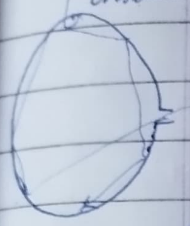
Quantum Physics

Kirchoff's Law of Heat Radiation:-

Good absorber ~~are always~~ are always, good emitter.

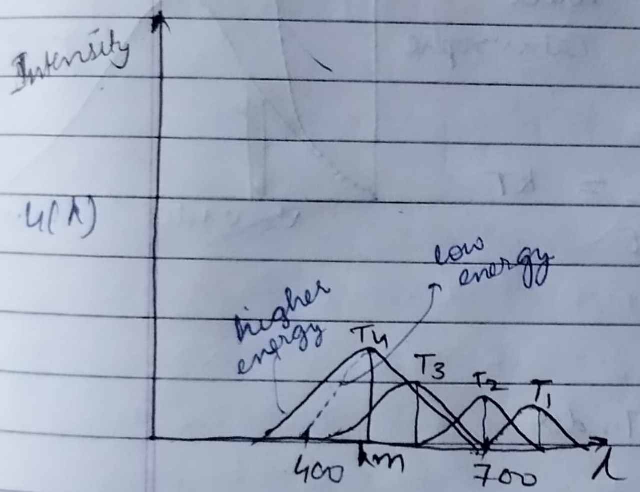
Eg: painted black inside -



At a given temp. the coefficient of absorption of a body is equal to its coefficient of emission.

light gets trap inside this. → perfectly absorbed → When this ~~container~~ heated at various temp.(T) → will emit radiations of all frequencies (or λ's) → Black body emits continous spectrum.

Wien's Displacement Law:-



here $T_1 < T_2 < T_3 < T_4$

$$\boxed{\lambda_m T = b = 2.898 \times 10^{-3}\ m\text{-}K.}$$

$u(\lambda) \rightarrow$ Energy per unit volume.

Experimental law:

$$\boxed{u(\nu)\,d\nu = \nu^3 f(\nu/T)}$$

Functional form

Stefan's Law -

$$u(\nu) = \underbrace{\sigma}_{\text{const.}} T^4$$

Wien's Radiation Laws:-

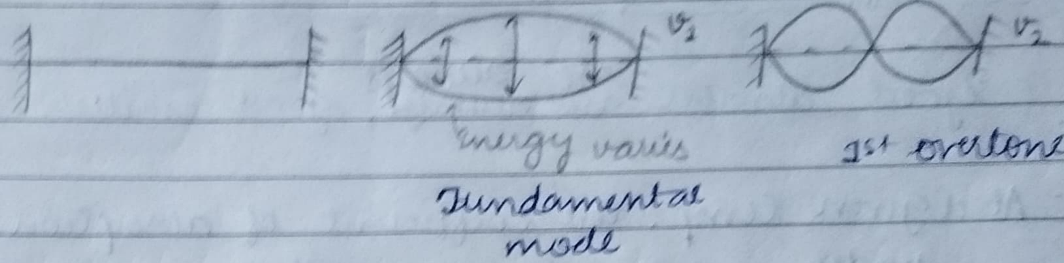
Empirical formula $\longrightarrow$ $\boxed{u_\nu = a\nu^3 e^{-b\nu/T}}$ → here a & b are constants.

Rayleigh-Jeans Law:-

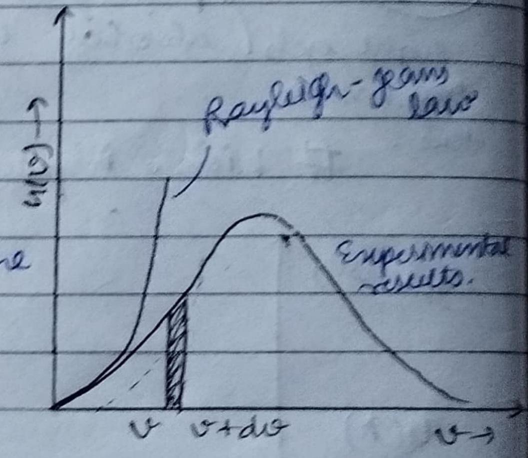
Due to numerous vertical & horizontal vibrations (wave nature), standing waves are produced & each standing wave consists of an oscillator.

Classical Mechanics fails to explain - 1) Stability of the atom. (motion of e⁻ in atom)
2) spectrum of hydrogen atom.

Vibrations in Strings :



Then, total no. of oscillators per unit vol. within ν to $\nu + d\nu$ $= \frac{8\pi\nu^2}{c^3} d\nu$



Deviation from ↑ freq. range - Ultra violet Catastrophe

Then,
Average Energy $\langle E \rangle = \dfrac{\int_0^\infty E \cdot e^{-E/KT} \cdot dE}{\int_0^\infty e^{-E/KT} \cdot dE} = KT$

$$\langle E \rangle = KT$$

$$\therefore \quad u(\nu) \cdot \cancel{d\nu} = \frac{8\pi\nu^2}{c^3} \cdot KT \cdot \cancel{d\nu}$$

$$\boxed{u(\nu) = \frac{8\pi\nu^2}{c^3} KT}$$ Rayleigh Jeans Law

Planck's Law :-

⊙ Assumptions : In order to explain experimentally observed distribution of energy in spectrum of black body, Planck suggested to take energy of oscillating e⁻ as discrete rather than continous to get results. Radiation law is derived by taking following assumptions:

(i) A chamber containing black body radiations also contains simple harmonic oscillators of molecular dimensions which can vibrate with all possible frequencies.

(ii) $\nu_{radiation}$ emitted by an oscillator = $\nu_{vibration}$ of oscillator.

(iii) An oscillator cannot emit energy in a continous manner, but only in discrete energy values En;

$$E_n = nh\nu = n\varepsilon \Rightarrow, \text{ where } h\nu = \varepsilon \; \{h = 6.625\times10^{-34} J/sec\}$$
$$\{n = 1, 2, 3, 4 \ldots\}$$

(iv) The oscillators can emit or absorb radiation energy in packets of $h\nu$ ⇒ change of energy between radiation & matter cannot take place continously but are limited to discrete set of values $0, h\nu, 2h\nu, 3h\nu \ldots n h\nu$

⊙ Derivation :- (Planck's Radiation Law).

$$E = n\, h\, \nu \rightarrow \text{Frequency}$$

n → Integral multiples; h → Universal constants

Let N → Total no. of Planck's oscillator
E → Total Energy.

Average Energy per planck's oscillator $\bar{\varepsilon} = \langle E \rangle = \frac{E}{N}$

Then, energy:
$N_0 \rightarrow 0$
$N_1 \rightarrow \varepsilon$
$N_2 \rightarrow 2\varepsilon$
$N_3 \rightarrow 3\varepsilon$
$\vdots$
$N_r \rightarrow r\varepsilon$

We have,

$$N = N_0 + N_1 + N_2 + \ldots + N_r + \ldots \quad -①$$

Then
$$E = 0\times\varepsilon + \varepsilon\times N_1 + 2\varepsilon\times N_2 + \ldots + N_r \times r\varepsilon + \ldots$$
$$= \varepsilon N_1 + 2\varepsilon N_2 + 3\varepsilon N_3 + \ldots + r\varepsilon N_r + \ldots \quad -②$$

~~From Maxwell's Distribution Law, we know that,~~

~~$N_r = N_0 e^{-r\varepsilon/RT} = N_0 \exp\left(\frac{-r\varepsilon}{RT}\right)$~~

, where $r\varepsilon$ is the energy & R is boltzman constant

From Maxwell's distribution law, we know that

$$N_r = N_0 e^{-r\varepsilon/KT} \quad \text{--- (3)}$$

N_r ↑ No. of oscillators having energy $r\varepsilon$

N_0 ↑ No. of oscillator in a system in Thermal Eq. T.

Substituting values of N_r from (3) in (1) & (2), we get.

$$N = N_0 + N_0 e^{-\varepsilon/KT} + N_0 e^{-2\varepsilon/KT} + N_0 e^{-3\varepsilon/KT} + \dots + N_0 e^{-r\varepsilon/KT} + \dots$$

Consider $e^{-\varepsilon/KT} = x$

in (1) Then,

$$N = N_0 (1 + x + x^2 + x^3 + \dots + x^r)$$

$$N = \frac{N_0}{(1-x)} \qquad \{1 + x + x^2 + \dots + x^r + \dots = \frac{1}{1-x}$$

$$\boxed{N = \frac{N_0}{(1 - e^{-\varepsilon/KT})}}$$

in (2) Then,

$$E = \varepsilon N_0 e^{-\varepsilon/KT} + 2\varepsilon N_0 e^{-2\varepsilon/KT} + 3\varepsilon N_0 e^{-3KT} + \dots + r\varepsilon N_0 e^{-r\varepsilon/KT} + \dots$$

$$E = \varepsilon N_0 (e^{-\varepsilon/KT} + 2e^{-2\varepsilon/KT} + 3e^{-3KT} + \dots + re^{-r\varepsilon/KT} + \dots)$$

(let $e^{-\varepsilon/KT} = x$)

$$E = \varepsilon N_0 (x + 2x^2 + 3x^3 + \dots + rx^r + \dots nx^n)$$

$$E = \varepsilon N_0 x (1 + 2x + 3x^2 + \dots + rx^{r-1} + \dots nx^{n-1})$$

$$\boxed{E = \frac{\varepsilon N_0 x}{(1-x)^2} = \frac{\varepsilon N_0 e^{-\varepsilon/KT}}{(1 - e^{-\varepsilon/KT})^2}}$$

$$\left(\because 1 + 2x + 3x^2 + \dots + rx^{r-1} = \frac{1}{(1-x)^2}\right)$$

Now, avg Energy:

$$\langle E \rangle = \frac{E}{N}$$

$$\langle E \rangle = \frac{\dfrac{\varepsilon N_0 e^{-\varepsilon/KT}}{(1 - e^{-\varepsilon/KT})^2}}{\dfrac{N_0}{(1 - e^{-\varepsilon/KT})}} = \frac{\varepsilon e^{-\varepsilon/KT}}{(1 - e^{-\varepsilon/KT})}$$

$$\langle E\rangle = \frac{\varepsilon e^{-\varepsilon/KT}}{(1-e^{-\varepsilon/KT})} \times \frac{e^{-\varepsilon/KT}}{e^{-\varepsilon/KT}} = \frac{\varepsilon}{(e^{\varepsilon/KT}-1)}$$

$$\langle E\rangle = \frac{\varepsilon}{(e^{\varepsilon/KT}-1)}$$

$$\langle E\rangle = \frac{h\nu}{(e^{h\nu/KT}-1)}$$

No. of oscillators per unit volume in frequency range from ν to $\nu+d\nu$ from Ray-leigh Jean's law will be same.

$$N = \frac{8\pi\nu^2}{c^3}.d\nu$$

$\therefore$ Total Energy $= \langle E\rangle . N$

$$= \frac{h\nu}{(e^{h\nu/KT}-1)} . \frac{8\pi\nu^2 . d\nu}{c^3}$$

$$(\text{Energy})_T = \frac{h\nu}{(e^{h\nu/KT}-1)} . \frac{8\pi\nu^2 . d\nu}{c^3}$$

$\nu = \frac{c}{\lambda}$, $d\nu = \frac{-c\,d\lambda}{\lambda^2}$

Also,

$$(\text{Energy})_T = \frac{hc}{\lambda} . \frac{8\pi . c^2}{\lambda^2} . \frac{(-c . d\lambda)}{\lambda^2} . \frac{1}{c^3 (e^{h\nu/k\lambda}-1)}$$

$$= \frac{-8\pi hc . d\lambda}{\lambda^5 (e^{hc/\lambda KT}-1)}$$

$$\therefore \boxed{u(\lambda) = \frac{-8\pi hc}{\lambda^5} \frac{1}{(e^{hc/\lambda KT}-1)} . d\lambda}$$

With the help of Planck's radiation law, $\rightarrow$ Wein's displacement law & Rayleigh-Jeans law can be derived. ~~in the foll~~

(1900)

Max Planck proposed quantum theory. According to this, matter is composed of a large no. of oscillating particles which vibrate with diff. frequencies while acc^n to classical theory, the particles can have any value of frequency & moreover it can have any value of energy but in quantum theory, energy is quantized, it is not continous and discrete.

- In 1909, it is concluded that emission & absorption of thermal energy is not a continous process but takes place in discrete amount.

de BROGLIE WAVES: Concept of matter waves :-

Relation b/w particles & waves.

$$E = h\nu \qquad \nu = \frac{c}{\lambda}$$

$$\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2mqV}} = \frac{h}{\sqrt{2mk_BT}}$$

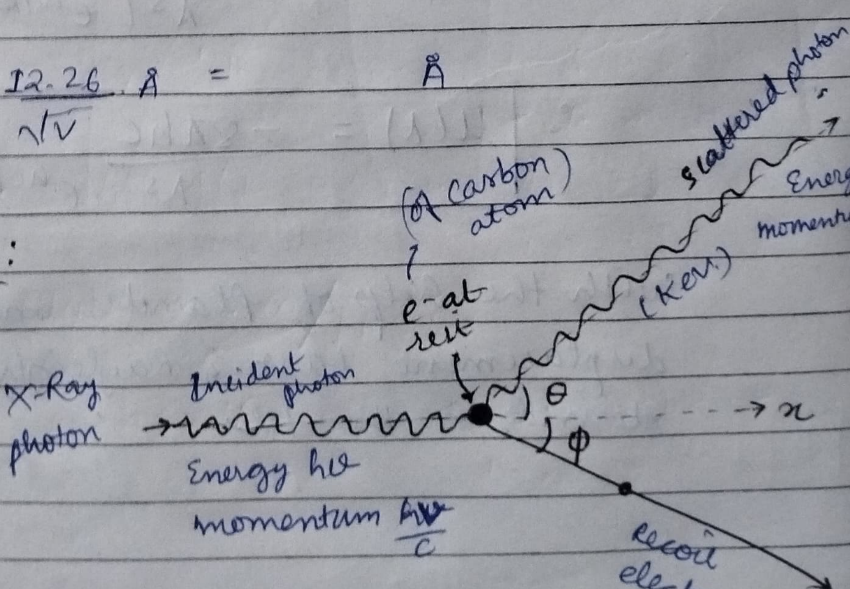
$$K.E. = \frac{1}{2}mv^2 \times \frac{2m}{2m} = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

$$p = \sqrt{2mE}$$

- $\frac{1}{2}m_0v^2 = eV \quad = 0.07724 \times 10^{-7}$

- For e^-, $\lambda = \frac{12.26}{\sqrt{V}}$ Å $=$ Å

Compton Effect:



When monochromatic beam of ~~light~~ high ν radiation (X Ray, γ-Ray) is scattered by a substance, the scattered radiation contains two components - one having a lower ~~or grea~~ frequency or greater λ which is known as modified radiation while other having same frequency or wavelength which is known as unmodified radiation. The modification in change in ν & λ is known as Compton effect.

→ ~~It~~.

It is due to elastic collision b/w two particles → photon of incident radⁿ. → e⁻ of scatterer.

- Before Collision

$(\text{Energy})_{\text{photon}} \Rightarrow E_p = h\nu$

$P_P = \frac{h\nu}{c} = \frac{h}{\lambda}$

$(\text{Energy})_{e^-} \Rightarrow E_e = m_0 c^2$

$(P_{e^-})_{\text{rest}} = 0.$

In case of photon

$E = \sqrt{p^2c^2 + m_0^2c^4}$

, m_0 is an inertial frame of reference

- After Collision

$E'_p = h\nu'$

$P_P = \frac{h\nu'}{c} = \frac{h}{\lambda'}$

$E_e = mc^2$

$= \frac{m_0}{\sqrt{1 - v^2/c^2}} \cdot c^2$

$p_e = mv = \frac{m_0}{\sqrt{1 - v^2/c^2}} \cdot v$

Relativistic mass

$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$ Rest mass

From Conservation of Energy, we get.

$$h\nu + m_0c^2 = h\nu' + \frac{m_0c^2}{\sqrt{1 - v^2/c^2}} \quad \left(\text{Before collision} = \text{After collision}\right)$$

$$h(\nu - \nu') = m_0c^2\left(\frac{1}{\sqrt{1 - v^2/c^2}} - 1\right) \quad \text{— (1)}$$

From conservation of momentum

along x axis $\quad \frac{h\nu}{c} + 0 = \frac{h\nu'}{c}\cos\theta + mv\cos\phi \quad$ — ②

along y axis $\quad 0 + 0 = \frac{h\nu'}{c}\sin\theta + (-mv\sin\phi) \quad$ —

$$\frac{h\nu'}{c}\sin\theta = mv\sin\phi \quad — ③$$

from ② : $\quad h\nu = h\nu'\cos\theta + mvc\cos\phi$

$h\nu - h\nu'\cos\theta = mvc\cos\phi \quad$ — ④

from ③ ; $\quad mvc\sin\phi = h\nu'\sin\theta \quad$ — ⑤

Now, square ④ & ⑤ & add them, we get

$(mvc)^2 = (h\nu'\sin\theta)^2 + (h\nu - h\nu'\cos\theta)^2$

$(mvc)^2 = h^2\nu'^2\sin^2\theta + h^2\nu^2 + h^2\nu'^2\cos^2\theta - 2h^2\nu\nu'\cos\theta$

$(mvc)^2 = h^2\nu'^2 + h^2\nu^2 - 2h^2\nu\nu'\cos\theta$

$(mvc)^2 = h^2(\nu'^2 + \nu^2 - 2\nu\nu'\cos\theta) \quad$ — ⑥

From ①. $\quad mc^2 = h(\nu - \nu') + m_0c^2$

Now, squaring both side, we get

$m^2c^4 = h^2(\nu^2 + \nu'^2 - 2\nu\nu') + m_0^2c^4 +$

$+ 2h(\nu - \nu')m_0c^2$

$c^4(m^2 - m_0^2) = h^2(\nu^2 + \nu'^2 - 2\nu\nu') + 2h(\nu - \nu')m_0c^2$

Eqⁿ ⑦ − ⑥.

$m^2c^2(v^2 - c^2) = -2h^2\nu\nu' + 2h^2\nu\nu'\cos\theta + 2h(\nu - \nu')m_0c^2$

$+ m_0^2c^4.$

$m^2c^2(c^2 - v^2) = -2h^2\nu\nu'(1 - \cos\theta) + 2h(\nu - \nu')m_0c^2$

$+ m_0^2c^4.$

Substitute $m = m_0/\sqrt{1 - v^2/c^2}$

$\frac{m_0^2c^2 \cdot c^2(c^2 - v^2)}{(c^2 - v^2)} = -2h^2\nu\nu'(1 - \cos\theta) + 2h(\nu - \nu')m_0c^2$

$+ m_0^2c^4.$

$$\cancel{2}h^2 \nu \nu' (1-\cos\theta) = \cancel{2}h(\nu-\nu') m_0 c^2$$

$$h \nu \nu' (1-\cos\theta) = (\nu-\nu') m_0 c^2$$

$$\frac{\nu - \nu'}{\nu \nu'} = \frac{h}{m_0 c^2}(1-\cos\theta)$$

$$\boxed{\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0 c^2}(1-\cos\theta)} \quad -(8)$$

Now, substituting in terms of λ & λ', we get.

$$\boxed{\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c}(1-\cos\theta)}$$, where $h = 6.6 \times 10^{-34}$ $m^2 kg/s$ or J sec

$c = 3 \times 10^8$ m/s

$m_0 = 9.1 \times 10^{-31}$ kg

Compton Shift:

$$\boxed{\lambda' - \lambda = 0.02426(1-\cos\theta)}$$

Modified Radiations :-

- For the inner shell (s-orbital) electrons to get recoil, the entire atoms get recoil.

mass of atom = 24000 mass of e^-

$$\therefore \downarrow(\Delta\lambda) = \frac{h}{\uparrow M_a c}(1-\cos\theta)$$

$$\therefore \lambda' \simeq \lambda \text{ (unmodified)}$$

The presence of unmodified original line may be explained by considering the scattering of the X-Ray photon with those e-s which are not free & are tightly bound to the nucleus. In such case, the whole atom will recoil instead of an e-. Now, the mass of the carbon atom is nearly 24000 times that of the mass of the e-. and hence the change in

Thus, the unmodified lines arises due to scattering of x-ray photon with the carbon atoms instead of free e-s present in it.

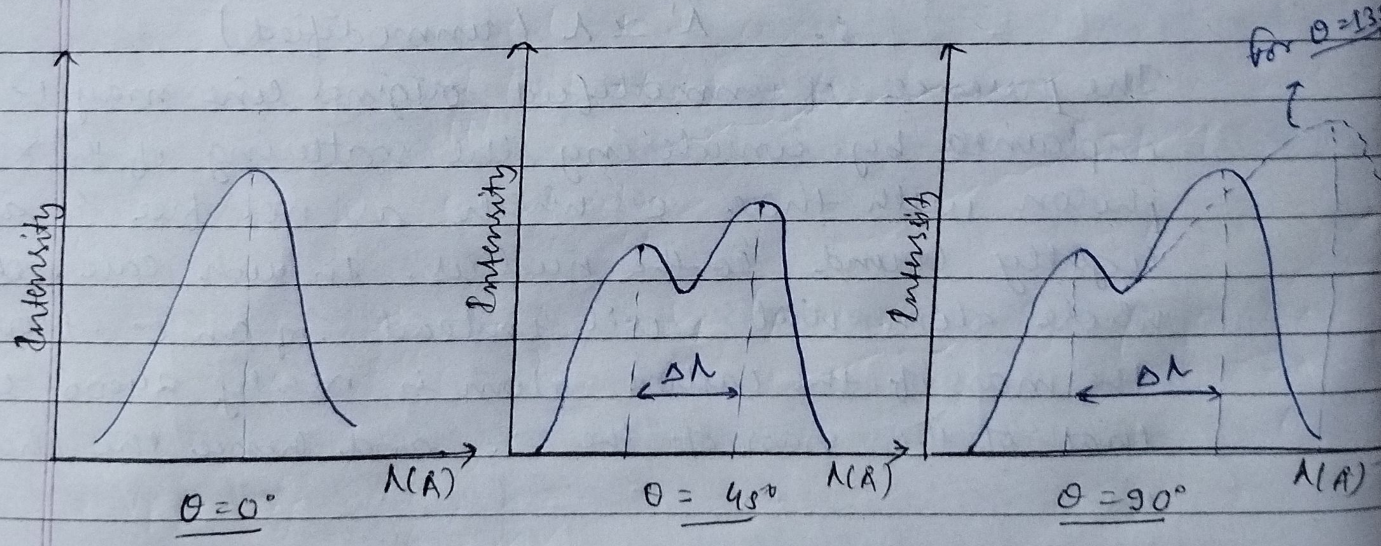
As per classical electromagnetic theory, when an EM radiation (with freq. ν) is incident on free charges (say e^-), the free charges absorb this radiation & start oscillating at freq. ν. Then these oscillating charges radiate em wave of the same freq. ν. This type of scattering where their is no change in ν & λ is called coherent scattering. This coherent scattering has been observed with the radiation in visible range & also at long wavelength. However, the prediction of classical theory fails in the case of scattering of range of short wavelengths etc. For X-Rays we obtain both modified & unmodified radiation which are classification of incoherent scattering.

Compton shift:

At $\theta = 0°$, $\Delta\lambda = 0$

At $\theta = 90°$, $\Delta\lambda = 0.02426$

At $\theta = \pi/max$, $\Delta\lambda = 0.04852$



at $\theta = 45°$, $\Delta\lambda = 0.00710818$

At $\theta = 135°$, $\Delta\lambda = 0.04141182$

* Compton shift is not observed for visible light?

It is observed that compton shift occurs only in case of X-Ray scattering & not in the case of visible light. This is because the quantity $\Delta\lambda$ will have a max change when $\theta = 180$ or π. & the corresponding value is $\Delta\lambda = 0.04852\,Å$. Now, in case of X-rays (where λ is of the order $1Å$) the percentage change is 4.852. This gives 5% change in the original value which is easily detected by instruments.
In case of visible light (say $\lambda = 4000Å$) the % change in the compton shift would be 0.0012131% & similarly for wavelength of 7000Å the % change will be 0.00069%.
Thus, it cannot be detected by any instrument because the compton shift for visible light is not significant.

→ Direction of Recoil Electron :-

From eqn (4) & (5)

$$mv\cos\phi = h\nu - h\nu'\cos\theta \quad \text{—— (4)}$$

$$mv\sin\phi = h\nu'\sin\theta \quad \text{—— (5)}$$

(5) ÷ (4)

$$\tan\phi = \frac{h(\nu'\sin\theta)}{h(\nu - \nu'\cos\theta)} \quad \text{—— (10)}$$

From (8),
$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0c^2}(1-\cos\theta)$$

$$\frac{1}{\nu'} = \frac{1}{\nu} + \frac{2h}{m_0c^2}\sin^2\theta/2$$

$$\frac{1}{\nu'} = \frac{(1 + h\nu/m_0c^2)\,2\sin^2\theta/2}{\nu}$$

$$\nu' = \frac{\nu}{[1 + h\nu/m_0c^2]\cdot 2\sin^2\theta/2} \quad \text{—— (8)}$$

Substitute value of ν' in eq^n (10), we get

$$\tan\phi = \frac{\sin\theta}{\left(\frac{1}{1+2\alpha\sin^2\theta/2}\right) - \cos\theta} \qquad \left\{\frac{h\nu}{m_0c^2} = \alpha\right\}$$

$$\tan\phi = \frac{\sin\theta}{(1+2\alpha\sin^2\theta/2) - \cos\theta}$$

$$\tan\phi = \frac{\sin\theta}{(1-\cos\theta) + 2\alpha\sin^2\theta/2} = \frac{2\sin\theta/2 \cdot \cos\theta/2}{2\sin^2\theta/2 + 2\alpha\sin^2\theta/2}$$

$$\tan\phi = \frac{\cos\theta/2}{\sin\theta/2(1+\alpha)}$$

$$\boxed{\tan\phi = \frac{\cot\theta/2}{1 + h\nu/m_0c^2}}$$

Phase Velocity & Group velocity.

$y = a\sin(\omega t - kx)$

- For a single monochromatic light (with fixed k → fixed wavelength → fixed angular freq. (ω))

$$\omega t - kx = \text{const.}$$

$$\frac{d}{dt}(\omega t - kx) = \text{const.}$$

$$\omega - k\cdot\frac{dx}{dt} = 0.$$

wave vector

k - propagational vector

ω - Angular freq.

$$\frac{dx}{dt} = \frac{\omega}{k} = v_p \text{ (phase velocity)} \qquad \left(\because \omega = 2\pi\nu,\ k = \frac{2\pi}{\lambda}\right)$$

$$V_p = \nu\lambda = \frac{E}{h}\cdot\frac{h}{mv}$$

$$V_p = \frac{mc^2}{mv} = \frac{c^2}{V}$$

$$V_p \cdot V = c^2 \qquad \left\{\begin{matrix} V_p > c \\ v <<< c \end{matrix}\right\}$$

$$\left\{ \lambda = \frac{h}{p} = \frac{h}{mv} \right\}$$

Since $V_p >> c$; which is practically impossible. Hence, it is not a single wave but a number of waves OR wave packets.

- Now considering superposition of two waves;

$$y_1 = a\sin(\omega_1 t - k_1 x),$$
$$y_2 = a\sin(\omega_2 t - k_2 x).$$
$$\therefore \quad y = y_1 + y_2$$
$$y = a[\sin(\omega_1 t - k_1 x) + \sin(\omega_2 t - k_2 x)]$$

$$\left(\therefore - \sin A + \sin B = 2\sin\left(\frac{C+D}{2}\right).\cos\left(\frac{C-D}{2}\right) \right)$$

$$y = a\left[2\sin\left(\frac{\omega_1 t - k_1 x + \omega_2 t - k_2 x}{2}\right).\cos\left(\frac{\omega_1 t - k_1 x - \omega_2 t + k_2 x}{2}\right)\right.$$

$$= \cancel{a}\, 2a.\sin\left(\left(\frac{\omega_1 + \omega_2}{2}\right)t - \frac{(k_1+k_2)}{2}x\right).\cos\left(\frac{(\omega_1 - \omega_2)t}{2} - \frac{(k_1 - k_2)x}{2}\right)$$

$\cancel{= 2a}$ let - $\Delta\omega = \omega_1 - \omega_2$, $\Delta K = K_1 - K_2$

$$\omega = \frac{\omega_1 + \omega_2}{2}, \quad K = \frac{K_1 + K_2}{2}$$

Putting these in eqn:-

$$\therefore y = 2a\sin(\omega t - Kx).\cos\left[\frac{\Delta\omega t}{2} - \frac{\Delta K x}{2}\right]$$

$$V_p \text{ (For 1st Wave)} = \frac{\omega}{K}$$

$$V_g \text{ (group velocity)} = \frac{\Delta\omega}{\Delta K}$$

~~R~~ Relation between V_p & V_g:-

$$V_p = \frac{\omega}{K}$$

$$V_g = \frac{\Delta\omega}{\Delta K} = \frac{d\omega}{dK} \qquad \{\omega = KV_p\}$$

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Now, $\frac{d}{dk}(kV_p) = V_p + k\frac{dV_p}{dk}$ — (1)

In terms of λ

We know that, $k = 2\pi/\lambda$

$\therefore\ dk = -\frac{2\pi}{\lambda^2}\cdot d\lambda$

put this in (1)

$\therefore\ V_g = V_p - \frac{\cancel{2\pi}}{\cancel{\lambda}}\cdot\frac{dV_p}{\cancel{2\pi}d\lambda}\cdot\lambda^2$

$$\boxed{V_g = V_p - \lambda\frac{dV_p}{d\lambda}}$$

Uncertainty principle

heisnberg's $\Delta x\cdot\Delta p_x \geq \frac{h}{4\pi}$ or $\frac{\hbar}{2}$, where $\hbar = \frac{h}{2\pi}$

since p is a vector quantity, that's why only momentum in x direction is considered.

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

$\langle x^2\rangle$: ~~squa~~ average of square

$\langle x\rangle^2$: square of average.

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

Statement: In 1927, Werner Heisenberg enunciated (declaring) an important principle which states "It is impossible to specify precisely and simultaneously the two canonically conjugate variables of a dynamical system."

here - momentum & position are c.c.v.

- angle & angular momentum are c.c.v. - $\Delta\theta\cdot\Delta L \geq \frac{h}{4\pi}$

for y direcn $\Delta y \cdot \Delta P_y \geq \frac{h}{4\pi}$

for z direcn $\Delta z \cdot \Delta P_z \geq \frac{h}{4\pi}$

→ If we go to measure momentum precisely, then we wont be able to measure position precisely & vice versa

Note:⇒ Energy & time are not C.C. variables but still follow this principle.

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

suppose for a free particle m, P_x

$$E = \frac{P_x^2}{2m} \Rightarrow \Delta E = \frac{2 p_x \Delta P_x}{2m}$$

∴

$$\Delta E \cdot \Delta t = \frac{P_x}{m} \cdot \Delta P_x \cdot \Delta t$$

$$= \Delta P_x \cdot \underline{v \cdot \Delta t}$$

$$\underline{\Delta E \cdot \Delta t} = \Delta P_x \cdot \Delta x \geq \frac{\hbar}{2}$$

↓ This is derived from the $\Delta P_x \cdot \Delta x$.

Schrödenger Wave Equation:

The function that represents state of a quantum mechanical system & contains all the information regarding that system is called a wave function or state function.

ψ → Psi → wave/ function state.

$$\psi = Ae^{i(kx-\omega t)} \text{ (say)} \quad \text{—— (A)}$$

$$= A \sin(kx-\omega t) \,/\, B \cos(kx-\omega t)$$

Diffrential Equation obtained is generalised.

Consider a free particle – (particle whose potential $V=0$)

Energy for particle $= E = K.E. = \frac{p^2}{2m}$

$$p = \frac{h}{\lambda} = \frac{h/2\pi}{\lambda/2\pi} = \frac{\hbar}{1/k} = \hbar k. \quad —— ① \quad \left(\hbar = \frac{h}{2\pi}\right)$$

$$E = h\nu = \frac{h}{2\pi} \cdot 2\pi\nu = \hbar \cdot \omega \quad —— ②$$

Put values of ① & ② in Ⓐ.

$$\psi = Ae^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}$$

$$\psi = Ae^{\frac{i}{\hbar}(px - Et)}$$

$$\frac{\partial\psi}{\partial x} = \frac{ip}{\hbar} e^{i/\hbar\,(px - Et)} = \frac{ip}{\hbar}(\psi) \quad —— ③$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{i^2}{\hbar^2} \cdot p^2 \, e^{\left(\frac{i}{\hbar}(px - Et)\right)} = \frac{i^2 p^2}{\hbar^2}(\psi) \quad (i^2 = -1)$$

from ③.

$$\frac{\partial\psi}{\partial x} = \frac{ip}{\hbar}(\psi)$$

$$p\psi = \frac{\hbar}{i} \cdot \frac{\partial\psi}{\partial x}$$

$$p\psi = -i\hbar \cdot \frac{\partial\psi}{\partial x} \quad —— ④$$

(Multiply i both in num & denom.)

$$\cancel{p^2\psi = -i\hbar p \cdot \frac{\partial\psi}{\partial x}}$$

$$p^2\psi = -\hbar^2 \cdot \frac{\partial\psi^2}{\partial x^2} \quad —— ⑤$$

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar}\left(e^{\frac{i}{\hbar}(px-Et)}\right) = \frac{-iE\psi}{\hbar}.$$

$$\boxed{E\psi = i\hbar \frac{\partial \psi}{\partial t}} \quad \text{—— (6)}$$

In Eqⁿ $E = \frac{p^2}{2m}$

$$E \cdot \psi = \frac{p^2}{2m} \cdot \psi.$$

Put (5) & (6) in this

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2}.$$

$$\boxed{\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi}{\partial x^2} + i\hbar \frac{\partial \psi}{\partial t} = 0}$$

Above is the differential Equation obtained for free particle.

- For a particle with potential V. ie. (not free particle)

Total Energy = K.E + P.E.

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

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

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

$$\boxed{\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + i\hbar \frac{\partial \psi}{\partial t} - V(x) \cdot \psi = 0}$$, where $\psi = \psi(x,t)$

This is time dependent Schrödenger wave equation in 1D.

Time dependent equation in 3D.

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2 \psi^2(\vec{r},t) + V(r)\,\psi(\vec{r},t) = i\hbar\,\frac{\partial \psi}{\partial t}(\vec{r},t)}$$

$$, \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

So, if a wave function is known at a particular time then how the wave function will change after time t, that we can say from this diffrential equation. This wave equation in terms of wave function predicts analytically & precisely the probability of events or outcomes

Schrödinger's Time Independent Wave equation:

For a particle with some $V(x)$, (potential), not free particle.

$$E = \frac{p^2}{2m} + V \quad , p = \hbar K$$

$$E = \frac{\hbar^2 K^2}{2m} + V.$$

$$K^2 = \frac{2m}{\hbar^2}(E-V). \quad —① $$

Wave funcⁿ - (as it is time independent, term of t will not be there.)

$$\psi = Ae^{ikx}$$

$$\frac{\partial \psi}{\partial x} = iKAe^{ikx} = iK\psi.$$

$$\frac{\partial^2 \psi}{\partial x^2} = i^2K^2Ae^{ikx} = i^2K^2\psi = -K^2\psi$$

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

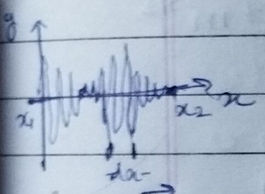
$$-\frac{\hbar^2}{2m}.\frac{\partial^2 \psi}{\partial x^2} = (E-V).\psi.$$

$$\boxed{-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi(x)}{\partial x^2} + V\psi_{(x)} = E\psi(x)} \quad \text{— (in 1D)}.$$

Time independent equation.

$$\boxed{-\frac{\hbar^2}{2m} \cdot \nabla^2 \psi(\vec{r}) + V(r) \cdot \psi(r) = E\psi(r)} \quad \text{(in 3D)}$$

★ $\psi = Ae^{i(kx-\omega t)}$, here ψ is a complex quantity, it can be real or imaginary. It has no physical meaning. For its physical ~~mean~~ existence,



→ $|\psi|^2_{(x,t)} \cdot dx$ = probability of finding the particle in small interval of space lying between x to $(x+dx)$. at time t.

→ $|\psi|^2$ = The probability of finding the particle at a particular position ~~a~~ x at time t.

→ for long time interval $x_1 \to x_2$.

$\int_{x_1}^{x_2} |\psi|^2 \cdot dx$ - The probability of finding the particle lying between x_1 to x_2 at time t.

$\psi^2 = \underbrace{\psi^*}_{\text{conjugate of } \psi} \cdot \psi$, $\psi^* = Ae^{-i(kx-\omega t)}$.

→ Normalisation condition : $\int_{-\infty}^{\infty} |\psi|^2_{(x,t)} \cdot dx = 1 = \int_{-\infty}^{\infty} \psi^*(x,t) \cdot \psi(x,t)\, dx$.

It states that the probability of finding the particle in a particular state in a quantum mechanical system at time t is unity.

Unit of normalized wave function :-

ψ - is a unitless quantity

<u>In 1d</u>

$$|\psi|^2 \cdot dx = 1$$

$$|\psi|^2 = \frac{1}{dist}$$

$$\psi = \frac{1}{\sqrt{dist}} = m^{-1/2}$$

<u>In 2D</u>

$$|\psi|^2 \cdot dxdy = 1$$

$$|\psi|^2 = \frac{1}{m^2}$$

$$\psi = \frac{1}{m} = m^{-1}$$

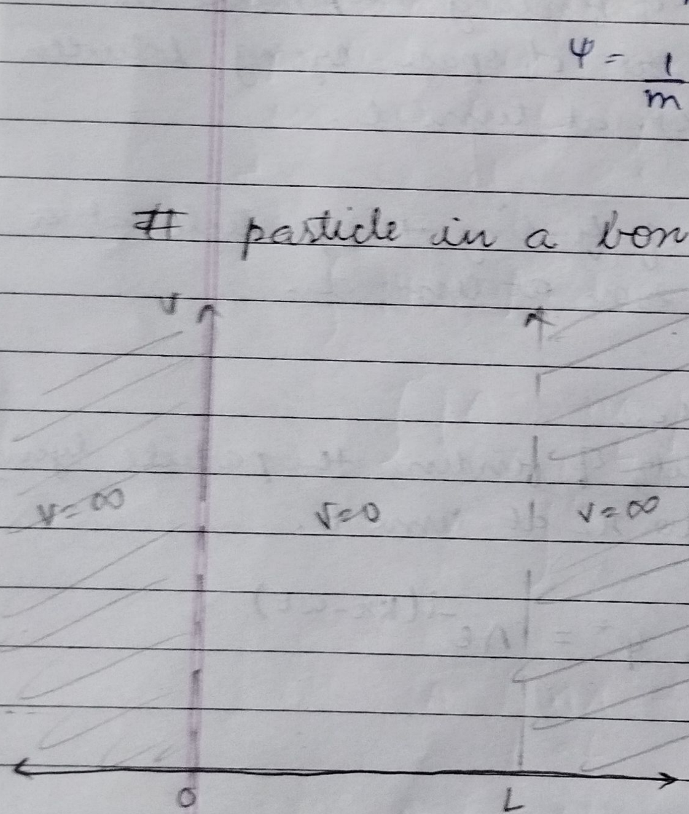
<u>In 3D</u>

$$|\psi|^2 \cdot dxdydz = 1$$

$$\psi = \frac{1}{\sqrt{m^3}}$$

$$\psi = m^{-3/2}$$

particle in a box (Infinite potential walls)



→ Hard Walls (perfectly elastic)

$V = 0, \quad 0 \leq x \leq L$

$V = \infty, \quad x \leq 0 \ \& \ x > L$

1D - $\frac{-\hbar^2}{2m} \cdot \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi$ ← Time independent eqn. (Scrödinger's Wave eqn)

$$\frac{\partial^2 \psi}{\partial x^2} + \underbrace{\frac{2mE}{\hbar^2}}_{k} \cdot \psi = 0.$$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0 \quad \text{(SHM)}$$

solution of this eqⁿ

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

, A & B are constants

Boundary conditions: , From the graph: At $x=0$ & $x=L$ → $\psi(x)=0$.

$0 = A\sin 0 + B\cos 0$, $A\sin KL = 0$

$\boxed{0 = B}$ ∴ ~~$A\sin KL = \sin(n\pi)$~~ 0

From this $A \neq 0$.

$\sin KL = 0$

$\sin KL = \sin(n\pi)$

$KL = n\pi$

$$\boxed{K = \frac{n\pi}{L}}$$

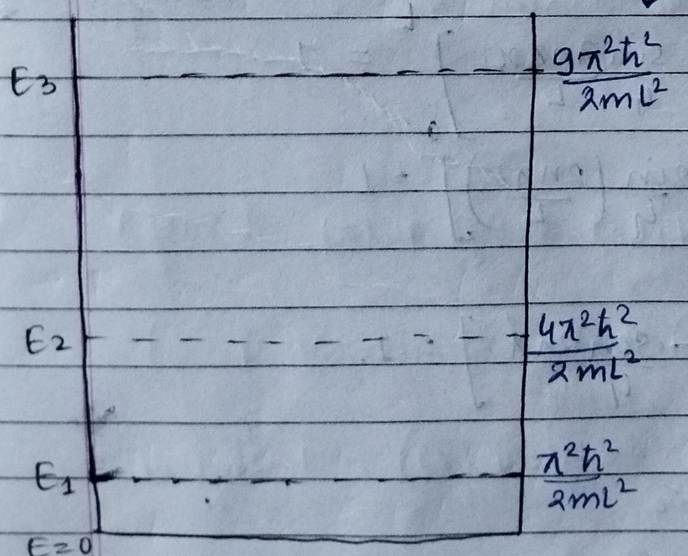
- To find energy of that free particle.

$$K^2 = \frac{n^2\pi^2}{L^2}$$

$$\boxed{E = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$ → Eigen Value , $n = 1, 2, 3, \ldots$

quantum no.

This energy will be discrete, its not continous



⊙ To find momentum :

$$p = \hbar k$$

$$\boxed{p = \frac{n\pi\hbar}{L}}$$

To find A :-

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

$$\psi(x) = A\sin kx + 0$$

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

In normalisation condition, probability of getting particle in range $-\infty$ to ∞ is 1. similarly here in 0 to L probability of getting particle is also 1. so, it $-\infty$ to ∞ will be replaced by 0 to L.

$$\int_0^L |\psi_n(x)|^2 \cdot dx = 1$$

$$\int_0^L \left|A\sin\frac{n\pi x}{L}\right|^2 \cdot dx = 1$$

$$\frac{x}{2} - \frac{\sin 2x}{4}$$

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

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

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

$$A^2\left[\frac{n\pi L}{2L} - \frac{\sin}{4}\left(\frac{2n\pi L}{L}\right)\right] = 1$$

$$A^2\left[\frac{n\pi}{2} - \frac{\sin(2n\pi)}{4}\right] = 1.$$

$$\sin 2n\pi = 0$$

$$A^2 \cdot \frac{n\pi}{2} = 1$$

$$A = \sqrt{\frac{2}{n\pi}}$$

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

$$\frac{A^2}{2}\left[x \mp \cancel{\cos}\,\sin\frac{2n\pi x}{L}\cdot\left(\frac{L}{2n\pi}\right)\right]_0^L = 1$$

$$A^2\left[(L-0) - \sin\left(\frac{2n\pi L}{L}\right)\cdot\frac{L}{2n\pi} - \sin 0\right] = 2$$

$$A^2\left[L - \frac{\sin(2n\pi)}{(2n\pi/L)}\right] = 2 \qquad (\because \sin(2n\pi) = 0)$$

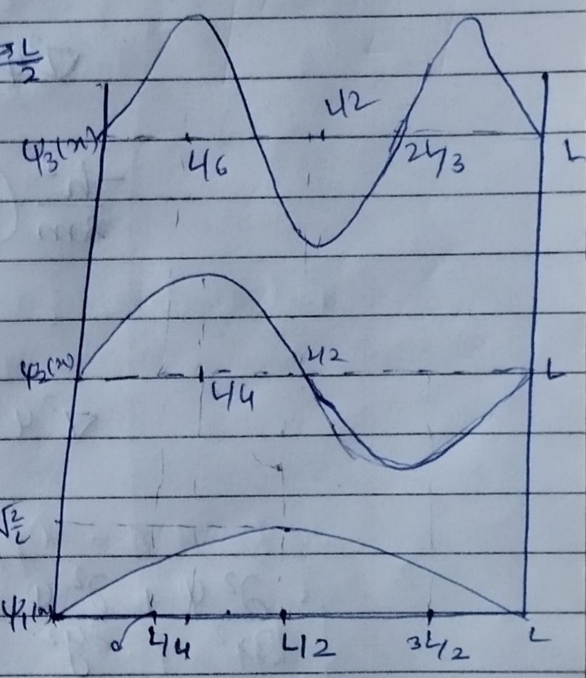
$$A^2[L] = 2 \Rightarrow \boxed{A = \sqrt{\frac{2}{L}}}$$

$\psi_n(x) = \sqrt{\frac{2}{L}}\cdot\sin\frac{n\pi x}{L}$, at $\frac{\pi}{2}, x \to \frac{L}{2}$

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

$\psi_2(x) = \sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}$, at $\frac{\pi}{4}$, $x \to \frac{L}{4}$

$\psi_3(x) = \sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}$, at $\frac{\pi}{6}$, $x \to \frac{L}{6}$

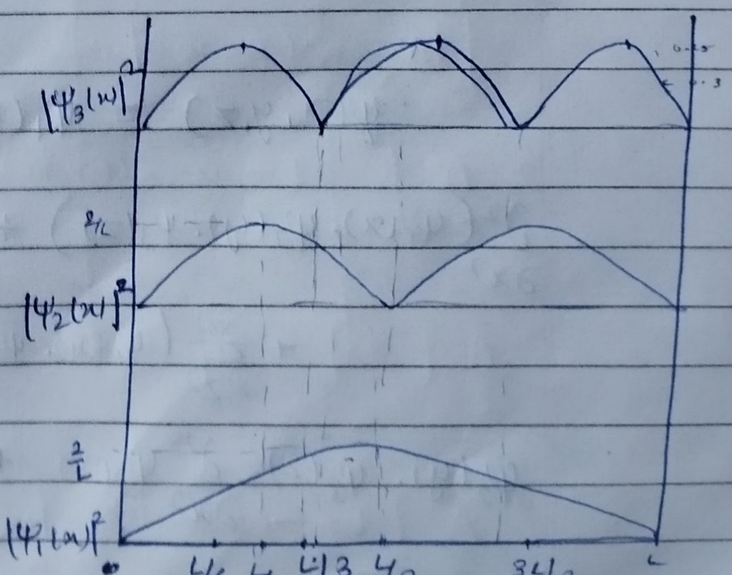


probability graph

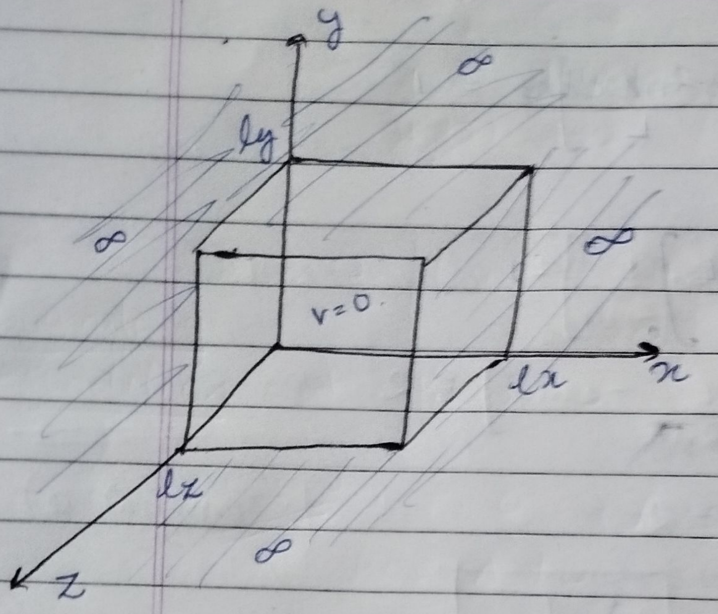
$|\psi_1(x)|^2 = \frac{2}{L}\sin^2\frac{\pi x}{L}$

$|\psi_2(x)|^2 = \frac{2}{L}\cdot\sin^2\frac{2\pi x}{L}$

$|\psi_3(x)|^2 = \frac{2}{L}\sin^2\frac{3\pi x}{L}$



In 3D System:



Cuboid

- $V(x,y,z) = 0$, for, $0 < x < lx$, $0 < y < ly$, $0 < z < lz$
- $V(x,y,z) = \infty$ for elsewhere.

Time independent equation for 3D system.

$$\cancel{\nabla^2\psi(x,y,z) + \frac{2mE}{\hbar^2}}$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \cancel{V(x,y,z).\psi(x,y,z)}^{\,0}$$
$$= E.\psi(x,y,z)$$

$$\nabla^2\psi(x,y,z) + \frac{2mE}{\hbar^2}.\psi = 0 \quad (\because V=0 \text{ in the box.})$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \underbrace{\frac{2mE}{\hbar^2}}_{K^2}.\psi = 0$$

$$\psi(x,y,z) = \psi_1(x).\psi_2(y).\psi_3(z) \quad (\text{say})$$

$$\frac{\partial^2}{\partial x^2}(\psi_1(x).\psi_2(y).\psi_3(z)) + \frac{\partial^2}{\partial y^2}(\psi_1(x).\psi_2(y).\psi_3(z))$$
$$+ \frac{\partial^2}{\partial z^2}(\psi_1(x).\psi_2(y).\psi_3(z)) + \frac{2mE}{\hbar^2}.\psi$$

$$\psi_2(y).\psi_3(z).\frac{d^2}{dx^2}\psi_1(x) + \psi_1(x).\psi_3(z).\frac{d^2}{dy^2}\psi_2(y).$$

$$+ \psi_1(x).\psi_2(y)\frac{d^2}{dz^2}\psi_3(z) + K^2.\psi_1(x).\psi_2(y).\psi_3(z) = 0.$$

$$\psi_1(x).\psi_2(y).\psi_3(z)\left[\frac{1}{\psi_1(x)}.\frac{\partial^2}{\partial x^2}\psi_1(x) + \frac{1}{\psi_2(y)}.\frac{\partial^2}{\partial y^2}\psi_2(y) + \frac{1}{\psi_3(z)}.\frac{\partial^2}{\partial z^2}\psi_3(z)\right] = -K^2\,\cancel{\psi_1(x).\psi_2(y).\psi_3(z)}$$

$$\frac{1}{\psi_1(x)}.\frac{d^2}{dx^2}\psi_1(x) + \frac{1}{\psi_2(y)}.\frac{d^2}{dy^2}\psi_2(y) + \frac{1}{\psi_3(z)}.\frac{d^2}{dz^2}\psi_3(z) = -K^2.$$

Taking x term on one hand.

$$\frac{1}{\psi_1(x)}.\frac{d^2\psi_1(x)}{dx^2} = -\frac{1}{\psi_2(y)}.\frac{d^2\psi_2(y)}{dy^2} - \frac{1}{\psi_3(z)}.\frac{d^2\psi_3(z)}{dz^2} - K^2 = -K_1^2 \text{ (say)}$$

$$\frac{1}{\psi_1(x)}.\frac{d^2\psi_1(x)}{dx^2} = -K_1^2$$

$$\frac{d^2\psi_1(x)}{dx^2} + K_1^2.\psi_1(x) = 0. \quad \text{—— (1).}$$

Taking y term on one hand.

$$\frac{1}{\psi_2}.\frac{d^2\psi_2}{dy^2} = \underbrace{-\frac{1}{\psi_1}.\frac{d^2\psi_1}{dx^2}}_{-K_1^2} - \frac{1}{\psi_3}.\frac{d^2\psi_3}{dz^2} - K^2 = -K_2^2 \text{ (say)}$$

$$\frac{1}{\psi_2(y)}.\frac{d^2\psi_2(y)}{dy^2} = -K_2^2 = \left(-K_1^2 - K^2 - \frac{1}{\psi_3}\frac{d^2\psi_3}{dz^2}\right)$$

$$\frac{d^2\psi_2(y)}{dy^2} + K_2^2.\psi_2(y) = 0 \quad \text{—— (2)}$$

Taking z term on one hand

$$\frac{1}{\psi_3}\frac{d^2\psi_3}{dz^2} = -\frac{1}{\psi_1}.\frac{d^2\psi_1}{dx^2} - \frac{1}{\psi_2}.\frac{d^2\psi_2}{dy^2} - K^2$$

$$\frac{1}{\psi_3}.\frac{d^2\psi_3}{dz^2} = K_1^2 + K_2^2 - K^2 = -K_3^2 \text{ (say)} \text{ —— (3)}.$$

$$\frac{1}{\psi_3(z)} \cdot \frac{d^2\psi_3(z)}{dz^2} + k_3^2 \psi_3(z) = 0 \quad \text{--- (3)}$$

From (1), solⁿ - $\psi_1(x) = A \sin(Bx + C)$ --- (4)

Boundary condition: $\psi_1(x) = 0$ if $x = 0$, $x = L_x$

at $x=0$: $0 = A \sin C$

here $A \neq 0$, $\sin C = 0 = \sin 0$

$$\boxed{C = 0}$$

at $x = L_x$: $0 = A \sin BL_x$

here as $A \neq 0$, $\sin BL_x = 0 = \sin n_x\pi$

$BL_x = n_x\pi$

$$\boxed{B = \frac{n_x\pi}{L_x}}$$

Put value of B & C in (4)

$$\psi_1(x) = A \sin\left(\frac{n_x\pi}{L_x} + 0\right)$$

To find A - Apply Normalisation condition.

$$\int_0^{L_x} |\psi_1(x)|^2 \cdot dx = 1$$

$$\int_0^{L_x} |A^2 \sin^2(Bx+C)| \cdot dx = 1$$

$$\frac{A^2}{2} \int_0^{L_x} \left(1 - \cos 2(Bx+C)\right) \cdot dx = 1$$

$$\frac{A^2}{2}\left[[x]_0^{L_x} - \left[\frac{\sin 2(Bx+\cancel{C})}{2B}\right]_0^{L_x} \right] = 1$$

$$\frac{A^2}{2}\left[L_x - \frac{\sin 2(BL_x + \cancel{C})}{B}\right] = 1$$

$\frac{A^2}{2}\left[Lx - \sin 2BLx\right]$

$$A = \sqrt{\frac{2}{Lx}}$$

eq^n will be ~~Similarly~~, $\psi_1(x) = \sqrt{\frac{2}{Lx}} \cdot \sin \frac{n_x \pi x}{Lx}$

similarly for y & z,

$$\psi_2(y) = \sqrt{\frac{2}{Ly}} \cdot \sin \frac{n_y \pi y}{Ly}$$

$$\psi_3(z) = \sqrt{\frac{2}{Lz}} \cdot \sin \frac{n_z \pi z}{Lz}$$

$$\psi = \psi_1 \cdot \psi_2 \cdot \psi_3 = \sqrt{\frac{8}{Lx \cdot Ly \cdot Lz}} \cdot \sin \frac{n_x \pi x}{Lx} \cdot \sin \frac{n_y \pi y}{Ly} \cdot \sin \frac{n_z \pi z}{Lz}$$

$$\frac{d^2\psi_1}{dx^2} = -k_1^2 \psi_1$$

$$k_1^2 = \frac{n_x^2 \pi^2}{Lx^2}$$

$$k_1^2 = -\frac{1}{\psi_1(x)} \cdot \frac{\partial^2 \psi_1}{dx^2}$$

$$\cancel{= \frac{+1}{\sqrt{\frac{2}{Lx}} \cdot \sin \frac{n_x \pi x}{Lx}} \cdot \sqrt{\frac{2}{Lx}} \cdot \sin \frac{n_x \pi x}{Lx} \cdot \frac{n_x^2 \pi^2}{L_x^2}}$$

$$k_1^2 = \frac{n_x^2 \pi^2}{Lx^2},$$

similarly, $k_2^2 = \frac{n_y^2 \pi^2}{Ly^2}$, $k_3^2 = \frac{n_z^2 \pi^2}{Lz^2}$

$$K^2 = K_1^2 + K_2^2 + K_3^2$$

$$\frac{2mE}{\hbar^2} = \pi^2 \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$\boxed{E = \frac{\pi^2 \hbar^2}{2m} \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2 \right]}$$

For cuboid.

For a cube :- $L_x = L_y = L_z = L$.

$$\boxed{E = \frac{\pi^2 \hbar^2}{2mL^2} \left[n_x^2 + n_y^2 + n_z^2 \right]}$$

	n_x	n_y	n_z	E_n	Degeneracy
Lowest Ground state E.	1	1	1	$\frac{3\hbar^2\pi^2}{2mL^2}$	1
1st Excited state	2	1	1	$\frac{6\pi^2\hbar^2}{2mL^2}$	3
	1	2	1		
	1	1	2		
2nd Excited state	2	2	1	$\frac{9\pi^2\hbar^2}{2mL^2}$	3
	1	2	2		
	2	1	2		
3rd excited state	3	1	1	$\frac{11\pi^2\hbar^2}{2mL^2}$	3
	1	3	1		
	1	1	3		
4th excited state	2	2	2	$\frac{12\pi^2\hbar^2}{2mL^2}$	1.