

Ques 4

Methods of Quantum Mechanics

Q. What are inadequacy of classical mechanics that gave rise to quantum mechanics?

→ First

The development of classical mechanics is based on Newton's three laws. These laws include the concept of ~~actual~~ absolute mass, absolute space (x, y, z coordinate) and absolute time. Classical physics can explain motion of the body with non relativistic speed i.e. $v \ll c$. But for the relativistic speed and microscopic world i.e. of atomic dimension, Classical mechanics is completely

failed.

The main inadequacy of classical mechanics are:-

1) Stability of the atom:-

According to classical mechanics electron moves around the nucleus and it loses the energy in the form of electromagnetic wave continuously. So its velocity decreases continuously and come closer and closer to the nucleus finally collapses. This shows Instability of atom.

But actually this doesn't happen. According to quantum mechanics electrons revolve on their fixed orbits and transition of electron is possible only when the energy get by electron is equal to energy difference of two orbits.

$$P.E = nhf \quad v \neq 0$$

Thus there is no continuous degradation of energy of electron.

2) Blackbody radiation:-

The spectrum of blackbody couldn't be explained by the concepts of classical mechanics due to its assumption that energy change of radiation takes place continuously.

In 1900 plunck's hypothesis considered every atom in solid emit energy only discretely in quanta. The energy of an individual quantum being equal to hf . This hypothesis explain spectrum of blackbody radiation.

3) Specific heat of solid at low temperatures

According to classical theory specific heat is a constant quantity. But it is found that specific heat of solid at low temperature is not constant, it varies with temperature. This cannot be explained by classical theory.

C.v

According to quantum theory each atom acts as a oscillator. As temperature is lower the amplitude of oscillation decreases. Thus C_v decreases as T decreases. As T increases the amplitude of oscillation reaches maximum value equal to natural frequency and hence at high temperature C_v is constant.

4) Photo Electric Effect, Compton effect, Zeeman effect

The kinetic energy of the emitted photo electron depends only on incident frequency and on the intensity of light. This is not explained by classical theory, but it was successfully explained by quantum mechanics.

When photon of energy (hf) and momentum ($\frac{h}{c}$) is incident on electron at rest, then the scattered photon will have low energy and hence longer wavelength. The shift in wavelength $\Delta\lambda = \frac{h}{mc} (1 - \cos\theta)$ is called Compton shift. It is not explained by classical theory. Similarly eddiesical physio

could not explain Zeeman effect, Raman effect etc.

Q2. What are the short comings of old quantum theory.

-) Main short comings of old quantum theory are:-
- 1) It couldn't be applied to non periodic system.
- 2) It couldn't explain spectral line of relatively simple cases like hydrogen molecule and Helium atom.
- 3) It couldn't explain relative intensities of spectral line at all.
- 4) It doesn't have any theoretical background so it is not unified or general theory.

The above difficulties have been resolved by development of new methods of approaches called wave mechanics.

~~Q3~~ what are the physical significance of wave function (ψ). Derive the time independent Schrodinger wave equation.

-) First part:-

In quantum mechanics a particle is characterised by wave function ($\psi_{(r,t)}$) which contains information about spatial state of the particle at time t .

The physical significance of wave function are:-

- 1) The square of its absolute value i.e. $|\psi(r,t)|^2$ at a point r,t proportional to probability of finding a particle in a small element of volume enclosed by that point.
- 2) Wave function ψ complex quantity & contains amplitude and phase.

Let us write,

$$\psi = A + iB$$

$$\psi^* = A - iB$$

then

$$\psi\psi^* = (A+iB)(A-iB)$$

$$|\psi\psi^*| = A^2 + B^2$$

$\therefore \psi\psi^* = \psi^*$, $\psi = |\psi|^2$ which is always a positive quantity.

\therefore probability density $= (\psi)^2 = \psi^*\psi$.

\therefore probability, $P(r,t)dv = |\psi|^2 dv$.

Since the total probability of finding the particle in entire space is unity.

$$\int_{-\infty}^{\infty} |\psi|^2 dv = 1 \quad \text{--- (1)}$$

Any wave function satisfying eqn (1) is called Normalized wave function
2. eqn (1) is normalized wave function

8 eqn ① Ps normalization condition.

Second part:

Schrodinger wave equation describes the motion of quantum mechanical particle as Newton's second law in quantum mechanics.

Let the wave function associated with the motion of free particle in one dimension be given by,

$$\psi(n, t) = A e^{-i(Et - \frac{p_n}{\hbar}x)} \quad \text{--- (i)}$$

we have,

$$E = hf = \frac{\hbar}{2\pi} Q\pi f = \hbar\omega$$

$$\therefore \omega = \frac{E}{\hbar}$$

$$\text{Similarly, } p_x = \frac{Q\pi}{\lambda} = \frac{\hbar}{2\pi} \cdot \frac{Q\pi}{\lambda} = \hbar k$$

$$\therefore k = \frac{p_x}{\hbar}$$

Equation (i) becomes,

$$\psi(n, t) = A e^{-i(\frac{E}{\hbar}t - \frac{p_n}{\hbar}x)}$$

$$\therefore \psi(n, t) = A e^{-i\hbar(Et - p_n x)} \quad \text{--- (ii)}$$

Differentiation (ii) w.r.t. x .

$$\frac{dp}{dx} = \frac{i}{\hbar} p_n A e^{-i\hbar(Et - p_n x)}$$

$$\text{or, } \frac{d\psi}{dx} = \frac{i}{\hbar} p_n \psi$$

$$\text{or, } \frac{\partial \psi}{dn} = \frac{i}{\hbar^2} P_n \psi$$

$$\text{or, } \frac{d\psi}{dn} = \frac{i}{\hbar^2} P_n \psi$$

$$\text{or, } i\hbar \frac{d\psi}{dn} = P_n \psi \quad \text{--- (iii)}$$

Again, dP_{ff} (ii) w.r.t $n!$

$$\therefore \frac{d^2\psi}{dn^2} = \left(\frac{i P_n}{\hbar} \right) \left(\frac{i P_n}{\hbar} \right) \psi.$$

$$\text{or, } \frac{d^2\psi}{dn^2} = - \frac{P_n^2 \psi}{\hbar^2}$$

$$\text{or, } -\hbar^2 \frac{d^2\psi}{dn^2} = P_n^2 \psi \quad \text{--- (iv)}$$

Total energy of particle,

$$T-E = K.E + pE$$

$$\text{or, } E = \frac{P_n^2}{2m} + V$$

Multiplying on both sides by ψ from right,

$$E\psi = \left(\frac{P_n^2}{2m} + V \right) \psi.$$

$$\text{or, } E\psi = \frac{P_n^2}{2m} \psi + V\psi$$

$$\text{or, } (E - V)\psi = \left(-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}\right) \frac{1}{2m}$$

$$\text{or, } (E - V)\psi = -\frac{\hbar^2}{2m} \cdot \frac{d^2\psi}{dx^2}$$

$$\text{or, } \frac{\hbar^2}{2m} \cdot \frac{d^2\psi}{dx^2} + (E - V)\psi = 0$$

$$\therefore \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0 \quad \text{--- (1)}$$

This is required time independent Schrödinger wave equation in one dimension.

In 3-dimension,

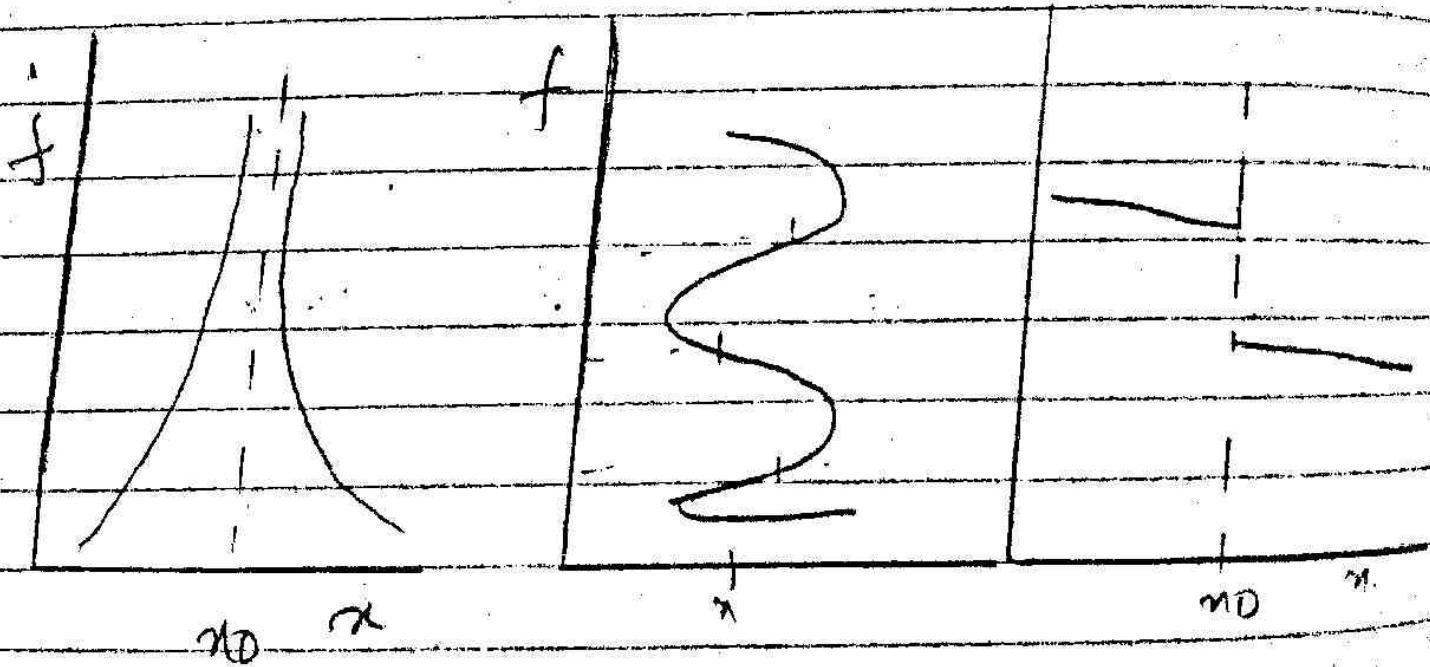
$$\nabla^2\psi + \frac{2m}{\hbar^2} (E - V)\psi = 0$$

$$\begin{aligned} \text{or, } \nabla^2 &= \text{Laplacian operator} \\ &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \end{aligned}$$

Q) What are the characteristics of wave function (ψ). Derive the time dependent Schrödinger wave equation.

Due to interpretation of $|\psi|^2$ as a probability density, the wave function ψ must satisfy the certain condition.

- 1) ψ must be finite for all values of x, y, z i.e. anywhere.
- 2) ψ must be single valued i.e. for each set of x, y, z ; ψ must have one value.
- 3) ψ must be continuous in all regions.
- (iv) The partial derivative of ψ . $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}$ also must be continuous.



fig(i)

 ψ is infinite

fig(ii)

 ψ has multivalued

fig(iii)

 ψ is discontinuous

A wave function satisfying these characteristics are called well behaved.

Second part:-

Schrodinger wave equation describes the motion of free particle in one dimension is given by

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

we have

$$E = hf = \frac{h}{2\pi} \cdot 2\pi f$$

$$= h \cdot \omega$$

$$\therefore \omega = \frac{E}{h}$$

$$p_x = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar \cdot k.$$

$$\therefore k = \frac{p_x}{\hbar}$$

then,

$$\psi = A e^{i\left(\frac{E}{\hbar} t - \frac{p_x}{\hbar} x\right)}$$

$$\psi = A e^{i\frac{\hbar}{\hbar}(Et - p_x x)}$$

(P)

Differentiating eqn ① w.r.t x ,

$$\frac{d\psi}{dx} = i \frac{\hbar}{\hbar} p_x A e^{i\frac{\hbar}{\hbar}(Et - p_x x)}.$$

$$\text{or, } \frac{d\psi}{dx} = i p_x \psi$$

$$\text{or, } \frac{d\psi}{dx} = -i \hbar p_x \psi$$

$$\text{or, } -\frac{\partial \psi}{\partial n} = P_{n1} \psi \quad \text{--- (iii)}$$

Again,
Differentiating eqn (ii) w.r.t n ,

$$\text{or, } \frac{d^2 \psi}{dn^2} = \left(\frac{i P_n}{\hbar} \right) \left(\frac{i P_n}{\hbar} \right) \psi$$

$$\text{or, } \frac{d^2 \psi}{dn^2} = \frac{P_n^2}{\hbar^2} \psi$$

$$\text{or, } \frac{d^2 \psi}{dn^2} = -\frac{1}{\hbar^2} P_n^2 \psi$$

$$\text{or, } -\frac{d^2 \psi}{dn^2} = \frac{P_n^2}{\hbar^2} \psi. \quad \text{--- (iv)}$$

Again, Differentiate ψ with respect to time t :

$$\frac{d\psi}{dt} = \frac{d A e^{i(Et - P_n n)}}{dt}$$

$$\text{or, } \frac{d\psi}{dt} = -\frac{\phi}{\hbar} E \psi$$

$$\text{or, } \frac{d\psi}{dt} = \frac{-\phi}{\hbar E} \psi$$

$$\text{or, } \frac{d\psi}{dt} = \frac{E\psi}{\hbar}$$

$$\text{or, } E\psi = \frac{\hbar}{\phi} \frac{d\psi}{dt} \quad \text{--- (v)}$$

Total energy for a particle moving non-relativistically

$$T.E = K.E + P.E$$

$$\text{Or, } E = \frac{P^2}{2m} + V$$

Multiplying by ψ on right sides,

$$E\psi = \left(\frac{P^2}{2m} + V \right) \psi$$

$$\text{Or, } E\psi = \frac{P^2}{2m}\psi + V\psi$$

$$\therefore i\hbar \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi$$

This is the required time dependent Schrödinger wave equation.

Now,

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

$$\text{Or, } E\psi = \hat{H}\psi$$

where, \hat{H} = Hamiltonian operation

$$\therefore \hat{H} = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right)$$

(show that $\hat{P}_x \hat{P}_y = \hat{P}_y \hat{P}_x$)

Q. 5 what are operator in quantum mechanics.
Derive an expectation value of momentum
and energy for a free particle.

→ First part:-

Any equation of the form

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

is called

eigen value equation.

\hat{A} is an operator.

ψ is called eigen function.

a is called eigen value.

Operator is a function over a space of physical states to another space of physical states.

The average or expectation value of a dynamical quantity is the mathematical expectation for result of single measurement.

Second part:-

Let we have a wave function,

$$\psi = A e^{-\frac{i}{\hbar}(Et - P_n x)}$$

Dif w.r.t n ,

$$\frac{d\psi}{dn} = \left(\frac{\hbar i}{\hbar} P_n\right) \psi.$$

$$\text{or, } \frac{d\psi}{P_n dn} = P_n \psi.$$

$$\text{or, } -\frac{\partial^2 \psi}{\partial x^2} \cdot \frac{d\psi}{dx} = P_n \psi$$

$$\text{or, } -i\hbar \frac{d\psi}{dx} = P_n \psi$$

$$\text{or, } \left(-i\hbar \frac{d}{dx} \right) \psi = P_n \psi$$

or, Comparing it with eigen value eqn,
 $\hat{A}\psi = a\psi$.

\therefore Momentum operator, $\hat{P}_x = \left(-i\hbar \frac{d}{dx} \right)$

Expectation value of P for a particle moving along x axis P_x given by,

$$\langle P \rangle \text{ or } \bar{P} = \int_{-\infty}^{\infty} \psi^* \hat{P} \psi dx$$

$$= \int_{-\infty}^{\infty} \psi^* \psi dx.$$

$$\text{For normalized wave, } \int_{-\infty}^{\infty} \psi^* \psi dx = 1,$$

$$\therefore \langle P \rangle \text{ or } \bar{P} = \int_{-\infty}^{\infty} \psi^* \hat{P} \psi dx.$$

$$= \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{d}{dx} \right) \psi dx$$

$$= \int_{-\infty}^{\infty} \psi^* (-i\hbar) \frac{d\psi}{dx} dx$$

$$= \int_{-\infty}^{\infty} \psi^* i \hbar \frac{\partial}{\partial x} \psi - \frac{1}{2m} P_n \psi d\eta.$$

$$= \int_{-\infty}^{\infty} \psi^* P_n \psi d\eta$$

$$= P_n \int_{-\infty}^{\infty} \psi^* \psi d\eta$$

$$= P_n$$

$$\therefore \langle P \rangle \text{ or } \bar{P} = P_n$$

so that

Again,

$$\psi = A e^{-\frac{i}{\hbar} (Et - P_n x)}$$

Differentiating w.r.t t.

$$\frac{d\psi}{dt} = -\frac{i}{\hbar} E \psi$$

$$\text{or, } -i \frac{d\psi}{dt} = E \psi$$

$$\text{or, } i \hbar \frac{d\psi}{dt} = E \psi$$

$$\text{or, } \frac{d\psi}{dt} \text{ or, } \left(\frac{d}{dt} \right) \psi = E \psi$$

Comparing with eigen value eqn.
 $\hat{A} \psi = a \psi$.

$$1. \text{ Energy operator } (\hat{E}) = \left(\frac{i\hbar}{m} \frac{d}{dt} \right)$$

Expectation value of E for a particle moving along x axis is given by,

$$\langle E \rangle \text{ or } \bar{E} = \int_{-\infty}^{\infty} \psi^* \hat{E} \psi dx$$

$$\int_{-\infty}^{\infty} \psi^* \psi dx$$

for normalized wave,

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

$$\therefore \langle E \rangle \text{ or } \bar{E} = \int_{-\infty}^{\infty} \psi^* \hat{E} \psi dx$$

$$= \int_{-\infty}^{\infty} \psi^* \left(i \frac{\hbar}{m} \frac{d\psi}{dt} \right) dx$$

$$= \int_{-\infty}^{\infty} \psi^* \left(i \frac{\hbar}{m} \frac{d\psi}{dt} \right) dx$$

$$= \int_{-\infty}^{\infty} \psi^* \left(i \frac{\hbar}{m} \frac{d\psi}{dt} \right) dx$$

$$= E \int_{-\infty}^{\infty} \psi^* \psi dx$$

$$\boxed{\therefore \langle E \rangle \text{ or } \bar{E} = E}$$

Expectation value of energy is energy itself.

~~VI~~

~~Application of Schrodinger Theory.~~

Show that the energy of an electron that is confined in an infinite potential well is quantized, and hence determine normalized wave function of an electron confined in an infinite potential well.

→ Let us consider a particle (electron) in an infinitely deep potential well defined by

$$V=0 \text{ for } 0 < n < \infty$$

$$V=\infty \text{ for } n < 0 \text{ & } n > \infty.$$

Now,

general time independent ^{V=0 n=1} electron in an infinitely deep potential well Schrodinger wave equation:

$$\frac{d^2\psi}{dn^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \text{--- (1)}$$

For electron inside well, $V=0$

$$\frac{d^2\psi}{dn^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \text{--- (ii)}$$

we have,

$$E - \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad [\because p = \hbar k]$$

$$\text{or, } k^2 = \frac{2mE}{\hbar^2}$$

Now, Substituting in eqn ⁽ⁱ⁾

$$\frac{d^2\psi}{dn^2} + k^2 \psi = 0 \quad \text{--- (iii)}$$

The solution of above differential equation is

$$\psi(n) = A \sin kn + B \cos kn \quad \text{--- (iv)}$$

where, A & B are constants that we have to calculate using boundary conditions.

Since the particle is confined within the well, the probability of finding the particle outside the wall or across the wall = 0, then we have following b.c's,

$$\psi(n)=0 \text{ when } n=0 \quad \text{--- (v)}$$

$$\psi(n)=0 \text{ when } n=L \quad \text{--- (vi)}$$

Using b.c's (v) in (iv),

$$\psi(0) := 0$$

$$\text{or, } A \sin k \times 0 + B \cos k \times 0 = 0$$

$$\text{or, } B \cos 0 = 0$$

$$\text{since } \cos 0 = 1$$

$$\text{Now, } \therefore B = 0.$$

$$\psi(n) = A \sin kn \quad \text{--- (vii)}$$

Applying b.c's (vi) in (vii)

$$\psi(L) = 0$$

$$\text{or, } A \sin kL = 0$$

$$\text{since } A \neq 0,$$

$$\sin kL = 0$$

$$\sin kL = \sin n\pi$$

$$\therefore kL = n\pi$$

$$\therefore k = \frac{n\pi}{L}$$

$$\begin{aligned}
 \text{we have, } E &= \frac{\hbar^2 k^2}{2m} \\
 &= \frac{\hbar^2 (n\pi)^2}{2m} \\
 &= \frac{\hbar^2 \cdot n^2 \pi^2}{2m} \\
 &\quad - \frac{n^2 h^2}{8mL^2}
 \end{aligned}$$

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

viii

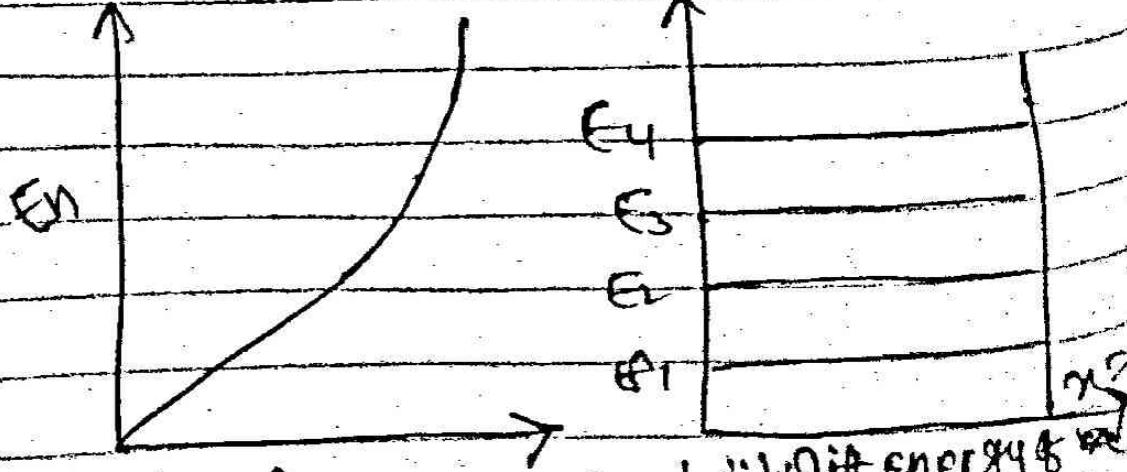
\therefore The energy eigen value of electron
in well are,

$$E_1 = \frac{h^2}{8mL^2}, E_2 = \frac{4h^2}{8mL^2}$$

$$\therefore E \propto n^2$$

\therefore The energy eigen value of electron
in infinite potential well is quantized.
is proportional to n^2 .

E



(i) Graph representing
reln b/w E_n & n

(ii) Diff energy of
electron in infinite
pot well.

Hence normalized wave function

$$f_n(r,n) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}r\right)$$

Q.1 Write radial part of Schrodinger equation for a spherically symmetric system. Explain the quantization of angular momentum of electron in the hydrogen atom.

→ The hydrogen atom consist of negatively charged electron moving around the positively charged nucleus. Electron is moving around the electric field of proton describe by columb potential.

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} \quad (\text{SI unit})$$

$$V(r) = \frac{-e^2}{r} \quad (\text{CGS unit})$$

It is two body problem but the mass of electron is neglected in comparison to proton.

The time independent schrodinger wave equation

$$\frac{d^2\psi}{dr^2} + \frac{2m(E-V)}{\hbar^2}\psi = 0$$

In 3-D

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

ψ is probability or
concentration.

$\Psi \rightarrow$ depends on
both initial & position.

where $\Delta \nabla^2 =$ laplacian operator
 $= \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right)$

$\psi = \psi(x, y, z)$ is cartesian co-ordinate system.

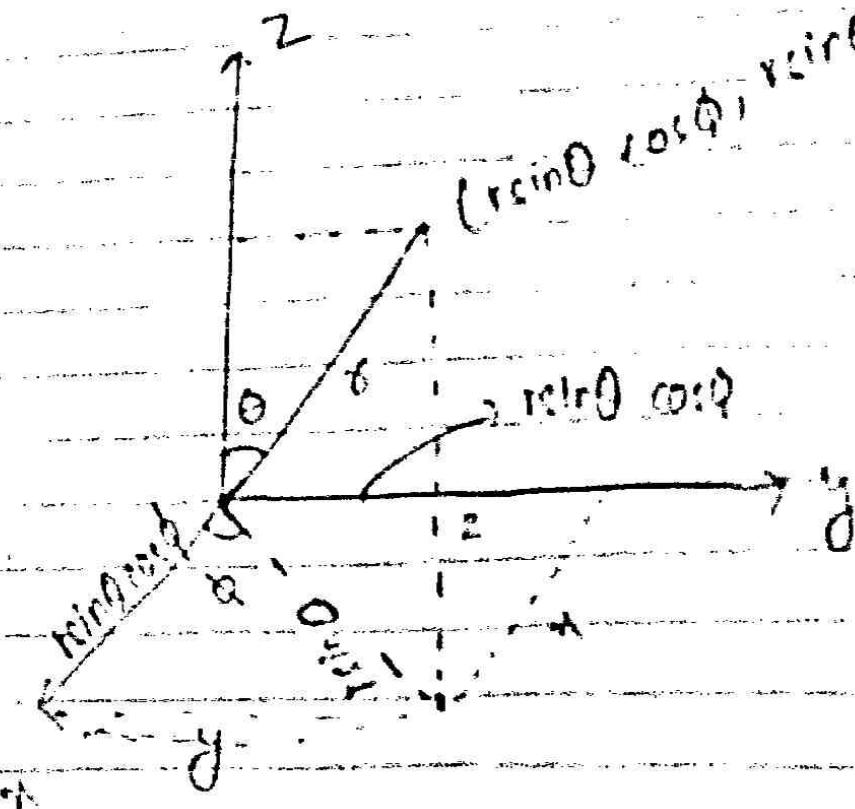
It is more easy to solve the problem in spherical polar co-ordinates system. The spherical polar co-ordinates are (r, θ, ϕ) .

Now, (x, y, z) related to (r, θ, ϕ) is

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

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

$$z = r \cos \theta$$



The Schrödinger's wave equation in spherical polar co-ordinate system is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} \left[E - V(r) \right] \psi = 0 \quad (i)$$

equation (i) can be solved by method of separation of variables.

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

where, $R(r)$ = Function of r only

$\Theta(\theta)$ = Function of θ only

$\Phi(\phi)$ = Function of ϕ only.

Using (ii) in (i) we get.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V(r)] R \Theta \Phi = 0 \quad (iii)$$

Multiplying (iii) by $\frac{r^2 \sin^2 \theta}{R \Theta \Phi}$ & replacing the partial derivative by total derivative.

$$\text{Or, } \frac{R^2 \sin^2 \theta}{r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2m}{\hbar^2} \left[E - V(r) \right] R \Theta \Phi = 0 \quad (iv)$$

$$+ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + \frac{2m}{\hbar^2} [E - V(r)] r^2 \sin^2 \theta = 0.$$

$$\text{or, } \frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\theta} \frac{d\theta}{d\phi} \left(\frac{\sin \theta}{\theta} \frac{d\theta}{d\phi} \right) + \frac{2m}{\hbar^2} [E - V(r)] r^2 \sin^2 \theta = - \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}$$

The L.H.S of equation \textcircled{v} is dependent on R & θ
 but the R.H.S of equation \textcircled{v} is dependent on
 Φ only.

Thus, they separately equal to some
 constants

i.e m_1^2 which is called magnetic
 orbital quantum number.

$$\therefore - \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_1^2$$

$$\text{or, } \frac{d^2 \Phi}{d\phi^2} = m_1^2 \Phi$$

$$\text{or, } \frac{d^2 \Phi}{d\phi^2} + m_1^2 \Phi = 0$$

it is called Azimuthal
 quantum number equation.

$$m\ddot{r} = \frac{\sin^2\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\theta}{d\phi} \right)$$

$$\rightarrow \frac{2m}{\hbar^2} [E - V(r)] r^2 \sin^2\theta = m\ddot{r}$$

vii.

Dividing egn (vii) by $\sin^2\theta$,

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] = \frac{m\ddot{r}}{\sin^2\theta} - \frac{1}{\theta \sin\theta} \frac{d\theta}{d\phi} \frac{d\phi}{d\theta}$$

Again, we obtain different variables appearing on each side.

Equating separately to $L(L+1)$ on each side,

$$\frac{m\ddot{r}}{\sin^2\theta} - \frac{1}{\theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\theta}{d\phi} \right) = L(L+1) \quad \text{--- (viii)}$$

It is called polar equation or θ equation,

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] = L(L+1)$$

It is called the radial equation. (ix)

Solution of azimuthal equation is

$$\Psi_m = Ae^{im\phi}$$

Since $\Psi(\theta, \phi, \psi)$ is single valued,

$\therefore \Phi_m$ must be single valued.
 \therefore When Φ increase by 2π radian
 $\Psi_m(\Phi)$ should have same value.

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

$$\text{or, } A e^{im\Phi} = A' e^{im(\Phi+2\pi)}$$

$$\text{or, } e^{im\Phi} = e^{im\Phi} \cdot e^{im2\pi}$$

$$\text{or, } e^{im2\pi} = 1$$

$$\text{or, } (\cos 2\pi m + i \sin 2\pi m) = 1 + i(0).$$

$$\therefore \cos(2\pi m) = 1 \quad \sin(2\pi m) = 0$$

$$\therefore m = 0, \pm 1, \pm 2, \pm 3, \dots$$

Thus Φ space is quantized.
 Thus constant m is called magnetic orbital quantum number.

Solving the polar equation (1), we get

$$L = 0, 1, 2, \dots$$

$$R \leq |m|$$

Again on solving the radial equation, we get
 the solution of R remain finite everywhere.

$$E_n = -\frac{z^2 \cdot me^4}{8\pi^2 h^2} \left(\frac{1}{n^2}\right) = -\frac{13.6}{n^2} \text{ eV}$$

for $n = 1, 2, 3, \dots$

$$g_n \geq (L+1)$$

This is in complete agreement with predictions of Bohr's theory (old quantum theory).

We arrived at a system of 3 quantum numbers for simple model of atom.
(Principal)

Total quantum number $n, n = 1, 2, 3, \dots$

Orbital quantum number $a_l = 0, 1, 2, \dots, n-1$

Magnetic orbital quantum number, $m_l, m_l = 0, \pm 1, \pm 2, \dots, \pm l$.

$$\text{Or, } Ae^{im\phi} = A e^{im\theta}$$

Q8

What are the physical significance of quantum numbers used in hydrogen atom problem. Also Explain degeneracy with the example of hydrogen atom

→ first part

When we solve each three part of Schrodinger equation of hydrogen atom we get three quantum numbers n, l, m_l .

(i) Principal quantum number (n):-

On solving the radial equation, the well behaved finite and physically acceptable solution of $R(r)$ of r can only be obtained (or possible only if) n is an integer. (greater than 0)
 $\therefore E_n = \frac{-me^4}{2\pi^2 n^2} = -\frac{13.6}{n^2}$ ev
 energy.

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

$$l \leq (n-1)$$

thus, (n) physically signifies the quantization of energy.

(ii) Orbital quantum number (l):- The solution of polar equation is only possible for

shape $l = 0, 1, 2, \dots$

- magnitude The quantum number ' l ' is called orbital angular momentum quantum number.

It defines orbital angular momentum of electron given by $L = \vec{l} \cdot \vec{r} \times \vec{l} / \hbar$

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

The orbital quantum number also defines shape of orbit.

Semi-major axis of ellipse is

$$b_n = a_n l(l+1)^{\frac{1}{2}}$$

n

where $n = l(l+1)$, $b_n = a_n$, the orbit is circle

(III) Magnetic quantum number (m_l):
The solution of azimuthal equation
is only possible
if $m_l = 0, \pm 1, \pm 2, \pm 3, \dots$
we get $\Psi(\phi) = A e^{im_l \phi}$

An electron revolving about a nucleus is a current loop & has a magnetic field.

Let the uniform magnetic field of flux density B & having its directions parallel to z-axis.

The magnetic orbital quantum number (m_l) specifies the direction of L determining the component of L in $z\text{-axis}$.

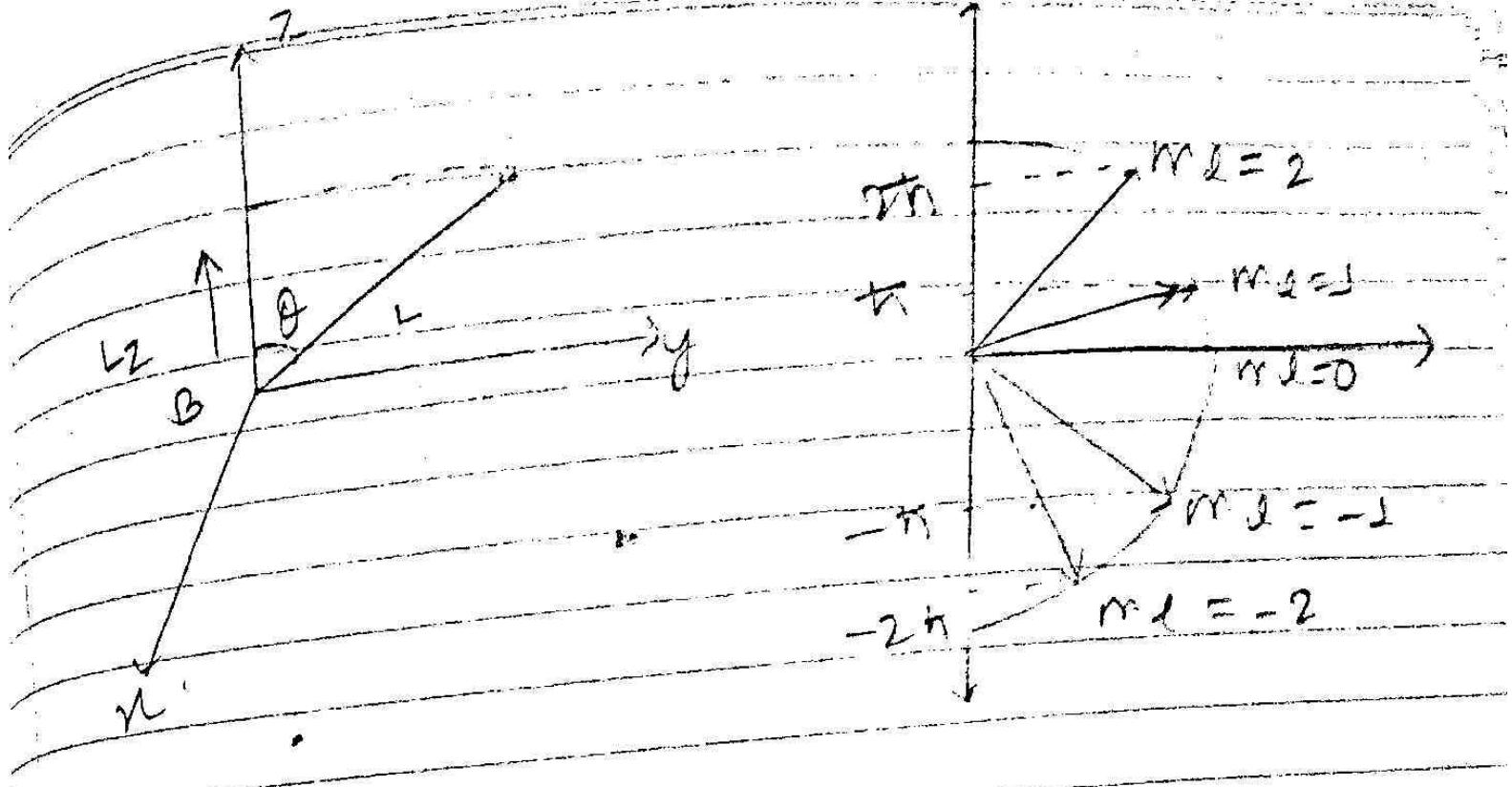
The component of L in $z\text{-axis}$ is also quantized.

$$\therefore L = m_l \hbar$$

Since for given value of ℓ there are $(2\ell+1)$ possible values of m_l .

The angular momentum vector L can have $(2\ell+1)$ discrete orientations with respect to magnetic field.

This quantization of orientation of atom is called space quantization or spatial quantization.



1) For $l=2$ orientation of angular momentum of electron.

Second part:-

The energy of hydrogen atom depends only on principal quantum number.

$$\therefore E_n = \frac{-13.6}{h^2} \text{ ev}$$

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

For a given value of n the possible values of orbital quantum number are,

$$l = 0, 1, 2, 3, \dots, (n-1)$$

Similarly for one value of l , the possible value of m_l is $(2l+1)$.

Thus, it is possible to have different state of electron having same energy. The phenomenon in which there are a number

of independent quantum states of a system
each belonging to same energy level
is called degeneracy.

An energy level which contains
more than one independent state is called
degenerate energy level & total number of
independent quantum states is called degree
of degeneracy of energy level.
 Ψ_{nlm} be wave function of hydrogen
atom.

If $n=1$, $l=0$ & $m=0$:
 $\therefore \Psi_{100}$ is only one stat.

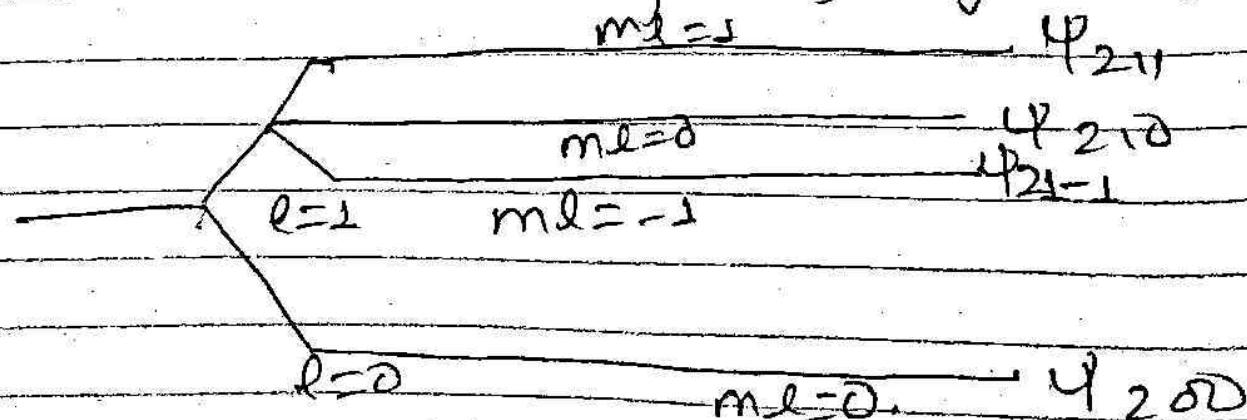
If $n=2$, $l=0, 1$

for $l=0$, $m=0$, Ψ_{200}

for $l=1$, $m=-1, 0, +1$.

i.e. Ψ_{2-1} , Ψ_{20} , Ψ_{2+1}

\therefore we have 4 fold degeneracy.



$n=2$ $l=0$ $m_l=0$ Ψ_{100}

(i) Degenerate energy level,

A state of energy E_n is said to be degenerated if there are two or more than two eigen functions corresponding to same energy.

Degree of degeneracy is given by n^2 .

Q9 Derive an expression for total energy of an electron revolving around the nucleus in an external magnetic field. Explain Pt.
(OR)

How Zeeman effect demonstrate the idea of space quantization.

→ Let an electron of mass 'm' revolving around the nucleus with velocity 'v' in a circular orbit of radius 'r'.

Magnetic dipole moment associated with it is called orbital magnetic dipole moment.

H_o

$$\therefore \text{H}_o = IA \quad \text{--- (i)}$$

where $I = \text{convention current}$
whose drxn is oppn to flow p

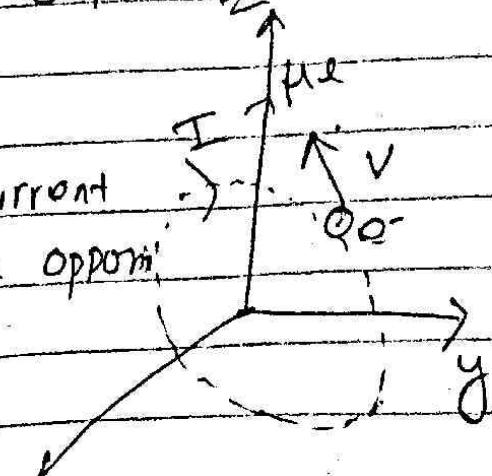
$$A = \text{Area of loop.}$$

we have,

$$\text{current}(I) = \frac{q}{t}$$

$$= \frac{|e|}{\left(\frac{2\pi r}{V}\right)} \quad [\because t = \frac{2\pi r}{V}].$$

Fig(i)



$$\therefore I = \frac{1e|v}{2\pi r} \quad \text{--- (ii)}$$

From eqn (ii),

$$H_2 = \frac{1ev}{2\pi r} \times A$$

$$= \frac{1ev}{2\pi r} \times \pi r^2$$

$$= \frac{1elvr}{2}$$

$$H_2 = \frac{1elmr}{2m}$$

$$H_2 = \frac{1elL}{2m}$$

$$\therefore H_2 = -\frac{1elL}{2m} \quad \text{--- (iii)}$$

where -ve sign signifies the direction of current is opposite to motion of current and drxn of L too.

Now, if external magnetic field is applied then electron will experience torque.

$$\vec{\tau} = \vec{H}_2 \times \vec{B}$$

(iv)

$$\therefore |\vec{\tau}| = H_2 B \sin \theta \quad \text{--- (v)}$$

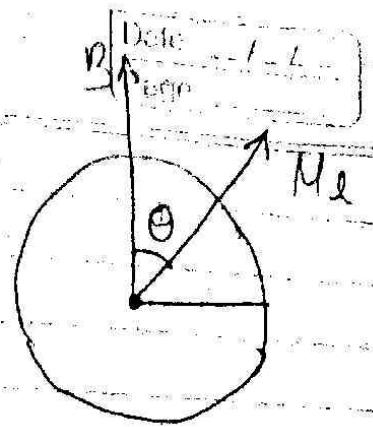
where θ is angle between H_2 & B .

From (v), if $\theta = 0$, i.e. He is parallel to B.

$$C = 0$$

If $\theta = 90^\circ$, i.e. He is perpendicular to B.

$$C_{\text{max}} = \mu_e B$$



Similarly, the associated potential energy that depends on orientation of He & B is given by.

$$E_p = -\vec{\mu}_e \cdot \vec{B}$$

$$E_p = \left[\frac{-|e|}{2m} \right] \vec{L} \cdot \vec{B}$$

$$= \frac{|e|}{2m} \vec{L} \cdot \vec{B}$$

$$= \frac{|e|}{2m} BL \cos \theta$$

$$E_p = \frac{|e|}{2m} BL_z$$

$$\text{where } L_z = L \cos \theta$$

It is seen that the total energy is the sum of:-

(i) Energy resulting from interaction of electron with nucleus E_n .

(ii) Energy resulting from interaction of magnetic dipole moment with external magnetic

field (B)

$$\therefore E_{\text{total}} = E_n + E_p \\ = E_n + \frac{1}{2m} e B L_z$$

we have,

$$L_z = m_s \hbar$$

$$E_{\text{total}} = E_n + \frac{1}{2m} e B m_s \hbar$$

VII

which is the required expression for total energy of electron in the presence of external magnetic field.

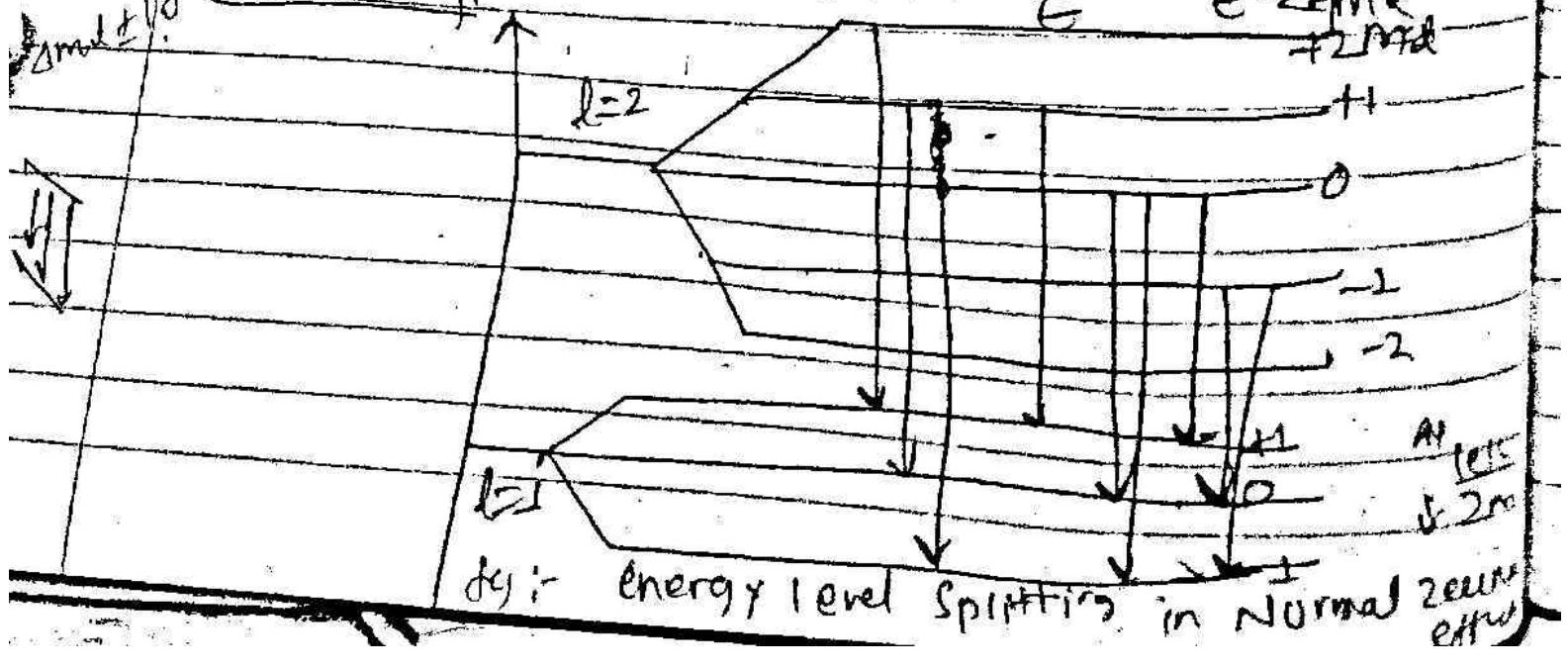
As m_s takes $0, \pm 1, \pm 2, \dots, \pm l$.

The energy levels of quantum states with orbital quantum number splits into several discrete sub levels as shown in figure. This effect of splitting of spectral lines due to presence of external magnetic field is called normal Zeeman effect.

$E + \Delta E$

$E - \Delta E$

$\pm 2m_s \hbar$



for $n=3$, $\ell=0, 1, 2$ - studying without presence of external magnetic field, there is no spectral lines.

But in presence of magnetic field there is energy gap between adjacent level i.e $\frac{eB}{2m}$ independent of ℓ .

Applying selection rule $\Delta m_l = 0, \pm 1$, restricts the number of possible lines. The line transition consistent with selection rule give only 3 diff. energies.

(D) Obtains an expression for the force experienced by an electron revolving around the nucleus in the presence of magnetic field gradient.

(OR)

Explain how Stern-Gerlach experiment describes the space quantization of spin angular momentum.

If a magnetic dipole is placed in uniform (constant) magnetic field, then it experiences torque.

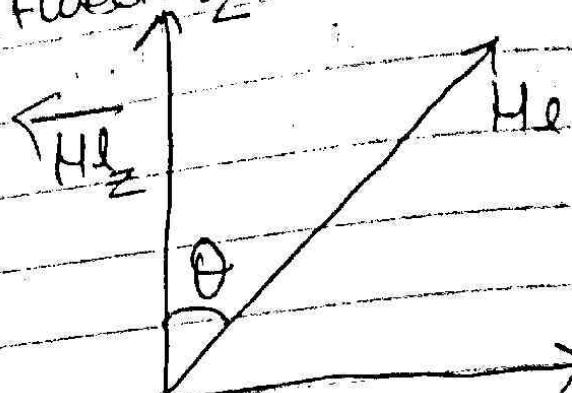
If field is not uniform (constant) the dipole will also experience net force.

Let us consider a magnetic field gradient $\left(\frac{dB}{dz}\right)$ is applied along z -axis, the force on magnetic dipole will be directed along z -axis.

$$\text{Magnitude of force, } F_z = \mu_0 \frac{dB}{dz} = \mu_0 \frac{dB}{dz} \cos \theta$$

where, θ is the angle between \vec{B} and \vec{H}_z

$$\therefore F_z = \frac{dB}{dz} (\mu_0 \cos \theta)$$



we have, $\vec{H}_z = -\frac{|e|}{2m} \vec{L}_z$ (Orientation of magnetic dipole in the presence of a homogenous magnetic field.)

$$\therefore F_z = -\frac{|e|}{2m} L_z \frac{dB}{dz}$$

Classically L_z varies from L & $-L$.

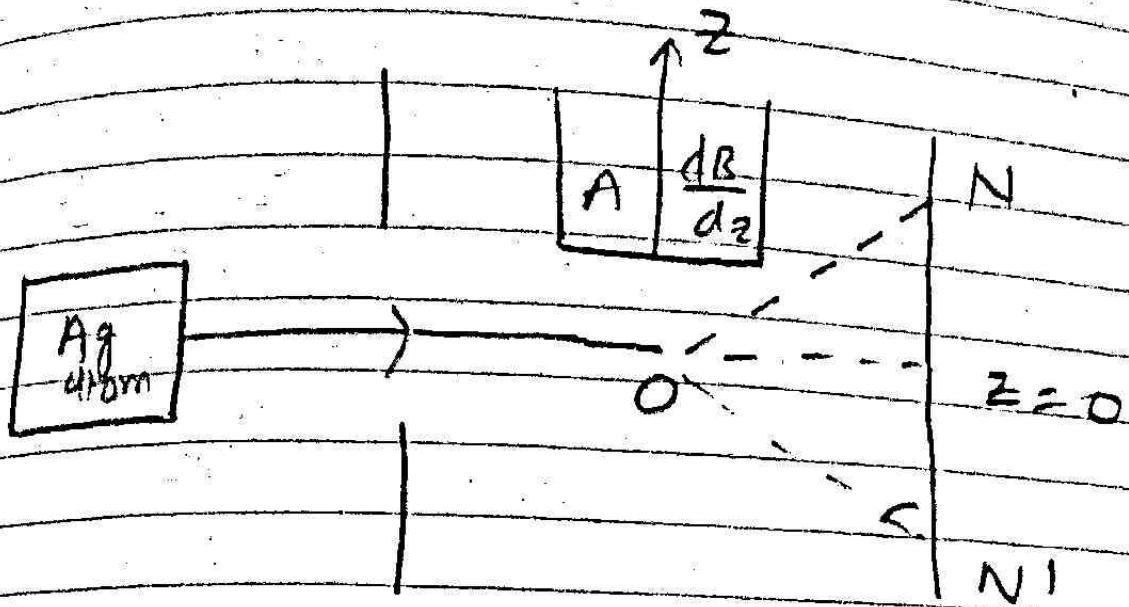
\therefore force has two extreme values.

$$\therefore F_z = \frac{|e|}{2m} L \frac{dB}{dz} \quad (i)$$

$$\therefore F_z = -\frac{|e|}{2m} L \frac{dB}{dz} \quad (ii)$$

Experimental verification.

Date / /
Page



fig(i) Stern-Gerlach screen.
experiment

This is the required expression for force experienced by an electron revolving around the nucleus in the presence of magnetic field gradient.

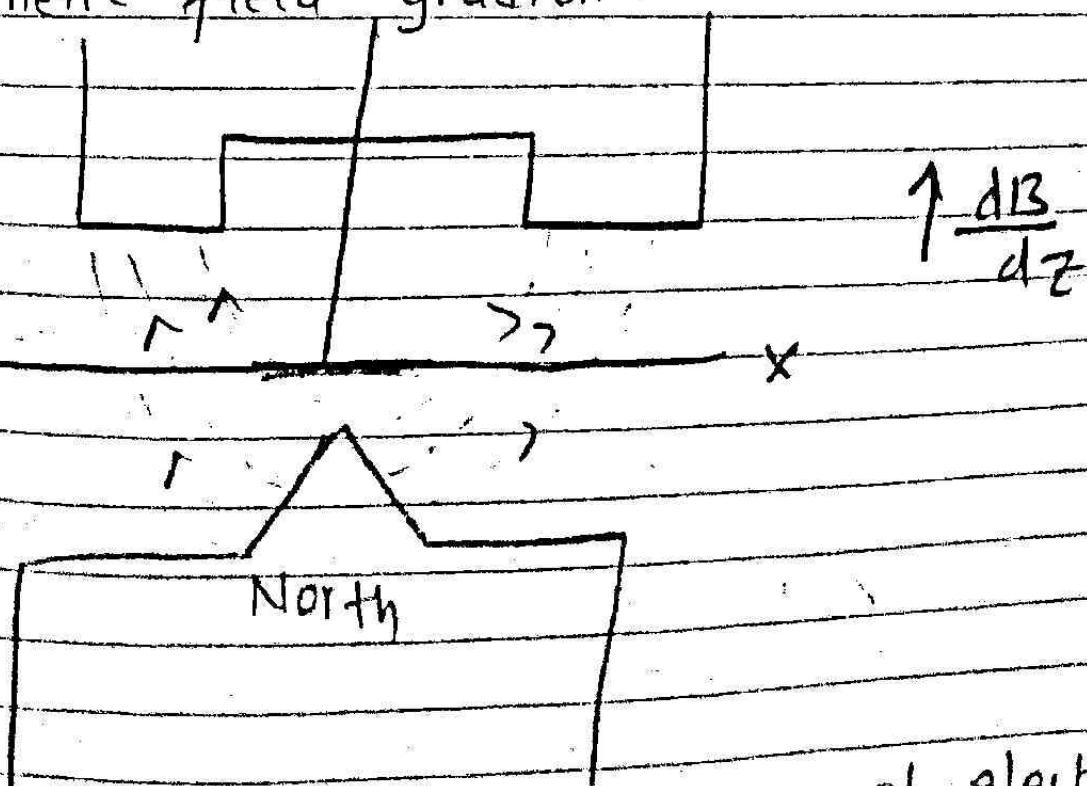


fig:- cross-section view of electromagnet

Stern and Gerlach form and experiment perform in 1921 and demon stated the space quantization of spin angular momentum of an electron.

The experiment consist of silver atoms in a furnace A, which heated to high temperature. Silver atoms leave through a small opening and propagate in the straight line in high vacuum which exist in the whole apparatus.

During the process silver atom sees non-uniform magnetic field having magnetic field gradient $\frac{dB}{dz}$ along z direction as shown in fig. dz

Silver atoms were collected on screen. Silver atoms are uncharge but as para-magnetic substance has magnetic dipole. The only force acting on them is the one resulting from inhomogeneity of magnetic field.

The stronger force (F_z), the more the atomic dipole will be deflected through the magnet.

When, $B=0$ a thin straight line trace obtain on screen as zero field pattern.

When $B \neq 0$, the trace is divided into two lines.

Classically the force varies continuously between two values.

For silver atom the outermost electron $p_s \ 2S_{1/2}$ i.e. $l=0$.

$$\text{thus, } H_0 = \frac{|e|L}{2m} = \frac{|e|l + \sqrt{e(l^2+1)}}{2m} = 0.$$

Thus it proves the electron of silver atom has only the spin magnetic dipole moment μ_s . This leads to the space quantization of the spin angular momentum.

Q1. Define electronic spin. Describe the atomic wave function and its importance in quantum mechanics.

→

An electron in an atom can be regarded as charged sphere rotating or spinning about an axis through its centre of mass it is called electronic spinning motion. Moreover, this spinning motion causes atom to have intrinsic spin angular momentum 's' and an intrinsic spin magnetic dipole moment ' H_s '.

$$M_s = \frac{-e h}{2m}$$

Analog with L.

$$S = \hbar \sqrt{s(s+1)} \text{ where } s = \frac{1}{2}$$

$$S_z = m_s \hbar \text{ where } m_s = \pm \frac{1}{2}$$

Second part

Atomic wave functions:

It is the solution of Schrödinger's equation which describes the wave-like behaviour of one electron or pair of electrons.

If it is used in quantum mechanics to find probability of finding any electron of an atom in a specific region around the atomic nucleus.

The wave function in spherical polar co-ordinate system is given by

$$\psi_{nlm}(r, \theta, \phi) = R_n(r) \Theta_{ml}(\theta) \cdot \Phi_{mlm}(\phi) \quad \text{①}$$

The probability density $P(r, \theta, \phi)$ of electron at a point (r, θ, ϕ) is defined as probability of finding the electron in a unit volume around a

given point:

$$P(r, \theta, \phi) = \psi \psi^*$$

$$= |\psi|^2$$

$$= R(r) R^*(r) \theta(\theta) \theta'(\theta) \Phi(\phi) \Phi^*(\phi)$$

$$= |R(r)|^2 |\theta(\theta)|^2 |\Phi(\phi)|^2$$

From the solution, of

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\Phi_m(\theta) \cdot \Phi_{m'}(\theta) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \times \frac{1}{\sqrt{2\pi}} e^{-im\phi}$$

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

$$\therefore P(r, \theta, \phi) = \frac{1}{2\pi} |R(r)|^2 |\theta(\theta)|^2 \quad (1)$$

It is seen that probability density is independent of azimuthal (0-ordinate). It means that electron distribution is symmetric about z-axis. Now, the probability of finding an electron in a small volume is,

$$P(r, \theta, \phi) dv = |\psi(r, \theta, \phi)|^2 dv$$

In spherical polar co-ordinate system
 $dv = r^2 dr \sin \theta d\theta d\phi$.

$$\therefore P(r, \theta, \phi) dv = |\psi(r, \theta, \phi)|^2 r^2 dr \sin\theta d\theta d\phi$$

The probability of finding the electron between r and $r+dr$ can be obtained by integrating above eqn with θ and ϕ .

$$P(r) dr = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta |\psi(r, \theta, \phi)|^2 dr$$

If it is seen that $P(r)$ varies with the distance from nucleus ' r ', with a maximum at a certain ' r ' values that depend on particular wave function.