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Name of Paper : Quantum Mechanics and Applications
Name of Course : B.Sc. (Hons.) Physics
Semester : V
Duration : 3 hours
Maximum Marks : 75

Solved Paper - 2018

1. Attempt any *five* of the following:

(a) State linearity and superposition principle.

(b) Prove that:

$$[x^n, \hat{p}] = -in\hbar x^{n-1}.$$

(c) What are stationary states? Why are they called so?

(d) What are the conditions for a wavefunction to be physically acceptable?

(e) What do you mean by space quantization? Explain.

(f) Write the quantum numbers for the state represented by:

$$3^2 D_{3/2}.$$

(g) Define group velocity and phase velocity.

5×3=15

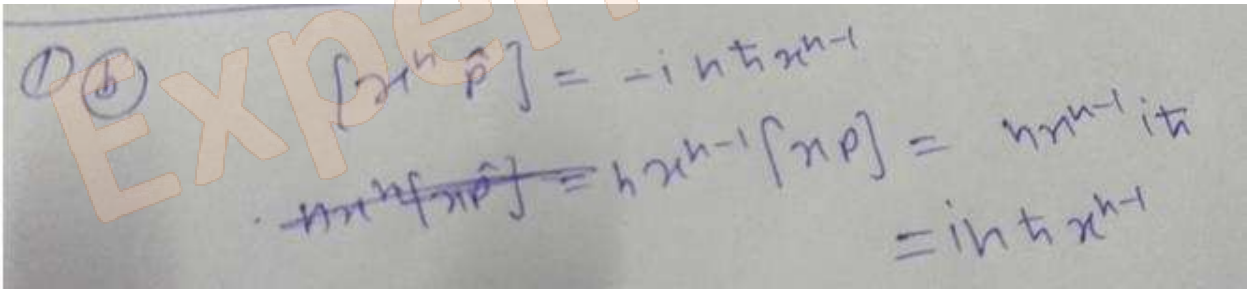
Ans. 1 (a).Linearity – It is defined as the property by virtue of which different states of quantum mechanical system function can be added together to create an additional state. This third edition treats first-order linearequations using the linearity principle and the extended linearity principle. The superposition principle states that a quantum mechanical system in different states describable by the wave functions $\psi_1, \psi_2, \ldots, \psi_n$, can be describe as the superposition of these states. The superposition is the state represented by the wavefunction

$$\psi = c_1\psi_1 + c_2\psi_2 \ldots + c_n\psi_n$$

where $c_1, c_2, \ldots, c_n$ are arbitrary complex numbers.

The states of a quantum
mechanical system should be represented by vectors in a linear space; in particular,by wave functions and that the operators of physical quantities must be linear. It follows from the superposition principle that any wave function can be expanded into a sum of
the eigenfunctions of the operator of any physical quantity.

1 (b)



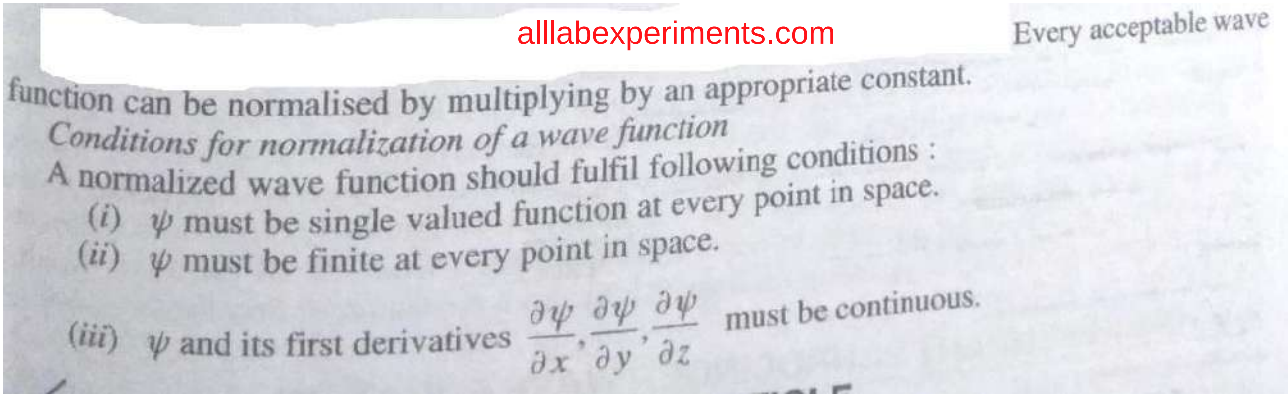
① ⓑ $[x^n, \hat{p}] = -i n \hbar x^{n-1}$

~~$n x^{n}[x\hat{p}]$~~ $= n x^{n-1}[x p] = n x^{n-1} i\hbar$

$= i n \hbar x^{n-1}$

1(c). Stationary state is a quantum mechanical state with all observables independent of time, it is an eigenvector of Hamiltonian. It is called stationary because the system remain in same state as time elapses, in every observable way, for a single particle Hamiltonian. This means that particle has a constant probability distribution for its position, velocity and spin etc.

1 (d).



Every acceptable wave function can be normalised by multiplying by an appropriate constant.

Conditions for normalization of a wave function

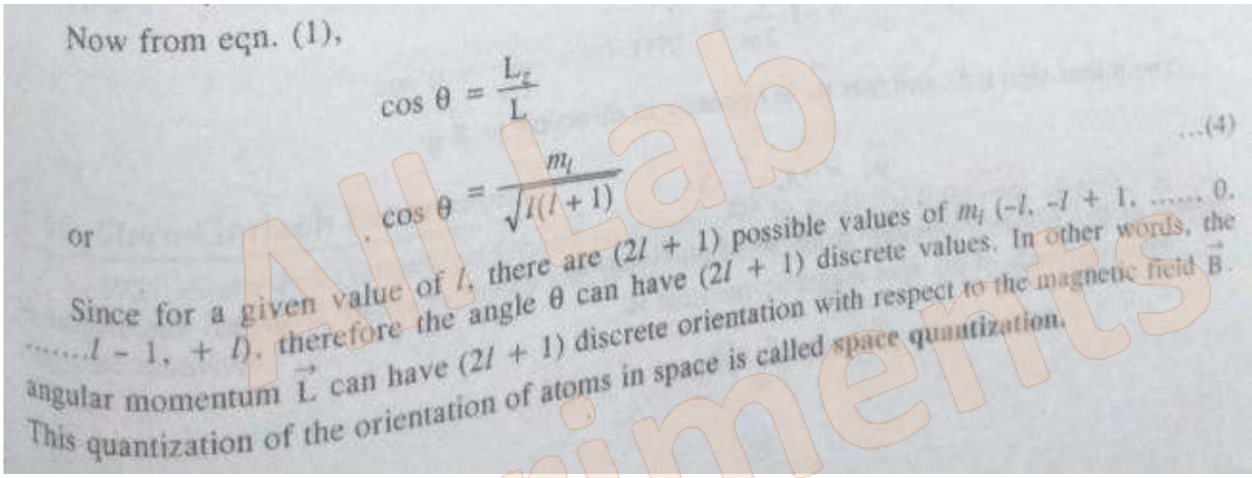
A normalized wave function should fulfil following conditions :

(*i*) ψ must be single valued function at every point in space.

(*ii*) ψ must be finite at every point in space.

(*iii*) ψ and its first derivatives $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ must be continuous.

1 (e).



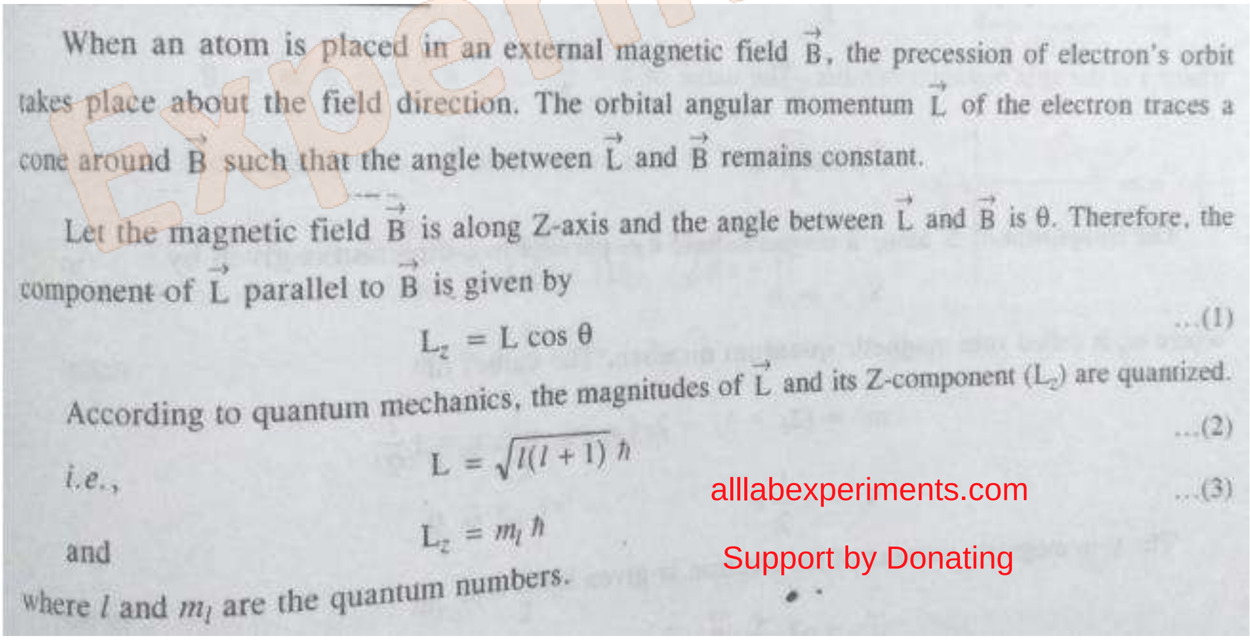
Now from eqn. (1),

$$\cos\theta = \frac{L_z}{L}$$

or

$$\cos\theta = \frac{m_l}{\sqrt{l(l+1)}} \qquad ...(4)$$

Since for a given value of l, there are $(2l + 1)$ possible values of m_l $(-l, -l + 1, ..., 0, ...l - 1, + l)$, therefore the angle θ can have $(2l + 1)$ discrete values. In other words, the angular momentum $\vec{L}$ can have $(2l + 1)$ discrete orientation with respect to the magnetic field $\vec{B}$. This quantization of the orientation of atoms in space is called space quantization.



When an atom is placed in an external magnetic field $\vec{B}$, the precession of electron's orbit takes place about the field direction. The orbital angular momentum $\vec{L}$ of the electron traces a cone around $\vec{B}$ such that the angle between $\vec{L}$ and $\vec{B}$ remains constant.

Let the magnetic field $\vec{B}$ is along Z-axis and the angle between $\vec{L}$ and $\vec{B}$ is θ. Therefore, the component of $\vec{L}$ parallel to $\vec{B}$ is given by

$$L_z = L\cos\theta \qquad ...(1)$$

According to quantum mechanics, the magnitudes of $\vec{L}$ and its Z-component (L_z) are quantized.

i.e.,

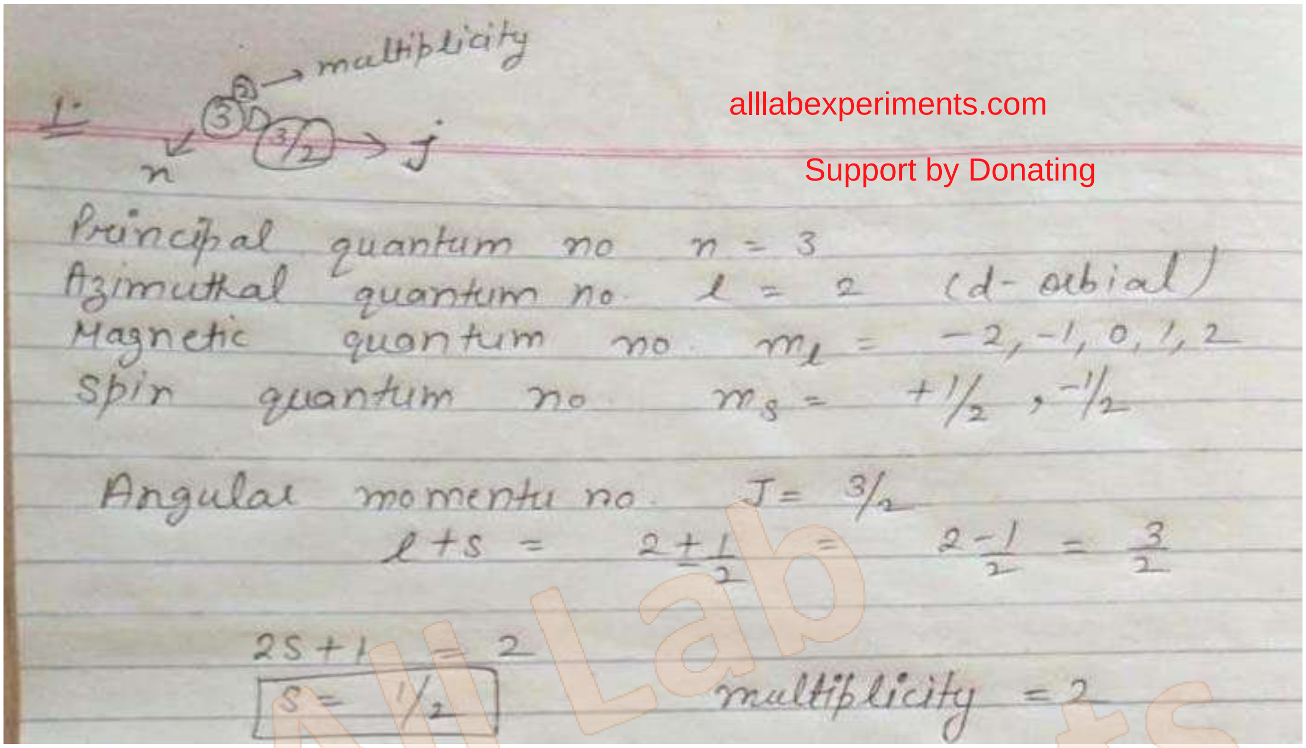
$$L = \sqrt{l(l+1)}\,\hbar \qquad ...(2)$$

and

$$L_z = m_l\,\hbar \qquad ...(3)$$

where l and m_l are the quantum numbers.

1(f)



1.

$$\underset{n}{\boxed{3}}\;{}^{\boxed{2}\rightarrow \text{multiplicity}}D_{\boxed{3/2}\rightarrow j}$$

Principal quantum no $n = 3$

Azimuthal quantum no $l = 2$ (d-orbial)

Magnetic quantum no $m_l = -2, -1, 0, 1, 2$

Spin quantum no $m_s = +1/2 , -1/2$

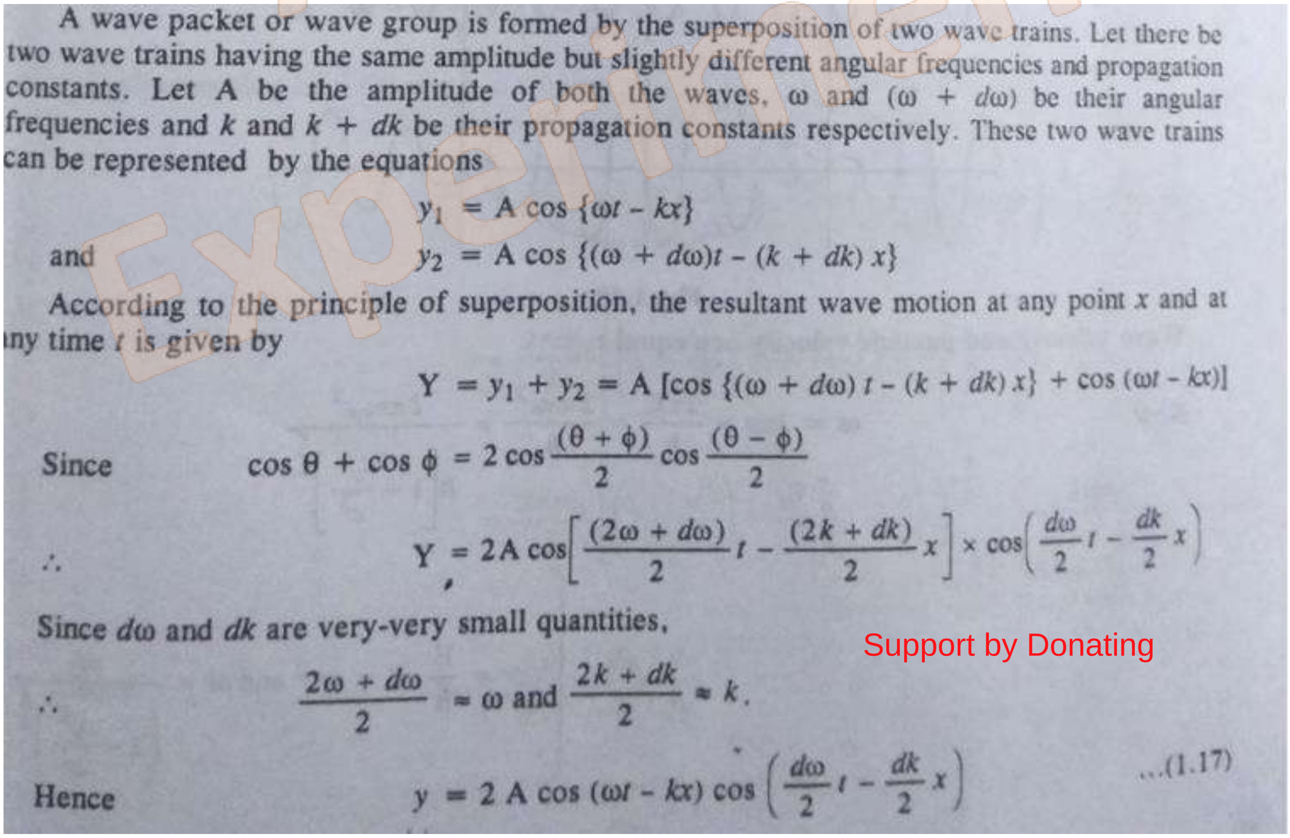
Angular momentu no $J = 3/2$

$$l + s = 2 + \frac{1}{2} = 2 - \frac{1}{2} = \frac{3}{2}$$

$$2S + 1 = 2$$

$\boxed{S = 1/2}$ multiplicity $= 2$

1(g)



A wave packet or wave group is formed by the superposition of two wave trains. Let there be two wave trains having the same amplitude but slightly different angular frequencies and propagation constants. Let A be the amplitude of both the waves, ω and (ω + dω) be their angular frequencies and k and $k + dk$ be their propagation constants respectively. These two wave trains can be represented by the equations

$$y_1 = A\cos\{\omega t - kx\}$$

and

$$y_2 = A\cos\{(\omega + d\omega)t - (k + dk)x\}$$

According to the principle of superposition, the resultant wave motion at any point x and at any time t is given by

$$Y = y_1 + y_2 = A\left[\cos\{(\omega + d\omega)t - (k + dk)x\} + \cos(\omega t - kx)\right]$$

Since $$\cos\theta + \cos\phi = 2\cos\frac{(\theta + \phi)}{2}\cos\frac{(\theta - \phi)}{2}$$

$$\therefore \quad Y = 2A\cos\left[\frac{(2\omega + d\omega)}{2}t - \frac{(2k + dk)}{2}x\right] \times \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$$

Since $d\omega$ and dk are very-very small quantities,

$$\therefore \quad \frac{2\omega + d\omega}{2} = \omega \text{ and } \frac{2k + dk}{2} \approx k.$$

Hence $$y = 2A\cos(\omega t - kx)\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \qquad \text{...(1.17)}$$

Eqn. (1.17) is the equation of motion of the wave of angular frequency ω and propagation constant k that has superimposed upon it a modulation of angular frequency $d\omega/2$ and propagation constant $dk/2$. This modulation produces successive wave groups as shown in fig. 1.19.

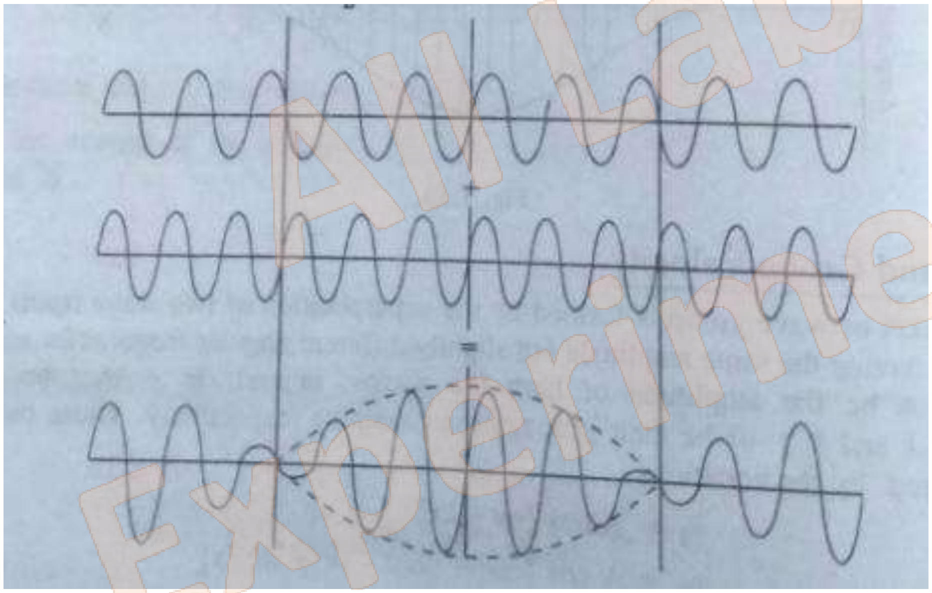
The *phase velocity* or *wave velocity* v_p *is given by*

$$v_p = \nu\lambda = \frac{2\pi\nu}{\left(\frac{2\pi}{\lambda}\right)} = \frac{\omega}{k} \qquad \text{...(1.18)}$$

where $k = \frac{2\pi}{\lambda}$.

and the *group velocity* of the group of waves is given by

$$v_g = \frac{\frac{d\omega}{2}}{\frac{dk}{2}} = \frac{d\omega}{dk} \qquad \text{...(1.19}$$



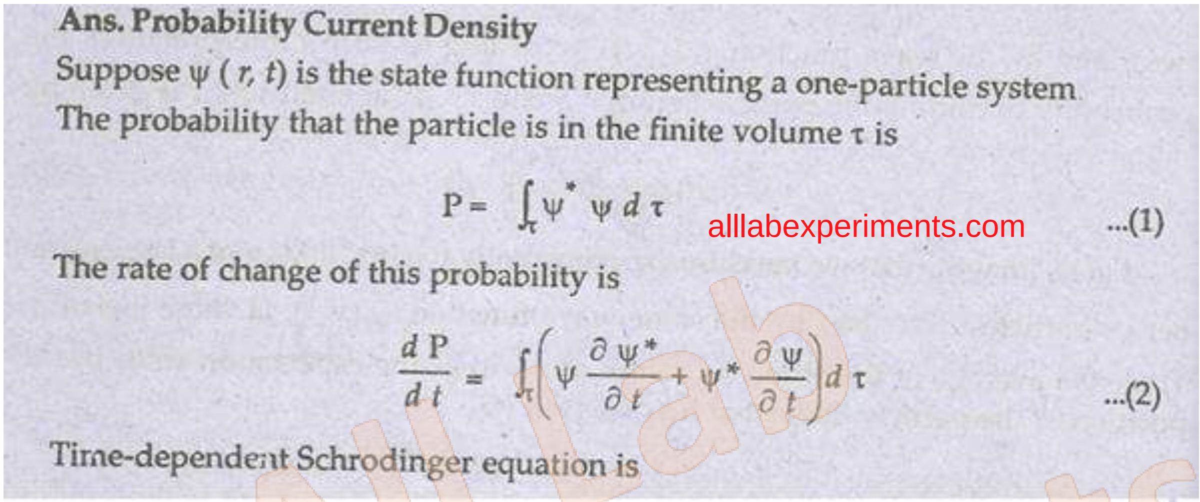
2. (a) Set up the time dependent Schrödinger equation and hence derive the time independent Schrödinger equation.

(b) Derive the expressions for probability density and probability current densities in three dimensions and hence derive the equation of continuity. 7,8

Q 2a Ans.

Find the solution to this question in the book.

2(b)



Ans. Probability Current Density

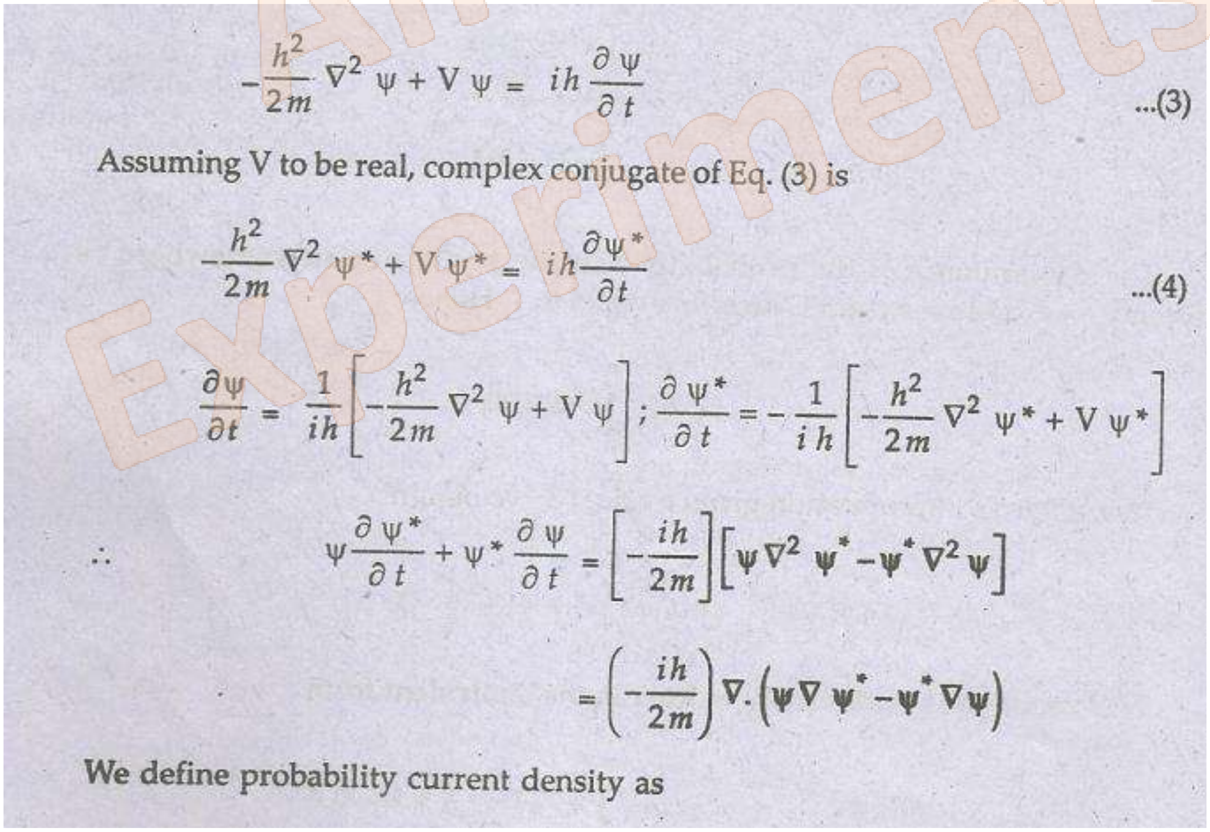
Suppose $\psi\ (r, t)$ is the state function representing a one-particle system. The probability that the particle is in the finite volume τ is

$$P = \int_\tau \psi^* \psi \, d\tau \qquad \text{...(1)}$$

The rate of change of this probability is

$$\frac{dP}{dt} = \int_\tau \left(\psi \frac{\partial \psi^*}{\partial t} + \psi^* \frac{\partial \psi}{\partial t} \right) d\tau \qquad \text{...(2)}$$

Time-dependent Schrodinger equation is



$$-\frac{h^2}{2m} \nabla^2 \psi + V \psi = ih \frac{\partial \psi}{\partial t} \qquad \text{...(3)}$$

Assuming V to be real, complex conjugate of Eq. (3) is

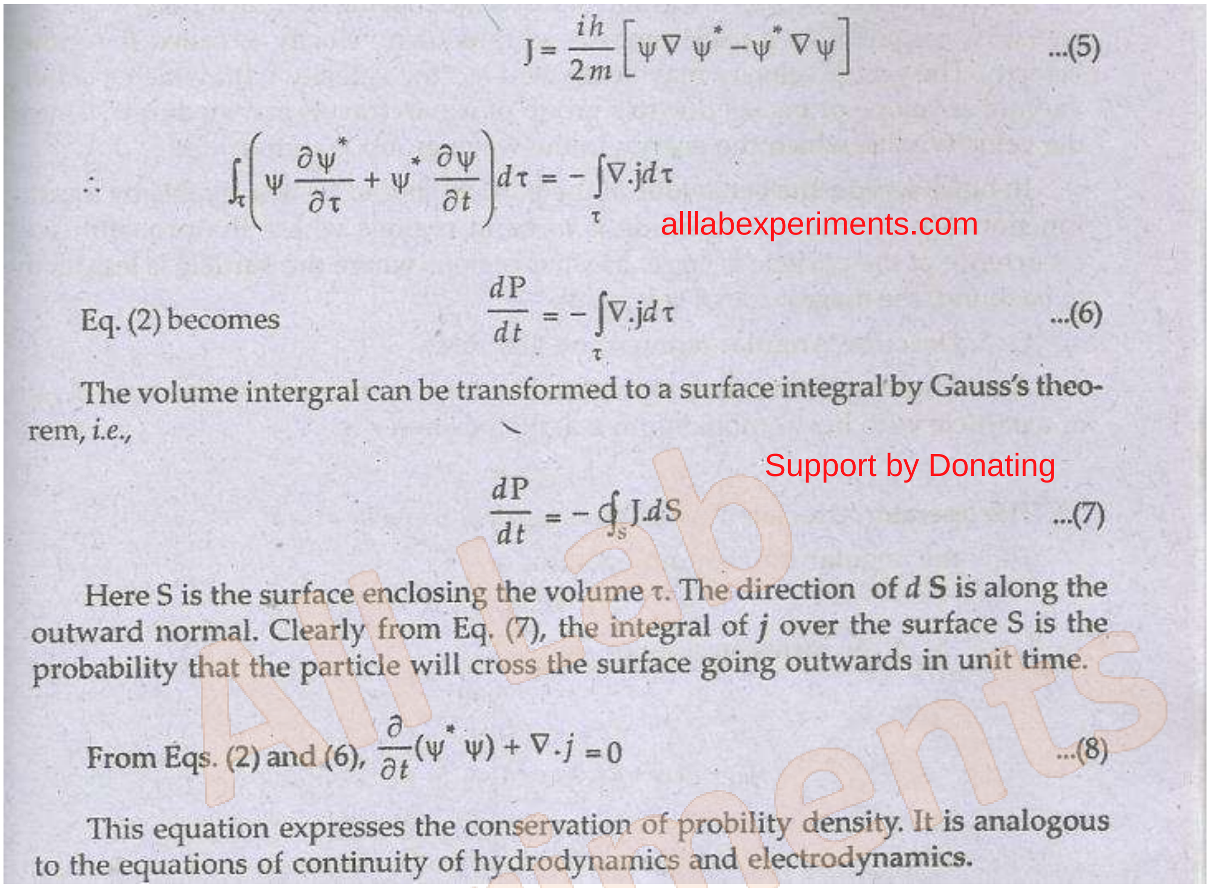
$$-\frac{h^2}{2m} \nabla^2 \psi^* + V \psi^* = ih \frac{\partial \psi^*}{\partial t} \qquad \text{...(4)}$$

$$\frac{\partial \psi}{\partial t} = \frac{1}{ih} \left[-\frac{h^2}{2m} \nabla^2 \psi + V \psi \right]; \quad \frac{\partial \psi^*}{\partial t} = -\frac{1}{ih} \left[-\frac{h^2}{2m} \nabla^2 \psi^* + V \psi^* \right]$$

$$\therefore \quad \psi \frac{\partial \psi^*}{\partial t} + \psi^* \frac{\partial \psi}{\partial t} = \left[-\frac{ih}{2m} \right] \left[\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi \right]$$

$$= \left(-\frac{ih}{2m} \right) \nabla . \left(\psi \nabla \psi^* - \psi^* \nabla \psi \right)$$

We define probability current density as



$$J = \frac{ih}{2m}\left[\psi\nabla\psi^* - \psi^*\nabla\psi\right] \qquad ...(5)$$

$$\therefore \quad \int_\tau\left(\psi\frac{\partial\psi^*}{\partial\tau} + \psi^*\frac{\partial\psi}{\partial t}\right)d\tau = -\int_\tau \nabla.j\,d\tau$$

Eq. (2) becomes $$\frac{dP}{dt} = -\int_\tau \nabla.j\,d\tau \qquad ...(6)$$

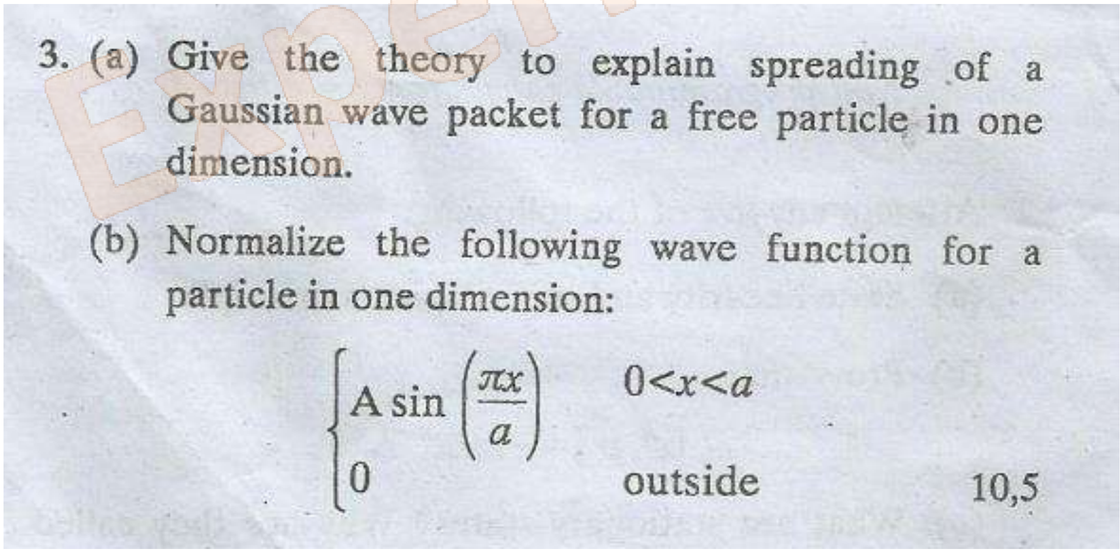
The volume intergral can be transformed to a surface integral by Gauss's theorem, *i.e.,*

$$\frac{dP}{dt} = -\oint_S J.dS \qquad ...(7)$$

Here S is the surface enclosing the volume τ. The direction of *d* S is along the outward normal. Clearly from Eq. (7), the integral of *j* over the surface S is the probability that the particle will cross the surface going outwards in unit time.

From Eqs. (2) and (6), $$\frac{\partial}{\partial t}(\psi^*\psi) + \nabla.j = 0 \qquad ...(8)$$

This equation expresses the conservation of probility density. It is analogous to the equations of continuity of hydrodynamics and electrodynamics.



3. (a) Give the theory to explain spreading of a Gaussian wave packet for a free particle in one dimension.

(b) Normalize the following wave function for a particle in one dimension:

$$\begin{cases} A\sin\left(\frac{\pi x}{a}\right) & 0<x<a \\ 0 & \text{outside} \end{cases}$$

10,5

Q 3a Ans. The solution to this question is in 2017 paper solution.

Q 3b

Solution.

The given function is

$$\psi(x) = \begin{cases} A\sin\dfrac{\pi x}{a} & \text{for } 0 < x < a \\ 0 & \text{outside} \end{cases}$$

The condition for normalization is

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

Here in this case, $$\int_{0}^{a} \psi^* \psi \, dx = 1$$

or $$\int_0^a A^* \sin\frac{\pi x}{a} \cdot A \sin\frac{\pi x}{a} \, dx = 1$$

Assuming that A is real, so we get

$$A^2 \int_0^a \sin^2\frac{\pi x}{a} dx = 1$$

or $$\frac{A^2}{2}\int_0^a \left(1 - \cos\frac{2\pi x}{a}\right) dx = 1$$

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

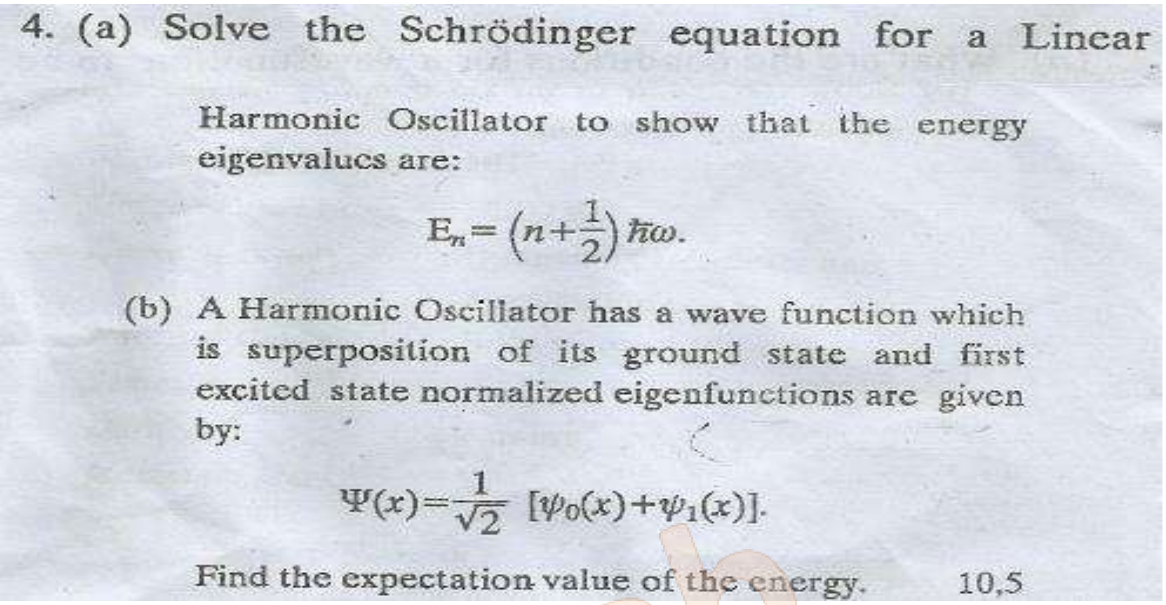
or $$\frac{A^2}{2}[a - 0] = 1$$

or $$A^2 = \frac{2}{a}$$

or $$A = \sqrt{\frac{2}{a}}$$

$\therefore$ Normalized wave function is

$$\psi = \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a}$$



4\. (a) Solve the Schrödinger equation for a Linear Harmonic Oscillator to show that the energy eigenvalues are:

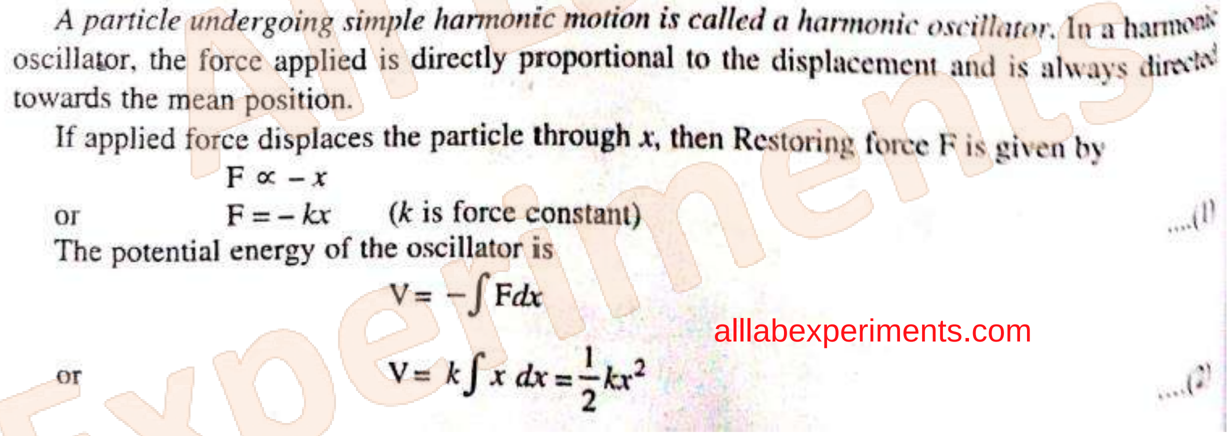
$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega.$$

(b) A Harmonic Oscillator has a wave function which is superposition of its ground state and first excited state normalized eigenfunctions are given by:

$$\Psi(x)=\frac{1}{\sqrt{2}}\,[\psi_0(x)+\psi_1(x)].$$

Find the expectation value of the energy. 10,5

4(a)



A particle undergoing simple harmonic motion is called a harmonic oscillator. In a harmonic oscillator, the force applied is directly proportional to the displacement and is always directed towards the mean position.

If applied force displaces the particle through x, then Restoring force F is given by

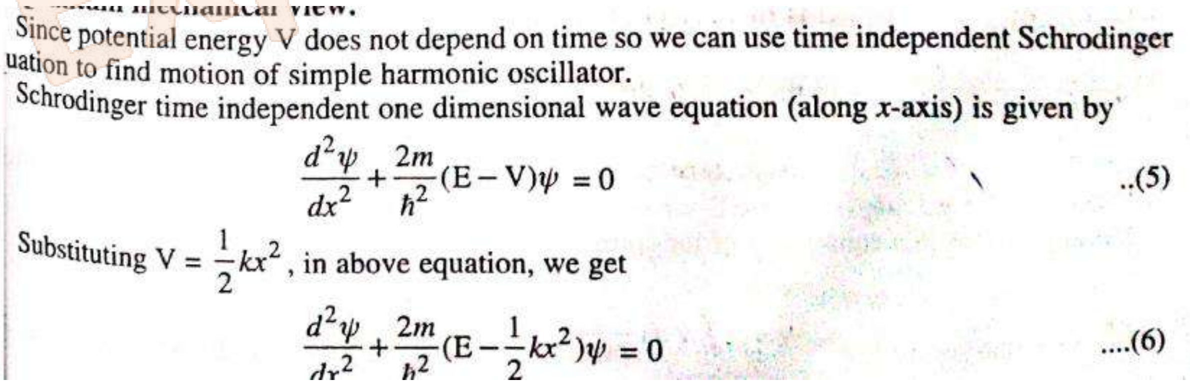
$$F \propto -x$$

or $$F = -kx \quad (k \text{ is force constant}) \qquad \ldots(1)$$

The potential energy of the oscillator is

$$V = -\int F\,dx$$

or $$V = k\int x\,dx = \frac{1}{2}kx^2 \qquad \ldots(2)$$



mechanical view.

Since potential energy V does not depend on time so we can use time independent Schrodinger uation to find motion of simple harmonic oscillator.

Schrodinger time independent one dimensional wave equation (along x-axis) is given by

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V)\psi = 0 \qquad ..(5)$$

Substituting $V = \frac{1}{2}kx^2$, in above equation, we get

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left(E-\frac{1}{2}kx^2\right)\psi = 0 \qquad \ldots(6)$$

Since $\omega = \sqrt{k/m}$, so $k = m\omega^2$

So equation (6), becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2x^2\right)\psi = 0$$

or

$$\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}x^2\right)\psi = 0 \qquad ...(7)$$

For convenience

let

$$\frac{2mE}{\hbar^2} = \alpha \text{ and } \frac{m\omega}{\hbar} = \beta \qquad ...(8)$$

So Eq. (7) becomes

$$\frac{d^2\psi}{dx^2} + \left(\alpha - \beta^2x^2\right)\psi = 0 \qquad ...(9)$$

Again for convenience, let us introduce a new variable q related to x such that

$$q = \sqrt{\beta}x$$

Now,

$$\frac{d\psi}{dx} = \frac{d\psi}{dq}\cdot\frac{dq}{dx} = \sqrt{\beta}\frac{d\psi}{dq}$$

and

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left[\frac{d\psi}{dx}\right] = \frac{d}{dx}\left[\sqrt{\beta}\frac{d\psi}{dq}\right]$$

or

$$\frac{d^2\psi}{dx^2} = \frac{d}{dq}\left[\sqrt{\beta}\frac{d\psi}{dq}\right]\frac{dq}{dx}$$

$$= \sqrt{\beta}\frac{d^2\psi}{dq^2}\sqrt{\beta}$$

or
$$\frac{d^2\psi}{dx^2} = \beta\frac{d^2\psi}{dq^2}$$

So Eq. (9) becomes

$$\beta\frac{d^2\psi}{dq^2} + \left(\alpha - \beta^2\frac{q^2}{\beta}\right)\psi = 0$$

or
$$\frac{d^2\psi}{dq^2} + \left(\frac{\alpha}{\beta} - q^2\right)\psi = 0 \qquad ...(10)$$

Asymptotic Solution.

To solve Eq. (10), let us make an attempt to obtain an expression for the asymptotic solution (the value of $\psi(q)$ for very large value of q), when $q^2 >> \frac{\alpha}{\beta}$. In this case, equation (10) becomes

$$\frac{d^2\psi}{dq^2} - q^2\psi = 0 \qquad ...(11)$$

The solution of this equation is of the form

$$\psi = e^{\pm q^2/2}$$

But here, the solution $e^{+q^2/2}$ is not acceptable because, it increases rapidly with increasing q,

but since $|\psi|^2$ is the probability of finding the particle and it must decrease as x increases.

$\therefore$ The particular acceptable solution is

$$\psi = e^{-q^2/2}$$

The general solution at any distance can be written as

$$\psi = H(q)e^{-q^2/2} \qquad ...(12)$$

where H(q) is a finite Hermite polynomial in q and can be written in a series of the form

$$H(q) = a_0 + a_1q + a_2q^2 + \ldots\ldots\ldots\ldots\ldots + a_nq^n$$

From Eq. (12), we have

$$\frac{d\psi}{dq} = -qe^{-q^2/2}H + e^{-q^2/2}\frac{dH}{dq}$$

and
$$\frac{d^2\psi}{dq^2} = q^2e^{-q^2/2}H - e^{-q^2/2}H - qe^{-q^2/2}\frac{dH}{dq} - qe^{-q^2/2}\frac{dH}{dq} + e^{-q^2/2}\frac{d^2H}{dq^2}$$

or $$\frac{d^2\psi}{dq^2} = \left(\frac{d^2H}{dq^2} - 2q\frac{dH}{dq} + q^2H - H\right)e^{-q^2/2}$$

Putting the values of ψ and $\frac{d^2\psi}{dq^2}$ in Eq. (10), we get

$$\left(\frac{d^2H}{dq^2} - 2q\frac{dH}{dq} + q^2H - H\right)e^{-q^2/2} + \left(\frac{\alpha}{\beta} - q^2\right)e^{-q^2/2}H = 0$$

or $$\frac{d^2H}{dq^2} - 2q\frac{dH}{dq} + \frac{\alpha}{\beta}H - H = 0$$

or $$\frac{d^2H}{dq^2} - 2q\frac{dH}{dq} + \left(\frac{\alpha}{\beta} - 1\right)H = 0 \qquad \text{...(13)}$$

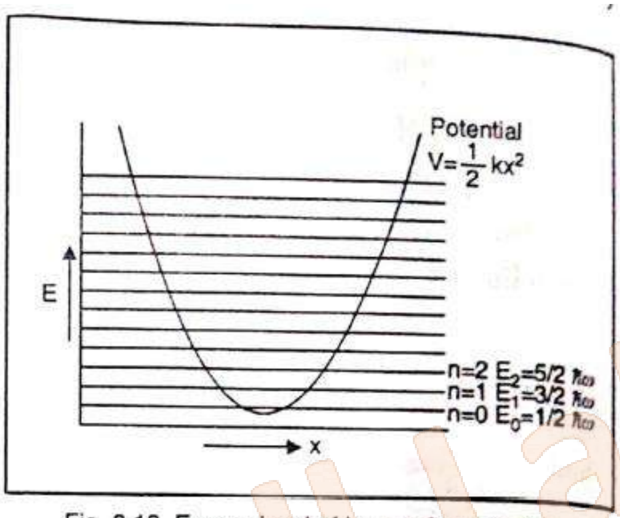
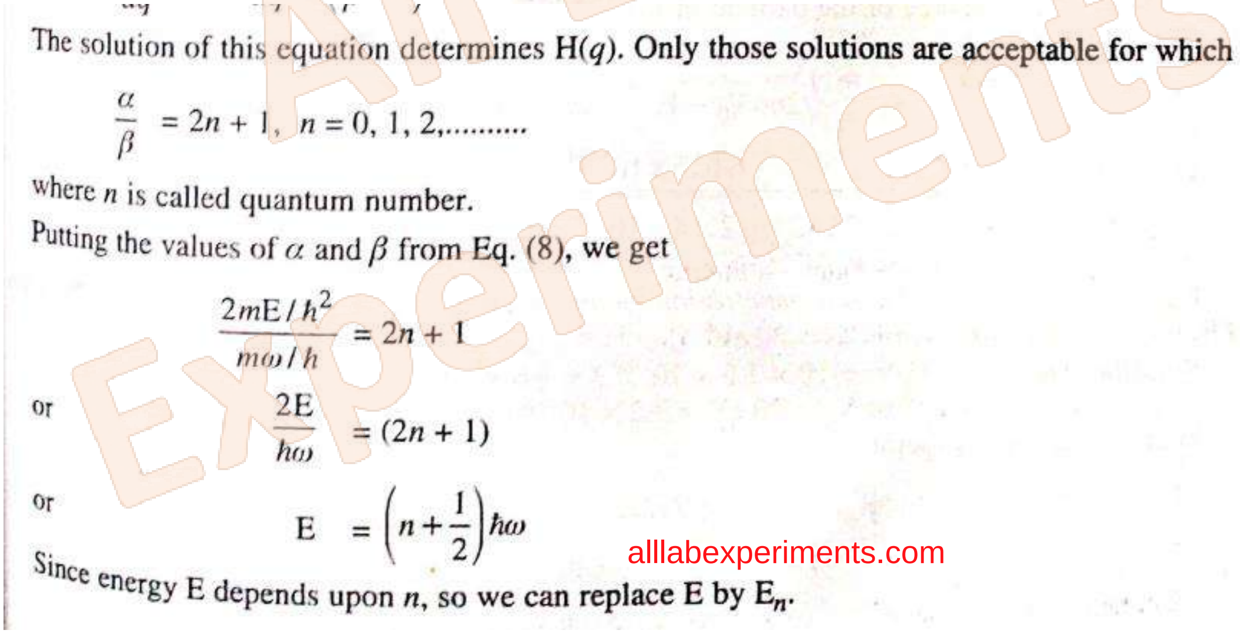


Fig. 3.13. Energy level of harmonic oscillator.



The solution of this equation determines H(q). Only those solutions are acceptable for which

$$\frac{\alpha}{\beta} = 2n+1, \quad n = 0, 1, 2, \ldots\ldots\ldots$$

where n is called quantum number.

Putting the values of α and β from Eq. (8), we get

$$\frac{2mE/\hbar^2}{m\omega/\hbar} = 2n+1$$

or

$$\frac{2E}{\hbar\omega} = (2n+1)$$

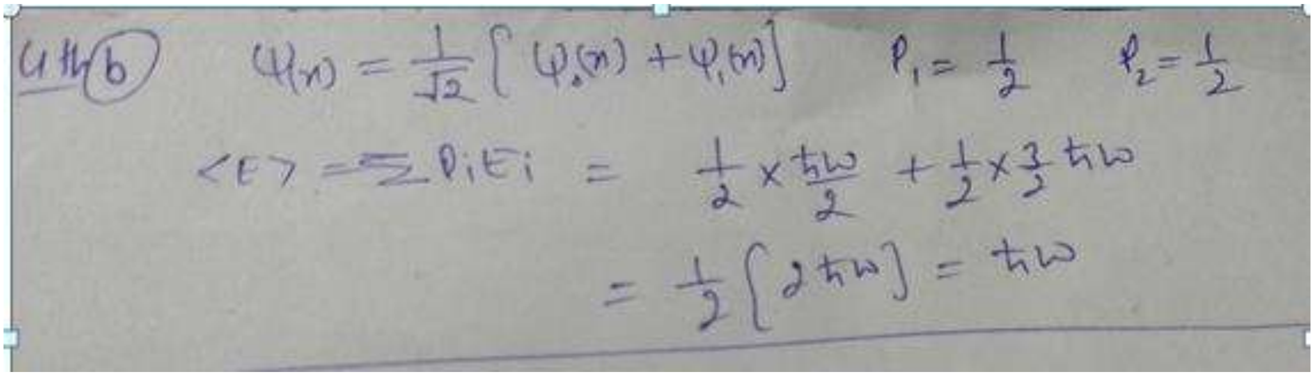
or

$$E = \left(n+\frac{1}{2}\right)\hbar\omega$$

Since energy E depends upon n, so we can replace E by E_n.

An alternate solution to the above question is in 2017 solved paper.

4(b)



4th (b) $\psi(x) = \frac{1}{\sqrt{2}}[\psi_0(x) + \psi_1(x)]$ $P_1 = \frac{1}{2}$ $P_2 = \frac{1}{2}$

$$\langle E\rangle = \Sigma P_i E_i = \frac{1}{2} \times \frac{\hbar\omega}{2} + \frac{1}{2} \times \frac{3}{2}\hbar\omega$$

$$= \frac{1}{2}[2\hbar\omega] = \hbar\omega$$

5. Write the Schrödinger equation for a 3D hydrogen atom in spherical polar coordinates. Derive three separate equations for r, θ, φ using the method of separation of variables. Solve the equation for φ to obtain the normalized eigenfunctions and show that they are orthogonal. 15

A hydrogen *atom* consists of one *proton* in the nucleus and only one *electron* in the surrounding space. The electron which carries a negative charge is bound to the nucleus due to the coulomb force of electrostatic attraction. Hence the electrostatic potential energy of an electron with charge $-e$ in the field of the nucleus with change $+Ze$ is given by

$$V(r) = \frac{-k\,e^2}{r},$$

where r is the distance between the electron and the nucleus both assumed to be point charges and k is a constant the value of which in S.I. unit is

$$\frac{1}{4\pi\,\varepsilon_0} = 9 \times 10^9\ \text{Nm}^2/\text{C}^2$$

$$\therefore \quad V = -\frac{e^2}{4\pi\,\varepsilon_0 r} \qquad \text{...(1)}$$

which is a *two* body problem but we can reduce it to a *one-body problem* by

(*i*) replacing the electron mass m_e by its *reduced mass m* given by

$$m = \frac{M\,m_e}{M + m_e},$$

where M is the mass of the nucleus.

(*ii*) by using the *centre of mass* as the origin of the co-ordinate system or by assuming the nucleus to be of an infinite mass.

As given by equation (1) the potential energy of the electron only depends upon the distance between the electron and the nucleus and is independent of any other factor like the angular position of the electron with respect to the nucleus. The value of V is the *same* at every point on the surface of a sphere of radius r. In other words, the potential is spherically symmetric and hence conservative in nature. The expression for V also does not involve time *explicitly*, the system is stationary and Schrodinger's time independent form of wave equation applies to it.

Because of spherical symmetry it is more convenient to deal with the problem in spherical polar co-ordinates defined by the variables r, θ and ϕ.

Schrodinger's time independent, three dimensional wave equation in cartesian co-ordinates is given by

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

where m is the reduced mass of the electron, E its total energy, V the potential energy and $\hbar = \frac{h}{2\pi}$.

In cartesian coordinate system, we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \text{...(3)}$$

Potential energy V is function of r (*i.e.* function of three coordinates x, y and z but it is not easy to solve Eq. (3) in cartesian coordinates. Also r is one of the co-ordinates in a spherical co-ordinate system (r, θ, ϕ), and due to spherical symmetry it is more convenient to deal with the problem in spherical polar co-ordinate system.

The spherical polar co-ordinates (r, θ, ϕ) of point P shown in fig. 4.1 have following interpretations.

r = length of radius vector from origin O to point P

θ = angle between radius vector and z-axis called zeneith angle.

ϕ = angle between the projection of the radius vector in the xy-plane and the x-axis called azimuth angle.

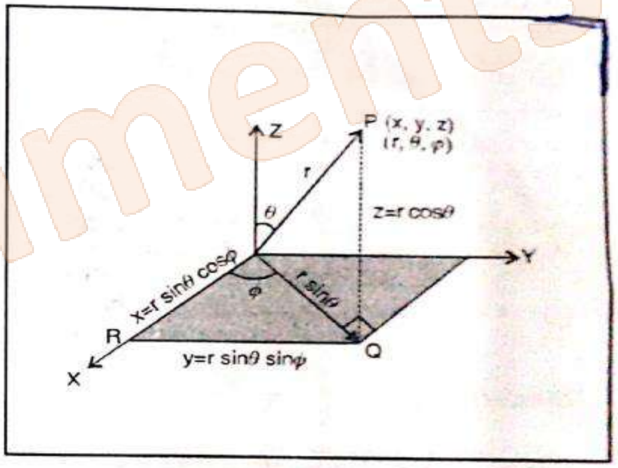


Fig. 4.1

From fig. 4.1, the relation between (x, y, z) and (r, θ, ϕ) are given by

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned} \qquad \text{...(4)}$$

Squaring and adding all the three terms of Eq. (4), we get

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

or

$$r = (x^2 + y^2 + z^2)^{1/2} \qquad \text{...(5)}$$

Also

$$\frac{\sqrt{x^2 + y^2}}{z} = \frac{\sqrt{r^2 \sin^2\theta(\cos^2\phi + \sin^2\phi)}}{r\cos\theta} = \tan\theta$$

or

$$\tan\theta = \frac{\sqrt{x^2 + y^2}}{z} \qquad \text{...(6)}$$

And

$$\frac{y}{x} = \frac{r\sin\theta\sin\phi}{r\sin\theta\cos\phi} = \tan\phi$$

$$\text{or} \qquad \tan\phi = \frac{y}{x} \qquad \text{...(7)}$$

Differentiating Eq. (5), partially w.r.t. x, we get

$$\frac{\partial r}{\partial x} = \frac{1}{2}(x^2+y^2+z^2)^{-1/2}2x = \frac{x}{\sqrt{x^2+y^2+z^2}} = \frac{x}{r} = \frac{r\sin\theta\cos\phi}{r}$$

$$\left.\begin{aligned} &\text{i.e.} && \frac{\partial r}{\partial x} = \sin\theta\cos\phi \\ &\text{Similarly,} && \frac{\partial r}{\partial y} = \sin\theta\sin\phi \\ &\text{and} && \frac{\partial r}{\partial z} = \cos\theta \end{aligned}\right\} \qquad \text{...(8)}$$

Differentiating Eq. (6) partially w.r.t. x, we get

$$\sec^2\theta\cdot\frac{\partial\theta}{\partial x} = \frac{\frac{1}{2}(x^2+y^2)^{-1/2}\,2x}{z} = \frac{x}{z\sqrt{x^2+y^2}} = \frac{r\sin\theta\cos\phi}{r\cos\theta\cdot r\sin\theta}$$

$$\text{or} \qquad \frac{\partial\theta}{\partial x} = \frac{1}{r}\frac{\cos\phi}{\cos\theta}\cdot\cos^2\theta = \frac{\cos\theta\cos\phi}{r}$$

$$\left.\begin{aligned} &\text{i.e.} && \frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r} \\ &\text{Similarly,} && \frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r} \\ &\text{and} && \frac{\partial\theta}{\partial z} = -\frac{\sin\theta}{r} \end{aligned}\right\} \qquad \text{...(9)}$$

Differentiating Eq. (7) partially w.r.t. x, we get

$$\sec^2\phi\,\frac{\partial\phi}{\partial x} = -\frac{y}{x^2} = -\frac{r\sin\theta\sin\phi}{r^2\sin^2\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta\cos^2\phi}$$

$$\text{or} \qquad \frac{\partial\phi}{\partial x} = -\frac{\sin\phi\cos^2\phi}{r\sin\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta}$$

$$\left.\begin{aligned} &\text{So} && \frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta} \\ &\text{Similarly,} && \frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta} \end{aligned}\right\} \qquad \text{...(10)}$$

and $$\frac{\partial \phi}{\partial z} = 0$$

With the help of above equations, we can find the value of $\frac{\partial^2 \psi}{\partial x^2}$, $\frac{\partial^2 \psi}{\partial y^2}$ and $\frac{\partial^2 \psi}{\partial z^2}$ as given ahead :

Since $$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial \psi}{\partial \phi}\frac{\partial \phi}{\partial x}$$

$$= (\sin\theta\cos\phi)\frac{\partial \psi}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial \psi}{\partial \theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial \psi}{\partial \phi}$$

$$\therefore \quad \frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial \phi}$$

Now

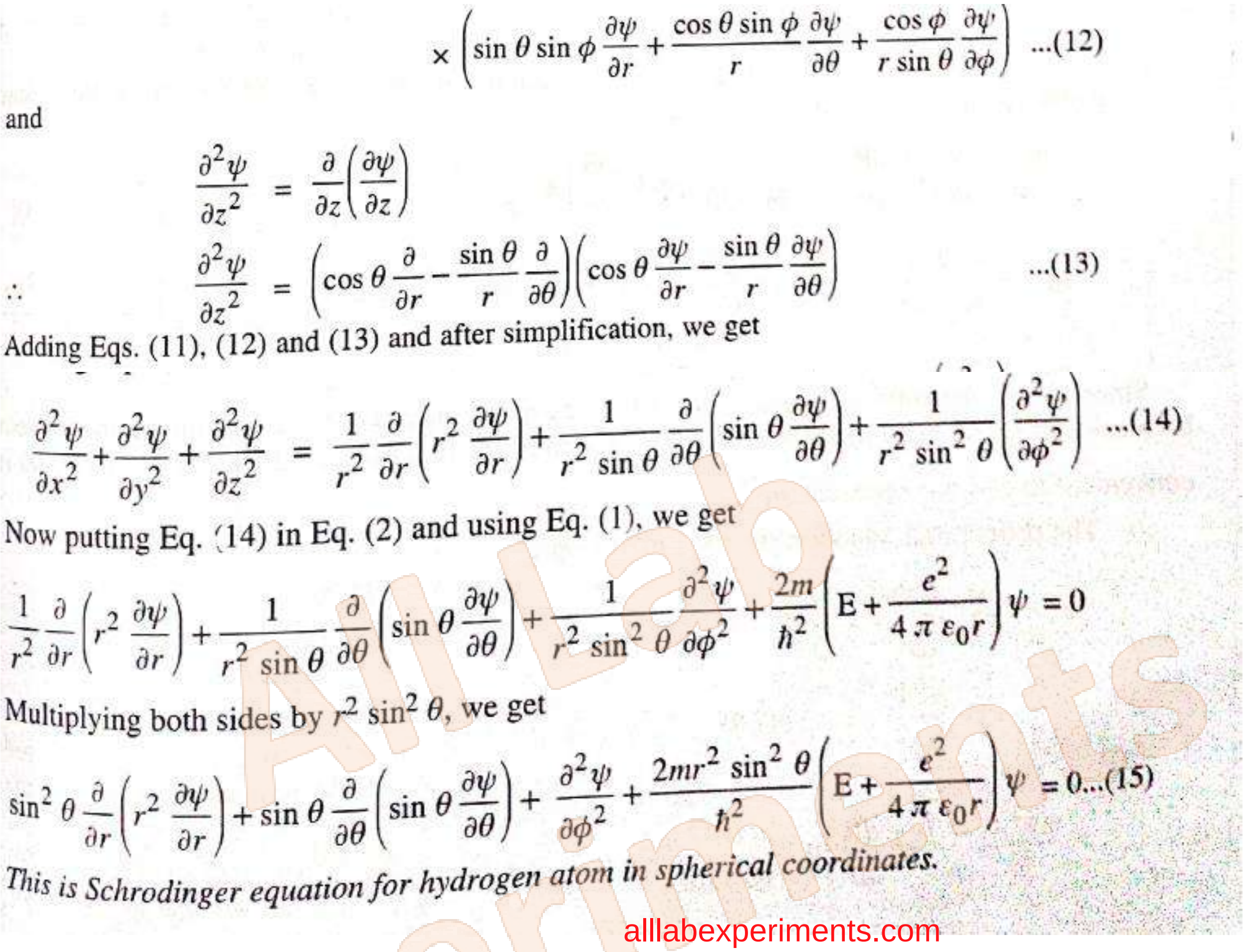
$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial x}\right)$$

$$\therefore \quad \frac{\partial^2 \psi}{\partial x^2} = \left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial \phi}\right)$$
$$\times\left(\sin\theta\cos\phi\frac{\partial \psi}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial \psi}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial \psi}{\partial \phi}\right) \quad \text{...(11)}$$

Similarly,

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

$$\therefore \quad \frac{\partial^2 \psi}{\partial y^2} = \left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial \phi}\right)$$



$$\times\left(\sin\theta\sin\phi\frac{\partial\psi}{\partial r}+\frac{\cos\theta\sin\phi}{r}\frac{\partial\psi}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}\right)\quad ...(12)$$

and

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

$$\therefore\quad \frac{\partial^2\psi}{\partial z^2}=\left(\cos\theta\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\left(\cos\theta\frac{\partial\psi}{\partial r}-\frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta}\right)\quad ...(13)$$

Adding Eqs. (11), (12) and (13) and after simplification, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\quad ...(14)$$

Now putting Eq. (14) in Eq. (2) and using Eq. (1), we get

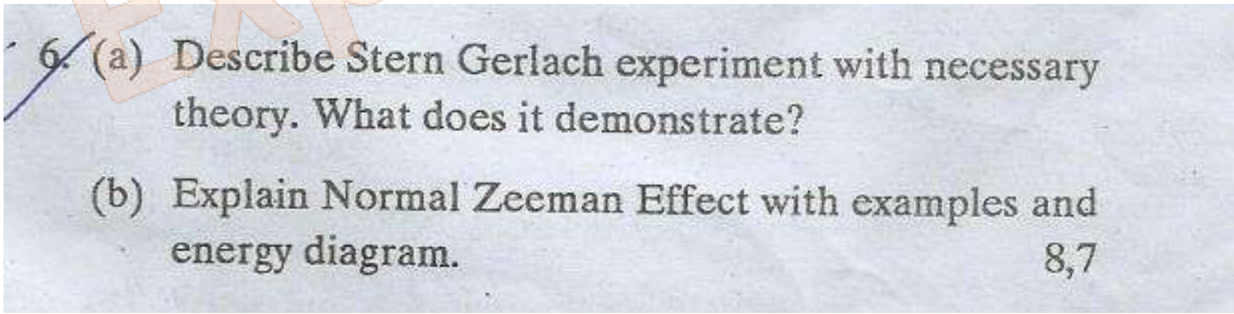
$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2m}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi=0$$

Multiplying both sides by $r^2\sin^2\theta$, we get

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi=0\quad ...(15)$$

This is Schrodinger equation for hydrogen atom in spherical coordinates.

Find the three Separate equations in the textbook.



6. (a) Describe Stern Gerlach experiment with necessary theory. What does it demonstrate?

(b) Explain Normal Zeeman Effect with examples and energy diagram. 8,7

6(a)

The deflection of atomic beam in a non-uniform magnetic field was studied by Stern and Gerlach and thus *proved the existence of electron spin and its space quantization.*

Experimental arrangement

The substance whose atomic beam is to be studied, is kept in the oven. In the original experiment silver was used for this purpose. A beam of neutral silver atoms when heated come out of the opening of the oven. The beam after collimation by passing through two slits S_1 and S_2 is passed through a non-homogeneous magnetic field produced by specially designed electromagnets as shown in fig. 5.28.

The outgoing beam is recorded on a suitable detector screen, which for silver is a cold glass plate.

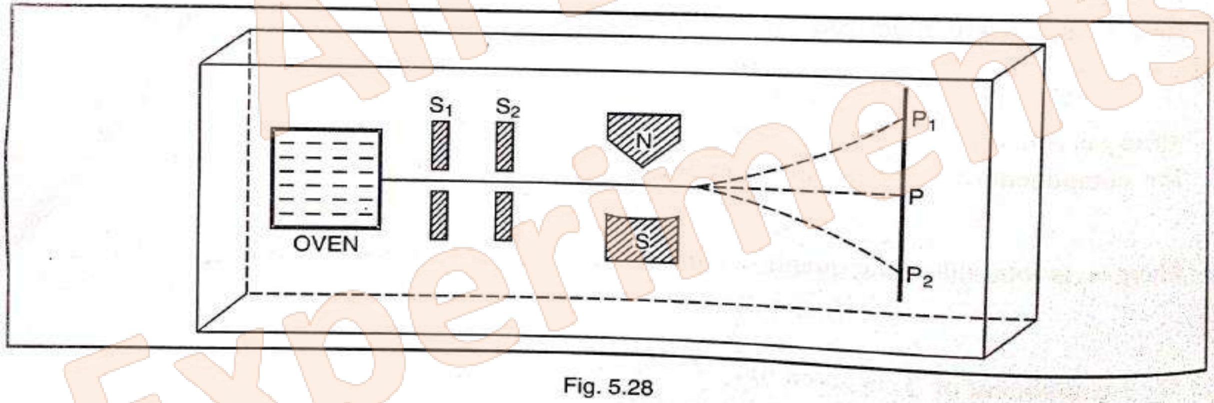
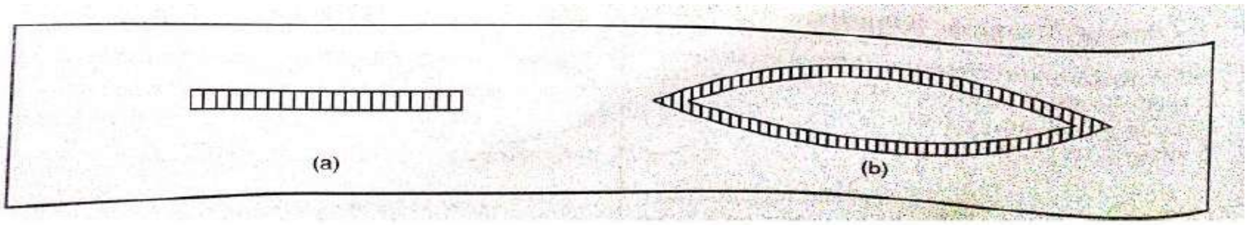


Fig. 5.28

WORKING

When the current in the electromagnet is switched off, the beam strikes at P and produces a narrow trace at the centre of the screen as in Fig. 5.28 (*a*). But as soon as the current is switched on, the beam spreads, producing two traces P_1 and P_2 on the screen. Both these traces are of equal intensity having patterns similar to shown in Fig. 5.29 (*b*).


(a) (b)

The spread in the two traces is due to the Maxwellian distribution of velocity of the atoms around some mean value. As each silver atom can possess only two possible values of spin *i.e.* $\frac{1}{2}$ and $-\frac{1}{2}$ the beam of atoms must split into two beams during its passage through the non-homogeneous magnetic field. The component μ of the magnetic moment of the atom in the direction of the field as studied by Stern-Gerlach was found to be one Bohr Magneton.

Explanation (*Quantum theory*)

The magnitude of total magnetic moment $\vec{\mu}_j$ of silver atom due the orbital and spin angular momenta and associated magnetic moment of its electrons is given by

$$\mu_j = -\mu_B\, g \sqrt{j(j+1)}, \qquad \text{... (1)}$$

where $\mu_B = \frac{eh}{2m} = 1$ Bohr magneton

and $g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$

or $V_m = \pm \mu_B B$ ...(3)

Let the silver atoms enter the magnetic field with velocity v along X-axis and let B varies at the rate of $\frac{\partial B}{\partial z}$ along Z-axis, then

Magnitude of the force acting on the atomic dipole along Z-axis is :

$$F_z = \pm \mu_B \frac{\partial B}{\partial z}$$

If M is the mass of silver atom, then
Acceleration of the atom,

$$a = \frac{F_z}{M} = \pm\mu_B \frac{\partial B}{\partial z} \cdot \frac{1}{M}$$

If l is the length of the path of the beam through the magnetic field, then
Time taken to travel the field

$$t = l/v$$

∴ The displacement of the atom along Z-axis

$$Z = \pm \frac{1}{2} at^2$$

or

$$Z = \pm\frac{1}{2}\mu_B \frac{\partial B}{\partial z} \cdot \frac{l^2}{Mv^2}$$

From Maxwell's law of distribution of velocities

$$v = \sqrt{\frac{3kT}{M}}$$

∴

$$Z = \pm\frac{1}{2}\mu_B \frac{\partial B}{\partial z} \cdot \frac{l^2}{M} \frac{M}{3kT}$$

or

$$Z = \pm\frac{1}{6}\mu_B \frac{l^2}{kT} \frac{\partial B}{\partial z} \qquad \text{... (3)}$$

The maximum displacement at the centre of the trace is given by the above equation.

The maximum displacement at the centre of the trace is given by the above equation.

Conclusions

(*i*) If either the magnetic field is uniform or magnetic field is zero, then

$$\frac{\partial B}{\partial z} = 0$$

∴

$$Z = 0$$

Hence there is no displacement of the atomic magnets along z-axis, hence we find a straight line Fig. 5.28 (*a*)

(*ii*) If the applied magnetic field is non-uniform, the displacement is either along + Z-axis or – Z-axis depending upon their orientations and we get a trace on plates.

Significance.

The displacement Z of the line from original position derived by quantum theory is in close agreement with experimental values and thus the above experiment give experimental confirmation of the interaction of orbital angular momentum and spin angular momentum and their associated magnetic moments as well as space *quantization of total* magnetic moment vector μ_j of the atom.

6(b)

Zeeman discovered in 1896 that *when a light source producing spectrum is brought into a magnetic field, each emitted spectral line is split into a number of components—doublets or triplets or even more complex arrangements.* This phenomenon is called *Zeeman effect*. The extent of the splitting depends on the strength of the magnetic field and on the nature of spectral lines, whether they are singlets or multiplets.

Normal Zeeman effect.

If the magnetic field is very strong, each spectral line splits into two components in the longitudinal view and in three components in transverse view. This is known as *Normal Zeeman effect*.

Experimental Arrangement.

The experimental arrangement to study normal Zeeman effect is shown in fig 3.19. The source of light such as a gas discharge tube is placed between the pole pieces of a strong electromagnet. The pole pieces of the magnet have an axial hole parallel to their length, so that light emitted from the source of light can pass through it. The spectral lines are observed with the help of a spectroscope of high resolving power.

When no field is applied, there is only a single (unpolarised) spectral line visible in the spectrum. When the field is switched on and the line is viewed perpendicular to the direction of magnetic field (*normal transverse Zeeman effect*), three component spectral lines are observed

One component in the same position as the original line (without field) having the same wavelength and frequency ν and other two component lines lie on either side of the original line. The

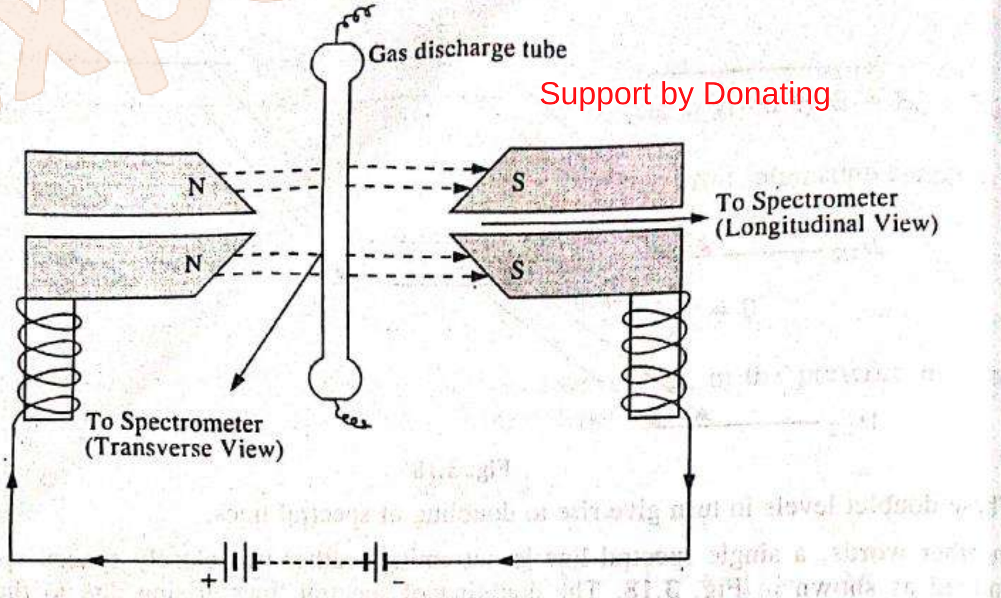


Fig. 3.19

frequency of the component line on the right side of original line is $\nu + \Delta\nu$ and that of on the left side of the original line is $\nu - \Delta\nu$. It is observed that the original line is linearly polarised, parallel to the direction of applied magnetic field, whereas the two component lines on either side of original line are linearly polarised at right angles to the magnetic field as shown in Fig. 3.20. When the light is viewed along the direction of the applied magnetic field (*normal langitudinal Zeeman effect*), the original (central) line is found missing but the other two component lines with frequency $(\nu - \Delta \nu)$ and $(\nu + \Delta \nu)$ are observed. These component lines are circularly polarised. One component is circularly polarised clockwise and other anticlockwise as shown in Fig 3.20.

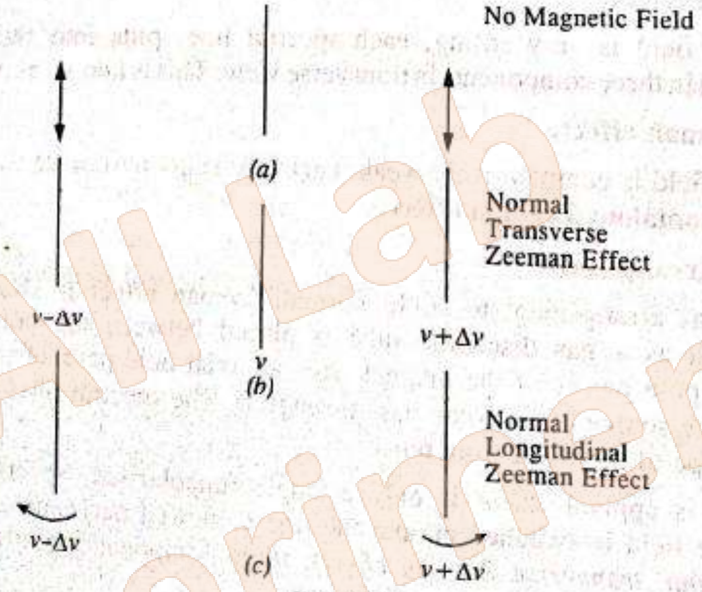


Fig. 3.20

3.23. Classical Theory Of Normal Zeeman Effect

The phenomenon of normal Zeeman effect was explained by Lorentz, on the basis of electronic theory of matter.

Consider an electron of mass m revolving a round the nucleus in a circular orbit of radius r with linear velocity v and angular velocity ω.

The centripetal force acting on the revolving electron is given by

$$F = \frac{mv^2}{r}$$

Since $$v = r\,\omega \quad \therefore \; F = m\,r\,\omega^2 \qquad \ldots(1)$$

Now let a magnetic field of uniform intensity $\vec{B}$ be applied at right angles to the plane of the orbit of the electron, then the additional force acting on the electron $= Bev = Ber\omega$, where e is the charge on the electron.

According to Fleming's left-hand rule, the direction of this additional force will be towards or away from the centre of the orbit depending upon the clockwise or anticlockwise motion of the electron. If the additional force is towards the centre of the atom (*i.e.*, motion is anticlockwise), the orbit contracts and hence the angular velocity of the electron increases as per law of conservation of angular momentum. On the other hand, if the additional force is away from the centre (*i.e.*, the motion is clockwise), the orbit expands and hence the angular velocity of the electron decreases.

velocity due to the additional force. Then the equation electron decreases.

Le $d\omega$ be the small change in angular velocity due to the additional force. Then the equation of motion in dynamic equilibrium becomes

$$F \pm B e v = m r (\omega + d\omega)^2$$

[Using eqn. (1)]

or $$m r \omega^2 \pm B e r \omega = m r (\omega + d\omega)^2$$

or $$m r \omega^2 - m r (\omega + d\omega)^2 = \pm B e r \omega$$

or $$-2 m r \omega d\omega - m r (d\omega)^2 = \pm B e r \omega$$

Since $d\omega$ is very small, so $(d\omega)^2$ can be neglected.

$\therefore$ $$-2 m r \omega d\omega = \pm B e r \omega$$

or $$d\omega = \pm \frac{Be}{2m} \quad \ldots(2)$$

– ve and + ve signs show the case of *retardation* and *acceleration respectively*.

But $\omega = 2\pi\nu$, where ν is the frequency of rotation of the electron.

$$\therefore d\omega = 2\pi d\nu \quad \ldots(3)$$

Comparing eqns. (2) and (3), we get

$$d\nu = \pm \frac{Be}{4\pi m} \quad \ldots(4)$$

Eqn. (4) represents the change in frequency of the spectral line

Since $\nu = \frac{c}{\lambda}$,

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

Substituting the value of $d\nu$ in eqn. (4), we get

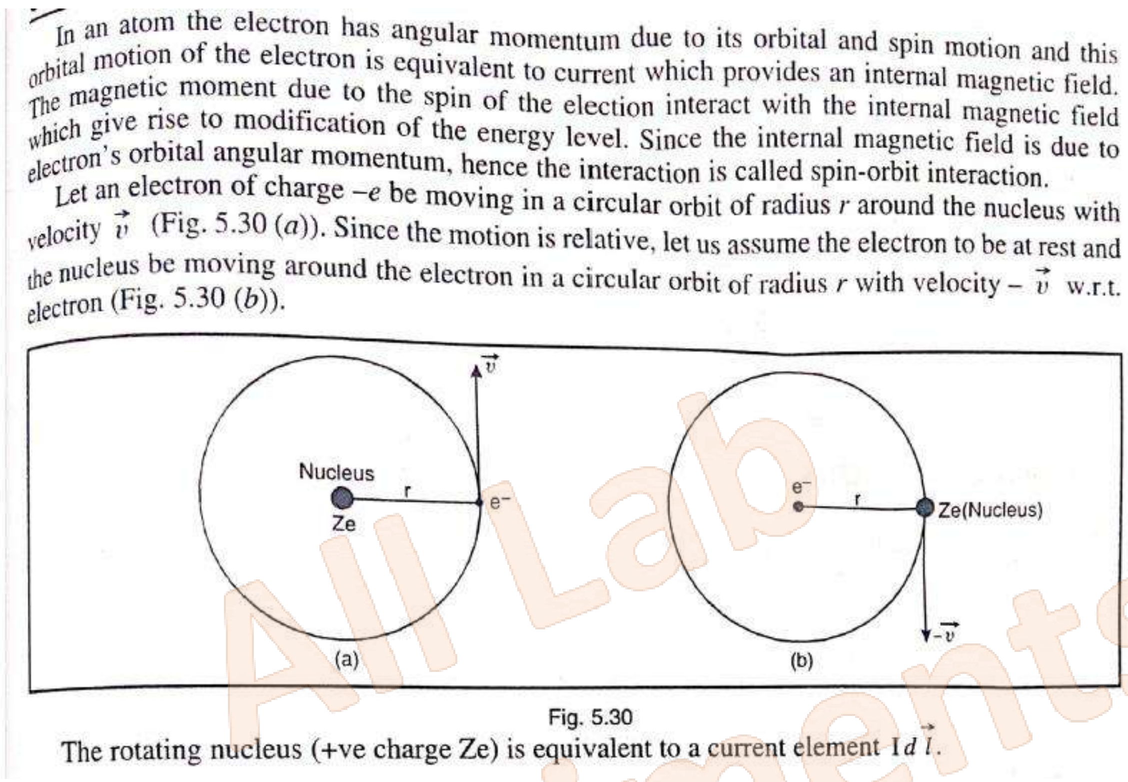
$$d\lambda = \pm \frac{Be}{4\pi m} \frac{\lambda^2}{c} \quad \ldots(5)$$

Eqn. (5) represents the change in wavelength or *Zeeman shift* of the spectral line. Thus, the spectral line of wavelength λ will be resolved under the action of an applied magnetic field B into either side of the original line.

The value of e/m given by eqn. (5) is

$$e/m \pm \frac{4\pi c}{B\lambda^2} d\lambda \quad \ldots(6)$$

The value of e/m obtained by this method is $1{\cdot}77 \times 10^{10}$ e.m.u. per gram or $1{\cdot}77 \times 10^{11}$ C kg^{-1}, which is same as that determined by J.J. Thomson.

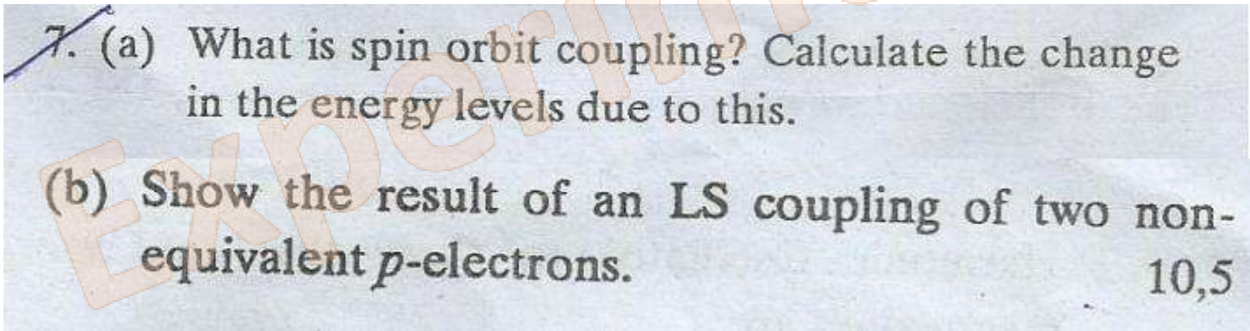


In an atom the electron has angular momentum due to its orbital and spin motion and this orbital motion of the electron is equivalent to current which provides an internal magnetic field. The magnetic moment due to the spin of the election interact with the internal magnetic field which give rise to modification of the energy level. Since the internal magnetic field is due to electron's orbital angular momentum, hence the interaction is called spin-orbit interaction.

Let an electron of charge $-e$ be moving in a circular orbit of radius r around the nucleus with velocity $\vec{v}$ (Fig. 5.30 (*a*)). Since the motion is relative, let us assume the electron to be at rest and the nucleus be moving around the electron in a circular orbit of radius r with velocity $-\vec{v}$ w.r.t. electron (Fig. 5.30 (*b*)).

Fig. 5.30

The rotating nucleus (+ve charge Ze) is equivalent to a current element $I\,d\vec{l}$.



7. (a) What is spin orbit coupling? Calculate the change in the energy levels due to this.

(b) Show the result of an LS coupling of two non-equivalent *p*-electrons. 10,5

7(a)

According to Biot-Savart law, the magnetic field at the centre of a current element $I d\vec{l}$ is given by

$$\vec{B} = \frac{\mu_0}{4\pi}\frac{I\, d\vec{l}\times\vec{r}}{r^3}$$

But $$I d\vec{l} = \frac{dq}{dt}\cdot d\vec{l} = dq.\frac{d\vec{l}}{dt} = -\mathrm{Ze}\,\vec{v}$$

$$\therefore \quad \vec{B} = -\frac{\mu_0}{4\pi}\frac{\mathrm{Ze}\,(\vec{v}\times\vec{r})}{r^3} \qquad \text{... (1)}$$

Since $$c^2 = \frac{1}{\mu_0\varepsilon_0} \qquad \therefore\ \mu_0 = \frac{1}{\varepsilon_0 c^2}$$

So Eq. (1) becomes

$$\vec{B} = -\frac{\mathrm{Ze}}{4\pi\varepsilon_0\, mc^2}\frac{(m\vec{v}\times\vec{r})}{r^3} = -\frac{\mathrm{Ze}}{4\pi\varepsilon_0\, mc^2 r^3}(\vec{p}\times\vec{r})$$

$$= \frac{\mathrm{Ze}}{4\pi\varepsilon_0\, mc^2 r^3}(\vec{r}\times\vec{p})$$

or $$\vec{B} = \frac{\mathrm{Ze}\,\vec{L}}{4\pi\varepsilon_0\, mc^2 r^3}, \qquad \text{...(2)}$$

where $\vec{L} = \vec{r}\times\vec{p}$ is the orbital angular momentum of the electron.

Spin-orbit interaction

The potential energy $\Delta E'_{ls}$ due to internal magnetic field is given by

$$\Delta E'_{ls} = -\vec{\mu}_s\cdot\vec{B}$$

The electron spin magnetic moment is given by

$$\vec{\mu}_s = \frac{-g_s\mu_B\vec{S}}{\hbar} = \frac{-2\mu_B}{\hbar}\vec{S} \qquad \text{... (3) } [\because g_s = 2]$$

Using Eqs. (2) and (3), we get

$$\Delta E'_{ls} = \frac{2\mu_B}{\hbar}\frac{\mathrm{Ze}}{4\pi\varepsilon_0\, mc^2 r^3}(\vec{S}\cdot\vec{L})$$

Since $$\mu_B = \frac{e\hbar}{2m}$$

$$\therefore \quad \Delta E'_{ls} = \frac{\mathrm{Ze}^2}{4\pi\varepsilon_0\, m^2c^2r^3}(\vec{S}\cdot\vec{L})$$

This value of energy is determined in the frame of reference in which electron is at rest. If we transform this frame to another in which nucleus is at rest, the potential energy will be reduced by a factor 2.

∴ Spin orbit interaction energy,

$$\Delta E_{ls} = \frac{1}{2}\Delta E'_{ls} = \frac{Ze^2}{8\pi\varepsilon_0 mc^2 r^3}(\vec{S}\cdot\vec{L}) \qquad \text{... (4)}$$

Since total angular momentum of an electron is the sum of orbital and spin angular momentum, so

$$\vec{J} = \vec{L} + \vec{S}$$

$$\therefore \quad \vec{J}\cdot\vec{J} = \left(\vec{L}+\vec{S}\right)\left(\vec{L}+\vec{S}\right) = L^2 + S^2 + 2\vec{S}\cdot\vec{L}$$

or

$$J^2 = L^2 + S^2 + 2\vec{S}\cdot\vec{L}$$

or

$$\vec{S}\cdot\vec{L} = \frac{1}{2}(J^2 - L^2 - S^2)$$

or

$$\vec{S}\cdot\vec{L} = \frac{1}{2}[j(j+1)\hbar^2 - l(l+1)\hbar^2 - s(s+1)\hbar^2]$$

$$\therefore \quad \vec{S}\cdot\vec{L} = \frac{\hbar^2}{2}[(j(j+1) - l(l+1) - s(s+1)]$$

So Eq. (4) becomes

$$\Delta E_{ls} = \frac{Ze^2\hbar^2}{16\pi\varepsilon_0 m^2c^2r^3}[j(j+1) - l(l+1) - s(s+1)] \qquad \text{... (5)}$$

If E_n = Energy of the atom in nth state, then total energy of the atom due to spin-orbit interaction will be

N.S

$$E = E_n + \Delta E_{ls}$$

(*a*) Without spin-orbit coupling

(*i*) Ground state

For ground state, $n = 1$

$$\therefore \quad l = 0 \quad \text{and} \quad j = l + s = 0 + \frac{1}{2} = \frac{1}{2}$$

Thus ground state is written as $1^2s_{1/2}$

And energy level of this state, $E_1 = -\frac{13.6}{1_2} eV = -13.6$ eV.

(*ii*) First excited state

First excited state has $n = 2$

So $\quad l = 0 \quad$ or $\quad l = 1$

For $l = 0$ (s-state)

$$j = l + s = \frac{1}{2}$$

$\therefore$ This state is written as

$$2\,{}^2s_{1/2}$$

For $l = 1$ (p-state)

$$j = l \pm s = \frac{1}{2} \quad \text{or} \quad \frac{3}{2}$$

$\therefore$ These states are written as

$2\,{}^2p_{1/2}$ and $2\,{}^2p_{3/2}$

The energy of all these three states is

$$E_2 = -\frac{13.6}{2^2} eV = -3.4\ eV$$

i.e. all these three states are degenerate states.

(*iii*) Second excited state

Second excited state has $n = 3$

$$\text{So} \quad l = 0, \ 1 \ \text{or} \ 2$$

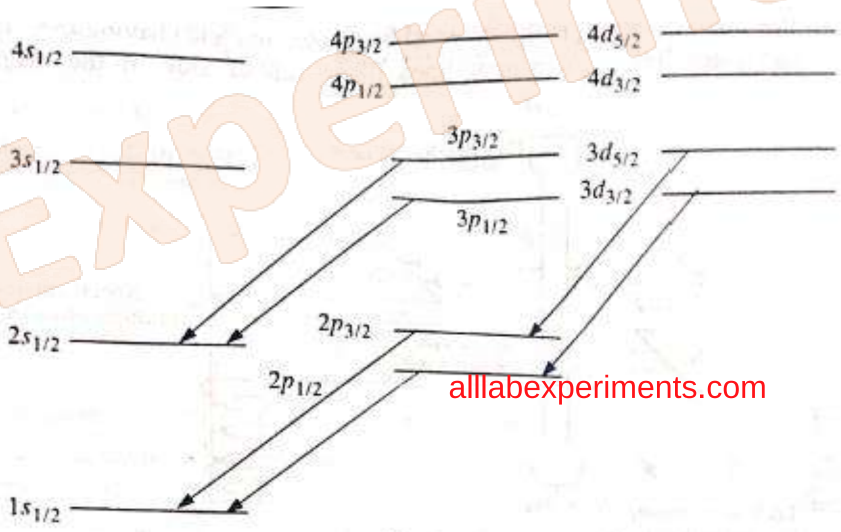
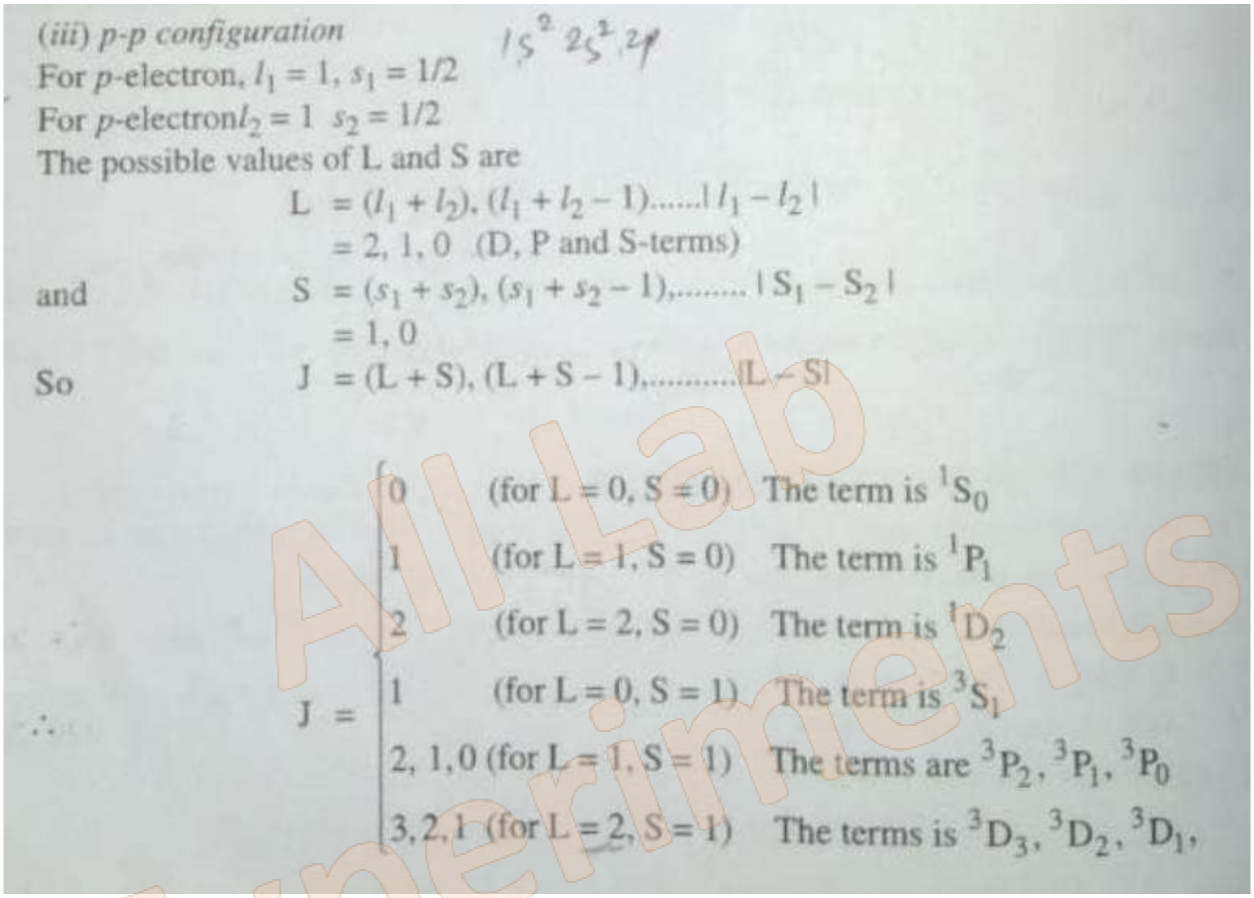


Fig. 3.18

These doublet levels in turn give rise to doubling of spectral lines.

In other words, a single spectral line is not emitted rather two closely spaced spectral lines are emitted as shown in Fig. 3.18. The doubling of spectral lines arising due to the spin-orbit coupling is called fine structure of a spectrum.

7(b)



(iii) p-p configuration $1s^2 2s^2 2p$

For *p*-electron, $l_1 = 1$, $s_1 = 1/2$

For *p*-electron$l_2 = 1 \quad s_2 = 1/2$

The possible values of L and S are

$$L = (l_1 + l_2), (l_1 + l_2 - 1)......| l_1 - l_2 |$$
$$= 2, 1, 0 \quad \text{(D, P and S-terms)}$$

and
$$S = (s_1 + s_2), (s_1 + s_2 - 1),......... | S_1 - S_2 |$$
$$= 1, 0$$

So
$$J = (L + S), (L + S - 1),...........|L - S|$$

$$\therefore \quad J = \begin{cases} 0 & \text{(for } L = 0, S = 0) \quad \text{The term is } {}^1S_0 \\ 1 & \text{(for } L = 1, S = 0) \quad \text{The term is } {}^1P_1 \\ 2 & \text{(for } L = 2, S = 0) \quad \text{The term is } {}^1D_2 \\ 1 & \text{(for } L = 0, S = 1) \quad \text{The term is } {}^3S_1 \\ 2, 1, 0 & \text{(for } L = 1, S = 1) \quad \text{The terms are } {}^3P_2, {}^3P_1, {}^3P_0 \\ 3, 2, 1 & \text{(for } L = 2, S = 1) \quad \text{The terms is } {}^3D_3, {}^3D_2, {}^3D_1, \end{cases}$$