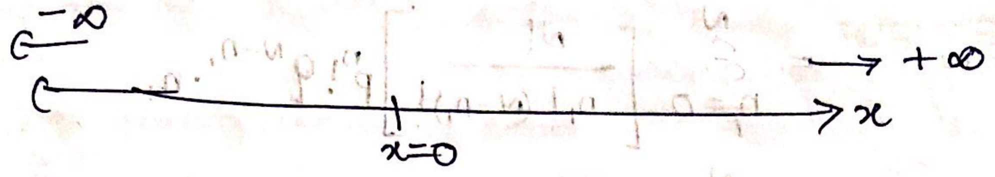
Mathematical Modeling.

Random Walk Problem: (1 Dimension)



→ A drunk starts out from $x=0$.
→ Each step is of equal length (l)
→ The direction of each step is completely independent of the preceding steps (random)
→ At each time, the probability of its being to the right is P, while the probability of its being to the left is Q

Question: After N steps, what is the probability that the man is located at a given distance ($x = ml$) from the origin? ($m>0 / m\leq 0$)

$n_1 \Rightarrow$ number of steps to the right $\qquad \dfrac{n!}{n_1!\, n_2!}$ $\qquad p+q=1$

$n_2 \Rightarrow$ number of steps to the left $\qquad pl - ql$

$$n_1 + n_2 = N$$

$\cancel{pl - (1-p)l}$

$\cancel{n(2p-l) = ml}$

$\cancel{m = (2p-1)n}$

$\cancel{= (p-q)n}$

$$m = n_1 - n_2 = n_1 - (N - n_2) = \underline{2n_1 - N}$$

Example: $\underbrace{N = 3,\ n_1 = 2,\ n_2 = 1}$

$$\left.\begin{array}{c} + + - \\ - + + \\ + - + \end{array}\right\} 3$$

Probability of taking n_1 steps to the right a total of N steps

$$W_N(n_1) = \frac{N!}{n_1!\, n_2!} \times p^{N_1} q^{N_2}.$$

$\langle\ \rangle$ = average

$\langle n_1 \rangle$ = average number of steps to the right.

$$\langle n_1 \rangle = \sum_{n_1=0}^{N} W_N(n_1)\, n_1$$

$n_1 + n_2 = N$

$$= \sum_{n_1=0}^{N} \left[\frac{N!}{n_1!\,(N-n_1)!}\right] p^{n_1} q^{N-n_1} \cdot n_1$$

$$= \sum_{n_1=0}^{N} {}^{N}C_{n_1}\, p^{n_1} q^{N-n_1} \cdot n_1$$

$(p+q)^N$

$1\, {}^{N}C_1 p^N + 2\, {}^{N}C_2$

$N\, {}^{N}C_N p^N$

$(p^{n_1} q^N)$

$(N-1) n_1$

<u>Hint:</u> use

$$n_1 p^{n_1} = p\frac{\partial}{\partial p}(p^{n_1})$$

$$= \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} \left(p\frac{\partial}{\partial p}(p^{n_1})\right) q^{N-n_1}$$

Interchange the order of summation & differential operation

$$= p\frac{\partial}{\partial p}\underbrace{\left[\sum_{n_1=0}^{N} \frac{N!}{n!(N-n_1)!} p^{n_1} q^{N-n_1}\right]}_{\text{binomial expression } (p+q)^N}$$

$$= p\frac{\partial}{\partial p}(p+q)^N.$$

$$= p \cdot N (p+q)^{N-1} \quad \left(\text{for arbitrary values of } p \,\&\, q\right)$$

[Special Case : $p+q=1$, where he has to take a step either right or left]

$$\langle n_1 \rangle = Np$$

$||^{ly}$

$$\langle n_2 \rangle = NQ = Nq$$

$$\langle m \rangle = \langle n_1 \rangle - \langle n_2 \rangle$$
$$= Np - Nq = N(p-q)$$

Mean Displacement $\equiv \langle m \rangle = N(p-q)$

(if $p=q$) ; $\langle m \rangle = 0$ (zero net displacement).

ink

→ why does the ink comes down? ← randomly walks down in 3D.

due to gravity, ink flows down

when ink is spilled in a cup of water

Ex: In a copper wire, $e^{\ominus}$ exhibit random walk property | thus the net current is zero. $\boxed{\langle m \rangle = 0}$.

$\sqrt{\dfrac{3 \times 8.314 \times 300}{28}}$

$$\langle m \rangle = \langle n_1 - n_2 \rangle$$

$$(\langle m \rangle)^2 = (\langle n_1 - n_2 \rangle)^2$$

$$\langle m^2 \rangle = \langle (n_1 - n_2)^2 \rangle$$

$(m - \langle m \rangle)^2$ ↗ similar to standard deviation.

$$\Delta m = m - \langle m \rangle$$

$$= n_1 - n_2 - \langle n_1 - n_2 \rangle$$

$$= 2n_1 - N - \langle 2n_1 - N \rangle$$

$$= 2(n_1 - \langle n_1 \rangle)$$

$$= 2(\Delta n_1)$$

$\Delta m = 2\Delta n_1$, where, $\Delta n_1 = n_1 - \langle n_1 \rangle$.

$\Delta n = n - \langle n \rangle$

$\Delta n^2 = n^2 - \langle n \rangle^2 - 2n\langle n \rangle$

$\langle \Delta n^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 - 2\langle n \rangle^2$

$= \langle n^2 \rangle - \langle n \rangle^2$

$\langle n^2 \rangle = NPQ + N^2P^2$

$\langle n \rangle = NP$

$\langle n \rangle^2 = N^2p^2$

$\langle \Delta n^2 \rangle = NPQ$

$$\langle (\Delta m)^2 \rangle = 4 \langle (\Delta n_1)^2 \rangle$$

$\langle (\Delta n_1)^2 \rangle$?

$$\Delta n_1 = n_1 - \langle n_1 \rangle$$

$$\Delta n_1^2 = (n_1 - \langle n_1 \rangle)^2$$

$$= n_1^2 + (\langle n_1 \rangle)^2 - 2 n_1 \langle n_1 \rangle$$

$$\langle \Delta n_1^2 \rangle = \langle n_1^2 \rangle + \langle n_1 \rangle^2 - 2 \langle n_1 \rangle^2$$

$$= \langle n_1^2 \rangle - (\langle n_1 \rangle)^2$$

$$<(\Delta n_1)^2> = <n_1^2> - (<n_1>)^2.$$

$$<n_1^2> = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} p^{n_1} \cdot q^{N-n_1} \cdot n_1^2.$$

$$= \sum_{n_1=0}^{N} {}^{N}C_{n_1} \cdot p^{n_1} \cdot q^{N-n_1} \cdot n_1^2.$$

Hint: $n_1^2 p^{n_1} = n_1 p \frac{\partial}{\partial p}(p^{n_1})$.

$$= \left(p\frac{\partial}{\partial p}\right)^2 p^{n_1} \qquad p\frac{\partial}{\partial p}\left(p\frac{\partial}{\partial p}\right)$$

$$n_1^2 p^{n_1} = \left(p\frac{\partial}{\partial p}\right)^2 p^{n_1}$$

$$<n_1^2> = \sum_{n_1=0}^{N} {}^{N}C_{n_1} \cdot (p^{n_1} \cdot n_1^2) \cdot q^{N-n_1}$$

$$= \sum_{n_1=0}^{N} {}^{N}C_{n_1} \cdot \left(p\frac{\partial}{\partial p}\right)^2 p^{n_1} \cdot q^{N-n_1}$$

$$= \left(p\frac{\partial}{\partial p}\right)^2 \underbrace{\sum_{n_1=0}^{N} {}^{N}C_{n_1} \cdot p^{n_1} \cdot q^{N-n_1}} \quad \Bigg\} \text{ interchange derivative \& summation.}$$

$$= \left(p\frac{\partial}{\partial p}\right)^2 (p+q)^{n_1}$$

$$= \cancel{p^2 n_1 (p+q)^{2(n_1-1)} (n_1-1)}$$

$$= \cancel{p^2 n_1 (n_1-1)}$$

$$= p\frac{\partial}{\partial p}\left[p\frac{\partial}{\partial p}(p+q)^{n_1}\right]$$

$$= p\frac{\partial}{\partial p}\left[p \cdot n_1 (p+q)^{n_1-1}\right]$$

$$= n_1 p \frac{\partial}{\partial p}\left(p(p+q)^{n-1}\right)$$

$$= n_1 p \cdot \left[(p+q)^{n-1} + (n-1)p(p+q)^{n_1-2}\right]$$

$$= n_1 p\left[1 + p(n_1-1)\right] = \cancel{n_1^2 p^2 - n_1 p^2 + n_1 p}$$

$= n_1 p[1 + n_1 p - p]$
$= n_1 p[q + n_1 p]$
$= n_1 pq + n_1^2 p^2$

$$\langle n_1^2 \rangle = n_1 pq + n_1^2 p^2.$$

$$\langle (\Delta n_1)^2 \rangle = \langle n_1^2 \rangle - (\langle n_1 \rangle)^2$$
$$= n_1 pq + n_1^2 p^2 - (n_1 p)^2$$
$$= n_1 pq$$

$$\Rightarrow \langle (\Delta m)^2 \rangle = 4 \langle (\Delta n_1)^2 \rangle$$
$$= 4NPQ.$$

$$\boxed{\langle (\Delta m)^2 \rangle = 4NPQ} \quad \text{if } p = q = 1/2$$

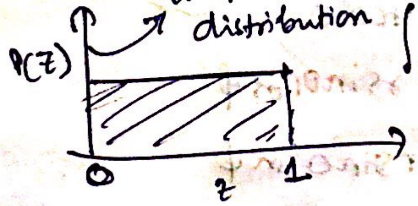
$$\boxed{\langle (\Delta m)^2 \rangle = N} \quad \boxed{t = N\Delta t}$$

* $\boxed{\langle x^2 \rangle \propto \text{time}}$ → random diffusive process

$\langle x^2 \rangle \propto N \propto$ time (Brownian movement/motion)

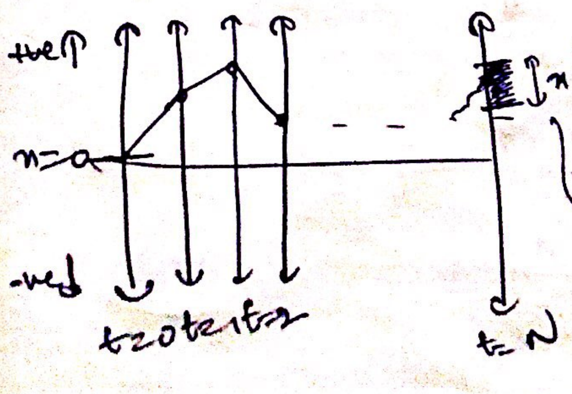
Coding it →

$0 \leq z \leq 1$



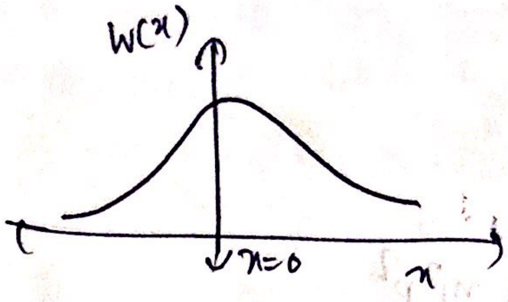
$$\int_0^1 P(z)\,dz = 1$$

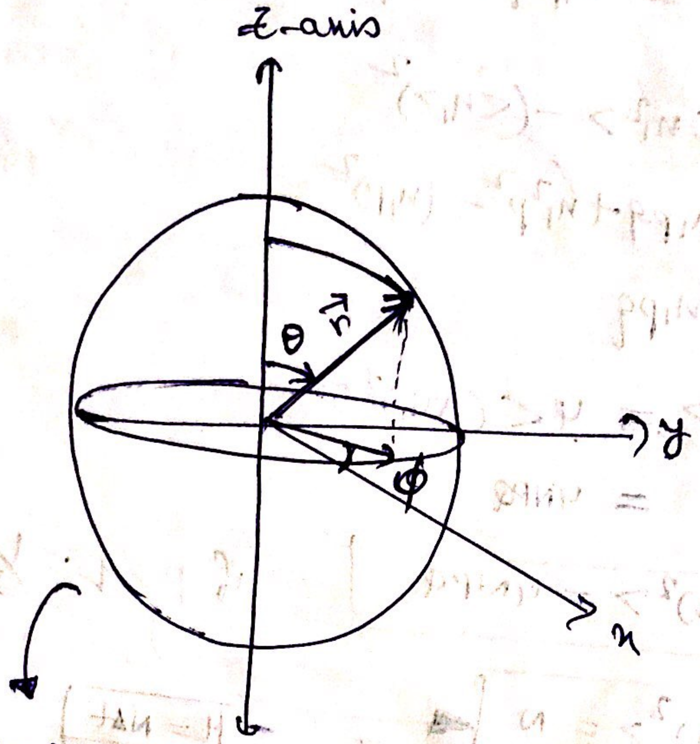
generate N random z values. ; if $z < 0.5 \Rightarrow x = x+1$
if $z \geq 0.5 \Rightarrow x = x-1$



Fluctuating trajectory.

→ how many trajectories hit a particular area of x?





Spherical Polar Co-ordinates –

$|\vec{r}| = r$

$\theta \rightarrow$ angle between the z axis & $\vec{r}$

$\phi \rightarrow$ angle between $\vec{r}_{xy}$ and x-axis.

$0 \leq \theta \leq \pi$

$0 \leq \phi \leq 2\pi$

$0 \leq r \leq \infty$

$z = r\cos\theta$

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

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

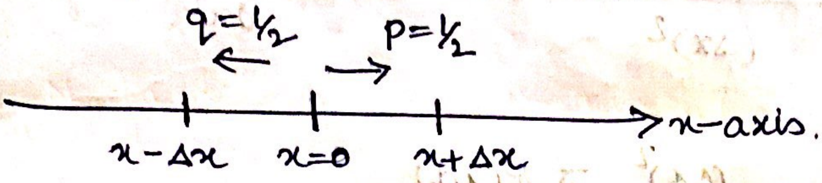
Diffusion Equation –

Aim :

① To derive the diffusion equation from the random walk method.

② Solving the diffusion equation.

1D Random Walk :



$\Delta t \Rightarrow$ time step

$\Delta x \Rightarrow$ step length.

$P(x,t) \longrightarrow$ Probability that the random walker is at x at time t

At the next instant;

$$P(x, t+\Delta t) = P(x-\Delta x \to x)\, P(x-\Delta x, t) + P(x+\Delta x \to x)\, P(x+\Delta x, t).$$

For any unbiased random walk –

$$P(x-\Delta x \to x) = 1/2 \quad \to p$$

$$P(x+\Delta x \to x) = 1/2 \quad \leftarrow q$$

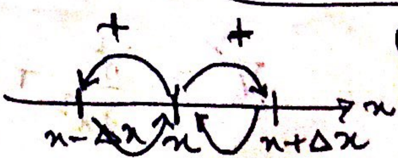
$$P(x, t+\Delta t) = \frac{1}{2} P(x-\Delta x, t) + \frac{1}{2} P(x+\Delta x, t).$$

Subtract $P(x,t)$ from both the sides.

$$P(x, t+\Delta t) - P(x,t) = \frac{1}{2}\left[P(x-\Delta x, t) - 2P(x,t) + P(x+\Delta x, t)\right]$$

Divide both sides of the equation by Δt & $(\Delta x)^2$

$$\frac{P(x, t+\Delta t) - P(x,t)}{\Delta t \cdot (\Delta x)^2} = \frac{1}{2\Delta t}\left[\frac{P(x-\Delta x, t) - 2P(x,t) + P(x+\Delta x, t)}{(\Delta x)^2}\right]$$



$\Delta t \to 0$; $\Delta x \to 0$. $\Rightarrow$ Continuous process.

$$\frac{P(x, t+\Delta t) - P(x,t)}{\Delta t \cdot \cancel{(\Delta x)^2}} \equiv \frac{\partial P(x,t)}{\partial t}$$

Since P is function of both x & t partial differentiation is the option

$$\frac{P(x-\Delta x, t) - 2P(x,t) + P(x+\Delta x, t)}{(\Delta x)^2} \equiv \frac{\partial^2 P(x,t)}{\partial x^2}.$$

$$\frac{\partial P(x,t)}{\partial t} = \underbrace{\frac{(\Delta x)^2}{2 \cdot \Delta t}}\cdot \frac{\partial^2 P(x,t)}{\partial x^2}.$$

$$D \equiv \frac{(\Delta x)^2}{2\Delta t} \Longrightarrow \text{diffusion constant.}$$

* $$\boxed{\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2}} \Rightarrow \text{DIFFUSION EQUATION}$$

wrt time — wrt distance.

3D Motion —

$$\frac{\partial P(x,y,z,t)}{\partial t} = D_x \frac{\partial^2 P(x,y,z,t)}{\partial x^2} + D_y \frac{\partial^2 P(x,y,z,t)}{\partial y^2} + D_z \frac{\partial^2 P(x,y,z,t)}{\partial z^2}.$$

for Isotropic diffusion →

$$D_x = D_y = D_z = D.$$

$$\frac{\partial P(x,y,z,t)}{\partial t} = D\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] P(\vec{r},t).$$

$$\vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

operator.

function — $f(x,y,z)$

gradient of a function : $\vec{\nabla} f(x,y,z)$.

in 3D, it has a direction. (towards the Maximum of a function).

$$\hat{i}\frac{\partial}{\partial x} f(x,y,z) + \hat{j}\frac{\partial}{\partial y} f(x,y,z) + \hat{k}\frac{\partial}{\partial z} f(x,y,z).$$

$$\nabla^2 = \vec{\nabla}.\vec{\nabla}$$

$$\Rightarrow \frac{\partial}{\partial t} P(x,y,z,t) = D.\nabla^2.P(\vec{r},t).$$

*
$$\boxed{\frac{\partial}{\partial t} P(\vec{r},t) = D.\nabla^2 P(\vec{r},t)}$$
(isotrophic diffusion)

Calculate $P(x,t)$: we need to solve the diffusion equation

initial condition: $t=0$; $P(x=0, t=0) = 1$

$P(x, t=0) = 0$ | for $x \neq 0$.

→ we need to use the fourier transformation to solve the diffusion equation.

Fourier Transformation — $P(x,t)$.

fourier tranformation of P.

$$F(k,t) = \int_{-\infty}^{\infty} P(x,t).\underbrace{e^{ikx}}_{\text{kernel}}.dx \equiv \tilde{P}$$

kphase. change of phase. xphase

$$P(x,t) = \int_{-\infty}^{\infty} F(k,t).e^{-ikx}.dk.$$

Properties of Fourier transformation –

① $\widetilde{\dfrac{\partial P}{\partial t}} = \dfrac{\partial}{\partial t}(\widetilde{P})$

use ;
$\propto$ product Rule →
$\int v u = u \int v - \int u' \int v$

② $\widetilde{\dfrac{\partial P}{\partial x}} = -ik\,\widetilde{P}$

③ $\widetilde{\dfrac{\partial^2 P}{\partial x^2}} = (-ik)^2\,\widetilde{P}$

Take the fourier transformation on both sides of the diffusion equation →

$$\widetilde{\frac{\partial P}{\partial t}} = \boxed{D\,\widetilde{\frac{\partial^2 P}{\partial x^2}}}$$

$$\frac{\partial \widetilde{P}}{\partial t} = -Dk^2\widetilde{P}$$

$$\frac{\partial}{\partial t}\widetilde{P} = -Dk^2\widetilde{P}$$

$\frac{\partial}{\partial t}\widetilde{P} = -Dk^2\widetilde{P}$

$\frac{1}{\widetilde{P}}\frac{\partial}{\partial t}\widetilde{P} = -Dk^2$

$\log\widetilde{P} = -Dk^2t$

$\widetilde{P} = ce^{-Dk^2t}$

$$\frac{1}{\widetilde{P}}\frac{\partial \widetilde{P}}{\partial t} = -Dk^2$$

$$\log\widetilde{P} = -Dk^2t$$

$$\widetilde{P} = ce^{-Dk^2t}$$

$$\widetilde{P} = ce^{-Dk^2t}.$$

$$\therefore \boxed{\widetilde{P} = \underbrace{c}_{\text{unknown constant}}e^{-Dk^2t}}$$

$\widetilde{P}(x=0, t=0) = 1$

$$\tilde{P} = \int_{-\infty}^{\infty} P(x=0, t=0)\, e^{ik(x=0)}\, dx$$

$P(x=0,t=0) = 1$.

$$= 1$$

Delta function:

$\delta(x - x_0) = 1$; $x = x_0$

$= 0$; $x \neq x_0$

$$f(x_0) = \int_{-\infty}^{\infty} f(x)\, \delta(x - x_0)\, dx$$

$\tilde{P}(x=0, t=0) = 1$

for any value other than x_0, $\delta(x - x_0) = 0$

So; the value of the derivative in any set of values $(-\infty, \infty)$ = $f(x_0)$

at $t = 0$;

$$\tilde{P} = c \cdot e^{-Dk^2 t} = c$$

$$\boxed{1 = c}$$

*

$$\boxed{\tilde{P} = e^{-Dk^2 t}}$$

$$P = \int_{-\infty}^{\infty} \tilde{P}\, e^{-ikx}\, dk$$

$$= \int_{-\infty}^{\infty} e^{-Dk^2 t}\, e^{-ikx}\, dk$$

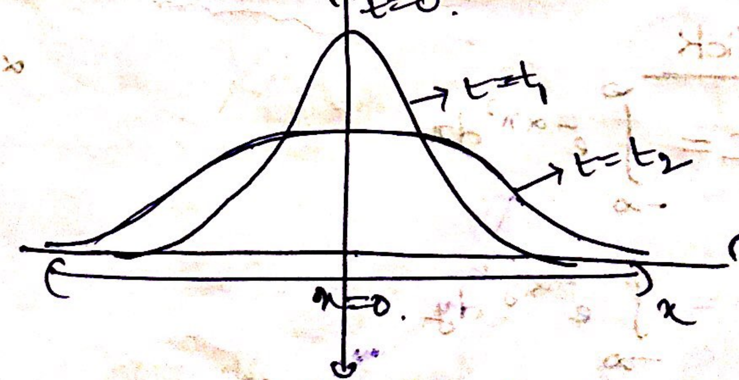
$$= \int_{-\infty}^{\infty} e^{-\left(Dk^2 + \frac{ikx}{t}\right)t}\, dk$$

$$= \frac{1}{\sqrt{4\pi D t}} \cdot e^{-\frac{x^2}{4Dt}}$$

$P(x,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{x^2}{4Dt}}$

Diffusion Equation :

$$\boxed{P(x,t) = \frac{1}{\sqrt{4\pi D t}} \cdot e^{-\frac{x^2}{4Dt}}}$$



$0 < t_1 < t_2 < t_\infty$

$t = t_\infty$ → uniform state → all the points have the same probability after long time.

$\langle x \rangle = 0.$

$\langle x^2 \rangle = 2Dt.$

- Ink in water vs ink in honey — water ✓ faster

→ Ink property (chemistry) doesn't change but the nature of the environment changed.

- Ink in water vs Ink in ice

→ Though ice and water have same chemical nature but still ink diffuses faster in water as "D" depends not only on external environment but also various other properties.

$$\boxed{P(x,t) = \int_{-\infty}^{\infty} e^{-ikx} \cdot e^{-Dk^2 t}\, dk.}$$

$$= \int_{-\infty}^{\infty} e^{-\left(Dk^2 t + ikx + \frac{i^2 x^2}{4Dt}\right) + \frac{i^2 x^2}{4Dt}}\, dk.$$

$$= \int_{-\infty}^{\infty} e^{-\left(Dk^2 t + ikx + \frac{i^2 x^2}{4Dt}\right)} \cdot e^{\frac{-x^2}{4Dt}}\, dk$$

$$= e^{-\frac{x^2}{4Dt}} \int_{-\infty}^{\infty} e^{-\left(\sqrt{Dt}\,k + \frac{ix}{2\sqrt{Dt}}\right)^2} dk$$

$P(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$

$$= e^{-\frac{x^2}{4Dt}} \int_{-\infty}^{\infty} e^{-\frac{(2Dt\,k + ix)^2}{4Dt}}\, dk$$

$$= \frac{e^{-\frac{x^2}{4Dt}}}{2Dt} \int_{-\infty}^{\infty} e^{-\alpha y^2}\, dy$$

$y = 2Dt\,k + ix$

$dy = 2Dt\,dk$

$dk = \frac{dy}{2Dt}$

$\alpha = 1/4Dt$

Feynman's Trick

$$I = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$$

$$= \int_{-\infty}^{\infty} e^{-\alpha y^2} dy$$

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\alpha(x^2 + y^2)}\, dy.\, dx.$$

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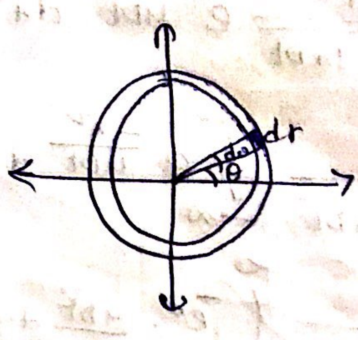
Cartesian to Polar Coordinate Space —

$x^2+y^2=r^2$

$$\underbrace{dx \cdot dy}_{\text{Area}} = r \cdot dr \cdot d\theta$$

$r \to [0 \to \infty]$



$$I^2 = \underbrace{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}}_{} e^{-\alpha r^2} \cdot r\,dr\,d\theta.$$

$-\infty \; -\infty \rightarrow$ limits change

$$I^2 = \int_0^{\infty}\int_0^{2\pi} \underbrace{e^{-\alpha r^2} \cdot r\,dr\,d\theta}_{\text{No } \theta \text{ involved}}.$$

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

$$= 2\pi \int_0^{\infty} e^{-\alpha r^2} \cdot r\,dr \qquad r^2 = t$$

$$2r\,dr = dt$$

$$= \pi \int_0^{\infty} e^{-\alpha t}\,dt \qquad r\,dr = \frac{dt}{2}$$

$$= \pi \left[\frac{-e^{-\alpha t}}{\alpha}\right]_0^{\infty} = -\frac{\pi}{\alpha}\left[\frac{1}{\infty} - \frac{1}{1}\right] = \frac{\pi}{\alpha}$$

$I^2 = \pi/\alpha$

$I = \sqrt{\pi/\alpha} = \sqrt{\pi/\tfrac{1}{4Dt}} = \sqrt{4\pi Dt}$

$$P(x,t) = \frac{e^{-\frac{x^2}{4Dt}}}{\cancel{\quad}} \times \frac{1}{\cancel{\sqrt{\pi}}\,2\cancel{Dt}} \times \sqrt{\frac{\pi}{1} \times 4Dt}.$$

$$= 1\Big/\sqrt{\pi 4Dt}\; e^{-\frac{x^2}{4Dt}} = \frac{1}{\sqrt{4\pi Dt}}\, e^{-\frac{x^2}{4Dt}}$$

$\int\int e^{-x^2-y^2} dx\,dy$

$\int_0^{\infty}\int_0^{2\pi} e^{-r^2} \cdot r \cdot dr \cdot d\theta$ — No θ in

$\int_0^{\infty} e^{-\alpha r^2} r\,dr$

$\pi \int_0^{\infty} e^{-\alpha t} dt = -\frac{\pi}{\alpha}[0-1]$

$= \pi/\alpha$

$I^2 = \pi/\alpha$

$I = \sqrt{\pi/\alpha}$

$= \sqrt{4\pi Dt}$

Calculate —

$\langle x \rangle \Rightarrow$ Mean displacement $= \int_{-\infty}^{\infty} x\,P(x,t)\,dx.$

$\langle x^2 \rangle \Rightarrow$ Mean square displacement $= \int_{-\infty}^{\infty} x^2\,P(x,t)\,dx.$

$$= \int_{-\infty}^{\infty} x \cdot \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}} dx .$$

$$= \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} x . e^{\frac{-x^2}{4Dt}} dx .$$

$$\frac{+x^2}{4Dt} = y$$

$$= \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} e^{-y} \cdot \frac{4Dt}{+2} dy$$

$$\frac{+2x}{4Dt} dx = dy$$

$$x dx = \frac{4Dt\, dy}{+2}$$

$$= \frac{4Dt}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} e^{-y} dy$$

$$= \sqrt{\frac{4Dt}{\pi}} \left[e^{-y} \right]_{-\infty}^{\infty} = \sqrt{\frac{4Dt}{\pi}} \left[0 \right]$$

$$\langle x^2 \rangle \Rightarrow \int_{-\infty}^{\infty} P(x,t) . x^2 dx$$

$$= \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi D t}} . e^{-\frac{x^2}{4Dt}} . x^2 dx$$

$$= \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$$

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

$$-\frac{\partial I}{\partial \alpha} = \int_{-\infty}^{\infty} + x^2 e^{-\alpha x^2} dx = \frac{1}{2} \left(\pi\right)^{1/2} . \alpha^{-3/2}$$

$$= \frac{1}{\sqrt{4\pi D t}} \times \frac{\sqrt{\pi}}{2} \times (4Dt)^{3/2}$$

$$= \frac{1}{2(4Dt)^{1/2}} . (4Dt)^{3/2} = \frac{4Dt}{2}$$

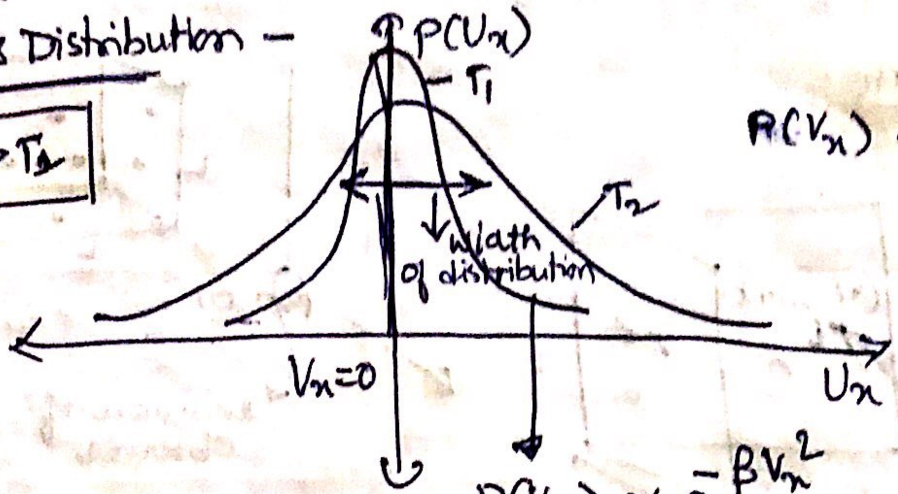
$$= 2Dt$$

$$\langle x^2 \rangle = 2Dt$$

Mean Square displacement varies linearly with time

Maxwell's Distribution –

$\boxed{T_2 > T_1}$



$$P(V_x) \propto e^{-\frac{1}{2}\frac{mV_x^2}{k_BT}}$$

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

k_B → Boltzmann's Constant

$$P(V_x) \propto e^{-\beta V_x^2}$$

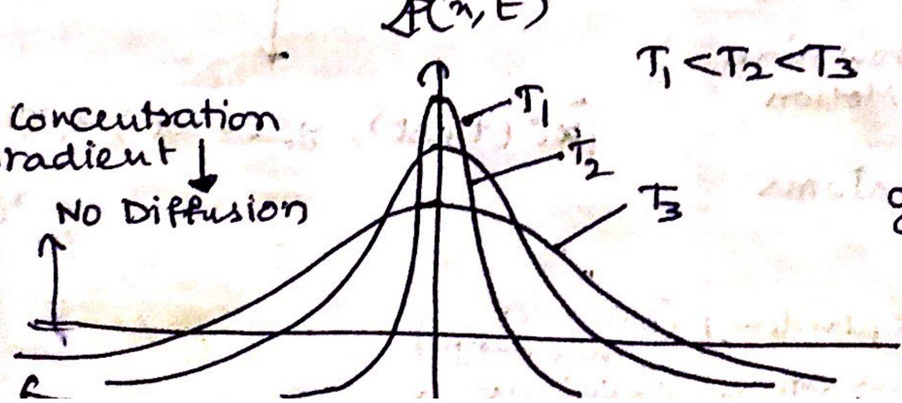
this represents the width of distribution.

$$P(V_x) = \sqrt{\frac{\beta}{\pi}}\, e^{-\beta V_x^2}$$

$$\frac{1}{2}m[V_x^2+V_y^2+V_z^2] \Leftarrow \langle V_x^2\rangle \propto T \quad \left(\text{as } \beta = \frac{m}{2k_BT}\right)$$

$$= \frac{1}{2}m\left[\langle V_x^2\rangle + \langle V_y^2\rangle + \langle V_z^2\rangle\right]$$

$$= \frac{1}{2}m[kT+kT+kT] = \frac{3}{2}mkT = \underline{\frac{3}{2}k_BT}$$



$T_1 < T_2 < T_3$

No concentration Gradient → No Diffusion

Ink molecules get diffused and stop forever.

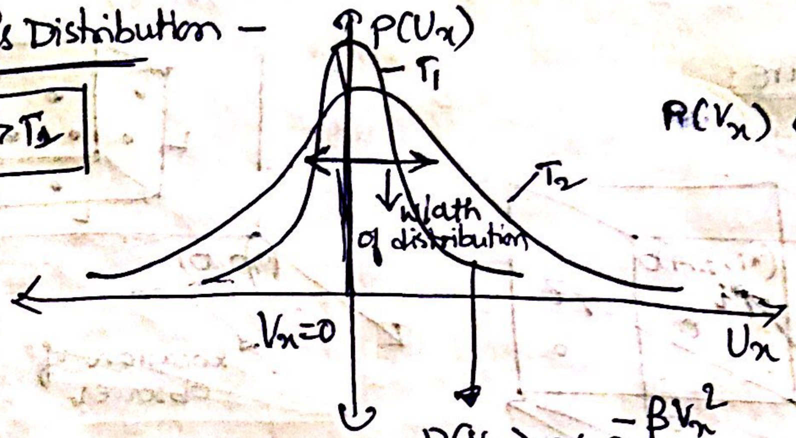
↑

Normalisation constant.

Probability distribution of gas molecules (velocity):

Maxwell's Distribution –

$\boxed{T_2 > T_1}$



$$P(V_x) \propto e^{-\frac{1}{2}\frac{mV_x^2}{k_B T}}$$

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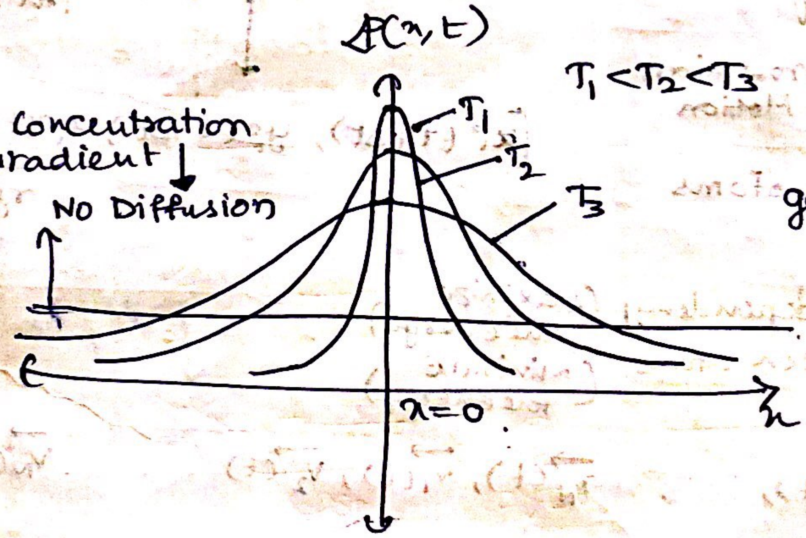
$T_1 < T_2 < T_3$

No concentration Gradient ↓ No Diffusion



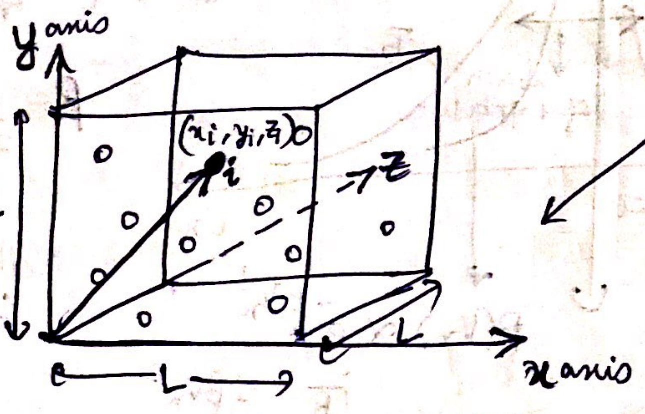
Ink molecules get diffused and stop forever.

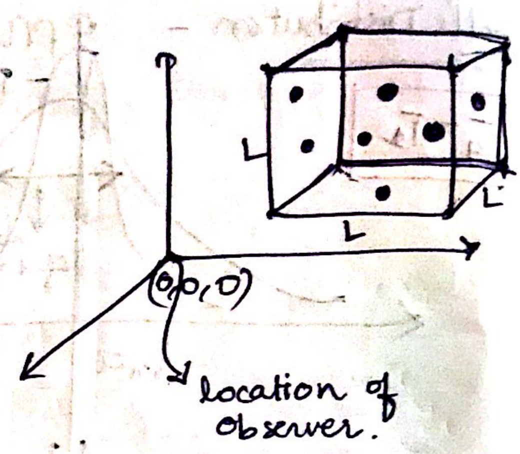
↑ Normalisation constant

$$\langle x^2\rangle = 2Dt$$

Microscopic or atomistic Model:

Detailed Picture:





Volume of the system $= L^3$ where $0 \leq L < \infty$

For an ith particle: $0 \leq x_i^o \leq L$ & $N \rightarrow$ no. of atoms in the system.

$0 \leq y_i^o \leq L$

$0 \leq z_i^o \leq L$

$(x_i^o(t), y_i^o(t), z_i^o(t)) \equiv \vec{r}_i^o($ — Position of the ith atom at time "t"

after time Δt

$[x_i^o(t+\Delta t), y_i^o(t+\Delta t), z_i^o(t+\Delta t)] = \vec{r}_i^o(t+\Delta t)$

Movement of atom
↓
proved by Brownian Motion.

Why do the atoms move?

* Temperature dependency (Maximize the energy)
* Forces between atoms (Minimize the energy).

$H(\vec{r}_1(t), \vec{r}_2(t), \ldots \vec{r}_N(t), \vec{v}_1(t), \vec{v}_2(t) \ldots \vec{v}_N(t))$

$\vec{v}_i(t)$ = Velocity of the ith atom at a time t.

$\vec{r}_i(t)$ = Position of the atom at time t.

→ Total Energy of the system at a time "t".

$\{\vec{r}(t)\} = (\vec{r}_1(t), \vec{r}_2(t), \ldots \ldots \vec{r}_N(t))$

$\{\vec{v}(t)\} = (\vec{v}_1(t), \vec{v}_2(t) \ldots \ldots \vec{v}_N(t))$

$$H(\{\vec{r}\}, \{\vec{v}\}) = U(\{\vec{r}\}) + K(\{\vec{v}\})$$

$U(\{\vec{r}\}) \downarrow$ Potential Energy, $K(\{\vec{v}\}) \downarrow$ Kinetic Energy.

· Kinetic Energy of the system $\Big\} = \sum_{i=1}^{N} \frac{1}{2} \times m \times \vec{v}_i^{\,2} = K(\{\vec{v}\})$.

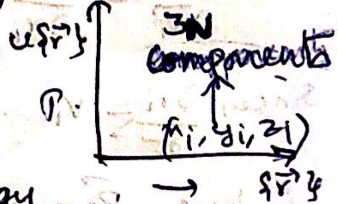
case 1:

$U\{\vec{r}\} = 0. \rightarrow$ ideal gas.

force on atom i at time t $\Big\}$ $\vec{F}_i(t) = -\left[\hat{i}\frac{\partial U(\{\vec{r}\})}{\partial x_i} + \hat{j}\frac{\partial U(\{\vec{r}\})}{\partial y_i} + \hat{k}\frac{\partial U\{\vec{r}\}}{\partial z_i}\right]$

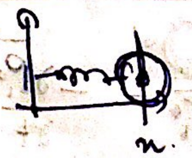
$$= -\vec{\nabla}_i U(\{\vec{r}\})$$

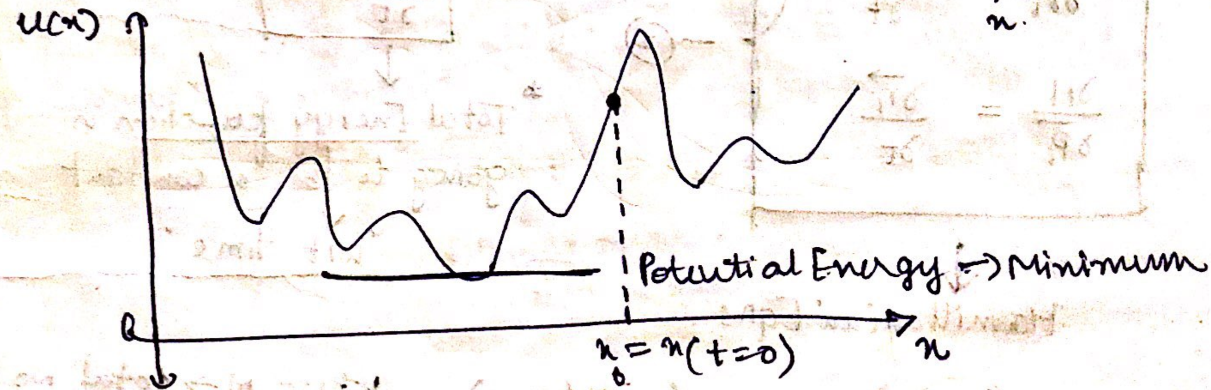
$$\vec{F}_i(t) = -\vec{\nabla}_i U(\{\vec{r}\})$$



* atoms try to have minimum potential energy.

$\downarrow$ not only atoms, any huge celestial bodies also (planets, galaxies)





assume.. kinetic energy = 0 [burner is off]
kinetic energy ≠ 0 [burner is on].

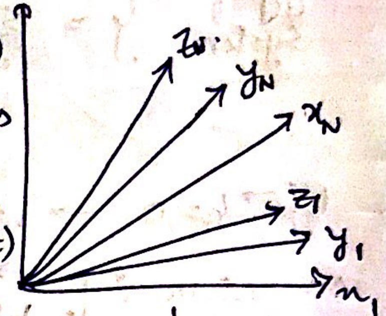
How does H change with time??

$$\frac{dH(\{\vec{r}\}, \{\vec{v}\})}{dt}$$

$U(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3 \ldots \ldots x_N, y_N, z_N)$

$\downarrow$

plotting $U(\{\vec{r}\})$



$\downarrow$

3N+1 dimensional hyper space.

$\frac{d}{dt} H(\{\vec{r}\}, \{\vec{v}\})$

$\downarrow$

after n steps

$t=0$	$t=\Delta t$	$t=2\Delta t$	...	$t=n\Delta t$
$H(0)$	$H(\Delta t)$	$H(2\Delta t)$	...	$H(n\Delta t)$

$$= \sum_{i=1}^{N} \frac{\partial H}{\partial \vec{r_i}} \cdot \frac{\partial \vec{r_i}}{\partial t} + \frac{\partial H}{m \partial \vec{v_i}} \cdot \frac{m \partial \vec{v_i}}{\partial t} \quad \text{— (1)}$$

here; $\frac{\partial H}{\partial \vec{r_i}} = \frac{\partial H}{\partial x_i} \cdot \frac{\partial x_i}{\partial t} + \frac{\partial H}{\partial y_i} \cdot \frac{\partial y_i}{\partial t} + \frac{\partial H}{\partial z_i} \cdot \frac{\partial z_i}{\partial t}$

Since; $\frac{\partial r_i}{\partial t} = v_i \qquad \frac{m \partial v_i}{\partial t} = \vec{F_i} = \frac{\partial \vec{P_i}}{\partial t}$

here $\vec{P_i} = m\vec{v_i}$

$\downarrow$

momentum of atom i.

$$\boxed{\begin{aligned} \frac{\partial H}{\partial \vec{r_i}} &= -\frac{\partial \vec{P_i}}{\partial t} \\ \frac{\partial H}{\partial \vec{P_i}} &= \frac{\partial \vec{r_i}}{\partial t} \end{aligned}} \quad \text{— (2)}$$

$\downarrow$

Hamiltonian's Eqns.

isolated systems

$\uparrow$

On substituting (2) in (1):

$$\boxed{\frac{\partial H}{\partial t} = 0}$$

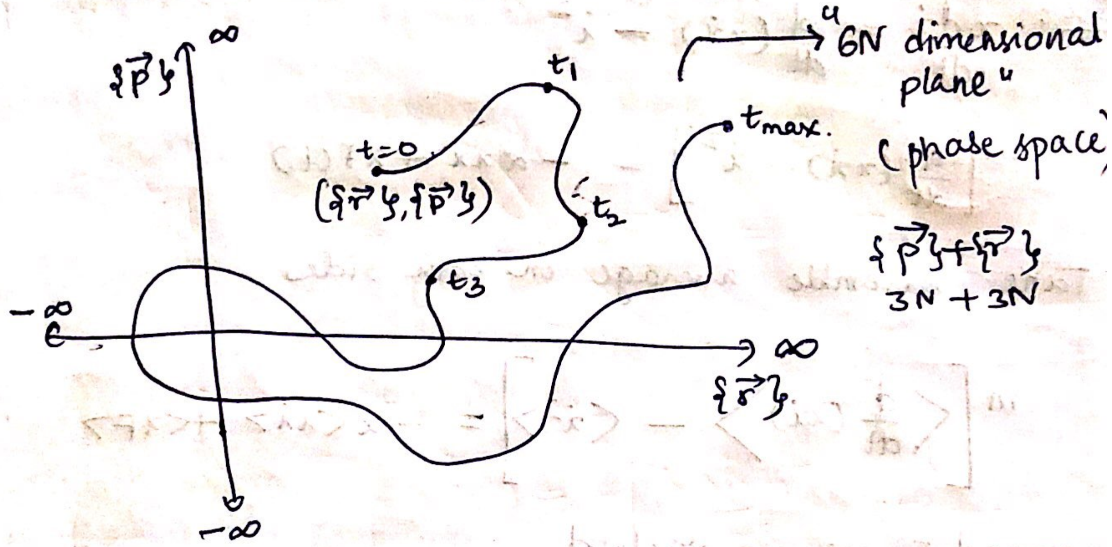
$\downarrow$

* Total Energy function is going to be a constant "wrt time"

$$\begin{pmatrix} F_{x,1} \\ F_{y,1} \\ F_{z,1} \\ F_{x,2} \\ F_{y,2} \\ F_{z,2} \\ \vdots \\ F_{x,N} \\ F_{y,N} \\ F_{z,N} \end{pmatrix} = \begin{pmatrix} -\partial H/\partial x_1 \\ -\partial H/\partial y_1 \\ -\partial H/\partial z_1 \\ -\partial H/\partial x_2 \\ -\partial H/\partial y_2 \\ -\partial H/\partial z_2 \\ \vdots \\ -\partial H/\partial x_N \\ -\partial H/\partial y_N \\ -\partial H/\partial z_N \end{pmatrix}$$

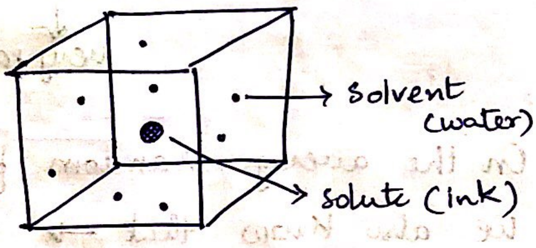
3N Components

where $N \to$ total no. of atoms in the system.



LANGEVIN'S EQUATION —

Equations of motion of the solute :



$$m\frac{d\vec{v}}{dt} = \vec{F}_{internal} + \cancel{\vec{F}_{external}}$$

$\vec{F}_{external} \to$ 0 (assume).

$$\vec{F}_{internal} = \vec{F}_{damping} + \vec{F}_{random}$$

$\vec{F}_{damping} + \vec{F}_{random} \to$ absence of random force

For the sake of simplicity, we can consider the problem in 1-dimension.

$$m\frac{dv}{dt} = -\alpha v + F(t)$$

$\alpha \to$ (Positive number) Friction constant

$F(t) \to$ Rapidly fluctuating force (noise).

$$v \equiv \frac{dx}{dt} = \dot{x}$$

$$\frac{dv}{dt} = \frac{d^2x}{dt^2} = \frac{d}{dt}(\dot{x}) = \ddot{x}$$

(1)
$$m\frac{d\dot{x}}{dt} = -\alpha\dot{x} + F(t).$$

multiply x on both the sides.

$$mx\frac{d\dot{x}}{dt} = -\alpha x\dot{x} + xF(t)$$

use: $x\frac{d\dot{x}}{dt} = \frac{d}{dt}(x\dot{x}) - \dot{x}^2$

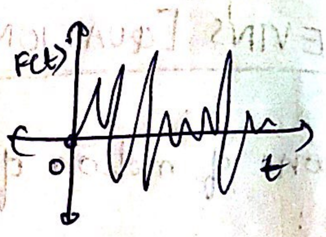
$$m\left[\frac{d}{dt}(x\dot{x}) - \dot{x}^2\right] = -\alpha x\dot{x} + xF(t).$$

Take ensemble average on both sides

$$m\left[\left\langle \frac{d}{dt}(x\dot{x})\right\rangle - \langle \dot{x}^2\rangle\right] = -\alpha\langle x\dot{x}\rangle + \langle xF\rangle$$

x and F are uncorrelated.

$$\langle xF\rangle = \langle x\rangle \underset{\text{very random}}{\underbrace{\langle F\rangle}} = 0.$$



On the average, random forces dont play any role.

We also know that $\rightarrow$ $\underbrace{\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}K_BT.}_{\text{Equipartition Theorem}}$

~~Eleeyg~~

$\rightarrow$ $m\left\langle\frac{d}{dt}(x\dot{x})\right\rangle - K_BT = -\alpha\langle x\dot{x}\rangle$

$\rightarrow$ $m\frac{d}{dt}\langle x\dot{x}\rangle - K_BT = -\alpha\langle x\dot{x}\rangle$

$$m.\frac{d}{dt}\langle x\dot{x}\rangle = K_BT - \alpha\langle x\dot{x}\rangle$$

$\langle xy\rangle = \iint xy\,P(x,y)d$

if x,y are statistic independent (uncorr

$P(x,y) = P(x).P(y$

$\langle xy\rangle = \int_x xP(x)dx\,.\int_y yP(y$

$= \langle x\rangle\langle y\rangle$

$$\frac{d}{dt}\langle y\rangle = \frac{d}{dt}\left(\frac{1}{N}\sum_{k=1}^{N} y_k(t)\right)$$

$$= \frac{1}{N}\sum_{1}^{N}\frac{d}{dt}y_k(t)$$

$$\frac{d}{dt}\langle x\dot{x}\rangle = \frac{K_BT}{m} - \frac{\alpha}{m}\langle x\dot{x}\rangle$$

define; $\Gamma = \frac{\alpha}{m}$

<u>Solve</u>; $$\langle x\dot{x}\rangle = ce^{-\Gamma t} + \frac{k_BT}{\alpha}$$

<u>Use</u>: $$\langle x\dot{x}\rangle = \frac{1}{2}\frac{d}{dt}(x^2)$$

$$\frac{1}{2}\cdot\frac{d}{dt}(x^2) = ce^{-\Gamma t} + \frac{k_BT}{\alpha}$$

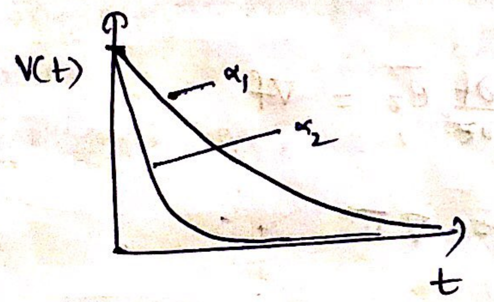
use the initial condition : at time $t=0, x=0$.

$t=0$;
$$c = -\frac{k_BT}{\alpha}.$$

$$\langle x^2\rangle = \frac{2k_BT}{\alpha}\left[t - \frac{(1-e^{-\Gamma t})}{\Gamma}\right]$$

$$\frac{dV}{dt} = -\frac{\alpha}{m}V$$

* Damping coeffient decreases with time whereas increases with temperature.



$\alpha_2 >> \alpha_1$

<u>Limiting cases:</u>

$$\Gamma t - \frac{1}{2}\Gamma^2 t^2$$

<u>case1</u> -

$$e^{-\Gamma t} = 1 - \Gamma t + \frac{1}{2}\Gamma^2 t^2 + \ldots$$

$$\langle x^2\rangle \cong \frac{k_BT}{\alpha}\Gamma t^2$$ (all higher powers of t are neglected).

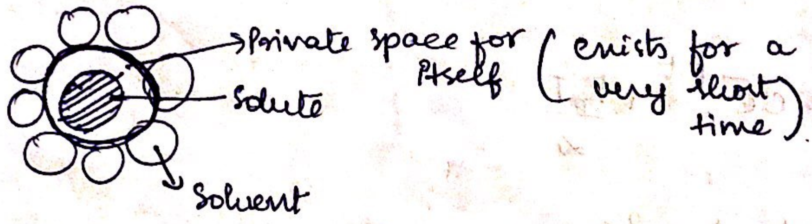
Short time dynamics.

<u>Case</u>: Free Particle (No force)

$$\frac{d^2x}{dt^2} = 0 \Rightarrow \frac{dx}{dt} = c_1 \Rightarrow x = c_1 t + c_2, \quad c_2 = 0 \text{ at } t=0, x=0$$

$$x = c_1 t$$

$\langle x^2 \rangle = c^2 t = Rt$



Case 2: Long time dynamics.

$\Gamma t \gg 1$

$t \gg \frac{1}{\Gamma}$

$e^{-\Gamma t} \longrightarrow 0.$

exponentially large.

$\langle x^2 \rangle = \frac{2 k_B T}{\alpha} t$

From the diffusion eq^n.

$\langle x^2 \rangle = 2Dt$

$\Rightarrow \boxed{D = \frac{k_B T}{\alpha}}$

$\langle x^2 \rangle \propto t \longrightarrow$ Linear dependence.

only for longtime case.

Gradient:

$$\text{grad} f = \frac{\partial f}{\partial x}\vec{e_x} + \frac{\partial f}{\partial y}\vec{e_y} + \frac{\partial f}{\partial z}\vec{e_z} = \nabla f$$

$$\text{div}\,\vec{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = \nabla \cdot \vec{v}$$

Laplace.

Assignment 2: Problem: 1.16, 1.18, 1.23, 1.24, 1.26

↓

Fundamentals of statistical thermal physics – F. Re

PROJECT 1 : Project Questions – (written + video) – 20/9/17

→ How does the survival probability of the rat vary with time?

→ Does the survival probability depend on:

ⓐ L of the square

ⓑ r of the sphere?

Derive the relationship

→ Can you determine the limiting value of the survival probability when the step length is infinitesimally small and the number of steps is sufficiently large?

(①,②,③ should be solved analytically)

→ Solve all the above problems computationally.

PROJECT 2 : Oxygen transport through myoglobin.

→ Using a spherical galton's board model, investigate the transport (for ex., mean displacement and mean square displacement of a spherical particle (representing an oxygen molecule) from the surface to the center (representing the binding site of the protein) of the sphere (representing a protein)).

Matter → bio, nonbio } building blocks ⇓ atoms.

Nature –

1. Stability
2. Symmetry → Diversity
3. Quantisation. (fixation of the object)
4. Homogeneity

} → all these factors help in understanding the "ATOM" → why understand → To understand the bulk property, you need to go to the deeper layers.

Complexity in nature

To understand Atoms, people developed "Model" → hypothesis, Theory, Law.

"Model" → simplest representation.

Atomic Models →

- Plum pudding model – J.J. Thompson
- Rutherford model
- Bohr's theory. → Quantisation of Angular Momentum.

  $mvr = \frac{nh}{2\pi}$, $n = 1, 2, \ldots \infty$

  explained
  - stability of atom
  - spectrum of H atom. $\bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$
- Sommerfeld → "Ellipse" = $\boxed{n = n_r + n_\phi}$ → $\boxed{n = n_r + n_\phi}$

Relativity theory → $m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$ } when a particle moves with a velocity comparable to that of light.

- Vector Atom Model
- Wave Mechanical Model.

Exercise –

→ Using bohr's theory, find the frequencies of all spectral lines (Lymann, Balmer, Paschen, Brackett, Pfund)

→ Allowed angles for "f" orbital using Vector Atom Model (possible orientations) –.

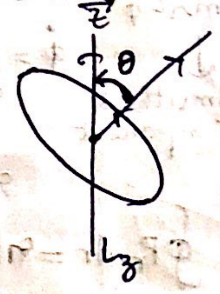
Scanned by CamScanner

Vector Atom Model →

(In bohr's theory, due to 'n', there's only one degree of freedom) and only "magnitude" is quantised.

Direction of Orbital is also quantized.

Rotating Orbital →



$\vec{L}$ (angular momentum associated)

$L_z = L\cos\theta$

$\cos\theta = \frac{L_z}{L}$ — L_z → z-component of total angular momentum; L → Total angular momentum

$L = \frac{lh}{2\pi}$ (allowed values of l →
$n=1,\ l=0.$
$n=2,\ l=1,0.$
$n=3,\ l=2,1,0.$)

modified

$L = \sqrt{l(l+1)}\,\frac{h}{2\pi}$

$= \sqrt{l(l+1)}\,\hbar$

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

$L_z = m_l \hbar$

$\cos\theta = \frac{m_l\hbar}{\sqrt{l(l+1)}\,\hbar} = \frac{m_l}{\sqrt{l(l+1)}}$ } Based on the values of l, m_l, the orientation is decided.

$\theta = 0°$; $m_l = \sqrt{l(l+1)} = \sqrt{l^2+l} \simeq l$

$\theta = 180°$; $m_l = -\sqrt{l(l+1)} = -\sqrt{l^2+l} \simeq -l$

m_l ranges from $\boxed{-l \text{ to } l}$

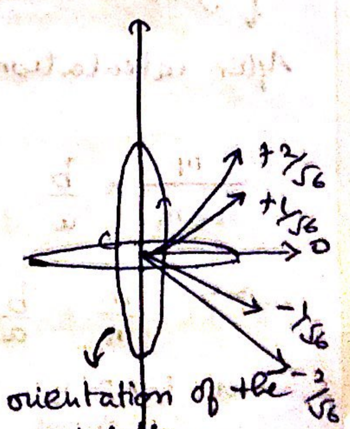
Called as **Magnetic quantum Number**

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

$l=2$; $\cos\theta = \frac{m_l}{\sqrt{6}}$; $m_l \in [-2, 2]$

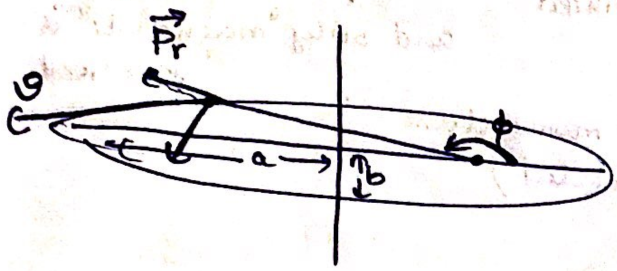
$= \underbrace{\frac{-2}{\sqrt6}, \frac{-1}{\sqrt6}, \frac{0}{\sqrt6}, \frac{1}{\sqrt6}, \frac{2}{\sqrt6}}$

$l=2 \equiv d$ → has 5 subshells oriented in these angles.



orientation of the subshells.

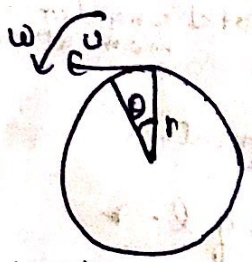
Sommerfeld Model →



$P_r = m\dot{r}$ → Radial Component

ϕ – Azimuthal Angle

$P_\phi = mr^2\dot{\phi}$ → Azimuthal Component ; $\dot{\phi} = \frac{d\phi}{dt}$



$\omega = \frac{d\theta}{dt}$

$V = r \times \omega = r\omega$

$L = r \times mv = mr^2\omega$.

$\oint P_r \cdot dr = rh$; $r = 1, 2, \ldots$

all over the surface

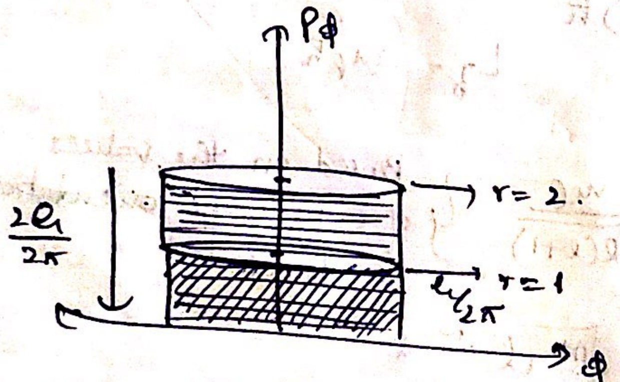
Azimuthal Component : $\oint P_\phi \, d\phi = mh$; $m = 1, 2, \ldots$

$\oint P_\phi \cdot d\phi = P_\phi \cdot 2\pi = mh$

$P_\phi = \frac{mh}{2\pi}$

angular momentum doesnt change for a given 'r'

Phase-base diagram



$m = 1$; $P_\phi = \frac{h}{2\pi}$

$m = 2$; $P_\phi = \frac{2h}{2\pi}$

$m = 3$; $P_\phi = \frac{3h}{2\pi}$

Radial Component :

$\oint P_r \cdot dr = rh$

After calculations;

$$\frac{m}{r+m} = \frac{b}{a} \quad ; \quad r+m = n$$

$$\rightarrow \frac{m}{n} = \frac{b}{a}$$

$m = 1, 2, 3, 4 \ldots\ldots$, $m \neq 0$ (electron moves in a straight line and during that it may collide with nucleus on the way)

	m	r
$n=1$	1	0
$n=2$	2,1	1,0

$$\frac{m}{r+m} = \frac{b}{a}$$

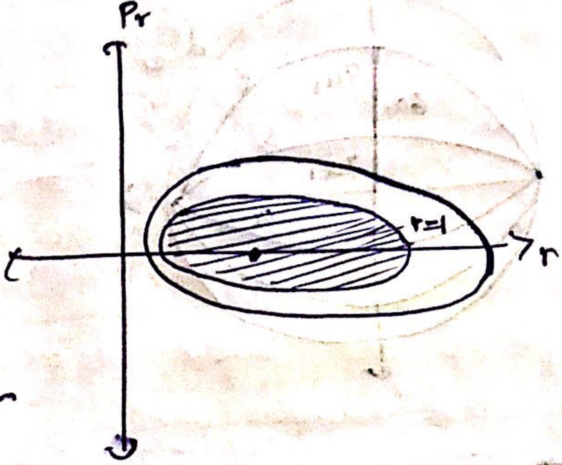
↓

Considering/comparing it to an ellipse

if $r\uparrow$ (increases) – semi-major axis increases.

↓

ellipticity ↑



away from the nucleus

↓

Radial component is low

near the nucleus

↓

Radial component is high.

↓

that is the reason why; $e^{\ominus}$ tries to stay away from the nucleus.

Radial Component is not constant like Azimuthal Component.

$a = a_1 \cdot \frac{n^2}{Z}$ [Semi-major axis]

$b = a_1 \cdot \frac{mn}{Z}$ [Semi-minor axis]

$a = a_1 \frac{n^2}{Z}$

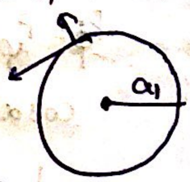
$b = a_1 \frac{kn}{Z}$

$Z = 1$ (Hydrogen atom).

$n=1,\ m=1,\ r=0.$

$a = a_1$

$b = a_1$

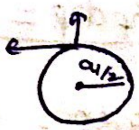


$Z = 2$

$n=1,\ m=1,\ r=0.$

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

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



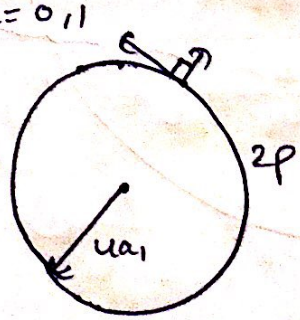
$n=2,\ m=2,1,\ r=0,1$

$a = \frac{a_1 4}{1} = 4a_1$

$b = 4a_1 = 4a_1$

↓

$(n=2, m=2, r=0)$



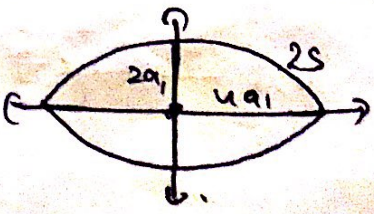
r value increased from 0, to 1, the ellipticity increased.

$a = a_1 4 = 4a_1$

$b = 2a_1 = 2a_1$

↓

$(n=2, m=1, r=1)$



→ {2s, 2p} acc^n to Sommerfeld Model

$n=3,\ m=3,2,1,\ r=0,1,2$

$n=3,\ m=3,\ r=0$ $[Z=1]$

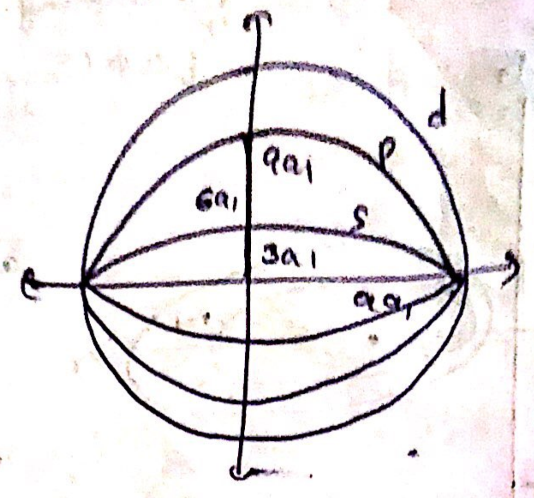
① $a=9a_1$ d
$b=9a_1$

② $n=3,\ m=2,\ r=1$

$a=9a_1$ p
$b=6a_1$

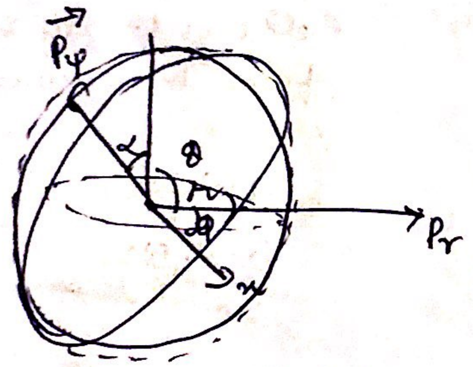
③ $n=3,\ m=1,\ r=2$

$a=9a_1$ s
$b=3a_1$



SPATIAL QUANTISATION →

Fixed orientation are allowed ↓



→ $P_r,\ P_\psi$

$\{r, \theta, \psi\}$

↓

$P_r,\ P_\theta,\ P_\psi$ → in spherical polar co-ordi

$\oint P_r\,dr = rh$

$\oint P_\psi\,d\psi = kh$ → $\boxed{k = t+m}$

$kh = th + mh$

$\oint P_\theta\,d\theta = th$

$\oint P_\phi\,d\phi = mh$

$\oint P_r\,dr = rh$

$\cancel{rh} + kh = \cancel{rh} + th + mh$

$kh = th + mh$

$P_\phi = P_\psi \cos\alpha$

$\cos\alpha = \dfrac{P_\phi}{P_\psi}$

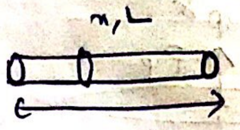
↓

$\cos\alpha = \dfrac{P_\phi}{P_\psi} = \dfrac{m}{t+}$

$\cos\alpha = \dfrac{m}{t+m} = \dfrac{m}{k}$

Heat Equation →

$$u(x,t) \Rightarrow \frac{\partial u}{\partial t} = -\alpha \frac{\partial^2 u}{\partial x^2}$$



Fourier's Law of heat transfer:

$$\frac{\text{Rate of heat transfer}}{\text{Area}} = -k_0 \times \frac{\partial u}{\partial t}$$

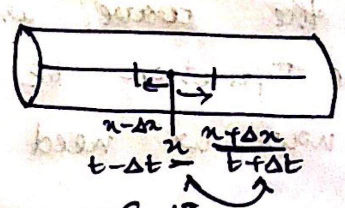
Conservation of Energy →

$$\Delta Q = \Delta U + \Delta W$$

$$\Delta Q = \boxed{\Delta U}$$

$$\downarrow$$

$$U = mC_p \times u \rightarrow \Delta U = m \times C_p \Delta T$$



$(x+\Delta x, t+\Delta t)$; $(x, \Delta t)$ $\qquad \Delta U = U_t - U_{t+\Delta t}$

$$\Delta t . \left(\frac{\partial U}{\partial t}\right)_{x+\Delta x} . A = \Delta t \left(\frac{\partial U}{\partial t}\right)_x \times A$$

$$\frac{\partial Q}{\partial t} = -k_0 \frac{\partial U}{\partial t} A$$

$$\Delta Q = Q_{x+\Delta x} - Q_x$$

$$= \left(\Delta t . \left(\frac{\partial U}{\partial t}\right)_{x+\Delta x} . A - \Delta t . \left(\frac{\partial U}{\partial t}\right)_x . A\right) k_0$$

$$Q = \Delta t . A \frac{\partial U}{\partial t} \times -k$$

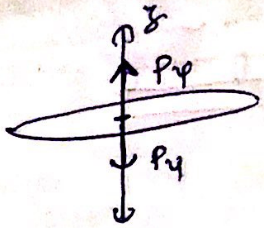
$$\Delta Q = Q_{t+\Delta t} - Q_t$$

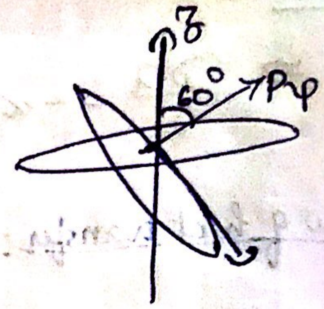
$$= \Delta x . \rho A . \left[u(x, t+\Delta t) - u(x,t)\right]$$

$$u = F(x) . G(t)$$

$$\frac{\partial U}{\partial t} = -c^2 \times \frac{\partial^2 U}{\partial x^2} \; ; \; c^2 = \alpha$$

$$\frac{\partial u}{\partial t} = -\alpha \frac{\partial^2 u}{\partial x^2}$$





$\cos\alpha = \pm 1 \rightarrow \alpha = 0.$

$\cos\alpha = -1 \rightarrow \alpha = 180^0$

$\cos\alpha = +\frac{1}{2}, -\frac{1}{2}, +1.$

$60^0 \quad 120^0 \quad 0^0$

All the above assumptions are before deBroglie wave Equation i.e no wave nature (matter waves). So now we need to see 'Wave Mechanical Model

<u>Correspondence with Classical Mechanics:</u>

$$E = \frac{1}{2}mv^2 + V$$
$$= \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

$n = 1, 2, 3, \ldots 100$

For large values of n:

ν = frequency of radiation → frequency of $e^\ominus$ (in the orbital) → classical theory

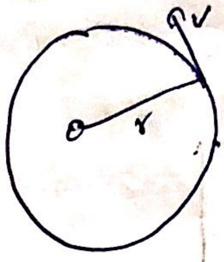
$$\nu = \frac{1}{T} = \frac{v}{2\pi r}$$

$$T_o\ominus(\text{Nucleus}) = \frac{e^2}{4\pi\varepsilon_0 \cdot r^2} = \frac{mv^2}{r} \quad \text{—①}$$

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

from ① & ② we get $v, r \longrightarrow$ find ν.

Scanned by CamScanner

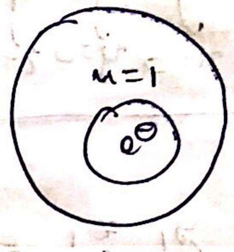


$$v = \frac{2\pi r}{T}$$

$$\frac{1}{T} = \frac{v}{2\pi r}$$

$$\nu = \frac{v}{2\pi r}$$

$$\nu = \frac{R}{h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$



$E_n =$ we can calculate

$$= R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$h\nu = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\nu = \frac{R}{h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{—④}$$

$$\nu = \frac{v}{2\pi r}$$

From ③ & ④ we see the same values.

$$\nu = \frac{v}{2\pi r} = \frac{1}{T}$$

Wave Mechanical Model :—

$$\boxed{\lambda = \frac{h}{mv}}$$

$$\lambda = \frac{h}{mv}$$

→ Representation of wave methematically

- Particle on a ring
- Wave function to represent $e^{\ominus}$
- Wave function of the system determines all the properties of the $e^{\ominus}$ (every-thing about the system).

Finding out wave function?
What is wave function? →

* **Wave Function :-** $\{\psi, \psi^2\}$

$\psi \rightarrow$ Represents the wave function

$$\boxed{\int_{x=0}^{\infty}\int_{y=0}^{\infty}\int_{z=0}^{\infty}\psi^2\,dx\,dy\,dz = 1}$$

$$\int_{x=0}^{x_1}\int_{y=0}^{y_1}\int_{z=0}^{z_1}\psi^2\,dx\,dy\,dz = \text{varies between } (0-1)$$

Wave function $\psi(x)$

↳ Single Valued, Continuous

→ $\int_{-\infty}^{+\infty} \psi.\psi^* \, dx = 0$. (particle cannot be found)

product of wavefunction and conjugate of wave function.

$$|\psi|^2 = \psi.\psi^*$$ → $\psi = A + iB$, $\psi^* = A - iB$.

→ $\psi \equiv$ Complex Number

→ Normalisation (to get valid results) $\underbrace{N\int_a^b \psi.\psi^* dv = 1}_{\text{Normalisation}}$

when a particle can be found

Wave Equation →

General Wave Eq^n: $y = Ae^{-i(\omega t - kx)}$

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

$\omega = 2\pi\nu$

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

$$= Ae^{-i(2\pi\nu t - \frac{2\pi}{\lambda}x)}$$

$$= Ae^{-2\pi i(\nu t - \frac{x}{\lambda})} \quad \text{— (1)}$$

$\omega = 2\pi\nu = \frac{2\pi E}{h}$

$K = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$

$E = h\nu$.

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

$$E = h\nu = \frac{h}{2\pi}.2\pi\nu = \hbar\, 2\pi\nu$$

$E = h\nu$

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

$$\nu = \frac{E}{\hbar 2\pi} = \frac{E}{2\pi\hbar} \quad \text{— (2)}$$

$\lambda = \frac{h}{E/\nu} = \frac{h}{p}$

$$\lambda = \frac{h}{p} = \frac{2\pi h}{2\pi p} = \frac{2\pi}{p}\left(\frac{h}{2\pi}\right) = \frac{2\pi\hbar}{p} \quad \text{— (3)}.$$

(2) & (3) in (1) :-

$$\psi(x,t) = A.e^{-2\pi i\left(\frac{E}{2\pi\hbar}t - \frac{xp}{2\pi\hbar}\right)}$$

$$= Ae^{-\frac{2\pi i}{2\pi}\left(\frac{E}{\hbar}t - \frac{xp}{\hbar}\right)}$$

$$= Ae^{-\frac{i}{\hbar}(Et - xp)}.$$

$$y = Ae^{-\frac{i}{\hbar}(Et - xp)}$$

$$E = \frac{p^2}{2m} + U(x). \quad \text{[General } E = K+U \text{ energy eq}$$

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

where $\psi(x,t) = Ae^{-i/\hbar(Et - px)}$.

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

$$\frac{\partial}{\partial t}\psi(x,t) = \psi(x,t)\cdot\left(\frac{-i}{\hbar}\right)\cdot E$$

$$E \cdot \psi(x,t) = -\frac{\hbar}{i}\cdot\frac{\partial}{\partial t}\psi(x,t) \quad \text{— (4)}$$

$$\frac{\partial}{\partial x}\psi(x,t) = Ae^{-i/\hbar(Et-px)} \times \frac{pi}{\hbar}$$

$$\frac{\partial}{\partial x}\psi(x,t) = \psi(x,t) \times p \times \left(\frac{i}{\hbar}\right)$$

$$\frac{\partial^2}{\partial x^2}\psi(x,t) = \frac{\partial}{\partial x}\psi(x,t)\cdot p\cdot\left(\frac{i}{\hbar}\right)$$

$$= \psi(x,t) \times p \times \frac{i}{\hbar} \times p \times \frac{i}{\hbar}$$

$$= \psi(x,t)\cdot p^2 \times \frac{-1}{(\hbar)^2}.$$

$$\psi(x,t)\cdot p^2 = -\hbar^2\cdot\frac{\partial^2}{\partial x^2}\psi(x,t). \quad \text{— (5)}$$

(4) (5) in eqⁿ →

Schrodinger's Time dependent Equation

$$-\frac{\hbar}{i}\cdot\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}\psi(x,t) + U(x)\cdot\psi(x,t)$$

$$\Downarrow$$

$$-\frac{\hbar}{i}\cdot\frac{\partial}{\partial t}\psi(x,t) = \frac{-\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}\psi(x,t) + \underbrace{U(x)\cdot\psi(x,t)}_{\text{Potential Energy varies among diff systems.}}$$

$$\psi(x,t) = Ae^{-i/\hbar(Et - px)}.$$

$$= Ae^{-\frac{iEt}{\hbar}} \cdot e^{\frac{ipx}{\hbar}}$$

$$\psi(x,t) = \psi(x) \cdot e^{-\frac{iEt}{\hbar}}$$

$$\frac{\partial \psi(x,t)}{\partial t} = \psi(x) \cdot e^{-\frac{iEt}{\hbar}} \cdot \left(-\frac{iE}{\hbar}\right)$$

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = e^{-\frac{iEt}{\hbar}} \cdot \frac{\partial^2 \psi(x)}{\partial x^2}$$

$$-\frac{\hbar}{i} \times \left[-\frac{i}{\hbar} E \cdot \psi(x) \cdot \cancel{e^{-\frac{iEt}{\hbar}}}\right] = -\frac{\hbar^2}{2m} \cdot \left[\frac{\partial^2 \psi(x)}{\partial x^2}\right] \cdot \cancel{e^{-\frac{iEt}{\hbar}}}$$

$$+ u(x) \cdot \psi(x) \cdot \cancel{e^{-\frac{iEt}{\hbar}}}$$

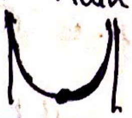
$$\longrightarrow \quad E \psi(x) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2 \psi(x)}{\partial x^2}\right] + u(x) \cdot \psi(x).$$

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

$$\frac{\partial^2}{\partial x^2} \psi(x) = -\frac{2m}{\hbar^2} [E - u(x)]\, \psi(x).$$

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

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

$\psi(x)$	$E < U(x)$	$E > U(x)$
$\psi > 0$	bound within the region $\boxed{\text{Max}}$ 	finding particle is low in high energy regions $\boxed{\text{Min}}$ 
$\psi < 0$.	$\boxed{\text{Min}}$ 	$\boxed{\text{Max}}$ 

Operators :-

$$\psi(x,t) = A.e^{-\frac{i}{\hbar}[Et - px]}$$

$\hat{P} \longrightarrow -i\hbar \frac{\partial}{\partial x}$ (operator)

$\hat{E} \longrightarrow i\hbar \frac{\partial}{\partial t}$ (operator)

x

$\hat{K.E} \longrightarrow -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2}$ (operator)

$$\frac{\partial \psi(x,t)}{\partial t} = A.e^{-\frac{i}{\hbar}[Et - Px]} \times \left(-\frac{i}{\hbar}\right) E$$

$$= \psi(x,t) \cdot \left(\frac{-i}{\hbar}\right) E$$

$$E\psi(x,t) = -\frac{\hbar}{i} \cdot \frac{\partial \psi(x,t)}{\partial t}$$

Eigen Value Eqn

$$E \cdot \psi(x,t) = i\hbar \frac{\partial}{\partial t} \psi(x,t).$$

$$\hat{\Theta}\, \psi(x,t) = m\, \psi(x,t).$$

Eigen Function

Eigen Value.

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

$$\frac{\partial \psi(x,t)}{\partial x} = A e^{-i/\hbar [Et - px]} \times \left(\frac{ip}{\hbar}\right)$$

$$= \psi(x,t) \times \left(\frac{i}{\hbar}\right) p.$$

$$p.(\psi(x,t)) = \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x,t)$$

$$= -i\hbar \frac{\partial}{\partial x} \psi(x,t)$$

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

$$KE = \frac{p^2}{2m}.$$

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = \left(\frac{i}{\hbar}\right)^2 p^2 . \psi(x,t)$$

$$= \frac{-1}{\hbar^2} . p^2 \psi(x,t).$$

$$= -\frac{2m}{\hbar^2} . \frac{p^2}{2m} \psi(x,t).$$

$$\frac{p^2}{2m} \psi(x,t) = -\frac{\hbar^2}{2m} . \frac{\partial^2}{\partial x^2} \psi(x,t).$$

$$K.E. \psi(x,t) = -\frac{\hbar^2}{2m} \times \frac{\partial^2}{\partial x^2} [\psi(x,t)]$$

$$\widehat{K.E} = \frac{-\hbar^2}{2m} . \frac{\partial^2}{\partial x^2}$$

$$\longrightarrow \frac{\partial^2 \psi(x)}{\partial x^2} \pm \frac{2m}{\hbar^2} (E - U) \psi(x) = 0.$$

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

$$E\psi(x) = \Big[\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_{\widehat{KE}} + U \Big] \psi(x).$$

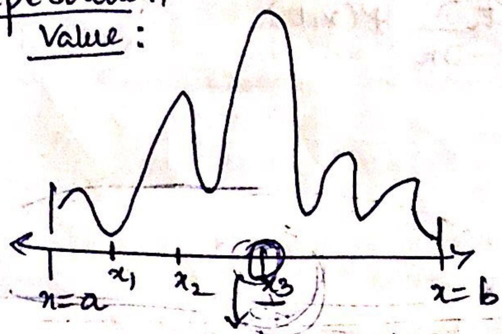
$$E.\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right]\psi(x).$$

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right]}_{\text{Hamiltonian operator}}$$

$$\hat{H} = -\frac{\hbar^2}{2m^2}\cdot\frac{\partial^2}{\partial x^2} + \hat{U}.$$

$$= \hat{K.E} + \hat{U}$$

Expectation Value:



most probable value.

Position →

Assume:

$x_1 - N_1$

$x_2 - N_2$

⋮

$x_n - N_n$.

$$x_{avg} = \frac{x_1 N_1 + \cdots x_n N_n}{N_1 + N_2 \cdots N_n}$$

particle picture

In quantum theory:

↓

particle i → at x_1 → $|\psi_1|^2$

→ x_2 → $|\psi_2|^2$

→ x_3 → $|\psi_3|^2$

⋮

Expectation value: $$\langle \bar{x} \rangle = \frac{x_1|\psi_1|^2 + x_2|\psi_2|^2 \cdots}{|\psi_1|^2 + |\psi_2|^2 \cdots}$$

$$= \frac{\int x_i |\psi_i|^2\, dx}{\int |\psi_i|^2\, dx}.$$

operator: x

$\{x, p, E \ldots\}$ $$\langle p \rangle = \frac{\int \psi^* \hat{p}\, \psi\, dx}{\int \psi.\psi^*\, dx}.$$

$\int \psi.\psi^* = 1$

$$\psi \cdot \psi^*\Big]_{-\infty}^{\infty} = |\psi^2|\Big]_{-\infty}^{+\infty} = 0. \qquad \int_{-\infty}^{+\infty} \frac{\partial}{\partial x}\psi^*\psi\, dx$$

$$\int_{-\infty}^{\infty} \psi^*\psi\ p\,dx = \int_{-\infty}^{\infty} \psi \cdot \psi^* \frac{\partial}{\partial x}\,dx \longrightarrow \text{Not useful.}$$

$$\langle \hat{\Theta} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{\Theta} \psi \cdot \partial \gamma$$

Problem : $\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$

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

$$\langle x \rangle = \int_{-\infty}^{+\infty} \hat{x}\, |\psi|^2 dx$$

$$= \int_0^L x|\psi|^2 dx = \frac{2}{L}\int_0^L x \sin^2 \frac{n\pi x}{L}\, dx.$$

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

$\int uv = u\int v - \int u' \cdot \int v$

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

$$= \frac{1}{L}\int_0^L x\,dx - x\cos\frac{2n\pi x}{L}\,dx$$

$$= \frac{L^2}{2} - \frac{1}{L}\int_0^L \underset{u}{x} \underset{v}{\cos\frac{2n\pi x}{L}}\, dx.$$

$$= \frac{L^2}{L2} - \frac{1}{L}\left[x \sin\left(\frac{2n\pi x}{L}\right)\Big]_0^L\right]$$

$$= \frac{L}{2} + \frac{1}{L}\int \frac{\sin\frac{2n\pi x}{L}}{\frac{2n\pi}{L}}\, dx$$

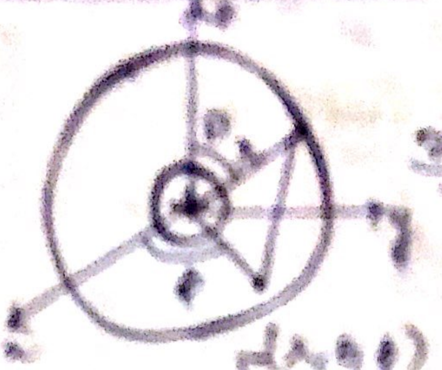
$$= \frac{L}{2} - \frac{1}{2n\pi}\cos\frac{2n\pi x}{L}\Big]_0^L$$

$$= \frac{L}{2} - \frac{1}{2n\pi}[1-1]$$

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

$$\langle x \rangle = \frac{L}{2}.$$

Quantum Theory of H atom:



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

$r(r,\theta,\phi)$

Spherical polar coordinates

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

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

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

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

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

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r}+E\right]=l(l+1)$$

$$\Phi=Ae^{im_l\phi}$$

$$\Phi(\phi)=\Phi(\phi+2\pi)$$

- Symmetric wave function : ψ_S
- Antisymmetric wave function : ψ_A

no Interaction — i.e. Independent

$$\psi = \psi(1)\,\psi(2)\,\psi(3)$$

system

State → $\{n, l, m_l\}$

Ex: system has 2 e⁻

$$\psi = \psi(1)\,\psi(2)$$

Identical particles → 1 – a state, 2 – b state

$$\psi_I = \psi_a(1)\,\psi_b(2)$$

$$\psi_{II} = \psi_a(2)\,\psi_b(1)$$

so states can be exchanged: 1 – b state, 2 – a state

Probability of e⁻ being in I state = Probability of e⁻ being in II state

Symmetric Wave function

$$\psi_S = \frac{1}{\sqrt{2}}\left(\psi_I + \psi_{II}\right)$$

Normalization constant (for 2 particles – $\frac{1}{\sqrt{2}}$)

$$= \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) + \psi_a(2)\cdot\psi_b(1)\right]$$

Antisymmetric Wave function –

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) - \psi_a(2)\cdot\psi_b(1)\right]$$

1, 2 ... n

$$\boxed{\psi(T) = \psi(1)\,\psi(2) \ldots \psi(n)}$$

$$\psi_I = \psi_a(1)\,\psi_b(2)$$

$$\psi_{II} = \psi_a(2)\,\psi_b(1)$$

$$|\psi(1,2)|^2 = |\psi|^2(2,1)$$

$$\psi(1,2) = \psi(2,1)$$

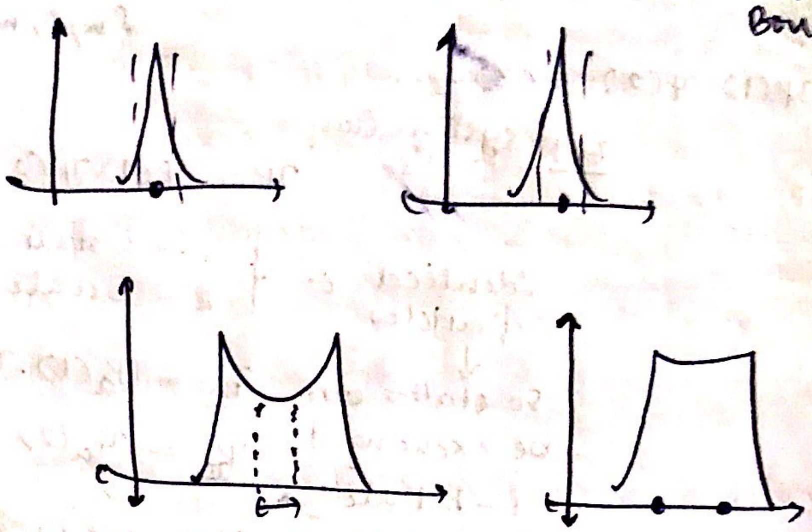
$$= -\psi(2,1)$$

Wave function of many $e^{\ominus}$ system :

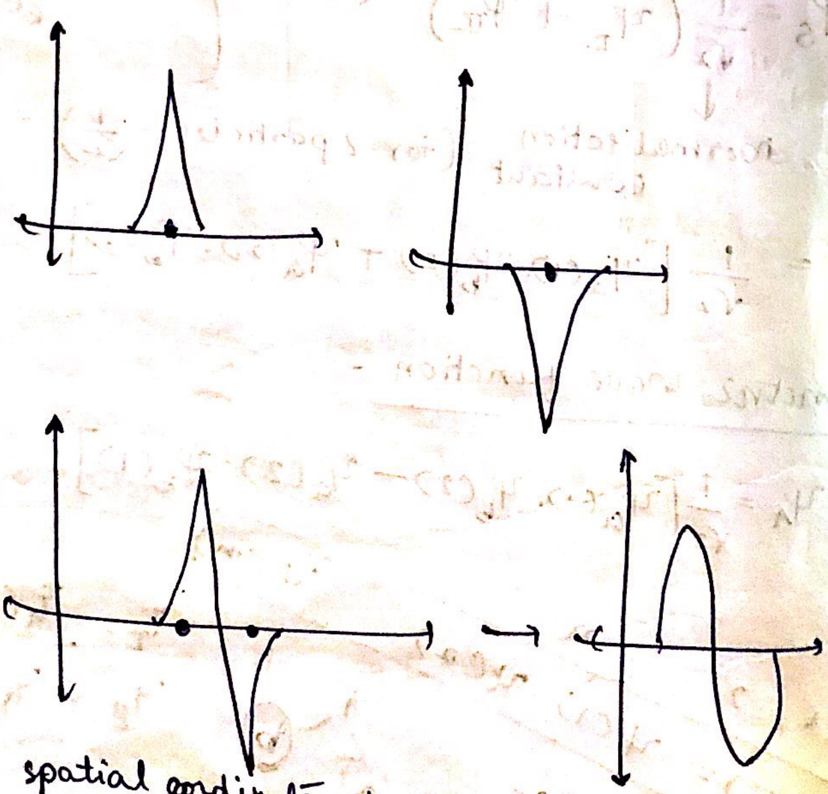
H_2^+

H —•— H ⤷ single $e^{\ominus}$ here.

Symmetric Overlapping : → Symmetric Wave function → Bond Formation



Antisymmetric overlapping :



$\Psi(r\ x)$ → spatial cordinates + spin co-ordinates = function of

Ψ_A → Antisymmetry wave function.

Rule 1:

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

wave function

Total Energy

Hamiltonian operator

Rule 2: Express all the physical / chemical properties of interest as operators.

$$P_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{P}_x^2 = \hat{P}_x . \hat{P}_x$$

$$\Rightarrow \quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \quad \text{[Hamiltonian operator]}$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\psi(x) + U(x)\psi(x) = \hat{H}\psi(x).$$

$$\Downarrow$$

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

Solve the differential equation to find $\psi(x)$ of the system of interest.

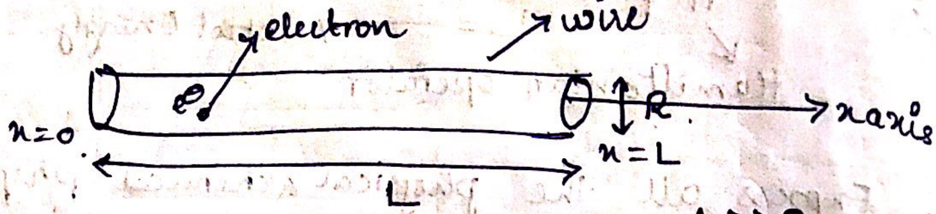
any physical quantity:

$$\hat{A}\psi(x) = A\psi(x).$$

This value can be compared of experimental values

Model System 1 →

↪ A particle in a one dimensional box →



L>>R.

L → length of the wire

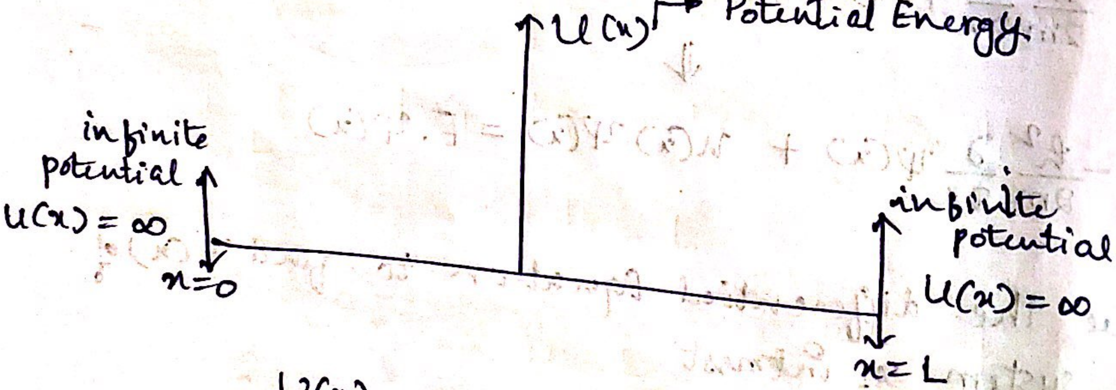
R → diameter of the wire.

Considering Quantum Mechanics →

let m be the mass of the electron

⟹ Schroedinger Equation →

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



$U(x) = 0; \quad 0 < x < L$

$U(x) = \infty; \quad x = 0$

$U(x) = \infty; \quad x = L.$

Inside the box:

As; $U(x) = 0.$

Eqn:

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

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) = 0.$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

$\frac{d^2}{dx^2}\psi(x) + k^2\psi(x) = 0$

general solution

$\psi(x) = B\sin kx + A\cos kx$

A & B are arbitrary constants

We know that $\psi(x=0) = 0$. (boundary condition).

$\rightarrow A = 0$

$\psi(x) = B\sin kx \quad (A=0)$.

since it is the boundary of the box

Secondary boundary condition $\rightarrow$ $\psi(x=L) = 0$

particle cannot be found outside or at the ends of the box

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

$B\sin kL = 0$

$B \neq 0$ so, $\sin kL = 0$.

$kL = n\pi \quad , n = 1, 2, 3, \ldots$ etc

$$\boxed{k = \frac{n\pi}{L}}.$$

k cannot take all possible values, only selected values.

Since ; $k = \frac{n\pi}{L}$ and $k = \sqrt{\frac{2mE}{\hbar^2}}$, k takes only discrete values so E also takes discrete values.

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

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

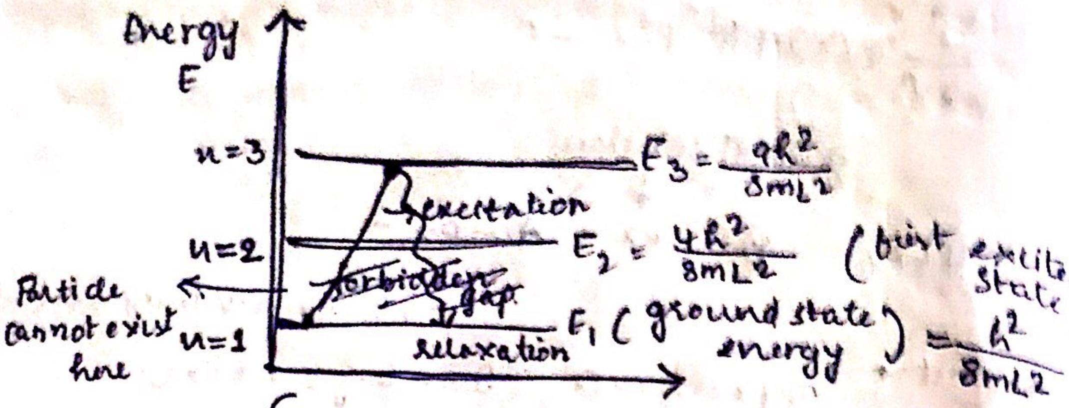
$$\boxed{\text{Since } \hbar = \frac{h}{2\pi}}$$

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

$$= \frac{n^2 \times h^2 \times \pi^2}{8mL^2\pi^2}$$

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

can take only selected values



Energy is being quantised in this model.

$$\psi(x) = B\sin\left(\frac{n\pi x}{L}\right).$$

→ What is B?

$\psi^*(x)\,\psi(x)\,dx.$ Probability that the particle is located between x and $x+dx$

Probability of finding the particle within the wire is

$$\int_0^L \psi^*(x).\psi(x).dx = 1.$$

$$B^2\int_0^L \sin^2\left(\frac{n\pi}{L}x\right).dx = 1 \;\rightarrow\; B^2 = \frac{2}{L}$$

$$B = \sqrt{\frac{2}{L}}$$

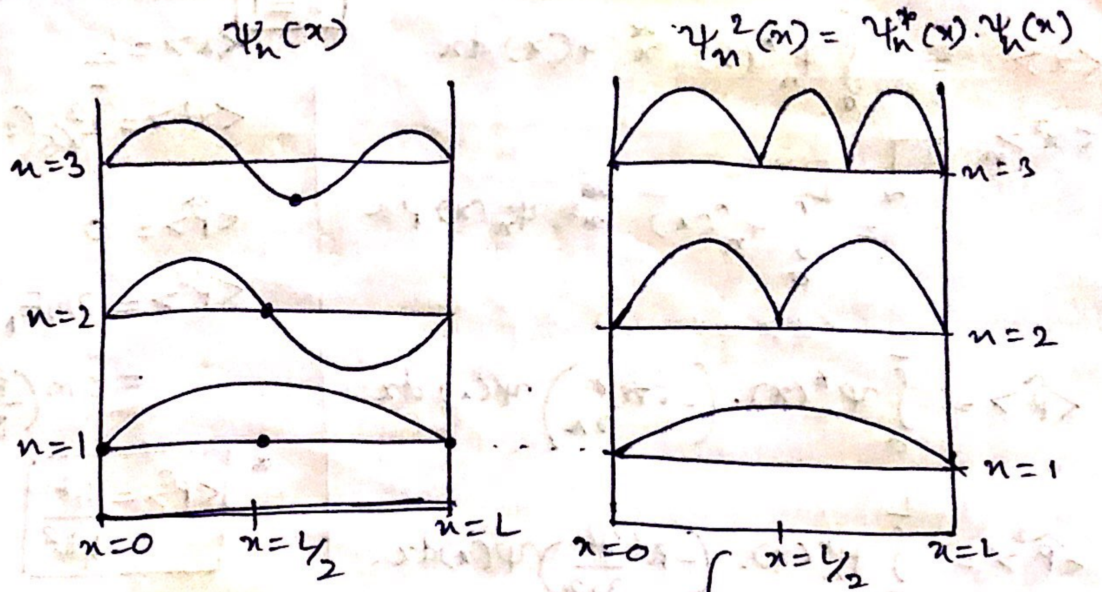
$$\psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right).$$

n can vary from $\{1, 2, 3, \ldots \infty\}$

$\psi_n(x)$ – solution of wave function in n^{th} state.

$\psi_1(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right).$ .... ground state

$\psi_2(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$ .... first excited state



Maximum probability at many locations (x).

<u>center of the box</u>

ground state ↘ first excited state ⟶ second excited state

<u>$\psi(x)$:</u> Max ↘ zero ↘ -ve Max ↗ zero ↗ Max

If $n \to \infty$ ↓ Classical Mechanics can be applied [Bohr's Correspondence Principle]

$$\hat{KE} = \frac{\hat{p}^2}{2m} = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x).$$

small n, quantum mechanics
large n, classical mechanics

} Quantum $\xrightarrow{n\to\infty}$ Classical Mechanics
↓
Bohr's Correspondence Principle.

<u>fix n & E_n:</u> (at a particular energy level).

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

increase m ⇒ increase n
increase L ⇒ increase n.

} increasing dimensions ↓ Bohr's Correspondence Principle.

Macroscopic systems do not require Quantum Mechanics ↓ Classical Mechanics should be sufficient.

$$\langle x \rangle = \int_0^L \psi_n^*(x) \cdot x \, \psi(x) \, dx.$$

$$\langle x^2 \rangle_n = \int_0^L \psi_n^*(x) \cdot x^2 \, \psi_n(x) \, dx$$

$$\langle \hat{p} \rangle = \int_0^L \psi_n^*(x) \cdot \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x) \, dx.$$

$$\langle \hat{p}^2 \rangle = \int_0^L \psi_n^*(x) \cdot \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \psi(x) \, dx.$$

$\boxed{n=1}$

$\langle x \rangle = \frac{L}{2}$

$\langle x^2 \rangle = L^2/6 \left(2 - \frac{3}{\pi^2}\right.$

$\langle \hat{p} \rangle = 0$

$\langle \hat{p}^2 \rangle = 2mE_1$

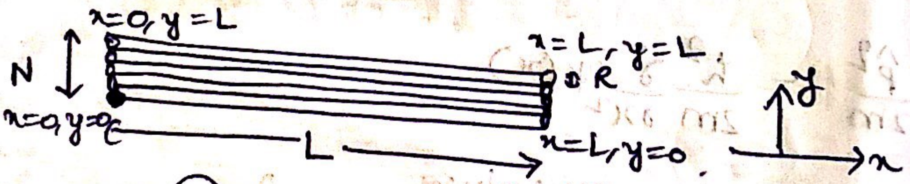
$= 2m\left(\frac{h^2}{8mL^2}\right)$

$$\boxed{\langle p^2 \rangle = \frac{h^2}{4L^2}}$$

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{[Energy is quantised]}$$

$\hookrightarrow |\psi|^2 = \frac{2}{L}\left[\sin \frac{n\pi x}{L}\right]^2.$

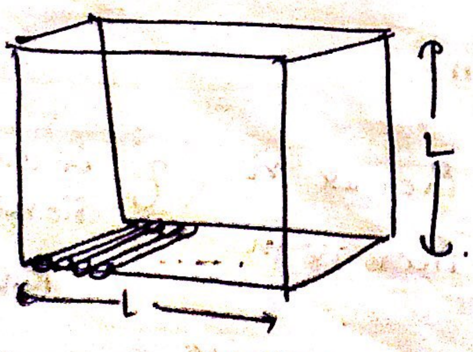
Two-dimensional box:



NR = L

q wires

Three dimensional box:



Two-dimensional box :

Inside the box — $V(x,y) = 0$. } $0 < x < L$, $0 < y < L$ (as long as e^- is inside the wire).

$V(x,y) = \infty$, otherwise.

$$\psi(x,y) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_1 \pi x}{L_x}\right) \sin\left(\frac{n_2 \pi y}{L_y}\right)$$

L_x - length across x

L_y - " " y

$L_x = L_y$ (square sheet).

$$\psi(x,y) = \frac{2}{L}\left[\sin \frac{n_1 \pi x}{L} \cdot \sin \frac{n_2 \pi y}{L}\right]$$

$[\psi(x,y) = X(x) \cdot Y(y)]$

$n_1 = 1, 2, 3, ..$

$n_2 = 1, 2, 3, ..$

ground state: $n_1 = 1, n_2 = 1$

$$\psi_{11}(x,y) = \frac{2}{L}\left(\sin \frac{\pi x}{L} \sin \frac{\pi y}{L}\right).$$

$$E_{n_1, n_2} = (n_1^2 + n_2^2)\frac{h^2}{8mL^2}$$

$$E_{1,1} = \frac{2h^2}{8mL^2} = \frac{h^2}{4mL^2}$$

First Excited state :

$(n_1 = 1, n_2 = 2) \Rightarrow E_{1,2} = \frac{5h^2}{8mL^2}$

$(n_1 = 2, n_2 = 1) \Rightarrow E_{2,1} = \frac{5h^2}{8mL^2}$

} Same energy states but different wave-functions.

$$\psi_{12}(x,y) = \frac{2}{L} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L}$$

$$\psi_{21}(x,y) = \frac{2}{L} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L}$$

* Degenerate states (Same energy values).

$\boxed{\text{Degeneracy} = 2}$ (2 such states have similar energy).

$\psi_{12}(x,y) \neq \psi_{21}(x,y)$

$E_{12}(x,y) = E_{21}(x,y)$

Three dimensional box :

$$\psi(x,y,z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \sin\left(\frac{n_3 \pi z}{L}\right)$$

$n_1 = 1, 2, 3, \ldots$

$n_2 = 1, 2, 3, \ldots$

$n_3 = 1, 2, 3, \ldots$

Two-dimensional box :

Inside the box – $V(x,y) = 0.$ $\Big\}$ $0 < x < L$, $0 < y < L$ (as long as $e^{\ominus}$ is inside the wire).

$V(x,y) = \infty$, otherwise.

$$\psi(x,y) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_1 \pi x}{L_x}\right) \sin\left(\frac{n_2 \pi y}{L_y}\right)$$

L_x – length across x

L_y – " " y

$L_x = L_y$ (square sheet).

$$\psi(x,y) = \frac{2}{L}\left[\sin \frac{n_1 \pi x}{L} \cdot \sin \frac{n_2 \pi y}{L}\right]$$

$[\psi(x,y) = X(x) \cdot Y(y)]$

$n_1 = 1, 2, 3, ..$

$n_2 = 1, 2, 3, ..$

ground state: $n_1 = 1, n_2 = 1$

$$\psi_{11}(x,y) = \frac{2}{L}\left(\sin \frac{\pi x}{L} \sin \frac{\pi y}{L}\right).$$

$$E_{n_1, n_2} = \left(n_1^2 + n_2^2\right) \frac{h^2}{8mL^2}$$

$$E_{1,1} = \frac{2h^2}{8mL^2} = \frac{h^2}{4mL^2}$$

First Excited state :

$(n_1 = 1, n_2 = 2) \Rightarrow E_{1,2} = \dfrac{5h^2}{8mL^2}$

$(n_1 = 2, n_2 = 1) \Rightarrow E_{2,1} = \dfrac{5h^2}{8mL^2}$

$\Big\}$ Same energy states but different wave-functions.

$\psi_{12}(x,y) = \frac{2}{L} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L}$

$\psi_{21}(x,y) = \frac{2}{L} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L}$

$\Downarrow$

* Degenerate states (same energy values).

$\boxed{\text{Degeneracy} = 2}$ (2 such states have similar energy).

$\psi_{12}(x,y) \neq \psi_{21}(x,y)$

$E_{12}(x,y) = E_{21}(x,y)$

Three dimensional box :

$$\psi(x,y,z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \sin\left(\frac{n_3 \pi z}{L}\right)$$

$n_1 = 1, 2, 3, \ldots$

$n_2 = 1, 2, 3, \ldots$

$n_3 = 1, 2, 3, \ldots$

Uncertainity Principle → Consider a particle in a 1D box in its ground state.

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L}$$

$$\langle x \rangle = \frac{\int_0^L \psi^* x \psi \, dx}{\underbrace{\int_0^L \psi \psi^* \, dx}_{1}}$$

1 (Normalised wave function)

$$\langle x \rangle = \int_0^L \frac{2}{L} x \sin^2\frac{\pi x}{L} \, dx = \frac{L}{2}.$$

$$\langle p \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L} \left(-i\hbar \frac{\partial}{\partial x} \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L}\right) dx$$

$$\boxed{\langle p \rangle = 0}$$

$$\langle x^2 \rangle = \int_0^L \frac{2}{L} \cdot x^2 \sin^2\frac{\pi x}{L} \, dx = \frac{L^2}{6}\left(2 - 3/\pi^2\right)$$

$$\langle p^2 \rangle = \frac{2}{L}\int_0^L \sin\frac{\pi x}{L} \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\left(\sin\frac{\pi x}{L}\right)\right) dx$$

$$= 2mE_1 = \frac{2m h^2}{8mL^2} = \frac{h^2}{4L^2}$$

$$\Delta x = x - \langle x \rangle.$$

$$(\Delta x)^2 = (x - \langle x \rangle)^2 \text{ variance}$$

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

Standard deviation: $\sigma_x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$

$$\sigma_p = \sqrt{\langle p^2\rangle - \langle p\rangle^2}.$$

$$\sigma_p = \sqrt{\langle p^2\rangle - \langle \underbrace{p}_{0}\rangle^2}$$

$$= \sqrt{\langle p^2\rangle} = \sqrt{\frac{\hbar^2}{4L^2}} = \frac{\hbar}{2L}.$$

$$\sigma_x = \sqrt{\langle x^2\rangle - (\langle x\rangle)^2} =$$

$$= \sqrt{\frac{L^2}{6}\left(2 - 3/\pi^2\right) - \frac{L^2}{4}}$$

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

$$= \sqrt{\frac{L^2}{12} - \frac{L^2}{2\pi^2}}$$

* $\sigma_x \sigma_p = 0$ [For classical sys. & Newtonian systems

If, $\boxed{\sigma_x \sigma_p = 0}$ Not for Quantum particle

then the ~~cert~~ position and momentum can be determined simultaneously without any error.

$$\sigma_x \sigma_p = \frac{\hbar}{2L}\sqrt{\frac{L^2}{12} - \frac{L^2}{2\pi^2}}$$

$$= \frac{\hbar}{2}\sqrt{\frac{1}{12} - \frac{1}{2\pi^2}} = 0.033$$

0.08333
0.05066

* $\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$

Uncertainity Principle.

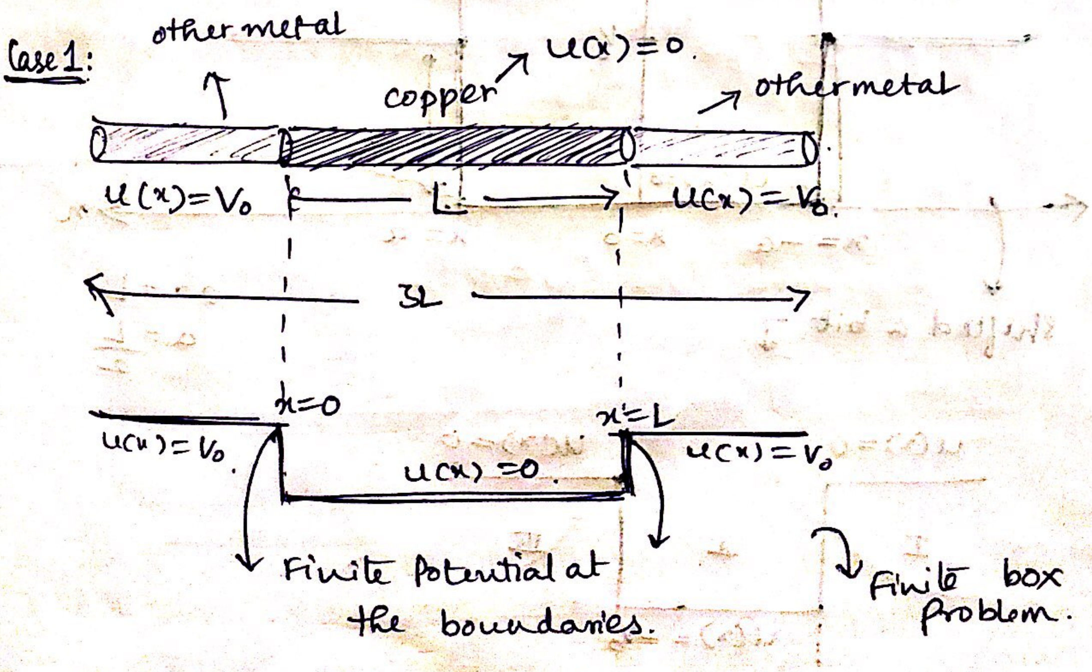
$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$ → uncertainity Principle.

Equality holds for Gaussian Wave functs

$\boxed{\hbar \sim 10^{-34}}$

→ By increasing the uncertainity in momentum, we can decrease the uncertinity in position or viceversee.

Case 1:

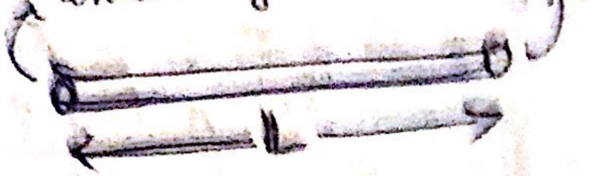


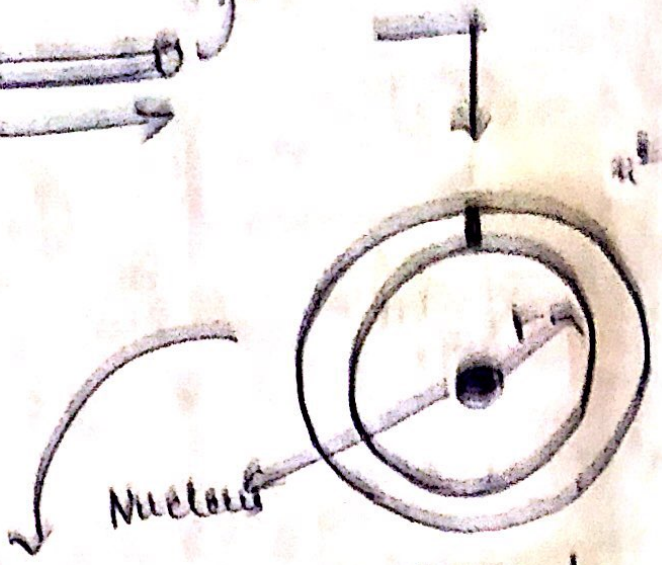
Case 2:

↓

No infinite barrier

connecting both the ends





$x^2+y^2=r^2$

[its a 1D problem] as $x^2+y^2=r^2$ though it is in x-y plane

$2\pi r = L$

$r = \frac{L}{2\pi}$

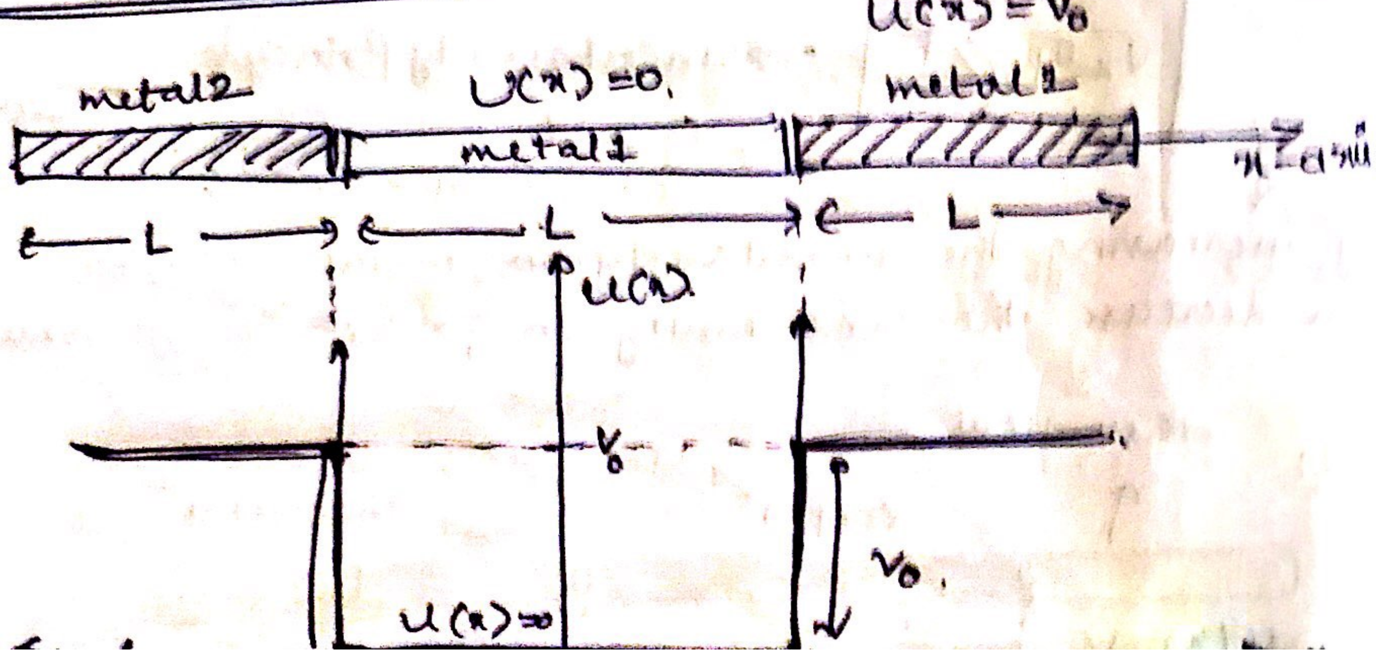
Flow of $e^{\ominus}$ → Flow of current

↓

creates magnetic field

(Magnet gets affected (spin))

Other Model Systems —



$U(x) = -V_0$ if $-a < x < a$ (Inside the box-metal1)

$= 0$, otherwise

Case 1: $E < 0$

total energy

Region 1 $\rightarrow$ $$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + \cancel{U(x)}\psi(x) = E.\psi(x)$$

$U(x) = 0$.

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

ϵ: positive quantity

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{2m\epsilon}{\hbar^2}\psi(x)$$

$$K_1 \equiv \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

$$\frac{\partial^2}{\partial x^2}\psi(x) = K_1^2\,\psi(x).$$

general solution: $\psi_I(x) = c_1 e^{K_1 x} + c_2 e^{-k_1 x}$

$x \rightarrow -\infty$; $\psi_I(x \rightarrow -\infty) = 0 \Rightarrow \boxed{c_2 = 0}$

$$\psi_I(x) = c_1 e^{K_1 x}$$

$$\frac{d\psi_I(x)}{dx} = c_1 K_1 e^{K_1 x}.$$

||ly for region III $\rightarrow$

$$\psi_{III}(x) = A_1 e^{K_1 x} + A_2 e^{-K_1 x}$$

$x \rightarrow \infty$; $\psi_{III}(x \rightarrow \infty) = 0 \Rightarrow \boxed{A_1 = 0}$

$$\psi_{III}(x) = A_2 e^{-K_1 x}.$$

$$\frac{d\psi_{III}(x)}{dx} = -A_2 K_1 e^{-k_1 x}$$

Region II $\rightarrow$ $U(x) \neq 0$.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) - V_0\,\psi(x) = E.\psi(x)$$

$E = -E$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) - V_0\psi(x) = -E\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\psi(x) + \underbrace{\frac{2m}{\hbar^2}\left[V_0 - E\right]}\psi(x) = 0.$$

$$K_2^2 = \frac{2m}{\hbar^2}[V_0 - E] \Rightarrow K_2 = \sqrt{\frac{2m}{\hbar^2}[V_0 - E]}$$

$$K_1^2 + K_2^2 = \frac{2m}{\hbar^2}(E + V_0 - E)$$

$$= \frac{2mV_0}{\hbar^2}$$

$$\frac{\partial^2}{\partial x^2}\psi(x) + K_2^2\psi(x) = 0.$$

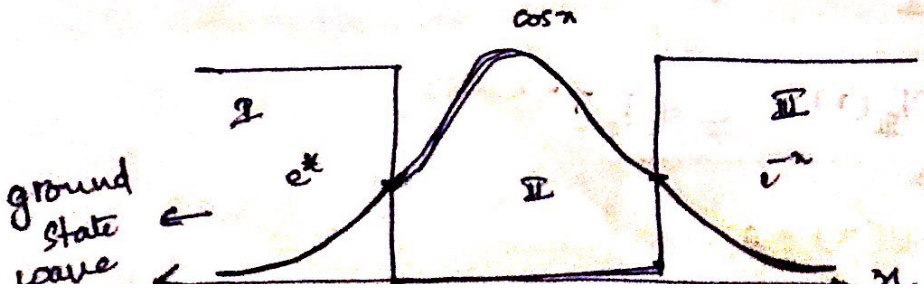
$$\psi_{II}(x) = B_1\cos(K_2 x) + B_2\sin(K_2 x).$$

$$\rightarrow \frac{d\psi_{II}(x)}{dx} = -B_1K_2\sin K_2 x + B_2K_2\cos K_2 x$$

$$\left.\begin{aligned} \psi_{III}(x) &= A_2 e^{-K_1 x} \quad (x>0) \\ \psi_I(x) &= C_1 e^{K_1 x}. \quad (x<0). \end{aligned}\right\}$$

$$\psi_{II}(x) = B_1\cos K_2 x + B_2\sin K_2 x$$

we can determine $A_2, C_1, B_1 \& B_2$

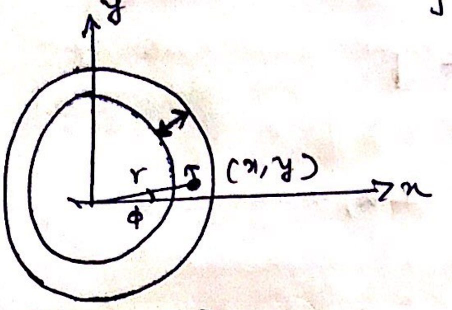


Particle in a wire:

$$x = r\cos\phi$$
$$y = r\sin\phi$$

$r \rightarrow$ fixed

$0 \leq \phi \leq 2\pi$



Kinetic Energy $\rightarrow$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \Rightarrow \text{Cartesian space.}$$

Polar space

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\cancel{\frac{\partial^2}{\partial r^2}} + \frac{1}{r}\cancel{\frac{\partial}{\partial r}} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

[r-fixed]

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right).$$

Schroedinger Equation :-

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = E\,\Phi(\phi)$$

wave function of particle in polar space since ["r fixed"]

* $I \equiv Mr^2 \Rightarrow$ moment of inertia.

$$\frac{\partial^2}{\partial \phi^2}\Phi = -\frac{2mEr^2}{\hbar^2}\Phi$$

$$\frac{\partial^2}{\partial \phi^2}\Phi = -\frac{2IE}{\hbar^2}\Phi$$

$$\Phi = Ae^{im_\ell \phi}$$

boundary condition $\rightarrow$

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

as after 1 rotation, it comes back to the same point

$$\rightarrow A e^{i m_\ell \phi} = A e^{i m_\ell (\phi + 2\pi)}$$

$$\rightarrow e^{i m_\ell 2\pi} = 1$$

$$e^{i m_\ell 2\pi} = 1$$

$$\downarrow$$

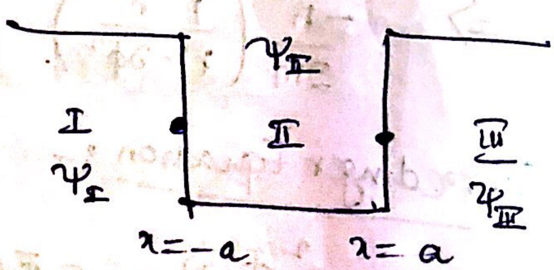
$$m_\ell = 0, \pm 1, \pm 2, \ldots$$

magnetic quantum number.

Applying Quantum Mechanics to Model Systems →

- → Identify the regions of interest
- → Solve the schrodinger equation for different regions seperately.
- → Apply → (i) ψ should be single valued
  (2) ψ should be continuous.

$$\psi_I(x) = \psi_{II}(x)$$



Continuity of ψ:-

at $x=-a$;

$$\frac{d\psi_I}{dx}(x=-a) = \frac{d\psi_{II}}{dx}(x=-a)$$

at $x=a$;

$$\frac{d\psi_{II}}{dx}(x=a) = \frac{d\psi_{III}}{dx}(x=a)$$

Single Valued ψ

at $x=-a$;

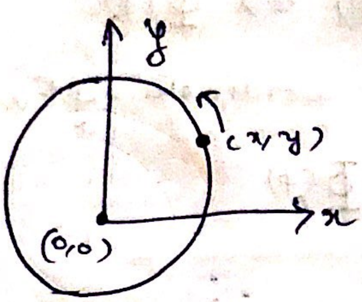
$$\psi_I(x=-a) = \psi_{II}(x=-a)$$

at $x=a$;

$$\psi_{II}(x=a) = \psi_{III}(x=a)$$

To determine $(A_2, B_1, B_2 \;\&\; C_1)$ 4 constants, solve 4 equation

Particle on a circular loop:—



Hamiltonian $\Rightarrow H = \frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right]$

$\left.\begin{matrix} x = r\cos\phi \\ y = r\sin\phi \end{matrix}\right\} \begin{matrix} x = x(r,\phi) \\ y = y(r,\phi) \end{matrix}$

$\downarrow$

r- fixed

$0 \leq \phi \leq 2\pi$

$$H = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right]$$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r} \times \underbrace{\boxed{\frac{\partial r}{\partial x}}}_{c_1(r,\phi)} + \frac{\partial f}{\partial \phi} \times \underbrace{\boxed{\frac{\partial \phi}{\partial x}}}_{c_2(r,\phi)} \; ; \; \frac{\partial^2}{\partial x^2} f = $$

$\cancel{\cos\phi} = x/r$

$-\sin\phi \, \partial\phi = \frac{\partial x}{r}$

$\cancel{\frac{\partial f}{\partial y}} =$

$\cancel{\frac{\partial x}{\partial r} = \cos\phi}$

$$\frac{\partial f}{\partial x} = c_1(r,\phi)\frac{\partial f}{\partial r} + c_2(r,\phi)\frac{\partial f}{\partial \phi}$$

$r = x/\cos\phi$

$$\boxed{\frac{\partial}{\partial x} = c_1\frac{\partial}{\partial r} + c_2\frac{\partial}{\partial \phi}}$$

$c_1 = \frac{\partial r}{\partial x} = \frac{1}{\cos\phi}$

$c_2 = \frac{\partial \phi}{\partial x} = \frac{-1}{r\sin\phi}$

$$\Rightarrow \frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left[c_1\frac{\partial f}{\partial r} + c_2\frac{\partial f}{\partial \phi}\right]$$

$$= c_1^2\frac{\partial^2 f}{\partial r^2} + c_1c_2[\bullet] + c_1c_2[\bullet] + c_2^2\frac{\partial^2 f}{\partial \phi^2}$$

$$= c_1^2\frac{\partial^2 f}{\partial r^2} + c_2^2\frac{\partial^2 f}{\partial \phi^2} + 2c_1c_2\frac{\partial}{\partial r}\left[\frac{\partial f}{\partial \phi}\right]$$

$$= \frac{1}{\cos^2\phi}\frac{\partial^2 f}{\partial r^2} + \frac{1}{r^2\sin^2\phi}\frac{\partial^2 f}{\partial \phi^2} + \frac{-2}{r\cos\phi\sin\phi}\left[\frac{\partial f}{\partial r\partial\phi}\right]$$

$\boxed{r \to \text{fixed}}$

$$\left.\begin{matrix} \Rightarrow \frac{\partial}{\partial r} = 0 \\ \frac{\partial^2}{\partial r^2} = 0 \end{matrix}\right\} \boxed{\hat{H} = -\frac{\hbar^2}{2m} \times \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}}$$

Cartesian | Polar

$$\psi(x,y) \Rightarrow \psi(r,\phi) \Rightarrow \Phi(\phi)$$

Schrodinger Equation in Polar Coordinate system

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2}\Phi(\phi) = E\Phi(\phi)$$

$I = mr^2 \equiv$ moment of inertia

$$\frac{\partial^2}{\partial\phi^2}\Phi(\phi) = -\frac{2IE}{\hbar^2}\Phi(\phi)$$

$$\Phi(\phi) = Ae^{im_\ell\phi} \longrightarrow \Phi(\phi) = \Phi(\phi+2\pi)$$

$m_\ell = 0, \pm 1, \pm 2 \ldots$

magnetic Quantum no.

Apply normalisation condition and calculate A

$$\hat{H}\Phi(\phi) = E\Phi(\phi)$$

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\Phi(\phi) = E\Phi(\phi)$$

$$\Downarrow$$

$$E_{m_\ell} = \frac{m_\ell^2\hbar^2}{2I}$$

Energy is quantised

$m_\ell = 0, \pm 1, \pm 2, \ldots$

Lowest Energy $\boxed{E_{m_\ell = 0} = 0}$

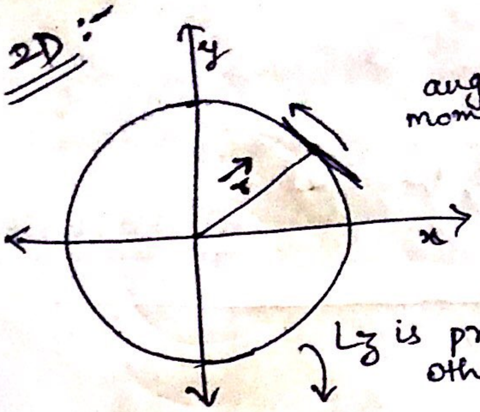
e^Θ } x is not fixed for an e^Θ acc^n to quantum theory

$$\Delta x \cdot \Delta p_x \geq \hbar/2$$

$$\Delta y \cdot \Delta p_y \geq \hbar/2$$

$$\Delta x \cdot \Delta p_y \ngeq \hbar/2$$

2D :-



angular momentum } $\hat{L} = \hat{i}\hat{L}_x + \hat{j}\hat{L}_y + \hat{k}L_z$

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

$$= \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

L_z is prominent, others are null

$$= \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ -\hbar\frac{\partial}{\partial x} & -\hbar\frac{\partial}{\partial y} & -\hbar\frac{\partial}{\partial z} \end{vmatrix}$$

$$\Rightarrow \hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

$$\Rightarrow \hat{L}_z = -i\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]$$ cartesian

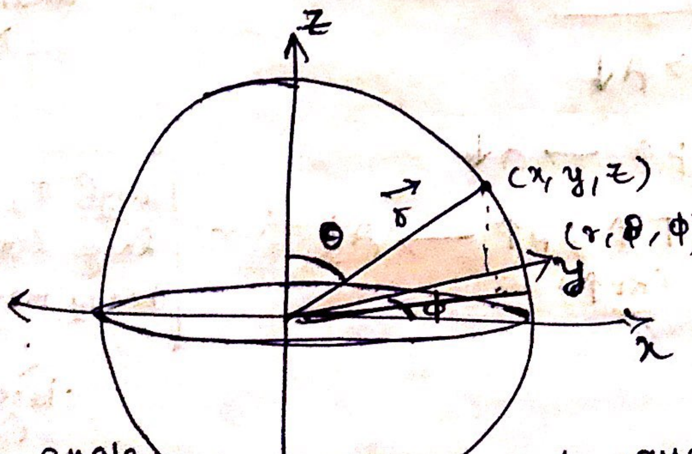
angular momentum is related to spin ← $\hat{L}_z = -i\hbar\frac{\partial}{\partial \phi}$ Polar.

$\hat{L}_z\,\Phi(\phi) = m_l\hbar\,\Phi(\phi)$; $m_l = 0, \pm 1, \pm 2 \ldots \ldots \pm\infty$? ($2l+1$)

quantisation of angular momentum.

m_l doesnt go to $\pm\infty$ but it is limited to $\pm l$.

3 Dimension (3D):-



$r \to$ radius $= |\vec{r}|$ $(-\infty \leq r \leq \infty)$

θ – angle between $\vec{r}$ & $\hat{z}$

$(0 \leq \theta \leq 2\pi)$

ϕ – angle between $\vec{r}$ projected on x-y plane and x-axis

$(0 \leq \phi \leq 2\pi)$

→ Express H in terms of θ, ϕ, r

$$\Rightarrow E_l = \frac{l(l+1)\hbar^2}{2I}$$

$$m_l = -l, -l+1 \ldots -1, 0, 1, \ldots l$$

<u>de Broglie →</u>

* Each Particle behaves like a wave.

$$\lambda = \frac{h}{p}$$

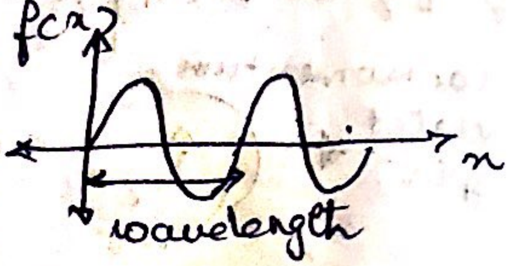
h → Plank's Constant.

λ → wavelength (wave property)

p → momentum (particle property)

<u>From particle in an infinite box problem;</u>

higher n → lower λ



$$k^2 = \frac{2mE}{\hbar^2}$$

$$\boxed{k = \frac{2\pi}{\lambda}}$$ (first excited State)

Smaller λ [higher
↓
Classical Mechanics

higher λ [smaller n
↓
Quantum Mechanics

How do we decrease λ →

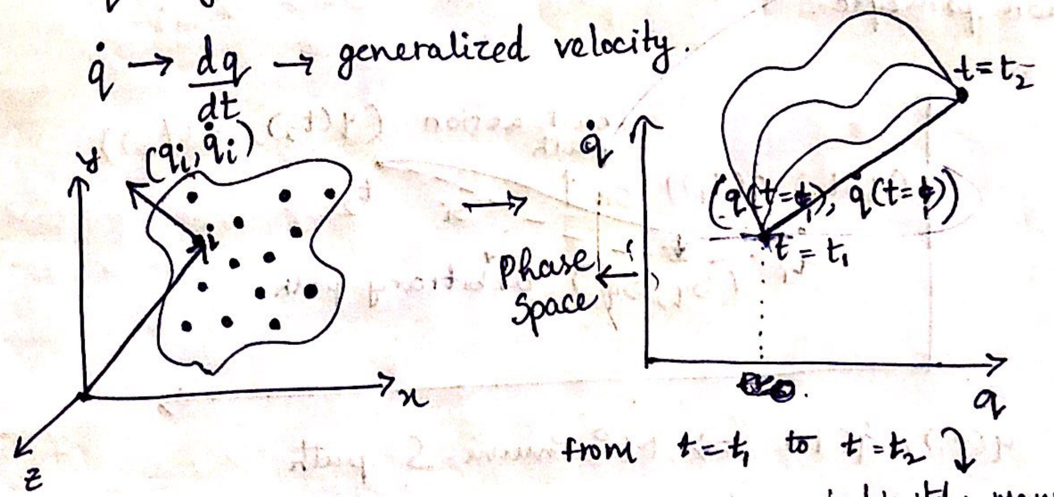
Classical Mechanics →

- → Lagrange's approach
- → Hamilton's approach

Generalized Co-ordinates & Momenta:

$q \rightarrow$ generalized co-ordinate

$\dot{q} \rightarrow \frac{dq}{dt} \rightarrow$ generalized velocity.



from $t = t_1$ to $t = t_2$ → infinitely many paths are possible.

Least Action Principle:

start $(q(t_1), \dot{q}(t_1))$

end $(q(t_2), \dot{q}(t_2))$

$L(q, \dot{q}, t) \rightarrow$ Lagrangian

define - $\underbrace{S}_{\text{action}} = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt$

$$L(q, \dot{q}, t) = \underbrace{K(\dot{q})}_{\text{Kinetic Energy}} - \underbrace{U(q)}_{\text{Potential Energy}}$$

→ whichever path has the least S value (action value) least, system would take that path.

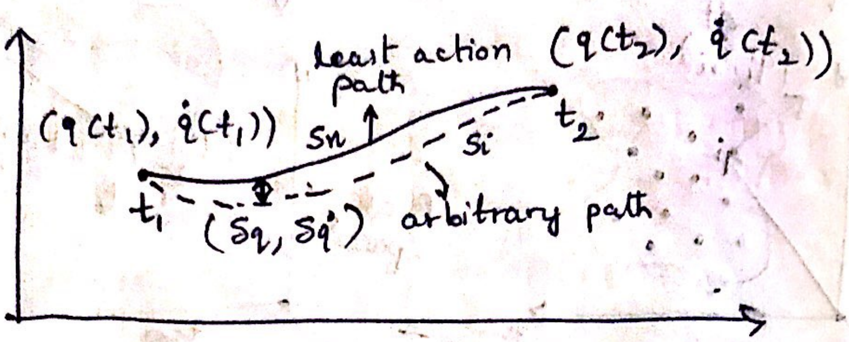
$$S = \int_{t_1}^{t_2} [K[\dot{q}] - U[q])\, dt$$

$$= \int_{t_1}^{t_2} K[\dot{q}]\, dt - \int_{t_1}^{t_2} U[q]\, dt$$

$$= \int_{t_1}^{t_2} K(\dot{q})\,dt - \int_{t_1}^{t_2} U(q)\,dt$$

average Kinetic Energy.   average Potential Energy

Obtain equations of motion from L and the least action principle.



$q(t), \dot{q}(t) \Rightarrow$ Minimum S path

$q(t) + \delta(q(t)), \dot{q}(t) + \delta(\dot{q}(t)) \longrightarrow$ neighboring path.

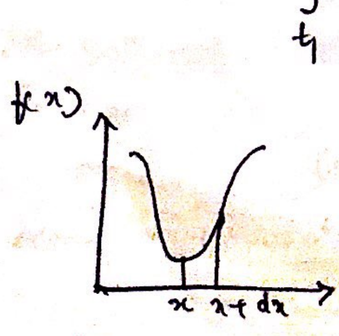
we also know that $\rightarrow \delta q(t_1) = \delta q(t_2) = 0$.

Change in S —

$$\delta S = \int_{t_1}^{t_2} L(q+\delta q, \dot{q}+\delta\dot{q}, t)\,dt - \int_{t_1}^{t_2} L(q, \dot{q}, t)\,dt$$

$$\hookrightarrow \delta S = \delta \int_{t_1}^{t_2} L(q, \dot{q}, t)\,dt = 0.$$

condition for a minimum.



$$= \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q} \right) dt = 0$$

$$\delta f = \frac{f(x+dx) - f(x)}{dx}$$

$\underline{dx \to 0}$

$df = 0$ (at the min).

Least Action Principle (or) Hamilton's Principle →

Laagrangian :- $L(q, \dot{q}; t) = K(\dot{q}) - U(q)$

- q → generalised co-ordinate
- $\dot{q}$ → generalised velocity
- $K(\dot{q})$ → Kinetic Energy
- $U(q)$ → Potential Energy.

Mechanical state $(q, \dot{q})$.

Least Action Principle →

$$\exists\, S_n \text{ st } S_n < S_i^0 \ \forall i^0$$

where S (action) $= \int_{t_1}^{t_2} L(q, \dot{q}, t)\,dt = \int_{t_1}^{t_2} K(\dot{q})\,dt - \int_{t_1}^{t_2} U(q)\,dt$

$\int_{t_1}^{t_2} K(\dot{q})\,dt$ ⇓ avg K; $\int_{t_1}^{t_2} U(q)\,dt$ ⇓ avg U.

? given L, least action principle, Can we determine the time evolution of q and $\dot{q}$?

$$\delta S = \delta \int_{t_1}^{t_2} L(q, \dot{q}; t)\,dt = 0.$$

$\delta(q(t_1)) = \delta q(t_2) = 0.$ → two paths intersect at $q(t_1)$ & $q(t_2)$

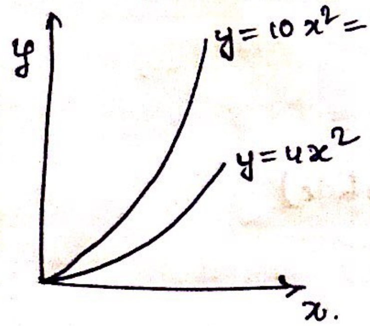
$$= \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \delta \dot{q} \right) dt = 0.$$

$\delta \dot{q} = \frac{d}{dt}(\delta q)$

Ex:

"Another path"

$y = 10x^2 = 4(x+\delta x)^2$ → changes for every value of x.



$q \to q + \delta q$

$\dot{q} \to \dot{q} + \delta \dot{q}$

Consider → $\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}} \frac{d}{dt}(\delta q)\,dt$

$$\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}} \left(\frac{d}{dt}(\delta q) \right) dt \qquad \frac{d}{dt}\left[\frac{\partial L}{\partial \dot{q}} \delta q \right] dt$$

↓

Integrate by parts

$$\left. \frac{\partial L}{\partial \dot{q}} \times \delta q \right]_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}} \right) \delta q\, dt$$

$0 \quad (\delta q(t_2) = \delta q(t_1) = 0)$

$$\delta S = \int_{t_1}^{t_2} \frac{\partial L}{\partial q}\, \delta q \, dt - \int_{t_1}^{t_2} \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) \delta q \, . dt.$$

$$\delta S = \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)\right] \delta q \, . dt$$

For the least action path $\longrightarrow$ $\Delta S = 0 \;\; \forall \, \delta q \;\; \forall \, \delta t$

$\delta S = 0$

$$\left[\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)\right] = 0. \implies \text{Lagrange's Equation.}$$

For more than one degree of freedom (n)

$(q_1, q_2, q_3, \ldots \ldots q_n, \dot{q}_1, \dot{q}_2, \dot{q}_3 \ldots \ldots \dot{q}_n)$

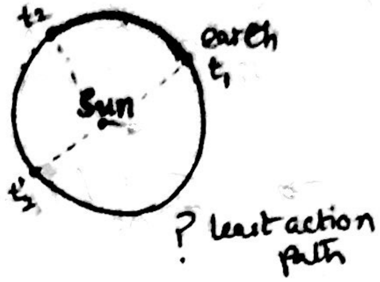
Mechanical state

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = 0 \qquad i = 1, 2, 3, \ldots n.$$

Lagrange's Equation:

$$\boxed{\frac{\partial L}{\partial q_i} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = 0, \quad i = 1, 2, \ldots n}$$

2. For a mass body interacting system



Kinetic Energy

$$K(\dot{q}_1, \dot{q}_2 \dots \dot{q}_n) = \sum_{i=1}^{n} \frac{1}{2} m_i \dot{q}_i^2$$

Cartesian co-ordinate system :-

N Particles —

$$K(\vec{v}_1, \vec{v}_2 \dots \vec{v}_n) = \sum_{i=1}^{n} \frac{1}{2} m_i \vec{v}_i^{\,2}$$

Potential Energy ; $U(\vec{r}_1, \vec{r}_2 \dots \vec{r}_n)$

Lagrange's Equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \vec{v}_i}\right) = \frac{\partial L}{\partial \vec{r}_i}$$

$$\Rightarrow \frac{d}{dt}\left(\frac{\partial K}{\partial \vec{v}_i}\right) = -\frac{\partial U}{\partial \vec{r}_i}$$

$$m_i \frac{d\vec{v}_i}{dt} = -\frac{\partial U}{\partial \vec{r}_i} = \vec{F}_i$$

force on atom i.

Equation of Motion.

Conservation Laws →

→ Homogeneity in time → energy conservation.

→ Homogeneity in space → momentum. Conservation

→ Isotropy in space → Angular momentum Conservation.

Homogeneity in Time →

$$\frac{dL}{dt} = \sum_i \left(\frac{\partial L}{\partial q_i} \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i\right)$$

Lagrange's Eqn:

$$\boxed{\frac{dL}{dq_i} = \frac{d}{dt}\left(\frac{dL}{d\dot{q}_i}\right)}$$

From Lagrange's Equation:

$$= \sum_i \left[\dot{q}_i \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) + \frac{\partial L}{\partial \dot{q}_i} \frac{d}{dt}(\dot{q}_i) \right]$$

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$$\frac{dL}{dt} = \sum_i \frac{d}{dt}\left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i}\right)$$

$$\Rightarrow \sum_i \frac{d}{dt}\left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i}\right) - \frac{dL}{dt} = 0$$

$$\frac{d}{dt}\left(\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L\right) = 0$$

$$\Rightarrow \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L \rightarrow$$ constant of motion (does not change with time)

We know that :-

$$L = K(\dot{q}) - U(q)$$

$$\frac{\partial L}{\partial \dot{q}} = \frac{\partial K}{\partial \dot{q}} = m\dot{q}$$

$$\Rightarrow \sum_i \dot{q}(m\dot{q}) - L = C$$

$$\underbrace{\sum_i m\dot{q}^2}_{2K} - L = C$$

$$2K - (K - U) = C$$

$$\boxed{K + U = C}$$

Total Energy is Constant $\Rightarrow$ $\boxed{K + U = C}$; Conservation of Energy.

$\Rightarrow$ L doesn't depend on time explicitly.

$\Rightarrow$ Total Energy, $H = K + U$ will be a constant of motion (law of conservation of energy)

Conservation of Momentum →

Homogeneity in space (the mechanical properties of a closed system are unchanged by any parallel displacement of the entire system in space).

→ Let us consider;

displace every particle by $\epsilon \Rightarrow q_i \to q_i + \epsilon$

Change in L → $\dot{q}_i \to$ fixed. (velocities are not changed) $\delta q_i = \epsilon$

$$\delta L = \sum_i \frac{\partial L}{\partial q_i} \delta q_i$$

$$= \epsilon \sum_i \frac{\partial L}{\partial q_i}$$

From Lagrange's Equation,

$$\rightarrow \delta L = \epsilon \sum_i \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)$$

Homogeneity in space $\Rightarrow \delta L = 0$.

$$\Rightarrow \frac{d}{dt}\left[\sum_i \frac{\partial L}{\partial \dot{q}_i}\right] = 0.$$

$L = K - U$

$L = \frac{m}{2} \Sigma \dot{q}_i^2 - U(q_i)$

$\frac{\partial L}{\partial \dot{q}_i} = m\dot{q}_i$

$$\Rightarrow \frac{d}{dt}\left[\sum_i m\dot{q}_i\right] = 0.$$

$m\dot{q}_i \to P_i$ (momentum of the i^{th} particle).

$$\frac{d}{dt}\left(\sum_i P_i\right) = 0.$$

This implies →

$$\sum_i P_i \equiv \text{Constant of Motion}$$

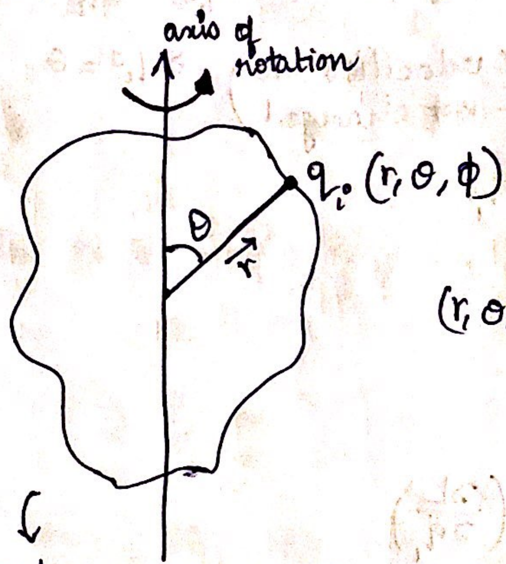
Law of Conservation of Momentum.

Conservation of Angular Momentum →

Isotropy in space (the mechanical properties of an isolated system would not change when rotated as a whole).

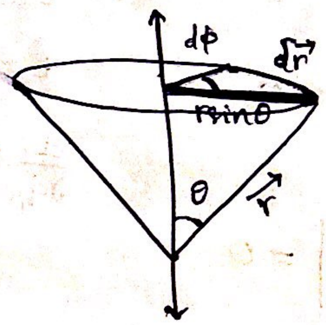
→ Let us consider;

Rotate a system about an axis.



$$(r, \theta, \phi) \xrightarrow{\text{rotation}} (r+\delta r, \theta, \phi+\delta$$

considering a single particle. →



$$\delta r = r\sin\theta\,\delta\phi$$

$$\delta\vec{r} = \delta\vec{\phi} \times \vec{r}$$

$$|\delta\vec{r}| = \delta r$$

$$\delta\vec{v} = \delta\vec{\phi} \times \vec{v}$$

$$L = L(\vec{r_i}, \vec{v_i})$$

change in L $\left\{ \delta L = \sum_i \frac{\partial L}{\partial \vec{r_i}} \cdot \delta\vec{r_i} + \frac{\partial L}{\partial \vec{v_i}} \cdot \delta\vec{v_i} \right.$

$$= \sum_i \vec{P_i} \cdot (\delta\vec{\phi} \times \vec{r_i}) + \vec{P_i} \cdot (\delta\vec{\phi} \times \vec{v_i})$$

$$= \delta\vec{\phi} \cdot \left(\sum \vec{r_i} \times \vec{P_i} + \vec{v_i} \times \vec{P_i} \right) = 0$$

⇒ $\delta\phi$ is arbitrary and isotropy in space

$\delta L = 0$

$$\Rightarrow \quad \frac{d}{dt}\left(\sum_i \vec{r_i} \times \vec{P_i}\right) = 0.$$

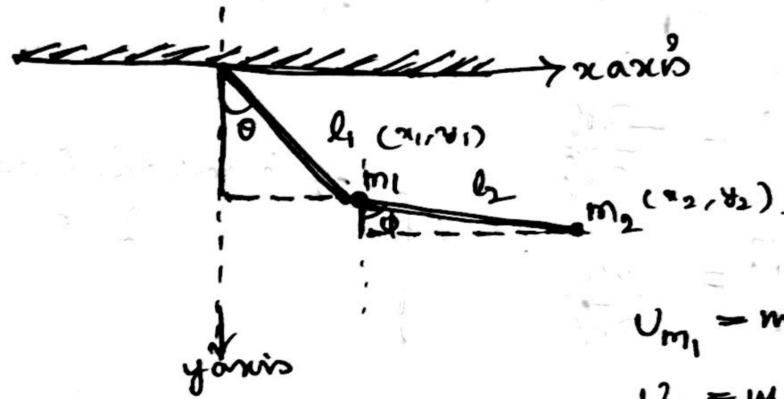
$\vec{r_i} \times \vec{P_i} \Rightarrow$ angular Momentum

$$\Rightarrow \quad \sum \vec{r_i} \times \vec{P_i} = \text{constant of Motion}$$

Law of Conservation of Angular Momentum

<u>Problem 1:-</u>

A Co-planar Pendulum $\rightarrow$



in plane motion

$U_{m_1} = m_1 g l_1 \cos\theta$

$U_{m_2} = m_2 g\,(h)$

$= m_2 g(l_1 \cos\theta + l_2 \cos\phi)$

$(U+K)_{system} = 0.$

$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$

Hamilton's Mechanics →

$$H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L \rightarrow \text{constant of motion}$$

total energy of the system $H = K(\{\dot{q}_i\}) + U(\{q_i\}) \rightarrow$ constant of motion

$H(\{\vec{r}_i\}, \{\vec{p}_i\})$

$$\frac{\partial}{\partial \vec{r}_i} = \frac{\partial}{\partial x_i} + \frac{\partial}{\partial y_i} + \frac{\partial}{\partial z_i}$$

$\frac{\partial H}{\partial t} = 0$ (isolated systems)

$$\frac{dH}{dt} = \sum_{i=1}^{N} \frac{\partial H}{\partial \vec{r}_i} \cdot \frac{d\vec{r}_i}{dt} + \frac{\partial H}{\partial \vec{p}_i} \frac{d\vec{p}_i}{dt} = 0$$

$$\left.\begin{aligned} \frac{d\vec{p}_i}{dt} &= -\frac{\partial H}{\partial \vec{r}_i} \\ \frac{\partial \vec{r}_i}{dt} &= \frac{\partial H}{\partial \vec{p}_i} \end{aligned}\right\} \Rightarrow \text{Hamilton's Equations of motion.}$$

RIGID BODY DYNAMICS →

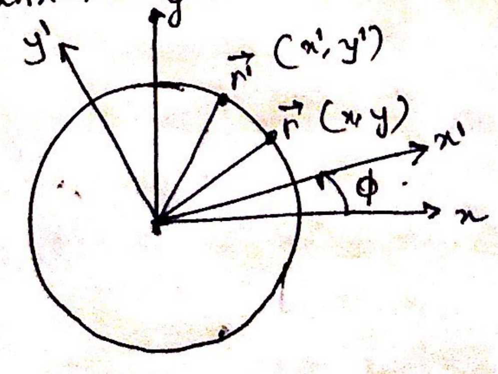
ROTATIONAL MOTION.

RIGIDBODY – Degrees of Freedom required $\} = 3 + 3 = 6$

Translational (↑ 3), Rotational (↓ 3)

→ Rotation Matrix →

Ex:



$\vec{r}$ = Position vec of a point before rotat

$\vec{r}'$ = Position vect after rotatic

with fixed frame of reference

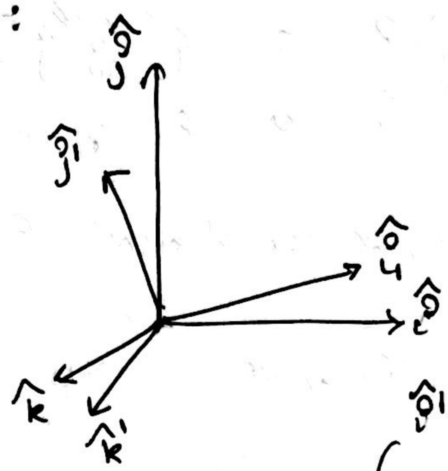
$$x' = x\cos\phi + y\sin\phi$$
$$y' = -x\sin\phi + y\cos\phi$$

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

Rotation Matrix $\equiv A$

$$\vec{r}' = A.\vec{r}$$

3D Rotation :



$\hat{i}, \hat{j}, \hat{k} \rightarrow$ before rotation

$\hat{i}', \hat{j}', \hat{k}' \Rightarrow$ after rotation.

$$\hat{i}' = (\hat{i}'.\hat{i})\hat{i} + (\hat{i}'.\hat{j})\hat{j} + (\hat{i}'.\hat{k}).\hat{k}$$

Using projection of that particular vector on the axes.

$$\hat{i}' = \cos(\hat{i}'.\hat{i})\hat{i} + \cos(\hat{i}'.\hat{j})\hat{j} + \cos(\hat{i}'.\hat{k})\hat{k}$$

$$\hat{i}' = \alpha_1\hat{i} + \alpha_2\hat{j} + \alpha_3\hat{k} \quad , \text{ where } \alpha_1 = \cos(\hat{i}'.\hat{i})$$

ully, $\hat{j}' = \beta_1\hat{i} + \beta_2\hat{j} + \beta_3\hat{k}$; where $\beta_1 = \cos(\hat{j}'.\hat{i})$
$\beta_2 = \cos(\hat{j}'.\hat{j})$
$\beta_3 = \cos(\hat{j}'.\hat{k})$

and

$\hat{k}' = \gamma_1\hat{i} + \gamma_2\hat{j} + \gamma_3\hat{k}$; where $\gamma_1 = \cos(\hat{k}'.\hat{i})$
$\gamma_2 = \cos(\hat{k}'.\hat{j})$
$\gamma_3 = \cos(\hat{k}'.\hat{k})$.

$$\begin{pmatrix} \hat{i}' \\ \hat{j}' \\ \hat{k}' \end{pmatrix} = \begin{pmatrix} \alpha_1 & \alpha_2 & \alpha_3 \\ \beta_1 & \beta_2 & \beta_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix} \begin{pmatrix} \hat{i} \\ \hat{j} \\ k \end{pmatrix}$$

$A \equiv$ general rotation matrix.

Matrix A has 9 elements involving 9 different angles.

↓

9 degrees of freedom

Question: Do we really need 9 degrees of freedom?

Orthogonal Conditions ⇒ $\hat{i}\cdot\hat{j} = 0$ & $\hat{i}\cdot\hat{i} = 1$

$\hat{j}\cdot\hat{k} = 0$ & $\hat{j}\cdot\hat{j} = 1$

$\hat{i}\cdot\hat{k} = 0$ & $\hat{k}\cdot\hat{k} = 1$

From these conditions, we can eliminate 6 degrees of freedom &

↓

thus, we are left with "3" degrees of freedom

$$\alpha_l \alpha_m + \beta_l \beta_m + \gamma_l \gamma_m = 0 \quad l, m = 1, 2, 3, \ldots l \neq m$$

$$\alpha_l^2 + \beta_l^2 + \gamma_l^2 = 1 \quad l = 1, 2, 3.$$

From these conditions:-

$$\alpha_l \alpha_m + \beta_l \beta_m + \gamma_l \gamma_m = \delta_{lm}$$

i.e $\delta_{lm} = 1 \, ; \, l = m$

$\delta_{lm} = 0 \, ; \, l \neq m$

→ Properties of A (Rotation Matrix):

→

$$(AB)C = A(BC)$$

→ $A \cdot A^{-1} = 1$

~~matrix~~ inverse of matrix A.

Standard rotation matrices →

→ Rotation about x-axis by ϕ

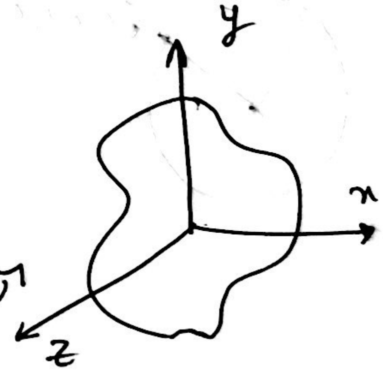
$$A_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & \sin\phi \\ 0 & -\sin\phi & \cos\phi \end{pmatrix}$$

lly rotation about y-axis by ϕ

$$A_y = \begin{pmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{pmatrix}$$

lly rotation about z-axis by ψ

$$A_z = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



Euler angles → (θ, ϕ, ψ)

* Any arbitrary rotation can be written as three successive rotations about x/y/z axes.

* Start from xyz

→ First rotation – rotate by ϕ counter clockwise about z-axis.
↳ new coordinate system = $x'y'z'$

→ Second rotation – rotate by θ counter clockwise about x'-axis
↳ new co-ordinate system = $x''y''z''$ $(x'' = x')$

→ Third rotation – rotate by ψ counter clockwise about z''-axis
↳ Final State – (XYZ)

XYZ → (xyz) [Multiplying all the three rotation matrices

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \overbrace{\big(\underbrace{A_3}_{\text{last rotation}} A_2 \underbrace{A_1}_{\text{first rotation}}\big)}^{E} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$A_1 = A_z(\phi)$

$A_2 = A_x(\theta)$

$A_3 = A_z(\psi)$

$E(\phi,\theta,\psi) = \cancel{A_z(\phi) \cdot A_x(\theta) \cdot A_z(\psi)}$

Euler Matrix: $A_z(\psi) \cdot A_x(\theta) \cdot A_z(\phi)$

$E(\phi,\theta,\psi) =$

$$\begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$