

2nd Semester.

Quantum physics

MARCH
MONDAY

02

Week 10 * Day 062-304

Date:
Mar 18, 2023
9.00

Inadequacy of classical mechanics:

- 10.00 : Classical mechanics / physics could not explain
- 11.00 the following:
 1. Observed spectrum of black body radiation.
 2. Stability of atom.
 3. Observed variation of specific heat of solid.
 4. Origin of discrete spectrum of atom.
- 14.00 Apart from this, classical mechanics could also not explain various phenomena like photoelectric effect, Compton effect, Raman effect, short wave length limit of X-ray spectrum.

* Phenomena of black body radiation:-

Rayleigh Jeans:

$$E_V dV = \frac{8\pi V^2}{c^2} K T \propto K T$$

A black body is an ideal body which allow the whole of the incident radiation to pass into itself without reflecting the energy & absorb within itself incident radiation (without energy). This property

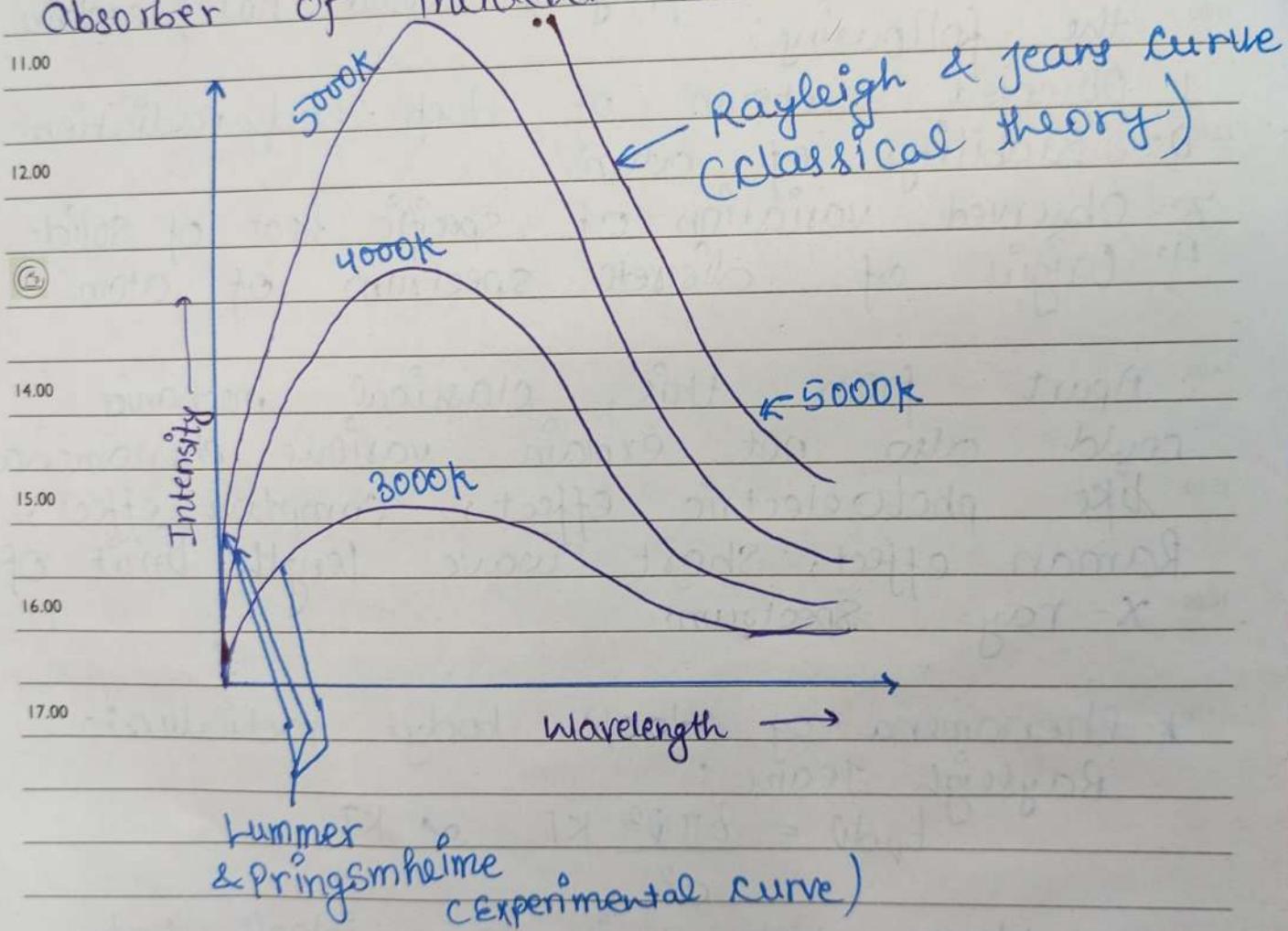
APRIL 20						
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03 | MARCH
TUESDAY

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Day 063-303 ♦ Week 10

- 9.00 is valid for radiations corresponding to all wavelengths & all angles of incidence
 10.00 Therefore, the black body is an ideal absorber of incident radiation.



Rayleigh & Jeans try to explain the above curve on the basis of classical theory. of electromagnetic radiation, which assume that all values of energy are possible in black body radiation.

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MARCH | 04

WEDNESDAY

Week 10 Day 064-302

Date

To
Lecture
Year
found
that the experimental data is
well fitted in long wavelength range but
give ridiculous prediction for short wavelength
region.

As according to classical theory, the
average energy associated with the degree
of freedom is " kT ". Therefore the energy
per unit volume in frequency range ν & $\nu + d\nu$ is given as:

$$E_{\text{av}} = \frac{8\pi V^2 k T}{c^2}$$

This is Rayleigh & jeans radiation law
derived from classical consideration which was
not capable in explaining the phenomena
of black body radiation.

Max Planck explained the black body
phenomena on the basis of his quantum
theory radiation.

Planck postulated from study of radiation
from hot bodies that the radiating atoms
can emit only discrete energy in discrete
amount (or) that atom exist only in discrete
states > called quantum theory.

APRIL 20
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05 MARCH
THURSDAY

Dinner

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close

Planck found that the black body could not radiate energy in continuous fashion, but only in discrete packets of energy that is emission of radiation from a black body taking place in bundles of energy or quanta known as photons.

Planck found an empirical formula based on following assumption to explain the experimentally observed distributed energy in spectrum of black body:

- (i) A chamber containing black body radiation also contains simple harmonic motion oscillator (or) molecular dimensions which can vibrate with all possible frequencies.
- (ii) An oscillator can't have any energy but have only energies given by :

$$E = nh\nu \text{ where } n = 1, 2, 3, \dots$$

According to Planck energy per unit volume in frequency range ν to $\nu + d\nu$ is

$$E_{\nu} d\nu = \frac{c^2}{c^2 \nu^5 k T} \frac{d\nu}{h}$$

The above relation is known as Planck's radiation law & explains all the experimentally observed facts.

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Went to see Dr. C. H. Smith, who could not explain such a

of an atom: that e- revolve.

L'U. R. P. 1

according to classical theory of ESR

given by Maxwell every known charge radiator electromagnetic energy.

Since e^- is performing circular motion

therefore e- will experience centripetal acceleration @ concentration. in accordance with classical theory

The e^- will radiate EM energy due to

...and the state of energy take

isoparbit will also be decrease, and ultimately

16. **very short** interval of time of order

¹⁷ physics required ¹⁸ for ¹⁹ classical

unstable e- could fall into the nucleus.

...
seconds but this never happens in
actual practice.

Therefore, on the basis of classical

explained, if an atom can't be

Neil's Bohr ex #8 P-9

Mo To	Nu	Fr	5n	5u
<u>macroscopic basis of quantum mechanics</u>				
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stability of atom				
of the Priority				
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96	97	98	99	100

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07 | MARCH
SATURDAY

Day 067-299 * Week 10

Applying

the concept of closed orbit &

the concept of angular momentum.

9.00 quantization of angular momentum can according to Bohr model e^- can revolve only in those orbits in which its angular momentum is an integral multiple of $\frac{h}{8\pi}$. $\Rightarrow m\lambda = \frac{nh}{8\pi}$

10.00 11.00 12.00

13.00 classical physics could not explain the theory of specific heat of solids.

14.00 At room temp, specific heat of solids at constant temp volume is given by Dulong & Petit law which was derived from classical assumption given by:

$$C_V = 3R$$

15.00 16.00 17.00

The above relation can be derived on the basis of kinetic theory according to which means kinetic energy per degree of freedom of a gas molecule temp at $\frac{3}{2}kT$ [K is Boltzmann constant]

For a monoatomic gas constant there are 3 degrees of motion of translation motion. Therefore total average kinetic energy per molecule is $\frac{3}{2}kT$.

Priority

For N atoms = $N(\frac{3}{2}kT)$

$$\Rightarrow \frac{3}{2}RT$$

$$[K = \frac{R}{N}]$$

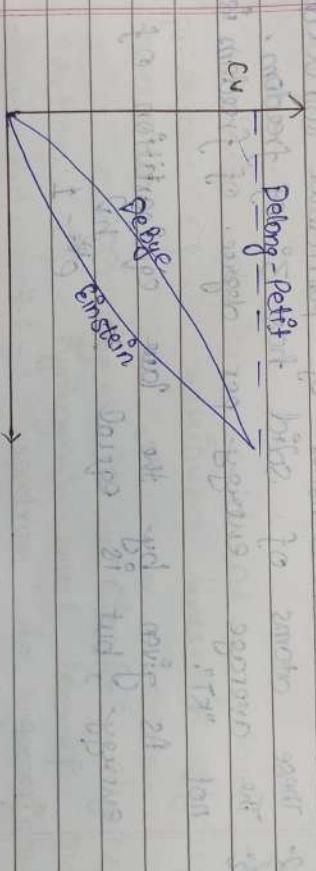
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The mean potential energy of each of the three components of vibration is equal to $\frac{1}{2} kT$ since average K.E. is equal to average potential energy in SHM.
So, therefore the potential energy of oxidation for 1 mole of atom will be $\frac{3}{2} kT$.

$$P.E. = N \cdot \frac{3}{2} kT = \frac{3}{2} RT \quad [\because k = \frac{R}{N}]$$

So, total energy = $3RT$.
Specific heat at constant volume

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R$$



This failure of law could not explain on the basis of classical theory which assume that the body absorbs heat continuously indefinitely small amount.

Dulong - Petit law however successfully explain why constant specific heat exists at room temp. at constant volume. But the behaviour of specific heat at low temp. can't be explained by

The law. The 1st attempt to explain the variation

of specific heat of solids with temp. was made of Einstein on the basis of Quantum theory.

Einstein assumed:

1. Atoms of solid are at rest under mutual attraction & repulsion. When the solid is heated, the atoms are set into simple harmonic motion about their position of equilibrium. The frequency of these "vibrations" is same characteristic of particular solid concerned.
2. These atoms of solid has 3° of freedom.
The average energy per degree of freedom is not " kT ".

As given by the law equipartition of energy, but is equal to $\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$

As calculated by Planck by application of Quantum theory

$$C_V = \frac{3Nk}{e^{\frac{h\nu}{kT}} - 1} \left(\frac{h\nu}{kT} \right)^2$$

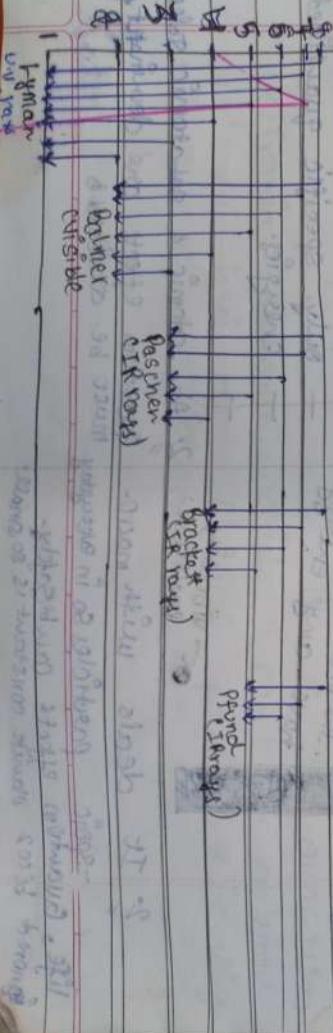
The above relation shows that specific heat of solids depends upon temperature. Although Einstein's theory predicts volume correctly, it fails to predict the variation of specific heat with temp. It was observed in certain case.

of elements like copper, aluminium etc, the specific heat at low temperatures decrease at more rapidly than that predicted by Einstein theory.

This agreement is due to neglecting mutual forces exerted by the atoms upon each other.

Dybe therefore modified Einstein theory by assuming that any solid is capable of vibrating elastically in many varying frequencies of limited no. of different modes. Dybe theory gives excellent experimental agreement over the whole observable range.

Up classical physics could not explain the presence of various lines in Hydrogen spectrum. According to classical physics, the spectrum of hydrogen must be of continuous type. But the spectrum is experimentally observed has discrete, i.e. the hydrogen spectrum is a line spectra consisting of large no. of lines known as Lyman, Balmer, Paschen, Pfund, Brackett.



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

for Lyman series :

$$n_1 = 1 \quad \& \quad n_2 = 2, 3, 4, 5, \dots$$

for Balmer series

$$n_1 = 2 \quad \& \quad n_2 = 3, 4, 5, 6, \dots$$

for Paschen series

$$n_1 = 3 \quad \& \quad n_2 = 4, 5, 6, 7, \dots$$

for Brackett series

$$n_1 = 4 \quad \& \quad n_2 = 5, 6, 7, 8, \dots$$

for Pfund series

$$n_1 = 5 \quad \& \quad n_2 = 6, 7, 8, 9, \dots$$

The presence of these series was ~~not~~ predicted by Neil Bohr on the basis of quantum theory of rad? Bohr derived the following eqn to explain the presence of various series in hydrogen spectrum.

Classical World

Quantum World

1. Before Planck's law possible could have any energy.
2. After Planck's law possible could have only specific quantized energies.

→ vibrating particle.

1. It deals with macroscopic particles so in everyday life, quantum effects can be safely ignored because Planck constant is so small.
2. At atomic & subatomic scales, quantum effects are dominant & specific particles so in everyday life, quantum effects must be considered.

classical world

3. It is based upon Newton's law of motion.
4. It is based on Maxwell's electromagnetic wave theory acc. to which any amount of energy may be emitted or absorbed continuously.
5. The state of a system is defined by specifying all the forces acting on a particle as well as their positions & velocity. The future state can then be predicted with certainty.

Mar. 15, 2023

Quantum world

3. It takes into account Heisenberg's uncertainty principle & De Broglie matter wave theory that is dual nature of matter.
4. It is based on Planck's quantum theory of rad. acc. to which only discrete values of energies are emitted or absorbed.
5. It gives probability of finding the particle at various location in space.

Practical

- # Photoelectric effect:
- When a light ray of suitable frequency is incident on a metal plate, then e⁻s are ejected. This phenomena is called photoelectric effect.

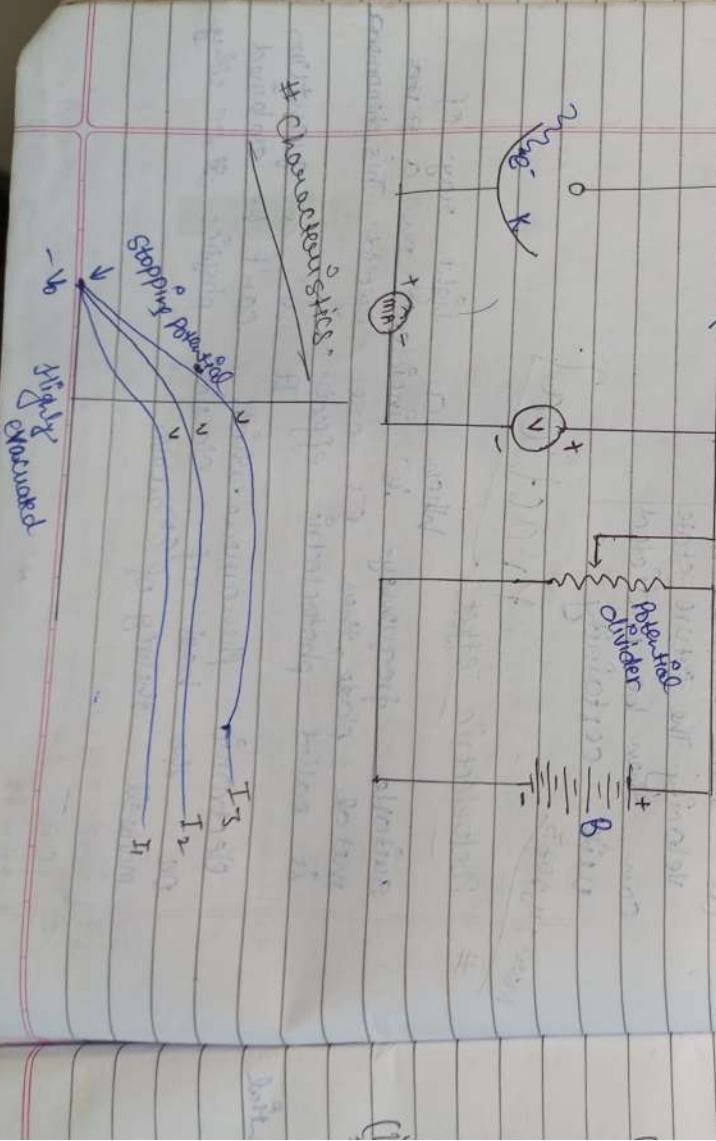
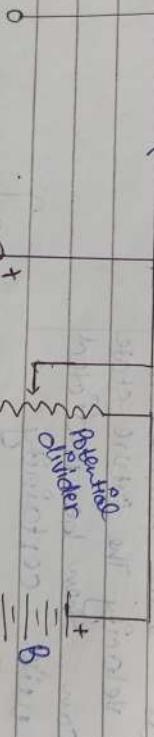
electronic phenomena which can't be explained on the basis of classical physics i.e. using Maxwell theory of EM waves.

Regarding photoelectric effect, the following points are worth noting:

- In 1905, Albert Einstein published a paper in which he explained experimental data from the photoelectric effect as the result of light energy being received in discrete quantized packets, known as photon. This discovery leads to quantum revolution.
- In 1914, Robert Millikan's experiment confirmed Einstein's law on photoelectric effect.

Experimental arrangement:

(photo current)



(i) For observing photoelectric characteristics we place cathode & anode in a highly evacuated glass tube as shown in figure before.

Here cathode & anode are maintained at -ve & +ve potential respectively by means of a high tension battery & through a potential divider, arrangement of experiment is such that potential can be kept reversed. Voltmeter can measure the difference between the cathode & plate & milliammeter measures the photocurrent in milliamperes.

Characteristic

(i) Photoelectric current =

The electric current flowing on account of photoelectrons in photoelectric effect is defined as photoelectric current.

(i)

(ii) Saturated photoelectric current =

The maximum constant current (or) constant value of photoelectric current, it is measured in saturated photoelectric current. In saturation stage, the value of photoelectric current is inversely proportional to square of distance b/w the light source & metal surface.

$$k \propto \frac{1}{d^2}$$

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* 3^o Stopping potential \Rightarrow

When negative potential (or) anode (plate) want cathode in a photocell is applied then at a certain ratio of this potential, photocurrent becomes zero. This value of voltage potential is defined as Stopping potential.

The minimum value of potential which is necessary to stop even one e- with the words "to stop even one e- with the maximum kinetic energy" from reaching the plate (cathode).

Stopping potential is the measure of the maximum value of kinetic energy of e- emitted as a result of photoelectric effect.

$$V = W$$

$$V = \frac{K_{max}}{e} \quad [K - \text{kinetic energy}]$$

$$\text{Given} \quad K_{max} = V_0 e \\ \therefore \frac{1}{2} m V_{max}^2 = V_0 e \\ \frac{1}{2} m V_{max} = V_0 e$$

Stopping potential depends on:

(i) Frequency of incident light.

(ii) Nature of cathode material used.

It is obvious that stopping potential doesn't depend upon intensity of light.

Ques. Q. 1. Define stopping potential & answer

(c) Minimum energy of incident photon required to release an e^- from the surface of a metal is called work function of the metal. And workfunction is given by $W = h\nu_0$ $\approx \text{AC} \times 10^3$

work

other

plate

of
y of
ctic

* Failure of (classical) electromagnetic theory in explaining photoelectric effect = According to Maxwell's theory of electromagnetism, if a substance is exposed to light, a substance is subjected to an oscillatory electric field, the intensity of light is proportional to square of amplitude of electric field. Due to interaction of e^- of substance with the electric field, the e^- gain kinetic energy. These e^- leave the substance as soon as their kinetic energy exceeds the binding energy of e^- . The electromagnetic energy gained by e^- depends upon

- i) Intensity of incident light.
- ii) Area of surface exposed to the light.
- iii) Time for which surface is illuminated

Potential

If we consider a light falling vertically on a sodium surface, a detectable photo electric current is obtained, when 10^{-6} W m^{-2} of electromagnetic energy is absorbed by the surface.

$$P = \frac{e}{t}$$

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A layer of sodium, one atom thick & one more square (cm^2) in area has 10^{19} atoms each atom will receive an average amount of energy = 10^{-25} watt, so that 1.6×10^6 seconds (nearly two weeks) will be required by an atom to emit energy & e- in action will gain sufficient energy will be liberated in about 2 months.

Hence, the E.M theory fails to explain why there is no time lag b/w the instant the light falls & that of emission of e- photo-e.

Secondly, according to E.M theory, the ejection of electron should depend upon the intensity of light & not on its frequency. In words, there should be no threshold frequency for any material. This is in contradiction to the observed fact.

Moreover there is no time limit only maximum energy to be transferred to the e- i.e. the e- can have only value of maximum energy. This is contradictory to the observed fact.

Hence, classical theory breaks E.M

Theory of light fails to explain the basic fact of photoelectric effect.

Einstein photoelectric laws:

For each emitting surface, there exist a threshold frequency (ν_0) at & above which e^- 's are emitted but below which no e^- is emitted. The number of e^- emitted for given surface of cathode per second is directly proportional to the intensity of incident light, not wavelength or frequency of light.

Maximum kinetic energy of the e^- increases with increase in frequency of incident light provided $\nu > \nu_0$. The value of maxⁿ kinetic energy doesn't depend upon intensity of incident light.

The stopping potential for a given metal surface is proportional to frequency of incident light. But is dependent of intensity of light.

There is practically no time lagging before incidence of light

& ejection of photo e^- from the cathode;
 If we use intensity of light $10^{-10} \text{ W m}^{-2}$
 (If we use 1 watt/m^2) then photo e^- are emitted
 within a very short interval of time
 3×10^9 second.

Einstein's photoelectric eqns - 1905

Q. When a photon of energy ' E ' is incident on a metal surface then a part of energy of photon is used up to liberate e^- from the surface of metal & the rest amount of energy provides the maximum value of kinetic energy of e^- .

$$E = W + E_{\max}$$

$$E = h\nu = h\nu + E_{\max}$$

$$h\nu = h\nu_0 + eV_0$$

(kinetic energy)

where ν_0 is the threshold frequency

for producing photo electrons

threshold frequency is $\nu_0 = \frac{h}{eV_0}$

W = work function

Date
Apr. 05, 2023

$p = mv$

Page No. 25
Date $p = mv$

De-Broglie principle -

According to De-Broglie there is a wave associate, energy with every matter particle. It is known as matter wave. Non-relativistic ($C \ll c$)
case. Its wavelength is $\lambda = \frac{h}{p}$

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$\text{Thus } \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

If voltage V is applied on a charge particle,

$$eV = \frac{h}{\sqrt{2mE}}$$

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

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$h = 6.626 \times 10^{-34} \text{ m}^2 \text{ kg/sec.}$$

$$p = D \cdot 882 \text{ eV} \quad (4) \quad \therefore \quad \lambda = \frac{h}{\sqrt{2mE}}$$

$$E = \frac{0.101}{\sqrt{V}} \text{ eV} \quad \left\{ \text{for partical} \right.$$

For gas molecule

$$(E = \frac{3}{2} k_B T)$$

$$T = \frac{h}{\sqrt{3mk_B}} = \frac{h}{\sqrt{3k_B}} + \frac{h}{\sqrt{3m}}$$

For neutron, $E = \hbar k_B T$

$$A_n = \frac{f_n}{\sqrt{m_n k_B T}}$$

Case 2: Relativistic case (where $\gamma \gg 1$)

$$E = \sqrt{p^2 c^2 + m_0^2 c^4} \quad \text{Eq (N)}$$

$$E = m_0 c^2 \left(1 + \frac{p^2}{m_0^2 c^2} \right)^{1/2}$$

$$(1+x)^n = 1 + nx + \frac{n(n-1)}{2!} x^2$$

$$E = m_0 c^2 \left[1 + \frac{p^2}{m_0^2 c^2} - \frac{1}{2!} \frac{p^4}{m_0^4 c^4} + \dots \right]$$

$$E = m_0 c^2 + \underbrace{\frac{p^2}{m_0}}_{\text{kinetic energy}} - \underbrace{\frac{1}{2!} \frac{p^4}{m_0^2 c^2}}_{\text{rest mass energy}}$$

$$E = m_0 c^2 + K \cdot E(k) \quad \text{Eq (Nc)}$$

From eqn (1) & (2), $(1) \cdot (2)$

$$\cancel{m_0 c^2} + K = \cancel{\int p^2 c^2 + m_0^2 c^4}$$

$$\text{Squaring both sides: } \cancel{p^2 c^2 + m_0^2 c^4} + K^2 = \cancel{p^2 c^2 + m_0^2 c^4}$$

$$p = \frac{1}{c} \sqrt{k^2 + 2km_0 c^2} = \frac{1}{c} \sqrt{k(k + 2m_0 c^2)}$$

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$$\checkmark 5.031 \times 10^{-21}$$

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{k(c^2 + m_0 c^2)}}$$

Q. Find de-Broglie wavelength of e- having energy of

$$12.27 \text{ eV} = \frac{12.27 \times 10^3 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} = 7.613 \times 10^{22} \text{ m}$$

$$12.27 \text{ eV} = 1.227 \times 10^{-19} \text{ J} \Rightarrow 0.613 \text{ Å}$$

$$\lambda = 6.626 \times 10^{-34} \times 3.8 \times 10^9$$

$$\sqrt{400(400 + 2 \times 9 \times 10^{-31}) \times (3.8 \times 10^9)^2}$$

$$\sin \theta = \frac{y}{r}$$

concept of wave packet $\psi(x, t)$ According to de-Broglie, there is a wave associate with every matter particle.

Let $\psi = A \sin(\omega t - kx)$ for phase velocity, v_p

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

$$\frac{dx}{dt} = \frac{\omega}{k} = v_p$$

$$\text{or, } \frac{v_p}{k} = \frac{\omega}{c} = \frac{h}{m} = \frac{mc^2}{mv} = \frac{c^2}{v} = \left(\frac{c}{v}\right)c$$

Since any matter particle velocity is less than the speed of light [According to Einstein's special theory of relativity (STR) so;

$$v \ll c$$

$$\Rightarrow v_p > c > v$$

So velocity of wave (phase velocity) & particle velocity are different; i.e., we can say that there is not a single wave associate with matter particle. Thus, there will be a group of wave associate with matter particle i.e. known as wave packet.

$$\text{Let } \Psi = A \sin(\omega_1 t - k_1 x)$$

$$\therefore \Psi_1 = A \sin(\omega_1 t - k_1 x)$$

from superpositn principle

$$\Psi = \Psi_1 + \Psi_2$$

$$\Psi = A [\sin(\omega_1 t - k_1 x) + \sin(\omega_2 t - k_2 x)]$$

$$\Psi = 2A \sin\left[\frac{(\omega_1 t - k_1 x) + (\omega_2 t - k_2 x)}{2}\right] \cos\left[\frac{(\omega_1 t - k_1 x) - (\omega_2 t - k_2 x)}{2}\right]$$

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

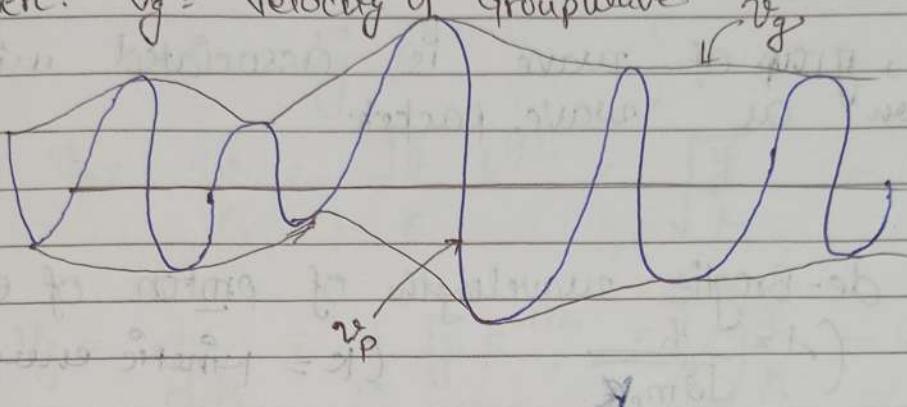
Let $\omega_1 \approx \omega_2$ & $k_1 \approx k_2$ then:

$$\rightarrow \frac{\omega_1 + \omega_2}{2} \approx \frac{\omega_1 + \omega_2}{2} = \omega ; \quad k_1 + k_2 \approx \frac{k_1 + k_2}{2} = K$$

$$\rightarrow \omega_1 - \omega_2 \approx \Delta\omega ; \quad \frac{k_1 - k_2}{2} \approx \Delta k$$

$$\psi = \underbrace{A \cos(\Delta\omega t - \Delta k x)}_{\text{Amplitude } (v_g)} \underbrace{\sin(\omega t - kx)}_{\text{wave } (v_p)}$$

Here: v_g = velocity of Groupwave.



For group velocity:

$$\Delta\omega t - \Delta k x = \text{constant}$$

$$\Delta\omega dt - \Delta k dx = 0$$

$$\frac{dx}{dt} = \frac{\Delta\omega}{\Delta k} = v_g$$

or; $v_g = \frac{d(\hbar\omega)}{d(\hbar k)} = \frac{dE}{dp}$

$$\therefore E = \frac{p^2}{2m}$$

$$v_g = \frac{dp}{dm} = \frac{p}{m} = \frac{mv}{m} = v$$

$$\Rightarrow v_g = v$$

For relativistic case: $E^2 = p^2 c^2 + m_0^2 c^4$

$$\frac{dE}{dp} = \frac{dp}{dp} c^2$$

$$\frac{dE}{dp} = c^2$$

PP. 1.67×10^{-29}

$$v_g = \frac{dE}{dp} = \frac{pc^2}{E} = \frac{mv^2c^2}{mc^2} = v$$

$$v_g = v$$

Thus, group of wave is associated with particle known as wave packet.

- Q. Find de-Broglie wavelength of proton of energy 1 MeV ($\lambda = \frac{h}{\sqrt{2m_p E}}$) [K = kinetic energy]

$$\Rightarrow \lambda = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-29} \times 1.6 \times 10^6}}$$

- Q. A ball of mass 10gm is moving with velocity 20m/sec. Then find de-Broglie wavelength ($\lambda = \frac{h}{mv}$)

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{20 \times \frac{10}{1000}} \text{ m} = \frac{6.626 \times 10^{-34}}{0.2} \text{ m} = 33.13 \times 10^{-34} \text{ m.}$$

$$\boxed{\lambda = 33.13 \times 10^{-34} \text{ m.}}$$

Q. If $\omega = \sqrt{gk}$, find value of k

$$v_g = \frac{v_p}{\lambda}$$

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Q. If $\omega = \sqrt{gk}$ then find (relation) b/w phase velocity & group velocity.

$$\text{Soln} : \omega = \sqrt{gk}^{1/2}$$

$$v_p = \frac{w}{k} = \frac{\sqrt{gk}}{k} = \sqrt{\frac{g}{k}} - \text{Eq}(1)$$

$$v_g = \frac{d\omega}{dk} = \frac{1}{2} \sqrt{gk} k^{-1/2} = \frac{1}{2} \sqrt{\frac{g}{k}} - \text{Eq}(2)$$

from Eqn (1) & (2)

$$v_g = \frac{v_p}{2}$$

Q. $\omega^2 = \alpha k + \beta k^2$ then value of wave no. at which phase velocity is equal to group velocity.

$$\omega^2 = \alpha k + \beta k^2$$

$$2\omega d\omega = \alpha dk + \beta k^2 dk$$

$$2\omega d\omega = (\alpha + \beta k) dk$$

$$\frac{d\omega}{dk} = \frac{\alpha + \beta k}{2\omega}$$

$$\text{Given } v_p = v_g$$

$$\frac{v_p}{v_g} = (\alpha + \beta k) \left(\frac{1}{A} \right) = \frac{1}{B}$$

$$\alpha + \beta k = \frac{1}{B}$$

$$\alpha + \beta k = \frac{1}{B}$$

$$\alpha + \beta k = \frac{1}{B}$$

$$= 2(\alpha k + \beta k^2) = \alpha k + 2\beta k^2$$

$$\partial \alpha k + \partial \beta k^2 = \alpha k + \partial \beta k^2$$

$$\alpha k = 0; \quad [k=0]$$

Q. If $\omega^2 = \alpha k + \beta k^2$ then find value of k for which $v_g = v_p$

$$\partial \omega / \partial k = (\alpha + 3\beta k^2) dk$$

$$v_g = \frac{\partial \omega}{\partial k} = \frac{\alpha + 3\beta k^2}{\partial \omega} = v_p \quad \text{Given}$$

$$\Rightarrow \partial \omega^2 = \alpha k + 3\beta k^3$$

$$\partial(\alpha k + \beta k^3) = \alpha k + 3\beta k^2 \quad \text{Given}$$

$$\alpha k = 3\beta k^3; \quad [k = \sqrt{\frac{\alpha}{\beta}}]$$

Uncertainty principle:

Let \vec{A} & \vec{B} are Hermitian operator.

Uncertainty in \vec{A} can be defined as :

$$\Delta \vec{A} = \sqrt{\langle (\vec{A} - \langle \vec{A} \rangle)^2 \rangle} \leftarrow \text{rms (Root mean square)}$$

$$(\Delta \vec{A})^2 = \langle (\vec{A} - \langle \vec{A} \rangle)(\vec{A} - \langle \vec{A} \rangle)^* \rangle$$

$$= \langle (\vec{A}^2 - \vec{A} \langle \vec{A} \rangle - \vec{A}^* \langle \vec{A} \rangle + \langle \vec{A} \rangle^2) \rangle$$

$$= \langle \vec{A}^2 \rangle - 2 \langle \vec{A} \rangle \langle \vec{A} \rangle + \langle \vec{A} \rangle^2$$

$$= \langle \vec{A}^2 \rangle - 2 \langle \vec{A} \rangle \langle \vec{A} \rangle + \langle \vec{A} \rangle^2$$

$$= \langle \hat{A}^2 \rangle - 2\langle \hat{A} \rangle^2 + \langle \hat{A} \rangle^2$$

$$(\Delta \hat{A})^2 = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2$$

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

Similarly,

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

General uncertainty principle:

$$\Delta \hat{A} \Delta \hat{B} \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|$$

Case 1: If $\hat{A} = \vec{x}$ & $\hat{B} = \vec{p}_x$, then ~~$\Delta x \Delta p_x$~~

$$\Delta x \Delta p_x \geq \frac{1}{2} |\langle [\vec{x}, \vec{p}_x] \rangle|$$

$$(\text{Dimensionless}) \quad \frac{1}{2} |\langle i \hbar \rangle|$$

$$\frac{\partial \vec{x}}{\partial t} = \vec{p}_x \quad \frac{\partial \vec{p}_x}{\partial t} = -\vec{x}$$

Case 2: $\hat{A} = \vec{E} \cdot \vec{r} + \vec{p} \cdot \vec{t}$ and $\hat{B} = \vec{t}$ then,

$$\Delta E \cdot dt \geq \frac{1}{2} |\langle [\vec{E}, \vec{t}] \rangle|$$

$$\frac{1}{2} |\langle [i \vec{p} + \vec{E}, \vec{t}] \rangle|$$

$$\frac{1}{2} \left(\frac{1}{m} \vec{p} \cdot \vec{t} + \vec{E} \cdot \vec{t} \right)$$

Case 3: If $\vec{A} = \hat{\phi}$ & $\vec{B} = \vec{L}_2 = i\hbar \frac{d}{d\phi}$ (Ans)

$$\text{then } \Delta\phi \Delta \vec{L}_2 \geq \left| \langle \hat{\phi}, i\hbar \frac{d}{d\phi} \rangle \right| \geq \frac{1}{2} \hbar^2$$

$$\geq \frac{1}{2} \hbar^2 (-1) \quad |$$

$$\leq \frac{1}{2} \hbar^2 \quad \text{which is}$$

Case 4: If $[\vec{A}, \vec{B}] = 0$, then $\Delta\vec{A}\Delta\vec{B} = 0$
 if operator \vec{A} & \vec{B} commute then we can
 measure simultaneously!

Application :-

↳ Ground state energy of one dimensional
 Harmonic oscillator - (1 DHO):

$$E = \frac{p^2x}{2M} + \frac{1}{2} M \omega^2 x^2$$

$$\Delta E = \left(\frac{\Delta p x}{\Delta m} \right)^2 + \frac{1}{2} M \omega^2 (\Delta x)^2$$

$$\text{Let } \Delta x \propto \Delta t \Rightarrow \Delta p \propto \frac{\partial}{\partial x} \Delta x$$

$$\Delta E = \frac{p^2}{8m(\Delta x)^2} + \frac{1}{2} M \omega^2 (\Delta x)^2 \rightarrow \text{Eqn (1)}$$

$$\text{Since } \frac{\partial(\Delta E)}{\partial(\Delta x)} = 0, \quad = -\frac{\partial p^2}{8M(\Delta x)^3} + \frac{1}{2} M \omega^2 \Delta x$$

$$\Rightarrow \frac{\hbar^2}{4m(\Delta x)^2} = m\omega^2 \Delta x, \text{ and}$$

$$\Rightarrow (\Delta x)^4 = \frac{\hbar^2}{4m^2\omega^2}$$

On Substituting in eqn (i) we get;

$$E_{min} = \frac{\hbar^2}{8m\left(\frac{\hbar}{2m\omega}\right)} + \frac{1}{2}m\omega^2 \frac{\hbar^2}{4m\omega}$$

$$= \frac{\hbar\omega}{4} + \frac{1}{4} \frac{\hbar\omega}{m}$$

$$= \frac{\hbar\omega}{2} \quad \text{(mean)}$$

Ground energy = minimum energy.

Q. Ground state energy of H₂ atom:

$$= E = \frac{p^2}{2m} - kze^2$$

$$\Delta E = \frac{(\Delta p)^2}{2m} - kze^2$$

Let $\Delta p_x \approx h \Rightarrow \Delta p_x = h$

for spherical symmetry
 $\Delta \epsilon \propto \frac{1}{r}$

$$\Delta \epsilon = \left(\frac{1}{\Delta r} \right)^2 - \frac{k_2 e^2}{\Delta m} - \epsilon_{pN}^N (i)$$

$$\frac{d\epsilon}{dr} = 0$$

$$\text{So, } \frac{d\Delta \epsilon}{dr} = \frac{-2 \frac{1}{r^2}}{\Delta m (\Delta r)^3} + \frac{k_2 e^2}{(\Delta r)^2}$$

$$\frac{k_2 e^2}{(\Delta r)^2} = \frac{4}{M (\Delta r)^3}$$

$$\Delta r = \frac{4}{k_2 e^2 M}$$

On substituting in $\epsilon_{pN}^N (i)$ we get

$$E_{min} = \frac{\frac{4}{r^2}}{\frac{8m}{M k_2 e^2}} - \frac{k_2 e^2}{r^2}$$

$$= \frac{m^2 k_2^2 e^4 r^2}{8m r^4} - \frac{M k_2^2 e^4 r^4}{r^2}$$

$$= \frac{1}{2} \frac{M k_2^2 e^4}{r^2} - \frac{M k_2^2 e^4}{r^2}$$

$$= -\frac{1}{2} \frac{M k_2^2 e^4}{r^2}$$

3. Non-existence of e^- in nucleus: Fermi theory

$$\Delta p \cdot \Delta x \approx \hbar$$

$$\Delta p \approx \frac{\hbar}{\Delta x}$$

Let e^- exists in nucleus & radius of nucleus is 8 fm

$$\Delta p = \frac{\hbar}{\Delta x} = \frac{6.626 \times 10^{-34}}{1.6 \times 10^{-19} \times 8 \pi \times 2 \times 10^{-15}}$$

As we know:

$$E = \sqrt{p^2 c^2 + m^2 c^4} \rightarrow \text{Neglect,}$$

$$E = pc$$

$$\Delta E = \Delta pc = \frac{hc}{\Delta x} = \frac{6.626 \times 3 \times 10^8}{1.6 \times 2 \pi \times 2 \times 10^{-15}} = \frac{1240 \text{ Mev}}{4\pi}$$

$$\sim = \frac{10^8 \text{ ev}}{100 \text{ mev}}$$

So, According to uncertainty principle e^- should have large energy around 100 mev to exist in nucleus. But we found in beta decay experiment that e^- has energy 2.3 Mev so, e^- doesn't exist in nucleus.

Natural width of spectral line :-
From uncertainty principle,

$$\Delta E \Delta t \sim \frac{\hbar}{\Delta}$$

$$\Delta(\hbar\nu) \Delta t \sim \frac{K}{4\pi}$$

$$\Delta\nu = \frac{1}{4\pi \Delta t}$$

for electronic transition $\Delta t \sim 10^{-7}$ sec

$$\Delta\nu = \frac{1}{4\pi \times 10^{-7}} = \frac{10^7}{4\pi}$$

$$\therefore \nu = \frac{c}{\lambda} = c \overline{\nu} \rightarrow \text{wave no.}$$

frequency

$$c \Delta \overline{\nu} = \frac{10^7}{4\pi} = \Delta \overline{\nu} = \frac{10^7}{4\pi \times 3 \times 10^8} = \frac{1}{120\pi}$$

Impedance of electromagnetic wave is 120π
because of gamma photon is coming out
when e^- move from excited state to
ground state so both are correlated.

Probability - Current Density = $i \nabla \psi^* \cdot \nabla \psi$

The motion of a material particle is associated with the motion of wave function. If the probability of finding a particle in some bounded region of space decreases with time then the probability of finding outside, thus "reg" must increase by same amount.

The time dependent Schrödinger eq^N:

$$i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi - E_N(t)$$

On multiplying both sides with ψ^* , we get:

$$i\hbar \psi^* \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \psi^* \nabla^2 \psi + \psi^* V\psi - E_N(t)$$

($\psi \rightarrow \psi^*$) On taking complex conjugate of eq^{N(1)}, we get:

$$-i\hbar \psi \frac{d\psi^*}{dt} = -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* - E_N(t)$$

On multiplying both sides with ψ , we get:

$$-i\hbar \psi \frac{d\psi^*}{dt} = -\frac{\hbar^2}{2m} \psi \nabla^2 \psi^* + V\psi \psi^* - E_N(t)$$

On subtracting eq^{N(4)} from eq^{N(2)}, we get:

$$i\hbar \psi^* \frac{d\psi}{dt} - (-i\hbar \psi \frac{d\psi^*}{dt}) = -\frac{\hbar^2}{2m} \psi^* \nabla^2 \psi + \left(-\frac{\hbar^2}{2m} \psi \nabla^2 \psi^*\right)$$

$$\Rightarrow i\hbar \left[\psi^* \frac{d\psi}{dt} + \psi \frac{d\psi^*}{dt} \right] = -\frac{\hbar^2}{2m} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*)$$

$$\Rightarrow \frac{\partial}{\partial t} (\psi^* \psi) = -\frac{\hbar}{2m} \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*)$$

$$\frac{d}{dt} (\psi^* \psi) + \nabla \cdot \vec{J} = (\psi^* \nabla \psi - \psi \nabla \psi^*) = 0 - \epsilon^{(5)}$$

We know that eqⁿ of continuity in hydrodynamics associated with conservation of fluid of density ρ & current density \vec{J} is given by

$$\frac{d\rho}{dt} + \nabla \cdot \vec{J} = 0 \quad \text{Eq } (6)$$

On comparing eqⁿ (5) & (6)
 $\rho = \psi^* \psi \rightarrow$ position probability density (ρ)

$$\& \vec{J} = \frac{\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) \rightarrow \text{probability current density } (s)$$

$$\frac{dp}{dt} + \vec{\nabla} \cdot \vec{S} = 0$$

$$\frac{dp}{dt} = -\vec{\nabla} \cdot \vec{S}$$

On taking volume integral both sides,

$$\int_V \frac{dp}{dt} dV = - \int_V (\vec{\nabla} \cdot \vec{S}) dV$$

$$\frac{d}{dt} \int_V p dV = - \int_V (\vec{\nabla} \cdot \vec{S}) dV$$

Using Gauss div theorem,

$$\frac{d}{dt} \int_V \psi(r, t) dV = - \int_S \vec{S} \cdot \vec{da}$$

$$\therefore \frac{dp}{dt} = - \int_S \vec{S} \cdot \vec{da}$$

$$\Rightarrow \oint \vec{S} \cdot d\vec{a} = - \frac{dP}{dt}$$

Thus, the flow of particles through a closed surface is equal to decrease in finding the particle inside close surface.

If $\oint S da = 0$, then $\frac{dP}{dt} = 0$

$$-\frac{dP}{dt} = 0$$

$P = \text{Constant}$

* So, probability of finding the particle in all space is always unity [constant]

Time dependent Schrödinger wave eqn:

Consider a particle of mass m , moving in +ve dirn with velocity v . According to De-Broglie Hypothesis every moving particle has a wave associated with it, is called matter wave. whose wavelength is given by:

$$\lambda = \frac{h}{mv} \Rightarrow p_x = \frac{h}{\lambda} = \frac{h}{mv} \cdot \frac{m}{m} = \frac{h}{m} = \frac{h}{p_x}$$

or $p_x = \frac{h}{\lambda}$

According to Quantum physics, a wave consists of tiny packets of energy. It is called photons. The energy

of each photon is given by:

$$E = h\nu = \frac{h\omega}{\theta} = \frac{h\theta\nu}{\theta} \Rightarrow \omega = E - \epsilon q^N(2)$$

The wave associated with moving particle can be represented by:

$$\psi(x, t) = Ae^{i(\omega t - kx)} - \epsilon q^N(3)$$

$$\psi(x, t) = Ae^{-i(Et - \frac{p_x}{\hbar})} - \epsilon q^N(4)$$

Now, total energy E of the particle is given by:

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

$$E\psi = \frac{\hbar^2}{2m}\psi + V\psi = \epsilon q^N(5)$$

On differentiating eqn (4) w.r.t. t ,

$$\text{Since } \frac{d\psi}{dt} = \frac{d}{dt} \left[Ae^{-i(Et - \frac{p_x}{\hbar})} \right] = \frac{i(-E)}{\hbar} A e^{-i(Et - \frac{p_x}{\hbar})} \Rightarrow i(-E) \frac{d\psi}{dt} = \epsilon q^N(6)$$

$$\text{On differentiating eqn (4) w.r.t. } x,$$

$$\frac{d\psi}{dx} = \frac{d}{dx} \left[Ae^{-i(Et - \frac{p_x}{\hbar})} \right] = \frac{-ip_x}{\hbar} A e^{-i(Et - \frac{p_x}{\hbar})} \Rightarrow \frac{-ip_x}{\hbar} \frac{d\psi}{dx} = \epsilon q^N(7)$$

$$\text{Now, On differentiating eqn (4) w.r.t. } x^2,$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx^2} \left[Ae^{-i(Et - \frac{p_x}{\hbar})} \right] = \frac{-ip_x^2}{\hbar^2} A e^{-i(Et - \frac{p_x}{\hbar})} \Rightarrow \frac{-ip_x^2}{\hbar^2} \frac{d^2\psi}{dx^2} = \epsilon q^N(8)$$

$$\frac{d^2\psi}{dx^2} = \frac{1}{\hbar^2} \frac{\partial^2 \psi}{\partial x^2} \quad \text{Eqn (8)}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-\hbar^2}{\hbar^2} \left(-\frac{i}{\hbar} \frac{\partial \psi}{\partial x} \right) = \frac{i^2}{\hbar^2} \psi \frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{\hbar^2} \psi \frac{\partial^2 \psi}{\partial x^2}$$

From eqn (7)

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \rightarrow \text{Eqn (9)}$$

On substituting Eqns (6) & (9) in Eqn (5), we get:

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m} \left(-\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \right) + V\psi$$

$$(6) \quad i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \rightarrow \text{This is Eqn (10)}$$

In SP; $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{V^2}{\hbar^2} \psi \right) + V\psi$

$$\Rightarrow i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi$$

$$\Rightarrow i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad \text{Dissolving } \psi$$

(6)

where $E = i\hbar \omega$ - Energy eigen value

$$H = -\hbar^2 \nabla^2 + V \rightarrow \text{Harmonic value.}$$

$$(H)\psi = E\psi$$

Time independent Schrödinger Eq'n:

Consider a particle of mass m , moving with velocity v in +ve 'x' dirn.
The wave function describing the behaviour of wave function associated with moving particle can be expressed as,

$$\psi(x, t) = Ae^{i\frac{p}{\hbar}(px - Et)} \quad \text{--- ①}$$

We know that the time dependent Schrödinger Eq'n is given by,

$$i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) - E \quad \text{--- ②}$$

on differentiating Eq'n ① w.r.t. t we get

$$\begin{aligned} i\hbar \frac{d\psi}{dt} &= A e^{i\frac{p}{\hbar}(px - Et)} \cdot \frac{i}{\hbar}(-E) \neq -iE\psi = \frac{-iE\psi}{\hbar} \\ &= \frac{E\psi}{\hbar} = i\hbar \frac{d\psi}{dx} = E\psi - Eq'(x) \end{aligned}$$

Let potential energy of particle depends only on position x & independent of time. Then this case $\psi(x, t)$ can be represented as:

$$\begin{aligned} \psi(x, t) &= \phi(x) \cdot u(t) - Eq'(x) \\ \frac{d\psi}{dx} &= u \frac{du}{dt} \end{aligned}$$

$$S = \frac{i\hbar}{2m} [\nabla^2 \psi - \psi \nabla^2 \phi]$$

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$$\frac{\partial^2 \psi}{\partial x^2} = \frac{i\hbar^2 \phi}{2m} + \text{Eqn (5)}$$

Now

On using eqns (5) & (5) in eqn (2), we get,

$$E\phi = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \phi}{\partial x^2} \right) + V\phi$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + (E-V)\phi = 0$$

This is 1D time independent Schrödinger Eq.

$$\text{In SP, } \frac{\hbar^2}{2m} \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \right) \phi + (E-V)\phi = 0$$

$$\Rightarrow \frac{\hbar^2}{2m} \nabla^2 \phi + (E-V)\phi = 0$$

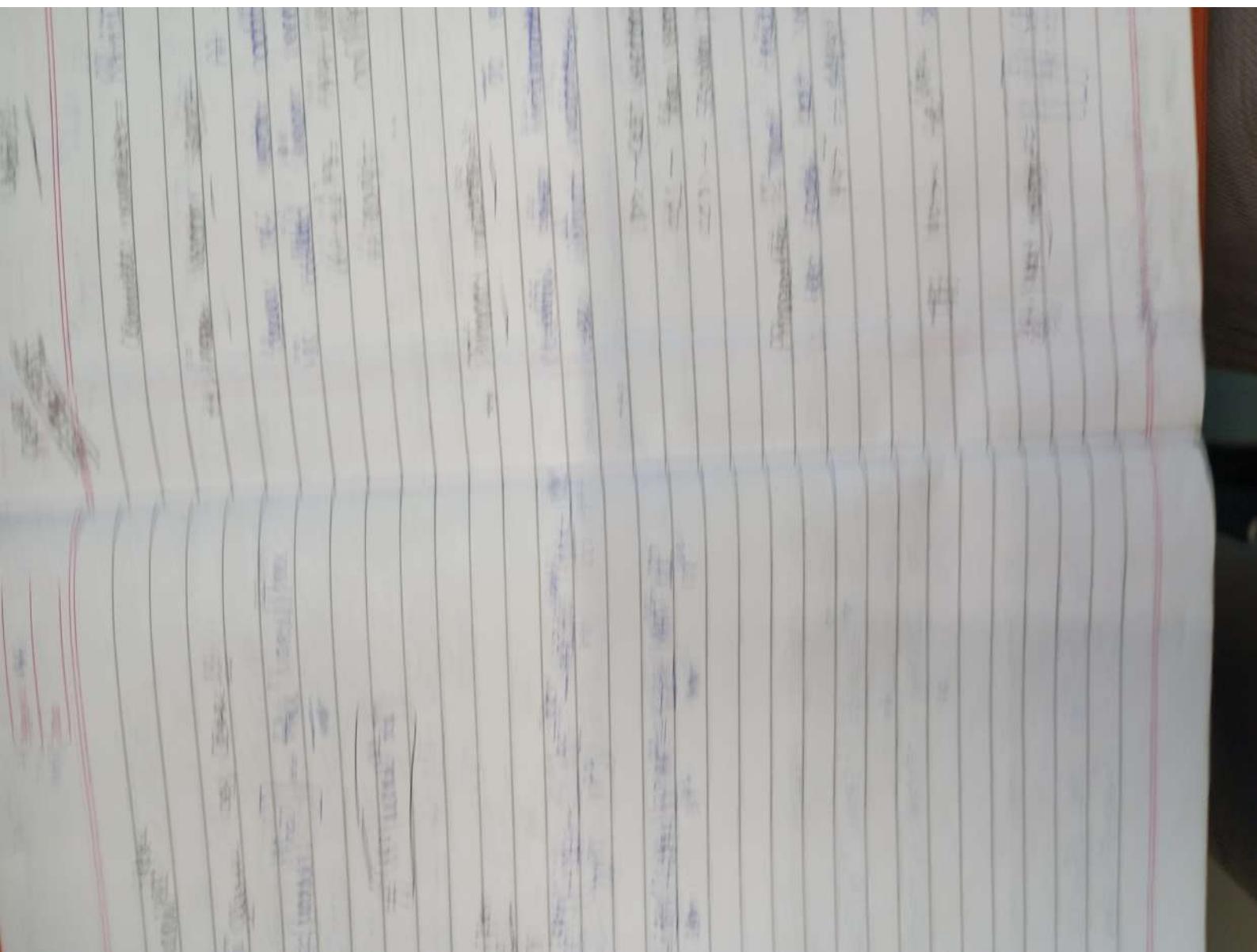
get,

$$\begin{aligned} \# \text{ Probability current density} \Rightarrow S &= -\frac{i\hbar}{2m} [\psi^* \nabla \psi - \psi \nabla \psi^*] \\ \psi(x) &= A e^{ikx} \\ S &= -i\hbar \left[C_A^* e^{-ikx} \right] \left(ik A e^{ikx} \right) - \left(A e^{ikx} \right) \left[-ik C_A^* e^{-ikx} \right] \\ &= -i\hbar [A k |A|^2 x^*] = \hbar k |A|^2 x^* = \hbar |A|^2 x^* \end{aligned}$$

Ans

$\therefore \psi(x) = u(x)$ real function.

$S = 0$ (For real f or there is no wave
(wave for complex function))



Complex number = $R + iI$

* Linear Vector space

A space that follows the laws of vector addition & scalar multiplication is called linear vector space.

$$(A + B)\psi = A\psi + B\psi$$

$$A(\alpha\psi) = \alpha(A\psi)$$

* Piact notation =>

To represent quantum state which gives information about the system we use piact notation.

$$\begin{pmatrix} -1 \\ r^2 \end{pmatrix} e^{i\theta}$$

$$\begin{aligned} |> &\rightarrow \text{Ket vector} \rightarrow |\psi\rangle = |\psi| \\ <1| &\rightarrow \text{Bra vector} \rightarrow \langle\psi| \\ <1> &\rightarrow \text{Scalar product} \rightarrow \langle\psi|\psi\rangle \end{aligned}$$

Properties:

- There exist a Bra vector corresponding to each ket vector such that:
- $|\psi\rangle^* = \langle\psi|$ (where \ast - transpose of conjugate)

If $|\psi\rangle = Ae^{ikx}$ then $\langle\psi| = A^*e^{-ikx}$

Q. Ket vector = $\begin{bmatrix} 5 \\ 3 \end{bmatrix} \langle\psi|$, bra vector = $\begin{bmatrix} 1 \\ 2 \end{bmatrix} |\psi\rangle$

$$\begin{aligned} \langle\psi| |\psi\rangle &= \begin{bmatrix} 5 \\ 3 \end{bmatrix} \langle\psi| \begin{bmatrix} 1 \\ 2 \end{bmatrix} = [5 \cdot 1 + 3 \cdot 2] = 13 \\ |\psi\rangle \langle\psi| &= \begin{bmatrix} 1 \\ 2 \end{bmatrix} |\psi\rangle \begin{bmatrix} 5 \\ 3 \end{bmatrix} = [1 \cdot 5 + 2 \cdot 3] = 11 \end{aligned}$$

$$\begin{aligned} \langle \psi | & \quad \langle u_i | = \begin{bmatrix} a^* & b^* & c^* \end{bmatrix} \quad \langle \psi | = \begin{bmatrix} a^* \\ b^* \\ c^* \end{bmatrix} = \begin{bmatrix} a^* & b^* & c^* \end{bmatrix}^\top \end{aligned}$$

Orthonormal Condition:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases} \quad (\text{Normalised})$$

The quantum state of a system is given by wavefunction ψ . It is a linear combination of orthogonal basis vectors.

$|\psi\rangle = C_1|u_1\rangle + C_2|u_2\rangle + C_3|u_3\rangle$ - linear combination of orthogonal basis vectors

$$\langle u_i | u_j \rangle = \delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases}$$

$$\begin{aligned} \langle \psi | \psi \rangle &= C_1 \langle u_1 | u_1 \rangle + C_2 \langle u_2 | u_2 \rangle + C_3 \langle u_3 | u_3 \rangle \\ &= C_1^2 + C_2^2 + C_3^2 \end{aligned}$$

Since $C_i = \langle u_i | \psi \rangle$

$$\begin{aligned} C_1 &= \langle u_1 | \psi \rangle \\ C_2 &= \langle u_2 | \psi \rangle \\ C_3 &= \langle u_3 | \psi \rangle \end{aligned}$$

$$\begin{aligned} P_1 &= |C_1|^2 = |\langle u_1 | \psi \rangle|^2 \\ P_2 &= |C_2|^2 = |\langle u_2 | \psi \rangle|^2 \\ P_3 &= |C_3|^2 = |\langle u_3 | \psi \rangle|^2 \end{aligned}$$

$P_n = |C_n|^2 = |\langle u_n | \psi \rangle|^2$ - probability of finding the particle in $|u_n\rangle$

i.e. $A^\dagger = A$ then it is known as Hermitian operator. It is also known as self adjoint operator.

Q: Spec or Anti Hermitian operator \Rightarrow

If an operator is such that $A^\dagger = -A$, then it is known as Anti or skew Hermitian operator.

\Rightarrow Projector Operator:

An operator P is said to be projection operator if
 a) $P^2 = P$ (Idempotent) & then P is projection operator.
 b) $P^\dagger = P$ (Hermitian)

$$P_x = -i \frac{d}{dx}$$

$$\left\{ P_x^\dagger = \left[-i \frac{d}{dx} \right]^\dagger = i \left(\frac{d}{dx} \right)^\dagger = i \frac{d}{dx} = P_x \right\} \Rightarrow P_x \text{ is Hermitian}$$

Q: If position \hat{x} & momentum \hat{p}_x are Hermitian operator then find that $x \hat{p}_x$ is Hermitian or not?

Soln:-

$$\begin{aligned} x^\dagger &= x \\ p_x^\dagger &= p_x \\ \text{We have to check if } &(x \hat{p}_x)^\dagger = (x \hat{p}_x) \text{ or not.} \end{aligned}$$

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$$\hat{p}_x \hat{x} \psi = \hat{x} \left(-i \frac{\partial}{\partial x} \right) \psi = -i \frac{\partial \psi}{\partial x}$$

$$\hat{p}_x \hat{x} \psi = -i \hbar \frac{\partial}{\partial x} (\hat{x} \psi) = i \hbar \left(\psi + x \frac{\partial \psi}{\partial x} \right)$$

is
operator

Q: If \vec{A} & \vec{B} are Hermitian then check $[\vec{A}, \vec{B}]$ is Hermitian or not?

Pd to

stop.

$$\text{soln: } [\vec{A}, \vec{B}]^\dagger = -i \left[(\vec{A}^\dagger \vec{B} - \vec{B}^\dagger \vec{A}) \right]^\dagger$$

$$= -i \left[(\vec{A} \vec{B})^\dagger - (\vec{B} \vec{A})^\dagger \right]$$

$$= -i \frac{\partial^2}{\partial i^2} \vec{A}^\dagger \vec{B} = \vec{A}^\dagger \vec{B}^\dagger$$

$$= -i \frac{\partial^2}{\partial i^2} \vec{B}^\dagger \vec{A} = \vec{B}^\dagger \vec{A}^\dagger$$

Hermitian

$$= \frac{\partial^2}{\partial i^2} \vec{B}^\dagger \vec{A}^\dagger = [\vec{A}^\dagger, \vec{B}^\dagger]^\dagger = -[\vec{A}, \vec{B}]$$

(operator)

(operator)

(operator)

(operator)

(operator)

(operator)

(operator)

(operator)

(operator)

Hermitian (or) Not

$$\begin{aligned}
 & \text{Q. } A^+ A \\
 & = i(A^+ - \bar{A}) \\
 & = i(A^+ - \bar{A}) \\
 & = i(A^+ + \bar{A}) \\
 & = i(A^+ + \bar{A})
 \end{aligned}$$

Q. If A & B are Hermitian then $[i(A^+ + \bar{B}) + (-i)\bar{B}A]$

$$\begin{aligned}
 & \Rightarrow \text{If } A^+ = B \text{ then } [i(A^+ + \bar{A})(i + \bar{A} + \bar{\bar{A}})]^+ = 0
 \end{aligned}$$

Note: If A^+ is Hermitian then $f(A^+)$ is also Hermitian.

$$\begin{aligned}
 & \text{Ex: } H = \hat{H}(x, p_x) \\
 & \text{Since } \hat{x} \text{ & } \hat{p}_x \text{ are Hermitian so } H \text{ is also Hermitian.}
 \end{aligned}$$

$$\begin{aligned}
 & \text{Q. Check: } H = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m \omega^2 \hat{x}^2 \\
 & \text{Since } \hat{x} \text{ & } \hat{p}_x \text{ are Hermitian so } H \text{ is also Hermitian.}
 \end{aligned}$$

Solution: \checkmark

$$\text{Q. } [A^+ A]^+ = A^+ (A^+)^+ = A^+ A \quad (\text{Hermitian})$$

$$\begin{aligned}
 & \text{Q. } [i(A^+ - A)]^+ = -i[(A^+)^+ - A^+] = -i(A - A^+) = -i(A^+ - A) \\
 & \quad (\text{Hermitian})
 \end{aligned}$$

$$\begin{aligned}
 & \text{Q. } [i(A^+ + \bar{A})]^+ = -i(A^+ + \bar{A})^+ = -i(A^+ + \bar{A}) = -i(A^+ + \bar{A}) \\
 & \quad (\text{Anti-Hermitian})
 \end{aligned}$$

$$Q. \left[\frac{1}{2}(A^* + A) \right]^* = -i[(A^*)^* + A^*] = -i(A + A^*) \Rightarrow \text{Anti-Hermitian.}$$

$$\text{Ans: } \left[\frac{p_x^2 - x}{2i} \right] = \left(p_x^2 \hat{x} - x p_x^2 \right)^* + \left(p_x^2 \hat{x} + x p_x^2 \right)^* \xrightarrow{\text{Anti-Hermitian}}$$

$$= \frac{p_x^2 \hat{x} - x p_x^2}{2i} \quad - 2i \quad - 2i \quad (\text{Hermitian})$$

C. If \vec{A} & \vec{B} are Hermitian then $[(1+i)\vec{A} + (1-i)\vec{B}]$

$$\text{Sol: } [(1+i)\vec{A} + (1-i)\vec{B}]^* = (1-i)(\vec{A}\vec{B})^* + (1+i)(\vec{B}\vec{A})^*$$

$$\begin{aligned} &\Downarrow \\ &\vec{B}^* \vec{A}^* + \vec{A}^* \vec{B}^* \\ &\Downarrow \quad \vec{A}^* \vec{A}^* \quad \vec{B}^* \vec{B}^* \\ &\vec{B}\vec{A} \quad \vec{A}\vec{B} \\ &\text{Hence } \vec{A} \text{ & } \vec{B} \text{ are Hermitian.} \end{aligned}$$

Q.7. If $\vec{A}^* = \vec{B}$ then $[(1+\vec{A})(1+\vec{A}^* + \vec{A}^2)]^* = ?$

$$\begin{aligned} &\stackrel{\text{given}}{=} \\ &[(1+\vec{A})(1+\vec{A} + \vec{A}^2)]^* = [(1+\vec{A} + \vec{A}^2)^*]^* \quad [1+\vec{A}]^* \\ &= [(1+\vec{A} + (\vec{A}^2)^*)^*][1+\vec{A}^*] \\ &= [(1+\vec{B} + \vec{B}^2)^*][1+\vec{B}] \end{aligned}$$

$\vec{A}^* = \vec{B}$

Unitary operator :- If $U^\dagger U = I$, then U^\dagger is known as ~~unitary~~ unitary

operator

$$U^\dagger U U^{-1} = I^\dagger U^{-1}$$

$$U^\dagger (UU^\dagger) = U^\dagger$$

$$U^\dagger I = U^{-1}$$

$$U^\dagger = \boxed{U^{-1}}$$

$$\text{Ex: } U^\dagger = e^{iHt/\hbar}$$

$$U^\dagger = e^{-iHt/\hbar} = e^{iHt/\hbar} = \frac{1}{e^{-iHt/\hbar}} = U^\dagger$$

$$|C_1\rangle$$

If $|C_1\rangle$ & $|C_2\rangle$ are orthogonal basis vector & $|\psi\rangle$ is state of a system such that $|\psi\rangle = \frac{1}{\sqrt{2}}|V_1\rangle + \frac{1}{\sqrt{2}}|V_2\rangle$, then find the probability of finding the system in $|V_1\rangle$ & $|V_2\rangle$.

Soln: $|C_1|^2 + |C_2|^2 = \frac{1}{4} + \frac{1}{4} = \frac{1}{2} \neq 1$ i.e. wave function is not normalized.

Let $|\psi\rangle = \frac{1}{\sqrt{2}}|V_1\rangle + \frac{1}{\sqrt{2}}|V_2\rangle$

$$|C_1|^2 + |C_2|^2 = \frac{1^2}{4} + \frac{1^2}{4} - 1 \quad \text{②} \quad \frac{\Delta A^2}{4} = 1$$

$$\textcircled{②} \quad A = \sqrt{2}$$

$$|\psi\rangle = \frac{1}{\sqrt{2}}|0\rangle + \frac{1}{\sqrt{2}}|1\rangle$$

\Rightarrow i.e. Normalized function
 $\left(\frac{1}{2} + \frac{1}{2} = 1 \right)$

$$P_1 = |C_1|^2 = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2}$$

$$P_2 = |C_2|^2 = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2}$$

Q. The component of initial state $|\psi_i\rangle$ are given in complete & orthogonal basis vector $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle$ as $|\psi_i\rangle = \frac{1}{\sqrt{3}}|\phi_1\rangle + \frac{1}{\sqrt{3}}|\phi_2\rangle + \frac{1}{\sqrt{3}}|\phi_3\rangle$

$\langle \phi_3 | \psi_i \rangle = 0$ when compared with $|\psi\rangle$

The probability of finding the system in final state $|\psi_f\rangle$ is also given in same basis state as:

$$\langle \phi_1 | \psi_f \rangle = \frac{1+i}{\sqrt{3}}, \quad \langle \phi_2 | \psi_f \rangle = \frac{1-i}{\sqrt{3}}, \quad \langle \phi_3 | \psi_f \rangle = \frac{1}{\sqrt{6}}$$

Soln: $P_1 = \langle \phi_1 | \psi_f \rangle = \frac{1+i}{\sqrt{3}}, \quad \langle \phi_2 | \psi_f \rangle = \frac{1-i}{\sqrt{3}}, \quad \langle \phi_3 | \psi_f \rangle = \frac{1}{\sqrt{6}}$

$$\langle \phi_3 | \psi_i \rangle = \frac{1}{\sqrt{3}}\langle \phi_1 | \psi_i \rangle + \frac{1}{\sqrt{3}}\langle \phi_2 | \psi_i \rangle + \frac{1}{\sqrt{3}}\langle \phi_3 | \psi_i \rangle$$

$$|\psi_i\rangle = \frac{1}{\sqrt{3}}|\phi_1\rangle + \frac{1}{\sqrt{3}}|\phi_2\rangle + \frac{1}{\sqrt{3}}|\phi_3\rangle$$

On

$$|\psi_4\rangle = \frac{1+i}{\sqrt{3}} |\phi_1\rangle + \frac{1}{\sqrt{6}} |\phi_2\rangle + \frac{1}{\sqrt{6}} |\phi_3\rangle$$

$$\langle \psi_4 | \psi_4 \rangle = \frac{1-i}{\sqrt{3}} \cdot \frac{i}{\sqrt{3}} + \frac{1}{\sqrt{6}} \cdot \frac{\sqrt{2}}{\sqrt{3}} + \frac{1}{\sqrt{6}} \cdot \frac{\sqrt{2}}{\sqrt{3}}$$

$$\begin{aligned} &= \frac{i}{3} + \frac{1}{3} + \frac{1}{3} = \frac{2}{3} + i\left(\frac{1}{3}\right) \quad \left(\because z = x+iy \right. \\ &\quad \left. \quad |z|^2 = x^2 + y^2 \right) \\ &= (x+iy)(x-iy) \\ &= x^2 + y^2 \\ &= 1 \end{aligned}$$

$$|\psi\rangle = \frac{1}{\sqrt{9}} |\psi\rangle = \frac{1}{3} |\psi\rangle = \frac{1}{3}$$

Th

at

Eigen value & Eigen vectors:-

Let our operator \hat{A}^\dagger is such that $\hat{A}^\dagger |\psi\rangle = \alpha |\psi\rangle$ then $|\psi\rangle$ is eigen state & α is eigen value.

Statement:

* Prove that eigen values of Hermitian operator are real.

Proof: Let \hat{A} is Hermitian operator i.e. $\hat{A} = \hat{A}^\dagger$

$$\hat{A} |\psi\rangle = \alpha |\psi\rangle \quad \text{--- (1)}$$

On taking scalar product with $\langle \psi |$, we get

$$\langle \psi | \hat{A}^\dagger |\psi\rangle = \alpha \langle \psi | \psi \rangle$$

$$\text{or } \alpha = \langle \psi | \hat{A}^\dagger |\psi\rangle - \text{--- (2)}$$

∴ $\alpha = \alpha$

Q.E.D

On taking \dagger of equation (a), we get:

$$(\hat{A}|\psi\rangle)^\dagger = (\alpha|\psi\rangle)^\dagger$$

$$\begin{aligned} \langle\psi|\hat{A}^\dagger &= \langle\psi|\alpha^* \\ \langle\psi|\hat{A}^\dagger &= \langle\psi|\alpha^\dagger \quad \therefore A^\dagger = A \end{aligned}$$

On taking scalar product with $|\psi\rangle$, we get
 $\langle\psi|\hat{A}|\psi\rangle = \alpha^* \langle\psi|\psi\rangle$

$$\alpha^* = \langle\psi|\hat{A}|\psi\rangle \quad \text{--- (c)}$$

From eqn (b) & (c):

$$\alpha = \alpha^*$$

Thus, eigen values of Hermitian operator are real.

Q. Statement :- Eigen states corresponding to different eigen values of Hermitian operator are orthogonal.

Proof:

Let \hat{A} is Hermitian operator $\hat{A}^\dagger = \hat{A}$
 let a_m & a_n are different eigen values
 corresponding to different eigen states $|\psi_m\rangle$ & $|\psi_n\rangle$.

$$\begin{aligned} |\psi_n\rangle &\quad \hat{A}|\psi_m\rangle = a_m|\psi_m\rangle \quad \text{--- (a)} \\ &\quad \hat{A}|\psi_n\rangle = a_n|\psi_n\rangle \quad \text{--- (b)} \end{aligned}$$

On taking scalar product with $\langle\psi_m|$ of eqn (a):

$$\langle \psi_n | \hat{A}^\dagger | \psi_m \rangle = \alpha_m \langle \psi_n | \psi_m \rangle \rightarrow \textcircled{2}$$

$$\begin{aligned} \text{On taking + of eqn (2), } \\ &= (\hat{A}^\dagger | \psi_n \rangle)^\dagger = (\alpha_n | \psi_n \rangle)^\dagger \\ &= \langle \psi_n | \hat{A}^\dagger = \langle \psi_n | \alpha_n \\ &\therefore \langle \psi_n | \hat{A}^\dagger = \langle \psi_n | \alpha_n \end{aligned}$$

On taking scalar product with $\langle \psi_m |$

$$\langle \psi_n | \hat{A}^\dagger | \psi_m \rangle = \alpha_n \langle \psi_n | \psi_m \rangle \rightarrow \textcircled{3}$$

from \textcircled{2} & \textcircled{3},

$$\begin{aligned} \alpha_m \langle \psi_n | \psi_m \rangle - \alpha_n \langle \psi_n | \psi_m \rangle &= 0 \\ (\alpha_m - \alpha_n) \langle \psi_n | \psi_m \rangle &= 0 \\ \therefore \alpha_m - \alpha_n &\neq 0 \\ \text{So, } \langle \psi_n | \psi_m \rangle &= 0 \end{aligned}$$

Expectation value :-

$$\begin{aligned} \langle \hat{A} \rangle &= \frac{\sum p_i \alpha_i}{\sum p_i} = \frac{\int \psi^* A \psi dV}{\int \psi^* \psi dV} \\ &= \langle \psi | \hat{A}^\dagger | \psi \rangle \end{aligned}$$

\textcircled{4}

for normalized wave function $\langle \psi | \psi \rangle = 1$

$$k \langle \hat{A} \rangle = \langle \psi | \hat{A}^\dagger | \psi \rangle$$

Sol:

Q. If wave fn. of a particle is given by:

$$|\psi\rangle = \frac{3}{5} |\psi_1\rangle + \frac{4}{5} |\psi_2\rangle$$

where $|\psi_1\rangle$ & $|\psi_2\rangle$ are eigen fn with energy eigen value - 1 eV & - 2 eV.

$$\text{Soln: } |C_1|^2 + |C_2|^2 = \frac{9}{25} + \frac{16}{25} = 1$$

$$\langle E \rangle = \sum p_i E_i = p_1 E_1 + p_2 E_2$$

$$\begin{aligned} &= |C_1|^2 E_1 + |C_2|^2 E_2 \\ &= \frac{9}{25} (-1) + \frac{16}{25} (-2) \end{aligned}$$

$$\langle E \rangle = -\frac{41}{25} \text{ ev.}$$

Q. If $|\psi_1\rangle$ & $|\psi_2\rangle$ are ground state & 1st excited state of particle in a pot, such that $\hat{A}|\psi_1\rangle = |\psi_2\rangle$ & $\hat{A}|\psi_2\rangle = |\psi_1\rangle$. Then calculate expectation value of \hat{A} in state

$$|\psi\rangle = \frac{3}{5} |\psi_1\rangle + \frac{4}{5} |\psi_2\rangle$$

$$\text{Soln: } |C_1|^2 + |C_2|^2 = \frac{9}{25} + \frac{16}{25} = 1 \quad (\text{i.e. Normalized})$$

$$|\psi\rangle = (3/5)|\psi_1\rangle + (4/5)|\psi_2\rangle$$

$$\langle \hat{A} \rangle = \langle \Psi_1 | \hat{A} | \Psi_2 \rangle = \left(\frac{3}{5} \langle \Psi_1 | + \frac{4}{5} \langle \Psi_2 | \right) \left(\frac{3}{5} |\Psi_2\rangle + \frac{4}{5} |\Psi_1\rangle \right)$$

$$\begin{aligned} &= \frac{3}{5} \cdot \frac{4}{5} + \frac{4}{5} \cdot \frac{3}{5} \\ &= \frac{12}{25} + \frac{12}{25} \\ &= \frac{24}{25} \end{aligned}$$

Special differential equation:
let differential eqn!

$$\frac{d^2y}{dx^2} + p(x)y' + q(x)y = 0$$

Where p & q are function of x :
About pt $x = x_0$

$$\lim_{x \rightarrow x_0} p(x) = \infty$$

$$\lim_{x \rightarrow x_0} q(x) = \text{finite}$$

When $x = x_0$ is known as ordinary point.
Otherwise it will be singular point.

Singular points are of 2 types:

- ① Regular
If $\lim_{x \rightarrow x_0} (x - x_0)p(x) = \text{finite}$
 $\lim_{x \rightarrow x_0} (x - x_0)q(x) = \text{finite}$

2^o Irregular :-

$$\lim_{x \rightarrow x_0} (x - x_0)^2 P(x) = \text{finite}$$

$$\lim_{x \rightarrow x_0} (x - x_0)^2 Q(x) = \text{finite.}$$

Then it will be regular singular point.
Otherwise, it will be irregular singular point.

Solution about ordinary point is given by power series solution or

$$y = \sum_k a_k x^k = a_0 + a_1 x + a_2 x^2 + \dots$$

Similarly, solution about singular point is given by Frobenius series soln,

$$y = \sum_k a_k x^{n+k}$$

$$\text{Ex: } (1-x^2) \frac{d^2y}{dx^2} - x \frac{dy}{dx} - y = 0$$

$$\frac{d^2y}{dx^2} - \frac{x}{(1-x^2)} \frac{dy}{dx} - \frac{1}{(1-x^2)} y = 0$$

$$P(x) = \frac{-x}{1-x^2}, Q(x) = \frac{1}{1-x^2}$$

$$\lim_{x \rightarrow 0} P(x) = \lim_{x \rightarrow 0} \frac{-x}{1-x^2} = 0, \lim_{x \rightarrow 0} Q(x) = \infty$$

$$\lim_{x \rightarrow 0} Q(x) = \lim_{x \rightarrow 0} \left(\frac{-1}{1-x^2} \right) (= +\infty)$$

So, $x=0$ is ordinary point.

Q: find power series solution of differential eq^N,
 $(1-x^2)y'' - 2xy' + 2y = 0$ about origin.

$$\text{Soln: } y'' - \frac{2x}{1-x^2} y' + \frac{2}{1-x^2} y = 0$$

$$P(x) = -\frac{2x}{1-x^2}, Q(x) = \frac{2}{1-x^2}$$

$$\lim_{x \rightarrow 0} P(x) = \lim_{x \rightarrow 0} \frac{2x}{1-x^2} = 2; \lim_{x \rightarrow 0} Q(x) = \lim_{x \rightarrow 0} \frac{2}{1-x^2} = 2$$

So, $x=0$ is ordinary point

$$y = \sum_k a_k x^k \quad ; \quad y' = \sum_k k a_k x^{k-1}, \quad y'' = \sum_k k(k-1) a_k x^{k-2}.$$

$$\text{So, } (1-x^2) \sum_k a_k x^k - 2x \sum_k k a_k x^{k-1} + 2 \sum_k a_k x^k = 0$$

$$\sum_k a_k x^k - \sum_k a_k x^{k-2} - 2 \sum_k a_k x^{k-1} + 2 \sum_k a_k x^k = 0$$

$$\sum_k a_k x^{k-2} = \sum_k a_k (k-1)(k+1) x^k$$

Since the power of x should be five in power series soln.

$$\text{So, let } k = k+2$$

$$\sum_k a_{k+2} (k+2) (k+1) x^k = \sum_k a_k (k-1) (k+2) x^k$$

$$a_{k+2} (k+1) (k+2) = a_k (k-1) (k+2)$$

$$a_{k+2} = \left(\frac{k-1}{k+2} \right) a_k$$

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May 05, 2022~~

$$K=0, \quad a_0 = -a_0$$

$$K=1, \quad a_1 = 0$$

$$K=2, \quad a_2 = -\frac{1}{3}a_0$$

$$K=3, \quad a_3 = \frac{2}{3}a_0$$

$$K=4, \quad a_4 = \frac{3}{5}(-\frac{1}{3})a_0 = -\frac{1}{5}a_0$$

$$K=5, \quad a_5 = \frac{8}{45}a_0$$

$$\begin{aligned} y &= \sum a_k x^k \\ &= a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5 + a_6 x^6 + \dots \\ &= a_0 + a_1 x + (-a_0)x^2 + 0 + \left(-\frac{1}{3}a_0\right)x^4 + \dots \\ &\approx a_0(1+x^2) + \frac{1}{3}x^4 - \frac{1}{3}x^6 + \dots \end{aligned}$$

$$x^{K=2}$$

Legendre Differential equation :-

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + n(n+1)y = 0 \quad (\text{where } n=0, 1, 2, \dots)$$

$$\frac{d^2y}{dx^2} - \frac{2x}{1-x^2}\frac{dy}{dx} + \frac{n(n+1)}{1-x^2}y = 0$$

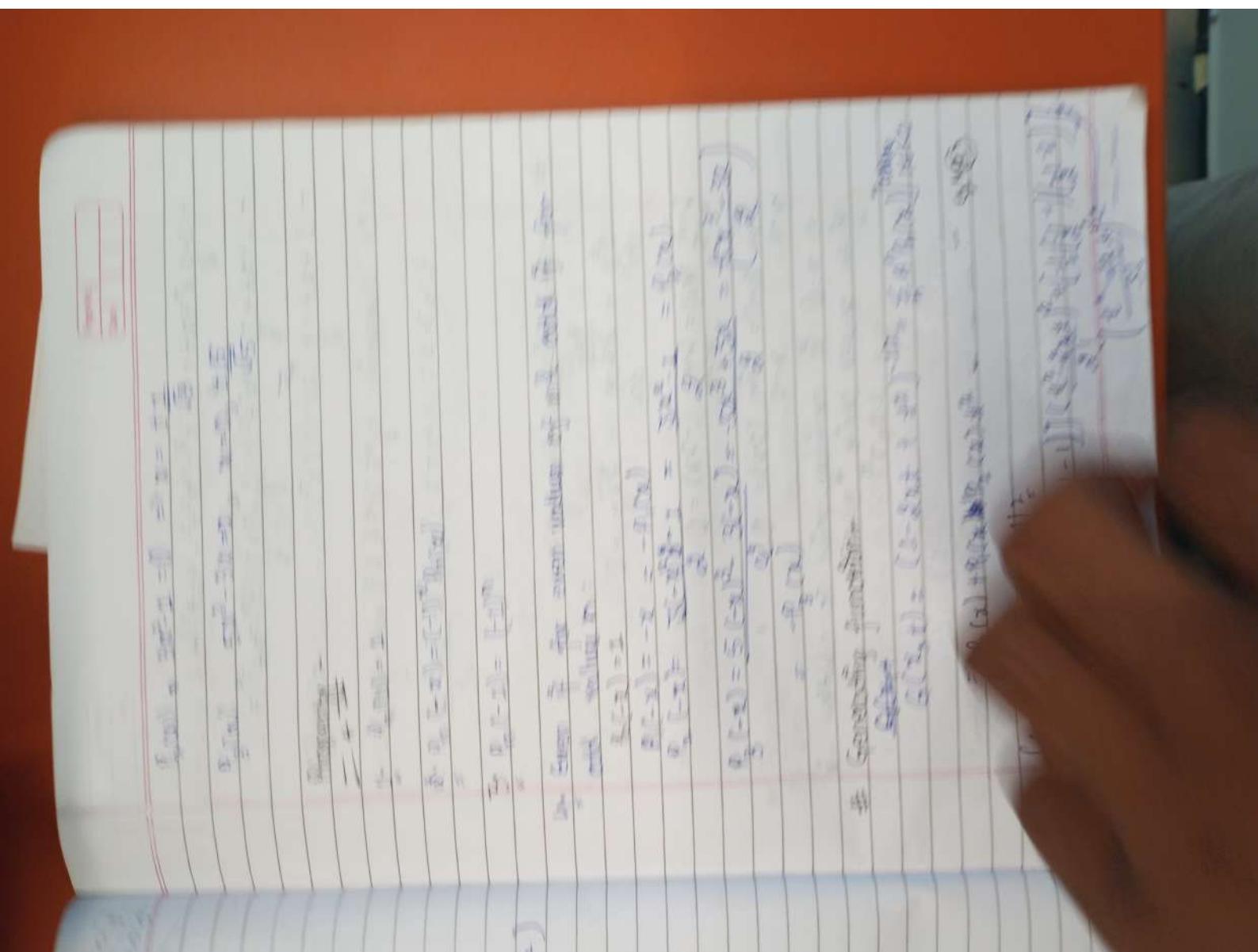
About Origin $x=0$;

$$\lim_{x \rightarrow 0} P(x) = \lim_{x \rightarrow 0} \frac{dx}{1-x^2} = 0$$

$$\lim_{x \rightarrow 0} Q(x) = \lim_{x \rightarrow 0} \frac{n(n+1)}{1-x^2} = n(n+1)$$

So; $x=0$ is ordinary point & solution about $x=0$ is given by power series soln;

$$y = \sum a_k x^k$$



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$$\begin{aligned}
 &= 1 - \frac{1}{2}x^2 + x^3 + \frac{3}{8}(x^4 - 4x^2x^2 - 4x^3) + \dots \\
 &= 1 + x^3 + \frac{3}{8}(4x^2x^2) - \frac{1}{2}x^2 + \frac{3}{8}(x^4 - 4x^3) + \dots \\
 &= 1 + x^3 + \frac{1}{2}(3x^2 - 1)x^2 + \dots \quad \text{--- Eqn 6}
 \end{aligned}$$

On comparing eqns (a) & (b) we get:

$$\rho_0(x) = 1 ; \rho_1(x) = x ; \rho_2(x) = \frac{3x^2 - 1}{2}$$

Hermite Differential eqn:

$$\frac{d^2y}{dx^2} - \frac{Q(x)}{2}y + \frac{Q'(x)}{2}y' = 0$$

$$\lim_{x \rightarrow 0} \rho(x) = \lim_{x \rightarrow 0} (-2x) = 0$$

$$\lim_{x \rightarrow 0} Q(x) = \lim_{x \rightarrow 0} (2x) = 0$$

$\Rightarrow x=0$ is ordinary point so solution is given power series solution if

$$y = \sum a_k x^k$$

(ii)

#

Rednidge formula:-

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2})$$

$$x=0, H_0(x) = (-1)^0 e^0 e^{-0^2} = 1$$

$$n=1, H_1(x) = (-1)^1 e^{x^2} \frac{d}{dx} (e^{-x^2}) = -e^{x^2} (2x)e^{-x^2} = 2x$$

$$n=2, H_2 = (-1)^2 e^{x^2} \frac{d^2}{dx^2} (e^{-x^2}) = e^{x^2} \frac{d}{dx} (-2x e^{-x^2}) = -2e^{x^2} (e^{-x^2} + 2x^2 e^{-x^2})$$

$$= -2(1 - 2x^2) = 4x^2 - 2$$

$$n=3, H_3 = (-1)^3 e^{x^2} \frac{d^3}{dx^3} (e^{-x^2}) = (-1) e^{x^2} \frac{d^2}{dx^2} (-2e^{-x^2} + 4x^2 e^{-x^2})$$

$$= (-1) e^{x^2} (4x e^{-x^2} + 8x e^{-x^2} - 8x^3 e^{-x^2})$$

$$= -1 \frac{(12x - 8x^3)}{(8x^3 - 12x)} = 12x^2 - 12x^4 - 8x^6$$

Property:
 (i)- Even function for even values of n & odd function
 for odd values of n.

$$(ii) H_1(0) = H_2(0) = H_3(0) = \dots = 0$$

Orthogonal condition:

$$\int_{-\infty}^{\infty} e^{-x^2} H_m(x) H_n(x) dx = 2^n n! \delta_{mn}$$

Q. Express function $(x^2 - 2)$ in terms of Legendre polynomial.

Soln: $P_0(x) = 1$

$$P_1(x) = x$$

$$P_2(x) = \frac{3x^2 - 1}{2}$$

$$x^2 = 2P_2(x) + 1$$

$$x^2 = \frac{2P_2(x) + P_0(x)}{3}$$

$$f''(x) = x^2 - 2 = 0$$

$$\left(\because P_0(x) = 1 \right)$$

$$(2x^2 - 2)$$

$$f(x) = \frac{2P_2(x) + P_0(x) - 2xP_0(x)}{3}$$

$$f(x) = \frac{2P_2(x) + P_0(x) - 6P_0(x)}{3}$$

$$f(x) = \frac{2P_2(x) - 5P_0(x)}{3}$$

Q. The generating function $Q = (1 - 2xt + t^2)^{-1/2}$

$$= \sum_n t^n P_n(x) |t| < 1$$

where $P_n(x)$ is Legendre polynomial.
Then find the value of $P_3(-1)$.

dre

Solⁿ: From property of Legendre polynomial.

$$\left\{ \begin{array}{l} P_n(-1) = (-1)^n \\ P_3(-1) = (-1)^3 = (-1) \end{array} \right.$$

$$P_2(x) = \frac{5x^3 - 3x}{2}$$

and

$$\text{Now } P_2(-1) = \frac{5(-1)^3 - 3(-1)}{2} = \frac{-5+3}{2} = (-1).$$

Q: Let $P_n(x)$ be a polynomial of order "n" defined in interval $a \leq x \leq b$ such that $\int_a^b P_m(x) P_n(x) dx = 0$ for all $m \neq n$.

$$a) P_0(x) = \frac{1}{\sqrt{2}}, \quad P_1(x) = \frac{\sqrt{3}}{2}(3-x)$$

$$b) P_0(x) = \frac{1}{\sqrt{2}}, \quad P_1(x) = \frac{\sqrt{3}}{3+x}$$

$$c) P_0(x) = \frac{1}{2}, \quad P_1(x) = \frac{\sqrt{3}}{2}(3-x)$$

$$d) P_0(x) = \frac{1}{2}, \quad P_1(x) = \frac{\sqrt{3}}{2}(3-x)$$

$$P_0(x) = \frac{1}{\sqrt{2}} \Rightarrow \int_a^b P_0(x) P_0(x) dx = \int_a^b \frac{1}{2} \cdot \frac{1}{2} dx = \frac{1}{2} (x)_a^b = \frac{1}{2} (b-a)$$

①

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Ques
Ans

$$\rho(x) = \frac{1}{\sqrt{2}} (3-x) \Rightarrow \int_2^4 \rho(x) dx = \int_2^4 \frac{3}{2} (3-x)^2 dx$$

$$= \frac{3}{2} \int_2^4 (9x^2 - 6x) dx = \frac{3}{2} \cdot (3x + \frac{x^3}{3} - 3x^2) \Big|_2^4$$

$$= \frac{3}{2} (36 + 64 - 48 - 18 - 8 - 12) = 1$$

$$\Rightarrow \int_2^4 \rho(x) dx = 0$$

So option (A) is correct

Ques

Ans

$$(x-3)^2 = (x^2 - 6x + 9) = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

$$= (x^2 - 6x + 9) + 1 - 1 = (x^2 - 6x + 9) + 1 - 1$$

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Legendre eqn & Spherical Harmonics:-

$$\begin{aligned} \langle \mathbf{L} | \mathbf{l}, m \rangle &= h^2 l(l+1) \delta_{l,m} \\ \langle \mathbf{L} | \lambda, m \rangle &= h m \delta_{\lambda,m} \end{aligned}$$

$$\vec{L} = i \hbar \vec{r} \times \vec{\nabla} \quad \text{where } \nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$$

$$\text{OR} \quad \vec{L} = -i\hbar \begin{vmatrix} i & j & k \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

$$\Rightarrow L_x = i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) ; L_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) ; L_z = i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

In spherical coordinates,

$$x = r \sin \theta \cos \phi ; y = r \sin \theta \sin \phi ; z = r \cos \theta \quad (\text{eqn (b)})$$

where $0 \leq r \leq \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$

$$\begin{aligned} \text{From eqn (b)} : r^2 &= x^2 + y^2 + z^2 \Rightarrow \frac{\partial r}{\partial x} = x, \frac{\partial r}{\partial y} = y, \frac{\partial r}{\partial z} = z \\ 2r \sin \theta &= x^2 + y^2 + z^2 \Rightarrow \frac{\partial r}{\partial x} = x, \frac{\partial r}{\partial y} = y, \frac{\partial r}{\partial z} = z \end{aligned}$$

$$\begin{aligned} \text{or, } \frac{\partial \theta}{\partial x} &= \frac{\partial x}{\partial r} = \frac{2r \sin \theta \cos \phi}{r^2 \sin^2 \theta} = \frac{2 \sin \theta \cos \phi}{r \sin^2 \theta} \\ &\Rightarrow \frac{\partial \theta}{\partial x} = \frac{(1 - \sin^2 \theta)}{r \sin^2 \theta} = \frac{2 \cos^2 \theta}{r^2} \end{aligned}$$

$$\begin{aligned} \text{Similarly : } \frac{\partial \theta}{\partial y} &= \frac{y \cos \theta}{r^2 \sin^2 \theta} \\ \text{Now, } z &= r \cos \theta \end{aligned}$$

On differentiating w.r.t Z: ($Z = r\cos\theta$)

$$\frac{1}{r} \frac{\partial}{\partial r} (r\sin\theta) - r\sin\theta \frac{\partial}{\partial \theta} \Rightarrow \frac{d\theta}{dr} = \frac{r\cos\theta - 1}{r\sin\theta}$$

$$r\sin\theta \quad \therefore r \cancel{\sin\theta}$$

$$z = \frac{-\sin\theta}{r}$$

Now, $\because x = r\sin\theta \cos\phi$

$$\Rightarrow \frac{dx}{d\theta} = -\frac{\sin\theta}{r} \cdot \frac{\partial\phi}{\partial\theta} = \frac{\cos\phi}{r\sin\theta} \Rightarrow \frac{\partial\phi}{\partial\theta} = 0$$

$$\begin{aligned}\therefore \frac{\partial}{\partial x} &= \frac{\partial}{\partial r} \left(\frac{\partial r}{\partial x} \right) + \frac{\partial}{\partial \theta} \left(\frac{\partial \theta}{\partial x} \right) + \frac{\partial}{\partial \phi} \left(\frac{\partial \phi}{\partial x} \right) \\ &= \frac{x}{r} \left[\frac{\partial}{\partial r} + \frac{\cos\theta}{r} - \frac{\sin\theta}{r} \cdot \frac{\partial}{\partial \theta} \right] \\ &\text{similarly } \frac{\partial}{\partial y} = y \left[\frac{\partial}{\partial r} + \frac{\cos\theta}{r} + \frac{\sin\theta}{r} \cdot \frac{\partial}{\partial \theta} \right]\end{aligned}$$

$$= \frac{\partial}{\partial z} = z \left[\frac{\partial}{\partial r} - \frac{\sin\theta}{r} \cdot \frac{\partial}{\partial \theta} \right]$$

Now, from eqn (a), $L_x = i\hbar \left(\sin\theta \frac{\partial}{\partial \theta} + \cos\theta \cos\phi \frac{\partial}{\partial \phi} \right)$

$$Ly = i\hbar \left(-\cos\theta \frac{\partial}{\partial \theta} + \cos\theta \sin\phi \frac{\partial}{\partial \phi} \right)$$
$$L_z = i\hbar \frac{\partial}{\partial \phi}$$

* Ladder operator :

$$L_+ = L_x + iL_y = \hbar \left[(\cos\phi + i\sin\phi) \frac{\partial}{\partial \theta} + i\cot\phi (\cos\phi + i\sin\phi) \frac{\partial}{\partial \phi} \right]$$

$$\Rightarrow L_+ = \hbar e^{i\phi} \left[\frac{\partial}{\partial \theta} + i\cot\phi \frac{\partial}{\partial \phi} \right]$$

$$\& L_- = L_x - iL_y = \hbar \left[-(\cos\phi - i\sin\phi) \frac{\partial}{\partial \theta} + i\cot\phi (\cos\phi - i\sin\phi) \frac{\partial}{\partial \phi} \right]$$

$$\Rightarrow L_- = -\hbar e^{-i\phi} \left[\frac{\partial}{\partial \theta} - i\cot\phi \frac{\partial}{\partial \phi} \right]$$

$$\text{Thus; } L_{\pm} = L_x \pm iL_y = \pm \hbar e^{\pm i\phi} \left[\frac{\partial}{\partial \theta} \pm i\cot\phi \frac{\partial}{\partial \phi} \right]$$

$$\text{Now; } L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\Rightarrow L^2 = \pm \hbar^2 \left[\left(\sin\phi \frac{\partial}{\partial \theta} + i\cot\phi \cos\phi \frac{\partial}{\partial \phi} \right) \left(\sin\phi \frac{\partial}{\partial \theta} + i\cot\phi \sin\phi \frac{\partial}{\partial \phi} \right) + \frac{\partial^2}{\partial \phi^2} \right]$$

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

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

Eigen value of L^2 :-
 $L^2 Y_m(\theta, \phi) = \lambda \hbar^2 Y_m(\theta, \phi)$ where $\lambda = l(l+1)$, for $l=0, 1, 2, \dots$

$$\Rightarrow -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial^2}{\partial \theta^2} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] Y_l(\theta, \phi) = \lambda \hbar^2 Y_l(\theta, \phi)$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + -1Y = 6$$

By using separation of variable method [let $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$]

$$\frac{\Phi(\phi)}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial (\Theta \Phi)}{\partial \theta} \right) + \Theta(\theta) \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} + -1\Theta \Phi = 0$$

On multiply by $\frac{\sin \theta}{\Theta \Phi}$:

$$\begin{aligned} & \Rightarrow \frac{\sin^2 \theta}{\Theta} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + 1 \right] = -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = M^2 \text{ (Let)} \\ & \Rightarrow \frac{\sin^2 \theta}{\Theta} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + 1 \right] = M^2 - N^2 \quad \text{Eqn @} \\ & \Rightarrow -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = M^2 ; \quad \frac{\partial^2 \Phi}{\partial \phi^2} = -N^2 \Phi \Rightarrow \Phi = C e^{im\phi} \end{aligned}$$

The constant C is determined by using Normalization condition:

$$1 = \int_0^{2\pi} \Phi^2 d\phi = \int_0^{2\pi} C e^{-im\phi} C e^{im\phi} d\phi = C^2 \int_0^{2\pi} d\phi = C^2 \times 2\pi$$

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

$$\text{Thus, } \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (\text{where } m=0, \pm 1, \pm 2, \dots)$$

As L^2 operate on $\gamma(\theta, \phi)$ solving it, we get!

$$L^2 \gamma(\theta, \phi) = -\ell^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \gamma(\theta, \phi)$$

By substituting $\gamma(\theta, \phi) = \Theta(\theta) \Phi(\phi)$

$$\Rightarrow L^2 \gamma(\theta, \phi) = -\ell^2 \left[\frac{\Phi(\phi)}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{\Theta(\theta)}{\sin^2 \theta} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right]$$

$$\Rightarrow L^2 \gamma(\theta, \phi) = -\ell^2 \left[\frac{\Phi(\phi)}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} + \Theta(\theta) \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right) - \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right] \quad [\text{from eqn (b)}]$$

$$= L^2 \gamma(\theta, \phi) = -\ell^2 \Phi(\phi) \left[\ell! \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{\Theta(\theta)}{\sin^2 \theta} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right) - \ell! \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) \right) \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right] \quad [\text{from eqn (a)}]$$

$$\therefore \sin^2 \theta \left[\frac{1}{\theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} + \Theta(\theta) \right) \right] = M^2 \left[\text{from eqn (a)} \right]$$

$$= \sin^2 \theta \left(\frac{1}{\theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \ell(\ell+1)\Theta \right) = M^2$$

$$= \frac{1}{\theta} \frac{\partial}{\partial \theta} \left(\sin^2 \theta - \frac{M^2 \Theta}{\sin^2 \theta} \right) = -\ell(\ell+1)\Theta - \Theta'' \quad [\text{from } (c)]$$

$$= L^2 \gamma(\theta, \phi) = -\ell(\ell+1) \Phi^2 \gamma(\theta, \phi)$$

$$= L^2 \gamma(\theta, \phi) = \ell(\ell+1) \Phi^2 \gamma(\theta, \phi)$$

(a) $\Phi(\phi) = (\ell!)^{1/2} Q_{\ell}(\cos \phi)$ (b) $\Theta(\theta) = (\ell!)^{1/2} P_{\ell}(\cos \theta)$

$\therefore \gamma(\theta, \phi) = (\ell!)^{1/2} Q_{\ell}(\cos \phi) P_{\ell}(\cos \theta)$

$\therefore \gamma(\theta, \phi) = (\ell!)^{1/2} Q_{\ell}(\cos \phi) P_{\ell}(\cos \theta)$

Eigen value or expectation value ($\langle L^2 \rangle$) of L^2 is $\lambda(l+1)$

where $l = 0, 1, 2, \dots, n-1$

Here; l - Orbital quantum no.

n - principle quantum no.

$$\text{Eigenvalues of } L_2: L_2 = i\hbar \frac{\partial}{\partial \theta}, \text{ so, } L_2 Y(\theta, \phi) = -i\hbar \frac{\partial Y(\theta, \phi)}{\partial \theta}.$$

By using separation of variable;

$$\Rightarrow L_2 Y(\theta) \frac{\partial}{\partial \theta} (Y(\phi)) = -i\hbar \frac{\partial Y(\theta)}{\partial \theta} Y(\phi) = i\hbar \Theta(\theta) \frac{\partial \Phi}{\partial \theta}$$

$$\Rightarrow L_2 \Theta(\theta) \Phi(\phi) = i\hbar \Theta(\theta) \frac{\partial}{\partial \theta} \left(\frac{1}{\sqrt{2\pi}} e^{im\phi} \right) = -i\hbar \Theta(\theta) \frac{1}{\sqrt{2\pi}} (im) e^{im\phi}$$

$$\Rightarrow L_2 \Theta(\theta) \Phi(\phi) = m \hbar \Theta(\theta) \Phi(\phi)$$

$$= L_2 Y(\theta, \phi) = m \hbar Y(\theta, \phi) \quad (\text{where } m = 0, \pm 1, \pm 2 \rightarrow)$$

Simi

Thus, eigen values of L_2 expectation value of L_2 is $m\hbar$.

Legendre differential eqn:-

$$\Rightarrow \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \left[\lambda(l+1) - \frac{m^2}{\sin^2 \theta} \right] \Phi_{l,m}(\theta) = 0 \quad (\text{from eqn C})$$

Sol' of this eqn of gen'ly

$$\Phi_{l,m}(\theta) = C_m P_l^m(\cos \theta), \text{ where } P_l^m(n) = (i-n) \frac{d^n}{dx^n} P_l(x)$$

where $P_l(x)$ is the l th legendre polynomial which is defined by Rodriguez formula,

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l$$

Thus, $P_0(x) = 1$

$$P_1(x) = \frac{1}{2} \frac{\partial}{\partial x} (x^2 - 1) = x \quad P_1(\cos\theta) = \cos\theta$$

$$P_2(x) = \frac{1}{8} \frac{\partial^2}{\partial x^2} (x^2 - 1)^2 = \frac{1}{8} (3x^2 - 1) \quad P_2(\cos\theta) = \frac{1}{8} (3\cos^2\theta - 1)$$

$$P_3(x) = \frac{1}{48} \frac{\partial^3}{\partial x^3} (x^2 - 1)^3 = \frac{1}{48} (5x^3 - 3x) \quad P_3(\cos\theta) = \frac{1}{48} (5\cos^3\theta - 3\cos\theta)$$

$$P_4(x) = \frac{1}{8} (35x^4 - 30x^2 + 3) \quad P_4(\cos\theta) = \frac{1}{8} (35\cos^4\theta - 30\cos^2\theta + 3)$$

$$P_5(x) = \frac{1}{48} (63x^5 - 70x^3 + 15x) \quad P_5(\cos\theta) = \frac{1}{48} (63\cos^5\theta - 70\cos^3\theta + 15\cos\theta)$$

* The Legendre polynomial satisfies the following properties:

$$= \frac{1}{2} \sum_{n=0}^{\infty} (2n+1) P_n(x) P_n(-x) = \int_{-1}^1 P_n(x) P_n(-x) dx = -1$$

\Rightarrow

Similarly:

$$\begin{aligned} P_1'(x) &= \sqrt{1-x^2} \quad P_1'(\cos\theta) = \sin\theta \\ P_2'(x) &= 3x\sqrt{1-x^2} \quad P_2'(\cos\theta) = 3\cos\theta \cdot \sin\theta \\ P_3'(x) &= 3(1-x^2) \quad P_3'(\cos\theta) = 8\sin^2\theta \\ P_4'(x) &= 3(5x^2-1)(5x^2-3) \quad P_4'(\cos\theta) = 3\sin\theta(5\cos^3\theta - 1) \end{aligned}$$

$$\begin{aligned} P_5'(x) &= 15x(1-x^2) \quad P_5'(\cos\theta) = 15\sin^2\theta \cos\theta \\ P_6'(x) &= 15(1-x^2)^{3/2} \quad P_6'(\cos\theta) = 15\sin^3\theta \end{aligned}$$

* Orthonormalization condition:

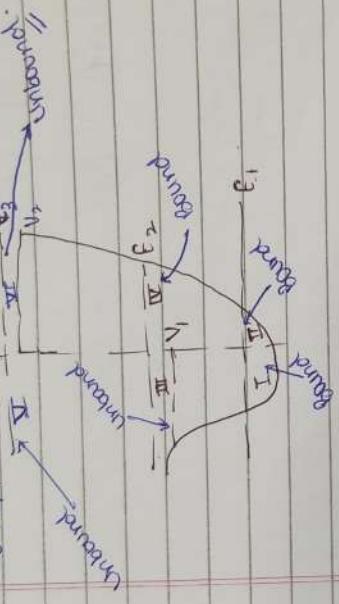
$$\langle P_m | P_m \rangle = \int_0^{2\pi} d\phi \sin\theta \int_0^\pi d\theta \int_0^\pi d\phi \sin\theta \sin m \cos m = \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\pi d\phi \sin^2\theta \sin m \cos m = 1$$

which can be written as:

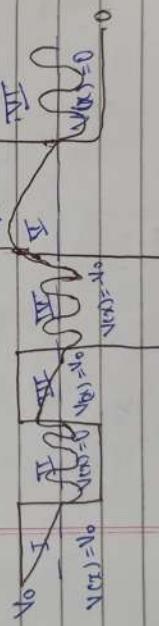
$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\pi d\phi \sin^2\theta \sin m \cos m = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin^3\theta$$

~~Ques~~
Ques

Bound state problem:
 $F \leq 0$ (i.e. $V(x) < E$) then particle is in bound state
 But in quantum mechanics, it may or
 may not be bound. However, if $E < V(x)$,
 then it will be in bound state.



Q. Find solution of Schrödinger eq. for an arbitrary potential as shown in figure.



$$\text{From TISE} \Rightarrow -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

$$= \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (\text{Another form of TISE})$$

Region (I) ($V_x = V_0$)

$$\Rightarrow \frac{\partial^2 \psi_1}{\partial x^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_1(x) = 0$$

$$= \frac{\partial^2 \psi_1}{\partial x^2} - \frac{2m}{\hbar^2} (V_0 - \epsilon) \psi_1(x) = 0$$

$$\Rightarrow \frac{\partial^2 \psi_1}{\partial x^2} - \alpha^2 \psi_1(x) = 0 \quad \text{where } \alpha = \sqrt{\frac{2m}{\hbar^2} (V_0 - \epsilon)}$$

$$\Rightarrow \psi_1 = A_1 e^{-\alpha x} + B_1 e^{\alpha x}$$

Similarly for region III, $\psi_3(x) = A_3 e^{-\alpha x} + B_3 e^{\alpha x}$

* Region (II) ($V_{(x)} = 0$)

$$\Rightarrow \frac{\partial^2 \psi_2}{\partial x^2} + \frac{2m}{\hbar^2} E \psi_2(x) = 0$$

$$= \frac{\partial^2 \psi_2}{\partial x^2} + k^2 \psi_2(x) = 0, \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\therefore \psi_2(x) = A_2 e^{-ikx} + B_2 e^{ikx}$$

Similarly for region III, $\psi_3(x) = A_3 e^{-ikx} + B_3 e^{ikx}$

Similarity for ψ_{ex}
Also, $\psi_{\text{ex}}(x) = A_1 e^{-ikx} + B_1 e^{ikx}$ (where: $k' = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$)

& $\psi_{\text{ex}}(x) = A_2 e^{-pkx} + B_2 e^{pkx}$ (where: $p = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$)



Free particle (Force = 0, pot can be zero or constant):

Free particle means net force on particle becomes zero.

$$\vec{F} = -\vec{\nabla} V = -\frac{\partial V}{\partial x} = 0$$

So, potential can be zero or constant.
let pot $V(x) = 0$, then using TISE,

$$\frac{\partial^2 \psi_{\text{ex}}}{\partial x^2} + k^2 \psi_{\text{ex}} = 0 \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

OR $E = \frac{\hbar^2 k^2}{2m} \rightarrow \text{continuous energy}$

$\psi_{\text{ex}} = A e^{ikx} + B e^{-ikx} \rightarrow \text{plane wave.}$

One dimensional infinite potential box:-

Consider a particle of mass m confined in a 1-D box of size a

$$\Psi(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

$$\text{Diagram: } \boxed{\begin{array}{c} \text{m} \\ \text{---} \\ \text{x} \end{array}}$$

$$\text{Using TISE: } \frac{\partial^2 \Psi}{\partial x^2} + \frac{2mE}{\hbar^2} \Psi(x) = 0$$

$$\text{Inside box } \Psi(x) = 0 \\ \frac{\partial^2 \Psi}{\partial x^2} + \frac{2mE}{\hbar^2} \Psi(x) = 0 \\ \text{constant} \quad \boxed{\begin{array}{c} \text{m} \\ \text{---} \\ \text{x} \end{array}} \quad \boxed{\begin{array}{c} \text{E} \\ \text{---} \\ \hbar^2 \end{array}} = 0 \\ \text{or, } \frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi(x) = 0, \text{ where } k = \sqrt{\frac{2mE}{\hbar^2}} = \text{constant}$$

General soln:

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

At boundary ($x=0, a$), $\Psi(x)|_{x=0} = 0$

At $x=0$, $\Psi(0) = A+0 = 0 \Rightarrow \Psi(x) = B \sin(kx)$

At $x=a$, $\Psi(a) = B \sin(ka) = 0$

$$\therefore B \neq 0, \sin(ka) = 0 \Rightarrow ka = n\pi \\ \text{or, } k = \frac{n\pi}{a} - \text{eq N(2)}$$

$$\boxed{\begin{array}{l} \Psi(x) = B \sin\left(\frac{n\pi x}{a}\right) \\ \text{or, } \Psi(x) = B \sin\left(\frac{n\pi}{a} x\right) \end{array}}$$

2nd Method:

$$\psi(x) = Ae^{-ikx} + Be^{ikx}$$

At $x=0$, $\psi(0)=0 \Rightarrow A+B=0$; $\text{① } A=-B$

$$\psi(x) = Ae^{ikx} - Ae^{-ikx}$$

$$\begin{aligned} \text{At } x=\alpha, \psi(\alpha) = 0 &\Rightarrow A(e^{i\alpha k} - e^{-i\alpha k}) = 0 \\ \therefore A \neq 0 &\Rightarrow e^{i\alpha k} - e^{-i\alpha k} = 0 \\ \therefore e^{i\alpha k} &= e^{-i\alpha k} \\ \Rightarrow e^{2i\alpha k} &= 1 \\ \Rightarrow e^{2i\alpha k} &= e^{i2n\pi} \end{aligned}$$

$$\begin{aligned} 2n\alpha &= 2n\pi \\ \alpha &= n\pi \quad (\text{for } n \in \mathbb{Z}) \\ \psi(x) &= A(e^{inx} - e^{-inx}) \times \frac{2i}{\alpha} \end{aligned}$$

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

Energy
1-p/p
un

From normalization condition;

$$\int_0^{\alpha} \psi_n^*(x) \psi_n(x) dx = 1 \quad \text{for } n \neq 0$$

$$\begin{aligned} |B|^2 \int_0^{\alpha} \sin^2\left(\frac{n\pi x}{\alpha}\right) dx &= 1 \quad (\text{since } B \neq 0) \\ |B|^2 \int_0^{\alpha} \left[1 - \cos\left(\frac{2n\pi x}{\alpha}\right) \right] dx &\neq 1 \end{aligned}$$

n=1

$$\begin{cases} \cos nx = 1 - \sin^2 x \\ \sin^2 x = 1 - \cos 2x \end{cases}$$

n=2

n=3

$$|B|^2 \left[\frac{1}{a} x - \frac{1}{2} \sin\left(\frac{2n\pi x}{a}\right) \right]^2 = 1$$

$$|B|^2 \frac{x}{a} = 1 \quad |B| = \sqrt{\frac{2}{a}}$$

$$\Rightarrow \psi_n(x) = \int_0^x \frac{d}{dx} \sin(n\pi x) \text{ where } n = 1, 2, 3 \dots$$

Energy eigen value =>
From eqns (1) & (2):

$$k = \frac{n\pi}{a} = \frac{2me}{\hbar^2} \quad n = 1, 2, 3 \dots$$

Energy levels of 1-D box are = $\frac{n^2\pi^2}{a^2} = \frac{2me}{\hbar^2}$
unequally spaced

$$\Rightarrow E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \text{ (where, } n = 1, 2, 3 \dots)$$

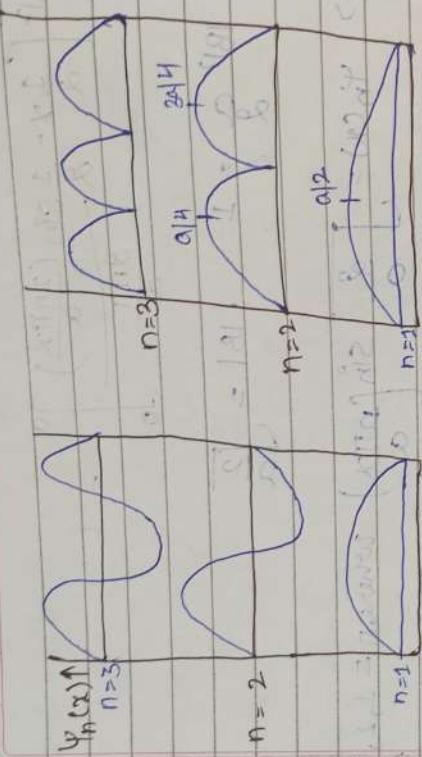
i.e. quantized energy

n $n=1$ $n=2$ $n=3$	Energy $E_1 = \frac{\pi^2\hbar^2}{8ma^2}$ $E_2 = \frac{4\pi^2\hbar^2}{8ma^2}$ $E_3 = \frac{9\pi^2\hbar^2}{8ma^2}$	wave function $\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$ $\psi_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$ $\psi_3(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right)$	state Ground 1st excited 2nd excited
--------------------------------	--	--	---

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

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

$$\psi_3(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right)$$



Nodes (Including boundary) = $n+1$
 - (Excluding boundary) = $n+1$

$\therefore K = \frac{n\pi}{a} \rightarrow$ Quantized

$$\frac{2\pi}{\lambda} = \frac{n\pi}{a}$$

$\lambda = \frac{da}{n}$ = Quantized

$$\lambda = \frac{da}{n}, \frac{da}{2}, \frac{da}{3}, \dots$$

$$n=1, \frac{d}{2} = a, \text{ and } \frac{d}{3}$$

$$n=2, d=a, \frac{da}{2}, \frac{da}{3}, \dots$$

$$n=3, \frac{3a}{2}, a, \frac{da}{3}, \dots$$

$$\left. \begin{array}{l} \text{Nodes} \\ \text{Boundary} \end{array} \right\} = \frac{2a}{\lambda} = \frac{2a}{(n+1)\pi} = \frac{2a}{\pi} \cdot \frac{1}{n+1}$$

* Energy Eigenvalues & Eigen functions for \hat{P}^z :

$$\text{For } \hat{P}_y, \psi_{x,y} = \begin{cases} 0 & 0 < x < a, 0 < y < b \\ 0 & \text{Otherwise} \end{cases}$$

$$\text{Wave function } \psi_{n_x n_y} (x, y) = \psi_n(x) \psi_m(y) =$$

$$= \frac{1}{a} \sin\left(\frac{n_x \pi x}{a}\right) \frac{1}{b} \sin\left(\frac{n_y \pi y}{b}\right)$$

$$\text{If } a = b, \text{ then, } \psi_{n_x n_y} (x, y) = \frac{1}{a} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right)$$

\Rightarrow Energy Eigen values:

$$\begin{aligned} E_{n_x n_y} &= E_{n_x} + E_{n_y} \\ &= \frac{n_x^2 \pi^2 \hbar^2}{8ma^2} + \frac{n_y^2 \pi^2 \hbar^2}{8mb^2} \\ &= \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right) \frac{\pi^2 \hbar^2}{8ma^2} \end{aligned}$$

If $a = b$ then:

$$E_{n_x n_y} = (n_x^2 + n_y^2) \frac{\pi^2 \hbar^2}{8ma^2}$$

Energy state	Energy	Degeneracy
(1,1)	Ground state	$\frac{2\pi^2 \hbar^2}{8ma^2}$
(1,2); (2,1)	1st excited state	$\frac{5\pi^2 \hbar^2}{8ma^2}$

(2,2)	Second excited state	$\frac{8\pi^2 \hbar^2}{8ma^2}$	Non-degenerate.
(1,3) (3,1)	3rd excited state	$\frac{10\pi^2 \hbar^2}{8ma^2}$	Two fold degenerate

Energy eigen value & eigen fn for three dimension:-

3-D potential infinite pot¹ box:

$$V(x,y,z) = \begin{cases} 0 & 0 < x < a, 0 < y < b, 0 < z < c \\ \infty & \text{otherwise,} \end{cases}$$

wave fn.

$$\Psi_{n_x n_y n_z}(x, y, z) = \frac{1}{a} \sin\left(\frac{n_x \pi x}{a}\right) \frac{1}{b} \sin\left(\frac{n_y \pi y}{b}\right) \frac{1}{c} \sin\left(\frac{n_z \pi z}{c}\right)$$

If $a=b=c$ then:

$$\Psi_{n_x n_y n_z} = \frac{1}{a} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

Energy eigen value!

$$\begin{aligned} E_{n_x n_y n_z} &= E_{n_x} + E_{n_y} + E_{n_z} \\ &= \frac{\hbar^2 \pi^2 k_x^2}{2ma^2} + \frac{\hbar^2 \pi^2 k_y^2}{2mb^2} + \frac{\hbar^2 \pi^2 k_z^2}{2mc^2} \end{aligned}$$

If $a=b=c$ then:

$$E_{n_x n_y n_z} = \left(n_x^2 + n_y^2 + n_z^2 \right) \left[\frac{\pi^2 k^2}{2ma^2} \right]$$

(l_1, m_1)	State	Energy	Degeneracy
$(1, 1, 1)$	Ground state	$3\pi^2 h^2 / 8ma^2$	Non-degenerate
$(1, 1, 2)$ $(2, 1, 1)$ $(1, 2, 1)$	First excited state	$6\pi^2 h^2 / 8ma^2$	3-fold degenerate

(j_2, j_2) $(2, 2, 1)$ $(2, 1, 2)$	Second excited state	$16\pi^2 h^2 / 8ma^2$	3-fold degenerate
$(1, 1, 3)$ $(3, 1, 1)$ $(1, 3, 1)$	Third excited state	$32\pi^2 h^2 / 8ma^2$	3-fold degenerate.

$(2, 2, 2)$	Fourth excited state	$12\pi^2 h^2 / 8ma^2$	Non-degenerate
$(2, 2, 3)$	Fifth excited state	$16\pi^2 h^2 / 8ma^2$	Non-degenerate

$$\Omega = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array} \right) \text{ (2) } \text{ (2) } \text{ (2) } \text{ (2) }$$

$$\Omega = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array} \right) \text{ (2) } \text{ (2) } \text{ (2) } \text{ (2) }$$

$$\Omega = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array} \right) \text{ (2) } \text{ (2) } \text{ (2) } \text{ (2) }$$

$$\Omega = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array} \right) \text{ (2) } \text{ (2) } \text{ (2) } \text{ (2) }$$

$$\Omega = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array} \right) \text{ (2) } \text{ (2) } \text{ (2) } \text{ (2) }$$

Date
May 18, 2023

of K_3
where
n=3

Page No.
Data

1-D symmetric infinite potential box :-

$$V(x) = \begin{cases} 0 & |x| < a/2 \\ \infty & |x| \geq a/2 \end{cases}$$

Using TISE : $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0$

$$-\alpha^2 \quad 0 \quad \alpha^2$$

$$\text{Now}, \frac{\partial^2 \psi}{\partial x^2} + 2m(E - V(x)) = 0$$

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

$$\text{This soln, } \psi(x) = A \cos(kx) + B \sin(kx)$$

Using boundary conditions:

$$\psi(a/2) = \psi(-a/2) = 0$$

$$\text{So, } \psi(-a/2) = A \cos(k \frac{a}{2}) - B \sin(k \frac{a}{2}) = 0 \rightarrow \text{Eqn(a)}$$

$$\& \psi(a/2) = A \cos(k \frac{a}{2}) + B \sin(k \frac{a}{2}) = 0 \rightarrow \text{Eqn(b)}$$

$$\text{from (a)+(b), } 2A \cos(k \frac{a}{2}) = 0$$

$$\text{From (a)-(b), } 2B \sin(k \frac{a}{2}) = 0$$

Now if $A=0$, then $B \neq 0 \Rightarrow \sin(k \frac{a}{2}) = 0$

$$\frac{ka}{2} = n_1 \pi, \quad K = \frac{2n_1 \pi}{a} \quad (\text{where } n_1 = 1, 2, 3, \dots)$$

$$\text{or } K = \frac{n_2 \pi}{a} \quad (\text{where } n_2 = 1, 2, 3, \dots)$$

$$\& \text{if } B=0, \text{ then } A \neq 0 \Rightarrow A \cos(k \frac{a}{2}) = 0 \rightarrow \frac{ka}{2} = \left(\frac{2n_2 - 1}{2} \right) \pi \quad K = \frac{2n_2 - 1}{a}$$

4

of $\frac{Kx \pi}{a}$
where
 $n=1, 2, 3$

$$\Psi(x) = \begin{cases} A \cos\left(2n_2 - 1\right)\pi x, & \text{where } n_2 = 1 \\ B \sin\left(2n_1\pi\right)x, & \text{where } n_1 = 1, 2, 3 \end{cases}$$

$$n = 2n_2 - 1 = 1, 3, 5, 7, \dots$$

$$n = 2n_1 = 2, 4, 6, 8, \dots$$

$$\Psi(x) = \begin{cases} A \cos\left(\frac{n\pi x}{a}\right) & \text{where } n = 1, 3, 5 \\ B \sin\left(\frac{n\pi x}{a}\right) & \text{where } n = 2, 4, 6 \end{cases}$$

On Normalizing, $\Psi_{n,0}(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right)$, where $n = 1, 3, 5, \dots$

$$\text{from eqn ① \& ②, } \frac{d^2E}{dx^2} = \frac{D^2\pi^2}{a^2}$$

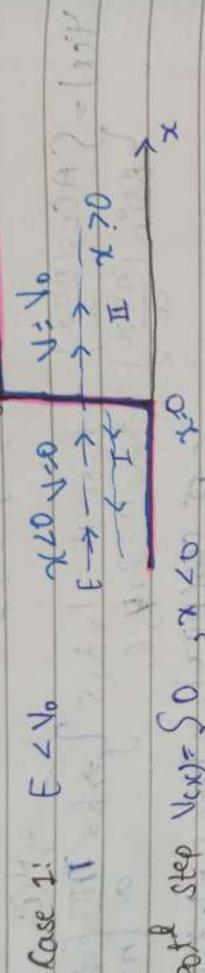
$$\text{energy eigen value } E = n^2 \frac{D^2 \pi^2}{a^2}$$

$$\begin{aligned} n & \quad \text{wave funcn} \quad \text{Energy} \\ 1 & \quad \int_a^0 \cos\left(\frac{n\pi x}{a}\right) \frac{\pi^2 k^2}{2m a^2} dx \\ 2 & \quad \int_a^0 \sin\left(\frac{2n\pi x}{a}\right) \frac{4\pi^2 k^2}{2m a^2} dx \\ 3 & \quad \int_a^0 \cos\left(\frac{3n\pi x}{a}\right) \frac{9\pi^2 k^2}{2m a^2} dx \\ 4 & \quad \int_a^0 \sin\left(\frac{4n\pi x}{a}\right) \frac{16\pi^2 k^2}{2m a^2} dx \end{aligned}$$

now we have to find $\int_a^0 \sin\left(\frac{4n\pi x}{a}\right) dx$

$$J = (\pi)^{1/2} \left(\frac{a}{\pi} - \frac{1}{4} \right) \cos \left(\frac{4n\pi a}{\pi} \right) + \frac{1}{4}$$

* Potential step:



$$\text{Using TISE: } \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0$$

$$\begin{aligned} \text{In region I: } & V(x) = 0 \\ \Rightarrow & \frac{\partial^2 \psi_I}{\partial x^2} + \frac{2m}{\hbar^2} E \psi_I(x) = 0 \\ \frac{\partial^2 \psi_I}{\partial x^2} + \frac{\hbar^2}{m} k^2 \psi_I(x) = 0 \end{aligned}$$

$$\psi_I = \underbrace{A e^{ikx}}_{\text{Incident}} + \underbrace{B e^{-ikx}}_{\text{Reflected}} + C e^{i\omega t}$$

Reflected.

$$\left\{ \begin{array}{l} p = -i\hbar \frac{\partial}{\partial x} \\ \psi_I = -i\hbar \frac{\partial \psi_I}{\partial x} = (-i\hbar)(ik) e^{ikx} = ik e^{ikx} \end{array} \right.$$

$$\begin{aligned} \text{In region II: } & V(x) = V_0 \\ \frac{\partial^2 \psi_{II}}{\partial x^2} + \frac{2m}{\hbar^2} [E - V_0] \psi_{II}(x) = 0 \end{aligned}$$

reflected wave.

$$\begin{aligned} \frac{\partial^2 \psi_{II}}{\partial x^2} + \frac{2m}{\hbar^2} [E - V_0] \psi_{II}(x) = 0 \end{aligned}$$

$$\frac{\partial^2 \Psi_I}{\partial x^2} - \frac{2m}{\hbar^2} (V_0 - \epsilon) \Psi_{II}(x) \neq 0, \text{ since } 2 \text{ are}$$

$$\frac{\partial^2 \Psi_{II}}{\partial x^2} - \alpha^2 \Psi_{II}(x) = 0 \quad \text{to obtain } \Rightarrow \Psi_{II}$$

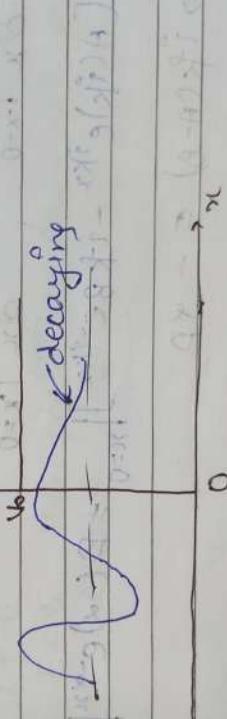
$$\Psi_{II} = C e^{\alpha x} + D e^{-\alpha x}$$

Boundary conditions : At $x \rightarrow 0, \Psi \rightarrow 0$

$$C e^{\alpha x} \Big|_{x \rightarrow 0} + D e^{-\alpha x} \Big|_{x \rightarrow 0} = 0$$

$$C e^{\alpha x} \Big|_{x \rightarrow \infty} = 0 \Rightarrow C = 0$$

$\Psi_{II} = D e^{-\alpha x}$ - transmitted decaying form



* Reflection coefficient :-

R = Reflected probability current density (S_R)
 I Incident probability current density (S_I)

$$\Psi_{ref} = B e^{-ikx} \Rightarrow S_R = \frac{\hbar k |B|^2}{m}$$

$$\Psi_{in} = A e^{ikx} \Rightarrow S_I = \frac{\hbar k |A|^2}{m}$$

$$R = \frac{|B|^2}{|A|^2}$$

Transmission coefficient $\Rightarrow (1 - R)$ or $\frac{R}{R+T}$

$T = \frac{\text{Transmitted probability}}{\text{Incident}}$ Current density (S_T)

$$\Rightarrow T=0$$

$\Rightarrow R+T=1 \Rightarrow R=1$ (Total reflection)

Using $\Psi_I \neq 0$ at $x=0$ (at boundary)

$$\Psi_I \Big|_{x=0} = 0 \Rightarrow \Psi_I \Big|_{x=0} = 0$$

$$(Ae^{ikx} + Be^{-ikx}) \Big|_{x=0} = Pe^{-\alpha x} \Big|_{x=0}$$

$$\Rightarrow A+B=P \quad \text{Eqn ②}$$

$$\frac{\partial \Psi_I}{\partial x} \Big|_{x=0} = \frac{\partial \Psi_R}{\partial x} \Big|_{x=0}$$

$$[A(\alpha) e^{ikx} - ikB e^{-ikx}] \Big|_{x=0} = P(-\alpha) e^{-\alpha x} \Big|_{x=0}$$

$$\Rightarrow ik(A-B) = -\alpha P$$

$$\text{Or } \frac{ik(A-B)}{\alpha} = -P \quad \text{Eqn ③}$$

On adding Eqns ② & ③

$$(A+B) + ik(A-B) = 0$$

$$\Rightarrow A = \frac{(1+ik)}{2} B$$

$$\begin{aligned} -P &= \frac{k-i\alpha}{k+i\alpha} \frac{\alpha+i\alpha}{\alpha-i\alpha} \\ &= \frac{i\alpha}{\alpha^2 - i^2 \alpha^2} = \frac{i\alpha}{\alpha^2 + \alpha^2} = \frac{i\alpha}{2\alpha^2} = \frac{i}{2\alpha} \end{aligned}$$

$$\Rightarrow \frac{B}{A} = \frac{k - i\alpha}{k + i\alpha} = 1 - \frac{2i\alpha}{k^2 + \alpha^2}$$

$$\text{where } k = \sqrt{\frac{mE}{\hbar^2}} \quad \& \quad \alpha = \frac{qV_0}{\hbar c}$$

$$\frac{\alpha}{k} = \frac{V_0 - E}{E} = \frac{V_0 - 1}{V_0 + 1}$$

$$\frac{B}{A} = \frac{1 - i \int_{V_0}^{V_0+1} \frac{V_0 - 1}{E} dV}{1 + i \int_{V_0}^{V_0+1} \frac{V_0 + 1}{E} dV}$$

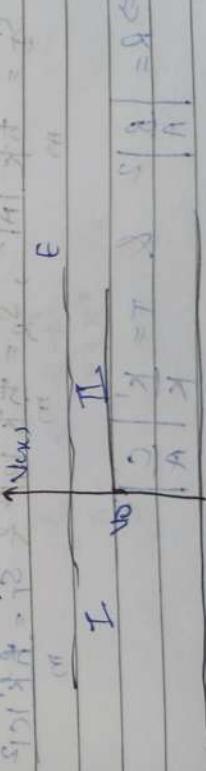
$$\text{Reflection coefficient: } R = \left| \frac{B}{A} \right|^2 = \left| \frac{k - i\alpha}{k + i\alpha} \right|^2 = \frac{k^2 + \alpha^2 - 2i\alpha k}{k^2 + \alpha^2}$$

$$R = 1 \quad \& \quad T = 0$$

Thus, if $E < V_0$, then particle can not go in region II (classical case)

~~initially~~: But according to Quantum mechanics, there is a probability of finding the particle in region II

Case II :- If $E > V_0$ then



Using TISE; $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\epsilon^2} [\epsilon - V(x)] \psi = 0$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\epsilon^2} [\epsilon - V_0] \psi = 0$$

In region I, $V=0 \Rightarrow \psi_I = A e^{ikx} + B e^{-ikx}$

In region II, $V(x) = V_0$

$$\frac{\partial^2 \psi_{II}}{\partial x^2} + \frac{2m}{\epsilon^2} (\epsilon - V_0) \psi_{II} = 0$$

$$\frac{\partial^2 \psi_{II}}{\partial x^2} + (k')^2 \psi_{II} = 0$$

$$\psi_{II} = C e^{ik'x} + D e^{-ik'x}$$

Incident reflected

$$D = T, S, R$$

In region II, there is no probability of reflection, so $D = 0$

$$\psi_{II} = C e^{ik'x}$$

Transmitted

So in region II, $\psi_{II} = C e^{ik'x}$ since $k' < k$ So amplitude will decrease & wavelength will increase.

$$S_I = \frac{\hbar k}{m} |A|^2, S_R = \frac{\hbar k}{m} |B|^2 \& S_T = \frac{\hbar k}{m} |C|^2$$

$$\Rightarrow R = \left| \frac{B}{A} \right|^2 \& T = \left| \frac{C}{A} \right|^2$$

Using θ/c , at $x=0$: $\Rightarrow \theta = 0$

$$Y_1|_{x=0} = 0 \Rightarrow Y_1|_{x=0} = \frac{Y_1}{x}|_{x=0} = 0 \quad (\text{eqn 9})$$

$$(Ae^{ikx} + Be^{-ikx})|_{x=0} = (e^{ikx})|_{x=0} \Rightarrow A = B$$

$$A+B = 2 \quad \text{eqn ②}$$

$$\frac{\partial Y_1}{\partial x}|_{x=0} = \left. \frac{\partial Y_1}{\partial x} \right|_{x=0} = \left. \frac{\partial}{\partial x} \left(\frac{A e^{ikx} - i k B e^{-ikx}}{k} \right) \right|_{x=0} = \left. i k A e^{ikx} - i k B e^{-ikx} \right|_{x=0} = i k (A e^{ikx} - B e^{-ikx})|_{x=0}$$

$$\frac{\partial Y_1}{\partial x}|_{x=0} = \left. \frac{\partial Y_1}{\partial x} \right|_{x=0} = \left. \frac{\partial}{\partial x} \left(\frac{A e^{ikx} - i k B e^{-ikx}}{k} \right) \right|_{x=0} = \left. i k A e^{ikx} - i k B e^{-ikx} \right|_{x=0} = i k (A e^{ikx} - B e^{-ikx})|_{x=0}$$

$$\text{from (a)-(b), } A+B - \frac{k}{k'} (A-B) = 0$$

$$= A - \frac{k}{k'} A + B - \frac{k}{k'} B = 0$$

$$= \left(1 - \frac{k}{k'} \right) A + B \left(1 - \frac{k}{k'} \right) = 0$$

$$= \frac{-B}{A} = \frac{k'-k}{k'+k}$$

$$B = \frac{A}{k'+k} \quad \text{eqn 10}$$

$$B = \frac{A}{k'+k} \quad \text{eqn 10}$$

$$B = \frac{A}{k'+k} \quad \text{eqn 10}$$

$$R = \left| \frac{B}{A} \right|^2 = \left| \frac{k - k'}{k + k'} \right|^2$$

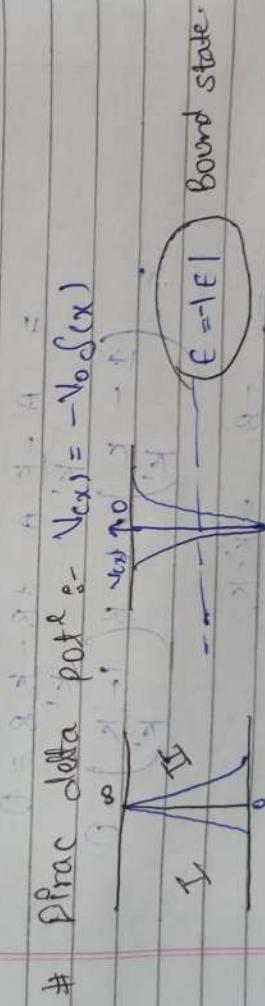
from eqn (8),
 $A - B = \frac{k'}{k} \left(C - \frac{k'}{k} \Psi \right) = \frac{(k' - k)(\Psi + k' \delta_{kk'})}{k^2}$

$$\frac{A + B}{2A} = \frac{C}{k} \left(1 + \frac{k'}{k} \right) \Psi$$

$$= \frac{C}{A} = \frac{gk}{k + k'} \left(\Psi + k' \delta_{kk'} - k' \delta_{kk'} \right)$$

$$= T = \frac{k'}{k} \left| \frac{\Psi}{A} \right|^2 = \frac{k'}{k} \frac{4k^2}{(k + k')^2} = \frac{4k^2}{(k + k')^2}$$

$$= T = \frac{4k'k}{(k + k')^2} \Psi - g_{kk'} (\delta_{kk'} - \delta_{kk'}) \text{ (now)}$$



Dirac delta pot. $\langle \Psi_{kk'} | \Psi_{kk'} \rangle = -N_0 \delta_{kk'}$

$$\delta_{kk'} = \begin{cases} 0, & k \neq k' \\ \infty, & k = k' \end{cases}$$

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{k} (E - \delta_{kk'}) \Psi = 0.$$

$$= \frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{k} [E + N_0 \delta_{kk'}] \Psi_{kk'} = 0$$

$$\text{for } x \neq 0, \frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi(x) = 0$$

For bound state, $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V(x)) \psi(x) = 0$

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{2mV(x)}{\hbar^2} \psi(x) = 0$$

$$= \frac{\partial^2 \psi}{\partial x^2} - K^2 \psi(x) = 0 \quad \text{where } K = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi(x) = Ae^{Kx} + Be^{-Kx}$$

In region (-∞ < x < 0)

At x → -∞, ψ(x) → 0

$$\Rightarrow Ae^{Kx} + Be^{-Kx} \Big|_{x \rightarrow -\infty} = 0 \quad \Rightarrow A = 0$$

$$\Rightarrow Be^{-Kx} \Big|_{x \rightarrow -\infty} = 0 \quad \Rightarrow B = 0$$

$$\Rightarrow Be^{-Kx} \Big|_{x \rightarrow -\infty} = 0 \quad \text{small}$$

$$\psi_1 = Ae^{Kx} \quad \text{at } x > 0$$

* Amount of discontinuity $\left(\frac{\partial \psi_1}{\partial x} \Big|_{x=0} - \frac{\partial \psi_1}{\partial x} \Big|_{x=0} \right) = ?$

Using TISE, $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E + V(x)] \psi(x) = 0$

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

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mV(x)}{\hbar^2} \psi(x) = \frac{2mE}{\hbar^2} \psi(x) \quad \Rightarrow \frac{\partial^2 \psi}{\partial x^2} \Big|_{x=0} = (0)V \quad \text{at } x=0$$

On integrating both sides, we get:

$$\lim_{\epsilon \rightarrow 0} \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \frac{2mV_0}{h^2} \int_{-\epsilon}^{\epsilon} \psi(x) dx \right] dx = \frac{2m|E|}{h^2} \int_{-\epsilon}^{\epsilon} |\psi(x)|^2 dx$$

$$\lim_{\epsilon \rightarrow 0} \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \frac{2mV_0}{h^2} \int_{-\epsilon}^{\epsilon} \psi(x) dx \right] \stackrel{\text{eqn 11.10}}{=} \frac{2m|E|}{h^2} \int_{-\epsilon}^{\epsilon} |\psi(x)|^2 dx$$

$$\lim_{\epsilon \rightarrow 0} \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial x} \right) \Big|_{x=-\epsilon} \Big|_{x=\epsilon} \right] + \frac{2mV_0}{h^2} \psi(0) = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} \Big|_{x=0} - \frac{\partial \psi}{\partial x} \Big|_{x=0} + \frac{2mV_0}{h^2} \psi(0) = 0$$

$$\frac{\partial \psi}{\partial x} \Big|_{x=0} - \frac{\partial \psi}{\partial x} \Big|_{x=0} = \frac{2mV_0}{h^2} \psi(0) \quad \text{--- eqn ②}$$

$$\text{Now: } \psi_I = Ae^{kx} \quad \& \quad \psi_{II} = Be^{-kx}$$

$$\begin{aligned} &\text{Using normalization condition we get, } A = B = \sqrt{K} \\ &\Rightarrow \psi_I = \sqrt{K} e^{kx} \quad \psi_{II} = \sqrt{K} e^{-kx} \end{aligned}$$

$$\frac{\partial \psi_I}{\partial x} \Big|_{x=0} - \frac{\partial \psi_{II}}{\partial x} \Big|_{x=0} = -\sqrt{K} e^{-kx}$$

$$\frac{\partial \psi_I}{\partial x} \Big|_{x=0} = \sqrt{K} e^{kx} \quad \frac{\partial \psi_{II}}{\partial x} \Big|_{x=0} = \sqrt{K} e^{-kx}$$

$$\Rightarrow \psi_I = \sqrt{K} e^{kx}$$

$$\text{or; } \psi(0) = \sqrt{K}$$

On substituting these values in eqn (c) we get:

$$K\sqrt{K} - (-1\sqrt{K}) = \frac{2mV_0}{h^2} \sqrt{K}$$

$$\Rightarrow K^2 = \frac{2mV_0}{h^2} \sqrt{K}$$

$$\Rightarrow K^2 = m^2 V_0^2$$

$$= \frac{\partial m|\psi|}{h^2} = m^2 V_0^2 \Rightarrow |\psi| = \frac{mV_0^2}{h^2}$$

$$= E = -|\psi| = -\frac{mV_0^2}{2h^2} - \text{It is bound state energy}$$

which is constant. So prob. of a particle has only one bound state.

Amount of discontinuity $\Rightarrow \left(\frac{\partial \psi}{\partial x} \right)_{x=0} - \left(\frac{\partial \psi}{\partial x} \right)_{x=0} = ?$

Using TISE; $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{h^2} [E + \text{hbar}] \psi(x) = 0$

$$= \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{h^2} [E + \text{hbar}] \psi(x) = -\frac{2m}{h^2} E \psi(x)$$

$$= \frac{\partial^2 \psi}{\partial x^2} + \frac{2mV_0}{h^2} \delta(x) \psi(x) = \frac{2m}{h^2} |E| \psi(x)$$

$$0 = \left(\psi'(0) \right)_{x=0} - \left(\psi'(0) \right)_{x=0} + (E)^{1/2}$$

On integrating both sides, we get

$$\lim_{h \rightarrow 0} \int_{-h/2}^{h/2} \frac{\partial^2 \psi}{\partial x^2} + \frac{2mV_0}{h^2} \delta(x) \psi(x) dx = \lim_{h \rightarrow 0} \int_{-h/2}^{h/2} (E)^{1/2} \psi(x) dx$$

May 26, 2021

1. One-dimensional Harmonic Oscillator (1DHO):
Suppose a particle of mass m is in 1DHO, i.e.
 $V(x) = \frac{1}{2}kx^2$ where $k = \sqrt{\frac{F}{m}}$

$$= \frac{1}{2}m\omega^2x^2 \quad \text{where } \omega = \sqrt{\frac{k}{m}}$$

T1 S.E.:-

$$\begin{aligned} &= \frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} (\epsilon - V(x)) \Psi(x) = 0 \\ &= \frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} (\epsilon - \frac{1}{2}m\omega^2x^2) \Psi(x) = 0 \end{aligned}$$

$$\text{Let: } y = x \quad \text{where } \alpha = \sqrt{\frac{m\omega}{\hbar^2}}$$

$$= \frac{\partial^2 \Psi(y)}{\partial y^2} + \frac{2m}{\hbar^2} \left(\epsilon - \frac{1}{2}m\omega^2\alpha^2y^2 \right) \Psi(y) = 0$$

$$= \frac{\partial^2 \Psi(y)}{\partial y^2} + \frac{2m}{\hbar^2} \left(\epsilon - \frac{1}{2}m\omega^2\alpha^2y^2 \right) \Psi(y) = 0$$

$$= \frac{\partial^2 \Psi(y)}{\partial y^2} + \left[\frac{2m\epsilon}{\hbar^2} - \frac{m^2\omega^2\alpha^2}{\hbar^2}y^2 \right] \Psi(y) = 0$$

$$= \frac{\partial^2 \Psi(y)}{\partial y^2} + \left(\frac{2\epsilon}{\hbar^2} - \frac{\omega^2\alpha^2}{\hbar^2}y^2 \right) \Psi(y) = 0 \quad \left(\because \alpha = \sqrt{\frac{m\omega}{\hbar^2}} \right)$$

$$= \frac{\partial^2 \Psi(y)}{\partial y^2} + \left(\frac{2\epsilon}{\hbar^2} - \alpha^2y^2 \right) \Psi(y) = 0$$

Now let $\frac{\partial \epsilon}{\partial \Omega} = \frac{1}{\hbar^2}$ (from power series soln)
 $\frac{\partial \Psi}{\partial y^2} = \frac{1}{\hbar^2}$ (from power series soln)

$$H_n(y) = \left[\frac{d^n}{dy^n} e^{-y^2/2} \right] H_0(y) = \left[\frac{d^n}{dy^n} e^{-y^2/2} \right] 1 = e^{-y^2/2}$$

where $H_n(y) \rightarrow$ Hermite polynomial.

$$\text{For } n=0, H_0(y) = 1 = H_0(x)$$

$$\text{For } n=1, H_1(y) = dy/dy = 2y = H_1(x)$$

$$\text{For } n=2, H_2(y) = d^2y/dy^2 = 4y^2 - 2 = 4x^2 - 2 = H_2(x)$$

$$\text{For } n=3, H_3(y) = d^3y/dy^3 = 8y^3 - 12y = 8x^3 - 12x = H_3(x)$$

$$\psi_0(x) = \left(\frac{\alpha}{2} \right)^{1/2} H_0(y) e^{-y^2/2} = \left(\frac{\alpha}{2\pi} \right)^{1/2} e^{-x^2/2} \rightarrow \text{Ground state wave function}$$

$$\psi_1(x) = \left(\frac{\alpha}{2} \right)^{1/2} H_1(y) e^{-y^2/2} = \left(\frac{\alpha}{2\pi} \right)^{1/2} 2y e^{-x^2/2} \rightarrow \text{1st excited state wave function}$$

$$\psi_2(x) = \left(\frac{\alpha}{2} \right)^{1/2} H_2(y) e^{-y^2/2} = \left(\frac{\alpha}{2\pi} \right)^{1/2} (4y^2 - 2) e^{-x^2/2} \rightarrow \text{2nd excited state wave function}$$

Energy eigen. value? -
(From power series soln $\psi_1 = 2(n+1) \psi_0$)

$$E = \frac{q\omega}{4\pi} = q(n+1) \psi_0^2$$

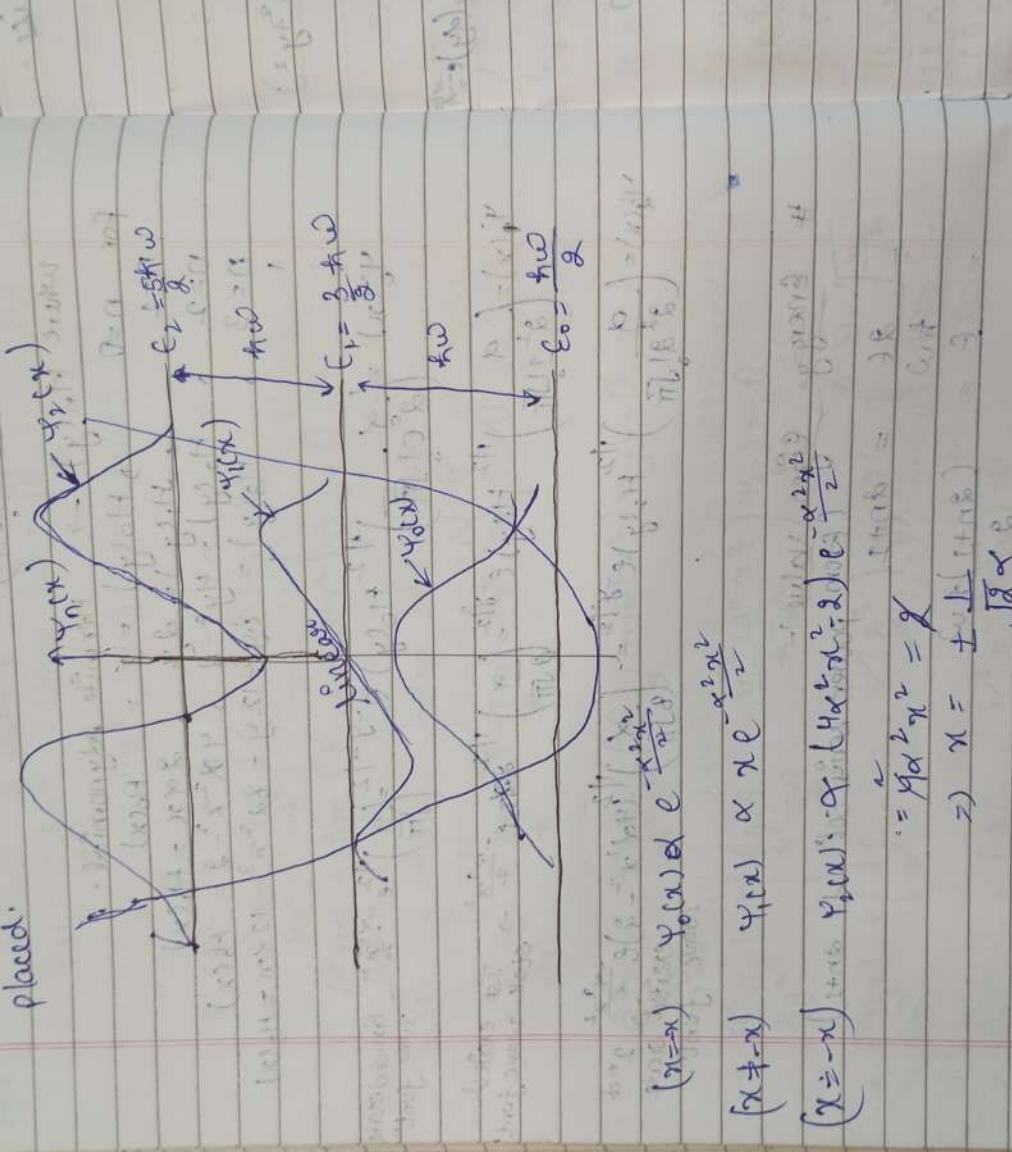
$$E = \left(n + \frac{1}{2} \right) \hbar\omega$$

In note 11/20, right hand side is $n+1$

$$\Rightarrow E = \frac{1}{2} \hbar\omega, \frac{3}{2} \hbar\omega, \dots \text{etc}$$

for $n=0, E_0 = E_1 = \frac{1}{2} \hbar\omega$

i.e. the energy levels of D_2HO are equally placed.



$$(n=0) \psi_0(x) \propto e^{-\frac{x^2}{2}}$$

$$(n \neq 0) \psi_{1,2}(x) \propto x e^{-\frac{x^2}{2}}$$

$$(\chi = -\alpha) \psi_{1,2}(\chi) \propto (4\alpha^2 \pi^2 - 2) e^{-\frac{\alpha^2 \chi^2}{2}}$$

$$\approx \frac{1}{2} \alpha^2 \pi^2 = \frac{1}{2}$$

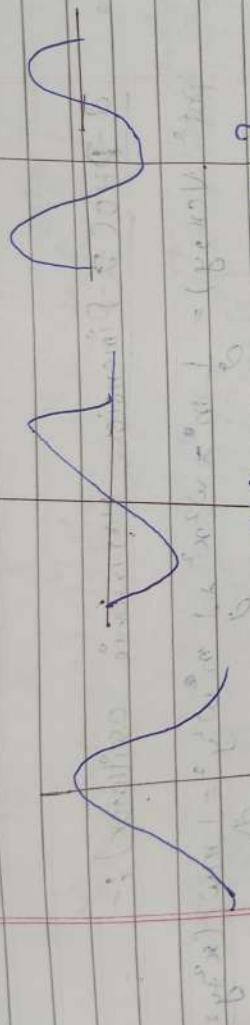
$$\Rightarrow \chi = \pm \sqrt{\frac{1}{2} \alpha^2} \approx \pm \frac{\alpha}{2}$$

$$\int \frac{dx}{\sqrt{1+x^2}}$$

$$\text{out}[1+1] = 9$$

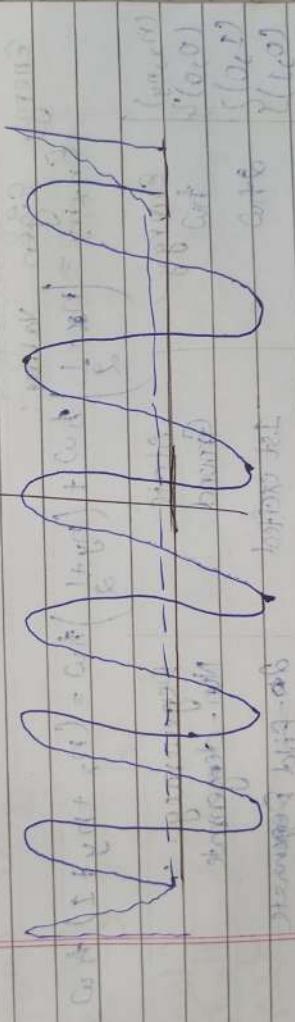
→ Wave function of Harmonic oscillator is even function of x with values of n & odd function for odd values of n .

→ Energy levels of harmonic oscillator are equally spaced.



$$n=0 \text{ (higher energy)} \quad n=1 \text{ (lower energy)}$$

• For higher 'n' values :-



According to Quantum mechanics probability of finding the particle is maximum at mid point in ground state of harmonic oscillator but according to Classical mechanics the probability of finding particle is maximum at end points. So this concept can't explain by using classical mechanics.

Q. For higher value of n the probability of finding particle is maximum at the end point, similar to classical mechanics.

* d-DHOC 2-Dimension Harmonic oscillator :-

$$\text{pot } V(x, y) = \frac{1}{2} m \omega^2 x^2 + \frac{1}{2} m \omega^2 y^2 = \frac{1}{2} m \omega^2 (x^2 + y^2)$$

$$\text{wave funt}, \Psi_{n_x n_y}(x, y) = \Phi_{n_x}(x) \Phi_{n_y}(y)$$

$$\Rightarrow \Psi_{n_x n_y}(x, y) = \left[\left(\frac{a}{2^{n_x} n_x! \sqrt{\pi}} \right)^{1/2} H_{n_x}(ax) e^{-\frac{x^2}{2}} \right] \left[\left(\frac{a}{2^{n_y} n_y! \sqrt{\pi}} \right)^{1/2} H_{n_y}(ay) e^{-\frac{y^2}{2}} \right]$$

Energy Eigen values:

$$E_{n_x n_y} = \left(n_x + \frac{1}{2} \right) \hbar \omega + \left(n_y + \frac{1}{2} \right) \hbar \omega = (n_x + n_y + 1) \hbar \omega$$

(n_x, n_y)	Energy $\hbar \omega$	State	Degeneracy	(n_x, n_y)
$(0, 0)$		Ground	Non-degenerate	$(1, 0)$
$(1, 0)$	$2\hbar \omega$	1st excited	2-fold degenerate	$(0, 1)$
$(0, 1)$				$(1, 1)$
$(1, 1)$				$(2, 0)$
$(2, 0)$	$3\hbar \omega$	2nd excited	3-fold degenerate	$(1, 0)$
$(0, 2)$				$(0, 1)$
$(2, 1)$				$(1, 1)$
$(1, 2)$	$4\hbar \omega$	3rd excited	4-fold degenerate	$(0, 2)$
$(3, 0)$				$(2, 0)$
$(0, 3)$				$(0, 1)$

3-DHO (3-dimension harmonic oscillator):-

$$V(x, y, z) = \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2)$$

$$\Psi_{n_x n_y n_z}(x, y, z) = \left[\left(\frac{\alpha}{d^{n_x} n_x! \sqrt{\pi}} \right)^{1/2} H_{n_x}(\alpha x) e^{-\frac{\alpha^2 x^2}{2}} \right]$$

$$\left[\left(\frac{\alpha}{d^{n_y} n_y! \sqrt{\pi}} \right)^{1/2} H_{n_y}(\alpha y) e^{-\frac{\alpha^2 y^2}{2}} \right] \left[\left(\frac{\alpha}{d^{n_z} n_z! \sqrt{\pi}} \right)^{1/2} H_{n_z}(\alpha z) e^{-\frac{\alpha^2 z^2}{2}} \right]$$

$$\Rightarrow E_{n_x n_y n_z} = \left(n_x + n_y + n_z + \frac{3}{2} \right) \hbar \omega$$

(n_x, n_y, n_z)	Energy	State	Degeneracy
-------------------	--------	-------	------------

$(0, 0, 0)$	$\frac{3}{2} \hbar \omega$	Ground	Non-degenerate
-------------	----------------------------	--------	----------------

$(1, 0, 0)$	$\frac{5}{2} \hbar \omega$	1st excited	3-fold degenerate.
$(0, 1, 0)$			
$(0, 0, 1)$			

$(1, 1, 0)$	$\frac{7}{2} \hbar \omega$	2nd excited	6-fold degenerate
$(1, 0, 1)$			
$(0, 1, 1)$			
$(2, 0, 0)$			
$(0, 2, 0)$			

Quantum Physics

Date:
June 05, 2023

APCO
Date: / /

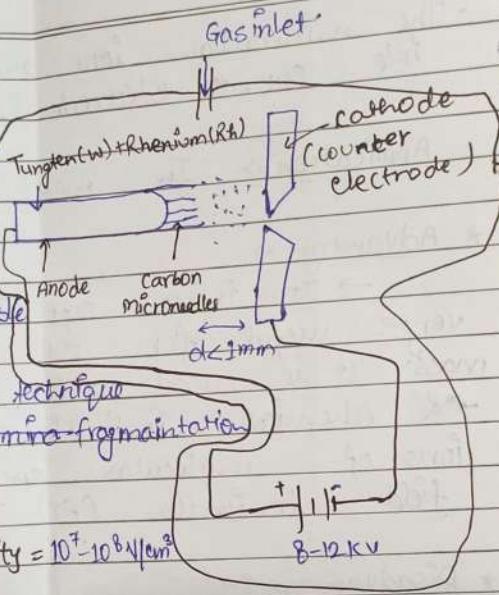
field Ionization (FI) \Rightarrow

* Application of strong electric field can induce emission of e^- from molecule.

* Molecules are used in FI should be volatile & thermally stable.

* It is soft ionization technique in which no or less fragmentation occurs.

$$\text{electric field intensity} = 10^7 - 10^8 \text{ N/cm}^2$$



* Construction:-

The instrument of FI consist of:

(i) 2 electrode - 1 is anode & other is cathode.

(ii) Anode is made up of tungsten (W) & Rhenium (Rh). And in the front of anode carbon microneedles are formed.

(iii) A battery is used having voltage (8-12) kV

(iv) A counter electrode (cathode) is present having -ve charge

(v) The distance b/w 2 electrode is less than 1mm.

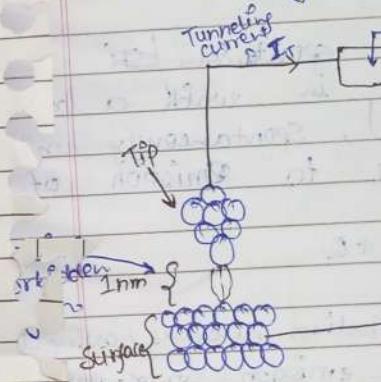
* Working:-

Gas is injected in ionization chamber. When strong electric field is applied, then the carbon microneedle induce the emission of e^- from the molecule & molecular ions are formed.

Date: June 07, 2023

Scanning Tunneling

In this micro very close to about 1 nm. The small gap



a classically However, quantum is finite through this are put tunneling cur the figure.

This curve the distance The :: surface keeping with the tunnel

Date
June 05, 2023

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- The molecular ions are ~~more~~ move from negative hole counter electrode & move further.

Application => In mass spectrometer.

* Advantage =)

→ It is a soft ionization technique so it very useful for the determination of molecular mass. It is used when e⁻ impact ionization (EI) & chemical ionization (CI) fail to give ions of molecular species then we used field ionization (FI).

* Disadvantage :-

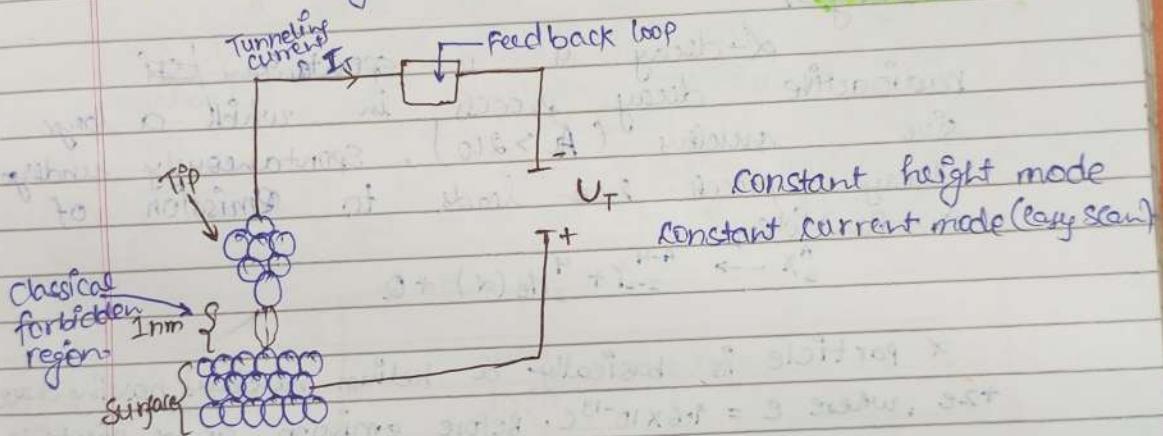
- It doesn't give any information for the structure of the molecule.
- Field ionization is not used for thermally, unstable & non-volatile molecules.
- The sensitivity of field ionization is less than sensitivity of e⁻ impact ionization (EI) & chemical ionization (CI).

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Scanning Tunneling microscope [Nobel prize: Binnig & Rohrer (1986)]:-

In this microscope, a small tip is brought very close to the sample, normally within about 1nm, i.e. ~~several~~ ^{several} atomic layers. The small gap b/w the tip & sample is



a classically forbidden region for the e⁻s. However, quantum mechanics tells us that there is finite probability that e⁻s can tunnel through this gap. If tip & sample surface are put under a small voltage U_T , a tunneling current I_T can flow as shown in the figure.

This current is strongly dependent on the distance b/w the tip & the surface. The surface can be scanned with the tip keeping either the height of the tip or the tunneling current constant.

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W-352

Jai Shri Krishan

The tumbling current or feedback parameters are detected. If the surface is scanned in parallel lines then a 3-D picture of the surface is generated.

α -decay $\Rightarrow \alpha$ -decay is a spontaneous decay process in which a large size nucleus ($A > 200$), spontaneously undergoes decay process α leads to emission of α -particle,

$$^{A-4}_{Z-2} \rightarrow ^{A-4}_{Z-2} \text{He}(\alpha) + Q$$

α particle is basically a helium nucleus having charge $+2e$, where $e = 1.6 \times 10^{-19} \text{ C}$. Before emission, an α -particle can be assumed to exist inside nucleus.

It is important to note that when different kinds of nuclei were studied then it is found that maximum kinetic energy of emitted α -particle usually ranges from 4-10 MeV.

Let us draw nuclear potential diagram with distance (r) from center of mass.

Length of nucleus of α -particle.

Potential energy = $Pot^2 \times charge = \frac{k_1}{r} \times 2e = k(2-2)e^2 r = k(2-2)2e^2$

$$For r = 32, Pot^2 = 9 \times 10^9 \times (9-2) \times 2 \times (1.6 \times 10^{-19})^2 \text{ J} = 10^{-24}$$

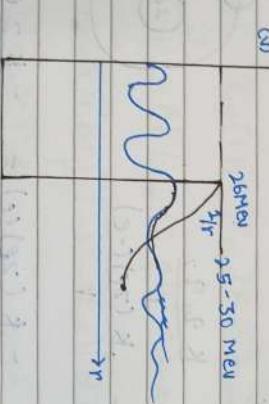
$$= \frac{9 \times 10^9 \times 900 \times 2 \times (1.6 \times 10^{-19})^2}{10^{-14} \times (1.6 \times 10^{-19}) \times 10^6} \text{ MeV} \approx 2.6 \text{ MeV}$$

Thus, α -particle experiences a pot. barrier of height 2.6 MeV inside a uranium nucleus before emission.

WAVE

But uranium emits α particles of energy 4 Mev. Classical mechanics can't explain that how a particle of energy 4 Mev can come out of potential barrier of height 26 Mev. But in 1928, George Gamow solved this puzzle by using wave mechanical consideration. This theory is based on quantum mechanics formed by combining de-Broglie Hypothesis and Schrödinger eqn.

A alpha particle has a wave associated with it. A wave fm (4) can describe the wave mechanical behav of wave. According to Gamow this wave has certain probability of penetrating (escaping) the barrier even through particle has k.e (4ev) less than height h(26Mev) of potential barrier.



6 Mev

$(2-2)2e^2$

α particle

not found

only

trans(r)

sc.

\rightarrow
• (2-2)2e² \rightarrow 1.6 Mev

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Radical

Hydrogen is the smallest atom which is bound state of e^- & proton. There is a bound state of e^- & proton. Now Coulomb attractive force provide centrifugal force. Here, we shall study about energy eigen value & eigen function of hydrogen atom for solving Schrodinger eqn. We have to size reduce mass as motion of both e^- & proton but mass of proton more 1838 me so we can consider proton at rest. Revision of e^- describe structure the structure of atom. So energy eigen value of e^- said to be energy state of atom.

$$V(r) = \frac{k_1 q_1 q_2}{r}$$

$$V(r) = -\frac{1}{r} \quad (r > a)$$

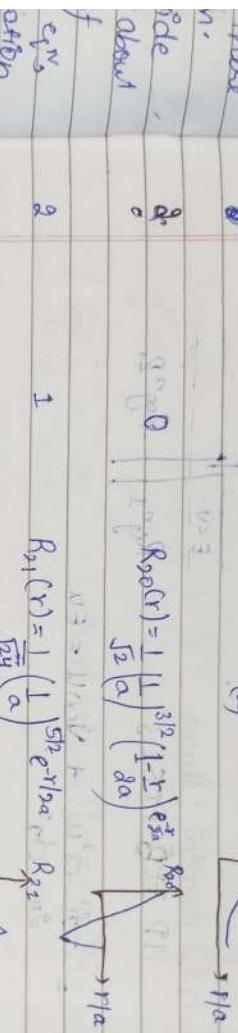
$$V(r) = -\frac{k(2e)(e)}{r} = -\frac{k}{2} \frac{e^2}{r}$$

For bound state, $E = -|E|$

$$\nabla \Psi(r_s, \theta_s, \phi) + \frac{\partial m}{\partial r} [E - V(r)] \Psi(r_s, \theta_s, \phi) = 0$$

Buddhist Canon

Graphs:



proton

portion
structure

eigen
State

1

1

1

1

1

1

1

6

N

1

1

$$\text{Probability} = P = \begin{cases} 1 & \text{when } Y_{\text{true}} \in T \\ 0 & \text{otherwise} \end{cases}$$

524 (a)

$\theta/2$

$$= \int_V R_{ne}(r) Y^*_L(\theta, \phi) R_{ne}(r) Y_{Lm}(\theta, \phi) d\Omega$$

$$= \lim_{n \rightarrow \infty} \left(\frac{1}{n} \sum_{k=1}^n \log \left(\frac{f(x_k)}{g(x_k)} \right) \right)$$

$$= \int_0^\infty \int_0^T \left[\int_0^{2\pi} |R_{\text{inel}}(r)|^2 |Y_{lm}(0, \phi)|^2 r^2 dr d\phi \right] dt$$

$$= \int_0^{\infty} r^2 |R_{\text{one}}(r)|^2 dr \int_0^{2\pi} |\chi_m(\theta, \phi)|^p d\theta. \quad \text{where } \partial T = S^1.$$

$$= \int r^2 |R_{\mu\nu}(r)|^2 dr$$

See paradr

where $p(r) = r^2 [R^2 \rho(r)]^2$ - probability density

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1-D delta potential well :-

$$E < V$$

$$1D \text{ Eqs TISE: } -\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial x^2} + V(x)u = Eu$$

$$\begin{aligned} &= -\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial x^2} + \delta(x)u = Eu \\ &= \frac{\partial^2 u}{\partial x^2} + \frac{2mE}{\hbar^2} u = \frac{2mV(x)}{\hbar^2} u \end{aligned}$$

$$\frac{\partial^2 u}{\partial x^2} - k^2 u = -\frac{2mE}{\hbar^2} u$$

where $E = -\hbar^2 k^2$ & $\delta(x) = -\frac{1}{\hbar^2} \delta(x)$

for $x \neq 0$, this eqn. reduces to $\frac{\partial^2 u}{\partial x^2} - k^2 u = 0$,

$$\text{having soln: } u = A e^{kx} + B e^{-kx}$$

As $x \neq 0$, this eqn. reduces to $\frac{\partial^2 u}{\partial x^2} - k^2 u = 0$

As the wave fn is finite everywhere so B is zero

so the soln in regions I & II are, $u_1(x) = A e^{kx}$ & $u_2 = B e^{-kx}$.

continuity of wave fn is not continuous at $x = 0$ result $A = B$. For simplicity, we choose $A = B = 1$.

The 1st derivative of wave f^n is not continuous because of presence of delta f^n .

Integration of eqn (1) in small intervals $[\epsilon, -\epsilon]$ gives,

$$\left(\frac{du}{dx} \right)_\epsilon + \left(\frac{du}{dx} \right)_{-\epsilon} - [k^2 u(\epsilon) + k^2 u(-\epsilon)] = -d \int_{-\epsilon}^{\epsilon} \delta(x-d) u(x) dx.$$

$$\therefore u(\epsilon) = u(-\epsilon) = 0 \quad &$$

$$\therefore u(\epsilon) = u(x-\epsilon) \approx 0 + \int_{-\epsilon}^{\epsilon} \delta(x-d) u(x) dx = u(d)$$

$$\text{So, } \left(\frac{du}{dx} \right)_\epsilon + \left(\frac{du}{dx} \right)_{-\epsilon} = -2 u(d)$$

$$\text{Or, } f' + K + K = -\frac{1}{d}$$

$$= \boxed{k = \frac{1}{d}}$$

Thus, the energy eigen value of particle is $E = -\frac{h^2 k^2}{8m} = -\frac{h^2}{8m} d^2$; The -ve energy indicates that the particle is bounded.

$$\begin{aligned} & (b > r > b-d) \quad \text{if } d < b \\ & (b < r > b-d) \quad \text{if } d > b \\ & (b < r) \quad \text{if } d > b \end{aligned}$$

Double delta pair & well defined

$\int_{-\infty}^{\infty} \delta(x-a) \delta(x-d) dx = \int_{-\infty}^{\infty} \delta(x-a) \delta(x-d) dx$

$\int_{-\infty}^{\infty} \delta(x-a) \delta(x-d) dx = \int_{-\infty}^{\infty} \delta(x-a) \delta(x-d) dx$

$$u(x) = -\alpha [\delta(x+a) + \delta(x-a)] \quad \text{where } a = \frac{\hbar^2}{m}$$

$$\text{TISE, } -\frac{\hbar^2}{m} \frac{d^2 u(x)}{dx^2} + V(x)u(x) = E u(x)$$

On replacing u by $(-x)$, we get:

$$-\frac{\hbar^2}{m} \frac{d^2 u(-x)}{dx^2} + V(-x)u(-x) = E u(-x)$$

$$\text{Since the pot } \frac{d^2}{dx^2} \text{ is symmetric, i.e., } V(x) = V(-x), \text{ so}$$

$$-\frac{\hbar^2}{m} \frac{d^2 u(-x)}{dx^2} + V(x)u(-x) = E u(-x)$$

In this case there are two solutions which are obtained as the linear combination of $u(x)$ & $u(-x)$ as:

$$u(x) = \frac{u(x) + u(-x)}{\sqrt{2}} \quad \text{&} \quad u(x) = \frac{u(x) - u(-x)}{\sqrt{2}}$$

even parity
odd parity

where $u(x)$ has even or odd parity.

$$\text{For such case, } E = -\frac{\hbar^2 k^2}{m} \quad \text{&} \quad \frac{d^2 u(x)}{dx^2} = \frac{-1}{m} [\delta(x+d) - \delta(x-d)]$$

$$\text{Even parity soln are, } u(x) = \begin{cases} e^{kx} & (x < -d) \\ \cos kx & (-d < x < d) \\ e^{-kx} & (x > d) \end{cases}$$

So,

* Boundary conditions at $x=d$ give,

$$c \cosh kd = e^{-kd} \quad \text{Eqn (a)}$$

$$c = \frac{e^{-kd}}{\cosh kd} \quad \text{using previous}$$

$\Rightarrow \cosh kd = \frac{e^{-kd}}{c}$?

$$e^{-kd} - c \sinh kd = -\frac{1}{d} e^{-kd} \quad \left(\frac{du}{dx} = -k e^{-kd}, \frac{d^2u}{dx^2} = c k^2 e^{-kd} \right)$$

$$\sinh kd = \left(\frac{1}{d} + \frac{c k^2}{d} \right) e^{-kd} \quad \left(\frac{d^2u}{dx^2} = u(d) = 0 \right)$$

$$\int_{-d}^d \sinh kd dx = 0$$

On substituting 'c' in Eqn (b), we get:

$$+k e^{-kd} + \frac{c}{d} \sinh kd = +\frac{1}{d} e^{-kd}$$

$$+k e^{-kd} + \frac{c}{d} \cosh kd = +\frac{1}{d} e^{-kd}$$

$$\text{or; } k + k \tanh kd = \frac{1}{d} : \text{by taking}$$

$$= \tanh kd = \frac{1}{kd} - \frac{1}{d} \quad \text{where } d = k d$$

$$\tanh d = \frac{1}{d} - 1 \quad \text{where } d = kd$$

On taking max. value of $\tanh d$ (i.e., 1), we get

$$1 < \frac{1}{d} \quad \text{or, } \frac{1}{d} < 1 \quad \text{or, } d > 1$$

i.e. for stable frequencies, d must be

So, ω 's energy eigen value value of $\tanh d$ is

$$E = -\frac{k^2 \omega^2}{m} < -\frac{\hbar^2 k^2}{8m d^2} \rightarrow \text{Energy in single delta pot well.}$$

June

* Odd parity solns are, defined as

$$u_o(x) = \begin{cases} e^{-kx} & (x < -d) \\ 0 & (-d < x < d) \\ e^{-kx} & (x > d) \end{cases}$$

Boundary conditions at $x=d$ gives:

$$c \sinh kd = e^{-kd} \quad (1)$$

$$\partial u / \partial x - ke^{-kd} + ck \cosh kd = -1/e^{kd} \quad (2)$$

$$(2) \Rightarrow \left\{ \begin{array}{l} \frac{\partial^2 u}{\partial x^2} + k^2 e^{-kd} u = ck \cosh kd \\ -\nu \left(\frac{\partial u}{\partial x} \right)_d = -1/e^{kd} \end{array} \right.$$

$$u(d+) = u(d-) = 0 \quad \text{and} \quad \int_d^{\infty} \delta(x+d) u(x) dx = u(d)$$

On eliminating c from eqn (1) we get;

$$-k - k \coth kd = -\frac{f_1}{d}$$

$$\text{or, } \coth kd = \frac{f_1}{kd} - 1 \quad (\# \text{ free param})$$

$$\text{Let } \rightarrow \text{then } \frac{t}{kd} - 1 = \lambda \text{ (const)}$$

Sol:

On taking minimum value of $\coth < 1$, we get.

$$f_1 > 2 \quad (1) \quad \frac{1}{d} > 2 \quad (2) \quad k < \frac{k_0}{2}$$

$$\frac{f_1^2}{4} - 1 > 2 \quad \frac{f_1^2}{4} > 3 \quad \frac{f_1^2}{4} > 3 \quad \frac{f_1^2}{4} = \frac{4}{d^2}$$

$$= -\frac{f_1^2}{4}$$

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So, the energy eigen value in this case is:

$$E = \frac{\hbar^2 k^2}{2m} + \sim \frac{\hbar^2 k^2}{2m} \rightarrow \text{Energy in single delta potential well.}$$

3-D problem in Cartesian coordinates:-

$$\begin{aligned} \text{Schr. Eqn} \quad \hat{H}\psi &= E\psi \quad \text{where } \psi(x,y,z) = \psi(x)\psi_y(y)\psi_z(z) \\ \Rightarrow \left[-\frac{\hbar^2}{2m} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) \right] \psi &= [E_x + E_y + E_z] \psi \\ \Rightarrow \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + E_x \psi(x) \right] \psi &= E_x \psi(x) \\ \Rightarrow -\frac{\hbar^2}{2m} \psi''(x) \psi(x, y, z) + V(x, y, z) \psi(x, y, z) &= E_x \psi(x, y, z) \end{aligned}$$

where: $\psi(x, y, z) = \psi_x(x) + \psi_y(y) + \psi_z(z)$

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + E_x \right) \psi(x) \approx E_x \psi(x) \quad [\text{Similarly for } y \text{ & } z]$$

for free particle:-

$$\frac{\partial^2 \psi}{\partial x^2} = -k_x^2 \psi \quad \text{where } k_x^2 = \frac{\partial m E_x}{\partial m}, \text{ i.e. } E_x = \frac{\hbar^2}{2m} k_x^2$$

$$\text{Sol. } \psi(x) = \frac{1}{J_{211}} e^{ik_x x} \Rightarrow \psi(x, y, z) = (2\pi)^{-3/2} e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

Coulomb potential (Spherical coordinates):- $V(\vec{r}) = V(r)$

$$\text{Schr. Eqn, } \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right\} \psi(r) = E \psi(r)$$

$$\begin{aligned} \Rightarrow \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{\partial}{\partial r} \frac{\partial}{\partial r} \right) \psi(r) + V(r) \psi(r) &= E \psi(r) \\ \Rightarrow \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) \psi(r) + V(r) \psi(r) &= E \psi(r) \\ \Rightarrow \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^4} \frac{\partial^2}{\partial \phi^2} \right) \psi(r) + V(r) \psi(r) &= E \psi(r) \end{aligned}$$

$$\text{where } L^2 = \frac{1}{r} \left(\frac{\partial}{\partial r} \frac{\partial}{\partial r} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$$\text{Radial eqn, } \left[-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2 R_{nlm}(r)}{\partial r^2} - \frac{L^2 + V(r)}{2mr^2} \right] Y_{lm}(r) = E_{nlm} Y_{lm}(r)$$

$$\text{Let } Y_{lm}(r) = R_{nlm}(r) Y_{lm}(\theta, \phi) + V(r) - E_g R_{nlm}(r) Y_{lm}(\theta, \phi)$$

$$+ \frac{L^2}{2mr^2} R_{nlm} Y_{lm}(\theta, \phi)$$

On dividing $\frac{d^2 Y_{lm}}{dr^2}$ by $R_{nlm}(r) Y_{lm}(\theta, \phi)$ & multiply by $\frac{1}{dmr^2}$, we get:

$$-\frac{\hbar^2}{2mr^2} \frac{d^2}{dr^2} (r R_{nlm}) + 2mr^2 E_{nlm} - E_g^2 + \frac{L^2}{2mr^2} Y_{lm}(\theta, \phi) = 0$$

On multiplying $\frac{1}{r} R_{nlm}(r)$, we get:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} (r R_{nlm}) + E_{nlm} + \frac{L^2}{2mr^2} Y_{lm}(\theta, \phi) = E_{nlm}$$

$$= -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} (r R_{nlm}) + V(r) + \frac{L^2}{2mr^2} Y_{lm}(\theta, \phi) = E_{nlm}$$

$$\text{where } V_{eff} = V(r) + \frac{L^2}{2mr^2}$$

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$$f(r) = E\psi(r)$$

$$\frac{d^2f}{dr^2} + \frac{2}{r} \frac{df}{dr} + \left[\frac{\mu(E - \epsilon_p)}{r^2} - \frac{L(L+1)}{r^2} \right] f(r) = 0$$

$\psi(r)$

Ansatz form

$\psi(r) = rR(r)$

where $U(r) = rR(r)$

$\mu = \text{Reduced mass}$

(θ, ϕ)

Case I: For $r \rightarrow 0$ (i.e. very small)

$- \frac{d^2 U(r)}{dr^2} + \frac{\mu(L+1)}{r^2} \psi(r) = 0$

$\frac{d^2 \psi}{dr^2} = \frac{\mu(L+1)}{r^2} \psi(r)$

Radial wave

functions

$$\text{soln } U(r) = A r^{L+1} + B r^{-2}$$

$$\partial_r \psi = A r^{L+2} - B r^{-3}$$

$$\partial_r \psi = 0$$

$$A r^{L+2} - B r^{-3} = 0 \Rightarrow A = B r^{5-L}$$

Case II: For $r \rightarrow \infty$ (i.e. very large)

$$E_n(r) R(r) = \frac{d^2 U}{dr^2} + \frac{2\mu E}{r^2} U(r) = 0$$

$$R(r) = 0$$

$$\text{soln } U(r) = e^{\pm ikr}$$

$$U(r) = e^{\pm ikr} \text{ (not possible for bound states)}$$

$$\text{as } r \rightarrow \infty \text{ so, } U(r) = e^{-ir} \rightarrow \text{Eqn (b)}$$

$$\text{from Eqn (a) \& (b), } U(r) = r^{L+1} f(r) e^{-ir} \rightarrow \text{Eqn (2)}$$

Where $f(r) = \sum_{k=0}^{\infty} b_k r^k$ (Power series soln for 3D H.O.)

On substituting Eqn (2) in Eqn (1); we get!

$$\frac{d^2 f}{dr^2} + 2 \left(\frac{L+1}{r} - 1 \right) \frac{df}{dr} + 2 \left[-1(L+1) + \mu e^2 / h^2 \right] f(r) = 0$$

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On substituting $f(r) = \sum_{k=0}^{\infty} b_k r^k$, we get

$$\begin{aligned} & \sum_{k=0}^{\infty} [k(k+2\lambda+1)b_k r^{k-2} + 2 \left\{ -\lambda(k+1+\lambda) + \mu e^2 \right\} \frac{b_{k-1}}{r}] = \\ & \text{by changing "K" to "K-1" in the last term,} \\ & \text{we get recurrence reln.} \\ & = k(k+2\lambda+1)b_k = 2 \left[1(k+\lambda) - \frac{\mu e^2}{r^{k-2}} \right] b_{k-1} \\ & = \underline{b_k} = 2 \left[1(k+\lambda) - \frac{\mu e^2}{r^{k-2}} \right] \underline{b_{k-1}} \\ & \quad \underline{r(k+\lambda+1)} \end{aligned}$$

$$\begin{aligned} & \text{On solving } f(r) = \sum_{k=0}^{\infty} b_k r^k \rightarrow e^{2\lambda r} \\ & \Rightarrow f(r) = r^{\lambda+2} e^{2\lambda r} e^{-\lambda r} = r^{\lambda+2} e^{\lambda r} \rightarrow \text{i.e., physically} \end{aligned}$$

To make it physically acceptable, let $b_{N+1}, b_{N+2}, \dots = 0$ i.e., unacceptable

$$f(r) = \sum_{k=0}^N b_k r^k$$

When $b_{N+1} = 0$, then recurrence reln reduces to,

$$1(N+1+\lambda) - \mu e^2 = 0$$

$$\text{or, } \lambda n + \mu e^2 = \frac{1}{r^2} \quad \text{where } n = N+1+\lambda$$

$$\lambda = \mu e^2$$

$$\text{Also } \lambda = \sqrt{\frac{-2\mu E}{r^2}}$$

$$\Rightarrow \mu e^2 = \frac{-2\mu E}{r^2} \rightarrow \frac{\mu^2 e^4}{r^2}$$

$$\mu e^2 = \frac{\mu e^4}{r^2} \rightarrow \frac{\mu^2 e^4}{r^2}$$

Eqn (8)

From Bohr theory of H₂ atom, $a_0 = \frac{4\pi^2}{\mu e^2}$

$$E_n = -\frac{e^2}{2a_0} \frac{1}{n^2}$$

$$\int f = 0$$

m_s

$$\lambda = \sqrt{-2\left(\frac{\mu}{\hbar^2}\right) E}$$

$$\lambda = \frac{1}{na_0}$$

$$\therefore N = 0, 1, 2, 3, \dots$$

$$n (=N+\lambda+1) = \lambda+1, \lambda+2, \lambda+3, \dots$$

Since n is a non zero integer quantity (allowed also allowed value of $\lambda = 0, 1, 2, 3, \dots, n-1$)

Since the Coulomb potential felt by the single "e" due to the charge "ze" is given by, $V(r) = -\frac{ze^2}{r}$, so energy can be inferred from eqns by simply replacing e^2 by ze^2 , i.e

$$E_n = -\frac{me(2e^2)^2}{2\hbar^2 n^2} = -\frac{ze^2}{n^2} \cdot \frac{2^2 E_0}{2a_0}$$

$$E_n = -13.6 \frac{z^2}{n^2}$$

Radial wave fn:

$$R_{nl} = \frac{1}{r} U_{nl}(r) = \frac{1}{r} A_{nl} r^{l+1} e^{-\lambda r} \sum_{k=0}^{\infty} b_{kl} r^k$$

$$R_{nl} = A_{nl} r^l e^{-\lambda r} \underbrace{\sum_{k=0}^{\infty} b_{kl} r^k}_{R_{nl}(r)} \quad \left\{ \begin{array}{l} \therefore \lambda = \frac{1}{na_0} \end{array} \right.$$

Lalit

$$R_{10}(r) = A_{10} e^{-r/a_0} \sum_{k=0}^0 b_k r^k = A_{10} b_0 e^{-r/a_0}$$

From Normalization conditions:-

$$= \int_0^{\infty} r^2 |R_{10}(r)|^2 dr$$

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$$\text{If } A_{10} = 1 \text{ then } b_0 = d(a_0)^{-3/2}$$

$$\Rightarrow R_{\text{outer}} = d(a_0)^{-3/2} e^{-r/a}$$

Similarly

$$R_{20}(r) = A_{20} e^{-r/b_{20}} \sum_{k=0}^4$$

By using references

Since b_1 , we can write

$$= \frac{1}{\sqrt{\frac{d\phi_0^2}{d\phi_0^2}}} \left(1 - \frac{r}{d\phi_0} \right) e^{-\frac{1}{2} d\phi_0}$$

Degeneracy of the bound state of

$$g_n = \sum_{k=0}^{n-1} (2k+1) = \sum_{k=0}^{n-1} 2k + \sum_{k=0}^{n-1} 1 = 2 \cdot \frac{n(n-1)}{2} + n - 1 = n^2 - n + n - 1 = n^2 - 1$$

$$d_n = n^2 - \eta^2 + \eta = [n^2]$$

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Molecules (Hydrogen molecule, valence bond, & molecular orbital picture), singlet / triplet state, chemical bonding & hybridization.

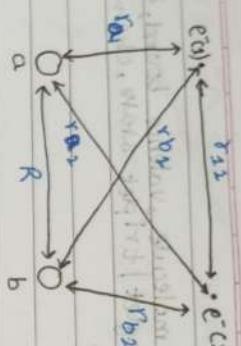
Valence bond method:-

In this method, atoms are assumed to maintain their individual identity in a molecule. And the bond arises due to the lesser interaction of balance e^- when the atoms come closer. It amounts to considering the molecule as composed of atomic cores & bonding valence e^- . Thus valence bond method considers bringing the atoms with their associated e^- together, & allowing them to interact to form the bond.

* Hydrogen molecule (Heitler London theory) \Rightarrow

To balance problem was first considered by Heitler & London, which is further extended by Slater & Pauling to give a general theory of chemical bonding. And the theory is known as the valence bond method.

Let us consider 2 hydrogen atoms far apart so that there is no interaction between them. Leveling the e^- as r_1 & r_2 , the nuclei as 'A' & 'B' & the nuclear distances are by r_{AB} , r_{1A} , r_{1B} ,



Sch. eqn:-

$$H_{\alpha(1)} \Psi_{\alpha(1)} = E_{\alpha} \Psi_{\alpha}(1)$$

$$\text{where } H(a_1) = -\frac{k^2}{2m} \nabla_1^2 - \frac{e^2}{4a_1}$$

When the 2 atoms are brought close & share
is not interaction b/w them, then the total
Hamilton of system is given by

It amounts to assuming that e_1 is moving about proton 'a' & e_2 is moving about 'b' - for the system of two hydrogen atoms can be described by wave function.

The e^- are indistinguishable & therefore can equally good description of the molecule with same energy is given by the structure. In which with energy eigen value, $E_a + E_b$. Since $[H_a(1) + H_b(2)] \Psi_a(1), \Psi_b(2) = H_a(1)[\Psi_a(1), \Psi_b(2)] + H_b(2)[\Psi_a(1), \Psi_b(2)] = E_a[\Psi_a(1), \Psi_b(2)] + E_b[\Psi_a(1), \Psi_b(2)]$

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ψ_1 is associated with atom 'b' & ψ_2 is associated with atom 'a'. Hence the wave function

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

The two f_3^3 's differ only in interchange of 2 e^- s in the orbitals. Hence this degeneracy is referred to as the exchange degeneracy.

$\psi_1(1,2)$ & $\psi_2(2,1)$ are eigen f_3^3 's of the Hamiltonian $H = H_a + H_b$, having eigen value $E_a + E_b$.

Now considering the hydrogen atoms the Hamiltonian of the system is given by:

$$H = \underbrace{H_a + H_b}_{\text{Unperturbed Hydrogen Hamiltonian}} + H' + \frac{e^2}{R} \rightarrow \text{Due to interaction between proton & proton}$$

$$\text{where } H' = -\frac{e^2}{r_{a_2}} - \frac{e^2}{r_{b_2}} + \frac{e^2}{r_{12}}$$

(2) The problem can be solved either by perturbation method or variational method. Heider & London follows the perturbation method.

As the hamiltonian does not change

on exchange of 2 e^- s, the wave f_3^3 's must either be symmetric or antisymmetric with respect to such an exchange. So the symmetric & antisymmetric combinations of wave f_3^3 's are:

$$\psi_S = N_S [\psi_{a(1)} \psi_{b(2)} + \psi_{a(2)} \psi_{b(1)}]$$

$$\psi_{AS} = N_{AS} [\psi_{a(1)} \psi_{b(2)} - \psi_{a(2)} \psi_{b(1)}]$$

where N_S & N_{AS} are normalization coefficient given by $N_S^2 = \frac{1}{2(S+1)}$ & $N_{AS}^2 = \frac{1}{2(1-S^2)}$ where $S = |\psi_a| \psi_b\rangle = \langle \psi_b | \psi_a\rangle$

The inclusion of e-spin & Pauli exclusion principle leads to Heitler London wave fn corresponding to singlet ($S=0$) & a triplet ($S=1$). In mode H atom

Since the Hamiltonian doesn't contain spin terms, the energy is not affected by the inclusion of spin parts. The space part alone can then be taken as the unperturbed wave fn for the evolution of energy. ($E' = \langle \Psi_h | H' | \Psi_m \rangle$)

$$E'_1 = N_3^2 \langle \Psi_a(1) \Psi_b(2) | H' | \Psi_a(1) \Psi_b(2) + \Psi_a(2) \Psi_b(1) | H' | \Psi_a(1) \Psi_b(2) + \Psi_a(2) \Psi_b(1) | H' | \Psi_a(2) \Psi_b(1) \rangle$$

$$\langle J = i \langle \Psi_a(1) \Psi_b(2) | H' | \Psi_a(1) \Psi_b(2) \rangle = \langle \Psi_a(2) \Psi_b(1) | H' | \Psi_a(2) \Psi_b(1) \rangle - K = \langle \Psi_a(1) \Psi_b(2) | H' | \Psi_a(2) \Psi_b(1) \rangle - E'_1 = N_3^2 (2J + 2K)$$

$$E'_1 = \frac{1}{1+S^2} \delta(J+K)$$

$$E'_1 = \frac{1}{1+S^2} \delta(J+K)$$

$$H_S = H_a + H_b + H' + e^2$$

$$E_S = 2E_H + \underbrace{J+K}_{R}$$

$$\text{Symmetric fn or } S^2 \text{ singlet state.}$$

$$E_2 = N_A^2 \langle \Psi_a(1) \Psi_b(2) - \Psi_a(2) \Psi_b(1) | H' | \Psi_a(1) \Psi_b(2) - \Psi_a(2) \Psi_b(1) \rangle$$

$$E_2 = N_A^2 (2J - 2K) = \frac{1}{1-S^2} 2(J-K)$$

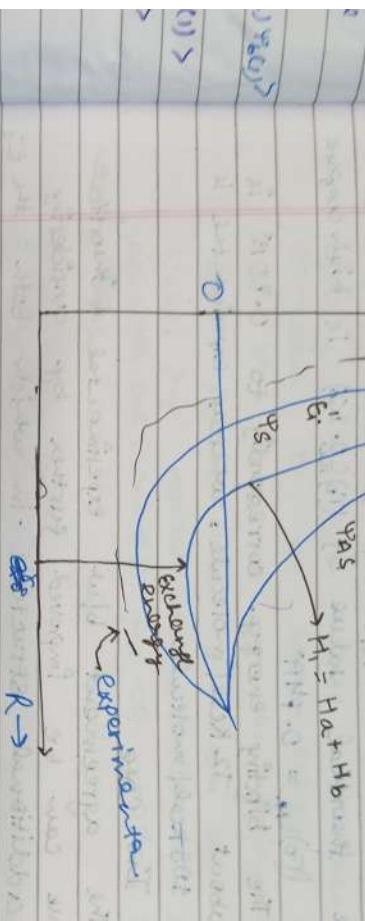
$$1 - S^2 = \frac{1}{(1-S^2)^2} = \frac{1}{2M} \rightarrow M = \frac{1}{2} (1 - S^2) \text{ And } \frac{1}{1-S^2} = \frac{1}{2M} \rightarrow M = \frac{1}{2} (1 - S^2) \text{ both}$$

Principle
to

$$E_{AS} = H_A + H_B + \frac{1}{R} + \frac{e^2}{R}$$

$$= \delta E_H + J - K + \frac{e^2}{1 - S^2} \quad \text{[For Antisymmetric wave function or triplet state]}$$

Plot of Energy Graph E_1 & E_2 against intermolecular distance 'R'.



The coulomb integral represents the interaction of classical e- charge electron cloud about one nucleus with the charge in other nucleus & the interaction of 2 charge clouds with one another. Exchange inter integral represents a non-classical interaction. It is a consequence of the inclusion of $\psi_{1(1,2)}$ & $\psi_{2(2,1)}$ in the unperturbed wave fn. The 2 ψ_i 's differ only in the interchange of e- between the orbitals ψ_A & ψ_B .

The overlap integral 'S' is zero, when the protons are fall apart.

$$S = \langle \psi_A | \psi_B \rangle = \langle \psi_B | \psi_A \rangle = 0$$

And when they are in contact, then $S = 1$. J & K both tends to zero for large 'R', while both are -ve for intermediate values.

The magnitude of K is several times large than that of ' J '. Thus ' E_3 ' can have a value less than $2E_H$, where as E_{HS} always shows a minimum for the 4^3_S combination corresponding to the formation of stable molecule. The equilibrium intermolecular distance r

the one correspondence. The one is

The theoretical value of $(n)_\text{ref}$: 0.85 is high compared to $(n)_\text{exp} = 0.749$.

The binding energy corresponding to 0.85 \AA° is about 72 Kcal/mole.

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agreement between experimental & theoretical value can be improved further by considering 2 additional structures in which both the electrons are associated with only one nucleus i.e. these are ionic structures.

Valence Bond method of hydrogen molecule Ion:-

The Hydrogen molecule ion is a system consisting of single p^- & p^+ .

The Schrödinger equation for the H_2^+ ion is given by:

$$-\frac{\hbar^2}{8m} \nabla^2 \psi + \left(-\frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{R}\right) \psi = E \psi$$

Consider the case of a single electron system.

• Wetland White tail

large

value shows strong leads to the structure of H_2H^+ . This is wave for the structure is assumed as $\psi_a = \psi_b$.

When the e^- is associated with nucleus ve. H_2 structure is described by H_2^+H with wave for ψ_b . Both these structures are correspond to the same energy & e^- wave for $1s$ is the same as the hydrogenic $1s$ will be the same as the e^- gets further when 2 nuclei are brought closer, they repelled one another but the e^- gets attracted due another. for to both the nuclei thereby creating a bond.



ex. i.e.

A hydrogen molecule now is formed when the energy of system is minimum. i.e. the wave function of system is described by a linear combination of ψ_a & ψ_b .

$\Psi = C_1\psi_a + C_2\psi_b$, where $C_1 = \pm C_2$. As both the states have same energy they contribute equally to Ψ . The 2 possible combinations are:

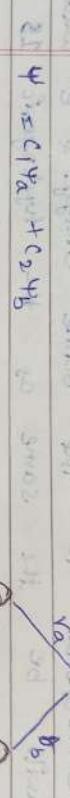
$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{2+2S}} (\psi_a + \psi_b) \\ \Psi_2 &= \frac{1}{\sqrt{2-2S}} (\psi_a - \psi_b) \end{aligned}$$

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The increase e^- charge density in case of ψ_1 is concentrated in the regn blue nuclei. In case of ψ_2 , the e^- charge density is pushed away from internuclear region.

Molecular orbital (MO) treatment of hydrogen ion:



$$\begin{aligned} \text{Sch. eqn: } & H\psi = E\psi \\ \Rightarrow & \langle \psi | H | \psi \rangle = \langle C_1 \psi_a + C_2 \psi_b | H | C_1 \psi_a + C_2 \psi_b \rangle \\ & \langle \psi | \psi \rangle = \langle (C_1 \psi_a + C_2 \psi_b) | (C_1 \psi_a + C_2 \psi_b) \rangle \end{aligned}$$

$$E = \frac{|C_1|^2 \langle \psi_a | H | \psi_a \rangle + C_1^* C_2 \langle \psi_a | H | \psi_b \rangle + C_2^* C_1 \langle \psi_b | H | \psi_a \rangle + |C_2|^2 \langle \psi_b | H | \psi_b \rangle}{|C_1|^2 + |C_2|^2 + C_1^* C_2 + C_2^* C_1}$$

where $\langle \psi_a | \psi_b \rangle = \langle \psi_b | \psi_a \rangle = S$ (overlap integral)

$\langle \psi_a | H | \psi_b \rangle = H_{ab}$ & $\langle \psi_b | H | \psi_a \rangle = H_{ba}$ (Resonance & exchange)

$\langle \psi_a | \psi_b \rangle = \langle \psi_b | \psi_a \rangle = S$ (Coverlap integral)

$$\Rightarrow E = C_1^2 H_{aa} + C_2^2 H_{bb} + 2C_1 C_2 H_{ab}$$

For minimum energy:

$$\begin{aligned} \frac{dE}{dC_1} &= 0 \Rightarrow E(C_1^* + 2C_2 S) = 2C_1 H_{aa} + 2C_2 H_{ab} \\ \Rightarrow & (H_{aa} - E)C_1 + (H_{bb} - E)C_2 = 0 \end{aligned}$$

$$\text{Similarly: } \frac{dE}{dC_2} = 0, \text{ gives } (H_{bb} - E)C_1 + (H_{aa} - E)C_2 = 0$$

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These simultaneous homogeneous eqn's in C_1 & C_2 have non-trivial soln. only if:

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{bb} - E \end{vmatrix} = 0$$

$$\text{Or, } (H_{aa} - E)(H_{bb} - E) - (H_{ab} - ES)^2 = 0$$

\because For homonuclear diatomic molecule H_2^+ , as the nuclei a & b are identical then $H_{aa} = H_{bb}$, which reduces above eqn to:

$$(H_{aa} - E)^2 - (H_{ab} - ES)^2 = 0 \quad \text{--- Eqn (2)}$$

$$\therefore a^2 - b^2 = (a+b)(a-b)$$

$$\Rightarrow (H_{aa} - E + H_{ab} - ES)(H_{aa} - E - H_{ab} + ES) = 0$$

$\psi_a + \psi_b < \psi_a |H| \psi_b$ On solving we get:

$$\begin{aligned} > & \text{From} \\ & \text{coulomb} \\ & \text{charge} \\ & \text{charge} \end{aligned} \quad \begin{aligned} E_1 &= \frac{H_{aa} + H_{ab}}{1+s} - E_{qN} \quad (3) \\ E_2 &= \frac{H_{aa} - H_{ab}}{1-s} - E_{qN} \quad (4) \end{aligned}$$

$$\begin{aligned} \text{from eqn (2), } H_{aa} &= H_{aa} - E = \pm(E_s - H_{ab}) \\ \text{from eqn (1), for +ve sign:-} \\ (E_{qN} - H_{ab})C_1 + (H_{ab} - E_{qN})C_2 &= 0, \Rightarrow C_1 = C_2 \end{aligned}$$

Similarly, for -ve sign!

Consequently, the wave fns corresponding to energies

E_1 & E_2 are respectively!

$$\psi_1 = C_1 (\psi_a + \psi_b) = \frac{\psi_a + \psi_b}{\sqrt{2+2s}} \quad \& \quad \psi_2 = C_2 (\psi_a - \psi_b) = \frac{\psi_a - \psi_b}{\sqrt{2-2s}}$$

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Coulomb integral: $\int \frac{e^2}{4\pi\epsilon_0 r^2} dV$

$$H_{aa} = \epsilon_a \int \frac{e^2}{4\pi\epsilon_0 r^2} dV = \epsilon_a \int \frac{e^2}{4\pi\epsilon_0 r^2} \frac{4\pi r^2}{R} dr = \epsilon_a \frac{4\pi e^2}{3\epsilon_0 R}$$

$$\text{Or, } H_{aa} = \epsilon_H - V_{aa} + \frac{k\epsilon^2}{R} - \text{eqn(5)}$$

Similarly: $H_{ab} = \epsilon_H - V_{ab} + \frac{k\epsilon^2}{R} - \text{eqn(6)}$

On substituting eqn(5) & (6) in eqn(3) & (4), we get

$$\epsilon_1 = \epsilon_H - (V_{aa} + V_{ab}) + \frac{k\epsilon^2}{R}$$

$$\epsilon_2 = \epsilon_H - (V_{aa} - V_{ab}) + \frac{k\epsilon^2}{R}$$

Hybridization:

$$(3) \quad u_p \rightarrow d_H + o_H = 13$$

3 + 1

$$(13) \quad u_p \rightarrow d_H + o_H = 13$$

2 + 1

$$(u_p) = 4 - 1 = 3$$

$$= 3 + 1 = 4$$

$$(d_H) = 3 + 1 = 4$$

$$= 3 + 1 = 4$$

$$= 3 + 1 = 4$$

$$= 3 + 1 = 4$$