sqrt{2}$
	$\boxed{E=75\sqrt{2}}$	$\boxed{E=-75\sqrt{2}}$

$\Rightarrow$ Energy of π-electrons for allylic system-

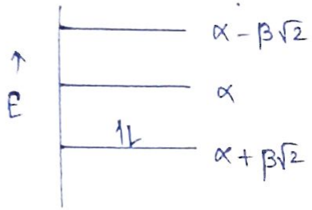


(Electron distribution is different for carbocation/ radical / carbanion - See the next page.)

⇒ Carbocation -

$H_2C = CH - \overset{+}{C}H_2$

number of π-electrons = 2



$E_{\pi e^-} = (\alpha + \beta\sqrt{2}) + (\alpha + \beta\sqrt{2})$

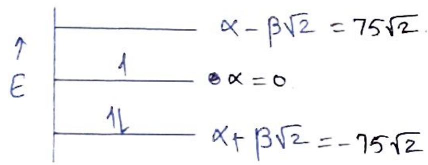
$\boxed{= 2(\alpha + \beta\sqrt{2})}$

$\boxed{2\alpha + 2\beta\sqrt{2}}$

⇒ Radical -

$H_2C = CH - \dot{C}H_2$

number of π-electrons = 3 ← Radical contributes 1 e^-.



$E_{\pi e^-} = 2(\alpha + \beta\sqrt{2}) + 1(\alpha)$

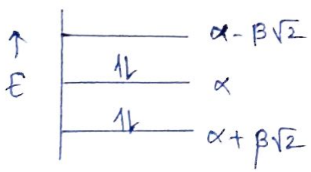
$\boxed{= \cancel{2(\alpha + \beta\sqrt{2})}}$

$\boxed{3\alpha + 2\beta\sqrt{2}}$

⇒ Carbanion -

$H_2C = CH - \bar{C}H_2$

number of π-electrons = 4 ← negative charge contributes 2 e's



$E_{\pi e^-} = 2(\alpha + \beta\sqrt{2}) + 2(\alpha)$

$\boxed{= \cancel{2(\alpha + \beta\sqrt{2})}}$

$\boxed{4\alpha + 2\beta\sqrt{2}}$

Trick - Energy Calculations

For open systems -

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

where, n = no. of carbon atoms

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

Ex. Ethene.

$H_2C = CH_2 \Rightarrow n = 2$

$K = 1, 2$

Case I - $n = 2$, $K = 1$

$E_\pi = \alpha + 2\beta \cdot \cos\left(\frac{\pi \cdot (1)}{2+1}\right)$

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

$= \alpha + \cancel{2}\beta \cdot \left(\frac{1}{\cancel{2}}\right)$

$\boxed{E_\pi = \alpha + \beta}$

Case II - $n = 2$, $K = 2$

$E_\pi = \alpha + 2\beta \cdot \cos\left(\frac{\pi(2)}{2+1}\right)$

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

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

$\boxed{E_\pi = \alpha - \beta}$

Ex 

$n = 4$

$k = 1, 2, 3, 4$

Case I - $n = 4$, $k = 1$

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

$= \alpha + 2\beta \cos \frac{\pi}{5}$

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

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

Case II - $n = 4$, $k = 2$

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

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

Case III - $n = 4$, $k = 3$

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

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

Case IV - $n = 4$, $k = 4$

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

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

For cyclic systems-

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

n = number of carbon atoms

k = → if (n = even) $0, (\pm 1), (\pm 2), \ldots\ldots (\pm \frac{n}{2})$

→ if (n = odd) $0, (\pm 1), \pm 2, \ldots\ldots, \pm\left(\frac{n-1}{2}\right)$

Ex. Benzene  $n = 6$ ↳ even

$k = 0, \pm 1, \pm 2, \pm 3$

① $n = 6$, $k = 0$

$E_\pi = \alpha + 2\beta \cos\left(\frac{2\pi(0)}{6}\right) = \alpha + 2\beta \cos 0 = \boxed{\alpha + 2\beta}$

$0 + 2(-75)$

-150

② $n = 6$, $k = 1$

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

$= \boxed{\alpha + \beta}$ -75

③ $n = 6$, $k = -1$

$\cos -\frac{\pi}{3} = \cos \frac{\pi}{3}$

$E_\pi = \alpha + 2\beta \cos \frac{2\pi(-1)}{6} = \alpha + 2\beta \cos \frac{-2\pi}{6} = \alpha + 2\beta\left(\frac{1}{2}\right)$

$= \boxed{\alpha + \beta}$ -75

④ $n = 6,\ r = 2$

$E_\pi = \alpha + 2\beta \cos \frac{2\pi(2)}{6}$

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

$= \boxed{\alpha - \beta}$ (75)

$\rightarrow \cos\frac{4\pi}{6} = \cos\left(\frac{\ldots}{6}\right)$

$= \cos\left(\pi - \frac{2\pi}{6}\right)$

$= -\cos\frac{2\pi}{6}$

$= -\cos \pi/3$

$= -1/2$

⑤ $n = 6,\ r = -2$

$E_\pi = \alpha + 2\beta \cos\frac{2\pi(-2)}{6}$

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

$= \boxed{\alpha - \beta}$ (75)

$\rightarrow \cos\frac{-4\pi}{6} = \cos\frac{4\pi}{6}$

$= -1/2.$

⑥ $n = 6,\ r = 3$

$E_\pi = \alpha + 2\beta \cos\frac{2\pi(3)}{6}$

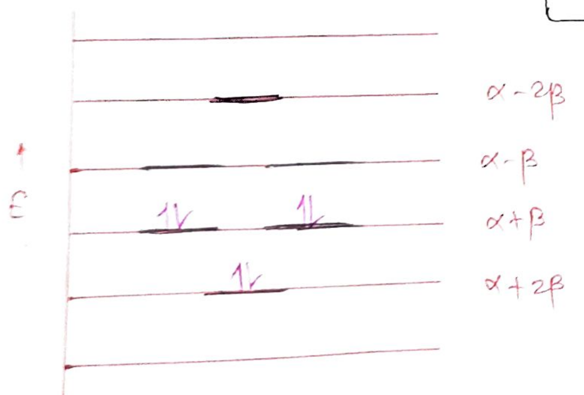
$= \alpha + 2\beta(-1)$

$= \boxed{\alpha - 2\beta}$ (+150)

$\rightarrow \cos\frac{6\pi}{6} = \cos\pi = -1$

$E_{\pi e^-} = 2(\alpha + 2\beta) + 4(\alpha + \beta)$

$\boxed{E_{\pi e^-} = 6\alpha + 8\beta}$



Perturbation theory -

⇒ Approximation method
- ↳ Perturbation theorem → first order ✓, → second order
- ↳ Variation principle

⇒ Need of approximation methods -

↳ To find the solution in cases where exact solutions cannot be obtained.

⇒ Perturbation ≡ disturbance / displacement (difference)

⇒ **Derivation -**

We have, Schrodinger wave equation -

$\hat{H}\psi = E\psi$ —— ①

↳ exact solution not known. ⇒ Perturbed eq^n

$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}.\psi^{(0)}$ —— ②

↳ exact solution is known. ⇒ unperturbed eq^n

↳ $\psi^{(0)}$ is normalised wave function.

Disturbance - Perturbation = (perturbed - unperturbed)

$\Delta H = \hat{H} - \hat{H}^{(0)}$

$\Delta E = E' - E^{(0)}$

$\Delta\psi = \psi - \psi^{(0)}$

$$\Rightarrow \hat{H} = \Delta H + \hat{H}^{(0)}$$
$$E = \Delta E + E^{(0)}$$
$$\psi = \Delta\psi + \psi^{(0)}$$

put these values in equation ①

$$(\Delta H + \hat{H}^{(0)})(\Delta\psi + \psi^{(0)}) = (\Delta E + E^{(0)})(\Delta\psi + \psi^{(0)})$$

$$\cancel{\Delta H\,\Delta\psi} + \Delta H.\psi^{(0)} + \hat{H}^{(0)}\Delta\psi + \cancel{\hat{H}^{(0)}\psi^{(0)}} = \underbrace{\Delta E\,\Delta\psi}_{\text{neglect}} + \Delta E.\psi^{(0)} + E^{(0)}\Delta\psi + \cancel{E^{(0)}\psi^{(0)}}$$

neglect

Since, product will be very very small.

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$
↳ from eqⁿ ②

∴ Above equation becomes

$$\Delta H\,\psi^{(0)} + \hat{H}^{(0)}\Delta\psi = \Delta E.\psi^{(0)} + E^{(0)}\Delta\psi$$

$$\Delta H.\psi^{(0)} + \hat{H}^{(0)}\Delta\psi - E^{(0)}.\Delta\psi = \Delta E\,\psi^{(0)}$$

$$\Delta H\,\psi^{(0)} + (\hat{H}^{(0)} - E^{(0)})\,\Delta\psi = \Delta E.\psi^{(0)}$$

Multiply by $\psi^{(0)*}$ -

$$\psi^{(0)*}\Delta H.\psi^{(0)} + \psi^{(0)*}(\hat{H}^{(0)} - E^{(0)}).\Delta\psi = \psi^{(0)*}.\Delta E.\psi^{(0)}$$

Integrating both sides -

$$\int_{-\infty}^{\infty}\psi^{(0)*}\Delta H.\psi^{(0)}d\tau + \int_{-\infty}^{\infty}\psi^{(0)*}(\hat{H}^{(0)} - E^{(0)}).\Delta\psi\,d\tau = \int_{-\infty}^{\infty}\psi^{(0)*}\Delta E.\psi^{(0)}d\tau$$

$$= \Delta E.\int_{-\infty}^{\infty}\psi^{(0)*}\psi^{(0)}d\tau$$

$$= \Delta E.(1)$$

∴ Since, wavefunction is normalised.

$$\Rightarrow \Delta E = \int_{-\infty}^{\infty}\psi^{(0)*}.\Delta H.\psi^{(0)}d\tau + \underbrace{\int_{-\infty}^{\infty}\psi^{(0)*}(\hat{H}^{(0)} - E^{(0)})\Delta\psi\,d\tau}$$

Hermitian operator-

Every operator in quantum is a hermitian.

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

∴ Now, in above equation,

consider $[\hat{H}^{(0)} - E^{(0)}]$ as a hermitian operator.

⇒ equation becomes

$$\Delta E = \int_{-\infty}^{\infty}\psi^{(0)*}.\Delta H.\psi^{(0)}d\tau + \int_{-\infty}^{\infty}\Delta\psi\,(\hat{H}^{(0)} - E^{(0)})^*\,\psi^{(0)*}\,d\tau$$

$$= \int_{-\infty}^{\infty}\psi^{(0)*}.\Delta H.\psi^{(0)}d\tau + \underbrace{\int_{-\infty}^{\infty}\Delta\psi\left[(\hat{H}^{(0)} - E^{(0)})\psi^{(0)}\right]^*d\tau}$$

$$\underbrace{\int_{-\infty}^{\infty}\Delta\psi\,(\hat{H}^{(0)}\psi^{(0)} - E^{(0)}\psi^{(0)})^*\,d\tau \qquad \int_{-\infty}^{\infty}\Delta\psi\,(0)\,d\tau}_{\text{zero}}$$

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$
↳ from eqⁿ ②

$$\boxed{\Delta E = \int_{-\infty}^{\infty}\psi^{(0)*}.\Delta H.\psi^{(0)}d\tau}$$ ← perturbation in energy. (ΔE)

$$E = \Delta E + E^{(0)}$$ ← unperturbed ene.

perturbed ene. ↑ perturbation

$$\boxed{E = \int_{-\infty}^{\infty}\psi^{(0)*}.\Delta H.\psi^{(0)}d\tau + E^{(0)}}$$ ← perturbed energy (E)

$$\boxed{\Delta E = \int_{-\infty}^{\infty} \psi^{(0)*}\, \Delta H .\, \psi^{(0)}\, d\tau}$$

Questions -

Que. If the value of $\frac{\nu x}{a}$ is perturbed in a 1D box having length "o to a"
What is the total energy of system?

Ans. = $\frac{n^2h^2}{8ml^2} + \frac{\nu}{2}$

Ans - For 1D-Box

$$\psi^{(0)} = \psi^{*(0)} = \sqrt{\frac{2}{a}}\, \sin\left(\frac{n\pi x}{a}\right)$$ ← unperturbed wave function since no disturbance.

$$\text{perturbation} = \frac{\nu x}{a} = \Delta H.$$

We know the energy for 1D Box -

$$E^{(0)} = \frac{n^2h^2}{8ml^2}$$ ← Since no disturbance it is unperturbed.

Also, we know,

$$\Delta E = E - E^{(0)}$$

$$\boxed{E = \Delta E + E^{(0)}}$$

$$\Rightarrow \Delta E = \int_0^a \psi^{(0)*}\, \Delta H .\, \psi^{(0)}\, d\tau$$

$$= \int_0^a \sqrt{\frac{2}{a}} \cdot \sin\frac{n\pi x}{a} \cdot \frac{\nu x}{a} \cdot \sqrt{\frac{2}{a}} \cdot \sin\frac{n\pi x}{a}\, dx$$

$$= \frac{2\nu}{a.a} \int_0^a x .\, \sin^2\frac{n\pi x}{a}\, dx$$

$$= \frac{2\nu}{aa} \cdot \left(\frac{a^2}{4}\right)$$

Since,
we have given the length of box = (o to a)
so, wave function must be like -

$$\psi^{(0)} = \sqrt{\frac{2}{a}} \cdot \sin\left(\frac{2\pi x}{a}\right)$$

Now,
$$\Delta E = \frac{2\nu}{a^2} \times \frac{a^2}{4} = \frac{\nu}{2}$$

∴ total energy of system -

$$E = \Delta E^{(0)} + \Delta E$$

$$= \frac{n^2h^2}{8ml^2} + \frac{\nu}{2}$$

Que The quantum state of particle moving in a circular path in a plane is given by

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} \cdot e^{im\phi} \quad , m = 0, \pm 1, \ldots$$

When perturbation $H_1 = P.\cos\phi$ is applied (P is constant) what will be the first order correction to the energy of m^{th} state?

perturbation.

Ans- Given wavefunction is

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} \cdot e^{im\phi}$$

$$\psi_m^*(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im\phi}$$

perturbation $= H_1 = P.\cos\phi$.

Since, particle is moving in circular path, limits of integration will be (0 to 2π)

To find ΔE.

$$\Delta E = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} \cdot e^{-im\phi} \cdot P.\cos\phi \cdot \frac{1}{\sqrt{2\pi}} \cdot e^{im\phi} \, d\phi$$

$$= \frac{P}{2\pi} \int_0^{2\pi} e^{-im\phi + im\phi} \cdot \cos\phi \, d\phi$$

$$= \frac{P}{2\pi} \int_0^{2\pi} (1) \cos\phi \, d\phi$$

$$= \frac{P}{2\pi} \left[\sin\phi\right]_0^{2\pi}$$

$$= 0. \qquad \boxed{\Delta E = 0}$$

$\therefore$ There will be no need of correction.

Variation Principle -

⇒ Approximation method.

⇒ deals with energy of ground state

Let us consider,

Schrodinger wave equation -

$$\hat{H}\psi_0 = E_0\psi_0$$

zero represents ground state.

Multiply by ψ_0^* -

$$\psi_0^* \hat{H} \psi_0 = \psi_0^* E_0 \psi_0$$

Now, integrate the above equation.

$$\int \psi_0^* \hat{H} \psi_0 d\tau = \int \psi_0^* E_0 \psi_0 \, d\tau$$

$$\int \psi_0^* \hat{H} \psi_0 \, d\tau = E_0 \int \psi_0^* \psi_0 \, d\tau$$

$$\boxed{E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 \, d\tau}{\int \psi_0^* \psi_0 \, d\tau}}$$

Now, we replace the function ψ_0 by another trial funⁿ ϕ,

$$\boxed{E_\phi = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau}}$$

Statement - The value of energy, when we replace the function (ψ_0) by another trial function, will be greater than or equal to the ene. (E_0) in the ground state

$$\boxed{E_\phi \geq E_0}$$

⇒ Statement of variation principle -

$E_\phi \geq E_0$

⇒ percentage error $= \frac{E_\phi - E_0}{E_0} \times 100$

↳ $\frac{\text{experimental} \times \text{actual}}{\text{actual}} \times 100$

⇒ If percentage error is position, then wave function is acceptable $(E_\phi > E_0)$

⇒ And if % error is negative, then wavefunction is not acceptable. $(E_\phi < E_0)$

Questions -

Que Using variation theorem, find the energy of a particle in 1 D box having $\psi = \sin\left(\frac{n\pi x}{l}\right)$

Ans. $= \frac{n^2h^2}{8ml^2}$

Ans - We have,

$$E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 \, d\tau}{\int \psi_0^* \psi_0 \, d\tau}$$

Replacing ψ_0 by $\psi = \sin\left(\frac{n\pi x}{l}\right)$.

$$E = \frac{\int_0^l \psi^* \hat{H} \psi \, d\tau}{\int_0^l \psi^* \psi \, d\tau}$$

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

$$E = \frac{\int_0^l \sin\left(\frac{n\pi x}{l}\right) \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2}\right)\left(\sin \frac{n\pi x}{l}\right) d\tau}{\int_0^l \sin \frac{n\pi x}{l} \cdot \sin \frac{n\pi x}{l} \, d\tau}$$

$$\text{Numerator} = -\frac{\hbar^2}{2m} \int_0^l \sin \frac{n\pi x}{l} \cdot \left(\frac{d^2}{dx^2} \sin \frac{n\pi x}{l}\right) d\tau x$$

$$= + \frac{\hbar^2}{2m} \cdot \left(\frac{n\pi}{l}\right)^2 \int_0^l \sin \frac{n\pi x}{l} \cdot \sin \frac{n\pi x}{l} \, d\tau x$$

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

$$\frac{1}{2} \int_0^l \left(1 - \cos \frac{2n\pi x}{l}\right) dx$$

$$= \frac{\hbar^2}{2m} \cdot \frac{n^2\pi^2}{l^2} \cdot \frac{1}{2} \left[x \, . - \frac{\sin 2n\pi x}{l} \times \frac{l}{2n\pi} \right]_0^l$$

$$\text{Numerator} = \frac{\hbar^2}{2m} \cdot \frac{n^2\pi^2}{l^2} \cdot \left(\frac{\cancel{l}}{2}\right)$$

$$\text{Denominator} = \frac{\cancel{l}}{2}$$

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

$$E = \frac{n^2 \pi^2 h^2}{2 m l^2 (4\pi^2)} \quad \ldots \hbar = \frac{h}{2\pi}$$

$$\boxed{E = \frac{n^2 h^2}{8 m l^2}}$$

* Energy of wavefunction $\left(\psi = \sin \frac{n\pi x}{l}\right) = \frac{n^2 h^2}{8 m l^2}$

Energy of normalized wavefunction $\left(\psi = \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l}\right) = \frac{n^2 h^2}{8 m l^2}$

* Conclusion -
The energy remains same, if the wavefunction is multiplied by some constant.

Que. Which of the following wave functions are acceptable in 1D Box of length 'l'.

i) $\psi = x^2$

ii) $\psi = x(l-x)$ (Find % error).

Ans. - We know,

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

①. $\psi = x^2$

$$E = \frac{\int_0^l x^2 \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2}\right) \cdot x^2 \, dx}{\int_0^l x^2 \cdot x^2 \, dx}$$

$$\int_0^l x^4 \, dx = \left[\frac{x^5}{5}\right]_0^l = \frac{l^5}{5}$$

$$E = -\frac{5}{l^5} \times \frac{\hbar^2}{2m} \cdot \int_0^l x^2 \cdot \left(\frac{d^2}{dx^2} \cdot x^2\right) dx$$

$$= -\frac{5\hbar^2}{\cancel{2} m l^5} \int_0^l x^2 (\cancel{2}) \, dx$$

$$= -\frac{5\hbar^2}{m l^5} \times \left[\frac{x^3}{3}\right]_0^l$$

$$= -\frac{5\hbar^2}{m l^5} \times \frac{l^3}{3} = \frac{-5\hbar^2}{3 m l^2}$$

$$\boxed{E = -5\hbar^2 / 3 m l^2}$$

Since, value of energy is negative percentage error comes out to be negative.
$\therefore \psi = x^2$ is not acceptable.

② $\psi = x(l-x)$

$$E = \frac{\int_0^l x(l-x)\left(-\frac{\hbar^2}{2m}\cdot\frac{d^2}{dx^2}\right) x(l-x)\,dx}{\int_0^l x(l-x)\cdot x(l-x)\,dx}$$

$\rightarrow \int_0^l x^2(l-x)^2\,dx$

$\int_0^l x^2(l^2-2lx+x^2)\,dx$

$\int_0^l (l^2x^2-2lx^3+x^4)\,dx$

$\left(l^2\cdot\frac{l^3}{3}-2l\cdot\frac{l^4}{4}+\frac{l^5}{5}\right)$

$\left(\frac{1}{3}-\frac{1}{2}+\frac{1}{5}\right)l^5$

$\frac{l^5}{30}$

$$= -\frac{30}{l^5}\times\frac{\hbar^2}{2m}\int_0^l x(l-x)\underbrace{\frac{d^2}{dx^2}x(l-x)\,dx}$$

$\frac{d^2}{dx^2}(lx-x^2)\,dx$

-2

$$= \frac{30}{l^5}\times\frac{\hbar^2}{2m}\times 2\int_0^l (lx-x^2)\,dx$$

$$= \frac{30\hbar^2}{ml^5}\times\left[\frac{lx^2}{2}-\frac{x^3}{3}\right]_0^l$$

$$= \frac{30\hbar^2}{ml^5}\times\left[\frac{l^3}{2}-\frac{l^3}{3}\right] \rightarrow \frac{3l^3-2l^3}{6} = \frac{l^3}{6}$$

$$= \frac{30\hbar^2}{ml^5}\times\frac{l^3}{6} \Rightarrow \boxed{E = \frac{5\hbar^2}{ml^2}}$$

$n=1 \leftarrow$ ground state

$$\text{\% error} = \frac{5\hbar^2}{ml^2} - \frac{h^2}{8ml^2} \Big/ \times 100$$

$$= \frac{5h^2}{4\pi^2ml^2} - \frac{h^2}{8ml^2} = \frac{10h^2-\pi^2h^2}{8\pi^2ml^2}$$

$$\text{\% error} = \frac{\left(\frac{5\hbar^2}{ml^2}\right)-\left(\frac{h^2}{8ml^2}\right)}{\left(\frac{h^2}{8ml^2}\right)}\times 100$$

$$= \frac{(10-\pi^2)\cancel{h^2}}{\cancel{8}\pi^2\cancel{ml^2}}\times\frac{\cancel{8ml^2}}{\cancel{h^2}}\times 100$$

$$= \left(\frac{10-\pi^2}{\pi^2}\right)\times 100$$

$$= \boxed{1.32\ \%}$$

percentage error is positive.

$\therefore\ \psi = x(l-x)$ is acceptable.

Hermitian Operator -

⇒ Hermitian Adjoint or Dagger (+) -

If A is any matrix

then Hermitian adjoint is $\underbrace{(A^T)^*}_{\text{conjugate}} = (A^*)^T = A^\dagger$ transpose

⇒ transpose -

If $A = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$ then $A^T = \begin{bmatrix} 1 & 3 \\ 2 & 4 \end{bmatrix}$

If $A = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}$ then $A^T = \begin{bmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{bmatrix}$

$R_1 \rightarrow C_1$
$R_2 \rightarrow C_2$
$R_3 \rightarrow C_3$

⇒ Conjugate -

$A = \begin{bmatrix} 2 & -i \\ i & 0 \end{bmatrix} \Rightarrow A^* = \begin{bmatrix} 2 & i \\ -i & 0 \end{bmatrix}$

$B = \begin{bmatrix} 0 & 3 \\ -3 & i \end{bmatrix} \Rightarrow B^* = \begin{bmatrix} 0 & 3 \\ -3 & -i \end{bmatrix}$

Condition for Hermitian Adjoint -

$$\boxed{A^\dagger = A}$$

Ex. $A = \begin{bmatrix} 2 & -i \\ i & 0 \end{bmatrix}$

Transpose of $A = A^T = \begin{bmatrix} 2 & i \\ -i & 0 \end{bmatrix}$

Conjugate of $A^T = (A^T)^* = \begin{bmatrix} 2 & -i \\ i & 0 \end{bmatrix}$

Since $\boxed{\boxed{(A^T)^* = A} = A^\dagger}$

Given matrix is a Hermitian matrix.

Ex. $B = \begin{bmatrix} 0 & 3 \\ -3 & i \end{bmatrix}$

$B^T = \begin{bmatrix} 0 & -3 \\ 3 & i \end{bmatrix} \Rightarrow (B^T)^* = \begin{bmatrix} 0 & -3 \\ 3 & -i \end{bmatrix}$

$$\boxed{(B^T)^* \neq B}$$

$$\boxed{B^\dagger = -B}$$

∴ Given matrix is Anti-Hermitian matrix.

⇒ Anti-Hermitian / Skew-Hermitian -

$$\boxed{A^\dagger = -A}$$

⇒ For Hermitian matrix ⇒ $\boxed{A^{n\dagger} = A}$ $A^{\dagger\dagger\dagger\dagger\cdots} = A$

For anti-hermitian matrix ⇒ $\boxed{A^{(\text{even})\dagger} = A}$ $A^{\dagger\dagger\dagger\dagger} = A$

$\boxed{A^{(\text{odd})\dagger} = -A}$ $A^{\dagger\dagger\dagger} = -A$

Properties of Dagger-

$$\boxed{(\hat{A}^{+})^{n} = (\hat{A}^{n})^{+}}$$

$$\boxed{(A+B)^{+} = A^{+} + B^{+}}$$

$$\boxed{(A-B)^{+} = A^{+} - B^{+}}$$

$$\boxed{(AB)^{+} = B^{+}A^{+}}$$

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

$$\boxed{(c.A)^{+} = c^{*}.A^{+}}$$

$$\boxed{c^{+} = c^{*}}$$

⇒ Hermitian Operator-

Condition-

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

⇒ Here, ψ must be normalised wave function

⇒ Hermitian operator will be applicable for normalised wave function only

⇒ All operators mentioned in postulates of quantum mechanics are Hermitian.

ex. $\hat{x}$, $\hat{P_x}$, $\hat{K_x}$, $\hat{V_x}$, $\hat{H}$

⇒ By operating Hermitian operator on any function the eigen value comes to be real numbers (value)

Ex. Operator- $\hat{P_x}$

We have to prove $\hat{P_x}$ as a Hermitial operator.

∴ Have to follow condition-

$$\boxed{\int_{-\infty}^{\infty} \psi^{*} \hat{P_x} \psi \, dx = \int_{-\infty}^{\infty} \psi \hat{P_x} \psi^{*} \, dx}$$

$$\int_{-\infty}^{\infty} \psi^{*} \left(-\hbar i \frac{d}{dx}\right) \psi \, dx = -i\hbar \int_{-\infty}^{\infty} \psi^{*} \frac{d}{dx} \psi \, dx$$

$$\int_{-\infty}^{\infty} \psi^* \hat{P}_x \psi \, dx = -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{d}{dx} \psi \, dx$$

$$= -i\hbar \left[\psi^* \int \frac{d\psi}{dx} dx - \left(\int \frac{d\psi^*}{dx} \left(\int \frac{d\psi}{dx} dx \right) \right) dx \right]$$

$$= -i\hbar \left[\psi^* . \psi - \int \frac{d\psi^*}{dx} . \psi \, dx \right]_{-\infty}^{\infty}$$

By condition of orthogonality

$[\psi^* \psi]_{-\infty}^{\infty} = \text{zero}.$

$$= i\hbar \left[\int_{-\infty}^{\infty} \frac{d\psi^*}{dx} \psi \, dx \right]$$

$$= \int_{-\infty}^{\infty} \psi . \left(i\hbar . \frac{d\psi^*}{dx} \right) \psi^* \, dx$$

$$= \int_{-\infty}^{\infty} \psi . (-i\hbar)^* \frac{d}{dx}^* \psi^* \, dx$$

$$= \int_{-\infty}^{\infty} \psi . \hat{P}_x^* \psi^* \, dx$$

$$\Rightarrow \boxed{\int_{-\infty}^{\infty} \psi^* \hat{P}_x \psi \, dx = \int_{-\infty}^{\infty} \psi . \hat{P}_x \psi^* \, dx}$$

Hydrogen Atom -

⇒ Wave function for hydrogen atom is written in variables r, θ and ϕ

⇒ From this wave function, we can find out values of quantum number n, l and m. value of spin quantum no. (s) cannot be calculated

⇒ Wave function -

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\substack{\text{radial part} \\ (n,l)}} . \underbrace{\Theta(\theta)\ \Phi(\phi)}_{\substack{\Theta:(l,m) \quad \Phi:(m) \\ \text{angular part} \\ \text{Spherical Harmonics} \\ (Y)}}$$

⇒ Values of Φ, Θ and R -

$$\Phi_{(m)}(\phi) = \frac{1}{\sqrt{2\pi}} \cdot e^{im\phi}$$

$$\Theta_{(lm)}(\theta) = \underset{\text{constant}}{\epsilon} \sqrt{\frac{(2l+1)}{2} \cdot \frac{\lfloor l-|m| \rfloor}{\lfloor l+|m| \rfloor}} \cdot \underbrace{P_l^m(\cos\theta)}_{\text{Legendre polynomial}}.$$

$$\epsilon \begin{cases} 1 & , m \leq 0 \\ (-1)^m & , m > 0 \end{cases}$$

Legendre Polynomial -

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

$$P_l(x) = \frac{1}{2^l . \lfloor l} \frac{d^l}{dx^l} (x^2-1)^l$$

$P_l(x)$

$\Rightarrow$ For $l=0$ $\quad P_0(x) = \frac{1}{2^0 \lfloor 0} \frac{d^0}{dx^0}(x^2-1)^0$

$$\boxed{P_0(x) = 1}$$

$\Rightarrow$ For $l=1$ $\quad P_1(x) = \frac{1}{2^1 \lfloor 1} \frac{d^1}{dx^1}(x^2-1)^1$

$$\boxed{P_1(x) = \frac{1}{2}(2x) = x}$$

$\Rightarrow$ For $l=2$ $\quad P_2(x) = \frac{1}{2^2 \lfloor 2} \cdot \frac{d^2}{dx^2}(x^2-1)^2$

$$= \frac{1}{4 \times 2 \times 1} \frac{d^2}{dx^2}(x^4 - 2x^2 + 1)$$

$$= \frac{1}{8}(12x^2 - 4)$$

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

Now, putting these values to get $P_l^m(x)$.

$$\boxed{P_l^m(x)}$$

For $l=0$, $m=0$

$$P_0^0(x) = (1-x^2)^{0/2} \cdot \frac{d^0}{dx^0} P_0(x)$$

or $P(0,0)$

$$= 1 \times 1$$

$$\boxed{P_0^0(x) = 1}$$

For $l=1$, $m=0$

$$P_1^0(x) = (1-x^2)^{0/2} \cdot \frac{d^0}{dx^0} P_1(x)$$

$$= 1 . \frac{d^0}{dx^0} x$$

$$\boxed{P_1^0(x) = x}$$

Conclusion - $\boxed{P_l^m(x) = P_l(x)}$ ...if $m=0$

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

For $l=1$, $m=1$

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

$$= \sqrt{1-x^2} \cdot \frac{d}{dx} \cdot x$$

$$\boxed{P_1^1(x) = \sqrt{1-x^2}}$$

Now, Value of Θ

$$\Theta(\theta) = \epsilon \sqrt{\frac{(2l+1)}{2} \frac{\lfloor l-|m|}{\lfloor l+|m|}} \; P_l^m(\cos\theta)$$

$l=0$, $m=0$

$$\Theta_{(0,0)} = 1 \cdot \sqrt{\frac{(0+1)}{2} \frac{0!}{0!}} \; P_0^0(\cos\theta)$$

$$= \sqrt{\frac{1}{2}}$$

Now, Spherical harmonics,

$$Y_{(l,m)} = \Theta_{(l,m)}{}^{\theta} \; \Phi_{(m)}(\phi)$$

$$Y(0,0) = \Theta_{(0,0)}{}^{\theta} \cdot \Phi_{(0)}{}^{\phi}$$

$\hookrightarrow \frac{1}{\sqrt{2\pi}} \cdot e^{im\phi}$

$$= \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2\pi}}$$

$$\boxed{Y(0,0) = \frac{1}{2\sqrt{\pi}}}$$

$l=2$, $m=0$

$\epsilon = 1 \quad \because m \leq 0$

$$\Theta_{(2,0)} = 1 \cdot \sqrt{\frac{(2\times 2+1)}{2} \cdot \frac{\lfloor 2-0}{\lfloor 2+0}} \cdot P_2^0(\cos\theta)$$

$\hookrightarrow \frac{3x^2-1}{2}$

$$\boxed{\Theta_{(2,0)} = \sqrt{\frac{5}{2}} \cdot \frac{3\cos^2 x - 1}{2}}$$

Trick

For calculating quantum numbers from given wavefunction ($R / \Theta / \Phi$)

(m) $\Rightarrow \Phi$

$$\Phi = \frac{1}{\sqrt{2\pi}} \cdot e^{im\phi}$$

For, $e^{2i\phi} \Rightarrow$ Value of $\boxed{m=2}$

$e^{-2i\phi} \Rightarrow$ Value of $\boxed{m=-2}$

(l) = Maximum power of sum of $\cos\theta$ & $\sin\theta$ terms when function is given in terms of $\Theta(\theta)$

(n) $\Rightarrow$ If radial part is given.

$$R(r) = \frac{Zr}{na_0}$$

For, $R(r) = \frac{Zr}{2a_0} \Rightarrow$ Value of $\boxed{n=2}$

Calculating the values of quantum numbers (n, l and m).

(m) $\Rightarrow e^{im\phi}$

(n) $\Rightarrow e^{-2r/na_0}$

(l)
- In terms of $\theta \Rightarrow$ Sum of powers of $\cos\theta$ & $\sin\theta$ (Maximum of)
- In terms of $R \Rightarrow$ Minimum value of power of r in pre-exponential factor.

Que. 1 $\Theta_{(l,m)} = \cos^4\theta + \cos^3\theta \cdot \sin\theta + \sin^2\theta - \sin\theta + 4$

($l \Rightarrow$ sum of power of $\cos\theta$ & $\sin\theta$)

4 + (3 + 1) + 2 + 1

maximum = 4

$\boxed{l = 4}$

Que. 2 $\Theta(l,m) = \underset{4}{\cos^4\theta} + \underset{3+2 = 5}{\cos^3\theta \cdot \sin^2\theta} + 4$

$\boxed{l = 5}$

Que 3 $\Theta(l,m) = 1$

$\boxed{l = 0}$

Que. 4 $\Theta(l,m) = \underset{4}{\cos^2\theta \sin^2\theta} + \underset{5}{\cos^5\theta}$

$\boxed{l = 5}$

Que. 5 $R = (r + r^2 - 3r^3) \cdot e^{-r/4a_0}$

$\boxed{n = 4}$

(l = min. value of power of r in pre-exp.)

$\boxed{l = 1}$

IMP ***

Que. 6 $R = (1 - r) \cdot e^{-r/4a_0}$

$\boxed{n = 4}$

* $(1-r)$ can be written as $(r^0 - r^1)$ also.

Hence, minimum power is 0. $\boxed{\text{Not } 1}$

$\boxed{l = 0}$

Que. 7 $R = r(1-r) \cdot e^{-r/2a_0}$

$\boxed{n = 2}$

$r(1-r) = r - r^2$

$\boxed{l = 1}$

Average value for Hydrogen-atom-

$\Rightarrow \langle \hat{x} \rangle = \int \psi^* \hat{x} \psi \, d\tau$

$\Rightarrow$ Volume element for Hydrogen atom-

$$d\tau = \int_{r=0}^{\infty} r^2 dr \int_{\theta=0°}^{\pi} \sin\theta \, d\theta \cdot \int_{\phi=0}^{2\pi} d\phi$$

$\Rightarrow$ For radial part only-

$$d\tau = 4\pi \int_{r=0}^{\infty} r^2 dr$$

Que Find the average value of radius vector of 1s orbital for H-atom

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} \cdot e^{-r/a_0}$$ ← radial part only.

Average value-

$$\langle \hat{r} \rangle = 4\pi \int_{r=0}^{\infty} \psi^* \hat{r} \psi \, r^2 dr$$

$$= 4\pi \int_{r=0}^{\infty} \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} \cdot e^{-r/a_0} \cdot r \cdot \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} \cdot e^{-r/a_0} \cdot r^2 dr$$

$$= \frac{4\cancel{\pi}}{\cancel{\pi} \times (a_0^{3/2})^2} \int_{r=0}^{\infty} r^3 \cdot e^{-2r/a_0} dr$$ ← Solve by Gamma function

$$= \frac{4}{a_0^3} \cdot \frac{\Gamma 3+1}{\left(\frac{2}{a_0}\right)^{3+1}} =$$

$$\langle \hat{r} \rangle = \frac{4}{a_0^3} \times \frac{3!}{2^4} \times a_0^4$$

$$= \frac{6}{4} \cdot a_0 = \frac{3}{2} a_0$$

$$\boxed{\langle \hat{r} \rangle = \frac{3}{2} a_0}$$

Que. Average value for r^2

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} \cdot e^{-r/a_0}$$

Ans. Same as above question. just power of r will increase by 1 as-

$$\langle \hat{r}^2 \rangle = \frac{4}{a_0^3} \int_{r=0}^{\infty} r^4 \cdot e^{-2r/a_0} dr.$$

$\Gamma 5 = 4!$

$$= \frac{4}{a_0^3} \cdot \frac{\Gamma 4+1}{\left(\frac{2}{a_0}\right)^{4+1}}$$

$$= \frac{\cancel{4}}{a_0^3} \cdot \frac{\cancel{4} \times 3 \times \cancel{2} \times 1}{2 \times \cancel{2} \times \cancel{2} \times \cancel{2} \times \cancel{2}} \times a_0^5$$

$$= 3 \cdot a_0^2$$

$$\boxed{\langle \hat{r}^2 \rangle = 3 a_0^2}$$

Que. Average value for $\frac{1}{r}$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} \cdot e^{-r/a_0}$$

Ans Same as the first question just power of r will decrease by 1 as-

$$\langle \tfrac{1}{r} \rangle = \frac{4}{a_0^3} \int_{r=0}^{\infty} r \cdot e^{-2r/a_0} \, dr$$

$$= \frac{4}{a_0^3} \frac{\Gamma 1+1}{\left(\frac{2}{a_0}\right)^{1+1}}$$

$$= \frac{\cancel{4}}{a_0^3} \times \frac{1}{\cancel{4}} \times a_0^2$$

$$= \frac{1}{a_0}$$

$$\boxed{\langle \tfrac{\hat{1}}{r} \rangle = \frac{1}{a_0}}$$

Trick

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

Now,
Calculating average value by using trick

1s $\Rightarrow$ $n=1$, $l=0$.

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

$$= \frac{1}{2} (3) a_0$$

$$\boxed{\langle r \rangle = 3/2 \, a_0}$$

2s $\Rightarrow$ $n=2$, $l=0$

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

$$= \frac{1}{2} (12) a_0$$

$$\boxed{\langle r \rangle = 6a_0}$$

3d $\Rightarrow$ $n=3$, $l=2$

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

$$= \frac{1}{2} \left[27 - 6 \right] a_0$$

$$\boxed{\langle r \rangle = \frac{21}{2} a_0}$$

Que. Average value for $\frac{1}{r}$.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a_0^{3/2}} \cdot e^{-r/a_0}$$

Ans. Same as the first question.
just power of r will decrease by 1 as-

$$\langle \frac{1}{r} \rangle = \frac{4}{a_0^3} \int_{r=0}^{\infty} r \cdot e^{-2r/a_0} \, dr$$

$$= \frac{4}{a_0^3} \frac{\lceil 1+1}{\left(\frac{2}{a_0}\right)^{1+1}}$$

$$= \frac{\cancel{4}}{a_0^{\cancel{3}}} \times \frac{1}{\cancel{4}} \times a_0^{\cancel{2}}$$

$$= \frac{1}{a_0}$$

$$\boxed{\langle \frac{\hat{1}}{r} \rangle = \frac{1}{a_0}}$$

Trick

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

Now,
Calculating average value by using trick.

1s $\Rightarrow$ $n=1$, $l=0$.

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

$$= \frac{1}{2} (3) a_0$$

$$\boxed{\langle r \rangle = 3/2 \, a_0}$$

2s $\Rightarrow$ $n=2$, $l=0$

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

$$= \frac{1}{2} (12) a_0$$

$$\boxed{\langle r \rangle = 6a_0}$$

3d $\Rightarrow$ $n=3$, $l=2$

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

$$= \frac{1}{2} \left[27 - 6 \right] a_0$$

$$\boxed{\langle r \rangle = \frac{21}{2} a_0}$$

Trick

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

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

$$\langle r^2 \rangle = \frac{1^2}{2}\left[5(1)^2+1-3(0)\right]a_0^2$$

$$= \frac{1}{2}(6)\,a_0^2$$

$$\boxed{\langle r^2 \rangle = \frac{3}{2}a_0^2}$$

Trick

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0}$$

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

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{(1)^2 . a_0} = \frac{1}{a_0}$$

$$\boxed{\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0}}$$

IMP

** $R \rightarrow (n,l)$ $\Theta \rightarrow (l,m)$ $\Phi \rightarrow (m)$

Nodes - $\rightarrow$ prob. of finding wavefunction = 0.

↳ Radial nodes = $n-l-1$

↳ Angular nodes = l

Total nodes (R+A) = $(n-l-1)+l$

$= (n-1)$

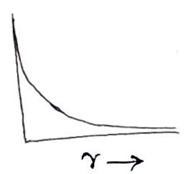
Radial Wave function plots-

$$\psi = \underbrace{R(r)}_{\text{Considering only radial part.}}\,\Theta(\theta)\,\Phi(\phi)$$

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

radial nodes $= n-l-1 = 1-0-1 = 0$

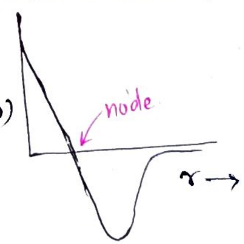
$R_{(1,0)}$



$\boxed{2s}$ $n=2,\ l=0$

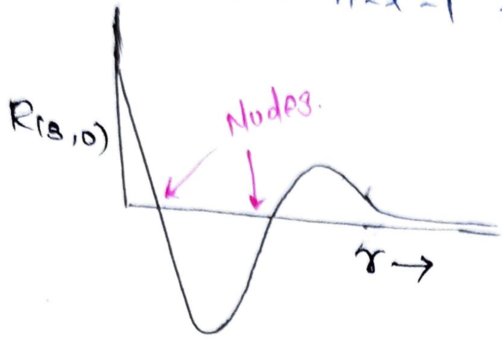
radial nodes $= n-l-1 = 2-0-1 = 1$

$R_{(2,0)}$



$\boxed{3s}$ $n = 3$, $l = 0$

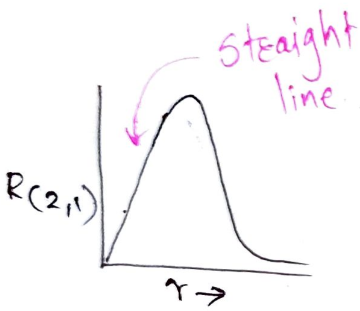
radial nodes $= n - l - 1 = 3 - 0 - 1 = 2$



$\boxed{2p}$

$n = 2$, $l = 1$

radial nodes $= 2 - 1 - 1 = 0$

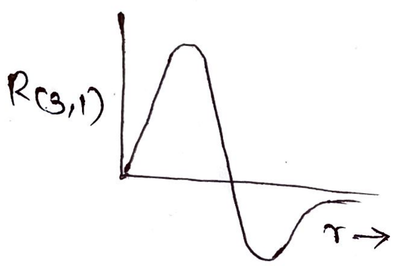


$\boxed{3p}$

$n = 3$, $l = 1$

$3 - 1 - 1$

1 node

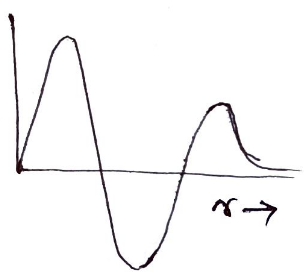


$\boxed{4p}$

$n = 4$, $l = 1$

$4 - 1 - 1$

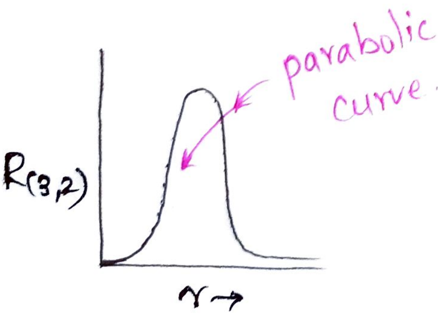
2 nodes



$\boxed{3d}$

$n = 3$, $l = 2$

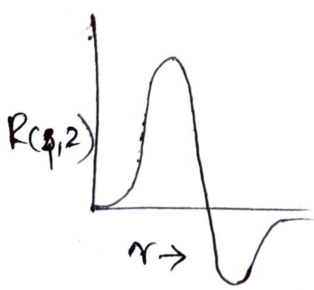
radial nodes $= 0$



$\boxed{4d}$

$n = 4$, $l = 2$

1 node



$\boxed{5d}$

$n = 5$, $l = 2$

2 nodes