• Maxwells Eqn: Relations :

→ Internal Energy

$U(S,V)$

$$\Rightarrow \frac{\delta^2 U}{\delta S\,\delta V} = \frac{\delta^2 U}{\delta V\,\delta S}$$

order is immaterial
∴ state functions (something to do with curvature)

$$dU = TdS - PdV. \quad — (1)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V \partial S + \left(\frac{\partial U}{\partial V}\right)_S \partial V. \quad — (2)$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad — (3)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P. \quad — (4)$$

Use $$\frac{\partial^2 U}{\partial S\,\partial V} = \frac{\partial^2 U}{\partial V\,\partial S}.$$

From (3) :-

$$\frac{\partial}{\partial V}\left(\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial T}{\partial V}\right)_S$$

From (4) :-

$$\frac{\partial}{\partial S}\left(\left(\frac{\partial U}{\partial V}\right)_S\right)_V = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

→ Using $H(S, P)$

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V.$$

Using exactness condition : $\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.}$

Similarly for A & G :-

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.}$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T}$$

× ———— ×

- LAGRANGIAN MECHANICS | DYNAMICS :

Newtonian mechanics
↓
Lagrangian mechanics
↓
Hamiltonian mechanics

} Chronology.

We define a new scalar function called Lagrangian

$$L(\underbrace{q}_{\text{generalised coordinates}},\ \underbrace{\dot{q}}_{\text{generalised velocity}};\ t)$$

↳ implicit time dependence.

→ Generalized coordinates: that describe the degrees of freedom of the system. that describe the mechanics of.
Eg: Pendulum you will have x, y, z.

→ $\dot{q} = \dfrac{dq}{dt}$.

No explicit dependence of L on t.
⇒ ~~α~~ L cannot be written as a function of t.
but q is a func. of time & $\dot{q}$ func. of time.

NOW:- ★

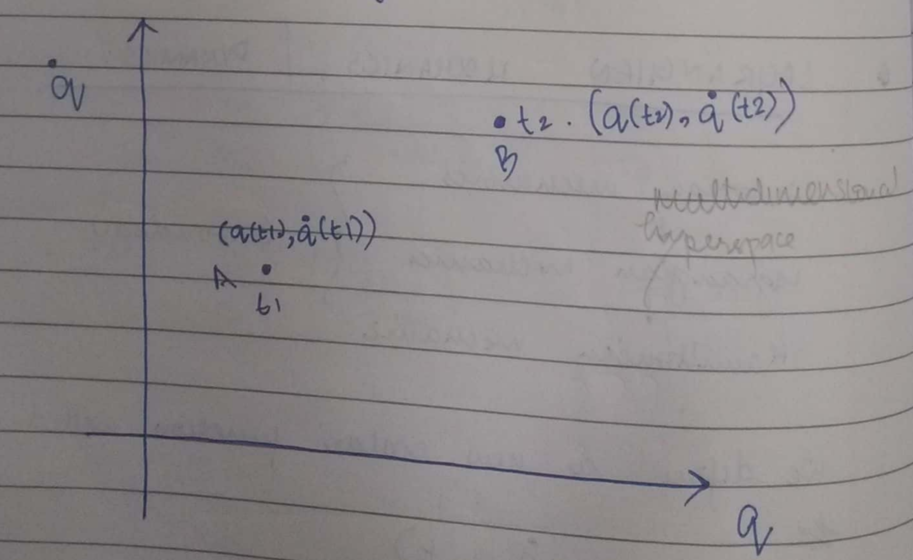
$$L(q, \dot{q}; t) = K(\dot{q}) - U(q)$$

$K(\dot{q})$: kinetic energy func.

$U(q)$: Potential energy function

[Only diff with Hamiltonian is the −ve sign for potential energy.]

In Lagrangian approach he defined phase space as a set of gen. coordinates & vel.



$t_2 > t_2$.

Q: what is the likely path the sys takes from $t_1 - t_2$

In principle from t_1

— Aim: To f
To do so,

▲ The principle

$S =$

The path probable

→ Consider

$(q(t)$

$(q(t) + \delta$

$\dot{q}$

Now

∴ change in S

In principle there can be infinitely many paths from t1 to t2

— Aim: To find the most probable path b/w A & B. To do so, we define a qty called action.

▲ <u>The principle of least action</u>:

$$S = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt.$$

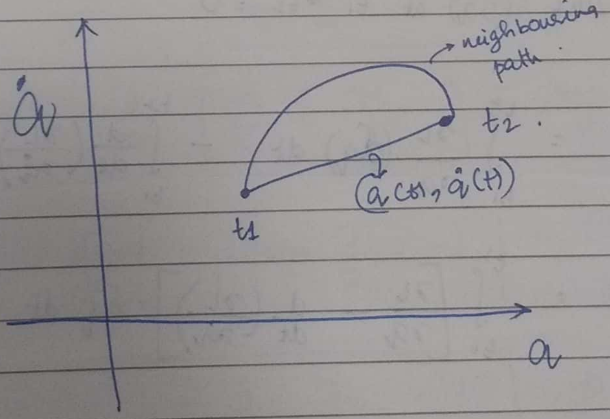
• sub KE & PE
• get avg. KE & PE

"The path with the least action is the most probable path"

→ Consider 2 paths:

$(q(t), \dot{q}(t)) \Rightarrow$ this ~~is~~ is least action path.

$(q(t) + \delta q(t), \dot{q}(t) + \delta \dot{q}(t)) \Rightarrow$ a neighbouring path.



Now the paths meet at t_1 & t_2.

$$\Rightarrow \delta q(t_1) = 0$$
$$\delta (q(t_2)) = 0$$

$\therefore$ change in S $= \delta S = \int_{t_1}^{t_2} L(q+\delta q, \dot{q}+\delta \dot{q}; t)\, dt - \int_{t_1}^{t_2} (q, \dot{q}; t)\, dt.$

$= \delta \int_{t_1}^{t_2} L(q,\dot{q};t)\,dt$

$= \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q}\right) dt$

But $\delta \dot{q} = \frac{d(\delta q)}{dt}$; see :-

$$\delta S = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q} \times \delta q + \frac{\partial L}{\partial \dot{q}} \times \frac{d}{dt}(\delta q)\right) dt$$

Consider the second term :-

$\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}} \times \frac{d}{dt}(\delta q)\,dt$ .... Integrating by parts

$$\cancel{\left[\frac{\partial L}{\partial \dot{q}}(\delta q)\right]_{t_1}^{t_2}} - \int_{t_1}^{t_2} \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)(\delta q)\,dt$$

0

since (δq) at t_1 & $t_2 = 0$

$$\Rightarrow \quad \delta S = \int_{t_1}^{t_2} \frac{\partial L}{\partial q}(\delta q)\,dt - \int_{t_1}^{t_2} \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)(\delta q)\,dt$$

$$\therefore \quad \delta S = \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)\right] \delta q \, dt$$

Because of least action ; ???

$\delta S = 0$

$\delta S = 0 \quad \forall q.$

$$\Rightarrow \quad \boxed{\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = 0}$$

Now KE doesnt de

∴ $\frac{\partial L}{\partial q} =$

$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) =$

→ How do we get

Let us calculate

$\frac{dL}{dt} = \sum_{i=1}^{N}$

n gene

Now from Lagrang

$\frac{dL}{dt} = \sum_{i=1}^{N} \dot{q}_i$

$\frac{dL}{dt} =$

Hamiltonian

Now KE doesnt depend on coordinates

$\therefore \quad \frac{\partial L}{\partial q} = -\frac{\partial U}{\partial q} = $ force — ①

$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = $ rate of change of generalized momentum — ②

→ How do we get Hamiltonian from Lagrangian ?

Let us calculate $\frac{dL}{dt}$

$$\frac{dL}{dt} = \sum_{i=1}^{N} \frac{\partial L}{\partial q_i}\dot{q}_i + \sum_{i=1}^{N} \frac{\partial L}{\partial \dot{q}_i}\ddot{q}_i$$

n generalized coords

Now from lagrangian equation

$$\frac{dL}{dt} = \sum_{i=1}^{N} \dot{q}_i \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) + \sum_{i} \frac{\partial L}{\partial \dot{q}_i}\frac{d}{dt}(\dot{q}_i)$$

$$\frac{dL}{dt} = \sum_i \frac{d}{dt}\left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i}\right)$$

$$\Rightarrow \frac{d}{dt}\left[\sum_i \dot{q}\frac{\partial L}{\partial \dot{q}_i}\right] - \frac{dL}{dt} = 0$$

$$\Rightarrow \frac{d}{dt}\left[\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L\right] = 0.$$

$$\Rightarrow \boxed{\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L} \Rightarrow \text{constant}$$

Hamiltonian.

[Law of conservation of energy]

$$\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial K}{\partial \dot{q}_i} = m\dot{q}_i$$

External forces acting on a system $\Rightarrow \frac{dL}{dt} \neq 0$

$\frac{dL}{dt} = 0 \quad \therefore$ isolated system.

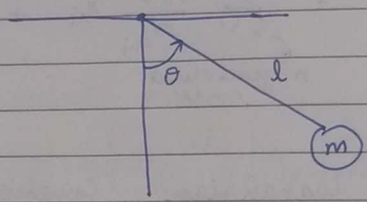
$$\sum \dot{q}_i (m \dot{q}_i) - L = \text{constant}$$

$$2K - K + U = \text{constant}$$

$$\Rightarrow \boxed{K + U = \text{constant}}$$

$$H = K + U$$

(I) Simple Pendulum :-



Construct L

$K(\dot{\theta})$, $L(\theta)$

$$L(\theta, \dot{\theta}) = K(\dot{\theta}) - L(\theta).$$

$\frac{\partial L}{\partial \theta}$ and $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right)$

$$\frac{\partial L}{\partial \theta} = -mgl\sin\theta$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) = ml^2 \ddot{\theta}$$

$$\boxed{ml^2\ddot{\theta} + mgl\sin\theta = 0}$$

Lagranges equ of motion.

→ Now going

$\frac{dL}{dt} \Rightarrow H$

? $\frac{dL}{dt}$ =

(For an syst

But if ∃ som with time

If implicit depen then $L(q, \dot{q}; t$

→ Homogenity

L of an on time e ⇒

→ Conservatio

→ Homogeni The mec change

→ Now going back to deriving the hamiltonian.

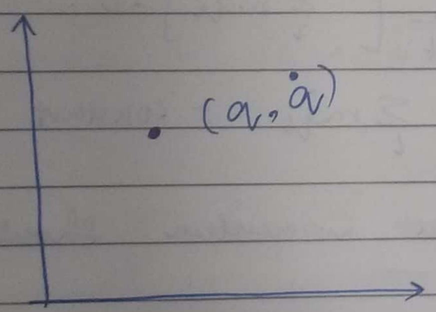
$$\frac{dL}{dt} \Rightarrow H \equiv \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = \text{constant}$$

? $$\frac{dL}{dt} = \sum_i \frac{\partial L}{\partial \dot{q}_i}\frac{d\dot{q}_i}{dt} - \frac{\partial L}{\partial \dot{q}_i}\frac{d\dot{q}_i}{dt} \Big] + \underbrace{\cancel{\frac{\partial L}{\partial t}}}_{0}$$

(For an isolated system) ⟵ ∵ L is not an explicit function of time

But if ∃ some external influence then L could vary with time.

If ~~...~~ implicit dependence, then each state would have unique L
$L(q, \dot{q}; t) \Rightarrow$ homogeneity in time.



→ Homogenity Of Time:

L of an isolated system does not ~~chan~~ depend on time explicitly
$\Rightarrow$ Energy will be conserved.

→ Conservation Of Momentum:

→ Homogenity of space:
The mechanical properties (i.e: L) would not change by any parallel displacement of the

entire system

Method: Displace every particle by ϵ; such that velocities are fixed then If

$$q_i \longrightarrow q_i + \epsilon$$

$$\delta L = \sum_i \frac{\partial L}{\partial q_i} (\delta q_i) \quad \delta q_i \rightarrow \epsilon$$

By homogenity of space

$$\Rightarrow \delta L = 0$$

$$\Rightarrow \epsilon \sum_i \frac{\partial L}{\partial q_i} = 0$$

$$\Rightarrow \epsilon \frac{d}{dt}\left[\sum_i \frac{\partial L}{\partial \dot{q}_i}\right] = 0.$$

$$\Rightarrow \frac{d}{dt}\left[\sum_i m\dot{q}_i\right] = 0.$$

$$\Rightarrow \sum_i m\dot{q}_i = \text{constant}$$

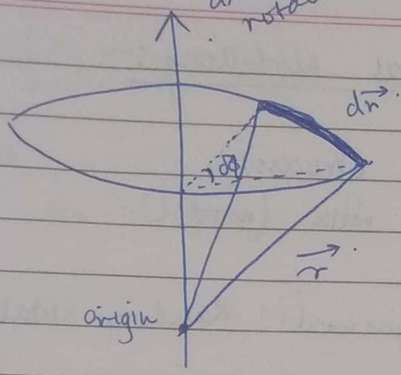
$\Rightarrow$ Total linear momentum should be conserved.

- **Conservation Of Angular Momentum:**

↳ Isotropy of space

↳ L is invariant under the rotation of the whole system by an arbitrary angle.

- Time & energy coupled.
- Impossible to measure energy & time together simultaneously



Change in $\vec{r}$ due to the rotation by $\delta\phi$ angle

$$\vec{\delta r} = \delta\vec{\phi} \times \vec{r}$$

where

$\delta\vec{\phi}$ => magnitude is $\delta\phi$
=> direction is axis of rotation.

|||ly change in velocity.

$$\vec{\delta v} = \vec{\delta\phi} \times \vec{v}$$

Now, $$\delta L = \sum_i \frac{\partial L}{\partial \vec{r_i}} \delta\vec{r_i} + \frac{\partial L}{\partial \vec{v_i}} \delta\vec{v_i}$$

Using isotropy of space => $\delta L = 0$.

$$\sum_i \dot{\vec{P_i}} \cdot (\delta\vec{\phi} \times \vec{r}) + \vec{P_i} \cdot (\delta\vec{\phi} \times \vec{v})$$

(see using lagranges)

[Permuting factors $a\cdot(\vec{b}\times\vec{c}) = b\cdot(\vec{c}\times a)$

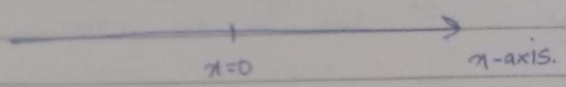
$$\delta\phi \sum_i \vec{r_i} \times \dot{\vec{P_i}} + \vec{v_i} \times \vec{P_i} = 0$$

$$= \delta\phi \cdot \underline{d}$$

- **Mathematical Modelling :-**

→ Diffusion (Process)
→ Random walk (model)

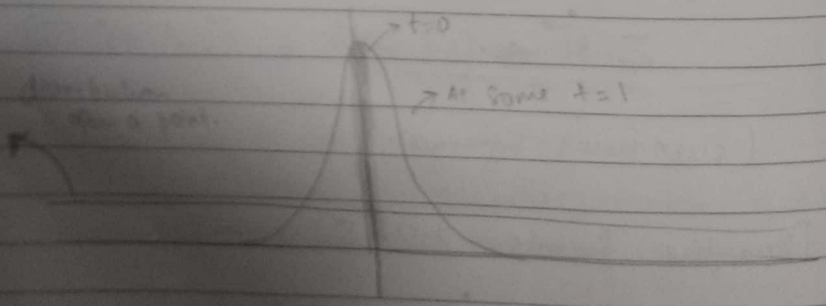
→ One dimensional Random Walk :-



- A drunkard starts from $x = 0$
- Each step he takes is of equal length l
- The direction of each step is random
- At each time the prob to go to the right is p while the probability to go left is q.

Q. After N steps what is the probability that the drunk is located at a given distance from the origin

At time $t=0$ → Dirac Delta function
$P(x=0) = 1$



Let N → total no. of steps
n_1 → no. of steps to right
n_2 → no. of steps to the left

$$\boxed{n_1 + n_2 = N}$$

convention of $\xleftarrow{-ve}$ $\xrightarrow{+}$

Net displacement

$$m = (n_1 - n_2)\, l$$

$$-Nl \le m \le Nl$$

The probability of taking n_1 steps to the right in a total of N steps $\Bigg\}$ $W_N(n_1) = \frac{N!}{n_1!\, n_2!}\, p^{n_1} q^{n_2}$

~ Simple case

$N = 3 \quad n_1 = 2, \quad n_2 = 1.$

3 possibilities

Here, $$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)!\,\left(\frac{N-m}{2}\right)!}\, p^{\frac{N+m}{2}}\, q^{\frac{n+m}{2}}$$

when $l = 1$.

Further $\rightarrow$ mean no. of steps to the right.

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

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

Use $$n_1 p^{n_1} = p \frac{\partial}{\partial p} p^{n_1}$$

$$\Rightarrow \langle n_1 \rangle = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\, p \frac{\partial p^{n_1}}{\partial p}\, q^{N-n_1}$$

→ Interchange the order of summation & differentiation

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

$$\langle n_1\rangle = p\frac{\partial}{\partial p}(p+q)^N.$$

$$\langle n_1\rangle = pN(p+q)^{N-1}.$$

For an unbiased random walk

$$p = q = \frac{1}{2}$$

$$\boxed{\langle n_1\rangle = Np}$$

Similarly, $\langle n_2\rangle = Nq.$

Mean displacement

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

$$= \langle n_1\rangle - \langle n_2\rangle \quad : \quad \mathbb{E}[n_1] - \mathbb{E}[n_2]$$

$\because$ $p = q$ for unbiased walker

$$\Rightarrow \langle m\rangle = 0.$$

This is why $\bar{e}$ in a metallic wire do not produce electricity unless biased.

Also, $\langle m^2\rangle \neq 0$

To calculate this introduce a stat. qty (basically same thing! -.-), dispersion of n_1:-

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

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

And: $\langle n_1^2 \rangle = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} n_1^2$

Use

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

we know; $n_1 p^{n_1} = p \frac{\partial}{\partial p} p^{n_1}$

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

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

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

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

$$= \left(p\frac{\partial}{\partial p} \right)^2 [p+q]^N.$$

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

$$p \left[p \, N(N-1)(p+q)^{N-2} + N(p+q)^{N-1} \right]$$

$$p \left[pN^2 - pN + N \right]$$

$$= (Np)^2 + Npq.$$

$$\langle n_1 \rangle^2 + Npq.$$

$$\Rightarrow \langle (\Delta n_1)^2 \rangle = Npq$$

Now, $m = n_1 - n_2$

$$= 2n_1 - N.$$

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

$$= 4Npq$$

But $p = 1/2 \quad q = 1/2$

$$\therefore \quad \langle m^2 \rangle = N.$$

Further $\quad m = 2n_1 - N.$

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

$$\langle (\Delta m)^2 \rangle = \langle (m - \underbrace{\cancel{\langle m \rangle}}_{0})^2 \rangle = \langle m^2 \rangle$$

$$\Delta m = 2 \Delta n_1$$

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

Mean square displacement varies linearly with time

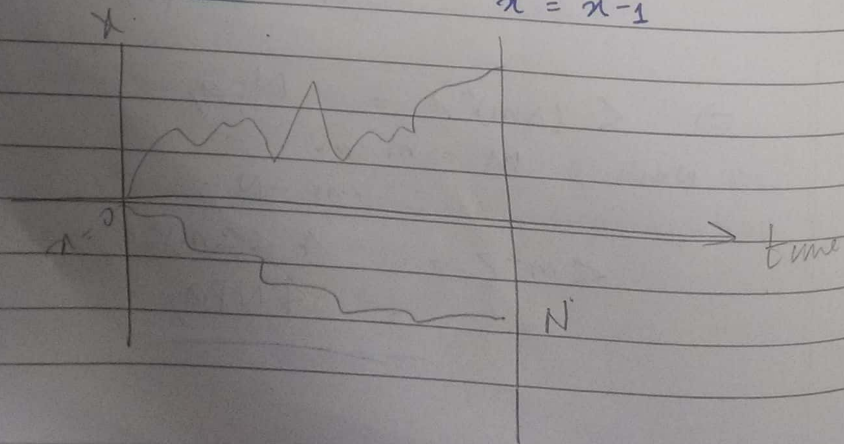
Code:

$S \rightarrow$ # of random walkers
$N \rightarrow$ # of steps.

~~xxxx~~

$N = 10{,}000$.

$i = 1, S$
$x = 0;$
$j = 1, N$
Call a random no: (P)
if(P > 0.5) $\Rightarrow$ $x = x+1$ (move right)
else $\quad x = x-1$



Recap:

N steps

$n_1 \Rightarrow$ right (p)

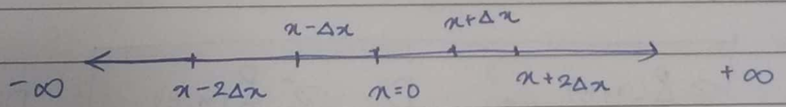
$n_2 \Rightarrow$ left (q).

qtys :- $\langle n_1 \rangle$, $\langle n_2 \rangle$, $\langle (\Delta n_1)^2 \rangle$; $\langle (\Delta n_2)^2 \rangle$

Also, • $\langle m \rangle = 0$ }
• $\langle m^2 \rangle$ } vary linearly with time N.

Fact: error $\propto \dfrac{1}{\sqrt{\text{samples}}}$.

• <u>Derive Diffusion Eqn. from Random Walk Model :-</u>



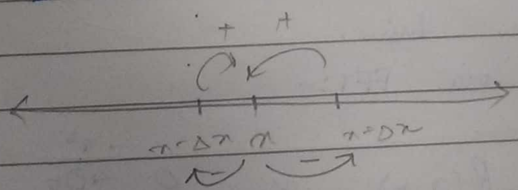
Δx : step length

Δt : time step.

$P(x,t) \rightarrow$ Probability of finding the random walker at x at time t.

Change in probability at x:-

$P(x, t+\Delta t) - P(x,t)$ —— (1)



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

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

time variation

$$P(x, t+\Delta t) - P(x,t) = \frac{1}{2}\Big[\underbrace{P(x+\Delta x, t) + 2P(x,t) + P(x-\Delta x, t)}_{\text{spatial var.}}$$

Diff. eqn couples spatial variation in probability with time variation.

Now ÷ by (Δt), $(\Delta x)^2$ on both sides

$$\Rightarrow \frac{P(x,t+\Delta t) - P(x,t)}{\Delta t} = \underbrace{\frac{(\Delta x)^2}{2\Delta t}}_{D}\left[\frac{P(x+\Delta x,t) + 2P(x,t) + P(x-\Delta x,t)}{(\Delta x)^2}\right] \quad (2)$$

In the limit $\Delta t \to 0$, $\Delta x \to 0$
(moving from discrete to continuous :
... converting random walk to diffusion.)

Eqn (2) becomes :-

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

Diffusion Equation

Diffusion constant $= \dfrac{(\Delta x)^2}{2\Delta t}$.

On solving the diff. eqn. we obtain the prob. of finding the random walker at a given x at a given time.
Solving via FFT :-

$$P(x,t) \propto e^{\frac{-x^2}{4Dt}}$$

Eg: consi

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Q: Two

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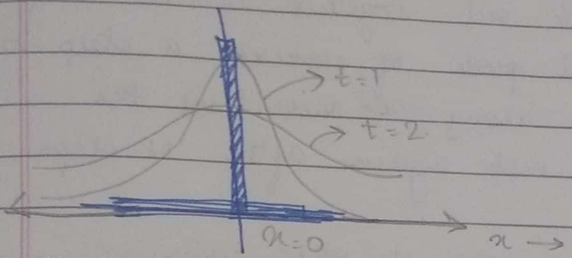
Eg: consider a drop of ink placed at the origin at $t=0$



→ $\langle x \rangle = 0$

$\langle x^2 \rangle \propto t$

→ ASSIGNMENT :

Q: Two drunks start out together at the origin, each having equal probability of making a step to the left or right along x-axis. Find the probability that they meet again after N steps

We know, $P_N(m) = \dfrac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}} q^{\frac{N-m}{2}}$

We can redefine the model as 2N steps being taken with disp $= 0$.

$$\therefore P_{2N}(0) = \frac{(2N)!}{\left(\frac{2N}{2}\right)!\left(\frac{2N}{2}\right)!} \times \left(\frac{1}{2}\right)^{2N}$$

$$= \frac{(2N)!}{2^{N \cdot 2}(N!)^2}$$ for every value of N.

Assignment: (Theoretical solution) :-

Q: Two drunks start out together at the origin, each having equal prob. of making a step to the left or right along x-axis. Find the prob. that they met again after N steps

Ans Let walker 1 & 2 take N steps each.
We can remodel the given scenario by considering their relative positions.

That is the no: of steps = N+N = 2N
& the net displacement = 0
[∵ they meet]

Now we know that for N steps & disp = m

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} \times p^{\left(\frac{N+m}{2}\right)} q^{\left(\frac{N-m}{2}\right)}$$

Sub N = 2N & m = 0 q = 1/2, p = 1/2
we get :-

$$P_{2N}(0) = \frac{(2N)!}{\left(\frac{2N}{2}\right)!\left(\frac{2N}{2}\right)!} \left(\frac{1}{2}\right)^N \cdot \left(\frac{1}{2}\right)^N$$

$$\boxed{P_{2N}(0) = \frac{(2N)!}{2^{2N}(N!)^2}}$$

→ Mathematical

↳ Diffusi

↳ Random

↳ Diffusi

One dimen

Three dime

3D diffu

$\frac{\partial \rho(\vec{r}, t}{\partial t}$

On solving
$\langle x \rangle$
$\langle x$

different w
• Ice hit with
a specific

→ Mathematical Modelling :

↳ Diffusion.

↳ Random Walk : Mean displacement $\langle m \rangle = 0$

Mean square displacement $\langle m^2 \rangle \propto N \propto t$

↳ Diffusion Equ $\dfrac{\partial P(x,t)}{\partial t} = D \dfrac{\partial^2 P(x,t)}{\partial x^2}$

$$\frac{\partial C}{\partial t}(x,t) = D \frac{\partial^2 C(x,t)}{\partial x^2}$$

One dimensional

$$P(x,t) \propto e^{-\frac{x^2}{4Dt}}$$

Three dimensional

$$P(\vec{r},t) \propto e^{-\frac{(x^2+y^2+z^2)}{4Dt}}.$$

3D diffusion eqn :-

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

On solving the diffusion eqn :-

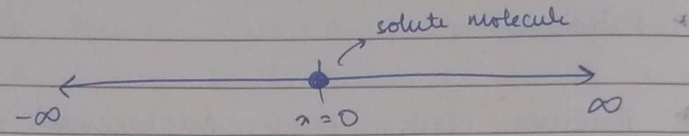
$\langle x \rangle = 0$

$\langle x^2 \rangle \propto t$ } mean square displacement varies linearly with time.

→ different values when measured in diff directions

- Ice hit with a hammer : cracks propagate in a specific manner (anisotropic)
- whereas for water the pressure is evenly dist

- **Example:**



- Mass of solute = m
- The solute is going to be executing random brownian motion
- Two forces drive this motion → damping force (medium resists the motion & fast) → Random force: changes direc & disp.

The pos. of the particle is going to vary as a function of time

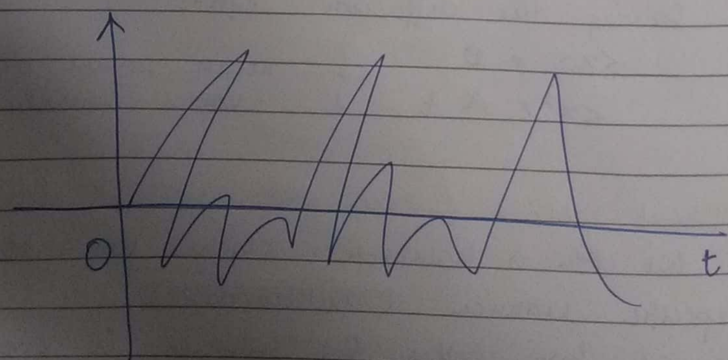
ie:-

$$m\frac{d\dot{x}}{dt} = \text{damping force} + \text{random force}$$

From the medium providing friction to the motion of solute

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

α : positive constant (friction constant)



The Random force : $\langle F \rangle = 0$

Step 1: $\times\ x$ on both sides

$$m x \frac{d\dot{x}}{dt} = -\alpha x \dot{x} + xF$$

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

Taking avg. on both sides :-

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

→ Uncorrelated noise.

$$\langle xF \rangle = \langle x \rangle \langle F \rangle = 0 \quad \text{(uncoupled)}$$

$$\left[\langle xy \rangle = \iint_{x\,y} xy\, P(x,y)\, dx\, dy = \quad P(x,y) = P(x) \cdot P(y)\right]$$

$$= \int_x x P(x)\, dx \times \int_y y P(y)\, dy.$$

From the equipartition th.

$$\frac{1}{2} m \dot{x}^2 = \frac{1}{2} k_B T$$

Sub in equ (2) :- we get :

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

NOTE: $\langle x\dot{x} \rangle = \frac{1}{2}\frac{d}{dt}\langle x^2 \rangle$ ★ $\left(\frac{d}{dt}(x^2) = 2x \cdot \frac{dx}{dt}\right)$

Left margin (facing page): motion of particle (medium) changes direc. disp. / force / (1)

$$\int x \frac{dx}{dt} = c e^{-\gamma t} dt + \frac{k_B T}{\alpha} dt$$

$$\frac{x^2}{2} = \frac{c e^{-\gamma t}}{\gamma} + \frac{k_B T t}{\alpha}$$

Now, $\langle x \dot{x} \rangle = c e^{-\Gamma t} + \frac{k_B T}{\alpha}$ —— ★

here, $\Gamma = \frac{\alpha}{m}$

At time $t = 0$, $x = 0$

$$\Rightarrow \boxed{c = -\frac{k_B T}{\alpha}}$$

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

Substitute ★ in ★ and integrate to solve.

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

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

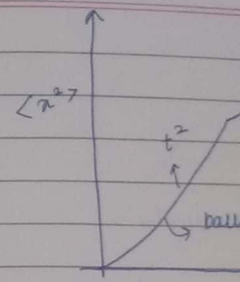
$$\Rightarrow \langle x^2 \rangle \simeq \frac{2 k_B T}{\alpha} t$$

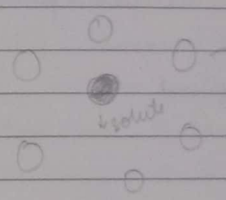
limit 2: $t \ll \frac{1}{\Gamma}$ (smaller time scale)

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

$$\Rightarrow \boxed{\langle x^2 \rangle \simeq \frac{k_B T}{m} t^2}$$

quadratic dependence on time for small time scales. ~~b/f~~ Happens when you have no forces acting on the particles





→ Heat Equation:

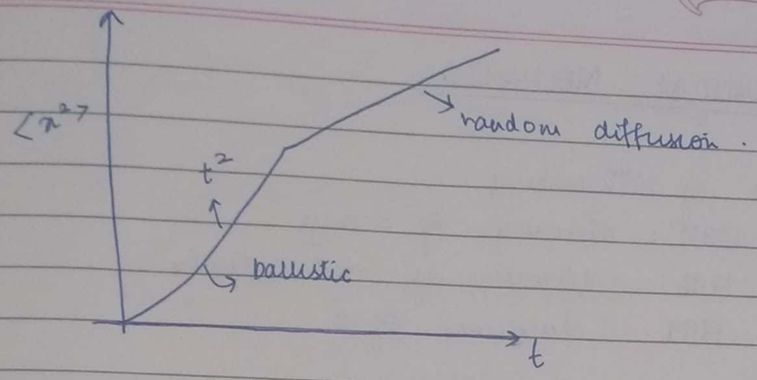
$T(x,t) \Rightarrow$

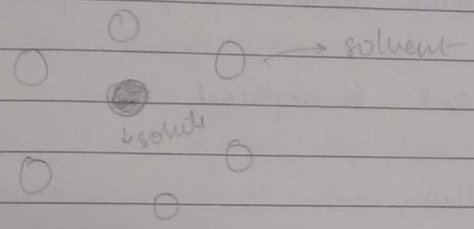
$\frac{\partial T(x,t)}{\partial t}$

Describes how
material

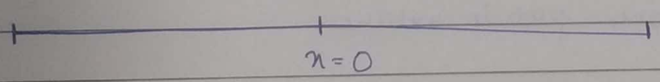
D

Where σ_t =
ρ =
C =





→ <u>Heat Equation:</u>



$T(x,t) \Rightarrow$ temperature at x at time t

$$\frac{\partial T(x,t)}{\partial t} = \underbrace{D_T}_{\text{thermal diffusability}} \frac{\partial^2 T(x,t)}{\partial x^2}$$

Describes how heat would flow through a given material

$$D_T = \boxed{\frac{\sigma_T}{\rho C}}$$ ... conductivity

where σ_t = thermal conductivity of the material

ρ = density of material

C = heat capacity of material.

QUANTUM MECHANICS:

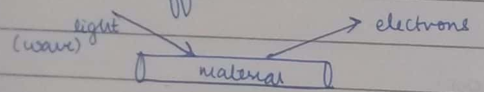
end of 19th century
- 1895 : discovery of X-Rays
- 1896 : discovery of radioactivity
- 1897 : discovery of $\bar{e}$

led to the belief that there are finer particles exist

Concepts that couldnt be explained

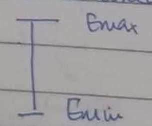
→ Black body Radiation.

→ Photoelectric effect



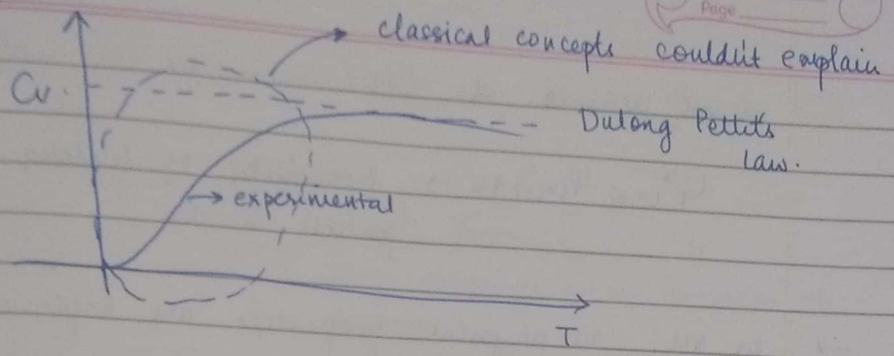
this made scientists think light could have particle nature

→ Hydrogen spectrum:
(To study the energies of H atom traditionally you'd create a Hamiltonian & define a range) like so:



thus you should get a continuous spectrum whereas on doing the exp it was found that light of only certain frequencies was emitted.

→ Heat capacity of solids (low temperatures)
For classical ideal gas model the heat capacity of the material at a constant volume is independent of the temperature (this is the expectation)



— Einstein used quantum principles to propose valid changes / reasoning.

→ Diffraction of $\bar{e}$s by crystals:
Discovery of $\bar{e}$ was believed that the $\bar{e}$ was a particle. But $\bar{e}$ diffraction indicates wave nature

→ Spin ~~of~~ / angular momentum could not be explained.

- <u>Framework of QM:</u>
To understand any quantum system, compute:-

analogous to Σ — $\Psi(x,t)$ ⇒ wave function (for one dim system)

spatial degree of freedom (x), time (t)

→ Properties of Ψ :
- finite
- ~~es~~ single valued → unique value for a given x — cannot have 2 diff probabilities
- continuous

Also, $\Psi^*(x,t)\ \Psi(x,t)$ ⇒ probability density

$\Psi^*(x,t)$: complex conjugate of $\Psi(x,t)$

Now multiplying this by a small length el $d(x)$ 1 dim

Quantum system → energy quantized

or vol element dv (3D) we get

$\Psi^*(x,t)\,\Psi(x,t)\,dx \Rightarrow$ Probability of finding the particle in dx

→ In QM, all physical properties are expressed as mathematical operators.

operation of P on the wave function

Eg: • momentum $\hat{P} = -i\hbar \frac{\partial}{\partial x}$??

operator — apply on the wave function

$\hbar = \frac{h}{2\pi}$ → plancks const

• Kinetic energy $\hat{K} = \frac{\hat{P}\cdot\hat{P}}{2m} = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

operate this on the wave function you'll get the K.E of the particle at that state which can be compared with experimental results.

Now, defining the hamiltonian : (operator

$$\hat{H} = \hat{K} + \hat{U}$$

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

For a quantum ideal gas $U(x) = 0$

• Schrodinger eqn:

transformation → $\hat{H}\,\Psi(x,t) = E\,\Psi(x,t)$ Eigen value problem

E → scalar total energy of the system

Time Indep S.Eqn.

Sub $\hat{H}$:-

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + U(x)\,\Psi(x,t) = E\,\Psi(x,t)$$

At a given time ↑ tells you how Ψ is distributed over x

Solve the differential eqn to find $\Psi(x,t)$ & E

In general: for any operator :-

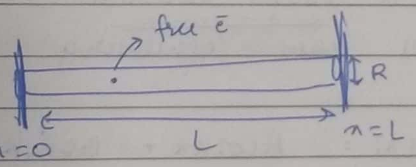
$$\hat{O}\,\Psi(x,t) = O\,\Psi(x,t)$$

scalar: measure of the property of interest.

■ <u>MODEL 1</u> :

Quantum particle in a 1-D box

Consider a metallic wire of length L & diameter R such that $L >> R$, ∴ can be treated as a 1-D object. Place 1 $\bar{e}$ in the wire (hypothetical) free $\bar{e}$. ∴ potential = 0 inside wire



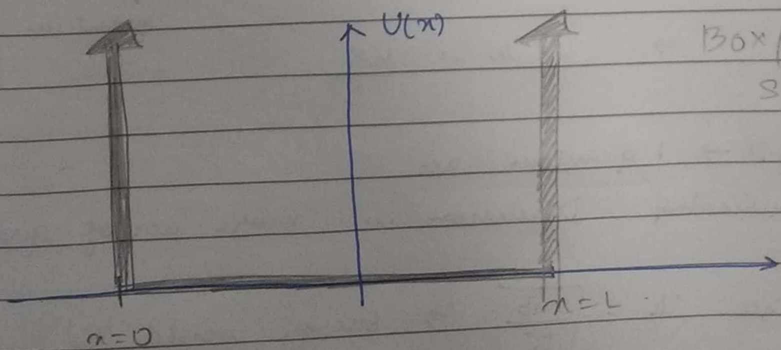
If the $\bar{e}$ executes random motion then

$\langle x \rangle = 0$ ... classical result

$U(x) = 0$ for $0 < x < L$ → free

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

$U(x) = \infty$ $x = L$. } $\bar{e}$ cannot come out of the wire



Box/well shaped

classmate
Date
Page

Solving the schrodinger eqn:

- Inside the box:-

$U(x) = 0$

$\therefore \quad \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = E\,\Psi(x,t)$ ... free particle whose dynamics controlled by kinetic energy

Rewriting this as:-

$$\frac{d^2}{dx^2}\Psi(x,t) + k^2\Psi(x,t) = 0 \quad \text{--- (1)} \quad \ldots \text{ where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

(will drop t $\because$ we're looking at a particular time instant)

This is a simple-harmonic osc. eqn — (1)

$\therefore$ it will have oscillating soln

ie:-

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

at $x = 0$, $\Psi(x=0) = 0 \Rightarrow \boxed{A = 0}$

$x = L$ $\quad \Psi(x=L) = 0 \Rightarrow B\sin kL = 0$

Here $B \neq 0$ $\because$ trivial

$\therefore \sin kL = 0$

ie: $kL = n\pi$ ... n is integer
↓
quantum number

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

1D → 1 quantum no:

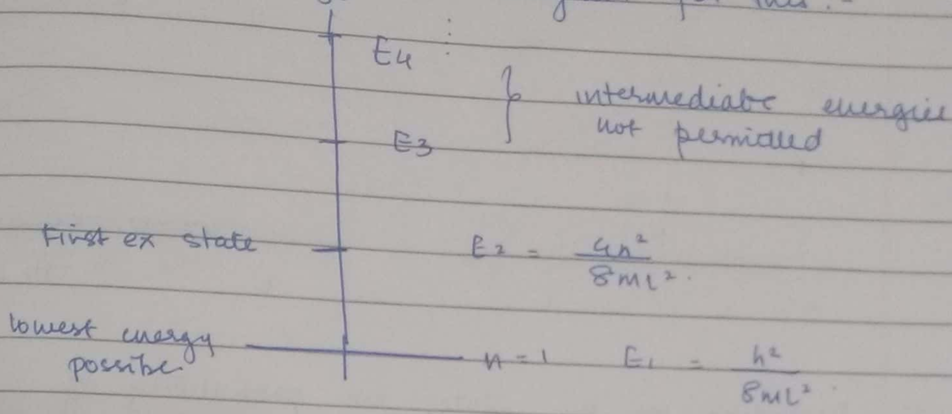
Increasing Dimension .... more no: of quantum nos:

Now, Since $k = \sqrt{\frac{2mE}{\hbar^2}}$ ⇒ Energy would be

$$\boxed{E = \frac{n^2h^2}{8mL^2}}$$ ⇒ Energy is quantised

$E = h\nu$

Drawing the energy level diagram for this :-



This explains why H atom on returning to the ground state emits radiations of only certain frequencies (discrete, not a spectrum)

∴ the solution becomes:-

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

Using normalization condition (of finding the electron within the wire = 1)

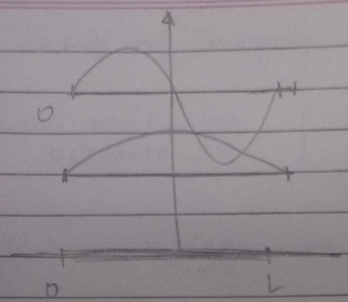
ie:
$$\int_{x=0}^{x=L} \psi^*(x) \cdot \psi(x)\, dx = 1$$
.... find B

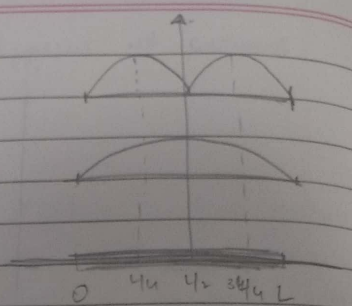
On solving we get $B = \sqrt{\frac{2}{L}}$

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

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

The system can exist in various states
∴ Now $\psi(x)$ depends on n, the state of the particle





- Depending on the state, the probability of finding the particle varies
- As $n \uparrow$, probability becomes delocalized

As $n \to \infty$, all points are equally likely and thats when you hit the classical limit

Classical concepts revert when $n \to \infty$