* De-Broglie Hypothesis :

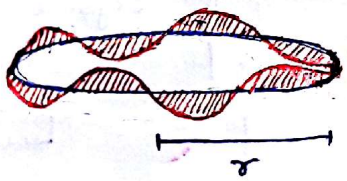
De Broglie applied the wave-particle dual nature of light to mass.

Any particle in motion can be associated with a wave.

$$\left[\lambda = \frac{h}{mv} \right]$$

λ = wavelength.
h = Planck's constant.
m = Mass.
v = Velocity.

→ De Broglie's Hypothesis explains the Bohr's postulate of Angular momentum quantization.



Let us consider an orbit of radius r in which the electron revolves around the nucleus.

The path traversed by the electron in one revolution = circumference of the orbit = $2\pi r$.

Let us assume that electron is a wave on a string of length $2\pi r$. The wave will only be stable for:

$$[2\pi r = n\lambda] \ldots \text{ condition for a standing wave}$$

If the condition is not satisfied, the opposite phases of wave will overlap and gradually cancel out each other thus decaying the wave.

⇒ Electron will be stable in the orbit only for: $[2\pi r = n\lambda]$.

Using De Broglie's Hypothesis : $\left[\lambda = \frac{h}{mv}\right]$.

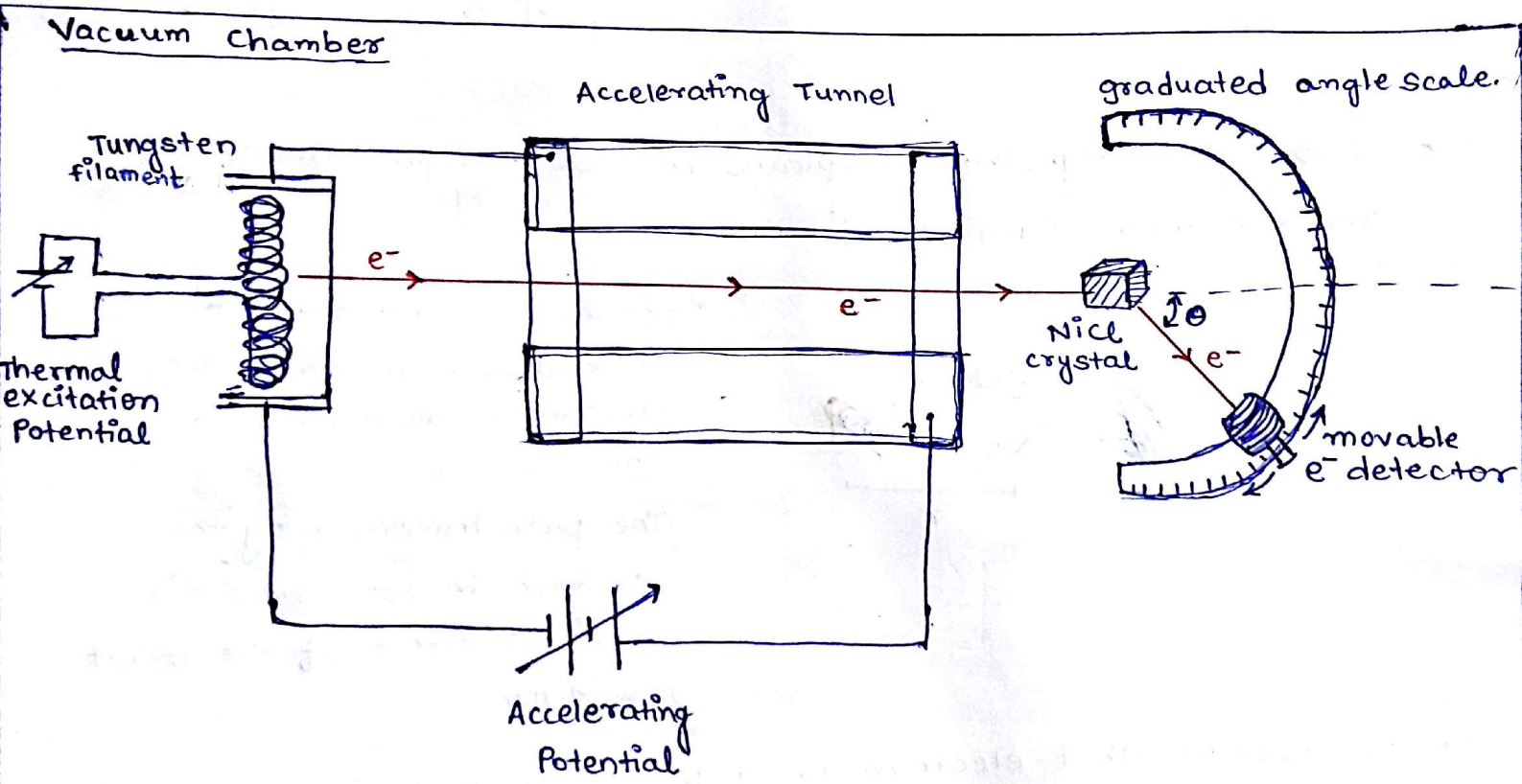
$$\therefore \quad 2\pi r = \frac{nh}{mv}$$

$$\Rightarrow \quad mvr = \frac{nh}{2\pi}$$

$$\therefore \left[l = n\left(\frac{h}{2\pi}\right) \right].$$

— Hence, the Quantization of Angular momentum as per Bohr's postulate.

* Davisson - Germer Experiment :



Expectations from the Experiment :

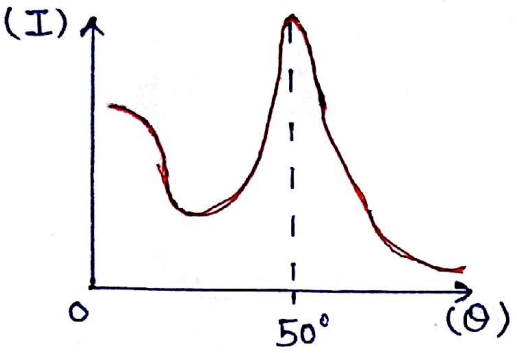
→ Electron beam will be diffusedly reflected (scattering + reflection) unevenly by the NiCl crystal such that roughly equal number of electrons are detected for any given angle to the normal.

→ The distribution of number of electrons / intensity of scattered + reflected beam would be smooth along the curved path of the detector indicating uniform e^- distribution.

Actual Results from the Experiment:

→ A sharp distinctive maxima was observed in the plot of the Intensity distribution with varying angle of detection. The maxima was at a particular value of Angle (θ) that depended on the Accelerating Potential

→ The Intensity versus Angle of detection plot for the experiment looked similar in nature to that from the X-ray diffraction results.



For 54 V.

→ The maxima occured at $\theta_{max.} = 50°$. at 54 V; As accelerating potential was increased / decreased from 54 V value, the maxima then occured at a $\theta < \theta_{max}$.

Conclusions:

→ The experiment involves diffraction of e^- through the NiCl crystal grating.

→ The e^- waves interfere constructively to give a maxima ($I_{max.}$) of intensity at a particular value of the angle (θ).

→ Mathematically,

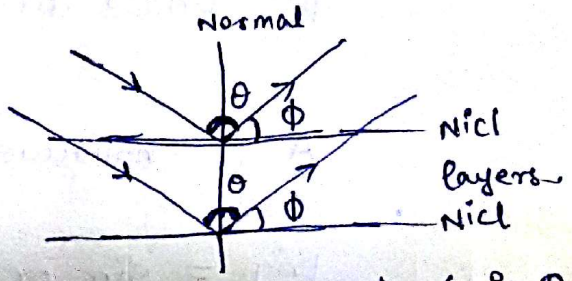
By Bragg's Law of Diffraction,

$$n\lambda = 2d \sin\left(90° - \frac{\theta}{2}\right) \Rightarrow \left[\lambda_{exp.} = 0.165 \text{ nm}.\right].$$

$n = 1 \Rightarrow$ considering adjacent layers of atoms in crystal.

$d = 0.091$ nm for NiCl crystal.

$\theta = 50°$.



$nd = 2d \sin\phi$, $\phi = (90° - \theta/2)$

By De-Broglie's Hypothesis.

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2 m K_E}} \Rightarrow \left[\lambda_{theo.} = 0.167 \text{ nm}\right].$$

m = mass of electron $= 9.1 \times 10^{-31}$ kg.

h = Planck's constant $= 4.14 \times 10^{-15}$ eV·s

K_E = Kinetic energy of e^- = 54 eV

Since $\lambda_{theo.} \simeq \lambda_{exp.}$

$\Rightarrow$ As theoretically expected,

e^- does behave as a wave.

$\Rightarrow$ e^- obeys wave-particle duality.

$\Rightarrow$ This proves De-Broglie's Hypothesis.

* <u>Waves</u> :

$$\left[y(x,t) = A \text{trig.}(Kx - \omega t + \phi)\right].$$

K = wave number $= \frac{2\pi}{\lambda}$

ω = Angular velocity $= \frac{2\pi}{T} = 2\pi\nu$.

ϕ = phase difference

A = amplitude

trig. = sin or cos trigonometric function.

Let, $y = A\cos(kx - \omega t + \phi)$.

$$\therefore \frac{dy}{dt} = -(-\omega) A \sin(kx - \omega t + \phi). = A\omega \sin(kx - \omega t + \phi).$$

$$\therefore \frac{d^2y}{dt^2} = -\omega A\omega \cos(kx - \omega t + \phi). = -A\omega^2 \cos(kx - \omega t + \phi).$$

$$\Rightarrow \frac{d^2y}{dt^2} = -\omega^2 y. \quad \text{—— (1)}.$$

$$\therefore \frac{dy}{dx} = -kA \sin(kx - \omega t + \phi).$$

$$\therefore \frac{d^2y}{dx^2} = -(k) kA \cos(kx - \omega t + \phi). = -k^2 A \cos(kx - \omega t + \phi).$$

$$\Rightarrow \frac{d^2y}{dx^2} = -k^2 y. \quad \text{—— (2)}.$$

From eqns. (1) and (2), we have,

$$\frac{1}{\omega^2}\frac{d^2y}{dt^2} = \frac{1}{k^2}\frac{d^2y}{dx^2}.$$

$$\Rightarrow \frac{d^2y}{dt^2} = \left(\frac{\omega^2}{k^2}\right)\frac{d^2y}{dx^2}.$$

$$\Rightarrow \frac{d^2y}{dt^2} = (V_p^2)\frac{d^2y}{dx^2}.$$

$$\Rightarrow \left[\frac{d^2y}{dx^2} = \frac{1}{V_p^2}\frac{d^2y}{dt^2}\right]$$

The above eqn. is called the "Wave eqn.".

V_p = phase velocity = $\frac{\omega}{K}$.

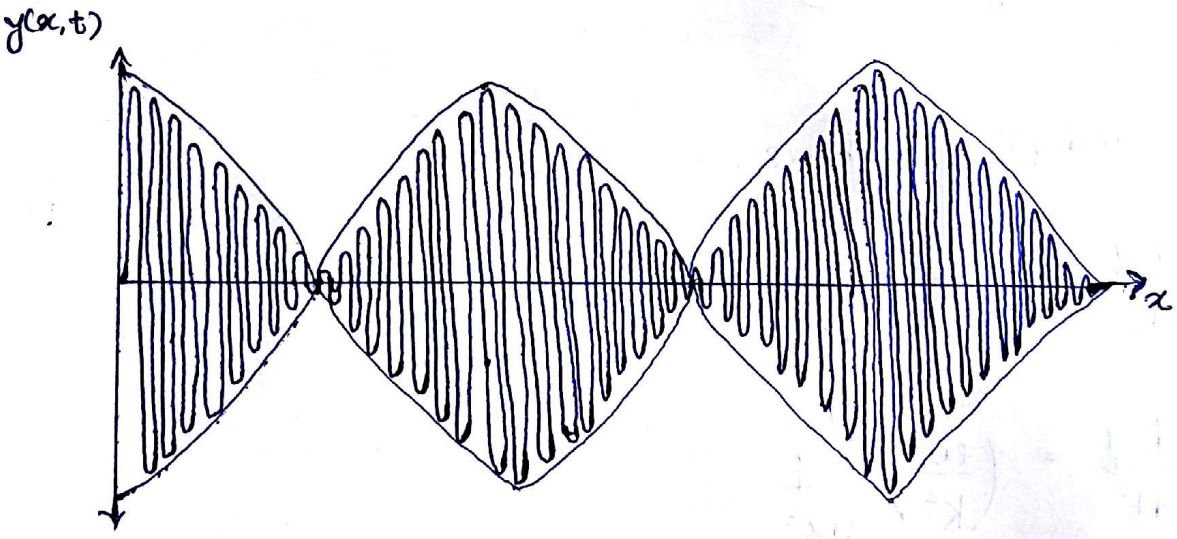
V_g = group velocity = $\frac{d\omega}{dK}$.

According to wave-particle duality,

$E = h\nu = \frac{h}{2\pi} \times 2\pi\nu$	$p = \frac{h}{\lambda} = \frac{h}{2\pi} \times \frac{2\pi}{\lambda}$
$\therefore \boxed{E = \hbar\omega}$	$\therefore \boxed{p = \hbar K}$.
Energy of a particle.	DeBroglie wavelength of a particle in motion.

$\Rightarrow$ $V_p = \frac{E}{P} = \frac{\omega}{K}$. $\simeq$ velocity of the wave propagation.

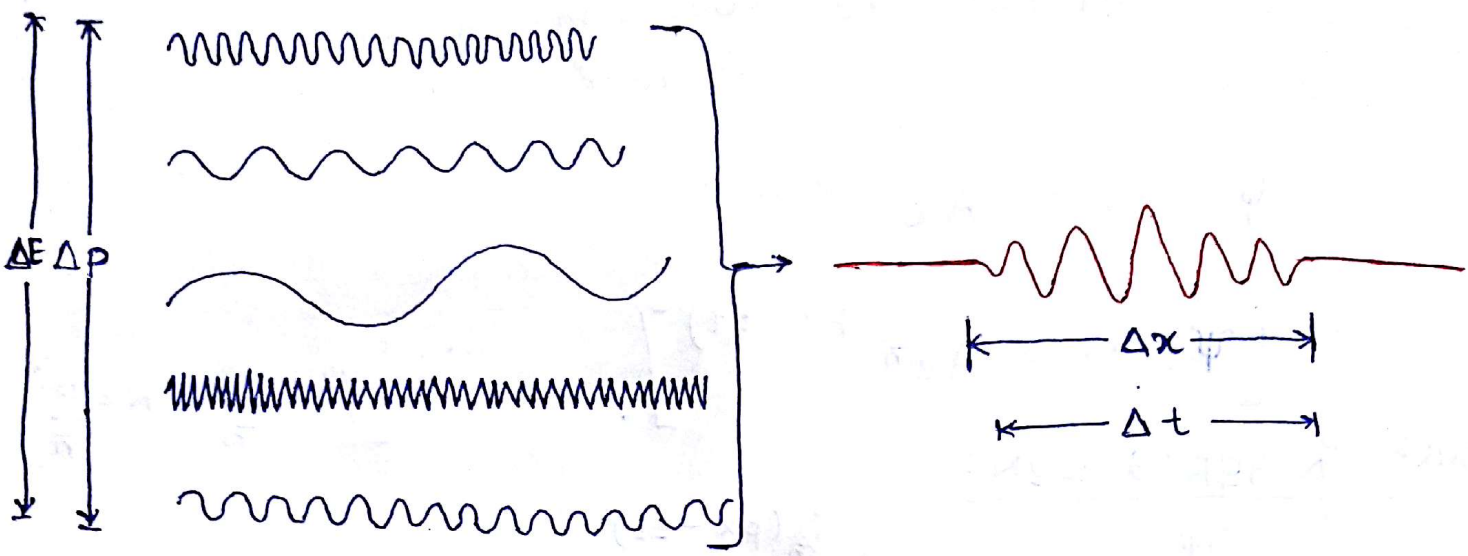
$\Rightarrow$ $V_g = \frac{dE}{dp} = \frac{d\omega}{dK}$. $\simeq$ velocity of the localized wave packet / particle.



"wavepacket" is a group of superposed waves that together form a travelling localized disturbance representing a "particle".

→ The wavepacket forms when several waves of distinct wavelengths and angular velocities superimpose to produce a localized wave pattern. (for length & time respt.)

→ More the number of waves superimposing, more localized is the wavepacket.



→ Each λ of the superimposing wave corresponds to a particular momentum (p) $\because \left[p = \frac{h}{\lambda}\right]$. ∴ Each ω of superimposing wave corresponds to $\left(E = \frac{h}{2\pi}\omega\right)$.

→ As number of participating waves ↑ ; the momentum (energy) value is more dispersed but the wavepacket is more localized. in length (or time).

→ As number of participating waves ↓ ; the momentum (energy) value is more centralized but the wavepacket is more disperesed. in length (or time)

→

∴ As $\Delta p \uparrow \Rightarrow \Delta x \downarrow$ and as $\Delta p \downarrow \Rightarrow \Delta x \uparrow$.

Also as $\Delta E \uparrow \Rightarrow \Delta t \downarrow$ and as $\Delta E \downarrow \Rightarrow \Delta t \uparrow$.

• <u>Heisenberg's Uncertainity principle</u>:

$$\left[\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}\right].$$

Δx & Δp_x are cannonical conjugate variables.

$$\left[\Delta E \cdot \Delta t \geq \frac{h}{4\pi}\right].$$

$$[\Delta x \Delta p_x = \Delta E \cdot \Delta t].$$

$$[\Delta x \cdot \Delta p_{y \text{ or } z} = 0].$$

$$y(x,t) = A\cos(kx - \omega t).$$

In Euler's notation, the above soln. of wave eqn. can be rewritten as.

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

$$\therefore \left[\psi(x,t) = A e^{\frac{i}{\hbar}(px - Et)}\right]. \qquad \because \left[\omega = \frac{E}{\hbar}\ ;\ k = \frac{p}{\hbar}\right].$$

SHRÖDINGER'S EQN:

$$\therefore \frac{\partial\psi}{\partial x} = \frac{i}{\hbar} p \cdot A e^{i/\hbar(px - Et)},$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} = \frac{i^2 p^2}{\hbar^2} \cdot A e^{i/\hbar(px - Et)}.$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} = \frac{-p^2}{\hbar^2} \cdot \psi.$$

$$\therefore \left[p^2\psi = -\hbar^2 \frac{\partial^2\psi}{\partial x^2}\right]. \quad \text{—— (1)}.$$

$$\therefore \frac{\partial\psi}{\partial t} = \frac{i}{\hbar}(-E) \cdot A e^{i/\hbar(px - Et)}$$

$$\therefore \frac{\partial\psi}{\partial t} = \frac{-iE}{\hbar} \cdot \psi.$$

$$\therefore \left[E\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}\right]. \quad \text{—— (2)}$$

We also know that;

$E_{tot.}$ = Kinetic Energy + Potential energy.

$$\therefore \left[E = \frac{p^2}{2m} + V(x)\right].$$

$$\Rightarrow \quad E\psi = \frac{p^2\psi}{2m} + V(x)\psi.$$

$$\therefore \quad -\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi.$$

$$\Rightarrow \quad \boxed{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi}.$$

The above eqn. is the <u>Time Dependant Shrödinger's Equation</u>.

$\psi(x,t)$ is called the wave function.

Using the wave function, assumed as

$$\psi(x,t) = f(x)\cdot g(t)$$

$\therefore$ substituting in the time dependant shrödinger's eqn.

$$i\hbar\frac{\partial f(x)\cdot g(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 f(x)\cdot g(t)}{\partial x^2} + V(x)\cdot f(x)\cdot g(t)$$

$$\Rightarrow \quad f(x)\cdot i\hbar\frac{\partial g(t)}{\partial t} = -g(t)\frac{\hbar^2}{2m}\frac{\partial^2 f(x)}{\partial x^2} + V(x)\cdot f(x)\cdot g(t).$$

Dividing both sides by $\psi = f(x)\cdot g(t)$, we get.

$$\frac{1}{g(t)}\, i\hbar\frac{\partial g(t)}{\partial t} = -\frac{1}{f(x)}\frac{\hbar^2}{2m}\frac{\partial^2 f(x)}{\partial x^2} + V(x).$$

clearly, above eqn. is such that

$$\text{LHS}(t) = \text{RHS}(x).$$

This can happen only when for any x, t.

$$\text{LHS} = \text{RHS} = \text{constant}.$$

$\therefore$ E_{tot} is a constant for a system.

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2} + V(x) = E_0 \quad \text{(const.)}.$$

E_0 = total Energy of the system.

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} f(x) + V(x) f(x) = E_0 f(x)$$

$$\Rightarrow \quad \boxed{E_0 f(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} f(x) + V(x) f(x)}$$

The above eqn. is the <u>time independant Shrödinger's eqn.</u>

Similarly,

$$\frac{1}{g(t)} i\hbar \frac{\partial}{\partial t} g(t) = E_0.$$

$$\therefore \quad \int \frac{\partial g(t)}{g(t)} = \frac{E_0}{i\hbar}\int \partial t.$$

$$\Rightarrow \quad \ln g(t) = \frac{E_0 t}{i\hbar} + \ln C_0$$

$$\Rightarrow \quad \ln\left(\frac{g(t)}{C_0}\right) = \frac{E_0 t}{i\hbar}.$$

$$\therefore \quad \boxed{g(t) = C_0 e^{-i/\hbar E_0 t}}$$

$$\Rightarrow \quad \Psi(x,t) = f(x) \cdot g(t).$$

Particular soln. $\longrightarrow$ $\left[\Psi(x,t) = C_0 f(x) \cdot e^{-i/\hbar E_0 t}\right]$.

Any linear combination of $f(x)$, $g(t)$ will satisfy the eqn.

$$\Rightarrow \quad \left[\Psi_n(x,t) = \sum C_n f_n(x) e^{-i/\hbar E_n t}\right] \longrightarrow \text{General soln.}$$

In 3-Dimensions

$$\left[\frac{P_x^2}{2m} + \frac{P_y^2}{2m} + \frac{P_z^2}{2m}\right] + V(x,y,z) = E_{tot}$$

$$\therefore \quad \psi(x,y,z,t) = A \cdot e^{i/\hbar\,[(P_x x + P_y y + P_z z) - Et]}.$$

$$\therefore \quad \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + V(x,y,z)\,\psi = +i\hbar\frac{\partial \psi}{\partial t} = E\psi.$$

$$\therefore \quad \left[\frac{-\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\,\psi = +i\hbar\frac{\partial \psi}{\partial t}\right].$$

<u>3D Shrödinger's eqn.</u>

→ <u>Probability Density</u>:

$\psi^*\psi$ ≃ Probability of finding the particle at that x, t.

$$\iiint \psi^*\psi \, dx\,dy\,dz = 1 = \int_{-\infty}^{\infty} \psi^*\psi \, dV$$ ≃ Total Probability of finding the particle in the given volume.

$$\psi^*\psi = \sum_{n=m} C_n^* C_m f_n^*(x) f_m(x) + \sum_{n \neq m} C_n^* C_m f_n^*(x) f_m(x)\, e^{i/\hbar (E_n - E_m)t}$$

i.e. $$\left[\psi^*\psi = \sum C_n^* C_m f_n^*(x) f_m(x)\, e^{i/\hbar (E_n - E_m)t}\right].$$

Stationary states :→

The states in which the probability of finding a moving electron is time independant.

i.e. $$\left[\psi^*\psi = \sum C_n^* C_m f_n^* f_m\right].$$

constraints on the wave function : $\psi(x,t)$.

→ must be soln. of Shrödinger's eqn.

→ must be normalizable i.e. as $x \to \infty$, $\psi(x,t) \to 0$.

→ must be continuous on x.

→ $\frac{\partial \psi(x)}{\partial x}$ must be continuous

.....

→ $\psi(x,y,z,t)$ should be finite at any x, y, z, t values.

→ $\psi(x,y,z,t)$ should be single valued at any x, y, z, t.

→ $\frac{\partial \psi}{\partial x}$, $\frac{\partial^2 \psi}{\partial x^2}$, $\frac{\partial \psi}{\partial t}$ should be finite and continuous.

→ $\iiint \psi^* \psi \, dx\, dy\, dz = 1$. (Normalisation constant).

→ $\psi(x,y,z,t)$ should $\to 0$ as $V(x) \to \infty$.

Postulates of Quantum mechanics :

(I) The state of a quantum mechanical system is completely specified by the wave function $\Psi(x,y,z,t)$. The function has a property that $\psi^*(x,y,z,t)\,\psi(x,y,z,t)\,dxdydz$ gives the probability that the particle lies in the volume $(dxdydz)$ element located at coordinates (x,y,z,t).

$$\therefore \left[\int_{-\infty}^{\infty} \psi^* \psi \, dV = 1\right].$$

i.e.

A unique $\psi(x,y,z,t)$ will be associated with every particle moving in a conservative field of a force.

(II) To every observable in classical mechanics there corresponds a linear operator in quantum mechanics.

Sr. no.	Observable	symbol	Operator	Operation
1)	Position	x	$\hat{x}$	multiply by x.
		$\vec{r}$	$\hat{\vec{R}}$	Multiply by $\vec{r}$.
2)	Momentum	P_x	$\hat{P}_x$	$-i\hbar \frac{\partial}{\partial x}$.
		$\vec{P}$	$\hat{\vec{P}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$.
3)	Kinetic Energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$.
		K	$\hat{K}$	$-\frac{\hbar^2}{2m}\nabla^2$.
4)	Potential Energy	$V(x)$	$\hat{V}(\hat{x})$	multiply by $V(x)$.
		$V(x,y,z)$	$\hat{V}(\hat{x},\hat{y},\hat{z})$	multiply by $V(x,y,z)$.
5)	Total Energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$.
6)	Angular Momentum	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$.
		l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$.
		l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$.

(III) The linear Operator will be Hermitian.

Hermitian matrix (HH)

$$H^{\dagger} = H$$

$$\therefore \Rightarrow (H^*)^T = H$$

→ H is a complex square matrix that is equal to its own conjugate-transpose.

→ H gives real eigenvalues. → need of operator to be Hermitian. Because, measured value of observable should be real.

→ H gives eigenvectors of two distinct eigenvalues such that they are orthonormal.

i.e. If $H\psi_{n_1} = n_1\psi_{n_1}$ and $H\psi_{n_2} = n_2\psi_{n_2}$ $\Rightarrow$ $\psi_{n_1} \perp \psi_{n_2}$ and $|\psi_n| = 1$ (orthonormal).

condition for Hermiticity:

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

$$\therefore \int \psi^* \hat{A} \psi \, dV = a \int \psi^* \psi \, dV = a \quad \text{—— (1)}$$

... Multiply by ψ^* from left and integrate. $\because \int \psi^* \psi \, dV = 1$.

$$\hat{A}^* \psi^* = a\psi^*$$

... Taking conjugate of Eigenequation.

$$\therefore \int \psi \hat{A}^* \psi^* dV = a \int \psi \psi^* dV = a \quad \text{—— (2)}$$

... Multiply by ψ from left and integrate $\because \int \psi \psi^* dV = 1$.

from eqn. (1) & (2), we get.

$$\int \psi^* \hat{A} \psi \, dV = \int \psi \hat{A}^* \psi^* dV$$

$$\therefore \left[\int_{-\infty}^{\infty} f^* \hat{A} f \, dV = \int_{-\infty}^{\infty} f \hat{A}^* f^* \, dV \right]$$

condition for Hermiticity.

$\therefore$ In 1D.

$$\left[\int_{-\infty}^{\infty} f^* \hat{A} f \, dx = \int_{-\infty}^{\infty} f \hat{A}^* f^* \, dx \right].$$

Assume as $x \longrightarrow \pm\infty$, $f \longrightarrow 0$, $f^* \longrightarrow 0$.

$$\therefore \quad \text{LHS} = \int_{-\infty}^{\infty} f^* \hat{A} f \, dx$$

$$= f^* \int_{-\infty}^{\infty} \hat{A} f \, dx - \int_{-\infty}^{\infty} \frac{df^*}{dx} \left(\int_{-\infty}^{\infty} \hat{A} f \, dx \right) dx \quad \text{——— (1)}$$

... solve further.

$$\text{RHS} = \int_{-\infty}^{\infty} f \hat{A}^* f^* \, dx$$

$$= f \int_{-\infty}^{\infty} \hat{A}^* f^* \, dx - \int_{-\infty}^{\infty} \frac{df}{dx} \left(\int_{-\infty}^{\infty} \hat{A}^* f^* \, dx \right) dx \quad \text{——— (2)}$$

... solve further.

u.v. Rule of Integration. ($\rightarrow$ ILATE rule of priority)

$$\left[\int \underset{(1)}{u} \cdot \underset{(2)}{v} \, dx = u \int v \, dx - \int u' \left(\int v \, dx \right) dx \right].$$

Iff eqn. (1) $\equiv$ eqn. (2) $\Rightarrow$ $\hat{A}$ is Hermitian.

More generalized condition for Hermiticity.

$$\left[\int \psi_m^* \hat{H} \psi_n \, dV = \int \psi_m \hat{H}^* \psi_n^* \, dV \right].$$

Note: 1. ψ_m and ψ_n are two well behaved wave functions.

2. $\iiint \psi_n^* \psi_n \, dx dy dz = 1$.

3. $\iiint \psi_m^* \psi_n \, dx dy dz = 0$.

- Dirac's <u>Bra-c-ket</u> notations:

$$\iiint \psi^* \psi \, dx dy dz \equiv \langle \psi | \psi \rangle$$

$$\int \psi_m^* \hat{H} \psi_n \, dV \equiv \langle \psi_m | \hat{H} | \psi_n \rangle$$

$$\int \psi_m \hat{H}^* \psi_n^* \, dV \equiv \langle \psi_m | \hat{H} | \psi_n \rangle^*$$

$$\because \int \psi_m \hat{H}^* \psi_n^* dV = \left(\int \psi_m^* \hat{H} \psi_n dV \right)^*$$

i.e.

$$\iiint \psi \psi^* dx dy dz \equiv \langle \psi | \psi \rangle^*$$

- Proof of Hermitian eigenvectors are orthogonal.

Let, $H r_1 = \lambda_1 r_1$ and $H r_2 = \lambda_2 r_2$; $\lambda_1 \neq \lambda_2 \neq 0$.

$\therefore$ $H \equiv$ Hermitian matrix.

$\lambda_1, \lambda_2 \in$ eigenvalues.

$r_1, r_2 \in$ eigenfunctions/eigenvectors

$\Rightarrow (H r_1)^\dagger = (\lambda_1 r_1)^\dagger$

$\therefore \; r_1^\dagger H^\dagger = \lambda_1^* r_1^\dagger$

$\therefore \; r_1^\dagger H = \lambda_1^* r_1^\dagger$

Multiplying both sides by r_2. on the right.

$\therefore \; r_1^\dagger H r_2 = \lambda_1^* r_1^\dagger r_2$

since λ_1 is real.

$\Rightarrow r_1^\dagger H r_2 = \lambda_1 r_1^\dagger r_2$ —— (1)

$(H r_2) = (\lambda_2 r_2)$

Multiplying both sides by $r_1^\dagger$. on the left.

$\Rightarrow r_1^\dagger H r_2 = \lambda_2 r_1^\dagger r_2$ —— (2).

from eqn. (1) and (2), we get.

$\lambda_1 r_1^\dagger r_2 = \lambda_2 r_1^\dagger r_2$

$\Rightarrow (\lambda_1 - \lambda_2) r_1^\dagger r_2 = 0.$

But $\lambda_1 \neq \lambda_2$.

$\therefore \; r_1^\dagger \cdot r_2 = 0.$

$\Rightarrow$ Dot product of $r_1^\dagger \cdot r_2 = 0.$

$\Rightarrow r_1 \perp r_2.$

— Hence r_1 & r_2 are orthogonal.

Thus proved.

(IV) If the system is in a state described by Ψ_n, an eigenfunction of Hermitian operator $\hat{A}$ describing some classical observable, then the measurement of the observable of the system in that state will be the eigenvalue a_n. (NO other value).

$$[\hat{A}\Psi_n = a_n \Psi_n].$$

The mathematical operator $\hat{A}$ extracts the observable value a_n by operating upon the wavefunction which represents that particular state of the system.

$$\hat{A}\psi_n = a_n \psi_n .$$

For example, the eigenequation for $Energy_{tot}$:

$$\hat{H}\psi_n = E_n \psi_n .$$

$\hat{H}$ = Hamiltonian operator = Total Energy Operator.

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(x, y, z) .$$

Thus, $\hat{H}\psi_n = E_n\psi_n$ is the shrödinger's equation.
i.e. Shrödinger's eqn. is the eigenequation of 'E_{tot}'.
∵ Energy is the most important property of the system, Shrödinger's eqn. is special amongst all the eigeneqns for different observable operators.

The set of all eigenvalues $\{a_n\}$ is called the spectrum of the operator $\hat{A}$.
Spectrum describes the measurement values of the observabl for all the possible states of the system.
The value of the observable at any given state of the system has to be an element of the spectrum of that operator.

(V) All the possible eigenfunctions of an operator for a given system form the basis (set of linearly independant functions).

Thus any wavefunction ψ describing a physical system can be expressed as a linear combination of the eigenfunctions of any physical observable of the system.

$$\psi = \sum_j c_j \psi_j .$$

A system need not be in a state described by any particular eigenfunction ψ_n.

i.e. a system can be in a state ψ that is not an eigenfunction of $\hat{A}$. The measured value 'a' of this system will still be an element of $\{a_n\}$ spectrum. But each element of a_n being the observed value of the system at the state given by ψ has distinct probabilities.

This enables us to calculate the "expectation value" (avg.) of the observable when the system is in a state ψ not an eigenfunction of the operator $\hat{A}$.

$$\langle a \rangle = \frac{\int \psi^* \hat{A} \psi \, dV}{\int \psi^* \psi \, dV \longrightarrow \simeq 1.}$$

conditions:

→ wavefunction ψ is normalized.

→ Integration is over all space.

→

$$\left[\psi = \sum_j c_j \psi_j \right]$$

where

$$\left[\hat{A} \psi_j = a_j \psi_j \right]$$

If $\psi = \psi_n$

$\langle a \rangle = a_n$

$\langle a^2 \rangle = a_n^2$

$Var(a) = \sigma^2 = 0.$

when system is in a state ψ_n $a = a_n$ but when $\psi = \sum c_j \psi_j$ then a = distribution of several values of $a_j \in$ spectrum with coeff. multiplied to indicate distinct level of prob. associated with that a_j. avg. of this distributn is $\langle a \rangle$

(VI) Evolution in time of the wavefunction ψ describing the system at an intial time 'to'; is given by the time dependant Shrödinger's equation.

$$\boxed{\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}}.$$

- <u>Commutativity</u>:

→ Operators $\hat{A}$ and $\hat{B}$ operating sequentially on a function $f(x)$.

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x) \quad \ldots \text{ commutative.}$$

$$\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x) \quad \ldots \text{ non commutative.}$$

If $\hat{A}$ and $\hat{B}$ are not commutative.

$$\hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) = f(x)$$

$$\Rightarrow (\hat{A}\hat{B} - \hat{B}\hat{A}) \cdot f(x) = \hat{I} \cdot f(x)$$

$\hat{I}$ = Identity operator. $\Rightarrow \hat{I}f(x) = f(x)\hat{I} = f(x)$.

If $\hat{A}$ and $\hat{B}$ are commutative.

$$\hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) = 0.$$

$$\Rightarrow (\hat{A}\hat{B} - \hat{B}\hat{A}) = 0.$$

$(\hat{A}\hat{B} - \hat{B}\hat{A}) = [\hat{A}, \hat{B}] \longrightarrow$ "commutator" representation.

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

$[\hat{A}, \hat{B}] = \hat{I}$ ... non commutative.

Algorithm to evaluate commutator :

- evaluate $\hat{A}(\hat{B}f(x)) = p$
- evaluate $\hat{B}(\hat{A}f(x)) = q$
- evaluate $(p - q)$
- evaluate $\dfrac{(p-q)}{f(x)} = r$
- $[\hat{A}, \hat{B}] = r\hat{I}$.
- $r = 0$ comm.
- $r = K$ non comm.

Role of commutator in uncertainity principle:

$\rightarrow [\hat{x}, \hat{P}_x]$

$\hat{x} = x$.

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

$\therefore [\hat{x}, \hat{P}_x]$

$= \left[x \cdot \left(-i\hbar \dfrac{\partial}{\partial x}\psi\right) - \left(-i\hbar \dfrac{\partial(\psi x)}{\partial x}\right)\right]$

$= -ix\hbar \dfrac{\partial \psi}{\partial x} + i\hbar\left[\psi(1) + x\dfrac{\partial \psi}{\partial x}\right]$

$= \cancel{-i\hbar x \dfrac{\partial \psi}{\partial x}} + \cancel{i\hbar x \dfrac{\partial \psi}{\partial x}} + i\hbar\psi \quad \Rightarrow [\hat{x}, \hat{P}_x] = i\hbar.$

$\rightarrow [\hat{H}, \hat{P}_x]$

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

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

$\therefore [\hat{H}, \hat{P}_x]$

$$= \left[\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\left(-i\hbar\frac{\partial}{\partial x}\psi\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V\cdot\psi\right)\right]$$

$$= \left[-i\hbar\left(\frac{-\hbar^2}{2m}\frac{\partial^3\psi}{\partial x^3} + V\frac{\partial\psi}{\partial x}\right)\right] - \left[\frac{+i\hbar^3}{2m}\frac{\partial^3\psi}{\partial x^3} - i\hbar V\frac{\partial\psi}{\partial x}\right]$$

$$= \cancel{\left[\frac{+i\hbar^3}{2m}\frac{\partial^3\psi}{\partial x^3} - i\hbar V\frac{\partial\psi}{\partial x}\right]} - \cancel{\left[\frac{+i\hbar^3}{2m}\frac{\partial^3\psi}{\partial x^3} - i\hbar V\frac{\partial\psi}{\partial x}\right]}.$$

$$= \underline{\underline{0}}.$$

$\Rightarrow [\hat{H}, \hat{P}_x] = 0.$

$\rightarrow [\hat{H}, \hat{x}]$

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

$$\hat{x} = x.$$

$\therefore [\hat{H}, \hat{x}]$

$$= \left[\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)x\cdot\psi\right] - \left[x\left(\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi\right)\right]$$

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

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

$\Rightarrow [\hat{H}, \hat{x}] = 0.$

$\rightarrow$

$[\hat{x}, \hat{P}_y]$

$\hat{x} = x.$

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

$\therefore [\hat{x}, \hat{P}_y]$

$= \left[x\left(-i\hbar \frac{\partial \psi}{\partial y}\right) - \left(-i\hbar \frac{\partial (x \cdot \psi)}{\partial y}\right) \right]$

$= \left[\cancel{-i\hbar x \frac{\partial \psi}{\partial y}} + \cancel{i\hbar x \frac{\partial \psi}{\partial y}} \right]$

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

$\therefore [\hat{x}, \hat{P}_y] = 0.$

Thus; If two quantities a, b are simultaneously measurable then $[\hat{A}, \hat{B}] = 0.$

ellf two quantities incite uncertainity when measured simultaneously then $[\hat{A}, \hat{B}] \neq 0.$

Some properties of commutators:

① $[\hat{A} \cdot \hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$

② $[\hat{A}, \hat{B} \cdot \hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$

③ $[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$

④ $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$

⑤ $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$

Probabilistic terms :

$$\langle a \rangle = \int \psi^* \hat{A} \psi \, dV \quad \ldots \text{ 3D.}$$

$$\langle a \rangle = \int \psi^* \hat{A} \psi \, dx \quad \ldots \text{ 1D.}$$

$$\sigma_a = \int \psi^* (\hat{A} - \langle a \rangle)^2 \psi \, dV \quad \ldots \text{ 3D.}$$

$$\sigma_a = \int \psi^* (\hat{A} - \langle a \rangle)^2 \psi \, dx \quad \ldots \text{ 1D.}$$

- Time Evolution of Operators :

$$\psi = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}_{n\times 1}$$ Column vector.

$$\psi^* = (\bar{x}_1 \ \bar{x}_2 \ \dots \ \bar{x}_n)_{1\times n}$$ Row vector. (complex conjugate of ψ.

$$\hat{O} = \begin{pmatrix} O_{11} & \dots & O_{1n} \\ \vdots & \ddots & \vdots \\ O_{n1} & \dots & O_{nn} \end{pmatrix}_{n\times n}$$ Operator Hermitian Matrix.

$$\therefore \quad \psi^* \hat{O} \psi = (\dots\dots)_{1\times n} \begin{pmatrix} \dots & \dots \\ \vdots & \ddots \\ \dots & \dots \end{pmatrix}_{n\times n} \begin{pmatrix} \vdots \end{pmatrix}_{n\times 1}$$

$$\therefore \quad \psi^* \hat{O} \psi = (.)_{1\times 1}.$$

Expected Mean of an operator is defined as :

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

$$\Rightarrow \langle \hat{O} \rangle = \int \psi^* \hat{O} \psi \, dx \quad \dots \text{ for 1D.}$$

... Differentiating both sides and applying u·v rule of diff.

$$\therefore \quad \frac{d}{dt}\langle \hat{O} \rangle = \int \frac{\partial}{\partial t}\psi^* \hat{O}\psi \, dx + \int \psi^* \frac{\partial}{\partial t}\hat{O}\psi \, dx + \int \psi^* \hat{O} \frac{\partial}{\partial t}\psi \, dx.$$

By v_{i}^{th} Postulate of Quantum Mechanics.

$$\hat{H} \equiv i\hbar \frac{\partial}{\partial t}.$$

$$\Rightarrow \frac{\partial()}{\partial t} \equiv \frac{\hat{H}}{i\hbar}$$

$$\Rightarrow \frac{d}{dt}\langle \hat{O} \rangle = \int \psi^* \frac{\partial}{\partial t}\hat{O}\psi \, dx + \int \frac{\hat{H}}{i\hbar}\psi^* \hat{O}\psi \, dx + \int \psi^* \hat{O}\frac{\hat{H}}{i\hbar} \, dx.$$

Now; $\hat{H}\psi^* = -\psi^* \hat{H}$ ... from operator property.

$$\therefore \frac{d\langle\hat{O}\rangle}{dt} = \int \psi^* \frac{\partial \hat{O}}{\partial t}\psi dx + \frac{1}{i\hbar}\int \psi^* \hat{O}\hat{H}\psi dx - \frac{1}{i\hbar}\int \psi^* \hat{H}\hat{O}\psi dx.$$

$$\therefore \frac{d\langle\hat{O}\rangle}{dt} = \underbrace{\int \psi^* \frac{\partial}{\partial t}\hat{O}\psi dx}_{\sim\left\langle\frac{\partial \hat{O}}{\partial t}\right\rangle} + \frac{1}{i\hbar}\int \underbrace{\psi^*[\hat{O}\hat{H} - \hat{H}\hat{O}]\psi dx}_{\sim[\hat{O},\hat{H}]}.$$

$$\sim\langle[\hat{O},\hat{H}]\rangle$$

$$\therefore \boxed{\frac{d\langle\hat{O}\rangle}{dt} = \left\langle\frac{\partial \hat{O}}{\partial t}\right\rangle + \frac{1}{i\hbar}\left\{\langle[\hat{O},\hat{H}]\rangle\right\}}$$

When the operators do not depend explicitly on time.

$$\left\langle\frac{\partial \hat{O}}{\partial t}\right\rangle = 0.$$

Under such case:

$$\boxed{\frac{d\langle\hat{O}\rangle}{dt} = \frac{1}{i\hbar}\left\{\langle[\hat{O},\hat{H}]\rangle\right\}}.$$

<u>The operators that commute with ($\hat{H}$) are constants of motion.</u>

i.e. if Operator $\hat{O}$ and Hamiltonian $\hat{H}$ commute.

$$\Rightarrow [\hat{O},\hat{H}] = [\hat{O}\hat{H} - \hat{H}\hat{O}] = 0 \text{(zero)}.$$

$$\therefore \boxed{\frac{d\langle\hat{O}\rangle}{dt} = 0 \text{ (zero)}}.$$

$\Rightarrow$ The physical quantity described by operator $\hat{O}$ is a constant of motion. i.e. it stays conserved throughout the motion (Does not vary with time).

Evaluating the following commutators:

$$\hat{x} = x.$$

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

$$\hat{H} = \frac{\hat{P}^2}{2m} + \hat{V}(x).$$

$$\hat{V}(x) = V(x).$$

Now;

$$\Rightarrow [\hat{P}_x, \hat{H}] = \left[\hat{P}_x, \frac{\hat{P}_x^2}{2m} + \hat{V}(x)\right] = \left[\hat{P}_x, \frac{\hat{P}_x^2}{2m}\right] + \left[\hat{P}_x, \hat{V}(x)\right].$$

$$= \cancel{\left[\hat{P}_x, \frac{\hat{P}_x}{\sqrt{2m}}\right]}^{\text{zero.}} \frac{\hat{P}_x}{\sqrt{2m}} + \frac{\hat{P}_x}{\sqrt{2m}} \cancel{\left[\hat{P}_x, \frac{\hat{P}_x}{\sqrt{2m}}\right]}^{\text{zero.}} + \left[\hat{P}_x, \hat{V}(x)\right].$$

$$= [\hat{P}_x, \hat{V}(x)].$$

$$= \left[\left(\frac{-i\hbar\partial}{\partial x}\right)(V(x)) - (V(x))\left(-i\hbar\frac{\partial}{\partial x}\right)\right]\psi(x).$$ taken only for commutator evaluation

$$= \left[-i\hbar\frac{\partial V}{\partial x} + i\hbar V(x)\cdot\frac{\partial}{\partial x}\right]\psi(x)$$

$$= -i\hbar\frac{\partial(V\psi)}{\partial x} + i\hbar V(x)\cdot\frac{\partial\psi(x)}{\partial x}$$

$$= -i\hbar\left(\psi\frac{\partial V(x)}{\partial x} + V(x)\cdot\frac{\partial\psi(x)}{\partial x}\right) + i\hbar V(x)\cdot\frac{\partial\psi(x)}{\partial x}$$

$$= -i\hbar\psi(x)\cdot\frac{\partial V(x)}{\partial x} - \cancel{i\hbar V(x)\frac{\partial\psi(x)}{\partial x}}^{0.} + \cancel{i\hbar V(x)\frac{\partial\psi(x)}{\partial x}}^{0.}.$$

$$= \left[-i\hbar\frac{\partial V(x)}{\partial x}\right]\psi(x)$$

$$\therefore [\hat{P}_x, \hat{H}] = -i\hbar\frac{\partial V(x)}{\partial x} \quad \text{—— (1)}.$$

Similarly;

$$\Rightarrow [\hat{x}, \hat{H}] = \left[\hat{x}, \frac{\hat{p}_x^2}{2m}, \hat{V}(x)\right] = \left[\hat{x}, \frac{\hat{p}_x^2}{2m}\right] + \left[\hat{x}, \hat{V}(x)\right].$$

$$= [\hat{x}, \hat{p}_x]\hat{p}_x + \hat{p}_x[\hat{x}, \hat{p}_x] + \underbrace{[xV - Vx]}_{\text{zero}}\psi.$$

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

$$\Rightarrow [\hat{x}, \hat{H}] = (i\hbar)\hat{p}_x + \hat{p}_x(i\hbar).$$

$$\therefore [\hat{x}, \hat{H}] = 2i\hbar\,\hat{p}_x \quad \text{—— (2)}.$$

$$\therefore \frac{d\langle\hat{p}_x\rangle}{dt} = \frac{1}{i\hbar}\langle[\hat{p}_x, \hat{H}]\rangle.$$

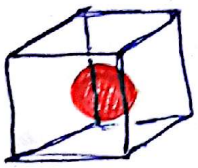
$$\therefore \frac{d\langle\hat{x}\rangle}{dt} = \frac{1}{i\hbar}\langle[\hat{x}, \hat{H}]\rangle.$$

Using eqns. (1) and (2), we get.

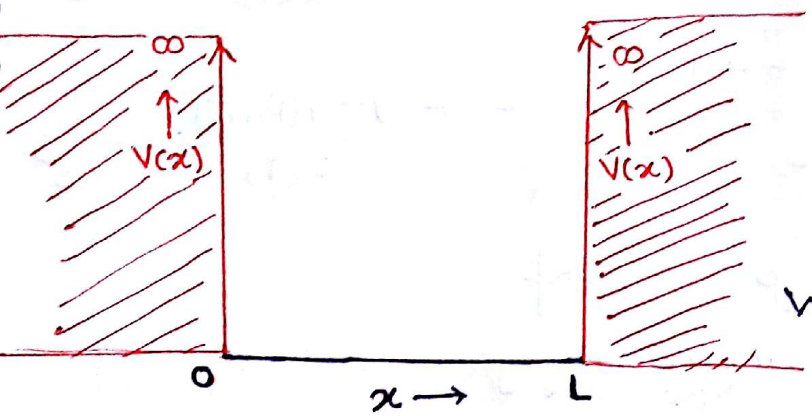
$$\left.\begin{aligned} \frac{d\langle\hat{p}_x\rangle}{dt} &= -\left\langle\frac{\partial V(x)}{\partial x}\right\rangle. \\ \frac{d\langle\hat{x}\rangle}{dt} &= \left\langle\frac{\hat{p}}{m}\right\rangle. \end{aligned}\right\} \text{Ehrenfest's theorem.}$$

$\Rightarrow$ Quantum Mechanical Expectations values obey Newton's second law.

* PARTICLE IN A BOX:



(1 Dimensional) Particle in a Box:



$$V(x) = \begin{cases} 0 \; ; & 0 < x < L. \\ \infty \; ; & x \geq L, \; x \leq 0. \end{cases}$$

Writing the time independant Shrödinger's eqn. for a free particle in the 1D Box. we have,

$$\hat{H}\Psi = E_{tot.}\Psi.$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) + \underbrace{V(x)}_{\text{zero.}}\cdot\Psi(x) = E_{tot.}\Psi(x)$$

Because we are solving the Shrödinger eqn. for $x \in (0, L)$. and $V(x)$ inside the box is: $V(x) = 0$.

Shrödinger's eqn. for free particle inside Box

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = E_{tot.}\Psi(x)$$

$$\Rightarrow \frac{\partial^2}{\partial x^2}\Psi(x) = -\frac{2mE}{\hbar^2}\Psi(x).$$

$$\therefore \frac{d^2}{dx^2}\Psi(x) = -k^2\Psi(x). \quad \ldots\ldots -k^2 = -\frac{2mE}{\hbar^2} = (\text{constant}).$$

The above simplified Diff. eqn. is a form of the general 2nd order D.E. of the form.

$$a_2\frac{d^2}{dx^2}y(x) + a_1\frac{d}{dx}y(x) + a_0 y(x) = 0.$$

where in our case $a_1 = 0$; $a_2 = 1$ and $a_0 = +k^2$.

We can <u>treat</u> diff. eqn. operators as algebraic symbols in Auxillary eqn.

$$(a_2 D^2 + a_1 D + a_0)y = 0.$$

The soln. of the Quad. Alg. eqn. $(a_2D^2 + a_1D + a_0) = 0$. is given by α, β.

$$\alpha = \frac{-a_1 + \sqrt{a_1^2 - 4a_2a_0}}{2a_2} = \frac{+\sqrt{-4(1)(k^2)}}{2(1)} = \frac{2ik}{2}.$$

$$\beta = \frac{-a_1 - \sqrt{a_1^2 - 4a_2a_0}}{2a_2} = \frac{-\sqrt{-4(1)(k^2)}}{2(1)} = \frac{-2ik}{2}.$$

$\therefore [\alpha = +i \cdot K]$; $[\beta = -i \cdot K]$.

clearly; α and β are complex conjugates of each other.

$\therefore$ The solns. of the 2nd order D.E. are.

$y_1 = c_1 e^{\alpha x}$.

$y_2 = c_2 e^{\beta x}$.

$\left.\begin{matrix} c_1 \\ c_2 \end{matrix}\right\}$ → Arbitrary constants.

The soln. of a linear O.D.E. can be written as a linear combo. of its other solns.

⇒ If y_1 & y_2 satisfy given ODE.

⇒ $[y_g = \bar{c}_1 y_1 + \bar{c}_2 y_2]$ will also satisfy O.D.E.

⇒ $y_g = c_1' e^{\alpha x} + c_2' e^{\beta x}$

y_g is soln. of ODE.

$[c' = c \times \bar{c}]$.

$\therefore y_g = c_1' e^{+ikx} + c_2' e^{-ikx}$.

Clearly; By Euler's notation : $e^{\pm i\theta} = \cos\theta \pm i\sin\theta$.

$\therefore$ we get; $y_g = c_1'(\cos kx + i\sin kx) + c_2'(\cos kx - i\sin kx)$.

⇒ $y_g = i(c_1' - c_2)\sin kx + (c_1' + c_2')\cos kx$.

⇒ $\boxed{y_g = A\sin(kx) + B\cos(kx)}$.

Thus general solution of our 2nd order D.E.

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

is $\psi_g(x) = A\sin(kx) + B\cos(kx)$ ... $A, B \in$ Arbitrary constants

Now applying Boundary conditions:

$\psi(x \leq 0) = 0 \Rightarrow \psi(0) = 0.$ since at $x = 0, L$; $V(x) = \infty$. $\therefore \psi(0; L) = 0$.

$\psi(x \geq L) = 0. \Rightarrow \psi(L) = 0.$

$$\therefore \quad \psi_g(0) \equiv A\sin(k*0) + B\cos(k*0) = 0.$$

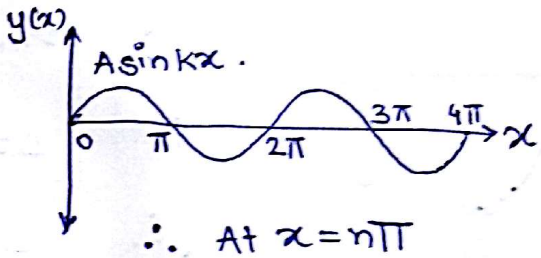
$$\therefore \quad A(0) + B(1) = 0.$$

$$\therefore \quad \boxed{B = 0}.$$

Thus, the boundary conditions demand that $B = 0$.

$\Rightarrow [\psi_g(x) = A\sin kx]$.

Now, $\psi_g(L) \equiv A\sin(KL) = 0$.



$\therefore$ At $x = n\pi$
$A\sin[k(x)] = 0$.

$$\therefore \quad \cancel{A}\cancel{\sin} KL = \cancel{A}\cancel{\sin}(n\pi).$$

$$\therefore \quad KL = n\pi$$

$$\Rightarrow \quad \therefore \boxed{k = \frac{n\pi}{L}}$$

Thus; the particular soln. is...

$$\psi_{p_n}(x) = A\sin\left(\frac{n\pi x}{L}\right).$$

The above eqn. gives the soln. for nth state of Energy of particle. A more general soln. would be the linear combination of all nth state solutions.

$$\psi_p(x) = \sum_1^{\infty} K_n A\sin\left(\frac{n\pi x}{L}\right).$$

$$K_n = \text{Fourier coeff.} = \left(\frac{1}{L/2}\right)\int_0^L \psi_p(x)\sin\left(\frac{n\pi x}{L}\right)dx.$$

Now, we know that $K = \frac{\sqrt{2mE}}{\hbar}$

$$\therefore \quad \frac{n\pi}{L} = \frac{\sqrt{2mE}}{\hbar}$$

$$\Rightarrow \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

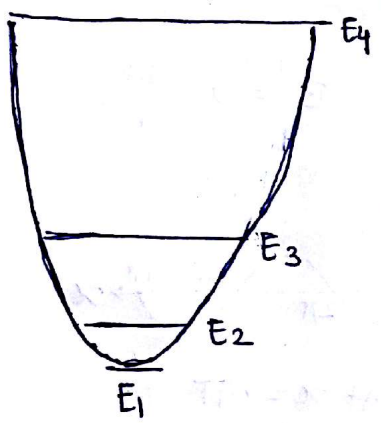
But $\hbar = \frac{h}{2\pi}$

$$\therefore \quad \boxed{E_n = \frac{n^2h^2}{8mL^2}}$$

This gives the energy of particle in the nth state.
$n = 1, 2, 3, \ldots$

Quadratic dependence of spacing of Energy levels further apart.

$$\therefore \quad E_1 = \frac{h^2}{8mL^2}$$



$$\Rightarrow \quad E_n = n^2 E_1$$

and $E_{n+1} = (n+1)^2 E_1$

$$\therefore \quad \Delta E = \left[(n+1)^2 - n^2\right] E_1$$

$$\therefore \quad \Delta E = (2n+1) E_1 = \frac{(2n+1)h^2}{8mL^2}.$$

- <u>Normalisation of Wave Function:</u>

Max Born's view:

$\psi(x)$ = The Amplitude of the particle wave.

$\therefore$ Intensity of the particle wave $= (\text{Amplitude})^2$.

But $\psi(x) \in \mathbb{C}$ i.e. $\psi(x) \equiv Re(x) + Im(x) \equiv A(x) + iB(x)$.

$\therefore [\psi(x)]^2 \in \mathbb{C}$ i.e. $[\psi(x)]^2 = (Re + Im)^2(x) \equiv A^2(x) - B^2(x) + 2iA(x)B(x)$

But Intensity cannot be a complex value.

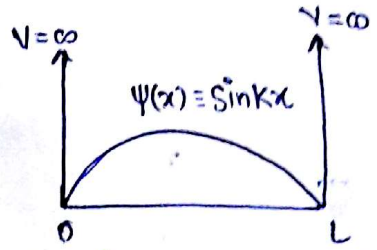
$\therefore$ instead of Intensity $= \psi(x)$ we take $\psi(x)\psi^*(x) =$ Intensity.

As $\psi(x)\psi^*(x) \in \mathbb{R}$ i.e. $\psi(x)\psi^*(x) = A^2(x) + B^2(x)$.

According to Max Born's view, the intensity of the particle wave gives the probability of finding the particle in element 'dx'.

$\Rightarrow \psi\psi^* dx \equiv$ Prob. of particle to be localized in dx.

Total probability $= 1$.

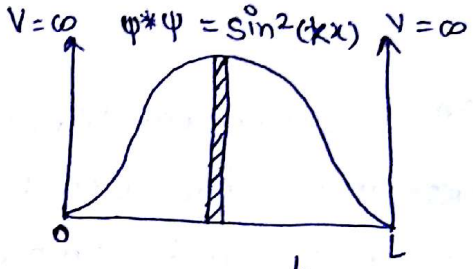


$$\Rightarrow \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = 1.$$

$\equiv$ Probability of finding the particle in the entire region.

In our case,

$$\int_{-\infty}^{0} \psi^*\psi\,dx = \int_{L}^{\infty} \psi^*\psi\,dx = 0 \quad \because V(x) \text{ is } \infty \text{ at } x \geq L, x \leq 0.$$



$$\therefore \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = \int_{0}^{L} \psi^*(x)\,\psi(x)\,dx = 1$$

$$\therefore \int_{0}^{L} \psi^*(x)\,\psi(x)\,dx \equiv \int_{0}^{L} \left[A \sin\left(\frac{n\pi x}{L}\right)\right]^2 dx = 1$$

$$A\int_{0}^{L} \sin^2(kx) = 1$$

$$\therefore \int_{0}^{L} A^2 \sin^2\left(\frac{n\pi x}{L}\right) = 1$$

Using $\sin^2\theta = \dfrac{1-\cos 2\theta}{2}$;

$$\therefore \frac{A^2}{2}\int_{0}^{L}\left[1-\cos 2\left(\frac{n\pi x}{L}\right)\right]dx = 1.$$

$$\therefore \frac{A^2}{2}\left[\int_{0}^{L} dx - \int_{0}^{L} \cos\left(\frac{2n\pi}{L}x\right)dx\right] = 1$$

$$\therefore \frac{A^2}{2}\left\{[x]_0^L - \frac{\left[\sin\left(\frac{2n\pi x}{L}\right)\right]_0^L}{\left(\frac{2n\pi}{L}\right)}\right\} = 1$$

Maximum Probability of finding the particle

Prob. $\equiv P(x)dx = \psi^*\psi\,dx$

It is max. where the function $\psi^*(x)\psi(x)$ is maximum.

$$\Rightarrow P(x)dx = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)dx$$

It is max. where $\sin^2\left(\frac{n\pi x}{L}\right)$ is max. (i.e. 1).

$\sin^2\left(\frac{n\pi x}{L}\right) = 1$

when $\frac{n\pi x}{L} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \ldots$

$$\Rightarrow x = \frac{L}{2n}, \frac{3L}{2n}, \frac{5L}{2n}, \ldots$$

Clearly ; $\sin(0) = 0$ at $x = 0$

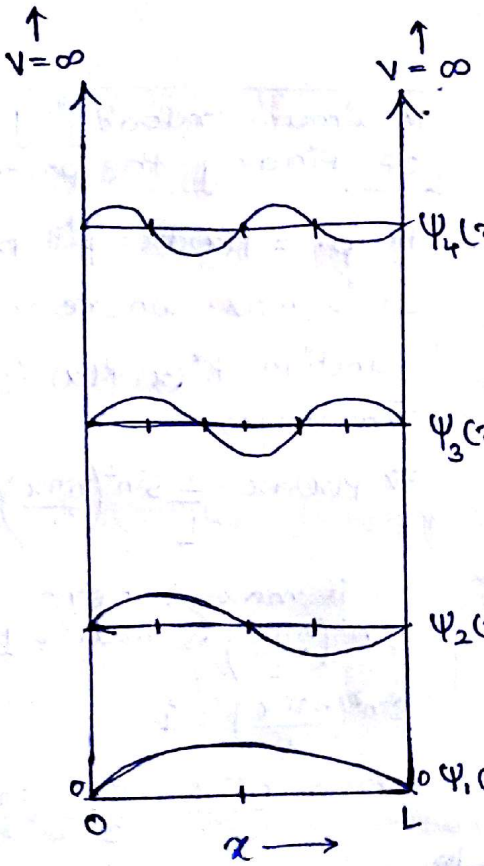
and $\sin(n\pi) = 0$ at $x = L$.

$$\therefore \quad \frac{A^2 L}{2} = 1$$

$$\Rightarrow \boxed{A = \sqrt{\frac{2}{L}}}$$

$$\therefore \quad \boxed{\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)} \longrightarrow \text{Normalized function.}$$

Thus Quantum Mechanics is Probabilistic as we cannot determine the exact trajectories of particles, we can only evaluate and compare the probability of finding the particle wave to be localized in a particular region.



$\psi_4(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{4\pi x}{L}\right)$, $E_4 = 16E_1$, $\frac{L}{8}, \frac{3L}{8}, \frac{5L}{8}, \frac{7L}{8}$

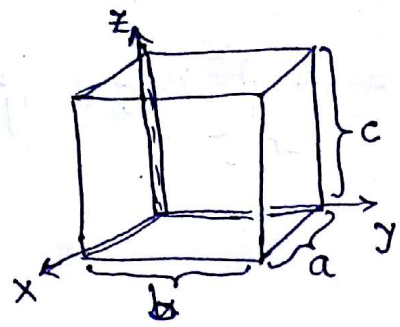
$\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right)$, $E_3 = 9E_1$, $\frac{L}{6}, \frac{L}{2}, \frac{5L}{6}$

$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$, $E_2 = 4E_1$, $\frac{L}{4}, \frac{3L}{4}$.

$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$, $E_1 = \frac{h^2}{8mL^2}$, $\frac{L}{2}$.

$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$, $E_n = \frac{n^2 h^2}{8mL^2}$, max. prob. at $x_n = \frac{L}{2n}, \frac{3L}{2n}, \frac{5L}{2n}, \ldots$

• Particle in a 3D Box:



The Shrödinger's eqn. for 3D Box of infinite potential walls and a free particle within.

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E_0\psi(x,y,z)$$

$\because$ $V(x,y,z) = 0$. within the boundries of the box.

Assuming the solution of the wavefunction to be explicitly dependant on the wavefunctions along each axes.

$$\psi(x,y,z) = u(x)\cdot v(y)\cdot w(z).$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{d}{dx^2}u(x) = E_x u(x). \Rightarrow u(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right).$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{d}{dy^2}v(y) = E_y v(y). \Rightarrow v(y) = \sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right).$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{d}{dz^2}w(z) = E_z w(z). \Rightarrow w(z) = \sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi z}{c}\right).$$

$$\therefore \left[\psi(x,y,z) = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right)\right].$$

$\ldots (n_x, n_y, n_z) \in \mathbb{N}$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c}\right]. = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right).$$

Thus, the energy of a particle in a 3D box is the function of 3 Quantum numbers n_x, n_y, n_z as well as the widths of the box along the 3 x, y, z axes.

Smaller the width of Box in a particular axes direction, more is the energy contribution of that axes to the overall energy of the wave packet.

If $a = b = c = L$; (cube). $\Rightarrow$ Degeneracy is result of symmetry in a system. It is lifted when symmetry is broken.

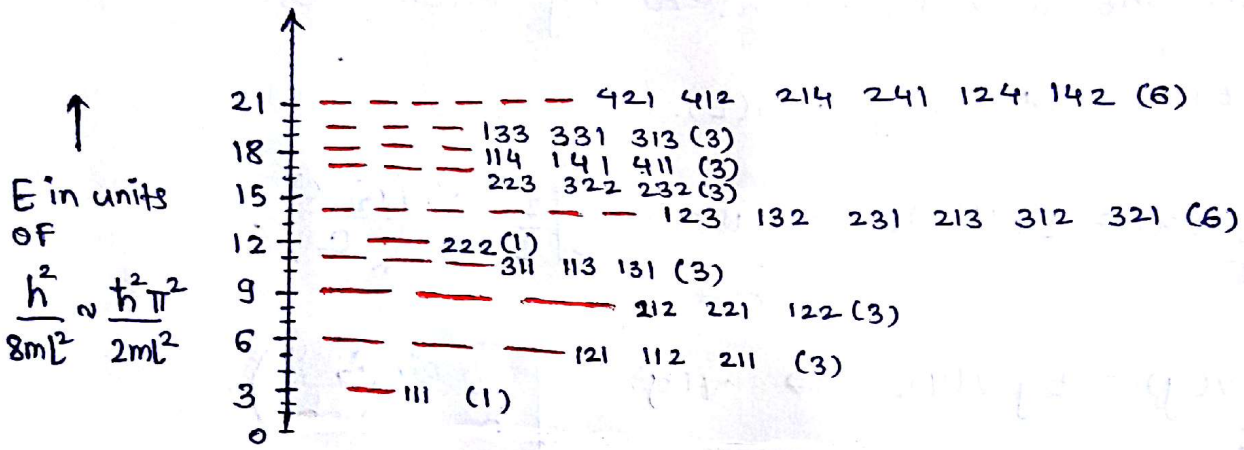
$$\therefore \quad E_{n_x n_y n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2). = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2).$$

The

$n_x \in (1, 2, 3, \ldots) \in \mathbb{N}$

$n_y \in (1, 2, 3, \ldots) \in \mathbb{N}$

$n_z \in (1, 2, 3, \ldots) \in \mathbb{N}$



Degeneracy:

The total number of possible states that belong to the same Energy level. It is a result of symmetry. It is possible only in a multidimensional box / surface / enclosure where atleast 2 more sides of the enclosure are equal.

Thus, the energy spacing diagram is more complex in a 3D box than in a 1D box. The complexity is brought by the symmetry possible in multidimensions.

Due to the symmetry; the three dimensional box problem reduces to three onedimensional box problems such that energy of the system is equal to the sum of energies along the three axes.

$\Rightarrow$ Hermitian operator is separable in case of degeneracy.

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

$\Rightarrow$ Their Eigenvalues are additive.

$$\therefore E_0 = E_x + E_y + E_z.$$

- <u>Orthogonality of Eigenvectors</u>:

$\hat{H} \equiv$ Hamiltonian operator.

$\psi_n = |n\rangle$ and $\psi_m = |m\rangle$ are eigenvectors (fncs.) of operator $\hat{H} \equiv \hat{A}$.

$\Rightarrow \hat{H}\psi_n = E_n\psi_n$, i.e. $\hat{H}|n\rangle = E_n|n\rangle$.

$\Rightarrow \hat{H}\psi_m = E_m\psi_m$, i.e. $\hat{H}|m\rangle = E_m|m\rangle$.

$E_n, E_m \in \mathbb{R}$. and $E_n \neq E_m$.

If $\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\,dx \equiv \langle m|n\rangle = 0$

$\Rightarrow |m\rangle \equiv \psi_m$ and $|n\rangle \equiv \psi_n$ are orthogonal.

$$\therefore \langle m|\hat{A}|n\rangle = \langle m|a_n|n\rangle = a_n\langle m|n\rangle.$$

Also, $\langle m|A|n\rangle = \langle n|\hat{A}|m\rangle^* = \langle n|a_m^*|m\rangle = a_m^*\langle n|m\rangle$.

$\Rightarrow \boxed{a_m^* = a_m \quad \because \quad a_m \in \mathbb{R}}$ And, $\boxed{\langle m|n\rangle = \langle n|m\rangle}$.

$$\therefore a_n\langle m|n\rangle = a_m^*\langle n|m\rangle = a_m\langle m|n\rangle$$

Reason: $\int_{-\infty}^{\infty} \psi_m^*\psi_n = \int_{-\infty}^{\infty} \psi_n^*\psi_m$...

$$\Rightarrow a_n\langle m|n\rangle = a_m\langle m|n\rangle.$$

$$\Rightarrow (a_n - a_m)\langle m|n\rangle = 0.$$

$\Rightarrow$ If $a_n \neq a_m$ i.e. ψ_m and ψ_n are non-degenerate.

then $\langle m|n\rangle = \int_{-\infty}^{\infty} \psi_m^*\psi_n\,dx = 0$.

Now, for a Particle in a Box.

$$E_m = \frac{m^2 \hbar^2 \pi^2}{2mL^2}$$

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2nL^2}$$

$\rightarrow$ clearly for $m \neq n$; $E_m \neq E_n$. E_m and E_n are the real Eigenvalues of Eigenvectors ψ_m, ψ_n.

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

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right).$$

$\rightarrow$ These are orthogonal eigenvectors of Operator $\hat{H}$ for $n \neq m$.

$\Rightarrow$ when ψ_m and ψ_n are not degenerate, they will be orthogonal for $n \neq m$.

In 1D particle box degeneracy is not observed due to absence of symmetry. Therefore any two eigenfunctions of 1D box are orthogonal given that they describe different energy states corresponding to E_n and E_m.

- **Probabilistic values of Position and Momentum for Particle in a Box.**

$$\text{Prob. Density} = \psi^*(x)\,\psi(x)\,dx = \begin{cases} \frac{2}{a}\sin^2\left(\frac{n\pi x}{a}\right) & \ldots\ 0<x<a \\ 0 & \ldots\ \text{otherwise.} \end{cases}$$

$$\therefore \langle x \rangle = \text{Mean pos. of Particle} = \int_0^a \frac{2}{a}\, x \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{2}{a}\int_0^a \underset{1.}{x}\ \underset{2.}{\sin^2 kx}\, dx \qquad k = \frac{n\pi}{a}.$$

$$= \frac{2}{a}\left[x\int \sin^2 kx\, dx - \int (1)\int \sin^2 kx\, dx\, dx\right].$$

$$= \frac{2}{a}\left[\frac{x}{2}\int (1-\cos 2kx)\,dx - \int \frac{1}{2}\int (1-\cos 2kx)\,dx\, dx\right].$$

$$= \frac{2}{a}\left[\frac{x}{2}\left(x - \frac{\sin 2kx}{2k}\right) - \int \frac{1}{2}\left(x - \frac{\sin 2kx}{2k}\right) dx\right].$$

$$= \frac{2}{a}\left[\frac{x^2}{2} - \frac{x\sin 2kx}{4k} - \frac{1}{2}\int\left(x - \frac{\sin 2kx}{2k}\right) dx\right]$$

$$= \frac{2}{a}\left[\frac{x^2}{2} - \frac{x\sin 2kx}{4k} - \frac{1}{2}\left(\frac{x^2}{2} + \frac{\cos 2kx}{4k^2}\right)\right].$$

$$= \frac{2}{a}\left[\frac{x^2}{2} - \frac{x\sin 2kx}{4k} - \frac{x^2}{4} - \frac{\cos 2kx}{8k^2}\right].$$

$$= \frac{2}{a}\left[\frac{x^2}{4} - \frac{x\sin 2kx}{4k} - \frac{\cos 2kx}{8k^2}\right]_0^a$$

$$= \frac{2}{a}\left[\frac{(a^2-0^2)}{4} - \cancel{\frac{(a\overset{0}{\sin 2n\pi} - \overset{0}{0})}{4k}} - \cancel{\frac{[\overset{1}{\cos(2n\pi)} - \overset{1}{\cos(0)}]}{8k^2}}\right]$$

$$\Rightarrow \langle x \rangle = \frac{2}{a}\cdot\frac{a^2}{4}$$

$$\Rightarrow \boxed{\langle x \rangle = \frac{a}{2}}.$$

Thus, the average position of the particle is at the mid point of the 1D Box of length a.

$$\therefore \langle x^2 \rangle = \text{Mean square pos. of particle} = \int_0^a \frac{2}{a} x^2 \cdot \sin^2\left(\frac{n\pi x}{a}\right).$$

$$= \frac{2}{a}\int_0^a \underset{1.}{x^2}\, \underset{2.}{\sin^2 kx}\, dx \qquad k = \frac{n\pi}{a}$$

$$= \frac{2}{a}\left[x^2 \int \sin^2 kx\, dx - \int (2x) \int \sin^2 kx\, dx\, dx\right].$$

$$= \frac{2}{a}\left\{\frac{x^2}{2}\left[\int (1-\cos 2kx)\, dx\right] - \int \frac{(2x)}{2} \int (1-\cos 2kx)\, dx\, dx\right\}.$$

$$= \frac{2}{a}\left\{\frac{x^2}{2}\left(x - \frac{\sin 2kx}{2k}\right) - \int x\left(x - \frac{\sin 2kx}{\cancel{2k}}\right) dx\right\}$$

$$= \frac{2}{a}\left\{\left(\frac{x^3}{2} - \frac{x^2 \sin 2kx}{4k}\right) - \int x^2 dx + \frac{1}{2k}\int \underset{1.}{x}\, \underset{2.}{\sin 2kx}\, dx\right\}.$$

$$= \frac{2}{a}\left\{\left(\frac{x^3}{2} - \frac{x^2 \sin 2kx}{4k} - \frac{x^3}{3}\right) + \frac{1}{2k}\left(x \int \sin 2kx\, dx - \int (1) \int \sin 2kx\, dx\right)\right\}$$

$$= \frac{2}{a}\left\{\left(\frac{x^3}{2} - \frac{x^2 \sin 2kx}{4k} - \frac{x^3}{3}\right) + \frac{1}{2k}\left(-\frac{x\cos 2kx}{2k} + \frac{1}{2k}\int \cos 2kx\, dx\right)\right\}$$

$$= \frac{2}{a}\left\{\left(\frac{x^3}{2} - \frac{x^2 \sin 2kx}{4k} - \frac{x^3}{3}\right) + \frac{1}{2k}\left(-\frac{x\cos 2kx}{2k} + \frac{1}{2k}\left(\frac{\sin 2kx}{2k}\right)\right)\right\}$$

$$\therefore \quad = \frac{2}{a}\left\{\frac{x^3}{2} - \frac{x^2\sin 2kx}{4k} - \frac{x^3}{3} - \frac{x\cos 2kx}{4k^2} + \frac{\sin 2kx}{8k^3}\right\}\Bigg|_0^a$$

$$= \frac{2}{a}\left\{\frac{x^3}{6} - \frac{x^2\sin 2kx}{4k} - \frac{x\cos 2kx}{4k^2} + \frac{\sin 2kx}{8k^3}\right\}\Bigg|_0^a$$

$$= \frac{2}{a}\left\{\frac{(a^3-0^3)}{6} - \frac{(a^2\cancel{\sin(2n\pi)}^{\,0} - 0)}{4k} - \frac{a\cancel{\cos(2n\pi)}^{\,1} - 0\cancel{\cos(0)}^{\,0}}{4k^2} + \frac{\cancel{\sin(2n\pi)}^{\,0} - \sin(0)}{8k^3}\right\}$$

$$= \frac{2}{a}\left\{\frac{a^3}{6} - \frac{a}{4\left(\frac{n\pi}{a}\right)^2}\right\}$$

$$= \frac{2}{a}\left\{\frac{a^3}{6} - \frac{a^3}{4n^2\pi^2}\right\}$$

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

$$\Rightarrow \boxed{\langle x^2\rangle = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}}.$$

$\therefore \langle p\rangle$ = Average momentum of particle $= \int_0^a \psi^*(x)\,\hat{p}\,\psi(x)\,dx.$

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

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

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

$\because \sin\theta\cdot\cos\theta = \dfrac{\sin 2\theta}{2}$

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

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

$$= \frac{-i\hbar}{n\pi} \left(-\cos 2\left(\frac{n\pi x}{a}\right)\right) \times \frac{a}{2n\pi}$$

$$= \frac{+i\hbar a}{2n^2\pi^2} \left[\cos\left(2\frac{n\pi x}{a}\right)\right]_0^a$$

$$= \frac{+i\hbar a}{2n^2\pi^2} \left(\underbrace{\cos(2n\pi)}_{1} - \underbrace{\cos(0)}_{1}\right)$$

$$\therefore \boxed{\langle p \rangle = 0 \cdot \text{Zero}}.$$

Thus, the average momentum of particle is zero.

$\Rightarrow$ It is equally likely that the particle will move in either direction.

$$\therefore \langle p^2 \rangle = \int_0^a \psi^*(x)\, \hat{p}_x^2\, \psi(x)\, dx.$$

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

$$= \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \left(+i^2\hbar^2 \frac{d^2}{dx^2} \sin\left(\frac{n\pi x}{a}\right)\right) dx.$$

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

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

$$= \frac{+2\hbar^2 n^2 \pi^2}{a^3} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

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

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

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

$$= \frac{\hbar^2 n^2 \pi^2}{a^3} \times a$$

$$\therefore \boxed{\langle p^2 \rangle = \frac{\hbar^2 n^2 \pi^2}{a^2}}$$

$$\Rightarrow \langle E \rangle = \left\langle \frac{\hat{p}^2}{2m} \right\rangle = \frac{\langle \hat{p}^2 \rangle}{2m} = \frac{\hbar^2 n^2 \pi^2}{2ma^2}.$$

— Hence verified.

Now: calculating standard deviations of $\hat{x}$ & $\hat{p}$.

Var(x)

$$\Rightarrow \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

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

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

$$= \frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}$$

$$= \frac{n^2\pi^2 a^2 - 6a^2}{12n^2\pi^2}$$

$$\therefore \sigma_x^2 = \frac{a^2}{12n^2\pi^2}(n^2\pi^2 - 6).$$

S.D.

$$\Rightarrow \sigma_x = \sqrt{Var(x)}$$

$$= \frac{a}{\sqrt{12}\, n\pi}(n^2\pi^2 - 6)^{1/2}$$

$$\boxed{\sigma_x = \frac{a}{2\sqrt{3}\, n\pi}(n^2\pi^2 - 6)^{1/2}}$$

Var(p)

$$\Rightarrow \sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$$

$$= \left(\frac{\hbar^2 n^2 \pi^2}{a^2}\right) - (0)^2$$

$$\therefore \sigma_p^2 = \frac{n^2\hbar^2\pi^2}{a^2}$$

S.D.

$$\Rightarrow \sigma_p = \sqrt{Var(p)} = \frac{n\hbar\pi}{a}$$

$$\boxed{\sigma_p = \frac{n\hbar\pi}{a}}$$

Now; $\sigma_x \sigma_p = \frac{\hbar}{2\sqrt{3}} (n^2\pi^2 - 6)^{1/2}$

$$\left[\sigma_x \sigma_p = \frac{\hbar}{2} \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2}\right].$$

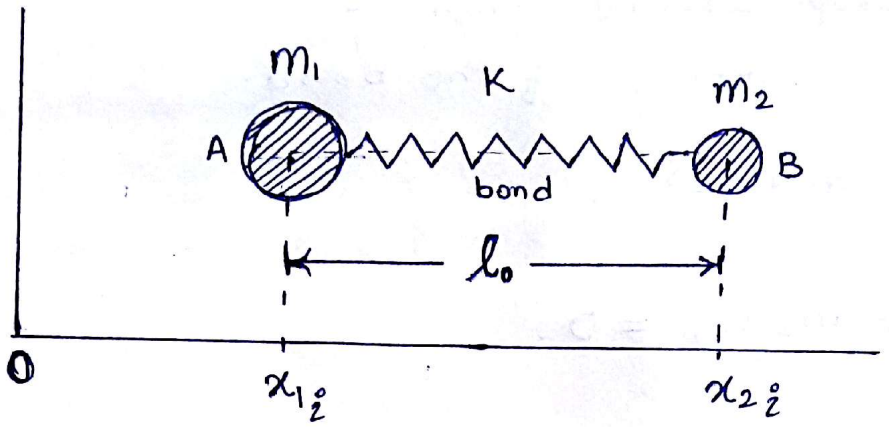
The value of square root term can never be less than 1.

$\Rightarrow \left[\sigma_x \cdot \sigma_p > \frac{\hbar}{2}\right]$ The Heisenberg's uncertainity principle

$\therefore$ When we localize a particle by minimizing (a) $\sigma_x \downarrow$ But then σ_p has to $\uparrow$ to maintain the Heisenberg's inequality (uncertainity principle).

S.D. σ gives the measure of how centralized or localized the variable is.

* Harmonic Oscillator:



The diagram shows two atoms A and B bonded to form a molecule. The bond length under undistorted conditions is l_0. Respectively, masses of atoms A and B are m_1 and m_2. These atoms vibrate along their bond to either stretch or compress the bond. During these vibrations, variables x_1 and x_2 denote the positions of atoms A and B respt. (with respect to an arbitrary origin).

$\Rightarrow$ if $(x_2 - x_1) > l_0$ $\therefore$ The bond is stretched.

$\Rightarrow$ elif $(x_2 - x_1) < l_0$ $\therefore$ The bond is compressed.

Thus equations of motion for each atom is as follows:
The restoring force acting on the atom is proportional to the displacement of atom from its mean/undistorted positions. but acts in direction opposite to the displacement.

$\therefore f_A \propto -(x_{2f} - x_{1f} - (x_{2i} - x_{1i}))$ $\qquad f_A \simeq m_1 \frac{d^2x_1}{dt^2}$.

$\Rightarrow f_A \propto +(x_2 - x_1 - l_0)$.

$\therefore f_B \propto -(x_{2f} - x_{1f} - (x_{2i} - x_{1i}))$ $\qquad f_B \simeq m_2 \frac{d^2x_2}{dt^2}$.

$\Rightarrow f_B \propto -(x_2 - x_1 - l_0)$.

$\because f_A$ & f_B in both elongation or compression act in opposite directions along the bond. Hence the Difference in sign in f_A and f_B.

$\therefore \Rightarrow$

$$m_1 \ddot{x}_1 = +K(x_2 - x_1 - l_0). \quad \text{—— (1)}.$$

$$m_2 \ddot{x}_2 = -K(x_2 - x_1 - l_0). \quad \text{—— (2)}.$$

K = (constant of prop.) ≡ Force constant.
A measure of the stiffness of the bond.

Adding eqns. (1) and (2),

$$\frac{d^2}{dt^2}(m_1 x_1 + m_2 x_2) = 0.$$

In the centre of Mass frame:

$$X_{COM} = \frac{m_1 x_1 + m_2 x_2}{(m_1 + m_2)}$$

$$X_{COM} = \frac{m_1 x_1 + m_2 x_2}{M_{system}}.$$

$\therefore$ Eqn. of Motion of COM becomes.

$$\frac{d^2}{dt^2} MX = 0.$$

$$\Rightarrow M \frac{d^2 X}{dt^2} = 0.$$

Clearly; the force term is zero. $\Rightarrow$ The COM moves uniformly with time with a constant momentum and no acceleration.

Dividing eqn. (1) with m_1 and eqn. (2) with m_2; we get.

$$\ddot{x}_2 = \frac{-K}{m_2}(x_2 - x_1 - l_0). \quad \text{—— (2')}.$$

$$\ddot{x}_1 = \frac{+K}{m_1}(x_2 - x_1 - l_0). \quad \text{—— (1')}.$$

Subtracting (1') from (2'); we get.

$$\ddot{x}_2 - \ddot{x}_1 = \left(\frac{-k}{m_2} - \frac{k}{m_1}\right)(x_2 - x_1 - l_0).$$

$$\frac{d^2}{dt^2}(x_2 - x_1) = -k\left(\frac{1}{m_2} + \frac{1}{m_1}\right)(x_2 - x_1 - l_0).$$

Since we have introduced COM frame, ∴ Only "RELATIVE" change in the coordinates of A and B is important not the absolute coordinate change.

$$\therefore \quad (x_2 - x_1 - l_0) = x.$$

Also, $\frac{1}{m_1} + \frac{1}{m_2} = \frac{m_2 + m_1}{m_1 * m_2}$

$$\therefore \quad \mu = \frac{m_1 * m_2}{m_1 + m_2} = \text{Reduced mass} =$$

Effective inertial mass appearing as the "Mass" in the force eqn.

Hence we basically reduce a two body problem to a single body of mass (μ) placed at the COM of the two body system.

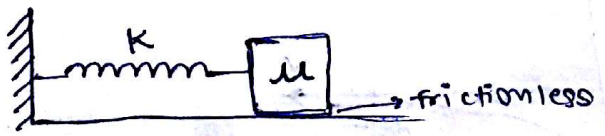
$$\therefore \quad \frac{d^2(x)}{dt^2} = \frac{-k}{\mu} x.$$

$$\Rightarrow \quad \boxed{\mu \frac{d^2x}{dt^2} = -kx}$$

This is the final eqn. of motion of the diatomic molecular vibration along the bond.

This gives the Classical Description of the system over time.

reduction to one body system.



To describe the system Quantum Mechanically i.e. using Shrödinger's eqn.

We need to know the Kinetic and Potential Energy operators to evaluate the Hamiltonian (Total Energy Operator). $\hat{H}$.

Since we reduced the two body problem to a one body problem under COM frame that performs uniform unaccelerated motion of constant momentum 'p'.

∴ We can write the K.E. of the system as.

$$E_K = \frac{p^2}{2\mu}.$$

We can guess the Potential Energy $V(x)$ of the system as:

For two atoms :

at infinitely great distances. → No interaction. ⇒ $V(\infty) = 0$.

at infinitesimally small distances → strong repulsion. ⇒ $V(0) = \infty$.

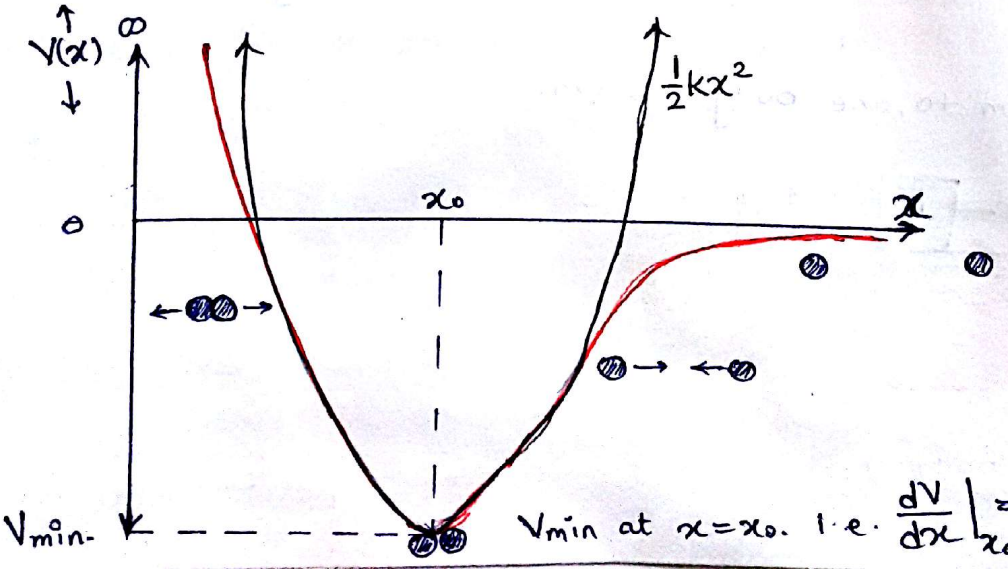
at considerably close distances → weak attraction. ⇒ $V(x > x_0) = -ve$

at optimally close distances → optimal attraction. $V(x_0) = \underline{\underline{min.}}$ (-ve).

i.e. Atoms form bonds to generate molecules

at distances closer than optimum → high repulsion. $V(x < x_0) = +ve$.

Thus, we can predict the curve of $V(x)$ to be:



V_{min} at $x = x_0$. i.e. $\left.\frac{dV}{dx}\right|_{x_0} = 0$; $\left.\frac{d^2V}{dx^2}\right|_{x_0} > 0$.

Describing the function $V(x)$ can be complicated. Thus we approximate it to $\left[V(x) \approx \frac{1}{2}kx^2\right]$.

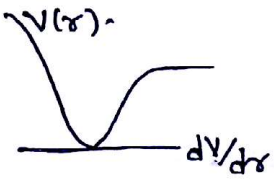
As is visible, the graph of approximatn and actual potential energy overlap closely at the low energy values i.e. at $x \in (x_0 - \Delta x, x_0 + \Delta x)$ where Δx is small. Precisely, this is the range of energy at which molecules can exist. Hence, under low energy constraint the approximation is fairly good for the vibrational case.

Mathematically,
Using Taylor series.

$$V(r) = V(r_0) + \left(\frac{dV}{dr}\right)_{r=r_0}(r-r_0) + \frac{1}{2!}\left(\frac{d^2V}{dr^2}\right)(r-r_0)^2 + \frac{1}{3!}\left(\frac{d^3V}{dr^3}\right)(r-r_0)^3 + \dots$$

The first term $V(r_0)$ describes the choice of the minimum. and is easy to be set at $V_{min} = 0$.

The second term vanishes at $r = r_0$. as $\left.\frac{dV}{dr}\right|_{r=r_0} = 0$.



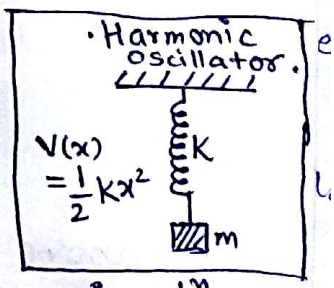
Therefore, the first two term vanish into zero.

In the third term; $\left(\frac{d^2V}{dr^2}\right) \approx k$.

and $(r - r_0) \approx x$.

Thus, we have;

$$V(r) = \frac{1}{2}kx^2 + \frac{1}{6}k'x^3 + \dots$$



For small displacements 'x'.

$\left[V(r) \approx \frac{1}{2}kx^2\right]$. is a good approximatn.

That is a general energy potential function $V(r)$ can be approximated as a Harmonic oscillator Potential.

At this point, we approximate the diatomic vibrations to be harmonic oscillations.

The higher order terms are "<u>AnHarmonic</u>" terms (that deviate the nature of vibrations from Harmonic oscillations).

$\therefore$ we get;

$$(\hat{H}) \equiv \left(\frac{\hat{p}^2}{2m_{red.}} + \hat{V}(x)\right) = \left(\frac{\hat{p}^2}{2m_{red}} + \frac{1}{2}kx^2\right).$$

$$\therefore \hat{H} = \frac{(-i\hbar)^2}{2\mu}\left(\frac{\partial}{\partial x}\right)^2 + \frac{1}{2}kx^2$$

$$\therefore \boxed{\hat{H} = \left(\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right)}.$$

Thus, time independant shrödinger's eqn. is :

$$\hat{H}\psi(x) = E_{tot.}\psi(x).$$

$$\therefore \frac{-\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E_0\psi(x).$$

$$\therefore \frac{-\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} = \left(E_0 - \frac{1}{2}kx^2\right)\psi(x).$$

$$\therefore -\frac{d^2}{dx^2}\psi(x) = \frac{2\mu}{\hbar^2}\left(E_0 - \frac{1}{2}kx^2\right)\psi(x).$$

$$\therefore \boxed{\frac{d^2}{dx^2}\psi(x) + \frac{2\mu}{\hbar^2}\left(E_0 - \frac{1}{2}kx^2\right)\psi(x) = 0.}$$

The above eqn. needs to be solved.
This diff. eqn. is of the form.

$$p(t)y'' + q(t)y' + r(t)y = 0.$$

where the coeff. are dependant funcs. and RHS = 0 in the 2nd order DE. Therefore, we will first convert it to a standard form and then solve for the particular soln. whose general soln. is known.

since our diatomic system is now reduced to a one body system performing SHM.

$$\therefore \quad \boxed{K = \mu \omega^2}$$

K = force constant.
μ = Mass red.
ω = Angular velocity or frequency of oscillation.

$$\Rightarrow \quad \frac{d^2\psi(x)}{dx^2} + \left(\frac{2\mu E_0}{\hbar^2} - \frac{\mu^2\omega^2}{\hbar^2}x^2\right)\psi(x) = 0.$$

Let, $\dfrac{E_0}{\hbar\omega} = \epsilon \quad \therefore \quad E_0 = \epsilon\hbar\omega$

$$\Rightarrow \quad \frac{d^2}{dx^2}\psi(x) + \left(\frac{2\mu\epsilon\omega}{\hbar} - \frac{\mu^2\omega^2}{\hbar^2}x^2\right)\psi(x) = 0$$

Let, $y = \sqrt{\dfrac{\mu\omega}{\hbar}}\cdot x \Rightarrow x = \sqrt{\dfrac{\hbar}{\mu\omega}}\cdot y. \Rightarrow \dfrac{dy}{dx} = \sqrt{\dfrac{\mu\omega}{\hbar}}.$

$$\therefore \quad \frac{d\psi}{dx} = \frac{d\psi}{dy}\cdot\frac{dy}{dx} = \frac{d\psi}{dy}\left(\sqrt{\frac{\mu\omega}{\hbar}}\right).$$

$$\therefore \quad \frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dy^2}\left(\frac{dy}{dx}\right)^2 = \frac{d^2\psi}{dy^2}\left(\frac{\mu\omega}{\hbar}\right).$$

$$\Rightarrow \quad \frac{\mu\omega}{\hbar}\frac{d^2\psi(y)}{dy^2} + \left(\frac{2\mu\epsilon\omega}{\hbar} - \frac{\mu\omega}{\hbar}y^2\right)\psi(y) = 0.$$

Dividing throughout by $\dfrac{\mu\omega}{\hbar}$, we get.

$$\boxed{\frac{d^2\psi(y)}{dy^2} + (2\epsilon - y^2)\psi(y) = 0}$$

The above eqn. is of the "Gaussian" D.E. form.

$\left[\dfrac{d^2\psi}{dy^2} + (1-y^2)\psi(y) = 0\right]$. whose soln. is $\left[y_g = e^{-y^2/2}\right]$.

Thus, our D.E. will have a soln. of the form

$$y_g = f(y)\, e^{-y^2/2}.$$

$$\Rightarrow \quad y_g' = \left(f'(y) - y f(y)\right) e^{-y^2/2}.$$

$$\Rightarrow \quad y_g'' = \left(f''(y) - 2y f'(y) - f(y) + y^2 f(y)\right) e^{-y^2/2}.$$

$\therefore$ DE becomes,

$$\left(f''(y) - 2y f'(y) - f(y) + y^2 f(y)\right) e^{-y^2/2} + \left(f'(y) - y f(y)\right) e^{-y^2/2}(2\epsilon - y^2) = 0.$$

$$\Rightarrow \left(f''(y) - 2y f'(y) + (2\epsilon - 1) f(y)\right) e^{-y^2/2} = 0.$$

$$\Rightarrow \left[f''(y) - 2y f'(y) + (2\epsilon - 1) f(y)\right] = 0.$$

Let, $2\epsilon - 1 = 2m$.

$$\Rightarrow \quad \boxed{f''(y) - 2y f'(y) + 2m f(y) = 0}$$

The above DE is of the form "Hermit" D.E.

Its general soln. is of the power series form.

$$f(y) = \sum_n A_n y^n.$$

Thus, The overall soln. of shrödinger DE for our H.O. system will be.

$$\psi_g = \left(\sum_{n=0}^{\infty} A_n y^n\right) e^{-y^2/2}.$$

$$\Rightarrow \quad \psi_g = \underbrace{H_n}_{\text{Hermit polynomial.}} e^{-y^2/2}$$

Solving Hermit DE.

$$f''(y) - 2y f'(y) + 2m f(y) = 0.$$

$$f(y) = \sum_{n=0}^{\infty} A_n y^n$$

$$\Rightarrow f'(y) = \sum_{n=1}^{\infty} n A_n y^{n-1}$$

$$\Rightarrow f''(y) = \sum_{n=2}^{\infty} n(n-1) A_n y^{n-2}.$$

Now, $2m f(y) = 2m \sum_{0}^{\infty} A_n y^n = \sum_{0}^{\infty} 2m A_n y^n.$

$$2y f(y) = \sum_{1}^{\infty} (2y) A_n n y^{n-1} = \sum_{0}^{\infty} 2n A_n y^n.$$

$$f''(y) = \sum_{2}^{\infty} n(n-1) A_n y^{n-2}.$$

$$\Rightarrow \sum_{2}^{\infty} n(n-1) A_n y^{n-2} - \sum_{0}^{\infty} 2n A_n y^n + \sum_{0}^{\infty} 2m A_n y^n = 0.$$

$$\Rightarrow \sum_{0}^{\infty} (n+1)(n+2) A_{n+2} y^n - \sum_{0}^{\infty} 2n A_n y^n + \sum_{0}^{\infty} 2m A_n y^n = 0.$$

$$\therefore \sum_{0}^{\infty} y^n \left[(n+1)(n+2) A_{n+2} - 2n A_n + 2m A_n\right] = 0.$$

$$y^n \neq 0.$$

$$\Rightarrow (n+1)(n+2) A_{n+2} - 2n A_n + 2m A_n = 0.$$

Now; $\left[2m = 2\epsilon - 1 = \frac{2E_0}{\hbar\omega} - 1\right]$

$$\Rightarrow \left[A_{n+2} = \frac{(2n - 2m)}{(n+1)(n+2)} A_n\right].$$

$$\Rightarrow 2n - 2m = 0$$

$$\Rightarrow \boxed{2m = 2n = \frac{2E_0}{\hbar\omega} - 1}.$$

Hermit Polynomials $H_n = \sum_{n=0}^{\infty} A_n y^n$.

$$\therefore H_n = A_0 + A_1 y + A_2 y^2 + A_3 y^3 + \dots$$

But $\because \left[A_{n+2} = \frac{2n-2m}{(n+1)(n+2)} A_n \right]$.

Recurrence relatn.

$$\therefore A_{\underset{(n)}{even}} = A_{\underset{(n-2)}{even}}.$$

$$\therefore A_{\underset{(n)}{odd}} = A_{\underset{(n)}{odd}}.$$

$$\therefore H_n = \underbrace{(A_0 + A_2 y^2 + \dots)}_{\text{even terms}} + \underbrace{(A_1 y + A_3 y^3 + \dots)}_{\text{odd terms}}.$$

we know that the lowest possible coeffs. A_n are : A_0 for even.

A_1 for odd.

[Let; $2m = (\lambda - 1)$]. $\Rightarrow$ $\left[A_{n+2} = \frac{2n+1-\lambda}{(n+1)(n+2)} A_n \right]$.

$$\therefore A_2 = \frac{(1-\lambda) A_0}{1 \cdot 2 \cdot} \qquad A_3 = \frac{(3-\lambda)}{1 \cdot 2 \cdot 3 \cdot} A_1$$

$$\therefore A_4 = \frac{(5-\lambda)(1-\lambda)}{1 \cdot 2 \cdot 3 \cdot 4 \cdot} A_0 \qquad A_5 = \frac{(7-\lambda)(3-\lambda) A_1}{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 \cdot}$$

$$\Rightarrow H = A_0 y^0 + A_1 y^1 + A_2 y^2 + A_3 y^3 + A_4 y^4 + A_5 y^5 + \dots$$

$$\therefore H = \left(A_0 + A_1 + \frac{(1-\lambda)}{1 \cdot 2} A_0 y^2 + \frac{(3-\lambda)}{1 \cdot 2 \cdot 3 \cdot} A_1 y^3 + \frac{(5-\lambda)(1-\lambda)}{1 \cdot 2 \cdot 3 \cdot 4} A_0 y^4 + \frac{(7-\lambda)(3-\lambda)}{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 \cdot} A_1 y^5 + \dots \right).$$

$$\left[H = \frac{A_0}{0!} + \frac{A_1 y}{1!} + \frac{(1-\lambda)A_0}{2!}y^2 + \frac{(3-\lambda)A_1 y^3}{3!} + \frac{(1-\lambda)(5-\lambda)A_0 y^4}{4!} + \frac{(3-\lambda)(7-\lambda)A_1 y^5}{5!} + \dots\right].$$

$$\therefore \psi_n = C_n H_n e^{-y^2/2}.$$

Using. $\lambda = 2m+1$ and $m = n \Rightarrow \boxed{\lambda = 2n+1}$.

$\therefore H_n = \sum_0^n A_n y^n. \Rightarrow \psi_n = C_n H_n e^{-y^2/2}.$

$\therefore H_0 = A_0. \Rightarrow \psi_0 = C_0 A_0 e^{-y^2/2}.$

$\therefore H_2 = A_0 + (-2)A_0 y^2. \Rightarrow \psi_2 = C_2 A_0 (1-2y^2) e^{-y^2/2}.$

$\therefore H_4 = A_0 + (-2)A_0 y^2 + \frac{}{3}A_0 y^4. \Rightarrow \psi_4 = C_4 A_0 (1-2y^2+\frac{y^4}{3}) e^{-y^2/2}.$

$\therefore H_1 = A_1 y \Rightarrow \psi_1 = C_1 A_1$

$\therefore H_3 = A_1 y + \left(\frac{-2}{3}\right)A_1 y^3. \Rightarrow \psi_3 = C_3 A_1 (y - 2/3\, y^3) e^{-y^2/2}$

$\therefore H_5 = A_1 y + \left(\frac{-2}{3}\right)A_1 y^3 + \left(\frac{4}{15}\right)A_1 y^5. \Rightarrow \psi_5 = C_5 A_1 e^{-y^2/2} \times (y - \frac{2y^3}{3} + \frac{4y^5}{15}).$

<u>Caution:</u> $\boxed{y = \sqrt{\frac{\mu\omega}{\hbar}}\, x.}$

Also, earlier relath states that:

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

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

$$\therefore \boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega} \rightarrow \text{Energy of the } n^{th} \text{ state.}$$

$(n = 0, 1, 2, \dots)$ (n = Principal Quantum Number)

In every Hermite polynomial $H_n = \sum_{i=0}^{n} A_i y^i$.

It is required that the last term (greatest degree term) follows the rule:

$$[A_n y^n = 2^n y^n].$$

Thus, the value of A_0 and A_1 gets changed for every polynomial uniquely.

Also, making use of $y = \sqrt{\frac{m\omega}{\hbar}}\, x \Rightarrow y \propto x$.

H_0: $A_0 y^0 = 2^0 y^0 \Rightarrow A_0 = 1. \therefore H_0 \equiv 1.$

H_1: $A_1 y^1 = 2^1 y^1 \Rightarrow A_1 = 2. \therefore H_1 \equiv 2x.$

H_2: $-2A_0 y^2 = 2^2 y^2 \Rightarrow A_0 = -2. \therefore H_2 \equiv 4x^2 - 2.$

H_3: $-\frac{2}{3} A_1 y^3 = 2^3 y^3 \Rightarrow A_1 = -12. \therefore H_3 = 8x^3 - 12x.$

H_4: $\frac{4}{3} A_0 y^4 = 2^4 y^4 \Rightarrow A_0 = 12. \therefore H_4 = 16x^4 - 48x^2 + 12.$

H_5: $\frac{4}{15} A_1 y^5 = 2^5 y^5 \Rightarrow A_1 = 120. \therefore H_5 = 32x^5 - 160x^3 + 120x.$

similarly, the discrete Energy levels of states are:

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

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

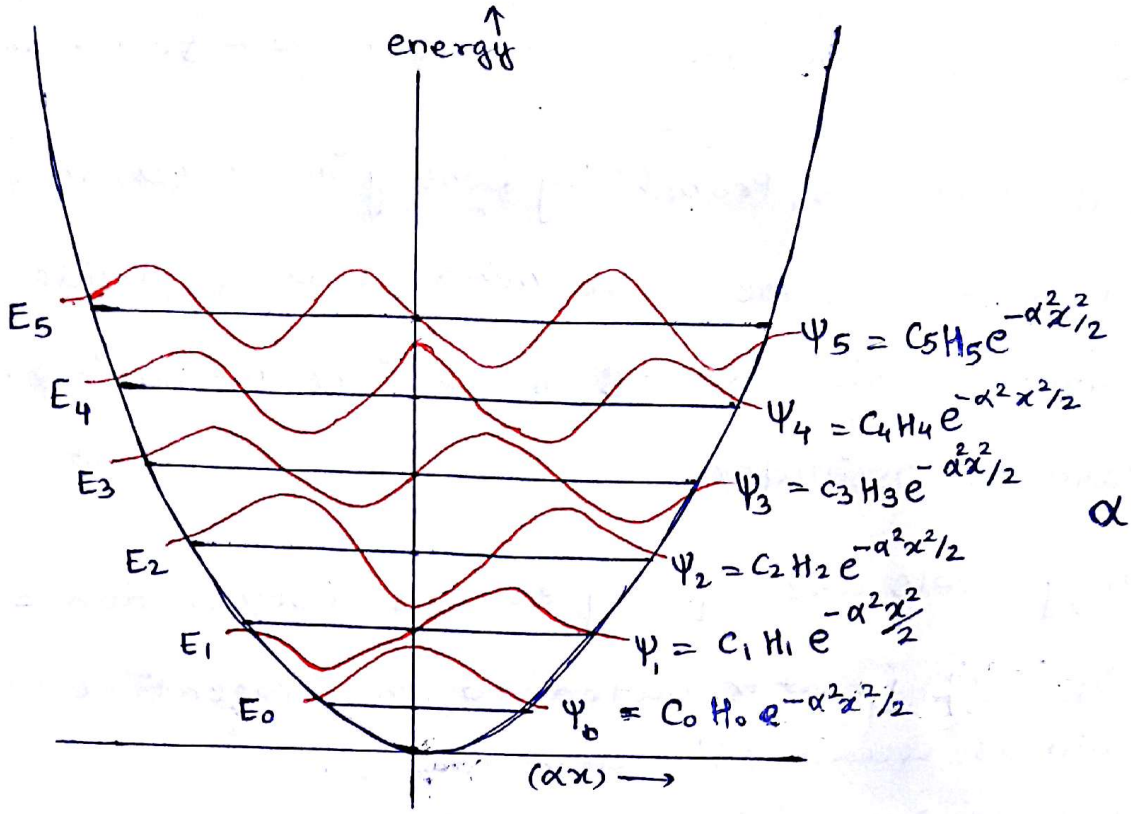
$E_2 = \frac{5}{2}\hbar\omega$

$E_3 = \frac{7}{2}\hbar\omega$

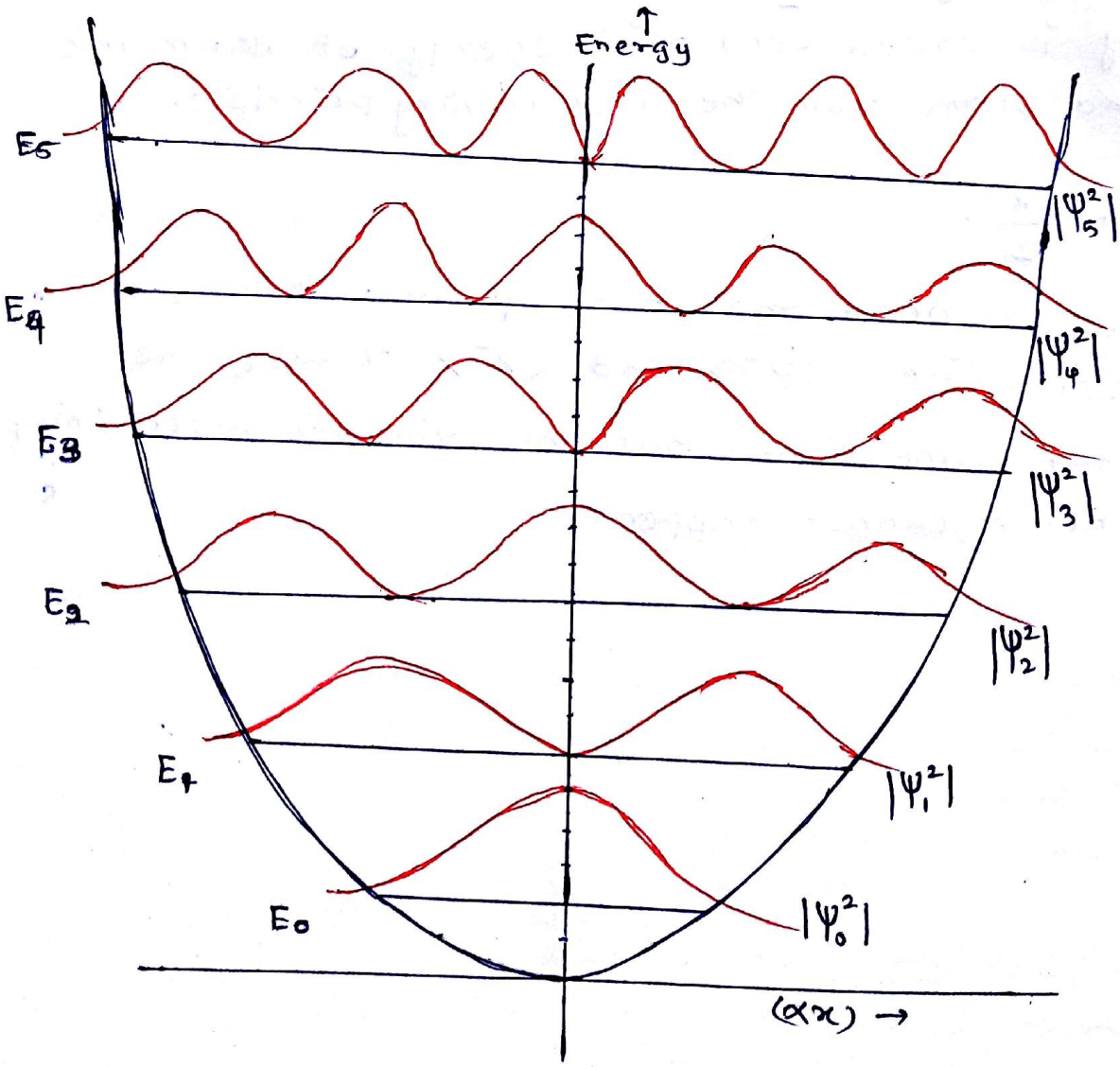
$E_4 = \frac{9}{2}\hbar\omega$

$E_5 = \frac{11}{2}\hbar\omega$

* Diagramatic representation of Harmonic Oscillator states.



$$\alpha = \sqrt{\frac{\mu \omega}{\hbar}}.$$



$H_{2n\,(even)}$ ≡ are even funcs. i.e. $f(x) = f(-x)$. symm. w.r.t. 0. (zero).

H_{2n+1} (odd) ≡ are odd func. i.e. $f(x) = -f(-x)$. antisymm. w.r.t. 0. (zero).

→ As the state increases, Probability Density increases. That is at higher energy states, the wave behaves as a particle and the quantum mechanics reduced to classical mechanical results of the Harmonic oscillator.

→ The energy levels are equally spaced. (separation $= h\nu$).

→ Equal spacing is attributed to the Potential energy that follows Quadratic dependance.

→ Ground state Energy is $\frac{1}{2}h\nu$ unlike 0 for classical result. This energy is called zero point energy. of Harmonic oscillator and stems from the uncertainity principle.

$$E = \frac{p^2}{2\mu} + \frac{kx^2}{2}.$$

for $E = 0$, we need that both p and x are equally zero. i.e. $\langle \hat{p}^2 \rangle$ and $\langle x^2 \rangle$ values are zero at the same time. But this violates uncertainity principle hence cannot happen.

* Vibrational Spectra:

The vibrational energy levels of a diatomic molecule are given by:

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

A molecule can make transition from one energy state to another by absorbing or emitting EM radiation of frequency ν_{photon}.

$$\Delta E_{transitn} = h\nu_{photon}.$$

The selection rules allow transition only between adjacent energy states.

$$\Rightarrow \Delta E = E_{n+1} - E_n = h\nu_{photon}.$$

$$\therefore \left[\nu_{photon} = \frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{-1/2}\right].$$

Frequence of radiation absorbed or emitted by Diatomic molecule for transitions between adjacent vibrational energy states.

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

$$\therefore \Delta E = \hbar\omega$$

$$\Rightarrow \hbar\omega = h\nu_{photon}$$

$$\therefore \omega = \sqrt{\frac{K}{\mu}}$$

$$\therefore \hbar = \frac{h}{2\pi}$$

$$\Rightarrow \frac{h}{2\pi}\sqrt{\frac{K}{\mu}} = h\nu_{photon}.$$

$$\therefore \boxed{\nu_{photon} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}}$$

Also, since all the energy states are equally spaced $\Delta E = \hbar\omega$ for any transition between adjacent states. And selection rule imposes only adjacent state transition allowance.

$\therefore$ The model predicts that the Diatomic molecule absorptn spectra will have only one line whose ν will be given ν_{photon}. for most Diatomic molecules this ν lies in the IR region. @ 10^{14} Hz.

$$\bar{\lambda} = \frac{1}{2\pi c}\left(\frac{K}{\mu}\right)^{-1/2}.$$

(K is of the order 10^2 or 10^3 N/m)

$$\nu = \frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{-1/2},$$

$$\omega = \left(\frac{K}{\mu}\right)^{-1/2}.$$

Also if the fundamental vibratn terms like wave number ($\bar{\lambda}$) or frequency (ν) is known then force constant of the molecule can be determined.

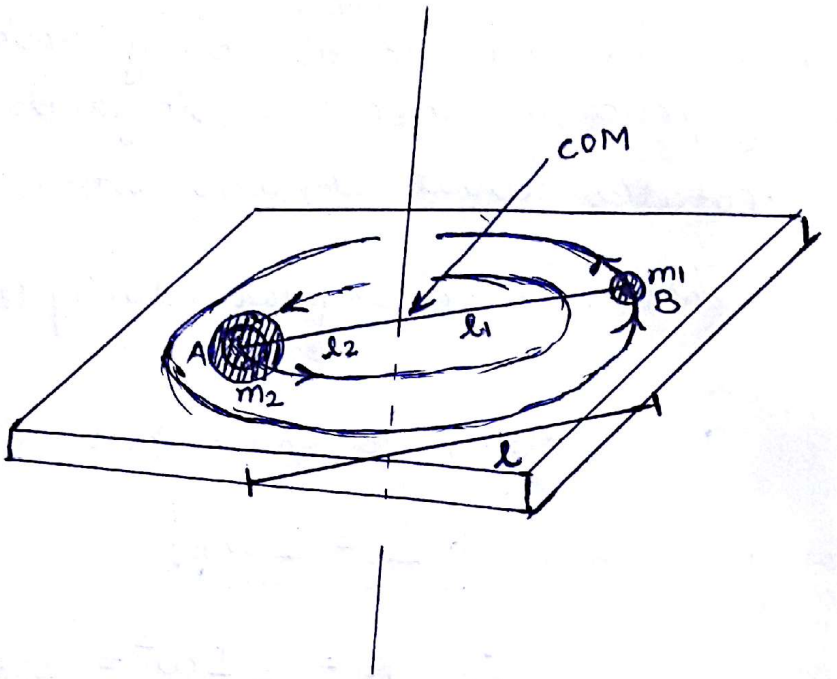
* Overtones in Vibrational spectra:

The Harmonic oscillator model predicts that there will be only one line in the vibrational spectra corresponding to the fundamental transition ($n=1$). But in reality there are also lines of weaker intensity at integral multiples of the fundamental. These are termed as overtones. These appear from the anharmonic higher order terms in the Taylor series of Potential function that we approximated to the quadratic term.

These overtones are not equally spaced. Their intensity as well as separation decreases with (n).

At room temperature, the Anharmonic terms can be safely ignored.

* Rigid Rotator :



The diagram shows two Atoms A and B of masses m_2 and m_1 respectively bonded together by a rigid bond of length l that cannot vibrate along the bond length. The COM is located at a distance l_2 away from atom A and at a distance l_1 away from atom B. [such that $l_2 + l_1 = l$].

The molecule rotates about its COM at a frequency ν_{rot}.

$\therefore$ Angular velocity of rotatn $(\omega) = 2\pi \nu_{rot}$.

Now we know that $v = \omega r$.

$\therefore$ The total Kinetic Energy of rotor system (K) is :

$$K = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} m_1 (l_1 \omega)^2 + \frac{1}{2} m_2 (l_2 \omega)^2$$

$$\therefore \quad K = \frac{1}{2} (m_1 l_1^2 + m_2 l_2^2) \omega^2 .$$

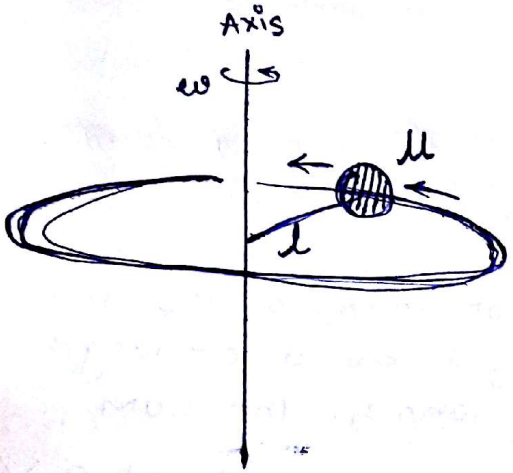
$$\therefore \quad K = \frac{1}{2} I \omega^2 \quad \ldots \quad I = \text{Moment of Inertia of the Rotor system.}$$

But also, $I = \mu l^2$. where μ = Reduced Mass of the system.
And l = Total Bond length between A & B

using : $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ and $m_1 l_1 = m_2 l_2$

$$\therefore K = \frac{1}{2}(\mu l^2)\omega^2 .$$

Therefore, we have reduced the two body problem into a one body problem where a single body/atom of mass (μ) rotates about an axis at a distance 'l' from the centre. at an angular velocity (ω).



Also, we know that.

$$\boxed{L = I\omega}.$$

$$\therefore \quad K = \frac{1}{2} I\omega^2 = \frac{1}{2}(I\omega)\cdot\omega .$$

$$\Rightarrow \quad K = \frac{1}{2} L\omega = \frac{1}{2} L\left(\frac{L}{I}\right).$$

$$\therefore \quad K = \frac{1}{2}\frac{L^2}{I}$$

$$\therefore \quad \boxed{K = \frac{L^2}{2I}}.$$

Since any external forces are absent like ($E\xi$, mg, $G\downarrow$) that would have created a field in the 3D space, the energy of the system is independent of the orientation of the system in 3D space.

Thus, analogous to a system in translational motion where $K = \frac{p^2}{2m}$ in the rotational kinetic energy term L (angular momentum) replaces p (linear momentum) and I (inertial moment) replaces m (Mass).

Therefore total energy of the system (E)

$$E = K + \cancel{U}^{\,0}$$

$$\Rightarrow E = K = \frac{L^2}{2I}.$$

since, $r = l$ = radial distance of rotating body from axis is constant.

$$\Rightarrow \frac{L^2}{2I} = \frac{l^2 p^2}{2\mu l^2}$$

$$\Rightarrow E = K = P^2/2\mu$$

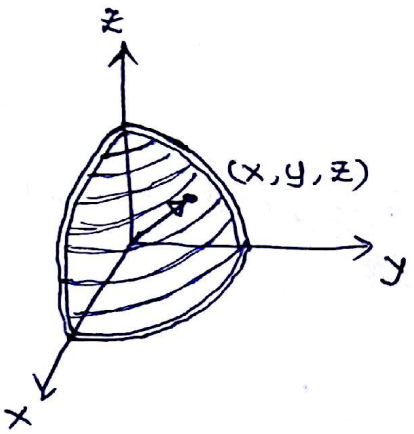
The Total Energy Hamiltonian Operator ($\hat{H}$) is:

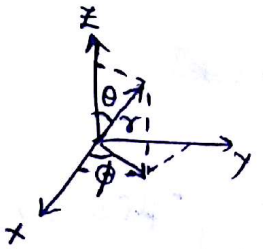
$$\hat{H} = \hat{K} = \frac{\hat{L}^2}{2I} = \frac{\hat{p}^2}{2\mu} = \frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$\therefore \hat{H} = \frac{-\hbar^2}{2\mu}\nabla^2.$$

We use spherical symmetry to exploit the naturally existing symmetry in the system.

$\therefore$





$\therefore x = r\cos\phi \sin\theta.$

$\therefore y = r\sin\phi \sin\theta.$

$\therefore z = r\cos\theta.$

$\therefore$ In spherical coord. sys.,

$$\hat{H} = \frac{-\hbar^2}{2\mu}\nabla^2$$

$$\nabla^2 = \frac{1}{l^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{l^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \cancel{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)} \rightarrow \text{zero.}$$

$\because r = \text{const.}$ $(r = l)$.

$$\therefore \nabla^2 = \frac{1}{l^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right).$$

$$\therefore \hat{H} = \frac{-\hbar^2}{2\mu}\cdot\frac{1}{l^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right).$$

$$\hat{H} = \frac{-\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right).$$

using $\hat{H} = \frac{\hat{L}^2}{2I}$; we get.

$$\left[\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right)\right] \rightarrow$$

The Operator $\hat{L}^2$ defined.

The orientation of the rigid rotator can be completely determined by the parameters θ and ϕ. Thus, rigid rotator wave functions depend on (θ, ϕ).

$$\therefore \hat{H}\psi(\theta,\phi) = E_0 \psi(\theta,\phi)$$

$$\Rightarrow \frac{-\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right)\psi(\theta,\phi) = E_0\psi(\theta,\phi).$$

Multiply throughout by $\sin^2\theta$.

$$\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi) = -\frac{2IE_0}{\hbar^2}\sin^2\theta\,\psi(\theta,\phi).$$

Let, $\frac{2IE_0}{\hbar^2} = \beta$

$$\therefore \left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi) + \beta\sin^2\theta\,\psi(\theta,\phi) = 0.$$

using separation of variables method:

Let, $\psi(\theta,\phi) = U(\theta)\,V(\phi)$.

$$\therefore \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}U\cdot V\right) + \frac{\partial^2}{\partial\phi^2}U\cdot V + \beta\sin^2\theta\cdot U(\theta)\cdot V(\phi) = 0.$$

$$\therefore \sin\theta\frac{\partial}{\partial\theta}\left(V(\phi)\sin\theta\frac{dU(\theta)}{d\theta}\right) + U(\theta)\frac{d^2}{d\phi^2}V(\phi) + \beta\sin^2\theta\cdot U(\theta)\cdot V(\phi) = 0.$$

$$\therefore V(\phi)\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}U(\theta)\right) + U(\theta)\frac{d^2}{d\phi^2}V(\phi) + \beta\sin^2\theta\,U(\theta)\cdot V(\phi) = 0.$$

$$\therefore V(\phi)\sin\theta\left(\cos\theta\frac{dU}{d\theta} + \sin\theta\frac{d^2U}{d\theta}\right) + U(\theta)\frac{d^2}{d\phi^2}V(\phi) + \beta\sin^2\theta\,UV = 0$$

$$\Rightarrow V(\phi)\sin\theta\cos\theta\frac{dU}{d\theta} + V(\phi)\sin^2\theta\frac{d^2U}{d\theta^2} + \beta\sin^2\theta\, U(\theta)V(\phi)$$

$$= -U(\theta)\frac{d^2V(\phi)}{d\phi^2}$$

Dividing throughout by $U(\theta)\cdot V(\phi)$, we get.

$$\frac{1}{U(\theta)}\sin\theta\cos\theta\frac{dU(\theta)}{d\theta} + \frac{1}{U(\theta)}\sin^2\theta\frac{d^2U}{d\theta^2} + \beta\sin^2\theta$$

$$= \frac{-1}{V(\phi)}\frac{d^2V(\phi)}{d\phi^2}.$$

clearly, LHS (θ) = RHS (ϕ).

This can happen only when

LHS (θ) = RHS (ϕ) = constant.

$$\therefore \frac{1}{U(\theta)}\sin\theta\cos\theta\frac{dU}{d\theta} + \frac{1}{U(\theta)}\sin^2\theta\frac{d^2U}{d\theta^2} + \beta\sin^2\theta = K^2$$

and

$$\frac{1}{V(\phi)}\frac{d^2V(\phi)}{d\phi^2} = -K^2$$

$$\Rightarrow \frac{d^2V(\phi)}{d\phi^2} + K^2V(\phi) = 0.$$

The above 2nd order ODE can be represented in the form of: $(a_2D^2 + a_1D + a_0)V(\phi) = 0.$

where $a_2 = 1$, $a_1 = 0$ and $a_0 = K^2$.

$\therefore$ Treating the Differentiation operators D and D^2 as algebraic variables and solving the Quadratic eqn.

$$a_2D^2 + a_1D + a_0 = 0.$$

$$\Rightarrow \alpha = \frac{-a_1 + \sqrt{a_1^2 - 4a_2a_0}}{2a_2} = \frac{\sqrt{-4K^2}}{2}$$

$$\Rightarrow \gamma = \frac{-a_1 - \sqrt{a_1^2 - 4a_1a_0}}{2a_2} = -\frac{\sqrt{-4K^2}}{2}$$

$$\therefore \alpha = \frac{i2K}{2} \; ; \; \gamma = -\frac{i2K}{2} \qquad \because (i = \sqrt{-1}).$$

$$\therefore (\alpha = iK \; ; \; \gamma = -iK)$$

Thus, the Quadratic roots α, γ are complex conjugates of each other.

Therefore solns. of the DE are:

$$\therefore y_1 = c_1 e^{\alpha t} \qquad c_1, c_2 \in \text{Arbitrary constants.}$$

$$\therefore y_2 = c_2 e^{\gamma t} \qquad \alpha, \gamma \in \text{Quad. roots.}$$

$$\therefore \left[y_g = c_1' y_1 + c_2' y_2\right]. \qquad \because (\text{linear combination of soln. of a linear DE is also a soln}).$$

$$\Rightarrow \left[y_g = \bar{c}_1 e^{\alpha t} + \bar{c}_2 e^{\gamma t}\right].$$

$$\Rightarrow y_g = \bar{c}_1 e^{ikt} + \bar{c}_2 e^{-ikt}$$

Using Euler's notation $\left[e^{\pm i\theta} = \cos\theta \pm i\sin\theta\right]$

$$\therefore \text{we get; } y_g = \bar{c}_1(\cos kt + i\sin kt) + \bar{c}_2(\cos kt - i\sin kt)$$

$$= (\bar{c}_1 + \bar{c}_2)\cos kt + i(\bar{c}_1 - \bar{c}_2)\sin kt.$$

$$\left[y_g = A\cos kt + iB\sin kt\right].$$

Thus, the general soln. of the DE is:

$$\left[y_g = A\cos k\phi + iB\sin k\phi\right] \qquad A, B \in \text{Arbitrary constants.}$$

$$\Rightarrow \frac{d^2 V(\phi)}{d\phi^2} + K^2 V(\phi) = 0.$$

Has soln.

$$[V(\phi)_g = A\cos K x(\phi) + iB\sin K x(\phi)].$$

But, It is required that the function $V(\phi)_g$ be one to one function (single valued). i.e. $V(\phi)$ is periodic $\Rightarrow V(\phi+2\pi) = V(\phi)$.

$$\therefore \boxed{V_m(\phi) = \Lambda_m e^{im\phi}} \quad m = 0, \pm 1, \pm 2, \ldots \; [m = K].$$

$$|\Lambda_m|^2 \int_0^{2\pi} V^*(\phi) V(\phi) d\phi = 1$$

$$\Rightarrow |\Lambda_m|^2 \int_0^{2\pi} e^{+im\phi - im\phi} d\phi = 1$$

$$\Rightarrow |\Lambda_m^2| \int_0^{2\pi} d\phi = 1$$

$$\therefore |A_m|^2 \, 2\pi = 1$$

$$\Rightarrow \Lambda_m^2 = \frac{1}{2\pi}$$

$$\Rightarrow \boxed{\Lambda_m = \frac{1}{\sqrt{2\pi}}}$$

$$\Rightarrow \left[V_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}\right] \ldots m = 0, \pm 1, \pm 2; \pm 3, \ldots (m = K).$$

m is the magnetic Quantum number.

Now; similarly,

$$\frac{d^2 U(\theta)}{d\theta^2} + \cot\theta \frac{dU(\theta)}{d\theta} + \left(B - \frac{K^2}{\sin^2\theta}\right) U(\theta) = 0.$$

The D.E. is of the form:

$$a_2(\theta) \frac{d^2 U}{d\theta^2} + a_1(\theta) \frac{dU(\theta)}{d\theta} + a_0(\theta) \frac{dU(\theta)}{d\theta} = 0.$$

The coeff. a_2, a_1 and a_0 are not constants but depend on θ.

Let, $\omega = \cos\theta$.

$$\Rightarrow \frac{d\omega}{d\theta} = -\sin\theta.$$

Also; $$\frac{dV}{d\theta} = \frac{dV}{d\omega} \cdot \frac{d\omega}{d\theta}$$

$$\Rightarrow \frac{dV}{d\theta} = \frac{dV}{d\omega}(-\sin\theta)$$

$$\therefore \frac{dV}{d\theta} = -(1-\cos^2\theta)^{1/2} \frac{dV}{d\omega}$$

$$\Rightarrow \frac{dV}{d\theta} = -(1-\omega^2)^{1/2} \frac{dV}{d\omega}.$$

Similarly; $$\cot\theta \frac{dV}{d\theta} = -\cancel{\sin\theta}\left(\frac{\cos\theta}{\cancel{\sin\theta}}\right)\frac{dV}{d\omega} = -\cos\theta \frac{dV}{d\omega}.$$

$$\therefore \left[\cot\theta \frac{dV}{d\theta} = -\omega \frac{dV}{d\omega}\right].$$

Also, $$\frac{d^2V}{d\theta^2} = \frac{d}{d\theta}\left(\frac{dV}{d\theta}\right) = \frac{d}{d\theta}\left(-\sin\theta \frac{dV}{d\omega}\right)$$

$$= -\cos\theta \frac{dV}{d\omega} - \sin\theta \frac{d}{d\theta}\frac{dV}{d\omega}.$$

$$= -\cos\theta \frac{dV}{d\omega} - \sin\theta \frac{d}{d\omega}\frac{dV}{d\omega}\left(\frac{d\omega}{d\theta}\right)$$

$$= -\omega \frac{dV}{d\omega} - \sin\theta\,(-\sin\theta)\frac{d^2V}{d\omega^2}.$$

$$= -\omega \frac{dV}{d\omega} + \sin^2\theta \frac{d^2V}{d\omega^2} = -\omega \frac{dV}{d\omega} + (1-\omega^2)\frac{d^2V}{d\omega^2}$$

$$\therefore \left[\frac{d^2V}{d\theta} = -\omega \frac{dV}{d\omega} + (1-\omega^2)\frac{d^2V}{d\omega^2}\right].$$

$$\therefore \left(\beta - \frac{k^2}{\sin^2\theta}\right) U(\theta) = \left(\beta - \frac{k^2}{1-\omega^2}\right) U(\theta).$$

$\therefore$ The D.E. becomes as follows:

$$\left[(1-\omega^2)\frac{d^2U(\theta)}{d\omega^2} - 2\omega\frac{dU(\theta)}{d\omega} + \left(\beta - \frac{k^2}{1-\omega^2}\right)U(\theta) = 0\right].$$

Thus our D.E. is in the Legendre eqn. form that yields solutions of the standard form described as:

$$U_l^{|m|}(\theta) = \underbrace{N_{lm}}_{\text{Normalization constant.}} \underbrace{P_l^{|m|}}_{\text{Associated Legendre polynomials in terms of } (\omega).} (\omega).$$

$\Rightarrow$ Soln. of our DE is

$$U_l^{|m|}(\theta) = N_{lm} P_l^{|m|}(\cos\theta).$$

Clearly, the solution $U(\theta)$ depends on two integers 'm' and 'l' that quantize the solution allowing only integral values of the fundamental.

$$N_{lm} = \text{Normalization constant} = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}}$$

$$\boxed{P_l^{|m|}(x) = \frac{(-1)^m}{2^l\, l!}(1-x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l} \rightarrow \text{General form of the Legendre Polynomial.}$$

m = magnetic Quantum number. $\in [-l, 0, +l]$

$l = J$ = Angular Quantum number. $= 0, 1, 2, \ldots$

For a state with Angular Quant. no. $= l$, total values that Magnetic Quant. no. can take $= 2l+1$. These values are:

$$[-l, -l+1, \ldots, -1, 0, +1, \ldots, l-1, l]$$

$\boxed{|m| \leq l}$ Always true.

$$\therefore \quad \Psi(r_0, \theta, \phi) = Y_l^m(\theta, \phi) = U_l^{|m|}(\theta) \cdot V(\phi)$$

$$\Rightarrow \quad Y_l^m(\theta, \phi) = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}} \cdot P_l^{|m|}(\cos\theta) \left(\frac{1}{\sqrt{2\pi}}\right) e^{im\phi}$$

$$\therefore \quad Y_l^m(\theta, \phi) = \underbrace{\sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-|m|)!}{(l+|m|)!}}}_{\text{Normalizat}^n \text{ const.}} \cdot \underbrace{P_l^{|m|}(\cos\theta)}_{\text{Polynomial}} \cdot \underbrace{e^{im\phi}}_{\text{complex exponential}}$$

Y_l^m functions are called <u>Spherical Harmonics.</u>

The soln. of the Legendre D.E. also yields an important fact that "β" is quantized.

$$\Rightarrow \quad \beta = l(l+1).$$

As per our previous assumption, $\beta = \frac{2IE}{\hbar^2} \Rightarrow E = \frac{\hbar^2}{2I}\beta.$

$$\Rightarrow \quad E_l = \frac{\hbar^2}{2I} l(l+1)$$

Energy is Quantized. It does not depend on 'm'.

Also, this implies that states $Y_l^m(\theta, \phi)$ with same l but different m are degenerate

The total number of degenerate states at energy level E_l is: $\boxed{g_l = 2l+1}$

Also, $E = hB\,l(l+1)$ where $B = \frac{h}{8\pi^2 I}$ (Hz)

Or, $E = hc\tilde{B}\,l(l+1)$ where $\tilde{B} = \frac{h}{8\pi^2 c I}$ (cm^{-1})

B and $\tilde{B}$ are called "Rotational constants".

Spherical Harmonics are special functions defined on the surface of a sphere. They are a complete set of orthonormal functions.

Orthogonality of the Spherical Harmonics:

$$Y_J^m(\theta,\phi) = \underbrace{\sqrt{\frac{2l+1}{4\pi}\cdot\frac{(l-|m|)!}{(l+|m|)!}}}_{\text{Normalization factor.}} \cdot \underbrace{P_l^{|m|}(\cos\theta)}_{\text{Associated Legendre Polynomial.}} \cdot \underbrace{e^{im\phi}}_{\text{complex exponential.}}$$

$l = 0, 1, 2, \ldots$

$m = 0, \pm 1, \pm 2, \ldots, \pm J.$

The legendre polynomials obey the property

$$\int_{-1}^{1} P_l(x) P_{l'}(x)\, dx = \delta_{ll'}$$

$$\delta_{ll'} = \text{Krönecker Delta} = \begin{cases} 1 & \forall\ l = l'. \\ 0 & \forall\ l \neq l'. \end{cases}$$

Thus, for associated Legendre polynomials we can write.

$x = \cos\theta$, $(-1, +1) \rightarrow (0, \pi)$, $dx = \sin\theta\, d\theta$.

$$\therefore \int_0^{\pi} P_l(\cos\theta)\cdot P_{l'}(\cos\theta)\sin\theta\, d\theta = \frac{\delta_{ll'}}{2l+1}$$

$$\Rightarrow \int_0^{\pi} P_l^{|m|}(\cos\theta)\cdot P_{l'}^{|m|}(\cos\theta)\sin\theta\, d\theta = \frac{2}{2l+1}\frac{(l+|m|)!}{(l-|m|)!}\delta_{ll'}.$$

Thus, for $l = l'$ ('m' may or may not be equal). $\Rightarrow \delta_{ll'} = 1$

$$\int_0^{\pi} P_l^{|m|}(\cos\theta)\cdot P_{l'}^{|m|}(\cos\theta)\sin\theta\, d\theta = \frac{1}{N_{lm}^2} \Rightarrow \text{Normalized.}$$

Also, for $l \neq l'$ ('m' may or may not be equal). $\delta_{ll'} = 0$.

$$\Rightarrow \int_0^{\pi} P_l^{|m|}(\cos\theta)\cdot P_{l'}^{|m|}(\cos\theta)\sin\theta\, d\theta = 0 \Rightarrow \text{orthogonal.}$$

Similarly,

$$\int_0^{2\pi} V_m(\phi)\cdot V_{m'}^*(\phi)\, d\phi = \langle m' | m \rangle. = \int_0^{2\pi} (e^{im\phi})(e^{-im'\phi})\, d\phi$$

$$\Rightarrow \langle m' | m \rangle = \int_0^{2\pi} e^{i(m-m')\phi}\, d\phi.$$

Thus for $m = m'$

$$\Rightarrow \langle m' | m \rangle = \int_0^{2\pi} e^0 \, d\phi = \int_0^{2\pi} d\phi = 2\pi = \frac{1}{(\Lambda_m)^2} \Rightarrow \text{Normalized}$$

$$\Rightarrow \langle m' | m \rangle = \delta_{mm'} \cdot \left(1/N^2\right).$$

Thus, for both 'l' and 'm' are equal

$$\psi_l^m(\theta, \phi) = \text{Normalized}$$

Also, for both 'l' and 'm' are unequal

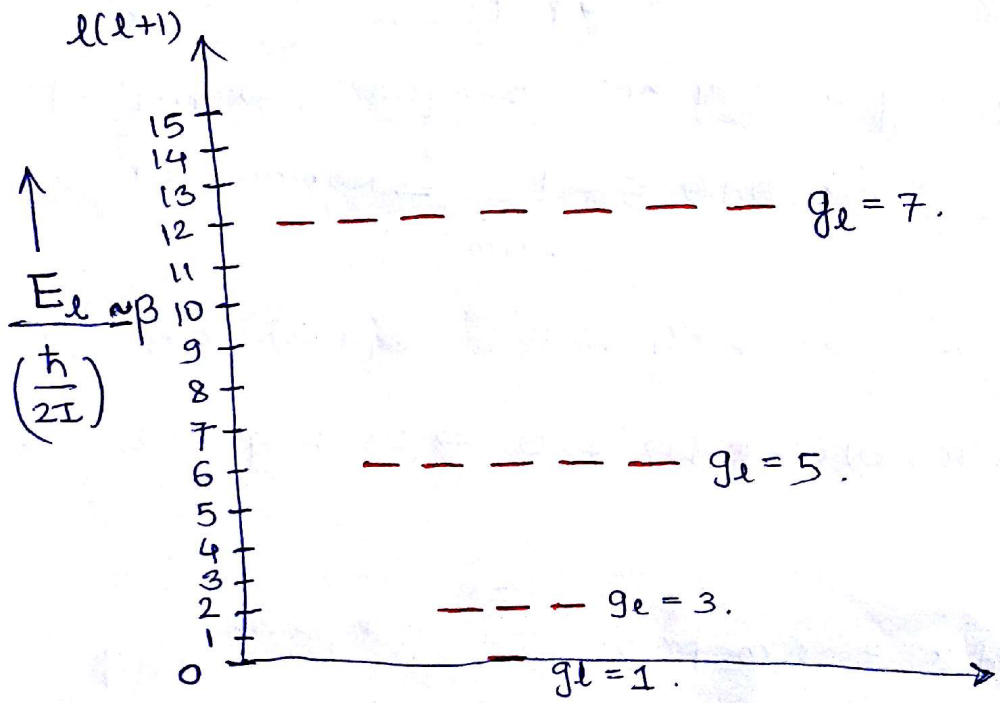
$$\psi_l^m(\theta, \phi) = \text{orthogonal}$$

$$\because \left[\langle \psi_l^m | \psi_{l'}^{m'} \rangle = \left(\frac{1}{N^2}\right) \cdot \delta_{ll'} \cdot \delta_{mm'} \right]$$

$\therefore \psi_l^m$ are orthonormal.

Thus, ψ_l^m form the eigenfunctions of the Hamiltonian ($\hat{H}$) for the rigid rotor model

* Energy levels of Rigid Rotor :



* Transitions & spectroscopy:

The selection rule states that transitions are allowed only between adjacent energy levels. $\Rightarrow \Delta l = \pm 1$.

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{I}(l+1) = \frac{h^2}{4\pi^2 I}(l+1).$$

$$\Delta E = h\nu_{photon}$$

$$\Rightarrow \nu_{photon} = \frac{h}{4\pi^2 I}(l+1)$$

$(l+1)$ → Angular Quantum Number

ν_{photon} = frequency of the photon emitted or absorbed. For most diatomic rigid rotors; $\nu_{photon} \in$ (μwave region).

$$I = \mu l^2$$

μ → Reduced mass, l → l = Internuclear distance

$$\tilde{\omega}_{photon} = 2\tilde{B}(l+1)$$

$\tilde{\omega}$ → Wave number of Radiation

$$\omega_{photon} = 2B(l+1)$$

ω → Angular frequency of radiation

Spacing in between adjacent lines of spectrum $= 2B$ (in Hz).
" " $= 2\tilde{B}$ (in cm^{-1})

* Vibrational AND Rotational Spectroscopy:

Rigid rotator – Harmonic oscillator model well approximates the motion of a diatomic molecule that rotates as well as vibrates. Under this model, we have.

$$E_{n,l} = \left(n + \frac{1}{2}\right)h\nu + Bh(l)(l+1).$$

$n = 0, 1, 2, \ldots$
$l = 0, 1, 2, \ldots$

$$E_{n,l} = \left(n + \frac{1}{2}\right)\hbar\omega + Bh(l)(l+1).$$

$$\omega = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \quad \text{and} \quad B = \frac{h}{8\pi^2 I}$$

$$\Rightarrow \Delta E = E_{n+1,l+1} - E_{n,l}.$$

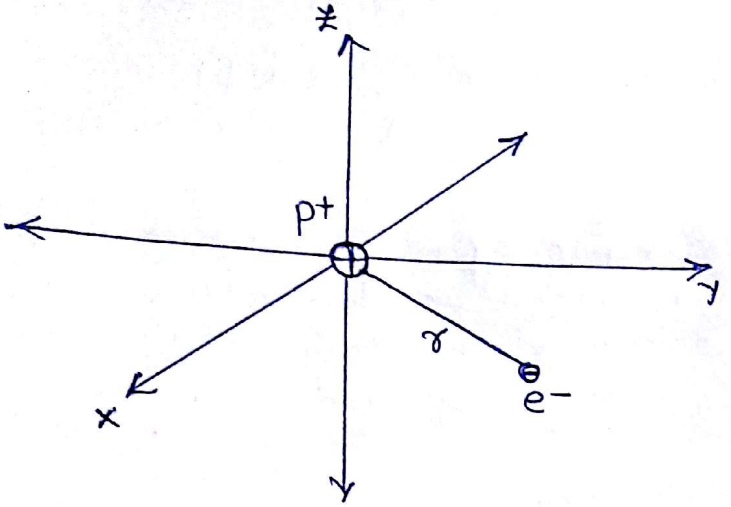
$$\therefore \boxed{h\nu_{obs.} = \hbar\omega + 2B(l+1)}.$$

Also, $\boxed{h\tilde{\nu}_{obs.} = \hbar\tilde{\omega} + 2\tilde{B}(l+1)}$.

$$B = \frac{h}{8\pi^2 I} \text{ (Hz)}.$$

$$\tilde{B} = \frac{h}{8\pi^2 c I} \text{ } (cm^{-1}).$$

* Hydrogen Atom system :



Consider a Hydrogen atom with one proton of mass m_p fixed at the centre of the atom while one electron of mass m_e revolving around the proton.

charge on $p^+ = +e$

charge on $e^- = -e$.

$|e| = 1.6 \times 10^{-19}$ C.

$m_p = 1.673 \times 10^{-27}$ kg.

$m_e = 9.109 \times 10^{-31}$ kg.

$\frac{m_p}{m_e} \approx 1823 \quad \therefore m_p = 1823 m_e$.

$\therefore$ Reduced Mass $(\mu) = \frac{m_p m_e}{m_p + m_e} = \frac{m_p m_e}{1824 m_e}$

$\Rightarrow \mu = m_e \frac{1823}{1824}$

$\Rightarrow [\mu = 0.999452\, m_e]$.

$\therefore \mu \simeq m_e$.

$$\hat{K} = \frac{-\hbar^2}{2\mu} \nabla^2$$

But $\mu = m_e$.

$$\Rightarrow \hat{K} = \frac{-\hbar^2}{2m_e} \nabla^2.$$

In spherical coordinates,

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

Also, Potential Energy of the system is :
using Coulombic interaction.

$$\hat{V}(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r} = \frac{-e^2}{4\pi\varepsilon_0 r}$$

ε_0 = permittivity of free space. $= 8.89 \times 10^{-12}\ Nm^2C^{-2}$.

$$\therefore \hat{H} = \hat{K} + \hat{V}(r).$$

$$\therefore \hat{H} = \frac{-\hbar^2}{2m_e}\nabla^2 + \left(\frac{-e^2}{4\pi\varepsilon_0 r}\right)$$

Hydrogen atom is case of non-rigid rotor model. where wavefunc. ψ depends on (r, θ, ϕ) all the polar/spherical coord.
Thus, the model expects the central proton to rotate about the COM of the system. However $m_p \ggg m_e$ so that m_p can be assumed to be stationary at the centre as the forces by e^- are negligibly small to move the proton.

Also, $m_1 l_1 = m_2 l_2$, Heavier the mass, closer it is to the COM. $\therefore$ COM overlaps closely on the pt. $\therefore$ we can assume pt is static at centre

Now, $\hat{H}\psi(r,\theta,\phi) = E_0\,\psi(r,\theta,\phi)$.

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

$$\left.-\frac{e^2}{4\pi\varepsilon_0 r}\right\}\psi(r_0,\theta,\phi) = E_0\,\psi(r_0,\theta,\phi).$$

But from the defination of $\hat{L}^2$ operator we have.

$$\hat{L}^2 = -\left(\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right)\hbar^2$$

$\therefore$ we get.

$$\left[\frac{-\hbar^2}{2m_e}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right) + \frac{\hat{L}^2}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(r,\theta,\phi) = E_0\,\psi(r,\theta,\phi).$$

$$\Rightarrow \therefore \left[\frac{-\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(r) - E_0\right]\psi(r,\theta,\phi) = \frac{-\hat{L}^2}{2m_e r^2}$$

Let By separation of variables method.

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{Radial wave fnc.}}\cdot\underbrace{Y(\theta,\phi)}_{\text{Spherical Harmonics}}.$$

$$\Rightarrow Y(\theta,\phi)\left[\frac{-\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + (V(r)-E_0)R(r)\right] = -R(r)\frac{\hat{L}^2 Y(\theta,\phi)}{2m_e r^2}$$

$$\Rightarrow \frac{1}{R(r)}\left[\frac{-\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + (V(r)-E_0)R(r)\right]$$

$$= \frac{-1}{Y(\theta,\phi)}\frac{\hat{L}^2 Y(\theta,\phi)}{2I}.$$

Clearly, $LHS(r) = RHS(\theta,\phi)$

This is possible only when: $LHS(r) = RHS(\theta,\phi) = \underline{\text{const}}$.

$$\Rightarrow \frac{-1}{Y(\theta,\phi)} \frac{\hat{L}^2}{2I} Y(\theta,\phi) = +K^2$$

$$\therefore \frac{1}{Y(\theta,\phi)} \frac{\hat{L}^2}{2I} Y(\theta,\phi) = -K^2 \quad \text{— eqn. ①}$$

Similarly; $$\frac{1}{R(r)}\left[\frac{-\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + (V(r) - E_0)R(r)\right] = -K^2 \quad \text{— eqn. ②}$$

Solns. of eqn. ① will be of the form of Legendre polynomials as evaluated in the Rigid rotor model.

To solve eqn. ② D.E.

$$\frac{-\hbar^2}{2m_e r^2}\left(2r\frac{dR(r)}{dr} + r^2\frac{d^2R(r)}{dr^2}\right) + (V(r) - E_0)R(r) = -K^2 R(r).$$

$$\frac{-\hbar^2}{2m_e}\frac{d^2}{dr^2}R(r) - \frac{\hbar^2}{m_e r}\frac{dR(r)}{dr} + (V(r) - E_0 + K^2)R(r) = 0.$$

we know that, from Rigid rotor model

$$\frac{\hat{L}^2}{2I}(Y\theta,\phi) = E_0 Y(\theta,\phi)$$

where E_0 = eigenvalue of $\frac{\hat{L}^2}{2I}$ operator on $Y(\theta,\phi)$.

E_0 = Angular kinetic energy of the rigid rotor system $= \frac{\hbar^2}{2I}(l)(l+1)$

$$\therefore K^2 = \left[\frac{\hat{L}^2 Y(\theta,\phi)}{2I}\right] \times \left(\frac{1}{Y(\theta,\phi)}\right) = E_0$$

$$\therefore \boxed{K^2 = \frac{\hbar^2}{2m_e r^2} l(l+1)} \qquad (l = 0, 1, 2, \ldots).$$

$$\therefore \left[\frac{-\hbar^2}{2m_e}\left(\frac{d^2}{dr^2}R(r)\right) - \frac{\hbar^2}{m_e r}\left(\frac{dR(r)}{dr}\right) + \left(\frac{-e^2}{4\pi\varepsilon_0 r} - E_0 + \frac{\hbar^2}{2m_e r^2} l(l+1)\right) = 0\right] \quad \text{— ☆}$$

The eqn. ★ is termed as the radial relation.
It can be physically interpreted as the Total Energy (E) is the sum of the radial kinetic energy, the angular kinetic energy and the potential energy of the system.

Let, $u(r) = r \cdot R(r)$.

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{-e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - E\right]u(r) = 0.$$

zero.

we define a new variable that expresses length in terms of Bohr's radius. Because Bohr's radius is a natural for the Hydrogen atom.

$$\left[a_0 = \frac{\hbar^2}{\mu e^2} = 0.529\,\text{Å}\right]$$

Also, we need this new variable to be unitless so as to function as a point of comparison in the limitting cases of the D.E.

$$\therefore \left[\rho = \frac{2r}{n a_0}\right].$$

$\therefore$ D.E. becomes,

$$\frac{d^2u}{d\rho^2} - \left[\frac{l(l+1)}{\rho^2} - \frac{n}{\rho} + \frac{1}{4}\right]u = 0.$$

This yields a solution of the form.

$$u(\rho) = \rho^{l+1} P(\rho)\, e^{-\rho/2}$$

$\therefore$ Expressing the DE with fnc. $P(\rho)$.

$$\Rightarrow \left[\rho\frac{d^2P}{d\rho^2} - (\rho - 2(l+1))\frac{dP}{d\rho} + [n-(l+1)]P = 0\right].$$

The above D.E. is a standard form of D.E. termed as Laguerre D.E.

Laguerre D.E. yields soln. of the form

$$P_{n+l}^{2l+1}(\rho) = \sum_{q=0}^{n-l-1} (-1)^q \frac{(n+3l+1)! \times \rho^q}{(n+l-q)! \times (q+2l+1)!}$$

$$\therefore u(\rho) = \rho^{l+1} P(\rho)\, e^{-\rho/2}$$

$$\therefore u\left(r = \frac{n\rho a_0}{2}\right) = \left(\frac{2r}{na_0}\right)^{l+1} \left[P_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)\right] e^{-r/na_0}$$

$$\Rightarrow R(r) \propto \frac{1}{r}\left(\frac{2r}{na_0}\right)^{l+1} \left[P_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)\right] e^{-r/na_0}$$

$$\therefore R(r) = N \frac{1}{r}\left(\frac{2r}{na_0}\right)^{l+1} \left[P_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)\right] e^{-r/na_0}$$

By Normalization,

$$N = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

$$\therefore R_{nl}(r) = \underbrace{\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}\left(\frac{2}{na_0}\right)^{l+\frac{1}{2}}}_{\text{Normalization constant}} \underbrace{P_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)}_{\text{associated Laguerre Polynomial}} \cdot \underbrace{r^l e^{-r/na_0}}_{\text{Decaying exponent term.}}$$

similarly,

$$Y_l^m(\theta,\phi) = \underbrace{\sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-|m|)!}{(l+|m|)!}}}_{\text{Normalization constant.}} \cdot \underbrace{P_l^{|m|}(\cos\theta)}_{\text{associated Legendre Polynomial}} \cdot \underbrace{e^{im\phi}}_{\text{complex exponent term.}}$$

$\therefore$ for Hydrogen: $\left[\psi(r,\theta,\phi) = R_{nl}(r)\cdot Y_l^m(\theta,\phi)\right]$.

Defining Quantum Numbers:

$(n, l, m) \propto$ Integers ($\mathbb{Z}$).

$n \in [1, 2, 3, \ldots]$

$l \in [0, 1, 2, 3, \ldots, n-1]$

$m \in [0, \pm1, \pm2, \pm3, \ldots, \pm l]$

n = Principal Quantum number.

l = Angular Quantum number.

m = Magnetic Quantum number.

$\therefore$ The total wavefunctions $\psi(r,\theta,\phi)$ can be described as:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\cdot Y_l^{m_l}(\theta,\phi).$$

These wave functions are orthonormal indicating that:

$$\boxed{\langle n\, l\, m_l \mid n'\, l'\, m_l' \rangle = \delta_{nn'}\,\delta_{ll'}\,\delta_{m_l m_l'}}.$$

$$\psi_{nlm}(r,\theta,\phi) = |n\, l\, m_l\rangle$$

That is, these wave functions depend on three quantum numbers n, l, m_l. This dependence arises from the quantizations of eigenfunctions of the three operators $\hat{H}, \hat{L}^2, \hat{L}_z$. ($n$ for $\hat{H}$, l for $\hat{L}^2$ and m_l for $\hat{L}_z$).

If two operators (representing two physical quantities) commute then it implies that these two physical quantities are simultaneously measurable without invoking uncertainity and that these operators have simultaneous eigenfunctions. Similarly, $\psi_{(nlm_l)}$ is a simultaneous eigenfunction of $\hat{H}, \hat{L}^2$ and $\hat{L}_z$ since they commute with each other.

$$[\hat{H}, \hat{L}^2] = [\hat{L}^2, \hat{L}_z] = [\hat{L}_z, \hat{H}] = 0 \text{ (zero)}.$$

i.e. $\hat{H}, \hat{L}^2$ and $\hat{L}_z$ commute mutually.

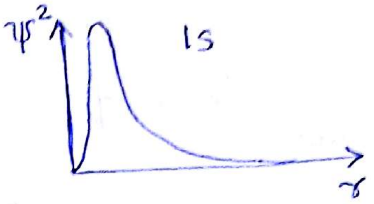
n, l and m_l are termed as good Quantum numbers.

* Total wavefunctions and Hydrogen orbitals:

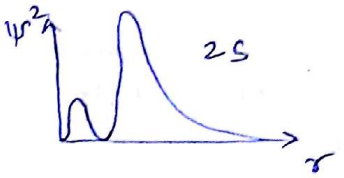
The total wavefunctions corresponding distinct values of quantum numbers describe particular orbitals of the Hydrogen atom. orbitals are the regions in 3D space in which the probability of finding an electron is maximum

s = sharp

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho} \qquad 1s$$



$$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (2-\rho) e^{-\rho/2} \qquad 2s$$

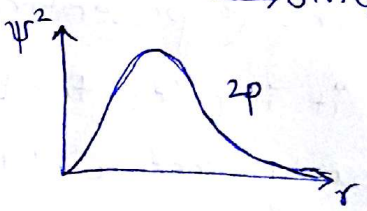


$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2} \cos\theta \qquad 2p_z$$

$$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2} \sin\theta \cdot e^{\pm i\phi}$$

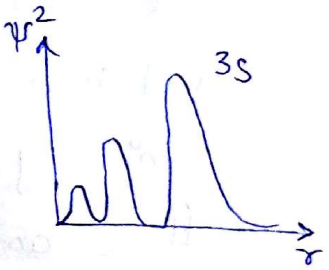
$\cos\phi$ $\quad \psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{211} + \psi_{21-1})$.

$\sin\phi$ $\quad \psi_{2p_y} = \frac{-i}{\sqrt{2}}(\psi_{211} - \psi_{21-1})$.

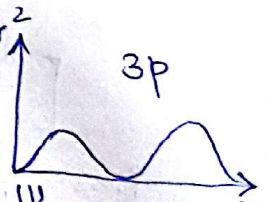


p = principal

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3} \qquad 3s$$



$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho(6-\rho) e^{-\rho/3} \cos\theta \qquad 3p_z$$



$\cos\phi$ $\quad \psi_{3p_x}$

$$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho(6-\rho) e^{-\rho/3} \sin\theta \, e^{\pm i\phi}$$

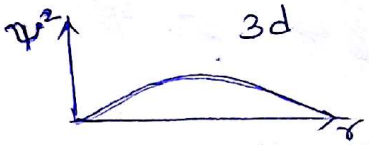
$\sin\phi$ $\quad \psi_{3p_y}$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3} (3\cos^2\theta - 1)$$

$$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3} \sin\theta\cos\theta \, e^{\pm i\phi}$$

$\cos\phi$ → $\psi_{3d_{xz}}$; $\sin\phi$ → $\psi_{3d_{yz}}$

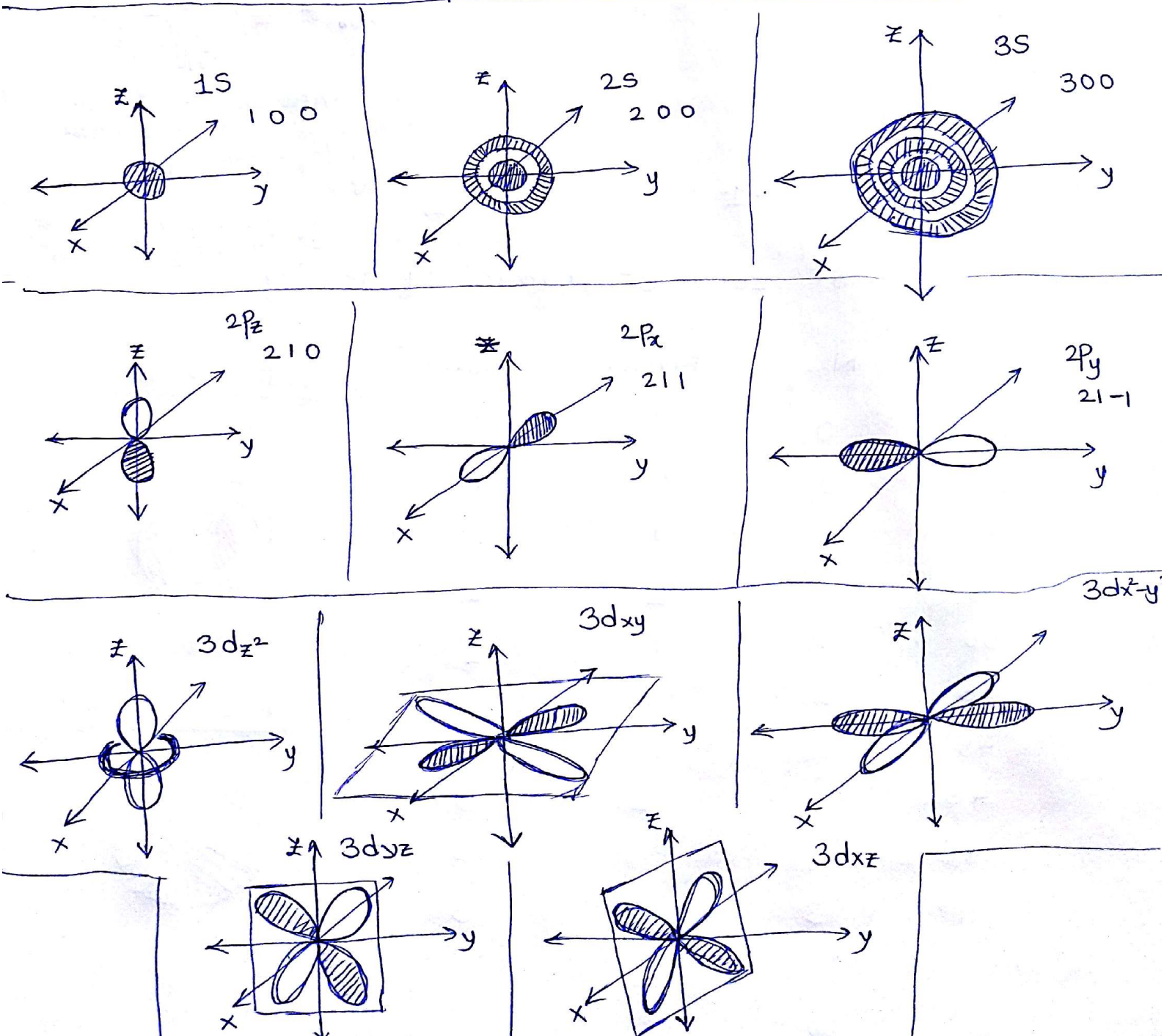
d = diffused



$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3} \sin^2\theta \, e^{\pm 2i\phi}$$

$\cos 2\phi$ → $\psi_{3d_{xy}}$; $\sin 2\phi$ → $\psi_{3d_{x^2-y^2}}$

SHAPES OF ORBITALS :



Each total wave function $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$ contains an algebraic polynomial term in terms of "r" coupled to a sinusoidal term in terms of "θ, ϕ".

The regions where the entire wavefunction $\psi(r,\theta,\phi) = 0$ are called nodes. Here, the probability (of finding an e^-) $\psi^*(r,\theta,\phi) \times \psi(r,\theta,\phi)$ is also zero.

The nodes may be "radial" (i.e. Algebraic "r" term becomes zero) or "angular" (i.e. sinusoidal "θ, ϕ" term becomes zero).

Number of nodes in an orbital:

Radial $= n - l - 1$.

Angular $= l$.

Total number of Nodes $= n - 1$.

$R_{nl}(r)$ for 1s orbital.

$$R_{10}(r) = \left(\frac{4}{a_0^3}\right)^{1/2} r \cdot e^{-2r/a_0}$$

$\therefore$ Prob. that an e^- will be found with r_1 & r_2 shell.

$$\frac{4}{a_0^3}\int_{r_1}^{r_2} r^2 e^{-2r/a_0}\, dr.$$

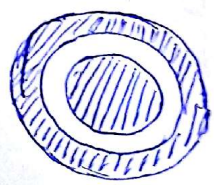
$\Rightarrow$ most prob. distance value of r for an e^- in 1s orb. is "a_0".

Nodes = region of zero e^- probability density.

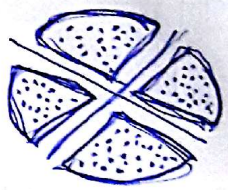
$\therefore$

Orbital	N_{ang}	$N_{rad.}$	$N_{tot.}$
1s	0	0	0
2s	0	1	1
2p	1	0	1
3s	0	2	2
3p	1	1	2
3d	2	0	2
4s	0	3	3
4p	1	2	3
4d	2	1	3
4f	3	0	3

Radial node



Angular node



• Energy levels of the Hydrogen atom :

Energy in terms of principal Quantum number (n).

$$E_n = \frac{-m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\left(\frac{1}{n^2}\right). \qquad n = 0, 1, 2, 3, \ldots$$

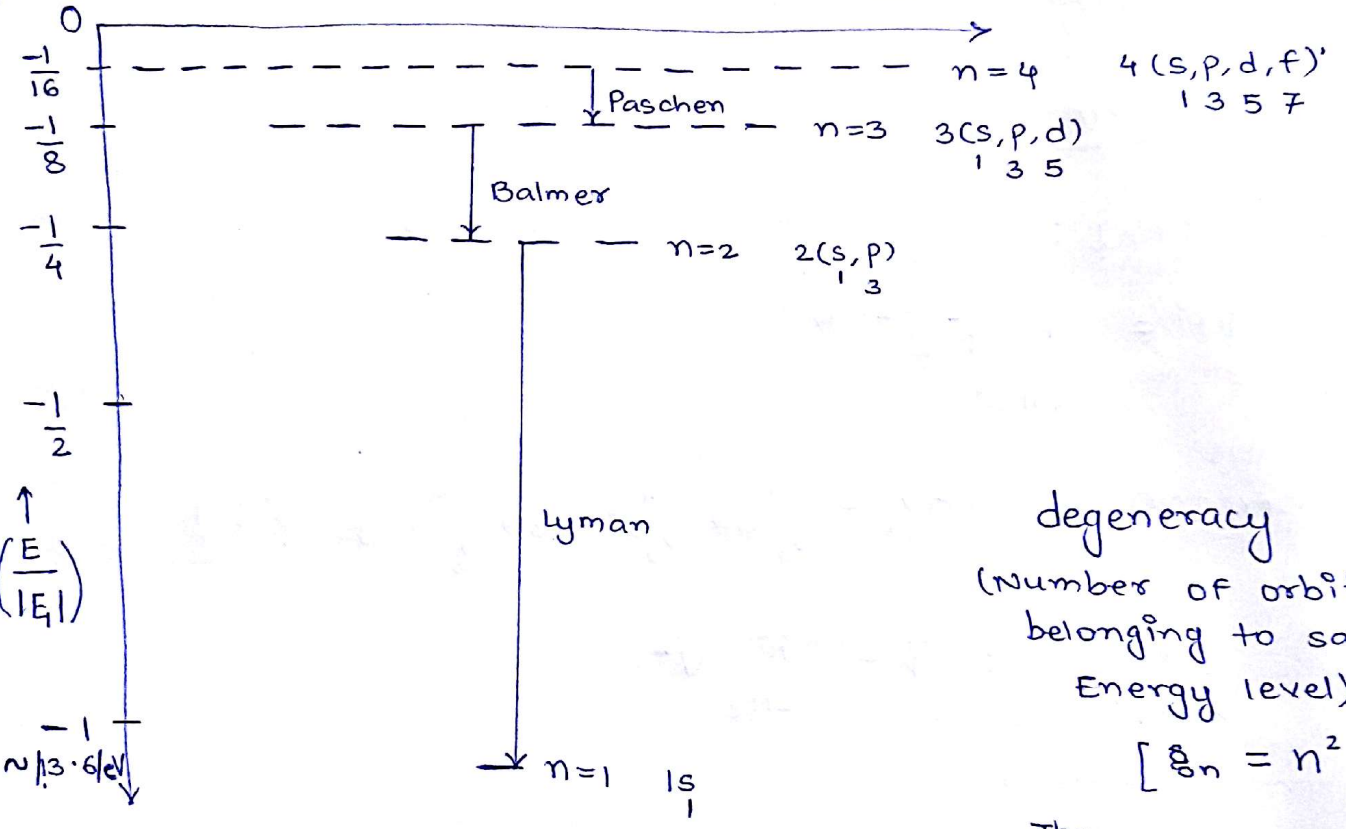
i.e. $E_1 = \dfrac{-m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}$

$\therefore \quad E_n = \left(\dfrac{E_1}{n^2}\right).$

Also, Quantum Theory agrees with Bohr's model as :

$E_n = \dfrac{-R_H}{n^2}$ where,

(R_H = rydberg's Constant).



degeneracy
(Number of orbitals belonging to same Energy level)
$[g_n = n^2]$.

Thus, each energy level describes one shell of orbitals (K, L, M, N...).

Bohr's radius $= a_0 = \dfrac{\varepsilon_0^2 \hbar^2}{\pi m_e e^2} = 0.529\ \text{Å}$

$\sim -E_1/n^2$

E_n is the value of Total energy in the nth shell/state. Thus 'E_n' is the eigenvalue of the $\hat{H}$ operator.

Similarly, eigenvalues of the $\hat{L}^2$ operator and the $\hat{L}_z$ operator are $\hbar^2 l(l+1)$ and $(\hbar m)$. respectively.

i.e.

$$\hat{H}\,\psi(r,\theta,\phi) = \left(-E_1/n^2\right)\psi(r,\theta,\phi)$$

$$\hat{L}^2\,\psi(r,\theta,\phi) = \hbar^2 l(l+1)\,\psi(r,\theta,\phi)$$

$$\hat{L}_z\,\psi(r,\theta,\phi) = \hbar m_l(\psi\, r,\theta,\phi)$$

Therefore the previous claim that $\psi(r,\theta,\phi)$ is the simultaneous eigenfunction of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ is justified. Also, we see that Eigenvalues of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ depend only on n, l and m_l respt.

From here we also get that

$$\left[L = \sqrt{\hbar^2\, l(l+1)}\right]$$

(Angular momentum of system H atom).

- <u>Virial Theorem</u> :

For 1s orbital :

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}\, r\, e^{-2r/a_0}$$

for an operator $\hat{A}$: $\langle A\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} r^2 dr\, \psi^* \hat{A}\, \psi$

$$\therefore\ \hat{V} = \frac{-e^2}{4\pi\varepsilon_0 r}\ ;\ \hat{T} = \frac{-\hbar^2}{2m_e}\nabla^2.$$

Now,

$$\langle\hat{V}\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} \frac{1}{\pi a_0^3}\left(\frac{-e^2}{4\pi\varepsilon_0 r}\right) r^2 e^{-2r/a_0} dr$$

$$= [\phi]_0^{2\pi}\,[-\cos\theta]_0^{\pi}\left(\frac{1}{\pi a_0^3}\right)\int_0^{\infty}\left(\frac{-e^2}{4\pi\varepsilon_0}\right) r e^{-2r/a_0} dr$$

$$= (\cancel{2\pi})\,(\cancel{+2})\left(\frac{1}{\pi a_0^3}\right)\left(\frac{-e^2}{\cancel{4\pi}\varepsilon_0}\right)\int_0^{\infty} r e^{-2r/a_0} dr.$$

$$\therefore\ \langle\hat{V}\rangle = \frac{-e^2}{\pi a_0^3 \varepsilon_0} \times \left(\frac{a_0^2}{4}\right)$$

$$\because\ \int_0^{\infty} x^n e^{-\alpha x}\, dx = \frac{n!}{\alpha^{n+1}}$$

$$\therefore \langle \hat{V} \rangle = \frac{-e^2}{4\pi\varepsilon_0 a_0} \quad ; \quad \text{Also, } \left(a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} \right).$$

$$\therefore \langle \hat{V} \rangle_{1s} = \frac{-m_e e^4}{16\pi^2\varepsilon_0^2 \hbar^2} \qquad \because \quad E_1 = \frac{-m_e e^4}{32\pi^2\varepsilon_0^2 \hbar^2}$$

$$\Rightarrow \langle \hat{V} \rangle_{1s} = 2\langle \hat{E} \rangle_{1s}$$

$$\Rightarrow \langle E \rangle_{1s} = \langle \hat{T} \rangle_{1s} + \langle \hat{V} \rangle_{1s}$$

where $\hat{E}$ = Total Energy.
$\hat{T}$ = Kinetic Energy.
$\hat{V}$ = Potential Energy.

$$\Rightarrow \langle \hat{T} \rangle_{1s} = \langle \hat{E} \rangle_{1s} - \langle \hat{V} \rangle_{1s}$$

$$\Rightarrow \langle \hat{T} \rangle_{1s} = \langle \hat{E} \rangle_{1s} - \left(2\langle \hat{E} \rangle_{1s}\right)$$

$$\Rightarrow \langle \hat{T} \rangle_{1s} = -\langle \hat{E} \rangle_{1s}.$$

$$\therefore \langle \hat{V} \rangle_{1s} = -2\langle \hat{T} \rangle_{1s}$$

$$\Rightarrow \boxed{\frac{\langle \hat{V} \rangle_{1s}}{\langle \hat{T} \rangle_{1s}} = -2}$$

This statement is valid for all energy levels and orbitals and is termed as Virial's Theorem.

- **Zeeman effect:**

Suppose an e^- revolves in an elliptical loop producing a mg dipole (m).

$$m = IA$$

I = current flow, A = Area of loop.

But $I = \dfrac{qv}{2\pi r}$

v = velocity of revolution
q = charge of e^- = $-e$
r = radius of circle of loop.

$$\therefore \vec{m} = \frac{q(\vec{r} \times \vec{v})}{2}$$

But, $m(\vec{r} \times \vec{v}) = \vec{l}$ = Angular momentum.

$$\therefore \vec{m} = \frac{-e\vec{l}}{2m_e}$$

Now V = potential energy of dipole in an external mg field $\vec{B}$ $= -\vec{m}\cdot\vec{B}$

Let $\vec{B}$ be along z axis,

$$\therefore \left[V = +\frac{eB_z}{2m_e} l_z \right].$$

Using operators in place of Physical Quantities, we get.

$$\hat{H} = \hat{H}_0 + \frac{|e| B_z}{2m_e} \hat{L}_z$$

$\hat{H}_0$ = initial total energy of dipole.

$\hat{H}$ = Total energy of dipole in ext. mg field B_z.

$$\Rightarrow \hat{H}\psi = \hat{H}_0\psi + \frac{eB_z}{2m_e} \hat{L}_z\psi.$$

$$\Rightarrow \hat{H}\psi = E_n\psi + \frac{eB_z}{2m_e} \hat{L}_z\psi.$$

Eigen value of $\hat{H}_0$ is E_n. and that of $\hat{L}_z$ is $m_l\hbar$.

$$\Rightarrow \hat{H}\psi = E_n\psi + \left(\frac{m_l \hbar e}{2m_e}\right) B_z\psi$$

$$\Rightarrow \boxed{\hat{H}\psi = (E_n + m_l \beta_B B_z)\psi}$$

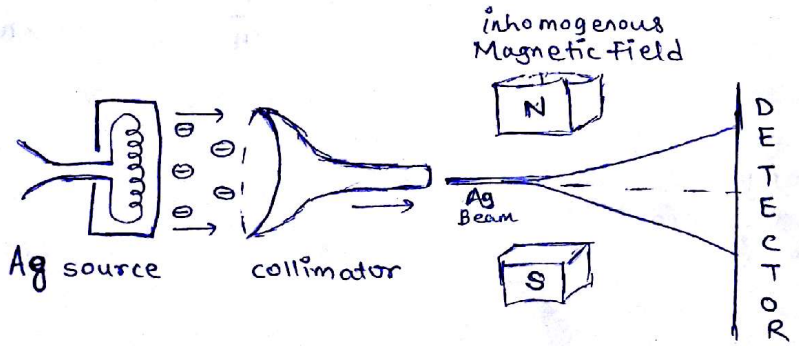
β_B = Bohr's magneton $\simeq \frac{e\hbar}{2m_e}$

Thus, the final total Energy of the Hydrogen atom after applying an external magnetic field 'B_z' depends on two Quantum numbers 'n' & 'm_l' (unlike initial case where E_n is only dependent on 'n'). Thus, previously in absence of ext. mg field, All energy levels or orbitals with different m_l & l but same n belonged to same degenerate energy level E_n. However, now the degeneracy gets lifted. Orbitals with different m_l have different energies. It causes 'splitting' of energy levels.

This is called Zeeman effect.

- <u>Spin of an electron:</u>

→ Stern - Gerlach experiment, 1922



- Ag (silver) has e^- config. $4d^{10}5s^1$ for outer e^- shell. that is it has only $1e^-$ in valence shell.
- A hot Electric (Ag) filament furnace used to generate a beam of silver atoms.
- A Detector plate used to mark the final point of trajectory.
- In absence of External magnetic field the trajectory is expected to be undeflected and linear.

- However, in the presence of an external magnetic field, Zeeman's effect expects that all unpaired electrons in a state described by unique 'n' and 'm_l' that is unpaired e^- of distinct orbitals will attain different energy decided by the value of m_l & n of the orbital in which that e^- lies. The e^- of same subshells will lift from degenerate level.
- In short, The ext. mg field will align each unpaired e^- uniquely (m_l & n dependent).
- However, an inhomogenous ext. mg field is used indicating that it will not just rotate each magnetic dipole to a unique alignment but also displace it in a translational fashion.
- The expected result is that if the atoms used in experiment have 'x' number of unpaired outermost e^- (And by Hund's rule all these 'x' e^- must belong to same subshell). and the subshell (s, p, d, f, ...) to which these e^- belong has Angular Quantum number 'l'. then after application of external $\vec{B}_{mg}$, $(2l+1)$ different trajectories are expected to be detected because $2l+1$ different magnetic quantum numbers belong to that subshell.
- Since Ag has outer shell config. $4d^{10}5s^1$. The only unpaired e^- belongs to 5s subshell that has $l=0$. Therefore $m_l = 0$ only one possible magnetic quantum number belongs to $l=0$. Hence, the final trajectory after mg field application should be unique.
- But experimentally the e^- beam of Ag split into two to yield two distinct final trajectories some how indicating two m_l values must be existing. This also means s subshell should have 2 orbitals which is impossible.

As per result obtained. $2l+1 = 2 \Rightarrow \left[l = \frac{1}{2}\right]$.

However this contradicts our defination of angular quantum number $l = 0, 1, 2, 3, \ldots, n-1$.

- This also reflected in the spectroscopy as transition line for $(n=1) \rightarrow (n=2)$ should have a unique spectral line but in reality it is split into two creating a Doublet.

Wolfgang Pauli found that the ambiguity disappeared if assume that the e^- exists in either of the $+\frac{1}{2}$ or the $-\frac{1}{2}$ states. Paul Dirac established the solid foundations of the Quantum number spin Quantum number (m_s).

- <u>Spin Quantum number:</u>

$$m_s = \pm \frac{1}{2} \quad \text{(only two values possible for } m_s\text{)}.$$

spin operators: $\hat{S}^2$ and $\hat{S}_z$ analogues of $\hat{L}^2$ and $\hat{L}_z$.

$\forall s = \frac{1}{2}$; $\hat{S}^2 \alpha(\theta, \phi) = \hbar^2 s(s+1)\alpha$; $\hat{S}^2 \beta(\theta, \phi) = \hbar^2 s(s+1)\beta$

$\forall s = \frac{1}{2}$; $\hat{S}_z \alpha(\theta, \phi) = \hbar s \alpha = \frac{1}{2}\hbar\alpha$; $\hat{S}_z \beta(\theta, \phi) = \hbar s \beta = -\frac{1}{2}\hbar\beta$

$|\alpha\rangle = Y_{1/2}^{-1/2}(\theta, \phi)$. ; $|\beta\rangle = Y_{1/2}^{-1/2}(\theta, \phi)$. ... spin eigenf

As, L = orbital Angular momentum $= \hbar\sqrt{l(l+1)}$. $l = 0, 1$

similarly, S = spin Angular momentum $= \hbar\sqrt{s(s+1)}$. $s = \frac{1}{2}$

Note: As s cannot attain large values thus spin cannot be classically explained. It is an exquisitely Quantum co developed to explain certain experimental observati

Also,
$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1.$$
$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0.$$

The Energy term is independent of spin Quantum numbe

$$\Rightarrow \quad \hat{H}|n\, l\, m_l\, m_s\rangle = \hat{H}|n\, l\, m_l\, -m_s\rangle.$$

$|n\, l\, m_l\rangle \Rightarrow$ Spatial Orbital.

$|n\, l\, m_l\, m_s\rangle \Rightarrow$ spin Orbital.

* Spin orbit coupling:

Now, from Zeeman's effect:

$$\vec{m}_l = \frac{-e}{2m_e}\vec{l} \Rightarrow m_l = \frac{-e}{2m_e}\hbar\,[l(l+1)]^{1/2} = -\beta_B[l(l+1)]^{1/2}$$

∴ similarly for $\vec{m}_s$ we can write,

$$\vec{m}_s = -\frac{g|e|}{2\,m_e}\vec{S} = -g\beta_B[s(s+1)]^{1/2}$$

g = Relativistic term. = 2.

Also,

$$|\vec{m}_{sz}| = -\frac{g|e|}{2m_e}S_z = \frac{-g e\hbar m_s}{2m_e} = -g m_s \beta_B$$

$$\therefore \left[m_{sz} = \pm\beta_B\right]$$

This matches the stern - Gerlach experimental results as the deviations from trajectory were $\pm\beta_B$.

Though, the spin (m_s) alone cannot affect the energy levels of the system, spin and Angular momentum coupling do affect it as evident from the anomalies of the Stern Gerlach experiment.

$$\therefore \hat{H} = \frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} + \underbrace{\xi(r)\,\vec{L}\cdot\vec{S}}_{\text{Spin orbit Interaction term.}}$$

$\xi(r)$ = Interactn func.

Thus, Hamiltonian gets a perturbation term. The Shrödinger now has to be solved by the perturbation theory solns.

$\hat{L}^2$ & $\hat{S}^2$ no longer commute with $\hat{H}$ after the interaction as the orbital Angular momentum and spin Angular momentum are no longer conserved independantly, only the total angular momentum remains conserved.

$$\hat{J}^2|jm_j\rangle = \hbar^2 j(j+1)|jm_j\rangle.$$

$$\therefore \left[\vec{J} = \vec{L} + \vec{S}\right] \Rightarrow \hat{J}_z|jm_j\rangle = \hbar m_j|jm_j\rangle.$$

Total m_j states possible:

$m_j \to m_s \to$ 2 states : $\pm\frac{1}{2}$

and

$m_l \to 2l+1$ states : $(-l, \ldots, 0, \ldots +l)$.

$\Rightarrow$ multiplicative rule $\Rightarrow$ Total $2\times(2l+1)$ possibilities

Two possibilities : $j = |l+s|$ or $|l-s|$.

Always $s = \left|\pm\frac{1}{2}\right|$.

$$m_j = (+j, j-1, j-2, \ldots, -j).$$

$\therefore\ l = 0 \longrightarrow j = \frac{1}{2} \to m_j = +\frac{1}{2}$, $m_j = -\frac{1}{2}$

$\therefore\ l = 1 \longrightarrow j = 3/2 \to 3/2,\ 1/2,\ -1/2,\ -3/2$

$\longrightarrow j = 1/2 \to 1/2,\ -1/2$

$\therefore\ l = 2 \longrightarrow j = 5/2 \to 5/2,\ 3/2,\ 1/2,\ -1/2,\ -3/2,\ -5/2$

$\longrightarrow j = 3/2 \to 3/2,\ 1/2,\ -1/2,\ -\frac{3}{2}$