Schrodinger equation and plane wave solution.

The time dependent schrodinger equation is given by

$$\left[\frac{-\hbar^2}{2m}\nabla^2+V\right]\psi = i\hbar\frac{\partial\psi}{\partial t} \rightarrow ①$$

This equation is a partial differential equation in four variables, three position co ordinates x, y, z and time t.

In the case the potential energy (V) is independent of time and depends only on position. Schrodinger sujested seeking the solution of the wave equation which represents standing waves (ψ). if ψ represents standing waves time must ~~cy~~ occur as a seperate factor.

If ~~W~~ V is independent of time the position and

time co-ordinates of separate equation ①.

$$\psi = \phi(x,y,z)\,u(t) \rightarrow ②$$

where $\phi(x,y,z) \Rightarrow$ Independent of time

$u(t) \Rightarrow$ Independent of position (x,y,z)

Sub the value of ψ from (2) in equ (1) we get.

$$\left[\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\phi(x,y,z)\,u(t) = i\hbar\frac{\partial}{\partial t}\phi(x,y,z)\,u(t) \hookrightarrow ③$$

$\div\ \phi(x,y,z)\ u(t)$

$$\frac{1}{\phi(x,y,z)u(t)}\left[\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\phi(x,y,z)\,u(t) = \frac{1}{\phi(x,y,z)u(t)}\,i\hbar\frac{\partial}{\partial t}\phi(x,y,z)\,u(t)$$

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$$\frac{1}{\phi(x,y,z)}\left[\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\phi(x,y,z) = \frac{1}{u(t)}\,i\hbar\frac{\partial u(t)}{\partial t} \rightarrow 3(a)$$

above equation the left hand side is independent of time while right hand side is on co-ordinate (x, y, z).

So if above eqn is should be satisfied eqn ③ is each side must be equal to the constant E.

$$\frac{1}{\phi(x,y,z)}\left[-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\phi(x,y,z)=E$$

$$\frac{1}{u(t)}\, i\hbar\, \frac{\partial u(t)}{\partial t} = E$$

$$\frac{1}{\phi(x,y,z)}\left[-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\phi(x,y,z)=E$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\phi(x,y,z)=E\,\phi(x,y,$$

$$-\frac{\hbar^2}{2m}\nabla^2\phi = E\phi - V\phi$$

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

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

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

$$\nabla^2\phi + \frac{2m}{\hbar^2}(E-V)\phi = 0 \rightarrow ④$$

$$\frac{1}{u(t)}\, i\hbar\, \frac{\partial u(t)}{\partial t} = E \rightarrow ⑤$$

$$u(t) = e^{Et/i\hbar} = e^{-iEt/\hbar} \rightarrow ⑥$$

If the comparison of this eqn with that of a plane wave E must have the dimension of energy with this value of u(t) and eqn ②

$$\psi = \phi(x,y,z)\,u(t)$$

$$\psi = \phi(x,y,z)\,e^{-iEt/\hbar} \rightarrow ⑦$$

The value of E is are the allowed the value of E of the particular system said to be characteristics (or) proper (or) eigen values. From the theory of part. linear partial differential eqn knows physically accepted most general solution eqn (2) can be written as linear super [illegible] of the solution of form of eqn ④.

The general solution ψ of Schrodinger equation for the time independent potential energy can be written as:

$$\psi = a_1 \phi_1 (x,y,z)\, e^{iE_1 t/\hbar} + a_2 \phi_2 (x,y,z)\, e^{iE_2 t/\hbar} + \dots\dots + a_n \phi_n (x,y,z)\, e^{iE_n t/\hbar}$$

$$\psi = \sum_{n=1}^{\infty} a_n \phi_n (x,y,z)\, e^{iE_n t/\hbar}$$

Expectation waves

2M

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

(or)

It may be defined as the average of the result of a large no. of measurement on independent system.

The expectation values of any observable f normalized wave function may be written as

$$\langle f \rangle = \int P_{(r,t)} f_{op}\, d\tau \rightarrow ①$$

$$= \int \psi^*_{(r,t)} f_{op}\, \psi_{(r,t)}\, d\tau \rightarrow ②$$

where f_{op} is operator associated with observable f

The E.V of position vectors

$$\langle r \rangle = \int \psi^*_{(r,t)}\, d\tau \rightarrow 3(a)$$

The $\langle r \rangle = \int \psi^*_{(r,t)}\, r\, \psi_{(r,t)}\, d\tau \rightarrow 3(a)$

$$\left.\begin{aligned} \langle x \rangle &= \int \psi^* x\, \psi\, d\tau \\ \langle y \rangle &= \int \psi^* y\, \psi\, d\tau \\ \langle z \rangle &= \int \psi^* z\, \psi\, d\tau \end{aligned}\right\} \rightarrow 3(b)$$

where $\langle x \rangle, \langle y \rangle, \langle z \rangle$ the expectation value of the co-ordinates x, y, z of particles

The E.V of Potential energy (V)

$$\langle V \rangle = \int \psi^*_{(r,t)}\, V \psi_{(r,t)}\, d\tau \rightarrow ④$$

The [illegible] of E is,

$$\langle E\rangle = \int \psi^* H \psi \, d\tau \rightarrow (5)$$

$$\langle E\rangle = \int \psi^* (i\hbar\, \partial/\partial t)\psi \, d\tau$$

$$\langle E\rangle = i\hbar \int \psi^* \frac{\partial \psi}{\partial t} d\tau \rightarrow (6)$$

The average (or) E.V of momentum (P)

$$\langle P\rangle = \int \psi^* P_{op} \psi \, d\tau$$

$[P = \frac{\hbar}{i}\nabla]$

$$= \int \psi^* \left(\frac{\hbar}{i}\nabla\right)\psi \, d\tau$$

$P = \frac{\hbar}{i}\nabla$

$$\langle P\rangle = \frac{\hbar}{i}\int \psi^* \nabla \psi \, d\tau \rightarrow (7)$$

The equ is equivalent to the components equ given by

$$\langle P_x\rangle = \frac{\hbar}{i}\int \psi^* P_x \psi \, d\tau$$

$$\langle P_y\rangle = \frac{\hbar}{i}\int \psi^* P_y \psi \, d\tau$$

$$\langle P_z\rangle = \frac{\hbar}{i}\int \psi^* P_z \psi \, d\tau$$

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where

$\langle P_x\rangle, \langle P_y\rangle, \langle P_z\rangle$ are the E.V of the components of the momentum along x, y, z axis respectively.

The above formula of E.V only hold if the wave function ψ is properly normalized otherwise we have the definition of E.V of any quantity of f.

$$\langle f\rangle = \frac{\int \psi^* f_{op} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \rightarrow (8)$$

therefore if the wave function is small normalized we have to use the definition given by equ (8) and equ (1) and equ 7(a) will be modified.

If the E.V are to be defined using operators the integrals will consist of the operator operating on ψ by multiply on the left by ψ*

① Commutation relation b/w position and momentum.

Let us purpose to find the commutator x and px

$x \to \hat{x}$ and $p_x \to \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

$[\hat{x}, \hat{p}_x]$ on a wave function $\psi(x)$

$$[\hat{x}, \hat{p}_x]\psi_{(x)} = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi_{(x)}$$

$$[\hat{x}, \hat{p}_x]\psi_{(x)} = x\frac{\hbar}{i}\frac{\partial\psi_{(x)}}{\partial x}$$

$$[\hat{p}_x, \hat{x}]\psi_{(x)} = \frac{\hbar}{i}\frac{\partial}{\partial x}(x\psi_{(x)})$$

$$= \frac{\hbar}{i}\left[x\frac{\partial\psi_x}{\partial x} + \psi_{(x)}\right]$$

$$[\hat{x}, \hat{p}_x]\psi_{(x)} = \left[x\frac{\hbar}{i}\frac{\partial\psi_{(x)}}{\partial x} - \frac{\hbar}{i}\left(x\frac{\partial\psi_x}{\partial x} + \psi_x\right)\right]$$

$$= \left[x\frac{\hbar}{i}\frac{\partial\psi_x}{\partial x} - \frac{\hbar}{i}x\frac{\partial\psi_x}{\partial x} - \frac{\hbar}{i}\psi_{(x)}\right]$$

$$[\hat{x}, \hat{p}_x]\psi_{(x)} = \frac{\hbar}{i}\left[\cancel{x\frac{\partial\psi_x}{\partial x}} - \cancel{x\frac{\partial\psi}{\partial x}} - \psi_x\right]$$

$$[\hat{x}, \hat{p}_x]\cancel{\psi_x} = -\frac{\hbar}{i}\cancel{\psi_x}$$

$$[\hat{x}, \hat{p}_x] = -\frac{\hbar}{i}$$

$$[\hat{x}, \hat{p}_x] = i\hbar$$

2. $[\hat{x}^2, \hat{p}_x] = [\hat{x}\hat{x}, \hat{p}_x]$

$$= [\hat{x}, \hat{p}_x)\hat{x} + \hat{x}(\hat{x}, \hat{p}_x)$$

$$= i\hbar\hat{x} + \hat{x}i\hbar$$

$$[\hat{x}^2, \hat{p}_x] = 2i\hbar\hat{x}$$

3. $[\hat{x}^3, \hat{p}_x] = [\hat{x}\hat{x}^2, \hat{p}_x] = \hat{x}(\hat{x}^2, \hat{p}_x) + (\hat{x}, \hat{p}_x)\hat{x}^2$

$$= \hat{x}\,2i\hbar\hat{x} + i\hbar\hat{x}^2$$

$$= 2i\hbar\hat{x}^2 + i\hbar\hat{x}^2$$

$$= 3i\hbar\hat{x}^2$$

4. $[\hat{x}, \hat{p}_x^2] = [\hat{x}, \hat{p}_x\hat{p}_x]$

$$[\hat{A}, \hat{B}\hat{C}] = (\hat{A}, \hat{B})\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

$$= (\hat{x}, \hat{p}_x)\hat{p}_x + \hat{p}_x[\hat{x}, \hat{p}_x]$$

$$= i\hbar\hat{p}_x + \hat{p}_x i\hbar$$

$$= 2i\hbar\hat{p}_x$$

$$[\hat{x}, \hat{p}_x] = i\hbar$$

(iii) Let us now consider the commutator position operator x, and momentum p

$$\hat{p}_y = \frac{\hbar}{i} \partial/\partial y$$

$$[\hat{x}, \hat{p}_y]\psi_y = [\hat{x}\hat{p}_y - \hat{p}_y \hat{x}]\psi_y$$

$$= \left[\hat{x} \frac{\hbar}{i} \partial/\partial y - \frac{\hbar}{i} \partial/\partial y \, \hat{x}\right](\psi_y)$$

$$= \hat{x} \frac{\hbar}{i} \frac{\partial}{\partial y} - \frac{\hbar}{i} \frac{\partial x}{\partial y} \frac{\hbar}{i}$$

$$\left(x \frac{\partial \psi}{\partial y} + \psi \frac{\partial x}{\partial y}\right)$$

$$= x \frac{\hbar}{i} \frac{\partial \psi}{\partial y} - \frac{\hbar}{i} x \frac{\partial \psi}{\partial y} - \frac{\hbar}{i} \psi \frac{\partial x}{\partial y}$$

$$= x \frac{\hbar}{i} \frac{\partial \psi}{\partial y} - x \frac{\hbar}{i} \frac{\partial \psi}{\partial y} = 0$$

$$[\hat{x}, \hat{p}_y] = 0$$

(iv)

$$[x, y] : (\hat{x}\hat{y} - \hat{y}\hat{x}) = 0$$

$$[\hat{p}_x, \hat{p}_y]\psi = (\hat{p}_x \hat{p}_y - \hat{p}_y \hat{p}_x]\psi$$

$$= \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \frac{\hbar}{i} \partial/\partial y - \frac{\hbar}{i} \partial/\partial y \frac{\hbar}{i} \partial/\partial x\right.$$

$$\Rightarrow -\hbar^2 \frac{\partial^2 \psi}{\partial x \partial y} + \hbar^2 \frac{\partial^2 \psi}{\partial x \partial y} = 0$$

(5) Commutator relation b/w momentum and Hamiltonian:

The Hamiltonian for a particle is given by

$$\hat{H} = \frac{\hat{p}^2}{2m}$$

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$$

$\hat{p}_x \Rightarrow$ momentum

$\hat{V}_x \Rightarrow$ potential energy operator

The commutator of $[\hat{H}, \hat{p}_x]$

(13)

$$[\hat{H}, \hat{p}_x] = \left[\frac{\hat{p}_x^2}{2m} + \hat{V}_{(x)}, \hat{p}_x\right]$$ → (i) [illegible]

$$[\hat{A}+\hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$$

$$= \left[\frac{\hat{p}_x^2}{2m}, \hat{p}_x\right] + \left[\hat{V}_{(x)}, \hat{p}_x\right]$$

$$= \frac{1}{2m}\left[\hat{p}_x^2, \hat{p}_x\right] + \left[\hat{V}_x, \hat{p}_x\right]$$

[since $[\hat{p}_x^2, \hat{p}_x] = 0$]

$$= 0 + [\hat{V}_x, \hat{p}_x]$$

$$= [\hat{V}_x, \hat{p}_x]$$

Now consider the operation of $[\hat{H}, \hat{p}_x]$ on $\psi_{(x)}$ we have,

$$[\hat{H}, \hat{p}_x]\psi_x = [\hat{V}_x, \hat{p}_x]\psi_{(x)}$$

$$[\hat{V}_x, \hat{p}_x]\psi_{(x)} = [\hat{V}_x \hat{p}_x$$

$$= [\hat{V}_x \hat{p}_x - \hat{p}_x \hat{V}_x]\psi_x$$

$$= \left[\hat{V}_x \frac{\hbar}{i}\partial/\partial x - \frac{\hbar}{i}\partial/\partial x\, \hat{V}_x\right]\psi_x$$

$$= \hat{V}_x \frac{\hbar}{i}\frac{\partial \psi_x}{\partial x} - \frac{\hbar}{i}\partial/\partial x(\hat{V}_x \psi_x)$$

$$= \hat{V}_x \frac{\hbar}{i}\frac{\partial \psi_x}{\partial x} - \frac{\hbar}{i}\left(\frac{\partial \psi_x}{\partial x}\hat{V}_x + \psi_x \frac{\partial V_x}{\partial x}\right)$$

$$= \hat{V}_x \frac{\hbar}{i}\frac{\partial \psi_x}{\partial x} - \frac{\hbar}{i} V_x \frac{\partial \psi_x}{\partial x} - \frac{\hbar}{i}\psi_x \frac{\partial V_x}{\partial x}$$

$$[\hat{H}, \hat{p}_x]\psi_x = -\frac{\hbar}{i}\psi_x \frac{\partial V_x}{\partial x}$$

$$[\hat{H}, \hat{p}_x] = -\frac{\hbar}{i}\frac{\partial V_x}{\partial x}$$

Case (i):

If a particle is free $V_x = 0$

$[\hat{H}, \hat{p}_x] = 0$ free particle

Case (ii) = if a particle momentum operator is three dimension and P.E fun $V = V(r)$

$$\hat{p} = \frac{\hbar}{i}\nabla$$

$$[\hat{H}, \hat{p}] = -i\hbar\nabla V_{(r)}$$

Commutator relation b/w Ladder operators $\hat{L}_+$ and $\hat{L}_-$.

Let us define the operators,

$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$

$\hat{L}_- = \hat{L}_x - i\hat{L}_y$

the commutation relation of $\hat{L}_z$ with $\hat{L}_+$ and $\hat{L}_-$

$[\hat{L}_z, \hat{L}_+] = [\hat{L}_z \hat{L}_+ - \cancel{\hat{L}_+ \hat{L}_z}]$

$= [\hat{L}_z(\hat{L}_x + i\hat{L}_y) - (\hat{L}_x + i\hat{L}_y)\hat{L}_z]$

$(L_z, \hat{L}_x + i\hat{L}_y) = [\hat{L}_z, \hat{L}_x] + i[\hat{L}_z, \hat{L}_y]$

$= +i\hbar\hat{L}_y + i\cancel{\hbar} - i\hbar\hat{L}_x$.

$= \hbar[\hat{L}_x - i\hat{L}_y]$

$(\hat{L}_z(\hat{L}_x + i\hat{L}_y) = \hbar\hat{L}_+$

$(\hat{L}_x + i\hat{L}_y, \hat{L}_z) = (\hat{L}_x, \hat{L}_z) + [i\hat{L}_y, \hat{L}_z]$

$= -i\hbar\hat{L}_y + i\, i\hbar\hat{L}_x$

$= -i\hbar\hat{L}_y - \hbar\hat{L}_x$

$= -\hbar[L_x + iL_y]$

$= -\hbar\hat{L}_+$

$[L_z, L_-] = L_z(\hat{L}_x - i\hat{L}_y)$

$= (L_z, \hat{L}_x) - i(L_z, \hat{L}_y)$

$= i\hbar\hat{L}_y - i\, -i\hbar\hat{L}_x$

$= i\hbar\hat{L}_y - \hbar\hat{L}_x$

$= -\hbar[\hat{L}_x - i\hat{L}_y]$

$= -\hbar\hat{L}_-$

Eqn ① and ② may be expressed in compact form

$[L_z, L_\pm] = \pm\hbar L_\pm$

The commutation b/w $\hat{L}_+$ and $\hat{L}_-$

$[\hat{L}_+, \hat{L}_-] = [(\hat{L}_x + i\hat{L}_y), (\hat{L}_x - i\hat{L}_y]$

$= [\hat{L}_x \hat{L}_x] - i[\hat{L}_x \hat{L}_y] + i[L_y L_x]$
$+ [L_y L_y]$

$= -i(\hat{L}_x, \hat{L}_y] + i[\hat{L}_y \hat{L}_x]$

$= -i \cdot i\hbar L_z + i\, -i\hbar L_z$

$= \hbar L_z + \hbar L_z = 2\hbar L_z$

[illegible] relation for the components of orbital angular momentum

Orbital angular momentum of a particle having p and position vector r and relative to an arbitrary orbitary any origin is defined as,

$$L = r \times p.$$

The components of angular momentum in cartesian co-ordinate may be obtain $(\hat{i} L_x + \hat{j} L_y + \hat{k} L_z) =$

$$(\hat{i} x + \hat{j} y + \hat{k} z) \times (\hat{i} p_x + \hat{j} p_y + \hat{k} p_z)$$

$$= \hat{i} (x, p_x) + \hat{j} (y, p_y) + \hat{k} (z, p_z)$$

$$= \hat{i} (y p_z - z p_y) + \hat{j} (z p_x - x p_z) + \hat{k} (x p_y - y p_x)$$

Comparing co-efficient i, j and k we get angular momentum component operator

$$L_x = y p_z - z p_y = y\left(\frac{\hbar}{i} \partial/\partial z\right) - z\left(\frac{\hbar}{i} \partial/\partial y\right)$$

$$L_y = z p_x - x p_z = z\left(\frac{\hbar}{i} \partial/\partial x\right) - x\left(\frac{\hbar}{i} \partial/\partial z\right)$$

$$L_z = x p_y - y p_x = x\left(\frac{\hbar}{i} \partial/\partial y\right) - y\left(\frac{\hbar}{i} \partial/\partial x\right)$$

Since, $p_x = \hbar/i \, \partial/\partial x$, $p_y = \hbar/i \, \partial/\partial y$, $p_z = \hbar/i \, \partial/\partial z$

Commutation relation $[\hat{L}_x, \hat{L}_y]$

$$= [\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x]$$

$$[\hat{L}_x, \hat{L}_y] = \left[y\left(\frac{\hbar}{i} \partial/\partial z\right) - z\left(\frac{\hbar}{i} \partial/\partial y\right), z\left(\hbar/i \, \partial/\partial x\right) - x\left(\frac{\hbar}{i}\right.\right.$$

$$= \frac{\hbar}{i}\left[(y \, \partial/\partial z - z \, \partial/\partial y), \frac{\hbar}{i}\left(z \, \partial/\partial x - x \, \partial/\partial z\right.\right.$$

$$= -\hbar^2 \left[yz \frac{\partial^2}{\partial z \partial x} - yx \frac{\partial^2}{\partial z^2} - z^2 \frac{\partial^2}{\partial y \partial x} + xz \frac{\partial^2}{\partial y \partial z}\right] + y\partial/\partial x$$

Adding R.H.S by $y \, \partial/\partial x$

$$[\hat{L}_y \hat{L}_x] = \left[\left(z \frac{\hbar}{i} \partial/\partial x - x \frac{\hbar}{i} \partial/\partial z\right), y \frac{\hbar}{i} \partial/\partial z - z \frac{\hbar}{i} \partial/\partial y\right]$$

$$= -\hbar^2 \left[zy \frac{\partial^2}{\partial x \partial z} - z^2 \frac{\partial^2}{\partial x \partial y} - xy \partial^2/\partial z^2 + xz \frac{\partial^2}{\partial z \partial y}\right]$$

Adding R.H.S. $\hbar^2 x \, \partial/\partial y$

$$= -\hbar^2 \left[zy \frac{\partial^2}{\partial x \partial z} - z^2 \frac{\partial^2}{\partial x \partial y} - xy \partial^2/\partial z^2 + xz \frac{\partial^2}{\partial z \partial y}\right] + \hbar^2 x \, \partial/\partial y$$

$$= -\hbar^2 \left[xy \frac{\partial^2}{\partial x \partial z} - x^2 \frac{\partial^2}{\partial x \partial y} + xy \frac{\partial^2}{\partial z^2} + xz \frac{\partial^2}{\partial x \partial y} + x \, \partial/\partial y \right]$$

$$= \left[-\hbar^2 \left[yz \frac{\partial^2}{\partial z \partial x} - yx \frac{\partial^2}{\partial z^2} - z^2 \partial/\partial y \partial x + xz \frac{\partial^2}{\partial y \partial z} + y \, \partial/\partial x \right] \right.$$

$$- \left[-\hbar^2 \left(xy \, \partial/\partial x \partial z - z^2 \frac{\partial^2}{\partial x \partial y} - xy \frac{\partial^2}{\partial z^2} + xz \frac{\partial^2}{\partial z \partial y} + x \partial/\partial y \right] \right.$$

$$= \hbar^2 \left[-\cancel{yz \frac{\partial^2}{\partial z \partial x}} + \cancel{yx \frac{\partial^2}{\partial x^2}} + \cancel{z^2 \frac{\partial^2}{\partial y \partial x}} - \cancel{xz \frac{\partial^2}{\partial y \partial z}} - y \, \partial/\partial x + \cancel{xy \frac{\partial^2}{\partial x \partial z}} - \cancel{z^2 \frac{\partial^2}{\partial x \partial y}} - \cancel{xy \frac{\partial^2}{\partial z^2}} + \cancel{xz \frac{\partial^2}{\partial z \partial y}} + x \, \partial/\partial y \right]$$

$$= \hbar^2 \left[x \, \partial/\partial y - y \, \partial/\partial x \right]$$

$$= -\frac{\hbar}{i} \frac{\hbar}{i} \left[x \, \partial/\partial y - y \, \partial/\partial x \right]$$

$$- \frac{\hbar}{i} \left(\underbrace{x \frac{\hbar}{i} \partial/\partial y - y \frac{\hbar}{i} \partial/\partial x}_{\hat{L}_z} \right]$$

$$= -\frac{\hbar}{i} \hat{L}_z$$

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[L_z, L_x] = i\hbar \hat{L}_y$$

$$[\hat{L}, \times \hat{L}] = i\hbar \hat{L}$$

Commutation relation of L^2 with components of $\hat{L}_x, \hat{L}_y, \hat{L}_z$

The total angular momentum is defined by the relation

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$[L^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x]$$

$$= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2$$

$$[L_x^2, L_x] = [L_x L_x, L_x] = L_x [L_x, L$$
$$+ [L_x, L_x] L_x = 0$$

$$[L_y^2, L_x] = [L_y L_y, L_x] = L_y [L_y, L$$
$$+ [L_y, L_x] L_y$$

$$= L_y \, {-i\hbar} L_z + {-i} \hbar L_z L_y$$

$$= -i\hbar L_y L_z - i\hbar L_z L_y$$

$$= \cancel{-} i\hbar \cancel{[} L_y L_z]$$

$$= -i\hbar L_y L_z + i\hbar L_y L_z = 0$$

$$[\hat{L}^2, \hat{L}_x] = 0$$

$$[\hat{L}^2, \hat{L}_y] = 0$$

$$[\hat{L}^2, \hat{L}_z] = 0$$

Hence L^2 commutator of any of three components of the angular momentum operator from eqn ① L^2 & L_z commutate so they have simultaneous eigen function and hence a simultaneously measura

② Q2 Uncertainty relation

Let f and g two acceptable function specify in connection with hermitian operation.

$$\int f^* f\,d\tau \int g^* g\,d\tau \ge \frac{1}{4}\left[\int (f^* g + g^* f)\,d\tau\right]^2 \to ①$$

This relation is due to Schwartz equality

$$f = (\hat{p} - \bar{p})\phi,\quad g = i(\hat{q} - \bar{q})\phi \to ②$$

where $\bar{p}, \bar{q}$ mean value associated with $\hat{p}$ & $\hat{q}$

$$\bar{p} = \lim_{\tau\to\infty} \frac{\int_\tau \phi^* \hat{p}\phi\,d\tau}{\int_\tau \phi^*\phi\,d\tau},\quad \bar{q} = \lim_{\tau\to\infty} \frac{\int \phi^* \hat{q}\phi\,d\tau}{\int_\tau \phi^*\phi\,d\tau}$$

Now sub the value of f & g from ② & ① we get

$$\int (\hat{p}-\bar{p})^* \phi^* (\hat{p}-\bar{p})\phi\,d\tau \int (\hat{q}-\bar{q})^* \phi^* (\hat{q}-\bar{q})\phi\,d\tau$$

$$\ge \frac{1}{4}\left[\int (\hat{p}-\bar{p})^* \phi^* i(\hat{q}-\bar{q})\phi\,d\tau - i(\hat{q}-\bar{q})^* \phi^* (\hat{p}-\bar{p})\phi\,d\tau\right]^2 \to ③$$

As $\hat{p}$ and $\hat{q}$ are hermitian equation operator satisfy the following condition

$$\int u^* \hat{p} v\,d\tau = \int \hat{p} u^* v\,d\tau \to ④$$

$\bar{p}$ & $\bar{q}$ are constant

Inequality equ ⑤ then reduce to

$$\int \phi^* (\hat{p} - \bar{p})^2 \phi \, d\tau \int \phi^* (\hat{Q} - \bar{q})^2 \phi \, d\tau \geq \frac{1}{4} \left[\int \phi^* (\hat{p}\hat{Q} - \hat{Q}\hat{p}) \phi \, d\tau \right]^2 \rightarrow ⑤$$

Let us consider meaning of the Quantity $\int \phi^* (\hat{p} - \bar{p})^2 \phi \, d\tau = \langle (\hat{p} - \bar{p})^2 \rangle$

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

$$= (\Delta p)^2$$

$$\int \phi^* (\hat{p} - \bar{p}^2) \phi \, d\tau = (\Delta p)^2$$

$$\int \phi^* (\hat{q} - \bar{q})^2 \phi \, d\tau = (\Delta q)^2$$

$$(\Delta p)^2 (\Delta q)^2 \geq -\frac{1}{4} \left[\int \phi^* (\hat{p}\hat{Q} - \hat{Q}\hat{p}) \phi \, d\tau \right]^2 \rightarrow ⑥$$

If $\hat{p}$ $\hat{Q}$ Commute right hand side is 0. since

$$\hat{p}\hat{Q} - \hat{Q}\hat{p}$$

$$\hat{p}\hat{Q} - \hat{Q}\hat{p} = 0$$

and its possible for $(\Delta p)^2$ or $(\Delta q)^2$ to be 0

$(\Delta p)^2 (\Delta q)^2 \geq 0$ zero or an both to vanish.

$$\int \phi^* (\hat{p} - \bar{p})^2 \phi \, d\tau \int \phi^* (\hat{Q} - \bar{q}) \phi \, d\tau \geq \frac{1}{4} \left[\int \phi^* (\hat{p}\hat{Q}$$

Uncertainity Relation for position and momentum.

Suppose for instance that is linear momentum operator

$$\hat{p} \rightarrow \frac{\hbar}{i} \partial / \partial q$$

Associated with position q and $\hat{Q}$ stands for the co-ordinate q then

$$(\hat{p}\hat{Q} - \hat{Q}\hat{p}) \psi = \left(\frac{\hbar}{i} \frac{\partial}{\partial q} q - q \cdot \frac{\hbar}{i} \partial / \partial q \right) \psi$$

$$= \frac{\hbar}{i} \partial / \partial q \, (q\psi) - q \cdot \frac{\hbar}{i} \frac{\partial \psi}{\partial q}$$

$$= \frac{\hbar}{i} \left[q \cdot \cancel{\frac{\partial \psi}{\partial q}} + \psi - q \cancel{\frac{\partial \psi}{\partial q}} \right]$$

$$(\hat{p}\hat{Q} - \hat{Q}\hat{p}) \cancel{\psi} = \frac{\hbar}{i} \cancel{\psi}.$$

$$(\hat{p}\hat{Q} - \hat{Q}\hat{p}) = \frac{\hbar}{i} \rightarrow ⑦$$

On substituting this result in equ (6) we get

$$(\Delta p)^2 (\Delta q^2) \geq -\frac{1}{4} \frac{\hbar^2}{i^2}$$

$$(\Delta p)^2 (\Delta q)^2 \geq \frac{\hbar^2}{4}$$

$$(\Delta P)(\Delta q) \geq \frac{\hbar}{2} \rightarrow 8(a)$$

This is Heisenberg uncertainity relation for position and momentum

This relation may alternatively be written in terms of position q and propagation vector $k = \frac{p}{\hbar}$

$$(\Delta k)(\Delta q) \geq \frac{1}{2} \rightarrow 8(b)$$

Uncertainity relation for Energy and time

Let operator $\hat{P}$ represents energy operator and $\hat{Q}$ time operator

$$\hat{P} = \hat{E} = i\hbar \, \partial/\partial t$$

$$\hat{Q} = t$$

$$(\hat{P}\hat{Q} - \hat{Q}\hat{P})\psi = (i\hbar \, \partial/\partial t \cdot t - t \cdot i\hbar \, \partial/\partial t)\psi$$

$$= i\hbar \, \partial/\partial t \, (t\psi) - t \, i\hbar \frac{\partial \psi}{\partial t}$$

$$= i\hbar \left[\partial/\partial t \, (t\psi) - t \cdot \frac{\partial \psi}{\partial t} \right]$$

$$= i\hbar \left[t \cdot \frac{\partial \psi}{\partial t} + \psi \frac{\partial t}{\partial t} - t \frac{\partial \psi}{\partial t} \right]$$

$$(\hat{P}\hat{Q} - \hat{Q}\hat{P})\psi = i\hbar \psi$$

$$(\hat{P}\hat{Q} - \hat{Q}\hat{P}) = i\hbar \rightarrow \textcircled{9}$$

Substituting this equation in (6 eq)

$$(\Delta E)^2 (\Delta t)^2 \geq \frac{1}{4} (\hbar)^2$$

$$\Delta E^2 \cdot \Delta t^2 \geq \frac{\hbar^2}{4}$$

$$(\Delta E)(\Delta t) \geq \frac{\hbar}{2} \rightarrow \textcircled{10}$$

This equation is called Heisenberg uncertainity relation of energy and time

Uncertainity relation for Number of photons and phase

The Uncertainity relation hold on all canonically conjugate Quantities product as dimension of joule second.

We consider the uncertainity relation for the no. of photons N and the phase ϕ

$\phi = \omega t$ of the wave

$\omega \rightarrow$ mono chromatic relation of frequency

On one hand wave may be considered as a collection of photons each having energy.

$E = \hbar\omega$

On the other hand it may be treated as a classical electromagnetic wave :

$$\Delta N \; \Delta\phi \geq 1/2 \quad (11)$$

eqn (11) we start from the uncertainity relation for energy and time

$$\Delta E \, \Delta t \geq \hbar/2$$

$$\Delta E = \Delta (N \hbar \omega) = \hbar \omega \Delta N$$

ΔN => Uncertainity in the no. of photons

Δt => measurement of the energy of the object with an accuracy ($\hbar\omega \Delta N$) phase ϕ of the wave changes . by the $\omega\Delta t$

$$\Delta E \; \Delta t \geq \hbar/2$$

$$(\cancel{\hbar}\omega \Delta N) \, \Delta t \geq \cancel{\hbar}/2$$

$$\Delta N \; \Delta(\omega t) \geq 1/2$$

$$\Delta N . \Delta\phi \geq 1/2 \rightarrow (12)$$

this relation is heisenberg uncertainity for no. of photons and phase.

---

② 2m

Bra and ket is vectors

Bra

$\langle | \rightarrow$ ket Bra

$| \rangle \rightarrow$ Bra ket

Accordingly each dir state may be represented by a certain type of vector known as ket vector (or) ket it represent by a simple symbol ($|\rangle$)

Ex:-

$|a\rangle$ $|b\rangle$ denotes the ket vector corresponding to state a , b of this system

d ket form a linear vector space. linear combination of several ket vectors is also a ket vector.

Ex:- let us consider three kets $|a\rangle$, $|b\rangle$, $|c\rangle$ and 3 arbitary complex numbers c_1, c_2, c_3 the linear combination

$$|v\rangle = c_1|a\rangle + c_2|b\rangle + c_3|c\rangle$$

Bra vectors

The vector of dual space are called Bra vectors. simply the Bras and denote in general one of them simply $\langle|$

ex:-

$\langle a|, \langle b|, \ldots$

Bra and Ket.

The two spaces Bra and ket said to be dual to each other if the ket space as a finite the number of a dimension. the Bra space has the same no. of dimension.

If the ket space has infinite no. of dimension the Bra space as the same property. ans

Bra and Ket associated by this one to one set to be conjugate of each other and are labled by the same indices. thus the Bra conjugate to ket. the ket B represents the symbol $|a\rangle \rightarrow \langle a|$

$$|a\rangle + |b\rangle \longleftrightarrow \langle a| + \langle b|$$

In complex conjugate,

$$c|a\rangle \longleftrightarrow c^*|a\rangle$$

Now we know the rules that the any complete bra ket expansion denote a number and the any incomplete denotes a vector of the bra of the space accordingly to contain the 1st or 2nd part of Braket

$$\overset{\text{complex}}{\overline{\langle a|b\rangle}} = \langle b|a\rangle^*$$

$$\langle a|\{c|b\rangle = c\langle a|b\rangle$$

the bra conjugate to ket

$$|v\rangle = c_1|a\rangle + c_2|b\rangle$$

$$\langle v| = c_1^*\langle a| + c_2^*\langle b|$$

③ Hermitian operator

The expectation average of a dinamical variable by definition is the arithmetic mean of possible result of a press of the variable. Each possible result being weighted by its probability. now if P is the schrodinger operator associated

5]

[illegible] [illegible] observable quantity then the value of observable quantity in to normalized state ψ. ψ is given by

$$\text{av } P_\psi = \langle p \rangle = \int \psi^* p \psi \, d\cancel{x} \Rightarrow ①$$

where $\psi^* \Rightarrow$ Complex conjugate of state ψ and operator $\hat{p}$ are associated with dynamical variable said to be hermitian. if its average value in any state ψ is real. if the average of p is the real. if the state ψ is two real state ψ

if $\int \psi^* \hat{p} \psi \, dx$ must be real. imaginary factor must be zero.

$$\text{Im} \int \psi^* p \psi \, dx = 0 \rightarrow ②$$

Complex conjugate of the system

$\int \psi^* \hat{p} \psi \, dx$ may be written as.

$$\int \psi^* \hat{p} \psi \, dx = \int (\psi^* \hat{p} \psi)^* dx$$

$$\int \psi^* \hat{p} \psi \, dx = \int \psi (\hat{p} \psi)^* dx \rightarrow ③$$

(35)

$$\int u^* \hat{p} u \, dx + \int u^* \hat{p} v \, dx + \int v^* \hat{p} u \, dx +$$

$$\int v^* \hat{p} v \, dx =$$

$$\int \hat{p}^* u^* u \, dx + \int \hat{p}^* u^* v \, dx +$$

$$\int \hat{p}^* v^* u \, dx + \int \hat{p}^* v^* v \, dx$$

$$\rightarrow ⑥$$

and p is hermitian operator in the state u and v therefore the relation ④ provides

$$\int u^* \hat{p} u \, dx = \int \hat{p}^* u^* u \, dx$$

$$\int v^* \hat{p} v \, dx = \int \hat{p}^* v^* v \, dx$$

in view above equation ⑥ gives

$$\int \psi^* \hat{p} u \, dx$$

$$\int \hat{p}^* \cancel{u^*} u \, dx + \int u^* \hat{p} v \, dx + \int v^* \hat{p} u \, dx$$

$$+ \int \hat{p}^* \cancel{v^* v} \, dx =$$

$$\int \hat{p}^* \cancel{u^* u} \, dx + \int \hat{p}^* u^* v \, dx$$

$$+ \int \hat{p}^* v^* u \, dx +$$

$$\int \hat{p}^* \cancel{v^*} v \, dx$$

$$\int u^* \hat{p} v \, dx + \int v^* \hat{p} u \, dx = \int \hat{p}^* u^* v \, dx + \int \hat{p}^* v^* u \, dx \rightarrow ⑦$$

We use the function (iv) instead of v in eqn ⑦ we get instead of eqn ⑧

$$\int u^* \hat{p}\,(iv)\,dx + \int (iv)^* \hat{p}\, u\,dx = \int \hat{p}^* u^* (iv)\,dx + \int \hat{p}^* (iv)^* u\,dx$$

$$i\int u^* \hat{p}\, v\,dx - i\int v^* \hat{p}\, u\,dx = i\int \hat{p}^* u^* v\,dx - i\int \hat{p}^* v^* u\,dx$$

Cancellation of factor (i) with the above

$$\int u^* \hat{p}\, v\,dx - \int v^* \hat{p}\, u\,dx = \int \hat{p}^* u^* v\,dx - \int \hat{p}^* v^* u\,dx \rightarrow ⑨$$

Adding equation ⑦ and ⑨

$$\int u^* \hat{p}\, v\,dx + \int v^* \cancel{\hat{p}}\, u\,dx + \int u^* \hat{p}\, v\,dx - \int v^* \hat{p}\, \cancel{u}\,dx = \int \hat{p}^* u^* v\,dx + \int \hat{p}^* v^* \cancel{u}\,dx + \int \hat{p}^* u^* v\,dx - \int \hat{p}^* v^* \cancel{u}\,dx$$

$$\cancel{2}\int u^* \hat{p}\, v\,dx = \cancel{2}\int \hat{p}^* u^* v\,dx$$

$$\int_{-\infty}^{\infty} u^* \hat{p}\, v\,dx = \int_{-\infty}^{\infty} \hat{p}^* u^* v\,dx \rightarrow ⑩$$

If an operator satisfy eqn ⑩ whenever u and v are normalizable we called it hermitian self adjoint (or) real. u and v are acceptable normalized wave function define over a certain range of configuration space τ then operator p associated with a dynamical variable is Hermitian

$$\int_{-\infty}^{+\infty} u^* \hat{p}\, v\,d\tau = \int_{-\infty}^{+\infty} \hat{p}^* u^* v\,d\tau \rightarrow ⑪$$

This equation may be expressed

$$(u, pv) = (\hat{p}u, v) \rightarrow ⑫$$

the operator can be applied either factor in the scalar product must hold for eqn ④ operator associated with schrodinger real dynamical variable we conclude every schrodinger operator is hermitian.

[illegible]//

Properties

Hermitian operators have real eigen value

Proof

Let ψ be an eigen values of Hermitian operator in the state described by normalized wave function ψ then eigen value equation is

$$\hat{P}\psi = \lambda\psi \rightarrow ①$$

Taking its complex conjugate

$$\hat{P}^*\psi^* = \lambda^*\psi^* \rightarrow ②$$

According to condition of Hermitian operator

$$\int \hat{P}\psi^*\psi\, d\tau = \int \hat{P}^*\psi^*\psi\, d\tau \rightarrow ③$$

using eqn ① and ② in ③ gives

$$\int \psi^*\lambda\psi\, d\tau = \int \lambda^*\psi^*\psi\, d\tau$$

$$\lambda\int \psi^*\psi\, d\tau = \lambda^*\int \psi^*\psi\, d\tau$$

$$\lambda\int \psi^*\psi\, d\tau - \lambda^*\int \psi^*\psi\, d\tau = 0$$

$$(\lambda - \lambda^*)\int \psi^*\psi\, d\tau = 0$$

$$\int \psi^*\psi\, d\tau = 0$$

$$\int \psi^*\psi\, d\tau = 1 \text{ (condition of normalisation)}$$

$$\lambda - \lambda^* = 0$$

$$\lambda = \lambda^*$$

This is only possible if λ is real number this proofs that the eigen value of each Hermitian operators is real.

Properties 2:-

The two eigen function of Hermitian operator, belonging to different eigen values, are orthogonal

let $\hat{P}$ be any Hermitian operator and ψ_1 and ψ_2 are two eigen function of operator if λ_1 and λ_2 are two eigen values of operator corresponding to eigen function ψ_1 and ψ_2 respectively then eigen value equation

$$\left.\begin{aligned} \hat{P}\psi_1 &= \lambda_1\psi_1 \\ \hat{P}\psi_2 &= \lambda_2\psi_2 \end{aligned}\right\} \rightarrow ①$$

Taking the complex conjugate of these equation

$$\hat{P}^* \psi_1^* = \lambda_1^* \psi_1^* \quad (\text{or})$$

$$\hat{P}^* \psi_1^* = \lambda_1 \psi_1^*$$

$$\hat{P}^* \psi_2^* = \lambda_2^* \psi_2^* \quad (\text{or})$$

$$\hat{P}^* \psi_2^* = \lambda_2 \psi_2^* \quad \rightarrow (2)$$

Since λ_1 and λ_2 being eigen value of hermitian operator are real.

According to general condition of Hermitian operator

$$\int \psi_2^* \hat{P} \psi_1 \, d\tau = \int \hat{P}^* \psi_2^* \psi_1 \, d\tau \rightarrow ③$$

Using eqn ① and ② in ③ gives

$$\int \psi_2^* \lambda_1 \psi_1 \, d\tau = \int \lambda_2 \psi_2^* \psi_1 \, d\tau$$

$$\lambda_1 \int \psi_2^* \psi_1 \, d\tau = \lambda_2 \int \psi_2^* \psi_1 \, d\tau$$

$$\lambda_1 \int \psi_2^* \psi_1 \, d\tau - \lambda_2 \int \psi_2^* \psi_1 \, d\tau = 0$$

(normalization

$$(\lambda_1 - \lambda_2) \int \psi_2^* \psi_1 \, d\tau = 0$$

$\lambda_1 \neq \lambda_2$ we have $\int \psi_2^* \psi_1 \, d\tau = 0$

Thereby indicating that ψ_1 and ψ_2 are orthogonal functions

This theorem orthogonality relation

$$\int \psi_i^* \psi_j \, d\tau = \delta_{ij}$$

are satisfied for a set of normalized eigen function belonging to different eigen values λ_i

Properties :

If two Hermitian operators commute, then their product is also hermitian operator:

Let ψ_1 and ψ_2 are two eigen function

$\hat{A}$ and $\hat{B}$ are two hermitian operator.

Now consider the integral

$$\int \psi_1^* \hat{A}\hat{B} \psi_2 \, d\tau$$

If $\hat{A}$ is hermitian operator

$$\int \psi_1^* \hat{A} \hat{B} \psi_2 \, d\tau = \int \psi_1^* \hat{A} (\hat{B}\psi_2) d\tau$$

$$= \int \psi_1^* \hat{A}^* (\hat{B} \psi_2) \, d\tau \rightarrow ①$$

If $\hat{B}$ is hermitian operator

$$\int \psi_1^* A^* B^* \psi_2 \, d\tau = \int \psi_1^* \hat{B} (\hat{A}\psi_2) d\tau$$

$$= \int \psi_1^* \hat{B}^* (\hat{A}\psi_2) \, d\tau \rightarrow ②$$

from eqn ① & ③

$$\int \psi_1^* \hat{A} \hat{B} \psi_2 \, d\tau = \int \psi_1^* \hat{A}^* \hat{B}^* \psi_2 \, d\tau \rightarrow ③$$

If operator $\hat{A}$ and $\hat{B}$ are be hermitian

$$\int \psi_1^* \hat{A} \hat{B} \psi_2 \, d\tau = \int \psi_1^* \hat{B}^* \hat{A}^* \psi_2 \, d\tau$$

$$\hat{A}\hat{B} = \hat{B}\hat{A}$$

$$\hat{A}^* \hat{B}^* = (\hat{B}^*)(\hat{A}^*) \rightarrow ④$$

In view of this equation ③

be comes $\int \psi_1^* \hat{A} \hat{B} \psi_2 \, d\tau = \int \hat{A}^* \hat{B}^* \psi_1^* \psi_2 \, d\tau$

$$\rightarrow ⑤$$

this condition product operator $(\hat{A}\hat{B})$ to be hermitian operator

Schrodinger picture (or) Representation

① In Schrodinger picture the state vectors are time dependent by the operators are time independent. In this picture, the state are the system at the given time t by the state vector $\psi_s(q,t)$ and the evaluation of the system described by the time dependents of $\psi_s(q,t)$

The Schrodinger equation in operator form

$$H_s \psi_s(q,t) = i\hbar \frac{\partial \psi_s(q,t)}{\partial t} \rightarrow ①$$

$H_s \rightarrow$ time independent Hamiltonian operator.

The special feature of the picture is that any operator Q_s corresponding to a given physical observable is time independent

$$\frac{\partial Q_s}{\partial t} = 0$$

Know consider a unitary transformation in which the state vector $\psi(q, t_0)$ is changed $\psi(q, t)$

$$\psi_s(q, t) = U(t, t_0)\psi(q, t_0) \rightarrow ②$$

where $U(t, t_0) \Rightarrow$ linear operator the operator $U(t, t_0)$ satisfy the following condition.

$$U(t_0, t_0) = 1 \rightarrow 3(a)$$

$$UU^{+} = U^{+}U = 1 \longrightarrow 3(b)$$

The condition 3(a) ; $t = t_0$ the function $\psi(q, t)$ and $\psi(q, t_0)$ must be identical

the condition 3(b) ; direct consequence of the independent of normalization amplitudes of the state from the choice of the

instant of time.

$$\int \psi_s^{*}(q, t)\,\psi_s(q, t)\,dq = \int \psi^{*}(q, t_0)\,\psi(q, t_0)\,dt = 1 \hookrightarrow ④$$

Now substituting eqn ② in ①

$$H_s\,U(t, t_0)\,\psi(q, t_0) = i\hbar\frac{\partial}{\partial t}\left\{U(t, t_0)\,\psi(q, t_0)\right\}$$

$$= \left\{i\hbar\,\frac{\partial U(t, t_0)}{\partial t}\right\}\psi(q, t_0) \hookrightarrow ⑤$$

As above eqn is true for all the state vector $\psi(q, t_0)$

$$H_s\,U(t, t_0) = i\hbar\,\partial/_{\partial t}\,U(t, t_0) \hookrightarrow ⑥$$

this eqn may be expressed

$$H_s\,U(t, t_0)\,U^{+}(t, t_0) = i\hbar\frac{\partial}{\partial t}U(t, t_0)\,U^{+}(t, t_0) \hookrightarrow ⑦$$

Using the condition,

$$U(t, t_0)\,U^{+}(t, t_0) = 1$$

$$U^{+}(t, t_0) = \frac{1}{U(t, t_0)} = U^{-1}(t, t_0)$$

We get from eqn ⑦

$$H_s = i\hbar\,\frac{\partial U(t, t_0)}{\partial t}\,\frac{1}{U(t, t_0)}$$

Separating the variables

$$\frac{\partial U(t,t_0)}{U(t,t_0)} = \frac{1}{i\hbar}\frac{i}{i} H_s \, \partial t$$

$$\frac{\delta U(t,t_0)}{U(t,t_0)} = \frac{-i}{\hbar} H_s \, \delta t$$

Integrating b/w the limits (t, t_0) we get

$$\left[\log_e U(t,t_0)\right]_{t_0}^{t} = \frac{-i}{\hbar} H_s [t]_{t_0}^{t}$$

$$\log_e U(t,t_0) - \log_e U(t_0,t_0)$$

$$= \frac{-i}{\hbar} H_s [t - t_0]$$

As $U(t_0,t_0) = 1$

$$\log_e U(t,t_0) - \log_e U(t_0,t_0) = -i/\hbar \; H_s \; t - t_0$$

$\log_e U(t_0 t_0) = 0$

$$\log_e U(t,t_0) = -i/\hbar \; H_s (t - t_0)$$

$$U(t,t_0) = \exp\left[-\frac{i}{\hbar} H_s (t - t_0)\right] \rightarrow ⑧$$

The exponential shown we treated here as an expansion into power series

Substituting equ ⑧ in equ ⑧ we see that the time development of state vector the schrodinger picture is given by

Sub

$$\psi_s(q,t) = \exp\left[-\frac{i}{\hbar} H_s (t - t_0)\right] \psi(q,t_0)$$

$\rightarrow$ ⑨

② Representation of operator in Schrodinger picture.

The expectation value of operator A in state $\psi_s(q,t)$ is given by,

$$\langle A_s \rangle = \int \psi_s^*(q,t) A_s \psi_s(q,t) \, dq$$

$$= \langle \psi_s(q,t) | A_s | \psi_s(q,t) \rangle \rightarrow ⑩$$

taking time differential of above equation

$$\frac{d}{dt}\langle A_s \rangle = \left\langle \psi_s(q,t) \middle| A_s \frac{\partial \psi_s(q,t)}{\partial t} \right\rangle + \left\langle \frac{\partial \psi_s(q,t)}{dt} \middle| A_s \psi_s(q,t) \right\rangle \rightarrow ⑪$$

As function $\psi_s(q,t)$ satisfies Schrodinger equation

H_s

$$H_s \psi_s (r,t) = i\hbar \frac{\partial \psi_s (r,t)}{\partial t}$$

$$H_s \psi_s = i\hbar \frac{\partial \psi_s}{\partial t}$$

$$H_s^* \psi_s^* = -i\hbar \frac{\partial \psi_s^*}{\partial t}$$

(or)

$$\frac{\partial \psi_s}{\partial t} = \frac{1}{i\hbar} H_s \psi_s$$

(or)

$$\frac{\partial \psi_s^*}{\partial t} = -\frac{1}{i\hbar} H_s^* \psi_s^*$$

$$\left| \frac{\partial \psi_s}{\partial t} \right> = \frac{1}{i\hbar} \left| H_s \psi_s \right>$$

$$\left< \frac{\partial \psi_s}{\partial t} \right| = -\frac{1}{i\hbar} \left< H_s \psi_s \right|$$

therefore the equation ⑪ takes the form

$$\frac{d}{dt} \langle A_s \rangle = \langle \psi_s | A_s \frac{1}{i\hbar} H_s \psi_s$$

$$+ \left(-\frac{1}{i\hbar} \langle \psi_s H_s | A_s \psi_s \rangle \right.$$

$$= \frac{1}{i\hbar} \langle \psi_s | A_s H_s - H_s A_s | \psi_s \rangle \rightarrow ⑫$$

In matrix representation the takes this form

$$i\hbar \frac{d}{dt} \langle A_s \rangle = \langle A_s H_s - H_s A_s \rangle$$

$$= \langle [A_s H_s] \rangle \rightarrow ⑬$$

It is well known that the bracket of the type < > indicate the expe value of operators enclosed by them.

If the operator A_s commute with hamiltonian H_s then $\frac{d}{dt} \langle A_s \rangle$ = E.V of operator in Schrodinger picture will be a constant of motion. The operator $\frac{dA_s}{dt}$ known as the total time derivative of operator A_s by imposing the condition of equality of E.V

$$i\hbar \frac{d}{dt} \langle A_s \rangle = \langle A_s H_s - H_s A_s \rangle + i\hbar \left< \frac{\partial A_s}{\partial t} \right> \rightarrow ⑭$$

$$\left< \frac{dA_s}{dt} \right> = \frac{d}{dt} \langle A_s \rangle \rightarrow ⑮$$

Substituting ⑮ into ⑭ we may write the dynamical law in operator form in Schrodinger picture

$$\left< \frac{dA_s}{dt} \right> = \frac{\langle A_s H_s - H_s A_s \rangle}{i\hbar} + \left< \frac{\partial A_s}{\partial t} \right>$$

$$\left< \frac{dA_s}{dt} \right> = \frac{d}{dt}$$

$$\frac{dA_s}{dt} = \frac{A_s H_s - H_s A_s}{i\hbar} + \frac{\partial A_s}{\partial t} \rightarrow ⑯$$

Heisenberg representation (or) picture

In heisenberg picture the state vectors are time independent and the time dependence is carried by the operators.

The equation of motion in Schrodinger picture is,

$$i\hbar \frac{\partial \psi_s(t)}{\partial t} = H_s \psi(t) \rightarrow ①$$

$H_s \rightarrow$ time independent hamiltonian operators.

The possibility of formulate of quantum dynamics in different pictures arises because the mathematical entities such as state vectors can't be measured directly.

Any formulation of quantum mechanics is equally suitable as the schrodinger picture if in the new picture

(i) The operators corresponding to the observables have the same eigen value spectrum as in Schrodinger picture

ii) The scalar products of vectors representing a state in new picture with new eigen vectors have the same values as the corresponding scalar products in schrodinger picture.

This two condition are satisfied by any unitary transformation U applied to vectors and operators in the schrodinger picture. It will be used with vector and operators in heisenberg picture.

Representation of state vectors in heisenberg picture:

Let us consider a time dependent unitary transformation U(t) on $\psi_s(t)$ which transforms $\psi_s(t)$ to new function of ϕ_H

$$\left.\begin{aligned} \phi_H &= U(t)\,\psi_s(t) \\ U^{-1}(t)\,\phi_H &= \psi_s(t) \end{aligned}\right\} \rightarrow ②$$

$$U(t)\,U^{\dagger}(t) = U^{\dagger}(t)\,U(t) = 1$$

$$U^{\dagger}(t) = U^{-1} \rightarrow ③$$

Also we can write,

$$U(i\hbar)\,\psi_s = U\, i\hbar \frac{\partial \psi_s}{\partial t}$$

$$= i\hbar \left[\partial/\partial t \, (U\psi_s) \right]$$

$$= i\hbar \left[\partial/\partial t \, (U\psi_s) - \psi_s \frac{\partial U}{\partial t} \right]$$

$$UH_s\psi_s = i\hbar \left[\frac{\partial \phi_H}{\partial t} - U^{-1}\phi_H \frac{\partial U}{\partial t} \right] \text{ using } \to ④$$

$$UH_s\psi_s = i\hbar \frac{\partial \phi_H}{\partial t} - i\hbar U^{-1}\phi_H \frac{\partial U}{\partial t}$$

Again

$$UH_s\psi_s = UH_s(U^{-1}U)\psi_s = UH_sU^{-1}(U\psi_s)$$

$$UH_s\psi_s = UH_sU^{-1}\phi_H \to ⑤$$

Comparing eqn ④ and ⑤

$$i\hbar \left[\frac{\partial \phi_H}{\partial U} - U^{-1}\phi_H \frac{\partial U}{\partial t} \right] = UH_sU^{-1}\phi_H$$

therefore transformed function ϕ obeys the equation.

$$i\hbar \frac{\partial \phi_H}{\partial U} - i\hbar U^{-1}\phi_H \frac{\partial U}{\partial t} = UH_sU^{-1}\phi_H$$

$$i\hbar \frac{\partial \phi_H}{\partial U} = UH_sU^{-1}\phi_H + i\hbar U^{-1}\hbar \frac{\partial}{\partial}$$

$$i\hbar \frac{\partial \phi_H}{\partial U} = \left[UH_sU^{-1} + i\hbar U^{-1}\frac{\partial U}{\partial t} \right) \phi_H \to ⑥$$

the transformation unitary operator U to satisfy the equation

$$UH_sU^{-1} + i\hbar U^{-1}\frac{\partial U}{\partial t} = 0$$

$$UH_sU^{-1} = -i\hbar U^{-1}\frac{\partial U}{\partial t}$$

$$(UH_sU^{-1})U = -i\hbar \frac{\partial U}{\partial t}$$

$$UH_s(U^{-1}U) = -i\hbar \frac{\partial U}{\partial t}$$

$$UH_s = -i\hbar \frac{\partial U}{\partial t} \; (t) \to ⑦$$

of the equation ⑥ gives

$$i\hbar \frac{\partial \phi_H}{\partial t} = 0$$

$$\frac{\partial \phi_H}{\partial t} = 0 \to ⑧$$

The transformed state vector the time independed as already pointed out the time dependence is carried by only the operator

Representation of operator in Heisenberg operator :-

The Expectation value of $\langle A\rangle$ can be written as ,

$$\langle A\rangle = \psi_s(t) A_s \psi_s(t)$$

$$\langle A\rangle = \int \psi_s^*(t) A_s \psi_s(t)\, dq \to ⑨$$

$$= \int \psi_s^*(t)(U^{-1}U)A_s(U^{-1}U)\psi_s(t)\, dq$$

$$\langle A\rangle = \int \phi_H^* U A_s U^{-1} \phi_H \, dq \to ⑩$$

we have derived

$$\phi_H = U\psi_s \; ; \; \phi_H^* = \psi_s^* U^{-1}$$

ψ_s^* being row matrix appearing on the left of U^{-1} know Now let us define

$$A_H(t) = U(t) A_s U^{-1}(t)$$

we can write equ ⑩

$$\langle A\rangle = \int \phi^*_H A_H(t) \phi_H \, da \rightarrow ⑪$$

thus from equation ⑨ and ⑪

$$\langle A\rangle = \psi_s(t) A_s \psi_s(t)$$

$$= \phi_H A_H(t) \phi_H \rightarrow ⑫$$

the time dependent of $A_H(t)$ the Heisenberg representation is the same expectation value in the terms of function ϕ_H as the operator independent operator in Schrodinger picture.

In terms of time dependent function.

In order to find the equation of motion in Heisenberg picture this

we use equation ⑦

$$-i\hbar \frac{\partial U}{\partial t} = U H_s \rightarrow 13(a)$$

$$i\hbar \frac{\partial U}{\partial t} = U^+ H_s^+ \rightarrow 13(b)$$

$$i\hbar \frac{\partial U^+}{\partial t} = U^+ H_s \rightarrow 13(b)$$

$$\frac{d}{dt} A_H(t) = \frac{d}{dt}\left(U U^+ A_H(t)\right)$$

$$\frac{d}{dt} A_H(t) = \frac{\partial U}{\partial t} U^+ A_H(t) + A_H(t) U \frac{\partial U^+}{\partial t} + U U^+ \frac{\partial A_H}{\partial t}$$

using equation 13 (a)(b) we get

$$\frac{d}{dt} A_H(t) = -\frac{1}{i\hbar} U H_s U^+ A_H(t) + A_H(t) U \frac{1}{i\hbar} U H_s + \frac{\partial A_H}{\partial t}$$

$$= -\frac{1}{i\hbar} (U U^+) H_s A_H(t) + \frac{1}{i\hbar} A_H(t) (U U^+) H_s + \frac{\partial A_H}{\partial t}$$

$$= -\frac{1}{i\hbar} H_H A_H + \frac{1}{i\hbar} A_H H_H + \frac{\partial A_H}{\partial t}$$

$$= \frac{1}{i\hbar} [A_H H_H - H_H A_H] + \frac{\partial A_H}{\partial t}$$

$$\frac{d}{dt} A_H(t) = \frac{1}{i\hbar} [A_H, H_H] + \frac{\partial A_H}{\partial t} \rightarrow ⑭$$

Comparing this equation (16) we note that in both the heisenberg and schrodinger picture the equ of motion has the same form if A_H is not an explicit fn function $\frac{dA_H}{dt} = 0$

$$\frac{d}{dt} A_H(t) = \frac{1}{i\hbar} [A_H, H_H] \rightarrow (15)$$

Equation (14), (15) representation of operator in heisenberg picture. equation (8) and (14) represents heisenberg picture from equation (15)

$$A_H = H_H$$

$$\frac{d}{dt} H_H(t) = \frac{1}{i\hbar} [H_H, H_H]$$

$$\frac{d}{dt} H_H(t) = 0 \quad (08)$$

$$H_H = \text{constant}$$

In both the schrodinger and heisenberg picture the constant of motion may be

---

represents any observable commutes with hamiltonian operator.

① Interaction picture.

This represents useful the hamiltonian's can be divided into two parts

$$H \left\langle \begin{matrix} H_0 \\ H' \end{matrix} \right.$$

$H_0 \Rightarrow$ unperturbed Hamiltonian

$H' \rightarrow$ interaction term

$$H = H_s = H_0 + H' \rightarrow ①$$

then the schrodinger eqn written as

$$i\hbar \frac{\partial \psi_s}{\partial t} = H\psi_s$$

$$i\hbar \frac{\partial \psi_s}{\partial t} = (H_0 + H')\psi_s \rightarrow ②$$

H_0 is assumed through a constant operator and H' may depend on time. Let us introduce a state vector

$$\psi_{int}(t) = U\psi_s(t) = e^{iH_0 t/\hbar} \psi_s(t) \rightarrow 3(a)$$

If the operator U, $U = e^{iH_0 t/\hbar}$ is a unitary operator since $UU^{-1} = e^{iH_0 t/\hbar} e^{-iH_0 t/\hbar}$

$$\psi_s = e^{-iH_0t/\hbar}\,\psi_{int}(t) \rightarrow ③(a)$$

using above equation ② reduces

$$i\hbar\frac{\partial}{\partial t}\left[e^{-iH_0t/\hbar}\,\psi_{int}(t)\right] = [H_0+H']\,e^{-iH_0t/\hbar}\,\psi_{int}$$

$$\Rightarrow$$

$$i\hbar\left[e^{-iH_0t/\hbar}\frac{\partial\psi_{int}}{\partial t} + \psi_{int}\left(\frac{-iH_0}{\hbar}\right)e^{-iH_0t/\hbar}\right] = H_0e^{-iH_0t/\hbar}\,\psi_{int} + H'e^{-iH_0t/\hbar}\,\psi_{int}$$

$$i\hbar\, e^{-iH_0t/\hbar}\frac{\partial\psi_{int}}{\partial t} + \psi_{int}\, i\cancel{\hbar}\left(\frac{-iH_0}{\cancel{\hbar}}\right)e^{-iH_0t/\hbar} = H_0e^{-iH_0t/\hbar}\,\psi_{int} + H'e^{-iH_0t/\hbar}\,\psi_{int}$$

$$i\hbar\, e^{-iH_0t/\hbar}\frac{\partial\psi_{int}}{\partial t} + \psi_{int}H_0e^{-iH_0t/\hbar} = H_0e^{-iH_0t/\hbar}\,\psi_{int} + H'e^{-iH_0t/\hbar}\,\psi_{int}$$

$$i\hbar\, e^{-iH_0t/\hbar}\frac{\partial\psi_{int}}{\partial t} = H'e^{-iH_0t/\hbar}\,\psi_{int}$$

$$i\hbar\frac{\partial\psi_{int}}{\partial t} = \frac{H'e^{-iH_0t/\hbar}}{e^{-iH_0t/\hbar}}\,\psi_{int}$$

$$i\hbar\frac{\partial\psi_{int}}{\partial t} = e^{iH_0t/\hbar}\,H'e^{-iH_0t/\hbar}\,\psi_{int} \rightarrow ④$$

let us introduce another operator

$$H'_{int} = e^{iH_0t/\hbar}\,H'e^{-iH_0t/\hbar} \rightarrow ⑤$$

equation of motion in the interaction picture.

$$i\hbar\frac{\partial}{\partial t}\psi_{int} = H'_{int}\psi_{int} \rightarrow ⑥$$

In fact all operator A of Schrodinger picture may be transform into interaction picture by the unitary transformation.

$$A_{int} = e^{iH_0t/\hbar}\,A_s\,e^{-iH_0t/\hbar} \rightarrow ⑦$$

$$\frac{d}{dt}A_{int} = \frac{1}{i\hbar}[A_{int}, H_0] + \frac{\partial A_{int}}{\partial t} \rightarrow ⑧$$

equation ⑥, ⑧ represent interaction picture both state vectors and operators are time dependent the motion of the state vector H' that of operators by H_0

the interaction picture is intermediate b/w the Schrodinger picture we obtain as a special case $A = H_0$

$H_{int}(t) = H_0$ the operator in interaction picture & the same in the Schrodinger picture.

88

	Schrodinger picture	Heisenberg picture	Interaction picture
Stat vectore	time dependent	time independent	time dependent
operators	time independent	time dependent	time dependent

k. Gayathri

$$\left.\begin{aligned} y_1 &= \tan\frac{p_2 a}{\hbar} \\ y_2 &= -\frac{2p_1p_2}{p_1^2 - p_2^2} \end{aligned}\right] \qquad ...(51)$$

y_1 and y_2 are plotted as function of p_2 for given values of a and p_1 on the same graph. The shape of curves also depends on the chosen values of a and p_1.

The points of intersections of these curves represent allowed value of p_2 for each set of values chosen for p_1 and a. it is observed from fig. 5.12 that there is but one allowed value of p_2 in every interval $\frac{n\pi\hbar}{2a} \leq p_2 \leq \frac{(2n+1)\pi\hbar}{2a}$, thus repersenting discrete energy levels.

unit-2

For an infinitely deep potential well $y_2 \to 0$, so

$$\tan\frac{p_2 a}{\hbar} = 0 \quad \text{or} \quad \frac{p_2 a}{\hbar} = n\pi$$

this gives

$$p_2 = \frac{n\pi\hbar}{a}$$

As $p_2 = \sqrt{\{2m(E+V_0)\}}$, we have

$$\frac{n\pi\hbar}{a} = \sqrt{\{2m(E+V_0)\}}$$

or

$$E + V_0 = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad ...(53a)$$

As total energy E is negative we may write equation (53a) as

$$V_0 - |E| = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad ...(53b)$$

Thus the energy difference of $|E|$ from the bottom of the well is just the kinetic energy of the particle in the well.

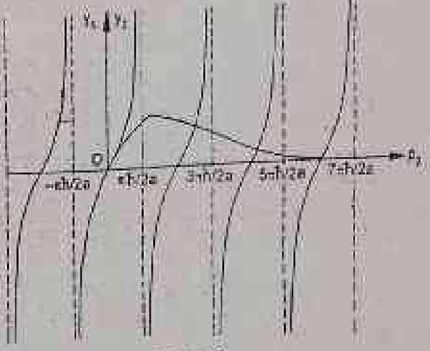

Fig. 5.12

From expression (53) it is clear that the energy levels of particle in the potential well coincide with the energy levels of the particle in the box. Moreover it may also be noted that the allowed value of p_2 given by (52) for an infinitely deep potential well would differ from the exact solution of (50) for a well of finite depth, by the maximum amount

$$\frac{(2n+1)\pi\hbar}{2a} - \frac{n\pi\hbar}{a} = \frac{\pi\hbar}{2a}$$

For small values of n, this difference is relatively large ; but for large values of n, equation (52) gives a reasonable approximation to the solutions given by equation (50).

ONE DIMENSIONAL LINEAR HARMONIC OSCILLATOR

The wave equation for an oscillator

A particle undergoing simple harmonic motion in one dimension is called one-dimensional harmonic oscillator.

In S. H. M the restoring force is proportional to displacement

$$F=-kx, \qquad \text{...(1)}$$

i.e.

where k is a positive constant, called the force constant.

RAM

According to Newton's II law $F=m\frac{d^2x}{dt^2}$

where m is the mass of the particle.

∴ From (1) we have equation of oscillator as

$$m\frac{d^2x}{dt^2}=-kx \quad \text{or} \quad m\frac{d^2x}{dt^2}+kx=0$$

or

$$\frac{d^2x}{dt^2}+\frac{k}{m}x=0. \qquad \text{...(2)}$$

This equation represents a periodic motion of angular frequency

$$\omega=\sqrt{\left(\frac{k}{m}\right)} \text{ or frequency } \nu=\frac{\omega}{2\pi}=\frac{1}{2\pi}\sqrt{\left(\frac{k}{m}\right)} \qquad \text{...(3)}$$

The potential energy of oscillator is

$$V=-\int_0^x kx\,dx, \text{ assuming zero P.E. at } x=0 \text{ (equilibrium state)} = k\left[\frac{x^2}{2}\right]_0^x$$

$$=\frac{1}{2}kx^2 \qquad \text{...(4)}$$

The one- dimensional Schrodinger time independent equation is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}(E-V)\,\psi=0. \qquad \text{...(5)}$$

Substituting $V=\frac{1}{2}kx^2$ in (5), the wave equation for an harmonic oscillator becomes

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}\left(E-\frac{1}{2}kx^2\right)\psi=0,$$

where E is given by eqn. (5).

$$\frac{\partial^2\psi}{\partial x^2}+2\sqrt{\left(\frac{m}{\hbar^2}\right)}\sqrt{\left(\frac{mk}{\hbar^2}\right)}\left[\frac{E}{\sqrt{k}}-\frac{1}{2}\sqrt{k}x^2\right]\psi=0 \qquad \text{...(6)}$$

or

$$\frac{1}{\sqrt{\left(\frac{mk}{\hbar^2}\right)}}\frac{\partial^2\psi}{\partial x^2}+2\sqrt{\left(\frac{m}{\hbar^2}\right)}\left[\frac{E}{\sqrt{k}}-\frac{1}{2}\sqrt{k}x^2\right]\psi=0$$

or

$$\frac{1}{\sqrt{\left(\frac{mk}{\hbar}\right)}}\frac{\partial^2\psi}{\partial x^2}+\left[2\sqrt{\left(\frac{m}{\hbar^2 k}\right)}E-\sqrt{\left(\frac{mk}{\hbar^2}\right)}x^2\right]\psi=0. \qquad \text{...(7)}$$

For convenience let us substitute

$$\left.\begin{aligned}\sqrt{\left(\frac{mk}{\hbar^2}\right)}&=\alpha^2 & \text{...(A)}\\ \text{and} \quad 2E\sqrt{\left(\frac{m}{\hbar^2 k}\right)}&=\lambda & \text{...(B)}\end{aligned}\right\} \qquad \text{...(8)}$$

in eqn. (7) ; then we have

$$\frac{1}{\alpha^2}\frac{\partial^2\psi}{\partial x^2}+(\lambda-\alpha^2x^2)\,\psi=0. \qquad \text{...(9)}$$

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

$$q=\alpha x, \qquad \text{...(10)}$$

where α is a constant given by eqn. (8).

Now

$$\frac{\partial\psi}{\partial x}=\frac{\partial\psi}{\partial q}\cdot\frac{\partial q}{\partial x}=\alpha\frac{\partial\psi}{\partial q} \qquad \text{...(11)}$$

from (10)

and

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

$$=\frac{\partial}{\partial q}\left(\alpha\frac{\partial\psi}{\partial q}\right)\alpha=\alpha^2\frac{\partial^2\psi}{\partial q^2} \qquad \text{from (10) and (11)}$$

Substituting these values in eqn. (9), we get

$$\frac{\partial^2\psi}{\partial q^2}+(\lambda-q^2)\,\psi=0. \qquad \text{...(12)}$$

Asymptotic solution

To solve eqn. (12) let us first make an attempt to obtain an asymptotic solution for the case when $q^2 >> \lambda$, in this case, eqn. (12) becomes

$$\frac{\partial^2\psi}{\partial q^2}-q^2\psi=0. \qquad \text{...(13)}$$

The solution of above equation is

$$\psi=e^{\pm q^2/2} \qquad \text{...(14)}$$

which may be verified by differentiating above equation twice with respect to q ; thus

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

$$=(q^2\pm1)\,e^{\pm q^2/2} \qquad \text{...(15)}$$

As q is very large, $q^2\pm1\approx q^2$ and so eqn. (15) becomes

$$\frac{\partial^2\psi}{\partial q^2}=q^2e^{+q^2/2}=q^2\psi.$$

which is same as eqn. (13).

Thus quantity $|\psi|^2$ represents the probability of finding the particle along X-axis ; therefore it must decrease continuously to zero as x, i.e., q approaches $\pm\infty$.

Clearly out of the two possible solutions represented by (14),

$$\psi = e^{q^2/2} \text{ and } \psi = e^{-q^2/2}, \qquad \text{...(16)}$$

the solution $\psi = e^{q^2/2}$ is not acceptable since it increases with increasing x, i.e. q, while the solution $\psi = e^{-q^2/2}$ satisfies the conditions and therefore is an asymptotic solution of the wave equation.

Recursion formula. From above consideration it is clear that the solution of eqn. (12) will contain the term $e^{-q^2/2}$ as a factor; the possible solution may be written as

$$\psi = e^{-q^2/2}\,\phi(q), \qquad \text{...(17)}$$

where $\phi(q)$ is a function of q, and hence of x.

Differentiating equations (17) twice with respect to q, we get

$$\frac{\partial^2\psi}{\partial q^2} = e^{-q^2/2}\left\{\frac{\partial^2\phi}{\partial q^2} - 2q\frac{\partial\phi}{\partial q} + (q^2-1)\phi\right\} \qquad \text{...(18)}$$

where ϕ is written for $\phi(q)$.

Substituting values of ψ and $\dfrac{\partial^2\psi}{\partial q^2}$ from (17) and (18) in eqn. (12) we get

$$e^{-q^2/2}\left\{\frac{\partial^2\phi}{\partial q^2} - 2q\frac{\partial\phi}{\partial q} + (q^2-1)\phi\right\} + e^{-q^2/2}(\lambda - q^2)\phi = 0$$

or

$$e^{-q^2/2}\left\{\frac{\partial^2\phi}{\partial q^2} - 2q\frac{\partial\phi}{\partial q} + (\lambda-1)\phi\right\} = 0.$$

∴

$$\frac{\partial^2\phi}{\partial q^2} - 2q\frac{\partial\phi}{\partial q} + (\lambda-1)\phi = 0 \qquad \text{...(19)}$$

(since $e^{-q^2/2} \neq 0$ except for $q = \pm\infty$)

Now let us assume that the function $\phi(q)$ may be expressed in the form of *power series in q*, i.e.

$$\phi(q) = q^s \sum_{r=0}^{\infty} a_r q^r = \sum_r a_r q^{s+r}.$$

Differentiating, we get

$$\frac{\partial\phi}{\partial q} = \sum_r a_r (s+r)\, q^{s+r-1} \qquad \text{...(21)}$$

and

$$\frac{\partial^2\phi}{\partial q^2} = \sum_r a_r (s+r)(s+r-1)\, q^{s+r-2}. \qquad \text{...(22)}$$

Substituting these values in (19), we get

$$\sum_r a_r (s+r)(s+r-1)\, q^{s+r-2} - 2q\sum_r a_r (s+r)\, q^{s+r-1} + (\lambda-1)\sum_r a_r q^{s+r} = 0$$

or

$$\sum_r a_r (s+r)(s+r-1)\, q^{s+r-2} - \sum_r a_r\{2(s+r) - (\lambda-1)\}\, q^{s+r} = 0. \qquad \text{...(23)}$$

This equation is a power series and is satisfied only if coefficient of each power in q must be separately equal to zero. Equating to the zero coefficient of lowest power of q (i.e. q^{s-2}); we get

$$a_0 s(s-1) = 0$$

As $a_0 \neq 0$ being first of power series, we have

$$s = 0 \text{ or } s = 1. \qquad \text{...(24)}$$

Now equating to zero the coefficient of q^{s-1} we get

$$a_1(s+1)(s) = 0.$$

This gives either $a_1 = 0$ or $s = 0$ or $s = -1$. ...(25)

As $s \neq -1$, we have either $a_1 = 0$ or $s = 0$ or both.

Now equating to zero the coefficients of q^{s+r}, we get

$$a_{r+2}(s+r+2)(s+r+1) - a_r\{2(s+r) - (\lambda-1)\} = 0$$

or

$$a_{r+2} = \frac{2s+2r+1-\lambda}{(s+r+2)(s+r+1)}\,a_r \qquad \text{...(26)}$$

where r is an integer or zero. This expression is called *recursion formula*. From this we can calculate the coefficients of q^2, q^4, q^6, etc. if that of q^0 is known . Similarly we calculate the coefficients of q^3, q^5, q^7 etc. if the coefficient of q^1 is known. Thus if we choose $a_1 = 0$, then all odd coefficients a_r will be zero.

Examining the series. If no restriction is placed on λ which is related to the energy E of the oscillator by eqn. (8) the series for $\phi(q)$ consists of infinite number of terms and does not correspond to a satisfactory wave-function. for large values of r which may be seen as follows :

Examining eqn. (26) for large values of n, we get

$$\lim_{n\to\infty} \frac{a_{n+2}}{a_n} = \frac{2}{n} \qquad \text{...(27)}$$

Now consider the series

$$e^{q^2} = 1 + q^2 + \frac{q^4}{2!} + \ldots + \frac{q^n}{(\frac{1}{2}n)!} + \frac{q^{n+2}}{(\frac{1}{2}n+1)!} + \ldots \qquad \text{...(28a)}$$

$$= 1 + b_2 q^2 + b_4 q^4 + \ldots + b_n q^n + b_{n+2} q^{n+2} + \ldots \qquad \text{...(28b)}$$

then the recursion formula for the exponential series for e^{q^2} is given by

$$\frac{b_{n+2}}{b_n} = \frac{(\frac{1}{2}n)!}{(\frac{1}{2}n+1)!} = \frac{1}{\frac{1}{2}n+1}$$

Where n is very large, so that unity is negligible in comparison with $\frac{1}{2}n$, then above equation gives

$$\lim_{n\to\infty} \frac{b_{n+2}}{b_n} = \frac{2}{n} \qquad \text{...(29)}$$

Thus we see that *for large values of n, the series for $\phi(q)$ will behave like e^{q^2}*. If this is the case, the eigen function ψ for large values of n will behave like

$$\psi = e^{-q^2/2}\,\phi(q) = e^{-q^2/2}\; e^{q^2} = e^{q^2/2} \qquad \text{...(30)}$$

According to this equation if $q \to \infty$, $\psi \to \infty$, thus making the wave function physically unacceptable. Thus the series governed by the recursion formula (25) does not lead to a satisfactory wave function unless some restriction is introduced which makes the series break off after a finite number of terms.

Eigen values of harmonic oscillator

From above discussion we have seen that in order to obtain a satisfactory wave-function, the series (20) must break off after a finite number of terms. The series will break off after rth term if we get the numerator in the recursion formula (26) equal to zero, *i.e.*

$$2r+2r+1-\lambda=0$$

i.e.
$$\lambda=2r+2r+1 \qquad ...(31)$$

For $r=0$, we have

$$\lambda=2r+1$$

For $r=1$, we have

$$\lambda=2r+3$$

This equation (31) may be written more generally as

$$\lambda=2n+1\,;\; n=0,1,2.... \qquad ...(32)$$

Substituting this value of λ in equation (88) we get

$$2E\sqrt{\left(\frac{m}{\hbar^2 k}\right)}=2n+1$$

or
$$2E\sqrt{\left(\frac{m}{\hbar^2(m\omega^2)}\right)}=2n+1 \qquad [\text{since } k=m\omega^2 \text{ from (3)}]$$

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

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

or
$$E_n=(n+\tfrac{1}{2})\hbar\omega \qquad (n=0,1,2,3,...) \qquad ...(33)$$

The allowed integral values of n lead to certain discrete values of energy, represented by equation (33), known as eigen *values of the harmonic oscillator*. Moreover equation (33) indicates that the *energy levels of harmonic oscillator are equally spaced.*

Significance of zero point energy

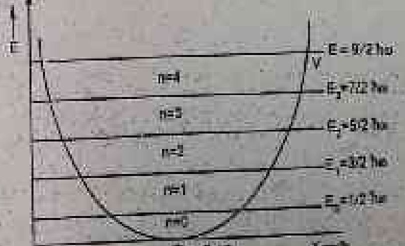

Fig. 5.16

For ground state (or lowest state) $n=0$, so that we have

$$E_0=\tfrac{1}{2}\hbar\omega \qquad ...(33a)$$

This is called zero point energy

A comparison with the result $E=n\hbar\omega_0$ obtained by old quantum theory shows that *the only difference is that all the equally spaced energy levels are shifted upward by an amount equal to half the separation of energy levels, i.e.* $\frac{1}{2}\hbar\omega$ *is equal to zero point energy.* Thus it is clear that

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ven in the lowest state, the harmonic oscillator has finite energy while according to classical mechanics the armonic oscillator possesses zero energy at lowest state. The existence of zero point energy is in agreement ith experiment and is important feature of quantum mechanics.

The energy levels of the harmonic oscillator according to wave mechanics are represented in fig. 16.

Eigen functions of harmonic osillator. We have seen that in order to have a satisfactory solution f wave equation (7), ϕ must break off after a finite number of terms, i.e. ϕ should be restricted in such manner so as to make it a polynomial rather than a power series. The best suitable polynomial is Hermite olynomial denoted by H_n (q). Then the eigen function ψ can be set equal to the product of polynomial I_n (q) and the factor $e^{-q^2/2}$, *i.e.*,

$$\psi_n(x)=N_n e^{-q^2/2} H_n(q) \qquad ...(34)$$

here N_n in a normalising factor and the *Hermite polynomial* $H_n(q)$ of degree n is defined by

$$H_n(q)=(-1)^n e^{q^2}\frac{d^n e^{-q^2}}{dq^n} \qquad ...(35)$$

Values of Hermite polynomials of different orders may be obtained by using above equation.

$n=0,\ H_0(q)=1$ (Hermite polynomial of order zero)
$n=1,\ H_1(q)=2q$ (Hermite polynomial of order one)
$n=2,\ H_2(q)=4q^2-1$ (Hermite polynomial of order two)
$n=3,\ H_3(q)=8q^3-12q$ (Hermite polynomial of order three)
$n=4,\ H_4(q)=16q^4-48q^2+12$ (Hermite polynomial of order four)

d so on.

The orthogonality condition of Hermite polynomials is

$$\int_{-\infty}^{+\infty} H_n(q)\,H_m(q)\,e^{-q^2}\,dq=2^n\,n\,!\sqrt{(\pi)}\,\delta_{mn} \qquad ...(36)$$

here δ_{mn} is Kronecker delta symbol defined as

$$\delta_{mn}=\begin{cases}1 \text{ for } m=n\\ 0 \text{ for } m\neq n\end{cases}$$

The normalising condition is

$$\int_{-\infty}^{+\infty}|\,\psi_n(x)\,|^2\,dx=1.$$

As $q=\alpha x$, we have $dq=\alpha dx$

$$dx=\frac{dq}{\alpha}$$

$$\frac{|N_n|^2}{\alpha}\int_{-\infty}^{+\infty} H_n^2(q)\,e^{-q^2}\,dq=1$$

But from orthogonality condition of Hermite polynomials

$$\int_{-\infty}^{+\infty} H_n^2(q)\,e^{-q^2}\,dq=2^n\,(n\,!)\sqrt{\pi}.$$

$$\therefore \quad \frac{N_n^2}{\alpha} \cdot 2^n (n!) \sqrt{\pi} = 1.$$

or

$$N_n = \left[\frac{\alpha}{2^n N! \sqrt{\pi}}\right]^{1/2} \quad \ldots(37)$$

Thus normalised wave-functions of harmonic oscillator are

$$\psi_n(x) = \left[\frac{\alpha}{2^n (n!) \sqrt{(\pi)}}\right]^{1/2} e^{-\alpha^2 x^2/2} H_n(\alpha x). \quad \ldots(38)$$

where α is given by equation (8).

The wave-function corresponding to the lowest state of energy is

$$\psi(x) = \left[\frac{\alpha}{\sqrt{\pi}}\right]^{1/2} e^{-\alpha^2 x^2/2} \quad \ldots(39)$$

since $H_0(q) = H_0(\alpha x) = 1$.

A few of these wave-functions are shown in figures 5·17 (a), (b), (c).

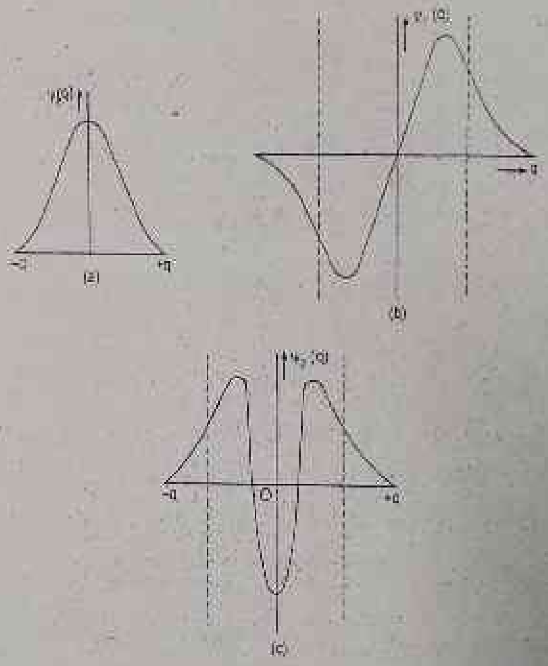

Fig. 5·17.

5

Physical Applications of Schroedinger's Equation to One and Three Dimensional Problems

5·1 THE FREE PARTICLE

The Schroedinger wave equation for a particle of mass m, total energy E and potential energy V is written as

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

where $\hbar = \frac{h}{2\pi}$, being Planck's constant.

A free particle is one for which potential energy V is quite independent of position and hence, for convenience, it may be set equal to zero, so that Schroedinger wave equation for a free particle becomes

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

or, in cartesian coordinates

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad \ldots(3)$$

This is a partial differential equation in three independent variables x, y and z and may be solved by the *method of separation of variables* imposing the boundary condition that ψ is infinite everywhere in space since the particle is free to move anywhere in space, so that we may write the solution of equation (3) in the form

$$\psi(x, y, z) = X(x)\, Y(y)\, Z(z), \quad \ldots(4)$$

where $X(x)$, $Y(y)$ and $Z(z)$ are functions of their respective co-ordinate alone.

Substituting this in equation (3) and dividing by $X(x)\, Y(y)\, Z(z)$ we get

$$\frac{1}{X}\frac{\partial^2 X(x)}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y(y)}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z(z)}{\partial z^2}+\frac{2m}{\hbar^2}E=0. \quad ...(5)$$

The equation may be written as

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}=-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}-\frac{2m}{\hbar^2}E. \quad ...(6)$$

In above equation L.H.S. is function of x along, while R.H.S. is function of y and z and is independent of x. It is, therefore, necessary that the value of the quantity to which each side is equal must be independent of x, y and z, *i.e.*, both sides must be equal to a constant k_x, (say), so that

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}=k_x \quad ...(7)$$

and

$$-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}-\frac{2m}{\hbar^2}E=k_x \quad ...(8)$$

Equation (8) may be written as

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=-k_x-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}-\frac{2m}{\hbar^2}E.$$

In above equation L.H.S. is independent of z while R.H.S. is independent of y. Therefore if above equation is to be satisfied both sides must be equal to constant k_y (say), so that

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=k_y. \quad ...(10)$$

$$-k_x-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}-\frac{2m}{\hbar^2}E=k_y. \quad ...(11)$$

Equation (11) may be written as

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=-k_x-\frac{2m}{\hbar^2}E-k_y.$$

In above equation R.H.S. is constant. Let this constant be k_z, so that we may write

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=k_z, \quad ...(12)$$

and

$$-k_x-k_y-\frac{2m}{\hbar^2}E=k_z$$

or

$$k_x+k_y+k_z=-\frac{2m}{\hbar^2}E. \quad ...(13)$$

For convenience let us substitute

$$k_x=-\frac{2m}{\hbar^2}E_x \quad ...(14)$$

Then the differential equation in x, from equation (7), may be written as

$$\frac{\partial^2 X}{\partial x^2}+\frac{2m}{\hbar^2}E_x X=0 \quad ...(15)$$

The general solution of above equation can be written as

$$X(x)=N_x \sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x-x_0)\right\}, \quad ...(16)$$

where N_x and x_0 are arbitrary constants.

Similarly we may obtain the differential equation in y and z by substituting $k_y=-\frac{2m}{\hbar^2}E_y$ and $k_z=-\frac{2m}{\hbar^2}E_z$ in equation (10) and (12) respectively, *viz.*,

$$\frac{\partial^2 Y}{\partial y^2}+\frac{2m}{\hbar^2}E_y Y=0. \quad ...(17)$$

and

$$\frac{\partial^2 Z}{\partial z^2}+\frac{2m}{\hbar^2}E_z Z=0. \quad ...(18)$$

The general solutions of above equations may be written as

$$Y(y)=N_y \sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y-y_0)\right\} \quad ...(19)$$

$$Z(z)=N_z \sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z-z_0)\right\}. \quad ...(20)$$

Substituting values of k_x, k_y and k_z in equation (13), we get

$$E_x+E_y+E_z=E. \quad ...(21)$$

As any sine function is single valued, finite and continuous for real values of its argument, therefore for finite values of X, Y and Z, (*i.e.*, ψ) E_x, E_y, E_z and hence E must be positive.

Thus the eigen (or wave or characteristic) functions and energy values of the free particle are

$$\psi=XYZ$$

$$=N\sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x-x_0)\right\}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y-y_0)\right\}\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z-z_0)\right\} \quad ...(22)$$

and

$$E=E_x+E_y+E_z, \quad ...(23)$$

where $N=(N_x N_y N_z)$ is a normalization constant, E_x, E_y, and E_z are positive. Clearly the Free particle has a continuous set of energy levels, however, the quantization may occur if the particle is not entirely free, but is constrained to remain in box, which we shall consider in the next section.

The complete wave functions with the time factor can be written as follows:

$$=N\sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x-x_0)\right\}e^{-iE_x t/\hbar}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y-y_0)\right\}e^{-iE_y t/\hbar}\times\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z-z_0)\right\}e^{-iE_z t/\hbar}$$

$$=N\sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x-x_0)\right\}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y-y_0)\right\}\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z-z_0)\right\}\times e^{-i(E_x+E_y+E_z)t/\hbar}$$

$$=N\sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x-x_0)\right\}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y-y_0)\right\}\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z-z_0)\right\}\times e^{-iEt/\hbar} \quad ...(24)$$

PARTICLE IN A BOX

Let a single particle, *e.g.*, a gas molecule of mass m, be confined within a *rectangular potential box* with edges parallel to the X, Y and Z-axes of lengths l_x, l_y and l_z respectively. The particle can move freely within the region $0 < x < l_x$, $0 < y < l_y$, $0 < z < l_z$, *i.e.*, inside the box the potential function $V(x, y, z)$ is equal to zero but rises suddenly to a very large value at the boundaries of this region remaining infinitely

The general solution of above equation can be written as

$$X(x) = N_x \sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x - x_0)\right\}. \qquad ...(16)$$

where N_x and x_0 are arbitrary constants.

Similarly we may obtain the differential equation in y and z by substituting $k_y = -\frac{2m}{\hbar^2}E_y$ and $k_z = -\frac{2m}{\hbar^2}E_z$ in equation (10) and (12) respectively, *viz*.,

$$\frac{\partial^2 Y}{\partial y^2} + \frac{2m}{\hbar^2}E_y Y = 0. \qquad ...(17)$$

and

$$\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2}E_z Z = 0. \qquad ...(18)$$

The general solutions of above equations may be written as

$$Y(y) = N_y \sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y - y_0)\right\} \qquad ...(19)$$

$$Z(z) = N_z \sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z - z_0)\right\}. \qquad ...(20)$$

Substituting values of k_x, k_y and k_z in equation (19), we get

$$E_x + E_y + E_z = E. \qquad ...(21)$$

As any sine function is single valued, finite and continuous for real values of its argument, therefore for finite values of X, Y and Z (*i.e.*, ψ) E_x, E_y, E_z and hence E must be positive.

Thus the eigen (or wave or characteristic) functions and energy values of the free particle are

$$\psi = XYZ$$

$$= N \sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x - x_0)\right\}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y - y_0)\right\}\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z - z_0)\right\} \qquad ...(22)$$

and

$$E = E_x + E_y - E_z. \qquad ...(23)$$

where $N = (N_x N_y N_z)$ is a normalization constant, E_x, E_y, and E_z are positive. Clearly the free particle has a continuous set of energy levels, however, the quantization may occur if the particle is not entirely free, but is constrained to remain in box, which we shall consider in the next section.

The complete wave- functions with the time factor can be written as follows :

$$= N \sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x - x_0)\right\} e^{-iE_x t/\hbar}\left\{\sin\frac{\sqrt{(2mE_y)}}{\hbar}(y - y_0)\right\} e^{-iE_y t/\hbar} \times \sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z - z_0)\right\} e^{-iE_z t/\hbar}$$

$$= N \sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x - x_0)\right\}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y - y_0)\right\}\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z - z_0)\right\} \times e^{-i(E_x + E_y + E_z)t/\hbar}$$

$$= N \sin\left\{\frac{\sqrt{(2mE_x)}}{\hbar}(x - x_0)\right\}\sin\left\{\frac{\sqrt{(2mE_y)}}{\hbar}(y - y_0)\right\}\sin\left\{\frac{\sqrt{(2mE_z)}}{\hbar}(z - z_0)\right\} \times e^{-iEt/\hbar} \qquad ...(24)$$

PARTICLE IN A BOX

Let a single particle, *e.g.*, a gas molecule of mass m, be confined within *a rectangular potential box* with edges parallel to the X, Y and Z-axes of lengths l_x, l_y and l_z respectively. The particle can move freely within the region $0 < x < l_x$, $0 < y < l_y$, $0 < z < l_z$ *i.e.*, inside the box the potential function $V(x, y, z)$ is equal to zero but it rises suddenly to a very large value at the boundaries of this region remaining infinitely

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large everywhere outside the boundaries. Therefore the particle will rebound when it will strike either of the boundaries.

If m is the mass of the particle and E its total energy, the Schrodinger wave equation, for the case under consideration may be written as (since $V = 0$)

$$\nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}E\psi = 0. \qquad ...(1)$$

This is a partial differential equation in three independent variables and may be solved by the method of separation of variables, so that we may write the solution of above equation in the form

$$\psi(x, y, z) = X(x)\,Y(y)\,Z(z), \qquad ...(2)$$

where $X(x)$ is a function of x alone, $Y(y)$ a function of y alone and $Z(z)$ a function of z alone.

Substituting value of ψ from equation (2) in (1) and dividing by $X(x)\,Y(y)\,Z(z)$, we get

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2}E = 0. \qquad ...(3)$$

Above equation may be writen as

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E. \qquad ...(4)$$

In above eqn. L.H.S. is a function of x alone, while R.H.S. is a function of y and z and is independent of x. It is, therefore, necessary that the value of the quantity to which each side is equal must be independent of x, y and z, *i.e.*, both sides must be equal to a constant, k_x (say), so that

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = k_x \qquad ...(5)$$

and

$$-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E = k_x \qquad ...(6)$$

Above equation may be written as

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E - k_x. \qquad ...(7)$$

In above equation L.H.S. is a function of y alone, while R.H.S. is a function of z and is independent of y. Therefore if above equation is to be satisfied both sides must be equal to a constant, k_y (say), so that

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = k_y \qquad ...(8)$$

and

$$-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E - k_x = k_y \qquad ...(9)$$

Eqn. (9) may be written as

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -k_x - k_y - \frac{2m}{\hbar^2}E = \text{constant } k_z \text{ (say)}$$

so that we have

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = k_z \qquad ...(10)$$

and
$$k_x + k_y + k_z = \frac{2m}{\hbar^2}E \qquad \text{...(11)}$$

For convenience let us substitute

$$\left.\begin{aligned} k_x &= -\frac{2m}{\hbar^2}E_x, \\ k_y &= -\frac{2m}{\hbar^2}E_y, \\ \text{and} \quad k_z &= -\frac{2m}{\hbar^2}E_z \end{aligned}\right\} \qquad \text{...(12)}$$

Then the differential equation in x, y and z from (5), (8) and (10) may be written as

$$\frac{\partial^2 X}{\partial x^2} + \frac{2m}{\hbar^2}E_x X = 0, \qquad \text{...(13A)}$$

$$\frac{\partial^2 Y}{\partial y^2} + \frac{2m}{\hbar^2}E_y Y = 0, \qquad \text{...(13B)}$$

and
$$\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2}E_z Z = 0. \qquad \text{...(13C)}$$

The general solution of equation (13A) will be sine function of arbitrary amplitude, frequency and phase, *i.e.*,

$$X(x) = A\sin(Bx + C) \qquad \text{...(14)}$$

where A, B and C are constants to be determined from the consideration of the boundary conditions.

According to quantum mechanics $|\psi|^2$ represents the probability of finding the particle at any point within the box. Therefore $|X(x)|^2$ which is a function of x coordinate only, represents the probability of finding the particle at any point along X-axis. As the potential is very high at the walls of the box, the probability of finding the particle at the walls will be zero *i.e.*,

$$|X(x)|^2 = 0 \text{ when } x = 0 \text{ and } x = l_x$$

or
$$X(x) = 0 \text{ when } x = 0 \text{ and } x = l_x$$

Using these boundary conditions, eqn. (14) gives

$$\sin C = 0$$

and
$$\sin(Bl_x + C) = 0,$$

which yields
$$C = 0$$

and
$$\sin Bl_x = 0$$

$$Bl_x = n_x\pi \text{ where } n_x \text{ is a + ve integer}$$

$$B = \frac{n_x\pi}{l_x}$$

Substituting values of B and C in eqn. (14), we get

$$X(x) = A\sin\frac{n_x\pi x}{l_x} \qquad \text{...(15)}$$

$X(x) = A\sin Bx + A\sin C$

$X(0) = A\sin B(0) + A\sin C$

$0 = A\sin C$ //

$= A\sin BX + A\sin C$

=

For simplicity we may assume A to be real number, then using the condition

$$\int_0^{l_x} |X(x)|^2\,dx = 1$$

we have
$$\int_0^{l_x}\left|A\sin\frac{n_x\pi x}{l_x}\right|^2 dx = 1$$

or
$$A^2\int_0^{l_x}\sin^2\frac{n_x\pi x}{l_x}\,dx = 1,$$

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

or
$$\frac{A^2}{2}\cdot l_x = 1$$

or
$$A = \sqrt{\left(\frac{2}{l_x}\right)} \qquad \text{...(16)}$$

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

Substituting this value of A in eqn. (15), the normalized function $X(x)$ is given by

$$X(x) = \sqrt{\left(\frac{2}{l_x}\right)}\sin\frac{n_x\pi x}{l_x} \qquad \text{...(17)}$$

Finding its second derivative, we have

$$\frac{\partial^2 X}{\partial x^2} = -\left(\frac{n_x\pi}{l_x}\right)^2 X(x) \qquad \text{...(18)}$$

Substituting values from (17) and (18) in (13A), we get

$$-\left(\frac{n_x\pi}{l_x}\right)^2 X(x) + \frac{2m}{\hbar^2}E_x X = 0,$$

or
$$E_x = \frac{1}{2m}\left(\frac{n_x\pi\hbar}{l_x}\right)^2 = \frac{n_x^2 h^2}{8ml_x^2} \qquad \text{...(19)}$$

since
$$\hbar = \frac{h}{2\pi}$$

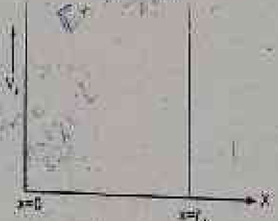

Fig. 5.1.

Similarly we may solve equations (13B) and (13C) and obtain

$$Y(y) = \sqrt{\left(\frac{2}{l_y}\right)}\sin\frac{n_y\pi y}{l_y} \qquad \text{...(20)}$$

$$n_y = 1, 2, 3, \ldots$$

$$Z(z) = \sqrt{\left(\frac{2}{l_z}\right)}\sin\frac{n_z\pi z}{l_z} \qquad \text{...(21)}$$

$$n_z = 1, 2, 3, \ldots$$

$$E_y = \frac{n_y^2 h^2}{8ml_y^2} \qquad \text{...(22)}$$

$$E_z = \frac{n_z^2 h^2}{8 m l_z^2} \qquad ...(23)$$

Using (11) and (12), we have

$$E = E_x + E_y + E_z \qquad ...(24)$$

Equations (19), (22) and (23) give the allowed values of energy levels along X, Y and Z axes respectively.

The allowed values of total energy are given by

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right] \qquad ...(25)$$

where n_x, n_y, n_z denote any set of three positive numbers.

The complete wave-function ψ_{n_x, n_y, n_z} has the form, for various values of the quantum numbers n_x, n_y, n_z

$$\psi_{n_x, n_y, n_z}(x, y, z) = X(x)\,Y(y)\,Z(z)$$

$$= 2\sqrt{\left(\frac{2}{l_x l_y l_z}\right)} \sin\frac{n_x \pi x}{l_x} \sin\frac{n_y \pi y}{l_y} \sin\frac{n_z \pi z}{l_z} \qquad ...(26)$$

Fig. 5.2 represents the first three normalized wave-functions $X(x)$ for a particle in a box.

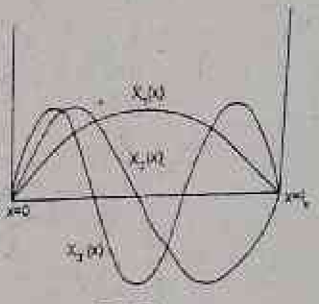

Fig. 5.2.

Ex.1 *Calculate the energy difference between the ground sate and the first excited state for an electron in one dimensional rigid box of length 10^{-10} m (mass of electron $= 9.1\times10^{-31}$ kg and $h = 6.626\times10^{-34}$ joule-sec)* **(Meerut 1987)**

Sol. The energy of a particle in one dimensional rigid box of side L is given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}, n = 1, 2, 3 ...$$

Substituting given values

$$E_n = n^2 \frac{(6.626\times10^{-34}\,J-s)^2}{8\,(9.1\times10^{-31}\,kg)\times(10^{-10}\,m)^2} = 0.603\times10^{-17}\,n^2 \text{ joule}$$

$$= \frac{0.603\times10^{-17}\,n^2}{1.6\times10^{-19}}\,eV = 37.7\,n^2\,eV$$

In the ground state $n = 1$, $E_1 = 37.7$ eV

For the first excited state $n = 2$, $E_2 = 37.7\times4$ eV $= 150.8$ eV

∴ The energy difference, $E_2 - E_1 = 150.8 - 37.7 = 113.1$ eV

Ex. 2. *Can you observe the energy state for a ball of mass 10 g moving in a box of length 10 cm. $h = 6.6\times10^{-34}$ J-s* **(Kanpur 1987)**

Sol. The energy state of a particle in the box are given by

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

Substituting given values, $E_n = \frac{n^2\times(6.6\times10^{-34})^2}{8\times10\times10^{-3}\times(10\times10^{-2})^2}\,J = 5.445\times10^{-64}\,n^2$

$$= \frac{5.445\times10^{-64}}{1.6\times10^{-19}}\,n^2\,eV = 3.4\times10^{-45}\,n^2\,eV$$

Substituting n = 1, 2, 3 ..., we get

$$E_1 = 3.4\times10^{-45}\,eV$$

$$E_2 = 13.6\times10^{-45}\,eV$$

$$E_3 = 30.6\times10^{-45}\,eV$$

These are so close to each other that they can not be observed separate and so a continuum will be observed.

5.3 POTENTIAL STEP

In the case of a potential step the potential function undergoes only one discontinuous change as shown in fig 5.3 and hence the potential function of a potential step may be represented as

$$V(x) = \begin{cases} 0 \text{ for } x < 0 \\ V_0 \text{ for } x > 0 \end{cases}$$

Let the electrons of energy E move from left to right, i.e., along the positive direction of X-axis. Let us apply quantum mechanics to the problem, according to which the electrons behave like a wave moving from left to right and face a sudden shift in the potential at $x = 0$.

The problem is analogous when light strikes a sheet of glass where there is a shift in the index of refraction and the wave is partly transmitted. Hence in this problem the electrons will be partly reflected and partly transmitted at the discontinuity.

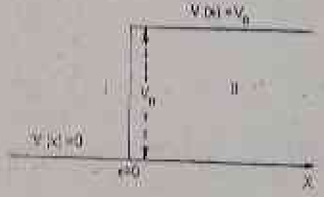

Fig. 5.3.

To solve the problem let us write the Schroedinger equation for two regions.

The Schroedinger equation for the first region is given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0, \qquad ...(1)$$

since for I region $V(x) = 0$.

The Schroedinger wave equation for II region is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0. \qquad ...(2)$$

The general solutions of equations (1) and (2) may be written

as $$\psi_1 = Ae^{ip_1x/\hbar} + Be^{-ip_1x/\hbar} \qquad ...(3)$$

and $$\psi_2 = Ce^{ip_2x/\hbar} + De^{-ip_2x/\hbar} \qquad ...(4)$$

where p_1 and p_2 are the moments in the I and II regions respectively and are given by

$$\left\{\begin{aligned} p_1 &= \sqrt{(2mE)} \\ p_2 &= \sqrt{[2m(E - V_0)]} \end{aligned}\right\} \quad ...(5)$$

ψ_1 and ψ_2 are functions for I and II regions respectively. A, B, C and D are constants and may be determind by boundary conditions.

In equation (3) the first term represents the wave travelling along +ve X-axis in first region, *i.e.*, the *incident* wave and the second term represents the wave travelling along –ve X-axis in the 1st region, *i.e.*, the *reflected wave*. In equation (4), the first term represents the wave travelling along +ve X-axis in 2nd region *i.e.*, transmitted wave while the second term represents the wave travelling along – ve X-axis in second region ; but there is no reflection of electrons in second region and hence there will be no wave travelling along – ve X-axis Consequently $D = 0$ so that the solution of equation (1), *i.e.*, equation (4) may be written as

$$\psi_2 = Ce^{ip_2x/\hbar} \quad ...(6)$$

According to probability interpretation of the wave function ψ must be finite, whereas E and V must be finite, because infinite energies do not exist in nature. Then from Schroedinger's equation we may conclude that $\partial^2\psi/\partial x^2$ is everywhere finite : but not necessarily continuous. But $\partial^2\psi/\partial x^2$ can only be finite if $\partial\psi/\partial x$ is *continuous everywhere*, this is *first boundary condition*. If $\partial\psi/\partial x$ is continuous everywhere, then necessarily ψ must be continuous. This is *second boundary* condition.

Now the boundary conditions, in this case may be represented as follows :

The continuity of ψ implies $\psi_1 = \psi_2$ at $x = 0$. ...(A)

The continuity of $\dfrac{\partial\psi}{\partial x}$ implies $\dfrac{\partial\psi_1}{\partial x} = \dfrac{\partial\psi_2}{\partial x}$ at $x = 0$. ...(B)

Applying boundary condition (A) to equations (3) and (6), we get

$$A + B = C \quad ...(7)$$

Differentiating equations (3) and (6), we get

$$\frac{\partial\psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[Ae^{ip_1x/\hbar} - Be^{-ip_1x/\hbar}\right], \quad ...(8)$$

$$\frac{\partial\psi_2}{\partial x} = \frac{ip_2}{\hbar}Ce^{ip_2x/\hbar} \quad ...(9)$$

Applying boundary condition (B) to (8) and (9), we get

$$p_2C = p_1(A - B). \quad ...(10)$$

Solving (7) and (10), we get

$$C = \frac{2p_1A}{p_1 + p_2} \quad ...(11)$$

$$B = \frac{p_1 - p_2}{p_1 + p_2}A, \quad ...(12)$$

where B and C represents the amplitudes of *reflected* and *transmitted* beams respectively in terms of the amplitude of incident wave.

The *reflectance* or *reflectivity* or *reflection coefficient* and the *transmittance* or *transmissivity* or *transmission coefficient* at the potential discontinuity may be defined as follows.

The reflectance, i.e., the fraction of electrons reflected is equal to the ratio of reflected current to the incident current i.e.

i.e., fraction of electrons reflected = 0.1

The fraction electrons transmitted

$$= \frac{4p_1p_2}{(p_1 + p_2)^2}$$

$$= \frac{4 \times 1.07 \times 10^{-25} \times 5.37 \times 10^{-26}}{(1.07 \times 10^{-25} + 5.37 \times 10^{-26})^2} = 0.9.$$

(b) In this case $E < V_0$.

∴ The transmission coefficient = 0,

i.e. The fraction of electrons transmitted = 0

and The reflection coefficient *i.e.*, the fraction of electrons reflected = 1.

(c) In this case $E = V_0$.

$$p_1 = \sqrt{(2mE)} = \sqrt{(2 \times 9 \times 10^{-31} \times 0.030 \times 1.6 \times 10^{-19})} \text{ kg-m/sec.}$$

$$p_2 = \sqrt{[2m(E - V_0)]} = 0 \; [\text{since } E = V_0].$$

∴ The fraction of electrons reflected $= \dfrac{(p_1 - p_2)^2}{(p_1 + p_2)^2} = 1.$

The fraction of electrons transmitted $= \dfrac{4p_1p_2}{(p_1 + p_2)^2} = 0.$ since $p_2 = 0$.

5 RECTANGULAR POTENTIAL BARRIER

Let us consider the one-dimensional problem where the potential function is defined as in fig. 5.4

$$\left\{\begin{aligned} V(x) &= 0 \quad \text{for } x < 0 \\ &= V_0 \text{ for } 0 < x < a \\ &= 0 \quad \text{for } x > a \end{aligned}\right\} \quad ...(1)$$

Here we have a potential barrier between $x = 0$ and $x = a$.

If a particle having energy less than V_0, *i.e.*, $E < V_0$, approaches this barrier from the left, *i.e.*, from 1st region, classically the particle will always be reflected and hence will not penetrate the barrier. However, wave mechanics predicts that the particle has some probability of penetrating to region 3rd, the probability of penetration being greater if $(V_0 - E)$ and a are smaller. Moreover if $E > V_0$ classical mechanics predicts

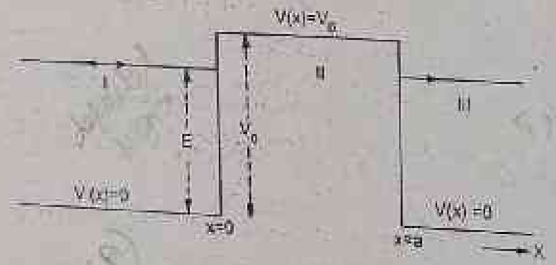

Fig. 5.4.

that the particle will always be transmitted ; while according to wave-mechanics, the particle has a finite probability of transmission and hence it is not certain that the particle will penetrate the barrier.

To solve the problem, let us write three schroedinger equations, one for each region.

The Schroedinger equation for I region is

$$\frac{\partial^2 \psi_1}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_1 = 0 \qquad \text{...(2)}$$

(since $V = 0$).

The Schroedinger equation for II region is

$$\frac{\partial^2 \psi_2}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\,\psi_2 = 0. \qquad \text{...(3)}$$

The Schroedinger equation for III region is

$$\frac{\partial^2 \psi_3}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_3 = 0 \qquad \text{...(4)}$$

Here ψ_1, ψ_2 and ψ_3 are wave-functions for I, II, and III regions respectively.

The general solutions of equations (2), (3) and (4) may be written as

$$\psi_1 = A_1 e^{ip_1 x/\hbar} + B_1 e^{-ip_1 x/\hbar} \qquad \text{...(5)}$$

$$\psi_2 = A_2 e^{ip_2 x/\hbar} + B_2 e^{-ip_2 x/\hbar} \qquad \text{...(6)}$$

$$\psi_3 = A_3 e^{ip_1 x/\hbar} + B_3 e^{-ip_1 x/\hbar} \qquad \text{...(7)}$$

where p_1 and p_2, the moments of particle in the corresponding regions, given by

$$\left.\begin{array}{l} p_1 = \sqrt{(2mE)} \\ p_2 = \sqrt{[2m(E - V_0)]} \end{array}\right\} \qquad \text{...(8)}$$

A_1, B_1, A_2, B_2, A_3 and B_3 are constants to be determined by boundary conditions.

In equation (5) the first term represents the wave travelling along (+) ve X-axis in the I region, *i.e., the incident wave* and second term represents the wave travelling along negative X-axis *i.e.*, wave reflected at $x = 0$.

In equation (6), the first term represents the wave travelling along (+)ve X-axis in II region, *i.e.*, the wave transmitted at $x = 0$ and second term represents the wave travelling along (−)ve X– axis in II region, *i.e.*, the wave reflected at $x = a$.

In equation (7) the first term represents the wave travelling along (+)ve X-axis in III region, *i.e.*, the wave transmitted at $x = a$ and the second term represents the wave travelling along (−)ve X-axis in III region, but no wave travels back from infinity in III region. Consequently $B_3 = 0$, so that the solution of equation (4), *i.e.*, equation (7) can be written as

$$\psi_3 = A_3 e^{ip_1 x/\hbar} \qquad \text{...(9)}$$

For evaluation the constants A_1, B_1, A_2, B_2 and A_3 we shall apply the conditions at the two boundaries $x = 0$ and $x = a$.

One conditions is that ψ must be continuous at the boundaries, *i.e.*

$$\left\{\begin{array}{ll} \psi_1 = \psi_2 \text{ at } x = 0 & \text{...(A)} \\ \psi_2 = \psi_3 \text{ at } x = a & \text{...(B)} \end{array}\right\} \qquad \text{...(10)}$$

The other condition is that $\partial\psi/\partial x$ must be continuous at the boundaries *i.e.*,

$$\therefore \quad \left\{\begin{array}{ll} \dfrac{\partial\psi_1}{\partial x} = \dfrac{\partial\psi_2}{\partial x} \text{ at } x = 0 & \text{...(A)} \\ \dfrac{\partial\psi_2}{\partial x} = \dfrac{\partial\psi_3}{\partial x} \text{ at } x = a & \text{...(B)} \end{array}\right\} \qquad \text{...(11)}$$

Applying boundary condition (10A) to equations (5) and (6), we have

$$A_1 + B_1 = A_2 + B_2 \qquad \text{...(12)}$$

Applying boundary condition (10B) to equations (6) and (9), we get

$$A_2 e^{ip_2 a/\hbar} + B_2 e^{-ip_2 a/\hbar} = A_3 e^{ip_1 a/\hbar} \qquad \text{...(13)}$$

Differentiating equations (5), (6) and (9), we get

$$\frac{\partial\psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[A_1 e^{ip_1 x/\hbar} - B_1 e^{-ip_1 x/\hbar}\right] \qquad \text{...(14)}$$

$$\frac{\partial\psi_2}{\partial x} = \frac{ip_2}{\hbar}\left[A_2 e^{ip_2 x/\hbar} - B_2 e^{-ip_2 x/\hbar}\right] \qquad \text{...(15)}$$

$$\frac{\partial\psi_3}{\partial x} = \frac{ip_1}{\hbar} A_3 e^{ip_1 x/\hbar} \qquad \text{...(16)}$$

Applying boundary conditions (11A) and (11B) to these equations, we get

$$p_1[A_1 - B_1] = p_2[A_2 - B_2]$$

and

$$p_2[A_2 e^{ip_2 a/\hbar} - B_2 e^{-ip_2 a/\hbar}] = p_1[A_3 e^{ip_1 a/\hbar}]$$

or

$$A_1 - B_1 = \frac{p_2}{p_1}(A_2 - B_2), \qquad \text{...(17)}$$

$$A_2 e^{ip_2 a/\hbar} - B_2 e^{-ip_2 a/\hbar} = \frac{p_1}{p_2} A_3 e^{ip_1 a/\hbar} \qquad \text{...(18)}$$

Solving (12) and (17) for A_1 and B_1, we get

$A_1 + B_1 + A_1 - B_1 = A_2 + B_2 + \frac{p_2}{p_1}(A_2 - B_2)$

$A_1 + B_1 - A_1 + B_1$

$$A_1 = \frac{A_2}{2}\left(1 + \frac{p_2}{p_1}\right) + \frac{B_2}{2}\left(1 - \frac{p_2}{p_1}\right) \qquad \text{...(19)}$$

$2A_1 = A_2 + B_2 + \frac{p_2}{p_1}A_2 - \frac{B_2 p_2}{p_1}$

$2B_1 = \frac{A_2}{2}\left(1 - \frac{p_2}{p_1}\right) + \frac{B_2}{2}\left(1 + \frac{p_2}{p_1}\right)$

$$B_1 = \frac{A_2}{2}\left(1 - \frac{p_2}{p_1}\right) + \frac{B_2}{2}\left(1 + \frac{p_2}{p_1}\right) \qquad \text{...(20)}$$

$= A_2 + \frac{A_2 p_2}{p_1} + B_2 - \frac{B_2 p_2}{p_1}$

$2A_1 = A_2\left(1 + \frac{p_2}{p_1}\right) + B_2\left(1 -\right.$

Solving (13) and (18) for A_2 and B_2, we get

$$A_2 = \frac{A_3}{2}\left(1 + \frac{p_1}{p_2}\right) e^{i(p_1 - p_2)a/\hbar}, \qquad \text{...(21)}$$

$$B_2 = \frac{A_3}{2}\left(1 - \frac{p_1}{p_2}\right) e^{i(p_1 + p_2)a/\hbar} \qquad \text{...(22)}$$

Substituting values of A_2 and B_2 from these equations in (19) and (20), we get

$$A_1 = \frac{A_3}{2} e^{ip_1 a/\hbar}\left[\left(1 + \frac{p_2}{p_1}\right)\left(1 + \frac{p_1}{p_2}\right) e^{-ip_2 a/\hbar} + \left(1 - \frac{p_2}{p_1}\right)\left(1 - \frac{p_1}{p_2}\right) e^{ip_2 a/\hbar}\right] \qquad \text{...(23)}$$

$$B_1 = \frac{A_3}{4} e^{ip_1 a/\hbar}\left[\left(1 - \frac{p_2}{p_1}\right)\left(1 + \frac{p_1}{p_2}\right) e^{-ip_2 a/\hbar} + \left(1 + \frac{p_2}{p_1}\right)\left(1 - \frac{p_1}{p_2}\right) e^{ip_2 a/\hbar}\right] \qquad \text{...(24)}$$

Equation (23) may be written as

$$\frac{A_3}{A_1}=\frac{4e^{-(ip_1a/\hbar)}}{\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2a/\hbar}+\left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2a/\hbar}}$$

$$=\frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1+p_2)^2e^{-ip_2a/\hbar}-(p_1-p_2)^2e^{ip_2a/\hbar}}$$

$$=\frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1^2+p_2^2)(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})+2p_1p_2(e^{-ip_2a/\hbar}+e^{ip_2a/\hbar})}$$

$$=\frac{2p_1p_2e^{-ip_1a/\hbar}}{(p_1^2+p_2^2)\frac{(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})}{2}+2p_1p_2\frac{(e^{-ip_2a/\hbar}+e^{ip_2a/\hbar})}{2}}$$

Dividing equation (24) by (23), we get

$$\frac{B_1}{A_1}=\frac{\left(1-\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2a/\hbar}+\left(1+\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2a/\hbar}}{\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2a/\hbar}+\left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2a/\hbar}}$$

$$=\frac{(p_1^2-p_2^2)(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})}{(p_1+p_2)^2e^{-ip_2a/\hbar}-(p_1-p_2)^2e^{ip_2a/\hbar}}$$

$$=\frac{(p_1^2-p_2^2)(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})}{(p_1^2+p_2^2)(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})+2p_1p_2(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})}$$

Now we consider the following two cases :

Case (i) $E > V_0$; in this case $p_1=\sqrt{2mE}$, $p_2=\sqrt{2m(E-V_0)}$, both are real so

$$\frac{A_3}{A_1}=\frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1^2+p_2^2)\left(-2i\sin\frac{p_2a}{\hbar}\right)+2p_1p_2\left(+2\cos\frac{p_2a}{\hbar}\right)}$$

$$=\frac{2p_1p_2e^{-ip_1a/\hbar}}{i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}+2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$$\frac{A_3^*}{A_1^*}=\frac{2p_1p_2e^{ip_1a/\hbar}}{i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}+2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$\therefore$ Transmission coefficient $T=\dfrac{\text{Transmitted flux}}{\text{Incident flux}}$

$$=\frac{A_3A_3^*\,p_1/m}{A_1A_1^*\,p_1/m}=\left(\frac{A_3}{A_1}\right)\left(\frac{A_3^*}{A_1^*}\right)$$

$$=\frac{4p_1^2p_2^2}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\cos^2\frac{p_2a}{\hbar}}$$

$$=\frac{4p_1^2p_2^2}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\left(1-\sin^2\frac{p_2a}{\hbar}\right)}$$

$$=\frac{4p_1^2p_2^2}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2}$$

Reflection Coefficient :

$$\frac{B_1}{A_1}=\frac{(p_1^2-p_2^2)\left(-2i\sin\frac{p_2a}{\hbar}\right)}{(p_1^2+p_2^2)\left(-2i\sin\frac{p_2a}{\hbar}\right)+2p_1p_2\left(2\cos\frac{p_2a}{\hbar}\right)}$$

$$=\frac{i(p_1^2-p_2^2)\sin\frac{p_2a}{\hbar}}{i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}-2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$$\frac{B_1^*}{A_1^*}=\frac{-i(p_1^2-p_2^2)\sin\frac{p_2a}{\hbar}}{-i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}-2p_1p_2\cos\frac{p_2a}{\hbar}}$$

Reflection Coefficient :

$$R=\frac{\text{Reflected flux}}{\text{Incident flux}}=\frac{B_1B_1^*\frac{p_1}{m}}{A_1A_1^*\frac{p_1}{m}}$$

$$=\frac{B_1B_1^*}{A_1A_1^*}$$

or

$$R=\frac{B_1}{A_1}\left(\frac{B_1^*}{A_1^*}\right)=\frac{(p_1^2-p_2^2)\sin^2\frac{p_2a}{\hbar}}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\cos^2\frac{p_2a}{\hbar}}$$

$$=\frac{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\left(1-\sin^2\frac{p_2a}{\hbar}\right)}$$

$$=\frac{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}}{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2}$$

Case (ii). $E < V_0$, then $p_1 = \sqrt{2mE}$ is real and $p_2 = \sqrt{[2m(E-V_0)]}$ is imaginary, therefore ip_2 is real, so that we have

$$\frac{A_3}{A_1} = \frac{2p_1p_2e^{-ip_1a/\hbar}}{-(p_1^2+p_2^2)\sinh(ip_2a/\hbar)+2p_1p_2\cosh(ip_2a/\hbar)}$$

$$= \frac{2p_1p_2e^{-ip_1a/\hbar}}{\cosh(ip_2a/\hbar)\,[-(p_1^2+p_2^2)\tanh(ip_1a/\hbar)+2p_1p_2]}$$

$$= \frac{2p_1p_2\,\mathrm{sech}(ip_2a/\hbar)\,e^{-ip_1a/\hbar}}{-(p_1^2+p_2^2)\tanh(ip_2a/\hbar)+2p_1p_2}$$

$$= \frac{-2p_1p_2\,\mathrm{sech}(ip_2a/\hbar)\,e^{-ip_1a/\hbar}}{(p_1^2+p_2^2)\tanh(ip_2a/\hbar)-2p_1p_2} \qquad ...(25)$$

The complex conjugate of above equation is written as

$$\frac{A_3^*}{A_1^*} = \frac{-2p_1p_2^*\,\mathrm{sech}(-ip_2^*a/\hbar)\,e^{ip_1a/\hbar}}{(p_1^2+p_2^{*2})\tanh(-ip_2^*a/\hbar)-2p_1p_2^*} \qquad ...(26)$$

But we have

[since $p_2 = \sqrt{[2m(E-V_0)]} = i\sqrt{[2m(V_0-E)]}$ as $V_0 > E$].

$$p_2^* = -i\sqrt{[2m(V_0-E)]} = -p_2$$

and so

$$p_2^{*2} = p_2^2$$

Then equation (26) becomes

$$\frac{A_3^*}{A_1^*} = \frac{2p_1p_2\,\mathrm{sech}(ip_2a/\hbar)\,e^{ip_1a/\hbar}}{(p_1^2+p_2^2)\tanh(ip_2a/\hbar)+2p_1p_2} \qquad ...(27)$$

The transmittance or the transmission coefficient is given by

$$T = \frac{\text{magnitude of transmitted current}}{\text{magnitude of incident current}}$$

$$= \frac{(A_3A_3^*)\,p_1/m}{(A_1A_1^*)\,p_1/m} = \frac{A_3A_3^*}{A_1A_1^*}$$

$$= \frac{\{-2p_1p_2\,\mathrm{sech}(ip_2a/\hbar)\,e^{-ip_1a/\hbar}\}\{2p_1p_2\,\mathrm{sech}(ip_2a/\hbar)\,e^{ip_1a/\hbar}\}}{\{(p_1^2+p_2^2)\tanh(ip_2a/\hbar)-2p_1p_2\}\{(p_1^2+p_2^2)\tanh(ip_2a/\hbar)+2p_1p_2\}}$$

[Using (25) and (27)]

or

$$T = \frac{-4p_1^2p_2^2\,\mathrm{sech}^2(ip_2a/\hbar)}{(p_1^2+p_2^2)^2\tanh^2(ip_2a/\hbar)-4p_1^2p_2^2} \qquad ...(28)$$

Here p_2 is imaginary, *i.e.*, ip_2 is real and so p_2^2 is real. Therefore T is real.

The reflectance of the barrier or the reflection coefficient is given by

$$R = \frac{\text{magnitude of reflected current}}{\text{magnitude of incident current}} = \frac{B_1B_1^*}{A_1A_1^*} \qquad ...(29)$$

---

sing equations (23) and (24), their conjuagates and remembering the fact that $p_2^* = -p_2$, equation (29) fter simplification yields

$$R = \frac{(p_1^2-p_2^2)^2\tanh^2(ip_2a/\hbar)}{(p_1^2+p_2^2)^2\tanh^2(ip_2a/\hbar)-4p_1^2p_2^2} \qquad ...(30)$$

The *reflection coefficient R* may be obtained by the fact [redacted]

$$R + T = 1, \qquad ...(31)$$

r,

$$R = 1 - T.$$

The property of the barrier penetration is entirely due to the wave nature of matter and is very similar the total internal reflection of light waves. If two plates of glass are placed close to each other with a yer of air as a medium between them, the light will be transmitted from one plate to another, even ough the angle of incidence is greater than the critical angle. However, the intensity of transmitted wave ill decrease exponentially with thickness of the layer of air. In this case the intensity of electron waves ecreases exponentially with the thickness of the barrier. The wave-function has the form more or less as own in fig. 5.5.

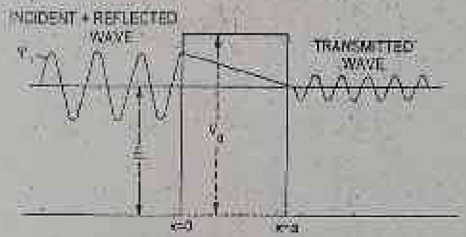

Fig. 5.5.

Now let us consider a special case when *the barrier is thick, i.e.,*

$$ip_2a >> \hbar \qquad \text{(since } a \text{ is very large).}$$

In this case $\tanh[(ip_2)\,a/\hbar] = 1$

and

$$\sec\left(\frac{(ip_2)\,a}{\hbar}\right) = 2e^{ip_2a/\hbar}$$

It is to be noted that p_2 is imaginary and so ip_2 and p_2^2 are real and negative. Then equations (21) and) yield

$$T = \frac{-16p_1^2p_2^2e^{2ip_2a/\hbar}}{(p_1^2+p_2^2)^2-4p_1^2p_2^2}$$

$$T = \frac{-16p_1^2p_2^2e^{2ip_2a/\hbar}}{(p_1^2-p_2^2)^2}$$

$$R = \frac{(p_1^2-p_2^2)^2}{(p_1^2+p_2^2)^2-4p_1^2p_2^2} = \frac{(p_1^2-p_2^2)^2}{(p_1^2-p_2^2)^2} = 1.$$

Substituting values of p_1 and p_2 from equation (8), equation (32) gives

$$T = \frac{-16\,(2mE)\,2m(E-V_0)\,e^{[2\sqrt{2m(E-V_0)}\,a/\hbar]}}{[2mE-2m\,(E-V_0)]^2}$$

$$= \frac{16E\,(V_0-E)}{V_0^2}\,e^{[-2\sqrt{2m\,(V_0-E)}\,a/\hbar]} \qquad ...(34)$$

This is the expression for transmission coefficient for a very large barrier. The phenomenon of the particle's (electrons, say) penetrating the potential barrier is called the "*tunnel effect*" and is specially important in thermionic and field emission.

5.5 APPLICATION OF BARRIER PENETRATION (α-DECAY)

It is known that certain nuclei emit α-particles, the process being known as *α-decay*. The theory of α-decay is based on the idea that α-particles are bound inside the nucleus by tremendous and enormous attractive forces which are very similar to those involved in the attraction of neutrons and protons. However, these attractive forces have a very short-range such that they are completely negligible unless the α-particle is inside the nucleus. As the α-particle and the nucleus are both positively charged, there must be repulsive forces. When α-particle is inside the nucleus, the nuclear attractive forces dominate over the electrical repulsive forces ; but when particle is outside the nucleus, the repulsive forces, dominate over the nuclear attractive forces. Therefore if an α-particle is brought from a long distance towards the nucleus, it will at first be repelled electrically and will possess potential energy $\frac{1}{4\pi\varepsilon_0}\frac{(2e)(Ze)}{r} = \frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{r}$ where Ze is the charge on the nucleus, $2e$ is the charge on α-particle and r the distance of the α-particle from the centre of the nucleus. When this α-particle reaches the nucleus, the attractive forces dominate over the repulsive forces. The potential curve as a function of r will be of the form as shown in fig. 5.6.

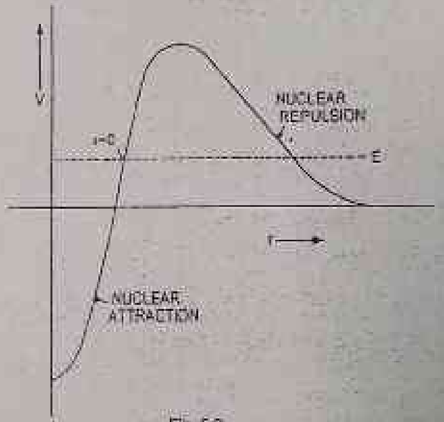

Fig. 5.6.

If an α-particle has energy E which is less than that required to carry it over the repulsive electrical barrier, than according to classical mechanics, the α-praticle, once got inside the nucleus, will be trapped in it. But according to quantum mechanics α-particle has a small but finite probability of penetrating the barrier.

The eigen values are given by

$$E_n = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\,\omega = \left(n + \frac{3}{2}\right)\hbar\,\omega, \qquad ...(17)$$

where $n = n_x + n_y + n_z$ may be called *total quantum number*. As the energy of this system depends only on the total quantum number, all the energy levels except the lowest one are *degenerate* with the quantum weight, $p = \frac{1}{2}[(n+1)(n+2)]$. Fig. 6.2 represents a few energy levels together with their quantum weights and quantum numbers.

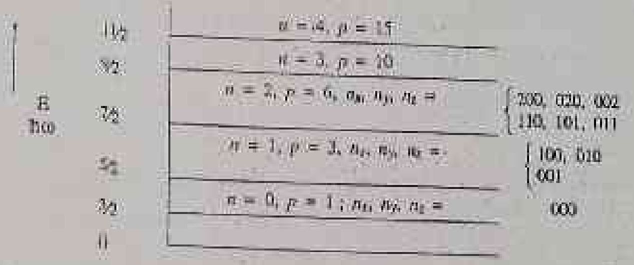

Fig. 6.2.

6.3 THE RIGID ROTATOR WITH FREE AXIS

The system, consisting of two spherical particles attached together, separated by finite fixed distance and capable of rotating about an axis passing through the centre of mass and normal to the plane containing the two particles, constitutes, a *rigid rotator*. If these two particles are constrained, to remain in one plane, then the direction of the axis of rotation is fixed and so the system is called the *rigid rotator with fixed axis*. If the plane of these two particles can move, then the axis of rotation is free to take any position in space and so the system is called the *rigid rotator with free axis*. In a diatomic molecule the atoms vibrate with respect to each other and so the distance between atoms will not be always constant; while the distance apart of the equilibrium position is constant. Thus the system of diatomic molecules is not really rigid; however, it may be treated, at least as a first approximation, as a *rigid rotator with free axis*.

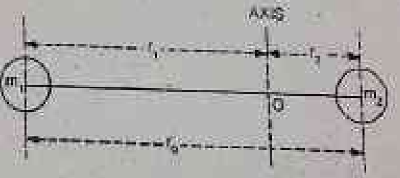

Fig. 6.3.

Energy for the rotator.

The kinetic energy of a particle of mass m can be expressed as

$$T = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) \qquad ...(1)$$

where $\dot{x}, \dot{y}, \dot{z}$ are the components of the velocity of a particle along X, Y and Z axes respectively.

The transformations between cartesian co-ordinates (x, y, z) and spherical co-ordinates (r, θ, ϕ) are given by

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right] \qquad ...(2)$$

so that the kinetic energy in spherical co-ordinates is expressed as

$$T = \frac{1}{2} m \left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2\right) \qquad ...(3)$$

If the distance r of the particle from the origin is fixed, its derivative $\dot{r}$ will be zero; thus from equation (3) the kinetic energy would be

$$T = \frac{1}{2} m r^2 \left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right) \qquad ...(4)$$

Taking O, the centre of mass of the rotator, as origin, the K.E. of the particle of mass m_1 is given by

$$T_1 = \frac{1}{2} m_1 r_1^2 \left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right)$$

Similarly the K.E. of the particle of mass m_2 is

$$T_2 = \frac{1}{2} m_2 r_2^2 \left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right)$$

Hence the total kinetic energy of the rotator will be

$$T = T_1 + T_2 = \frac{1}{2} m_1 r_1^2 \left(\dot{\theta}^2 + \sin^2\dot{\phi}^2\right) + \frac{1}{2} m_2 r_2^2 \left(\dot{\theta}^2 + \sin^2\dot{\phi}^2\right)$$

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2\right)\left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right) \qquad ...(5)$$

As there is no potential energy of the rotator, total energy is given by

$$E = T + V = T \qquad \text{(since } V = 0\text{)}$$

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2\right)\left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right) \qquad ...(6)$$

But $m_1 r_1^2 + m_2 r_2^2 = I$ the moment of inertia of the system about the axis passing through the centre of mass and perpendicular to the line joining the two masses.

Then equation (6) may be written as

$$E = T = \frac{1}{2} I \left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right) \qquad ...(7)$$

The moment of inertia of the rotator may be expressed in a more convenient form as follows :

According to definition of centre of mass, $r_{cm} = \dfrac{m_1 r_1 + m_2 r_2}{m_1 + m_2}$, we have

$$0 = \frac{-m_1 r_1 + m_2 r_2}{m_1 + m_2}$$

i.e. $$m_1 r_1 = m_2 r_2 \qquad ...(8)$$

But $$r_0 = r_1 + r_2$$

i.e. $$r_2 = r_0 - r_1$$

Substituting this in eqn. (8) we get

$$m_1 r_1 = m_2 (r_0 - r_1)$$

$\therefore$ $$r_1 = \frac{m_2}{m_1 + m_2} r_0 \qquad ...(9)$$

Similarly

$$r_2 = \frac{m_1}{m_1 + m_2} r_0 \qquad ...(10)$$

Then the moment of inertia of the rotator may be expressed as

$$I = m_1 r_1^2 + m_2 r_2^2 = m_1\left(\frac{m_2}{m_1 + m_2} r_0\right)^2 + m_2\left(\frac{m_1}{m_1 + m_2} r_0\right)^2$$

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$I = \mu r_0^2 \qquad ...(11)$$

where $$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad ...(12)$$

is called the *reduced mass* of the system.

From equations (4) and (7) it is evident that the *rigid rotator behaves like a single particle of mass μ given by eqn. (11) placed at a fixed distance, equal to unity (since $r = 1$) from the origin, which in this case is the centre of mass of the system.*

Wave equation for the rotator : The Schroedinger wave equation in three dimensions in spherical co-ordinates is given by

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad ...(13)$$

For a rigid rotator we have seen that potential energy is zero, $r = 1$ and the mass m may be replaced by the moment of inertia I. Therefore the Schroedinger wave equation for a rigid rotator becomes

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2I}{\hbar^2}E\psi = 0. \qquad ...(14)$$

This equation consists of two variables θ and φ which represent the precessional motion of the rotator's free axis and the rotation of the system respectively.

Solution of wave equation : Eigen function for the Rotator

Equation (14) may be solved by the method of separation of variables, *i.e.*, the wave-function ψ (θ, φ) may be represented by

$$\psi(\theta, \phi) = \Theta(\theta)\,\Phi(\phi) \qquad ...(15)$$

where Θ (θ) is function θ of alone and Φ (φ) is the function of φ alone.

Substituting in equation (14) and dividing by ΘΦ, we get

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\phi\sin^2\theta}\cdot\frac{\partial^2\Phi}{\partial\phi^2} + \frac{2IE}{\hbar^2} = 0 \qquad ...(16)$$

Multiplying this equation by $\sin^2\theta$ we get

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

or $$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{2IE}{\hbar^2}\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad ...(17)$$

In this equation L.H.S. is a function of θ alone, while R.H.S. is a function of φ alone. Therefore if this equation is to be satisfied, both sides must be equal to the same constant, m^2 (say) *i.e.*

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2IE}{\hbar^2}\sin^2\theta=m^2$$

and

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m^2 \qquad ...(18)$$

Equation (19) may be rewritten as

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi=0$$

the solution of above equation may be written as ...(19)

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

where $m = 0, \pm 1, \pm 2, \pm 3$ etc.

A is any arbitrary constant which may be chosen in such a way that the function is normalised, *i.e.*, ...(20)

$$\int_0^{2\pi}\Phi_m\Phi_m^*\,d\phi=1$$

or

$$\int_0^{2\pi}Ae^{im\phi}Ae^{-im\phi}\,d\phi=1,$$

i.e.,

$$A^2\int_0^{2\pi}d\phi=1$$

or

$$A^2\,2\pi=1$$

i.e.

$$A=\frac{1}{\sqrt{(2\pi)}}$$

Thus the normalised function is ...(21)

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

Multiplying equation (18) by $\frac{\Theta}{\sin^2\theta}$, we get

$$\frac{1}{\sin\theta}\left\{\sin\theta\frac{\partial\Theta}{\partial\theta}\right\}+\left(\frac{2IE}{\hbar^2}-\frac{m^2}{\sin^2\theta}\right)\Theta=0.$$

Let us now define a new variable x such that ...(22)

$$x=\cos\theta$$

so that

$$\sin\theta=\sqrt{(1-x^2)}$$

Then

$$\frac{\partial\Theta}{\partial\theta}=\frac{\partial\Theta}{\partial x}\cdot\frac{\partial x}{\partial\theta}=-\sin\theta\frac{\partial\Theta}{\partial x} \qquad ...(23)$$

and hence in general, we have ...(24)

$$\frac{\partial}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x} \qquad ...(25)$$

$$\sin\theta\frac{\partial\Theta}{\partial\theta}=-\sin^2\theta\,\frac{\partial\Theta}{\partial x}=-(1-x^2)\frac{\partial\Theta}{\partial x} \qquad ...(26)$$

using (24)

---

* Here the constant m is not related to the mass and it is actually a quantum number.

Using equations (24), (25) and (26) equation (22) can be written in terms of variable x as

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\}+\left(\beta-\frac{m^2}{1-x^2}\right)\Theta=0 \qquad ...(27)$$

where

$$\beta=\frac{2IE}{\hbar^2} \qquad ...(28)$$

Equation (28) is known as **Legendre's equation.** It has physical significance only for values of x between the limits of -1 and $+1$ since x is equal to $\cos\theta$ [refer equation (23)].

In order to solve eqn. (28) let us subsitute, for convenience,

$$\Theta(\theta)=(1-x^2)^{m/2}X(x), \qquad ...(29)$$

where $X(x)$ is the function of x only.

Equation (29) yields

$$\frac{\partial\Theta}{\partial x}=-mx(1-x^2)^{(m/2)-1}X+(1-x^2)^{m/2}\frac{dX}{dx} \qquad ...(30)$$

$$\therefore\quad \frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\}=\frac{\partial}{\partial x}\left\{-mx(1-x^2)^{m/2}X+(1-x^2)^{(m/2)+1}\frac{dX}{dx}\right\}$$

$$=\{-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{(m/2)-1}\}X$$

$$-\{2x(m+1)(1-x^2)^{m/2}\}X'+(1-x^2)^{(m/2)+1}X'' \qquad ...(31)$$

where

$$X'=\frac{dX}{dx}\text{ and }X''=\frac{d^2X}{dx^2} \qquad ...(32)$$

Using equations [29] and [31], equation [27] becomes

$$\{-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{(m/2)-1}\}X-\{2x(m+1)(1-x^2)^{m/2}\}X'$$

$$+(1-x^2)^{(m/2)-1}X''+\left(\beta-\frac{m^2}{1-x^2}\right)(1-x^2)^{m/2}X=0.$$

Dividing this by $(1-x^2)^{m/2}$, we get

$$(1-x^2)X''-2(m+1)xX'+\{\beta-m(m+1)\}X=0$$

or

$$(1-x^2)X''-2\alpha xX'+\lambda X=0 \qquad ...(33)$$

$$\left.\begin{aligned}\text{where}\quad \alpha&=m+1\\ \text{and}\quad \lambda&=\beta-m(m+1)\end{aligned}\right\} \qquad ...(34)$$

Now let us assume that $X(x)$ may be expressed as a power series, *i.e.*

$$X=a_0+a_1x+a_2x^2+a_3x^3+.... \qquad ...(35)$$

so that

$$X'=a_1+2a_2x+3a_3x^2+.... \qquad ...(36)$$

and

$$X''=2a_2+6a_3x+12a_4x^2+.... \qquad ...(37)$$

Substituting these values in equation [33] and simplifying, we get

$$(2a_2+\lambda a_0)+\{6a_3+(\lambda-2\alpha)a_1\}x+\{12a_4+(\lambda-4\alpha-2)a_2\}x^2+\{20a_5+(\lambda-4\alpha-6)a_3\}x^3+....$$

$$+\{(n+1)(n+2)a_{n+2}+\{\lambda-2n\alpha-n(n-1)\}a_n\}x^n+....=0. \qquad ...(38)$$

In order that the series may be zero for all possible values of x, the coefficients of individual powers of x must vanish separately, *i.e.*, in general

$$(n+1)(n+2)\,a_{n+2} + \{\lambda - 2n\alpha - n(n-1)\}\,a_n = 0$$

where $n = 0, 1, 2, 3, \ldots$

or

$$a_{n+2} = \frac{2n\alpha + n(n-1) - \lambda}{(n+1)(n+2)}\,a_n$$

Substituting values of α and λ in above equation, we get

$$\frac{a_{n+2}}{a_n} = \frac{(n+m)(n+m+1) - \beta}{(n+1)(n+2)} \qquad \ldots(39)$$

This is called *recursion formula* for the coefficients in power series for $X(x)$.

In order to obtain a satisfactory wave function ψ it is necessary that $X(x)$ should be a polynomial breaking off after a finite number of terms, as in the case of harmonic oscillator. The series will break after nth term if the nominator of equation [39] is zero

i.e.

$$(n+m)(n+m+1) - \beta = 0$$

or

$$\beta = (n+m)(n+m+1) \qquad \ldots(40)$$

It has already been pointed out that m is zero or an integer and n is also zero or integer. Therefore, the sum $(n+m)$ may be replaced by l, where l is also zero or an integer.

Then equation [40] gives

$$\beta = l(l+1),$$
$$l = m+n = 0, 1, 2, 3, \ldots \qquad \ldots(41)$$

Substituting this value of β in equation [27], we get

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\} + \left\{l(l+1) - \frac{m^2}{1-x^2}\right\}\Theta = 0 \qquad \ldots(42)$$

The solution of above equation contains the factor called the *associated Legendre function* $P_l^m(x)$ which may be defined as

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

where $P_l(x)$ is *Legendre polynomial* of degree l.

The solution of equation [42] is written as

$$\Theta = BP_l^m(x) = BP_l^m(\cos\theta) \qquad \ldots(43)$$

[since $x = \cos\theta$]

where B is a constant which may be normalizing factor.

According to orthogonal properties of associated Legendre's Polynomials,

$$\left.\begin{aligned} &\int_{-1}^{+1} P_k^m(x)\,P_l^m(x)\,dx = 0 && \text{for } k \neq l \\ \text{and} \quad &\int_{-1}^{+1} P_k^m(x)\,P_l^m(x)\,dx = \frac{2}{(2l+1)}\frac{(l+m)!}{(l-m)!} && \text{for } k = l \end{aligned}\right\} \qquad \ldots(44)$$

According to normalizing condition,

$$\int \Theta_{ml}\,\Theta_{ml}^*\,d\theta = 1$$

i.e.

$$B^2\int_{-1}^{+1} P_l^m(x)\,P_l^m\,dx = 1$$

i.e.

$$B^2 \cdot \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!} = 1 \qquad \text{from [44]}$$

i.e.

$$B = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)} \qquad \ldots(45)$$

Substituting value of B in [34], the normalized wave function Θ is given by

$$\Theta(\theta) = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)}P_l^m(\cos\theta) \qquad \ldots(46)$$

The complete wave-function or eigen-function for the rigid rotator is given by

$$\Psi = \Theta(\theta)\,\Phi(\phi) = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)}P_l^m(\cos\theta)\cdot\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

or

$$\Psi_{ml}(\theta, \phi) = \frac{1}{\sqrt{(2\pi)}}\sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l-m)!}\right)}P_l^m(\cos\theta)\,e^{im\phi} \qquad \ldots(47)$$

Eigen values or energy levels of the rigid rotator. From equations (28) and (41), we have

$$\frac{2IE}{\hbar^2} = l(l+1)$$

or

$$E = E_l = \frac{l(l+1)\hbar^2}{2I} \qquad \ldots(48)$$

$$l = 0, 1, 2, 3, \ldots$$

This equation gives allowed values for the energy (*i.e.* eigen values) of a rigid rotator with free axis.

6.4 RIGID ROTATOR IN A FIXED PLANE

If we consider the rotator to be only in XY plane, then $\theta = 90°$ and hence the Schroodinger's equation in this case may be written as

$$\frac{\partial^2\psi}{\partial\phi^2} + \frac{2IE}{\hbar^2}\psi = 0 \qquad \ldots(1)$$

In this case $\psi = \Phi_m(\phi)$, so that

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -\frac{2IE}{\hbar^2} = \text{constant} = -m^2 \text{ (say)}$$

so that we have

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} + m^2 = 0$$

i.e.

$$\frac{\partial^2\Phi}{\partial\phi^2} + m^2\Phi = 0 \qquad \ldots(2)$$

where

$$\frac{2IE}{\hbar^2} = m^2 \qquad \ldots(3)$$

Eigen functions : The solution of equation (2) can be written as

$$\Phi_m = Ae^{im\phi} \qquad \ldots(4)$$

where A is arbitrary constant and $m = 0, \pm 1, \pm 2, \ldots$

According to normalisation condition,

$$\int_0^{2\pi} \Phi_m \Phi_m^* \, d\phi = 1$$

or

$$\int_0^{2\pi} Ae^{+im\phi} Ae^{-im\phi} \, d\phi = 1$$

or

$$A^2 . 2\pi = 1$$

i.e.

$$A = \frac{1}{\sqrt{(2\pi)}}$$

∴ The eigen functions are given by

$$\psi = \Phi_m(\phi) = Ae^{im\phi}$$

$$= \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad \text{...(5)}$$

$$m = 0, \pm 1, \pm 2, \ldots$$

Eigen values : From equation (3), we have

$$E = E_m = \frac{m^2 \hbar^2}{2I} \qquad \text{...(6)}$$

This equation represents the rotational energy eigen values of the rigid rotator.

THE HYDROGEN ATOM

Hydrogen atom may be regarded as a system of two interacting point charges, the positively charged nucleus consisting of a proton and negatively charged electron, revolving around the nucleus.

For a system of two or more particles the equation of motion can be more conveniently written in the form

$$H\psi = E\psi \qquad \text{...(1)}$$

where H is the Hamiltonian operator, ψ is the eigen function and E is the energy of the whole system.

If (x_1, y_1, z_1) (x_2, y_2, z_2) are the cartesian co-ordinates of the nucleus and the electron and m_1 and m_2 their masses respectively. The Hamiltonian of the system is given by

$$H = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right) + V \qquad \text{...(2)}$$

where V is the potential energy.

So the Schroedinger wave equation for the whole system is written as

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)\psi_T - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)\psi_T + V = E_T\psi_T \qquad \text{...(3)}$$

where ψ_T and E_T are the total eigen function and the total energy respectively.

Equation (3) may be written as

$$\frac{1}{m_1}\left(\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{\partial^2\psi_T}{\partial z_1^2}\right)+\frac{1}{m_2}\left(\frac{\partial^2\psi_T}{\partial x_2^2}+\frac{\partial^2\psi_T}{\partial y_2^2}+\frac{\partial^2\psi_T}{\partial z_2^2}\right)+\frac{2}{\hbar^2}(E_T - V)\psi_T = 0 \qquad \text{...(4)}$$

In general the potential energy V of the system may be written as

---

$$V = \frac{(Ze)(-e)}{|\mathbf{r}|}$$

$$= \frac{(Ze)(-e)}{|\mathbf{r}_2 - \mathbf{r}_1|}$$

$$= -\frac{Ze^2}{\sqrt{\{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\}}} \qquad \text{...(5)}$$

Equation (4) can be separated into two equations one of which represents translational motion of the whole system *i.e.*, the centre of mass and the relative motion of the two particles. In order to separate the two equations let us introduce the new variables $\bar{x}, \bar{y}, \bar{z}$, the cartesian co-ordinates of the *centre of mass* of the system and (r, θ, ϕ) the polar co-ordinates of the electron relative to the nucleus. These new co-ordinates are related to the cartesian co-ordinates of the two particles by the equations.

$$\left.\begin{aligned} \bar{x} &= \frac{m_1x_1+m_2x_2}{m_1+m_2} \\ \bar{y} &= \frac{m_1y_1+m_2y_2}{m_1+m_2} \\ \bar{z} &= \frac{m_1z_1+m_2z_2}{m_1+m_2} \end{aligned}\right\} \qquad \text{...(6)}$$

$$\left.\begin{aligned} x_2 - x_1 &= r\sin\theta\cos\phi \\ y_2 - y_1 &= r\sin\theta\sin\phi \\ z_2 - z_1 &= r\cos\theta \end{aligned}\right\} \qquad \text{...(7)}$$

Introducing these new variables in equation (4), we get

$$\frac{1}{m_1+m_2}\left(\frac{\partial^2\psi_T}{\partial \bar{x}^2}+\frac{\partial^2\psi_T}{\partial \bar{y}^2}+\frac{\partial^2\psi_T}{\partial \bar{z}^2}\right)+\frac{1}{\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_T}{\partial r}\right)+\frac{1}{r^2\sin\theta}\left(\sin\theta\,\frac{\partial\psi_T}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_T}{\partial r}\right\}$$

$$+\frac{2}{\hbar^2}\{E_T - V(r)\}\psi_T = 0 \qquad \text{...(8)}$$

when $\mu = \dfrac{m_1m_2}{m_1+m_2}$ = *reduced mass of the system.* ...(9)

Let us now apply the principle of separation of variables to separate the two equations. For the urpose let us assume

$$\psi_T(\bar{x}, \bar{y}, \bar{z}, r, \theta, \phi) = f(x, y, z)\,\psi(r, \theta, \phi) \qquad \text{...(10)}$$

Substituting this value of ψ_T in equation (8) and dividing by $f\psi$, we get

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}\right)+\frac{1}{\mu\psi}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}$$

$$+\frac{2}{\hbar^2}\{E_T - V(r)\} = 0$$

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}\right)+\frac{2}{\hbar^2}E_T$$

$$= -\frac{1}{\mu\psi}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{2}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}+\frac{2}{\hbar^2}V(r) \qquad \text{...(11)}$$

In above equation L.H.S. is a function of $(\bar{x}, \bar{y}, \bar{z})$ while R.H.S. is a function of (r, θ, ϕ) and is independent of $(\bar{x}, \bar{y}, \bar{z})$. Therefore if above equation is to be satisfied both sides must be equal to a constant $2E/\hbar^2$, (say) *i.e.*

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}\right)+\frac{2}{\hbar^2}E_T = \frac{2}{\hbar^2}E$$

or

$$\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}+\frac{2}{\hbar^2}(m_1+m_2)(E_T-E)f = 0 \qquad ...(12)$$

and

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

or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}[E-V(r)]\,\psi = 0 \qquad ...(13)$$

Equation (12) represents the equation of motion of a free particle of mass m_1+m_2 and energy (E_T-E); thus the translational motion of the centre of mass is the same as that of a free particle of mass m_1+m_2 and energy (E_T-E). This result corresponds to the classical result that the centre of mass moves in a straight line with constant speed. Equation (13) is identical with Schroedinger's wave equation for a single particle of mass μ and total energy E (exclusive of the translational energy) moving under the influence of a potential function $V(r) = -e^2/r$ since for hydrogen atom $Z = 1$. The energy E of the relative motion is determined as the eigen value of this equivalent problem.

In order to solve equation (13), let us express eigen function $\psi(r, \theta, \phi)$ as the product of three functions, *viz.* $R(r)\,\Theta(\theta)\,\Phi(\phi)$, each of which is function of the one indicated variable, thus

$$\psi(r, \theta, \phi) = R(r)\,\Theta(\theta)\,\Phi(\phi) \qquad ...(14)$$

Substituting this in equation (13) and dividing by $R\,\Theta\,\Phi$, we get

$$\frac{1}{r^2 R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{r^2\sin\theta\,\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta\,\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}(E-V(r)) = 0 \qquad ...(15)$$

Multiplying this equation by $r^2\sin^2\theta$ and rearranging, we get

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+r^2\sin^2\theta\cdot\frac{2\mu}{\hbar^2}(E-V(r)) = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad ...(16)$$

In this equation L.H.S. is function of r and θ is independent of ϕ, while R.H.S. is function of ϕ alone. Therefore if this equation is to be satisfied each side must be equal to same constant m^2 (say), *i.e.*

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+r^2\sin^2\theta\,\frac{2\mu}{\hbar^2}(E-V(r)) = m^2 \qquad ...(17)$$

and

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = m^2$$

or

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi = 0 \qquad ...(18)$$

Dividing equation (17) by $\sin^2\theta$ and rearranging, we get

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$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\,\frac{2\mu}{\hbar^2}(E-V(r)) = \frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) \qquad ...(19)$$

The L.H.S. of this equation is a function of the variable r only while R.H.S. is a function of the variable θ only. Therefore if above equation is to be satisfied each side must be equal to the same constant, β (say) *i.e.*

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2\mu}{\hbar^2}(E-V(r)) = \beta$$

or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{\beta R}{r^2}+\frac{2\mu}{\hbar^2}(E-V(r))\,R = 0 \qquad ...(20)$$

and

$$\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) = \beta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta = 0. \qquad ...(21)$$

The solution of ϕ equation. As discussed in last article the solution of eqn. (18) can be written as

$$\Phi_m(\phi) = \frac{1}{\sqrt{(2\pi)}}\,e^{im\phi}, \qquad ...(22)$$

where the constant $m = 0, \pm 1, \pm 2, \pm 3, ...$ and is called the *magnetic quantum number.*

The solution of Θ equation. Let us substitute a new variable x such that

$$x = \cos\theta \qquad ...(23)$$

n equation (21), then we have

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial\theta}\right\}+\left\{\beta-\frac{m^2}{1-x^2}\right\}\Theta = 0. \qquad ...(24)$$

This equation is same as equation (27) of last article.

Therefore we must have

$$\beta = l\,(l+1) \qquad ...(25)$$

here $l = 0, 1, 2, 3, ...$ and is called the *azimuthal quantum number.*

Also solution of equation (21) may be written as

$$\Theta_{ml}(\theta) = \sqrt{\left\{\frac{(2l+1)}{2}\,\frac{(l-|m|)!}{(l+|m|)!}\right\}}\,P_l^{|m|}(\cos\theta). \qquad ...(26)$$

iere $P_l^{|m|}$ is called the *associated Legendre function.*

Solution of radial equation

Substituting value of β in equation (20), we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\frac{\partial R}{\partial r}\right\}-\frac{l(l+1)}{r^2}R+\frac{2\mu}{\hbar^2}(E-V(r))\,R = 0$$

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[\frac{-l(l+1)}{r^2}+\frac{2\mu}{\hbar^2}(E-V(r))\right]R = 0 \qquad ...(27)$$

This equation with $V(r) = -\frac{Ze^2}{r}$ is called the *radial equation for hydrogen-like atoms* and for I it is radial equation for hydrogen atom.

Substituting $V(r) = -\frac{Ze^2}{r}$ in equation (27), we get

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[\frac{-l(l+1)}{r^2} + \frac{2\mu}{\hbar^2}E + \frac{2\mu Ze^2}{\hbar^2 r}\right]R = 0. \qquad ...(28)$$

According to classical mechanics $E < 0$, *i.e.*, negative energies correspond to elliptical orbits representing bound states in atomic system : while $E > 0$, *i.e.*, positive energies correspond to hyperbolic orbits representing unbound states.

In this case let us consider that the electron is bound is the hydrogen atom, *i.e.*, $E < 0$. Then let us substitute

$$\left.\begin{aligned} \alpha^2 &= -\frac{2\mu E}{\hbar^2} \\ \text{and} \qquad \lambda &= \frac{\mu Ze^2}{\hbar^2 \alpha} \end{aligned}\right\} \qquad ...(29)$$

in equation (28), so that we have

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[-\frac{l(l+1)}{r^2} - \alpha^2 + \frac{2\lambda\alpha}{r}\right]R = 0. \qquad ...(30)$$

Let us now introduce a new independent variable ρ such that

$$\rho = 2\alpha r, \Rightarrow \frac{\partial \rho}{\partial r} = 2\alpha \qquad ...(31)$$

$r = \rho/2\alpha$

so that we have

$$\frac{\partial R}{\partial r} = \frac{\partial R}{\partial \rho}\frac{\partial \rho}{\partial r} = 2\alpha\frac{\partial R}{\partial \rho} \qquad ...(32)$$

$$\frac{\partial^2 R}{\partial r^2} = \frac{\partial}{\partial r}\left\{\frac{\partial R}{\partial r}\right\} = \frac{\partial}{\partial \rho}\left\{2\alpha\frac{\partial R}{\partial \rho}\right\}\cdot\frac{\partial \rho}{\partial r} = 4\alpha^2\frac{\partial^2 R}{\partial \rho^2} \qquad ...(33)$$

Substituting these values of $\frac{\partial R}{\partial r}$ and $\frac{\partial^2 R}{\partial r^2}$ in equation (30) and dividing by $4\alpha^2$, we get

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left\{-\frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right\}R = 0. \qquad ...(34)$$

Asymptotic behaviour : If $\rho \to \infty$, equation (34) approaches the form

$$\frac{\partial^2 R(\rho)}{\partial \rho^2} - \frac{1}{4}R(\rho) = 0.$$

The solution of above equation is

$$R(\rho) = e^{+\rho/2} \quad \text{and} \quad R(\rho) = e^{-\rho/2}$$

As ρ may vary from 0 to ∞, former of these solutions will increase as ρ increases and so it will lead to an unacceptable wave function. On the other hand second solution decreases to zero as ρ (and hence r) increases to infinity. Consequently second solution is satisfactory.

Recursion Formula : Keeping in mind the asymptotic solution, the exact solution of equation (34), must be of the form

$$R(\rho) = F(\rho)\, e^{-\rho/2} \qquad ...(35)$$

where $F(\rho)$ is another function of variable ρ.

Substituting this in equation (34), we get

$$F'' + \left\{\frac{2}{\rho} - 1\right\}F' + \left\{-\frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{\rho}\right\}F = 0 \qquad ...(36)$$

where

$$F' = \frac{dF}{d\rho} \quad \text{and} \quad F'' = \frac{d^2F}{d\rho^2}.$$

Let us now find a solution for F in the form

$$F(\rho) = \rho^s\, G(\rho), \qquad ...(37)$$

where $G(\rho)$ is a power series in ρ, begining with a non-vanishing constant, *i.e.*,

$$G(\rho) = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots = \sum_{k=0}^{\infty} a_k\rho^k,\ a_0 \neq 0. \qquad ...(38)$$

Differentiating equation (37), w.r. to ρ, we get

$$F'(\rho) = s\rho^{s-1}\,G + \rho^s\,G'$$

and

$$F''(\rho) = s(s-1)\,\rho^{s-2}\,G + 2s\rho^{s-1}\,G' + \rho^s\,G''.$$

Substituting these values of F, F' and F'' in equation (36) we get

$$\rho^{s+2}\,G'' + 2s\rho^{s+1}\,G' + s(s-1)\,\rho^s G + 2\rho^{s+1}\,G' + 2s\rho^s G - \rho^{s+2}G' + s\rho^{s+1}\,G$$
$$+ (\lambda - 1)\rho^{s+1}\,G - l(l+1)\,\rho^s G = 0$$

Dividing above equation by ρ^s and arranging the terms, we get

$$\rho^2 G'' + \rho\,[2(s+1) - \rho]\,G' + [\rho\,(\lambda - s - 1) + s(s+1) - l\,(l+1)]\,G = 0. \qquad ...(39)$$

If ρ is set equal to zero in above equation, we get

$$\{s(s+1) - l\,(l+1)\}\,a_0 = 0$$
$$s(s+1) - l\,(l+1) = 0 \qquad \text{[using (38)]}$$

hich yields

$$s = l \quad \text{or} \quad -(l+1). \qquad ...(40)\ \text{[since } a_0 \neq 0]$$

The boundary condition that $R(\rho)$ be finite at $\rho = 0$ requires that $s = l$ so that

$$\rho\,G'' + [2\,(l+1) - \rho]\,G' + (\lambda - l - 1)\,G = 0. \qquad ...(41)$$

Differentiating equation (38) w.r. to ρ, we get

$$G = \sum_k a_k\,.\,k\rho^{k-1} \qquad ...(42)$$

$$G'' = \sum_k a_k\,.\,k\,(k-1)\,\rho^{k-2} \qquad ...(43)$$

Substituting value of G, G' and G'' from (38), (43) and (44) in equation (42), we get $\qquad ...(44)$

$$\sum_k a_k\,k\,(k-1)\,\rho^{k-1} + (2\,(l+1) - \rho]\sum_k a_k\,k\,.\,\rho^{k-1} + (\lambda - l - 1)\sum_{k=0}^{\infty} a_k\,\rho^k = 0 \qquad ...(45)$$

If this equation is to be satisfied the coefficients of various powers of ρ must vanish separately.

Collecting the coefficients ρ^k and equating them to zero, we get

$$a_{k+1}\,k\,(k+1) - a_k\,k + 2(l+1)\,a_{k+1}\,(k+1) + (\lambda - l - 1)\,a_k = 0$$
$$a_{k+1}\,\{2l+2)\,(k+1) + k\,(k+1)\} + (\lambda - l - 1 - k)\,a_k = 0$$

or
$$a_{k+1} = \frac{k+l+1-\lambda}{(k+1)(2l+k+2)}\, a_k \qquad \text{...(46)}$$

This expression is called recursion formula. Here k is an integer or zero.

For any value of λ and l the series for $F(\rho)$ consists of infinite number of terms and does not correspond to a satisfactory wave-function; because value of the series as shown below, increases with increasing ρ and consequently with increasing r with the result that the function $R(\rho)$, i.e. $e^{-\rho/2}\rho^l\, G(\rho)$ increases without limit as ρ increases.

To prove this consider the series

$$\rho^l e^{\rho} = \rho^l\left[1+\rho+\frac{\rho^2}{2!}+\frac{\rho^3}{3!}+\dots+\frac{\rho^k}{k!}+\frac{\rho^{k+1}}{(k+1)!}+\dots\right]$$

so that
$$\frac{a_{k+1}}{a_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1}$$

If k is large $k+1 \cong k$, then

$$\lim_{k\to\infty}\frac{a_{k+1}}{a_k} \to \frac{1}{k}$$

Also from (46), we have

$$\lim_{k\to\infty}\frac{a_{k+1}}{a_k} \to \frac{1}{k}$$

Thus the series for $F(\rho)$ i.e. $\rho^l\, G(\rho)$, for large values of ρ behaves like $\rho^l e^{\rho}$. If this is the case, the function $R(\rho)$ for the large values of ρ will behave like $e^{-\rho/2}\rho^l e^{\rho} = \rho^l e^{\rho/2}$ which approaches infinity as ρ approaches infinity : thus making the wave-function physically unacceptable. Thus the series governed by the recursion formula (46) does not lead a satisfactory wave-function unless some restriction is introduced which makes the series break off after finite number of terms.

Energy Eigen-values for the hydrogen atom

From the above discussion we have seen that in order to obtain a satisfactory wavefunction the series will break off after a finite number of terms. The series will break off after ρ^k if we set the numerator in the recursion formula (46) equal to zero, i.e.

$$k+l+1-\lambda = 0$$
or
$$\lambda = k+l+1 = n \text{ (say)}. \qquad \text{...(47)}$$

Here k is called the *radial quantum number* and can have the values 1,2,3,..., while n is called the *total quantum number* and can have the values 1, 2, 3...

$$\lambda^2 = \frac{\mu^2 Z^2 e^4}{\hbar^4\alpha^2} = \frac{\mu^2 Z^2 e^4}{\hbar^4\left(-\frac{2E\mu}{\hbar^2}\right)}$$

or
$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2\lambda^2}$$

so that
$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad \text{...(48)}$$

[using (47)]

The equation gives the *energy eigen values for hydrogen atom* with $Z = 1$ and is in agreement with the old quantum theory and experiment.

Radial wave-function : Substituting $\lambda = n$ in equation (42) we get

$$\rho G'' + \{2(l+1)-\rho\}\, G' + (n-l-1)\, G = 0. \qquad \text{...(49)}$$

$$\begin{aligned}\text{Substituting}\quad & 2l+1 = p\\ \text{and}\quad & n+l = n'\end{aligned}\Bigg\} \qquad \text{...(50)}$$

in equation (49), we have

$$\rho G'' + \{p+1-\rho\}\, G' + (n'-p)\, G = 0. \qquad \text{...(51)}$$

The solution of this equation will be the *associated Laguerre polynomial* or more correctly the associated Laguerre polynomial multiplied by a constant factor i.e.

$$\begin{aligned} G(\rho) &= C L_{n'}^{p}(\rho)\\ &= C L_{n+l}^{2l+1}(\rho) \end{aligned} \qquad \text{...(52A)}$$

where C is constant and may be made equal to the normalization factor

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1}\frac{(-1)^{k+1}\,[(n+l)!]^2\,\rho^k}{[(n-l-1-k)]!\,[(2l+1+k)]!\,k!} \qquad \text{...(52B)}$$

Thus the total wave-function $R(r)$ is given by

$$R_{nl}(r) = e^{-\rho/2}\rho^l\, G(\rho) = Ce^{-\rho/2}\rho^l L_{n+l}^{2n+l}(\rho). \qquad \text{...(53)}$$

The normalization condition, for the physically significant interval of zero to infinity is

$$\int_0^{\infty} R(r)\, R^*(r)\, r^2\, dr = 1. \qquad \text{...(54)}$$

Here the factor r^2 is necessary to convert the length dr into an element of volume.

We have

$$\begin{aligned}\rho = 2\alpha r &= 2.\frac{\mu Z e^2}{\hbar^2\lambda}\, r = \frac{2\mu Z e^2}{\hbar^2 n}\, r \qquad \text{from (29) and (47)}\\ &= \frac{2r}{n}\,\frac{\mu Z e^2}{\hbar^2}\\ &= \frac{2Zr}{n}\cdot\frac{1}{a_0},\end{aligned} \qquad \text{...(55)}$$

$\therefore \frac{1}{a_0} = \frac{\mu e^2}{\hbar^2}$, a_0 being Bohr's radius.

rom (55)

$$r = \frac{na_0}{2Z}\,\rho$$

$$dr = \frac{na_0}{2Z}\, d\rho$$

stituting values of $R(r)$, $R^*(r)$, r and dr in equation (54), we get

$$C^2\int_0^{\infty} e^{-\rho}\rho^{2l}\left[L_{n+l}^{2l+1}(\rho)\right]^2\left(\frac{na_0}{2Z}\,\rho\right)^2\left(\frac{na_0}{2Z}\right)d\rho = 1$$

i.e.
$$C^2\left(\frac{na_0}{2Z}\right)^3\int_0^\infty e^{-\rho}\,\rho^{2l}\left[L_{n+l}^{2l+1}(\rho)\right]^2\rho^2\,d\rho=1$$

i.e.
$$C^2\left(\frac{na_0}{2Z}\right)^3\left[\frac{2n\,\{(n+l)!\}^3}{(n-l-1)!}\right]=1$$

or
$$C=\sqrt{\left[\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n\,\{(n+l)!\}^3}\right]}$$

Substituting this value of C in (53), the radial wave-function may be represented by

$$R_{nl}(r)=\sqrt{\left[\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n\,\{(n+l)!\}^3}\right]}\,e^{-Zr/na_0}\left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)\qquad ...(56)$$

The first three radial functions, found from equn. (56), are

$$\left.\begin{aligned}R_{10}(r)&=\left(\frac{Z}{a_0}\right)^{3/2}\cdot 2e^{-Zr/a_0}\\R_{20}(r)&=\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/a_0}\\R_{21}(r)&=\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0\sqrt{3}}\,e^{-Zr/a_0}\end{aligned}\right\}\qquad ...(57)$$

Complete wave-function : The complete wave-function or the normalised eigen functions for hydrogen-like atoms are

$$\psi_{nlm}(r,\theta,\phi)=R_{nl}(r)\,\Theta_{ml}(\theta)\,\Phi_m(\phi)\qquad ...(58)$$

with
$$\Theta_{ml}(\theta)=\sqrt{\left(\frac{(2l+1)\,(l-|m|)!}{2\,(l+|m|)!}\right)}\,P_l^{|m|}(\cos\theta)$$
$$\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}\,e^{im\phi}$$

and
$$R_{nl}(r)=\sqrt{\left[\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n\,\{(n+l)!\}^3}\right]}\,e^{-Zr/na_0}\left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

The real forms of the complete eigen functions ψ_{nlm} exclusive of spin, for various values of n, l and m are given below :

n	l	m	State	Eigen function
1	0	0	1s	$\psi_{100}=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$
2	0	0	2s	$\psi_{200}=\frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/a_0}$
2	1	0	2p	$\psi_{210}=\frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}e^{-Zr/2a_0}\,r\cos\theta$
2	1	1	2p	$\psi_{211}=\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}e^{-Zr/2a_0}\sin\theta\,e^{i\phi}$

Unit-3

11

The Independent Quantum Approximation Methods

(Stationary Perturbation Theory, Variation Method and W. K. B. Method)

11.1 INTRODUCTION

In Quantum Mechanics as in Classical Mechanics exactly solvable problems are rare and one must frequently resort to approximation. Approximations are therefore expected to play an important part. So various methods of approximate solution of the wave equation have been devised, leading to the more or less accurate approximate evaluation of energy values and wave-functions. Of these methods the first and in many respects the most interesting is simple wave mechanical perturbation theory developed by Schroedinger. Perturbation theories are to two kinds : time independent or stationary perturbation theory and time dependent. In this chapter we shall discuss several time independent quantum approximation methods and apply them to problems.

11.2 STATIONARY PERTURBATION THEORY (NON-DEGENERATE CASE)

The stationary perturbation theory is concerned with finding the changes in the energy levels and eigen functions of a system when a small disturbance is applied. In such cases, the Hamiltonian can be broken up into two parts, one of which is large and represents a system for which the Schroedinger equation can be solved exactly, while other part is small and can be treated as perturbation term. If the potential energy is disturbed by the influence of additional forces, the energy levels are shifted and for a weak perturbation, the amount of shift can be estimated if the original unperturbed states are known.

Consider a physical system subjected to a perturbation which shifts the energy levels slightly : of course the arrangement remains the same : Mathematically the effect of perturbation is to introduce additional terms in the Hamiltonian of the unperturbed system (or unchanged system). This additional term may by constant or it may be a function of both the space and momentum co-ordinates.

In other words, the Hamiltonian H in the Schroedinger equation can be written as the sum of two parts ; one of these parts H^0 corresponds to unperturbed system and other part H' corresponds to perturbation effect. Let us write Schroedinger wave equation

$$\hat{H}\,\psi = E\,\psi, \qquad \ldots(1)$$

which Hamiltonian $\hat{H}$ represents the operator

$$\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 + V. \qquad \ldots(2)$$

Let E be the eigen value and ψ is eigen function of operator $\hat{H}$. $\hat{H}$ is the sum of two terms H^0 and already defined

$$H = H^0 + H' \qquad \ldots(3)$$

where H' is small perturbation term.

Let ψ_k^0 and E_k^0 be a particular orthonormal eigen function and eigen value of unperturbed Hamiltonian , *i.e.*,

$$H^0\,\psi_k^0 = E_k^0\,\psi_k^0$$

If we consider *non-degenerate system* that is the system for which there is one eigen function rresponding to each eigen value. In the stationary system, the Hamiltonian H does not depend upon ne and it is possible to expand H in terms of some parameter λ yielding the expression

$$H = H^0 + \lambda H' + \lambda^2 H'' + \ldots \qquad \ldots(4)$$

which λ has been chosen in such a way that equation (1) for $\lambda = 0$ reduces to the form

$$H^0\psi^0 - E^0\psi^0 = 0 \qquad \ldots(5)$$

It is to be remembered that there is one eigen function ψ and energy level E^0 corresponding to operator . Equation (5) can be directly solved. This equation is said to be the "*wave equation of unperturbed stem*" while the terms $\lambda H' + \lambda^2 H'' + \ldots$ are called the *perturbation terms*.

The unperturbed equation (5) has solutions

$$\psi_0^0,\ \psi_1^0,\ \psi_2^0,\ \ldots,\ \psi_k^0,\ \ldots$$

led the unperturbed eigen functions and corresponding eigen values are

$$E_0^0,\ E_1^0,\ E_2^0,\ \ldots,\ E_k^0,\ \ldots$$

The functions ψ_k^0 form a complete orthonormal set, *i.e.* they satisfy the condition

$$\int \psi_i^{0*}\,\psi_j^0\,d\tau = \delta_{ij} \qquad \ldots(6)$$

ere δ_{ij} is Kronecker delta symbol defined as

$$\begin{aligned}\delta_{ij} &= 0 \ \text{ for } \ i \neq j\\ &= 1 \ \text{ for } \ i = j\end{aligned}$$

Now let us consider the effect of perturbation. The application of perturbation does not cause large anges ; hence the energy values and wave-functions for the perturbed system will be near to those for unperturbed system. We can expand the energy E and the wave-function ψ for the perturbed system terms of λ, so

$$\psi_k = \psi_k^0 + \lambda\psi_k' + \lambda^2\psi_k'' + \ldots \qquad \ldots(7)$$

$$E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots \qquad \ldots(8)$$

If the perturbation is small, then terms of the series (7) and (8) will become rapidly smaller *i.e.*, the ies will be convergent.

Now substituting (6), (7) and (8) in equation (1), we get

$$(H^0 + \lambda H' + \lambda^2 H'' + \ldots)\,(\psi_k^0 + \lambda\psi_k' + \lambda^2\psi_k'' + \ldots) = (E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots)\,(\psi_k^0 + \lambda\psi_k' + \lambda^2\psi_k'' + \ldots)$$

On collecting the coefficients of like powers of λ.

$$(H_0\psi_k^0 - E_k^0\psi_k^0) + (H^0\psi_k' + H'\psi_k^0 - E_k^0\psi_k' - E_k'\psi_k^0)\,\lambda + (H^0\psi_k'' + H'\psi_k' + H''\psi_k^0 - E_k^0\psi_k'' - E_k'\psi_k' - E_k''\psi_k^0)\,\lambda^2 + \ldots = 0.$$

If this series is properly convergent *i.e.*, equal to zero for all possible values of λ, then coefficients of various powers of λ must vanish separately. These equations will have successively higher orders of the perturbation. The coefficient of λ^0 gives

$$(H^0 - E_k^0)\,\psi_k^0 = 0 \qquad \ldots(10a)$$

The coefficient of λ gives the equation.

$$(H^0\psi_k' + H'\psi_k^0 - E_k^0\psi_k' - E_k'\psi_k^0) = 0$$

or

$$(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0 \qquad \ldots(10b)$$

The coefficient of λ^2 gives the equation

$$(H^0\psi_k'' + H'\psi_k' + \psi_k' + H''\psi_k^0 - E_k^0\psi_k'' - E_k'\psi_k' - E_k''\psi_k^0) = 0$$

$$(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' + (H'' - E_k'')\,\psi_k^0 = 0 \qquad \ldots(10c)$$

Similarly, the coefficient of λ^3 yield

$$(H^0 - E_k^0)\,\psi_k''' + (H' - E_k')\,\psi_k'' + (H'' - E_k'')\,\psi_k' + (H''' - E_k''')\,\psi_k^0 = 0 \qquad \ldots(10d)$$

But if we limit the total Hamiltonian H upto $\lambda\,H'$, *i.e.*, if we put $H = H^0 + \lambda\,H'$, then equations (10) will be modified as

$$\left.\begin{aligned}&(H^0 - E_k^0)\,\psi_k^0 = 0 && \ldots(a)\\ &(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0 && \ldots(b)\\ &(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' - E_k''\,\psi_k^0 = 0 && \ldots(c)\\ &(H^0 - E_k^0)\,\psi_k''' + (H' - E_k')\,\psi_k'' - E_k''\,\psi_k' - E_k'''\,\psi_k^0 = 0 && \ldots(d)\end{aligned}\right] \qquad \ldots(11)$$

First order perturbation : Equation (11 b) is

$$(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0$$

To solve this equation we use *expansion theorem*. As perturbation is very small, the deviations from unperturbed state are small, therefore the first order perturbation correction function ψ_k' can be expanded in terms of unperturbed functions $\psi_1^0,\ \psi_2^0,\ \ldots,\ \psi_l^0,\ \ldots$, since ψ_l^0 form a normalized orthonormal set. Hence we write

$$\psi_k' = \sum_{l=0}^{\infty} a_l\,\psi_l^0. \qquad \ldots(12)$$

Substituting ψ_k' from (12) in (11 b), we get

$$(H^0 - E_k^0)\sum_l a_l\,\psi_l^0 + (H' - E_k')\,\psi_k^0 = 0$$

$\psi_k' = \sum_{l=0} a_l \psi_l^0$

e. $$\sum_l a_l H^0 \psi_l^0 - E_k^0 \sum_l a_l \psi_l^0 + (H' - E_k') \psi_k^0 = 0.$$

sing $H^0 \psi_l^0 = E_l^0 \psi_l^0$, we get

$$\sum_l a_l E_l^0 \psi_l^0 - E_k^0 \sum_l a_l \psi_l^0 + (H' - E_k') \psi_k^0 = 0.$$

$$\sum_l a_l (E_l^0 - E_k^0) \psi_l^0 = (E_k' - H') \psi_k^0 \qquad ...(13)$$

Multiplying above equation by ψ_m^{0*} and integrating over configuration space, we get

$$\sum_l a_l (E_l^0 - E_k^0) \int \psi_m^{0*} \psi_l^0 \, d\tau = \int \psi_m^{0*} (E_k' - H') \psi_k^0 \, d\tau$$

Using the *condition of orthonormalisation* of ψ_0's.

$$\int \psi_i^{0*} \psi_j^0 \, d\tau = \delta_{ij} = \begin{cases} 0 \text{ for } i \neq j \\ 1 \text{ for } i = j \end{cases}$$

get $$\sum_l a_l (E_l^0 - E_k^0) \delta_{ml} = \int \psi_m^{0*} E_k' \psi_k^0 \, d\tau - \int \psi_m^{0*} H' \psi_k^0 \, d\tau$$

$$= E_k' \delta_{mk} - \int \psi_m^{0*} H' \psi_k^0 \, d\tau$$

Using the notations

$$\int \psi_m^{0*} H' \psi_k^0 \, d\tau = \langle m \mid H' \mid k \rangle.$$

we get

$$\sum_l a_l (E_l^0 - E_k^0) \delta_{ml} = E_k' \delta_{mk} - \langle m \mid H' \mid k \rangle. \qquad ...(14)$$

Evaluation of first order energy E_k' : Setting $m = k$ in eqn. (14), we observe that

$$\sum_l a_l (E_l^0 - E_k^0) \delta_{kl} = 0 \text{ always.}$$

Since for $l = k$, $E_l^0 - E_k^0 = 0$ and for $l \neq k$, $\delta_{kl} = 0$ so that, we get

$$0 = E_k' - \langle k \mid H' \mid k \rangle,$$

$$E_k' = \langle k \mid H' \mid k \rangle = \int \Psi_k^{0*} H' \Psi_k^0 \, d\tau. \qquad ...(15)$$

This expression gives first order perturbation energy correction. Accordingly the *"first order urbation energy correction for a non-degenerate system is just the expectation value of first order urbed hamiltonian (H') over the unperturbed state of the system."*

Evaluation of first order correction to wave function :

Equation (14) may be expressed as

$$a_m (E_m^0 - E_k^0) = E_k' \delta_{mk} - \langle m \mid H' \mid k \rangle \qquad ...(16)$$

$$\text{Since } \delta_{ml} \begin{cases} = 0 \text{ for } l \neq m \\ = 1 \text{ for } l = m \end{cases}$$

For $m \neq k$, equation (16) gives

$$a_m (E_m^0 - E_k^0) = - \langle m \mid H' \mid k \rangle$$

or $$a_m = - \frac{\langle m \mid H' \mid k \rangle}{E_m^0 - E_k^0} = \frac{\langle m \mid H' \mid k \rangle}{E_k^0 - E_m^0}$$

Setting

$$m = l, \; a_l = \frac{\langle l \mid H' \mid k \rangle}{E_k^0 - E_l^0} \qquad ...(17)$$

If we retain only first order correction terms, then

$$\left. \begin{aligned} E_k &= E_k^0 + \lambda E_k' & ...(a) \\ \psi_k &= \psi_k^0 + \lambda \psi_k' & ...(b) \end{aligned} \right| \qquad ...(18)$$

∴ Keeping in view equations (12) and (17), we get from (18b),

$$\psi_k = \psi_k^0 + \lambda \sum_l{}' \frac{\langle l \mid H' \mid k \rangle}{E_k^0 - E_l^0} \psi_l^0 + \lambda a_k \psi_k^0 \qquad ...(19)$$

where prime (or dash) on summation indicates that the term $l = m$ has been omitted from the summation (or it reminds that $l \neq k$).

The value of constant a_k may be evaluatd by requiring that ψ_k is normalised, *i.e.*

$$\int \psi_k^* \psi_k \, d\tau = 1 \qquad ...(20)$$

Substituting ψ_k from (19) and retaining only first order terms in λ ; we get

$$\int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda a_k \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda a_k^* \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda \sum_l{}' \frac{\langle l \mid H' \mid k \rangle}{E_k^0 - E_l^0} \delta_{lk}$$

$$+ \lambda \sum_l{}' \frac{[\langle l \mid H' \mid k \rangle]^*}{E_k^0 - E_l^0} \delta_{lk} = 1$$

or $$\lambda a_k + \lambda a_k^* = 0 \quad i.e. \; a_k + a_k^* = 0 \qquad ...(21)$$

This equation indicates that the real part of a_k is zero and still it leaves an arbitrary choice for the imaginary part.

Let us take $a_k = i\gamma$.

The wave function ψ_k can then be expressed as

$$\psi_k = \psi_k^0 + \lambda i \gamma \psi_k^0 + \lambda \sum_l{}' \frac{\langle l \mid H' \mid k \rangle}{E_k^0 - E_l^0} \psi_l^0$$

$$= \psi_k^0 (1 + i\lambda\gamma) + \lambda \sum_l{}' \frac{\langle l \mid H' \mid k \rangle}{E_k^0 - E_l^0} \psi_l^0 \qquad ...(22)$$

The term containing γ merely gives a phase shift in the unperturbed function ψ_k^0 and for normalisation, this shift can be put equal to zero, so that equation (22) gives

$$\psi_k = \psi_k^0 + \lambda \sum_l{}' \frac{\langle l \mid H' \mid k \rangle}{E_k^0 - E_l^0} \psi_l^0 \qquad ...(23)$$

The arbitrary λ can be put equal to 1 and it may be included in symbols, *i.e.* $\lambda H' \rightarrow H'$; then eigen values and eigen functions of the system upto first order perturbation correction terms are expressible as

$$E_k = E_k^0 + <k\,|H'|\,k> \qquad \text{...(a)}$$

$$\text{and} \qquad \psi_k = \psi_k^0 + \sum_l{}' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 \qquad \text{...(b)} \qquad \text{...(24)}$$

Second Order Perturbation : The second order perturbation equation (11 c) is

$$(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' - E_k''\,\psi_k^0 = 0 \qquad \text{...(11c)}$$

Expanding second order wave functions ψ_k'' as a linear combination of unperturbed orthonormal wave functions ψ_m^0 by expansion theorem, i.e.

$$\psi_k'' = \sum_m b_m\,\psi_m^0 \qquad \text{...(25)}$$

Substituting $\psi_k' = \sum_l{}' \dfrac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0$; $\psi_k'' = \sum_m b_m\,\psi_m^0$

and $E_k' = <k\,|H'|\,k>$ in (11c), we get

$$(H^0 - E_k^0)\sum_m b_m\,\psi_m^0 + (H' - <k\,|H'|\,k>)\sum_l{}' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 - E_k''\,\psi_k^0 = 0$$

or $$\sum_m b_m\,H^0\,\psi_m^0 - E_k^0 \sum_m b_m\,\psi_m^0 + (H' - <k\,|H'|\,k>)\sum_l{}' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 - E_k''\,\psi_k^0 = 0$$

Using unperturbed Schroedinger equation

$H^0\,\psi_m^0 = E_m^0\,\psi_m^0$, we get

$$\sum_m b_m\,E_m^0\,\psi_m^0 - E_k^0 \sum_m b_m\,\psi_m^0 + (H' - <k\,|H'|\,k>)\sum_l{}' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 - E_k''\,\psi_k^0 = 0$$

or $$\sum_m b_m\,(E_m^0 - E_k^0)\,\psi_m^0 + (H' - <k\,|H'|\,k>)\,\Sigma' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 - E_k''\,\psi_k^0 = 0$$

Multiplying by ψ_n^0 and integrating over all space, we get

$$\sum_m b_m\,(E_m^0 - E_k^0)\int \psi_n^{0*}\,\psi_m^0\,d\tau + \int \psi_n^{0*}\,(H' - <k\,|H'|\,k>)\,\Sigma' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0\,d\tau$$
$$- E_k'' \int \psi_n^{0*}\,\psi_k^0\,d\tau = 0$$

Using orthonormal property of unperturbed wave functions ψ^0's, we get

$$\sum_m b_m\,(E_m^0 - E_k^0)\,\delta_{nm} + \sum_l{}' \frac{<l\,|H'|\,k><n\,|H'|\,l>}{E_k^0 - E_l^0} - \sum_l{}' \frac{<k\,|H'|\,k><l\,|H'|\,k>}{E_k^0 - E_l^0}\,\delta_{nl}$$
$$- E_k''\,\delta_{nk} = 0 \qquad \text{...(26)}$$

Evaluation of second order energy correction :

Setting $n = k$ in (26), we get

$$\sum_m b_m\,(E_m^0 - E_k^0)\,\delta_{km} + \sum_l{}' \frac{<l\,|H'|\,k><k\,|H'|\,l>}{E_k^0 - E_l^0} - \sum_l{}' \frac{<k\,|H'|\,k><l\,|H'|\,k>}{E_k^0 - E_l^0}\,\delta_{kl}$$
$$- E_k''\,\delta_{kk} = 0 \qquad \text{...(27)}$$

As $\delta_{kk} = 1$ and $\sum_m b_m\,(E_m^0 - E_k^0)\,\delta_{km} = 0$ for all values of m, equation (27) gives

$$E_k'' = \sum_l{}' \frac{<l\,|H'|\,k><k\,|H'|\,l>}{E_k^0 - E_l^0} - \sum_l{}' \frac{<k\,|H'|\,k><l\,|H'|\,k>}{E_k^0 - E_l^0}\,\delta_{kl} \qquad \text{...(28)}$$

Considering the second term in equation (28), we note that this term is zero since $\delta_{kl} = 0$ for all values of l except for $l = k$ and this term is not included in the summation. Then equation (28) gives

$$E_k'' = \sum_l{}' \frac{<l\,|H'|\,k><k\,|H'|\,l>}{E_k^0 - E_l^0}$$

If we assume that H' is *Hermitian operator*, we may write

$$E_k'' = \sum_l{}' \frac{|<k\,|H'|\,l>|^2}{E_k^0 - E_l^0} \qquad \text{...(29)}$$

This equation gives second order energy correction term E_k''. The prime on summation reminds the omission of the term $l = k$ in the summation.

Evaluation of second order correction to wave function :

For $m \neq n$, equation (26) gives

$$b_n\,(E_n^0 - E_k^0) + \sum_l{}' \frac{<l\,|H'|\,k><n\,|H'|\,l>}{E_k^0 - E_l^0} - \sum_l{}' \frac{<k\,|H'|\,k><l\,|H'|\,k>}{E_k^0 - E_l^0}\,\delta_{nl} = 0$$

or $$b_n\,(E_n^0 - E_k^0) + \sum_l{}' \frac{<l\,|H'|\,k><n\,|H'|\,l>}{E_k^0 - E_l^0} - \frac{<k\,|H'|\,k><n\,|H'|\,k>}{E_k^0 - E_n^0} = 0$$

This gives

$$b_n = \sum_l{}' \frac{<l\,|H'|\,k><n\,|H'|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_n^0)} - \frac{<k\,|H'|\,k><n\,|H'|\,k>}{(E_k^0 - E_n^0)^2}$$

Setting $n = m$, we get

$$b_m = \sum_l{}' \frac{<l\,|H'|\,k><m\,|H'|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|H'|\,k><m\,|H'|\,k>}{(E_k^0 - E_m^0)^2} \qquad \text{...(30)}$$

This equation determines all coefficients b_m's but not b_k. The coefficient b_k is determined by the normalization condition for ψ_k retaining only terms upto second order in λ.

$$\psi_k = \psi_k^0 + \lambda\,\psi_k' + \lambda^2\,\psi_k'' = \psi_k^0 + \lambda\,\psi_k' + \lambda^2 \sum_m b_m\,\psi_m^0$$
$$= \psi_k^0 + \lambda\,\psi_k' + \lambda^2\,b_k\,\psi_k^0$$
$$+ \lambda^2 \sum_m{}' \left[\sum_l{}' \frac{<l\,|H'|\,k><m\,|H'|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|H'|\,k><m\,|H'|\,k>}{(E_k^0 - E_m^0)^2} \right] \psi_m^0 \qquad \text{...(31)}$$

The normalization condition for ψ_k gives

$$\int \psi_k^*\,\psi_k\,d\tau = 1$$

Substituting ψ_k from (31), we get

$$\int \psi_k^{0*}\,\psi_k^0\,d\tau + \lambda \int \psi_k^{0*}\,\psi_k'\,d\tau + \lambda^2\,b_k \int \psi_k^{0*}\,\psi_k^0\,d\tau + \lambda^2 \sum_m{}' \left[\sum_l{}' \frac{<l\,|H'|\,k><m\,|H'|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} \right.$$

So far we have not considered the effect of electron spin. The complete and generalised solution can be found by taking the spin contribution as well. The resulting effect gives rise to so called ***anomalous Zeeman effect.***

Ex. 1. *Apply the perturbation theory to evaluate the first order energy shift in the ground state of a linear harmonic oscillator by a small perturbing potential* Cx^4 *in the Hamiltonian.* **(Rohilkhand 2001, 97, 98)**

Solution. The Hamiltonian of the system can be expressed as

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 + Cx^4 \qquad \ldots(1)$$

$$= H_0 + H' \text{ (say)}, \qquad \ldots(2)$$

where unperturbed Hamiltonian

$$H^0 = \frac{p^2}{2m} + \frac{1}{2}kx^2 \qquad \ldots(3)$$

and small perturbation

$$H' = Cx^4$$

The unperturbed normalised wavefunctions of harmonic oscillator are given by

$$\psi_n(x) = \left[\frac{\alpha}{2^n\, n!\, \sqrt{\pi}}\right]^{1/2} e^{-\alpha^2 x^2/2} H_n(\alpha x)$$

where

$$\alpha^2 = \sqrt{\left(\frac{mk}{\hbar^2}\right)} = \frac{m\omega}{\hbar}; \qquad \text{so that}$$

$$\psi_n(x) = \left(\frac{m\omega}{\hbar}\right)^{1/4} \cdot \frac{1}{[2^n\, n!\, \sqrt{\pi}]^{1/2}}\, e^{-(m\omega/2\hbar)x^2} H_n\left\{\left(\frac{m\omega}{\hbar}\right)^{1/2} x\right\} \qquad \ldots(5)$$

For ground state $n = 0$; so that the wavefunction of harmonic oscillator for ground state takes the form

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} \qquad \ldots(6)$$

The first order energy correction, according to perturbation theory, is given as

$$E' = <\psi_0 \mid H' \mid \psi_0> = \int_{-\infty}^{+\infty} \psi_0^*\, H'\, \psi_0\, dx$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} C \int_{-\infty}^{+\infty} e^{-m\omega x^2/2\hbar}\, Cx^4\, e^{-m\omega x^2/2\hbar}\, dx$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} C \int_{-\infty}^{+\infty} x^4 e^{-m\omega x^2/\hbar}\, dx$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{3}{4}\sqrt{\left(\frac{\pi}{(m\omega/\hbar)^5}\right)} \qquad \left[\text{Since } \int_{-\infty}^{+\infty} x^4 e^{-\beta x^2}\, dx = \frac{3}{4}\sqrt{\left(\frac{\pi}{\beta^5}\right)}\right]$$

$$E' = \frac{3}{4} C \left(\frac{\hbar}{m\omega}\right)^2 = \frac{3}{4} C \left(\frac{\hbar\omega}{k}\right)^2$$

This is required result.

11.4 STATIONARY PERTURBATION THEORY : DEGENERATE CASE

In the preceding discussion we have assumed that there is one eigen function for one eigen value and have found for the first order correction to wavefunction as

$$\psi_k' = \Sigma\, a_l \psi_l^0$$

where

$$a_l = \frac{<l \mid H' \mid m>}{E_m^0 - E_l^0}.$$

This causes difficulty if the two states ψ_l^0 and ψ_m^0 correspond to same energy $E_m^0 = E_l^0$ unless $<l \mid H' \mid m> = 0$. As $<l \mid H' \mid m> \neq 0$, the results obtained for non-degenerate case would not be applicable to such cases. If actual physical situations there are systems in which a number of orthogonal eigen functions correspond to the same eigenvalue. Such a system is called *degenerate system*; the order of degeneracy being equal to the number of eigen states corresponding to same eigenvalue. In such case the perturbation method is as follows.

Let us consider two eigen states ψ_1^0 and ψ_2^0 having same eigenvalue in unperturbed system i.e. $E_1^0 = E_2^0 = E^0$ (say); so that

$$H^0\psi_1^0 = E^0\psi_1^0 \quad \text{and} \quad H^0\psi_2^0 = E^0\psi_2^0 \qquad \ldots(1)$$

As eigenfunction which is linear combination of these two functions, will also be an eigenfunction corresponding to this energy. Thus

$$\psi^0 = \alpha_1\psi_1^0 + \alpha_2\psi_2^0$$

and

$$H^0\psi^0 = H^0(\alpha_1\psi_1^0 + \alpha_2\psi_2^0)$$

$$= \alpha_1 H^0\psi_1^0 + \alpha_2 H^0\psi_2^0 = \alpha_1 E^0\psi_1^0 + \alpha_2 E^0\psi_2^0$$

$$= E^0(\alpha_1\psi_1^0 + \alpha_2\psi_2^0)$$

i.e.

$$H^0\psi^0 = E^0\psi^0 \qquad \ldots(3)$$

Using orthonormal properties of ψ_1^0 and ψ_2^0, we have

$$\alpha_1^*\alpha_1 + \alpha_2^*\alpha_2 = 1. \qquad \ldots(4)$$

There may be an infinite number of eigen functions which may be built out of these two eigenfunctions corresponding to same eigenvalue E^0. Such a set of n-functions is linearly independent if there exists no relation of the form

$$\alpha_1\psi_1^0 + \alpha_2\psi_2^0 + \ldots + \ldots + \alpha_n\psi_n^0 = 0. \qquad \ldots(5)$$

If there are n linearly independent eigenfunctions corresponding to the same eigenvalue, the state is said to be n-fold degenerate and any other function possessing the same energy can be expressed as

$$\psi^0 = \alpha_1\psi_1^0 + \alpha_2\psi_2^0 + \ldots + \alpha_n\psi_n^0 \qquad \ldots(6)$$

From the normalisation condition of ψ's we get

$$\alpha_1^*\alpha_1 + \alpha_2^*\alpha_2 + \ldots + \alpha_n^*\alpha_n = 1. \qquad \ldots(7)$$

Let us now consider the *perturbed system* for which the Schroedinger equation is

$$H\psi = E\psi$$

where

$$H = H^0 + \lambda H'.$$

So that

$$(H^0 + \lambda H')\psi = E\psi. \qquad \ldots(8)$$

For λ → 0, the system tends to the unperturbed state and let for this case the system be s-fold degenerate. Then the unperturbed Schroedinger equation

$$H^0\psi^0 = E^0\psi^0 \qquad \ldots(9a)$$

the solutions

$$\psi_{11}^0,\ \psi_{12}^0,\ \psi_{13}^0 \ldots \psi_{1s}^0;\ \psi_{21}^0,\ \psi_{22}^0,\ \psi_{23}^0 \ldots \psi_{2r}^0;\ \ldots\ldots\ \psi_{k1}^0,\ \psi_{k2}^0,\ \psi_{k3}^0 \ldots \psi_{kr}^0,\ \ldots \qquad \ldots(9b)$$

Corresponding to eigen values

$$E_1^0,\ E_2^0,\ \ldots,\ E_k^0,\ \ldots \text{ respectively.} \qquad \ldots(9c)$$

Let ψ_{k1}^0, ψ_{k2}^0, ψ_{k3}^0 ... ψ_{ks}^0 represent some arbitrary chosen orthonormal set of eigenfunctions. The blem in degenerate system is to find the set of unperturbed wavefunctions to which the perturbed ctions reduce when the perturbation vanishes i.e. the evaluation of the coefficients in the linear ibination converting the initially chosen wavefunctions into the *correct zeroth order wavefunctions*, the correct eigenfunction in zero approximation be represented by the linear combination

$$\psi_k^{(0)} = \sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 \qquad \ldots(10)$$

The eigenvalue and eigenfunction of perturbed system may be expressed as

$$E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots \qquad \ldots(11)$$

$$\psi_k = \psi_k^{(0)} + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots$$

$$= \sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots \qquad \ldots(12)$$

Substituting these values in (8), we get using (10)

$$(H^0 + \lambda H')\left(\sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots\right)$$

$$= (E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots)\left(\sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots\right) \qquad \ldots(13)$$

Equating coefficients of like powers of λ, we get

$$H^0 \sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 = E_k^0 \sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 \qquad \ldots(14a)$$

$$(H^0 - E_k^0)\psi_k' = \sum_{l=1}^{s} \alpha_{kl} (E_k' - H')\psi_{kl}^0 \qquad \ldots(14b)$$

d so on.

As in non-degenerate case, the perturbation is small and the perturbed system is very near to the perturbed system, therefore the perturbed wavefunctions may be expressed in terms of unperturbed vefunctions like

$$\psi_k' = \sum_{m,j} C_{mj} \psi_{mj}^0 \qquad \ldots(15)$$

ere C_{mj} are constants and ψ_{mj}^0 correspond to *m*th state. Then

$$H^0 \psi_k' = H^0 \sum_{m,j} C_{mj} \psi_{mj}^0$$

$$= \sum_{m,j} C_{mj} H^0 \psi_{mj}^0 = \sum_{m,j} C_{mj} E_m^0 \psi_{mj}^0 \qquad \ldots(16)$$

Substituting these values in (14b), we get

$$(H^0 - E_k^0) \sum_{m,j} C_{mj} \psi_{mj}^0 = \sum_l \alpha_{kl} (E_k' - H')\psi_{kl}^0$$

i.e.

$$\sum_{m,j} C_{mj} (E_m^0 - E_k^0)\psi_{mj}^0 = \sum_l \alpha_{kl} E_k' \psi_{kl}^0 - \sum_l \alpha_{kl} H' \psi_{kl}^0 \qquad \ldots(17)$$

Multiplying both sides by ψ_{np}^{0*} and integrating over all configuration space, we get

$$\sum_{m,j} C_{mj} (E_m^0 - E_k^0) \int \psi_{np}^{0*} \psi_{mj}^0 \, d\tau = \sum_l \alpha_{kl} E_k' \int \psi_{np}^{0*} \psi_{kl}^0 \, d\tau - \sum_l \alpha_{kl} \int \psi_{np}^{0*} H' \psi_{kl}^0 \, d\tau$$

or

$$\sum_{m,j} C_{mj} (E_m^0 - E_k^0)\delta_{nm}\delta_{pj} = \sum_l \alpha_{kl} E_k' \delta_{nk}\delta_{pl} - \sum_l \alpha_{kl} \int \psi_{np}^{0*} H' \psi_{kl}^0 \, d\tau \qquad \ldots(18)$$

Energy correction : Let us choose $n = k$, then

$$\sum_{m,j} C_{mj} (E_m^0 - E_k^0)\delta_{km}\delta_{pj} = \sum_l \alpha_{kl} E_k' \delta_{pl} - \sum_l \alpha_{kl} \int \psi_{kp}^{0*} H' \psi_{kl}^0 \, d\tau \qquad \ldots(19)$$

In this equation L.H.S. is always zero since when $k = m$, it is zero due to $(E_m^0 - E_k^0)$ and when $k \neq m$, it is zero due to δ_{km}. Therefore equation (19) gives

$$\sum_l \alpha_{kl} \int \psi_{kp}^{0*} H' \psi_{kl}^0 \, d\tau - \sum_l \alpha_{kl} E_k' \delta pl = 0$$

Using notations

$$\int \psi_{kp}^{0*} H' \psi_{kl}^0 \, d\tau = \langle p \,|\, H' \,|\, l \rangle = H'_{pl}$$

we get

$$\sum_{l=1}^{s} (H'_{pl} - E_k' \delta_{pl})\alpha_{kl} = 0 \qquad \ldots(20)$$

This equation gives *s*-simultaneous equations in α_{kl} and has *s*-solutions for E_k'. These simultaneous equations can be written as

$$\left.\begin{array}{l} (H'_{11} - E_k')\alpha_{k1} + H'_{12}\alpha_{k2} + H'_{13}\alpha_{k3} + \ldots + H'_{1s}\alpha_{ks} = 0 \\ H'_{21}\alpha_{k1} + (H'_{22} - E_k')\alpha_{k2} + H'_{23}\alpha_{k3} + \ldots + H'_{2s}\alpha_{ks} = 0 \\ \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots \\ \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots\quad \ldots \\ H'_{s1}\alpha_{k1} + H'_{s2}\alpha_{k2} + H'_{s3}\alpha_{k3} + \ldots + (H'_{ss} - E_k')\alpha_{ks} = 0 \end{array}\right\} = 0 \qquad \ldots(21)$$

If neither of coefficients α_{kl} is *zero*, the determinant of coefficients of α_{kl} $(l = 1, 2, \ldots s)$ must vanish i.e.

$$\begin{vmatrix} (H'_{11} - E_k') & H'_{12} & H'_{13} & \ldots & H'_{1s} \\ H'_{21} & (H'_{22} - E_k') & H'_{23} & \ldots & H'_{2s} \\ H'_{31} & H'_{32} & (H'_{33} - E_k') & \ldots & H'_{3s} \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots & \ldots\ldots \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots & \ldots\ldots \\ H'_{s1} & H'_{s2} & H'_{s3} & \ldots & (H'_{ss} - E_k') \end{vmatrix} = 0 \qquad \ldots(22)$$

2m

Since H'_{pl} are known, it is an equation of *s*th degree in E_k' and has *s*-solutions of E_k' given by E_{k1}', E_{k2}', E_{k3}' ... E_{ks}'. Such an equation is called **secular equation** and the perturbation of this type is called **secular perturbation.**

If this equation gives all the roots E_k' different, the solutions have completely removed degeneracy ; it may happen that not all the root E_k' are distinct in which case perturbation has not completely moved degeneracy.

It is remarkable that in case the secular equation has the form

$$\begin{vmatrix} (H'_{11}-E_k') & 0 & 0 & \cdots & 0 \\ 0 & (H'_{22}-E_k') & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & (H'_{ss}-E_k') \end{vmatrix} = 0 \qquad \ldots(23)$$

Then initially chosen functions ψ_k^0 are correct zeroth order functions for the perturbation H'. For such equation the roots of E_k' can be given by following equations

$$(H'_{11}-E_k')(H'_{22}-E_k') \ldots (H'_{ss}-E_k') = 0 \qquad \ldots(24)$$

that

$$E_{k1}' = H'_{11},\ E_{k2}' = H'_{22} \ldots \text{ and } E_{ks}' = H'_{ss}$$

To solve the eigenfunctions corresponding to roots E_{k1}', E_{k2}', ... E_{ks}', a particular root is substituted (20) and solved for the ratios

$$\frac{\alpha_{kp}}{\alpha_{kl}} = \frac{\sum\limits_{l=1}^{s} H_{pl}'}{E_k'} \qquad \ldots(25)$$

The knowledge of the normalisation condition

$$\alpha_{k1}^* \alpha_{k1}^+ + \alpha_{k2}^* \alpha_{k1} + \ldots + \alpha_{ks}^* \alpha_{ks} = 1$$

elps in determining α_{kp}.

For $p > s$, $\alpha_{kp} = 0$, so that we get from (18) $m = n$

$$C_{np}(E_n^0 - E_k^0) = -\sum_{l=1}^{s} \alpha_{kl} H_{pl}'$$

e.

$$C_{np} = \frac{\sum\limits_{l=1}^{s} \alpha_{kl} H_{pl}'}{(E_k^0 - E_n^0)}, \quad i.e. \quad C_{ml} = \frac{\sum\limits_{l=1}^{s} \alpha_{kl} H_{jl}'}{E_k^0 - E_m^0} \qquad \ldots(26)$$

For normalisation of ψ_k, $C_{np} = 0$ for $p \leq s$ and we can write the first order perturbation eigen unction and eigen value as

$$\psi_k = \sum_{l=1}^{s} \alpha_{kl} \psi_{kl}^0 + \lambda \sum_{m,j>s} \frac{\sum\limits_{l=1}^{s} \alpha_{kl} H_{jl}'}{E_k^0 - E_m^0} \psi_{mj}^0 \qquad \ldots(27)$$

and

$$E_k = E_k^0 + \lambda E_k' \qquad \ldots(28)$$

11.5 FIRST ORDER STARK EFFECT IN HYDROGEN ATOM AS AN APPLICATION OF STATIONARY DEGENERATE PERTURBATION THEORY

The splitting of energy levels of an atom caused by a uniform external electric field **E** *is called Stark-Effect.* It was discovered by Stark in 1413, while observing Balmer lines of hydrogen with an electric field of strength 10^5 volt/cm. Here we shall discuss the energy shifts of Stark effect by perturbation theory. As in Zeeman effect let us choose the unperturbed initial states with a direction of the perturbing electric field along the **z-axis** and use the eigen states of L_z.

The force on electron of charge ($q = -e$; e being positive quantity) in an electric field of strength **E** is

$$\therefore \quad \mathbf{F}_e = q\mathbf{E} = -e\mathbf{E}$$

As field is along z-axis, therefore extra-energy of electron in electric field $= F_e z = -eEz$.

The Schroedinger equation for this case is

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left(W + \frac{Ze^2}{r} + eEz\right)\psi = 0 \qquad \ldots(1)$$

where W is total energy and $-\dfrac{Ze^2}{r} - eEz$ is potential energy of electron in atom.

Equation (1) may also be written as

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} - eEz\right)\psi = W\psi$$

i.e.

$$(H_0 + H')\psi = W\psi \qquad \ldots(2)$$

where the unperturbed Hamiltonian ;

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r},$$

and the first order perturbed Hamiltonian term

$$H' = -eEz$$

If we use polar co-ordinates (r, θ), then $z = r\cos\theta$

and so

$$H' = -eEz = -eEr\cos\theta, \qquad \ldots(4)$$

e being again a positive quantity.

Here the potential energy is spherically symmetric. We know that the wave functions for any spherically symmetric potential energy when expressed in spherical harmonics, have even or odd parity according as the azimuthal quantum number is even or odd.

1st Order Stark effect in Ground state of Hydrogen Atom :

The ground state of H-atom is specified by

$$n = 1,\ l = 0,\ m = 0$$

The ground stat ($n = 1$, $l = 0$, $m = 0$) of hydrogen atom is *non-degenerate state* and the corresponding spherically symmetric function is given by

$$\psi_{100} = R_{10}(r)\,Y_{100}(\theta,\phi) = \frac{1}{\sqrt{(\pi a_0^3)}}e^{-r/a_0}$$

where $a_0 = \dfrac{\hbar^2}{\mu e^2}$ is radius of Bohr's first orbit.

The first order perturbation energy correction is given by

$$E' = \int \psi_{100}^* H' \psi_{100}\, d\tau$$

$$= \iiint \frac{1}{\sqrt{(\pi a_0^3)}} e^{-r/a_0} (-eEr\cos\theta) \frac{1}{\sqrt{(\pi a_0^3)}} e^{-r/a_0} r^2\, dr \sin\theta\, d\theta\, d\phi$$

$$= -\frac{eE}{\pi a_0^3}\int_0^\infty r^3 e^{-r/a_0}\,dr \int_0^\pi \sin\theta\cos\theta\,d\theta \int_0^{2\pi} d\phi = 0$$

Since $\int_0^\pi \sin\theta\cos\theta\,d\theta = 0$

Thus for ground state of hydrogen there is no first order Stark effect. Hence we may say that only the non-zero matrix elements of H' are those that have odd parity since the perturbation term H' is odd with respect to inversion (odd parity).

1st Order Stark Effect in First Excited State :

Let us now consider the first excited state $n = 2$ for Hydrogen atom. Since $n = 2$, therefore $l = 0$, 1 and $m = 1, 0, -1$ and hence the quantum numbers (l, m) can have the following combinations.

$$(0, 0),\ (1, 0),\ (1, 1) \text{ and } (1, -1)$$

Thus the wave-function ψ_{nlm} is four-fold degenerate *i.e.*, the wave-function ψ_{200}, ψ_{210}, ψ_{211} and $\psi_{21,-1}$ all have same energy.

The secular equation refer eqn. (22) of section (11.4) for the first order stark effect in the form of determinant is

$$\begin{vmatrix} <0,0\,|H'|\,0,0> - W_1 & <0,0\,|H'|\,1,0> & <0,0\,|H'|\,1,1> & <0,0\,|H'|\,1,-1> \\ <1,0\,|H'|\,0,0> & <1,0\,|H'|\,1,0> - W_1 & <1,0\,|H'|\,1,1> & <1,0\,|H'|\,1,-1> \\ <1,1\,|H'|\,0,0> & <1,1\,|H'|\,1,0> & <1,1\,|H'|\,1,1> - W_1 & <1,1\,|H'|\,1,-1> \\ <1,-1\,|H'|\,0,0> & <1,-1\,|H'|\,1,0> & <1,-1\,|H'|\,1,1> & <1,-1\,|H'|\,1,-1> - W_1 \end{vmatrix} = 0$$

Let us now calculate the elements of the secular determinant, we have

$$\left.\begin{aligned} \psi_{200} &= \frac{1}{\sqrt{(32\pi a_0^3)}}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0} \\ \psi_{210} &= \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0}\cos\theta\right)e^{-r/2a_0} \\ \psi_{211} &= \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0\sqrt{2}}\sin\theta\, e^{i\phi}\right)e^{-r/2a_0} \\ \text{and}\quad \psi_{21-1} &= \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0\sqrt{2}}\sin\theta\, e^{-i\phi}\right)e^{-r/2a_0} \end{aligned}\right\} \quad ...(5)$$

$$\therefore\quad <0,0\,|H'|\,0,0> = \int \psi_{200}^{*}\, H'\, \psi_{200}\, d\tau = 0 \quad ...(6)$$

[Since $(\psi_{200}^{*}.\ \psi_{200})$ have even parity].

On similar grounds all the elements except

$$<1,0\,|H'|\,0,0> \text{ and } <0,0\,|H'|\,1,0>^{*}$$

of the secular determinant are zero.

The non-vanishing elements of H' are

$$<1,0\,|H'|\,0,0> = <0,0\,|H'|\,1,0>^{*}$$

$$= \int \psi_{210}^{*}\,(-eEr\cos\theta)\,\psi_{200}\,d\tau$$

$$= -\iiint \frac{1}{\sqrt{(32\pi a_0^3)}}\frac{r}{a_0}\cos\theta\, e^{-r/2a_0}\,(eEr\cos\theta)\ \frac{1}{\sqrt{(32\pi a_0^3)}}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

[Since $d\tau = dr\, r d\theta\, r\sin\theta\, d\phi = r^2 \sin\theta\, dr\, d\theta\, d\phi$]

$$= -\frac{eE}{32\pi a_0^4}\int_0^\infty\left(2 - \frac{r}{a_0}\right) r^4 e^{-r/a_0}\,dr \int_0^\pi \cos^2\theta\sin\theta\,d\theta \int_0^{2\pi} d\phi \quad ...(7)$$

We have

$$\int_0^\pi \cos^2\theta\sin\theta\,d\theta = -\frac{1}{3}\left[\cos^3\theta\right]_0^\pi = \frac{2}{3} \quad ...(8)$$

$$\int_0^{2\pi} d\phi = 2\pi \quad ...(9)$$

and

$$\int_0^\infty\left(2 - \frac{r}{a_0}\right) r^4 e^{-r/a_0}\,dr$$

$$= \int_0^\infty (2 - \eta)\,(\eta a_0)^4\, e^{-\eta}\,(a_0\, d\eta) \qquad \text{where } \frac{r}{a_0} = \eta$$

$$= a_0^5\left[2\int_0^\infty \eta^4 e^{-\eta}\,d\eta - \int_0^\infty \eta^5 e^{-\eta}\,d\eta\right]$$

$$= a_0^5\,[2\Gamma 5 - \Gamma 6]\left(\text{since } \int_0^\infty x^{n-1} e^{-x}\,dx = \Gamma n\right) \quad ...(10)$$

$$= a_0^5\,[48 - 120] = -72 a_0^5$$

Using (8), (9) and (10) equation (7) yields

$$\left.\begin{aligned} <1,0\,|H'|\,0,0> &= <0,0\,|H'|\,1,0>^{*} \\ &= -\frac{eE}{32\pi a_0^4}(-72 a_0^5).\left(\tfrac{2}{3}\right).2\pi \\ &= 3eEa_0 \end{aligned}\right| \quad ...(11)$$

So the secular equation is

$$\begin{vmatrix} -W_1 & 3eEa_0 & 0 & 0 \\ 3eEa_0 & -W_1 & 0 & 0 \\ 0 & 0 & -W_1 & 0 \\ 0 & 0 & 0 & -W_1 \end{vmatrix} = 0 \quad ...(12)$$

i.e.

$$-W_1^2\left[W_1^2 - (3eEa_0)^2\right] = 0$$

This gives

$$W_1 = 0,\ 0 \text{ and } W_1 = \pm\, 3eEa_0$$

The splitting of energy levels is shown in Fig. 11.3. The electric potential energy of a dipole of moment **p** is $-\mathbf{p}.\mathbf{E}$.

In this case the energy of splitted levels is ± $3ea_0E$. Hence *the behaviour of hydrogen atom in first excited state* ($n = 2$) *is like a permanent electric dipole moment of magnitude* $3ea_0$ which can be oriented in three different ways :

Fig. 11.3. First order splitting of energy level.

(1) One state parallel to the external electric field.
(2) One state antiparallel to the external electric field and
(3) Two states perpendicular to external electric field.

Correct Eigen Functions : In order to find the correct unperturbed eigen functions corresponding to $W_1 = 0, 0, 3\,eEa_0$ and $-3\,eEa_0$; we use secular equation and proceed as follows :

(i) When $W_1 = 0$, the secular equation (12), gives

$$\begin{bmatrix} 0 & 3eEa_0 & 0 & 0 \\ 3eEa_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \alpha_1\ \psi_{200} \\ \alpha_2\ \psi_{210} \\ \alpha_3\ \psi_{211} \\ \alpha_4\ \psi_{2,1,-1} \end{bmatrix} = 0$$

This is equivalent to

$$3eEa_0\,\alpha_2\,\psi_{210} = 0 \text{ and } 3eEa_0\ \alpha_1\,\psi_{200} = 0$$

Thus giving $\alpha_2 = \alpha_1 = 0$

But there is no restriction on the values of α_3 and α_4. The corresponding linear combination is written as

$$\psi = \alpha_3\,\psi_{211} + \alpha_4\,\psi_{21-1}$$

The normalisation condition $\int \psi^* \psi\ d\tau = 1$ gives

$$\alpha_3^2 + \alpha_4^2 = 1$$

In particular $\alpha_3 = \frac{1}{\sqrt{2}}, \alpha_4 = \frac{1}{\sqrt{2}}$ in first case

and $\alpha_3 = \frac{1}{\sqrt{2}}, \alpha_4 = -\frac{1}{\sqrt{2}}$ in second case.

Thus the correct linear combinations for $W_1 = 0$ are

$$\frac{1}{\sqrt{2}}(\psi_{211} + \psi_{21-1}) \quad \text{and} \quad \frac{1}{\sqrt{2}}(\psi_{211} - \psi_{21-1})$$

(ii) When $W_1 = 3\,eEa_0$, the secular equation gives

$$\begin{bmatrix} -3eEa_0 & 3eEa_0 & 0 & 0 \\ 3eEa_0 & -3eEa_0 & 0 & 0 \\ 0 & 0 & -3eEa_0 & 0 \\ 0 & 0 & 0 & -3eEa_0 \end{bmatrix} \begin{bmatrix} \alpha_1\ \psi_{200} \\ \alpha_2\ \psi_{210} \\ \alpha_3\ \psi_{211} \\ \alpha_4\ \psi_{21-1} \end{bmatrix} = 0$$

Thus is equivalent to

$$-3eEa_0\ \alpha_1\ \psi_{200} + 3eEa_0\ \alpha_2\ \psi_{210} = 0 \text{ or } \alpha_1\ \psi_{200} - \alpha_2\ \psi_{210} = 0$$

$$3eEa_0\ \alpha_1\ \psi_{200} - 3eEa_0\ \alpha_2\ \psi_{210} = 0 \text{ or } \alpha_1\ \psi_{200} - \alpha_2\ \psi_{210} = 0$$

$$-3eEa_0\ \alpha_3\ \psi_{211} = 0 \text{ or } \alpha_3 = 0$$

and

$$-3eEa_0\ \alpha_4\ \psi_{21-1} = 0 \text{ or } \alpha_4 = 0$$

Thus the required linear combination is

$$\psi = \alpha_1\ \psi_{200} - \alpha_2\ \psi_{210}$$

The normalisation condition gives $\alpha_1^2 + \alpha_2^2 = 1$

Thus

$$\alpha_1 = \alpha_2 = \frac{1}{\sqrt{2}}.$$

Thus the correct linear combination for $W_1 = 3\,eEa_0$ is

$$\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$$

(iii) Similarly when $W_1 = -3\,eEa_0$, the correct normalised linear combination is

$$\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$$

11.6 THE VARIATION (RAYLEIGH-RITZ) METHOD

There are many problems of Quantum Mechanics which cannot be conveniently solved either by direct solution of wave equation or by the use of perturbation theory. The Helium atom is such a system. No direct method of solving the wave-equation has been found for this atom and the application of perturbation theory is unsatisfactory because the first oder approximation is not accurate enough while it is troublesome to calculate the higher order approximations. An approximation method, which is conveniently used for such system is *variation method*. The variation method is specially applicable for the interest in chemical problems. In special cases variation method can be extended to the state of the system other than lowest one. The variation method may also be applied to the lowest state of the given resultant angular momentum and of given electron spin multiplicity.

The expectation value of energy in normalised state ψ is given by

$$<E> = \int \psi^* H \psi\ d\tau \qquad ...(1)$$

If we choose the wave functioin ψ as variable function, then the integral (1) is known as *variational integral* and gives an upper limit to the energy E_0 of the lowest state of the system. The function ψ is the *variation function* and its choice may be quite arbitrary, but more wisely, it is chosen such that E approaches more closely to E_0.

If the variation function ψ equals the function ψ_0 of the lowest state, then energy E will be equal to E_0, *i.e.*

$$<E> = \int \psi_0^*\ H\,\psi_0\ d\tau = E_0 \qquad ...(2)$$

If $\psi \neq \psi_0$, then by expansion theorem ψ may be expanded in terms of a complete set of orthonormal functions $\phi_0, \phi_1, \phi_2 \ldots$ obtaining

$$\psi = \sum_n a_n\ \phi_n \text{ with } \sum_n a_n a_n^* = 1 \text{ and } H\phi_n = E_n\,\phi_n \qquad ...(3)$$

or

$$\frac{(2\alpha+1)^4}{\alpha} = \frac{24V_0ma^2}{\hbar^2} \qquad ...(7)$$

Given $\frac{\hbar^2}{mV_0a^2} = 0{\cdot}75$

$$\frac{(2\alpha+1)^4}{\alpha} = \frac{24}{0{\cdot}75} \Rightarrow \frac{(2\alpha+1)^4}{\alpha} = 32$$

Solving for α, we get $\alpha = \frac{1}{2}$ ...(8)

Substituting this value in (6), we get minimum energy

$$E_{\min} = \frac{\hbar^2}{8ma^2} - \frac{8V_0\left(\frac{1}{2}\right)^3}{(2)^3}$$

$$= \frac{\hbar^2}{8ma^2} - \frac{V_0}{8}$$

$$= \frac{V_0}{8}\left[\frac{\hbar^2}{ma^2V_0} - 1\right]$$

Using (2), we get

$$E_{\min} = \frac{V_0}{8}[0{\cdot}75 - 1]$$

$$= -\frac{0{\cdot}25}{8}V_0 = -0{\cdot}031\ V_0$$

THE WKB METHOD

Wentzel-Kramers-Brillouin (WKB) approximation is a final type of time independent approximate calculations. It applies to only situations in which the potential energy is slowly varying function of position. Problems of one dimension and also of three dimensions reducible in one dimension (radial) are solved by this method.

A slowly changing potential means the variation of potential energy $V(r)$ slightly over several wavelengths (de Broglie waves) of the particles shown in fig. 11·7.

The de Broglie wavelength associated with a particle moving with energy E in a region of potential V is

$$\lambda = \frac{h}{p} = \frac{h}{[2m(E-V)]^{1/2}}, \qquad ...(1)$$

since

$$\frac{1}{2}mv^2 = E - V,$$

$$m^2v^2 = 2m(E - V),$$

$$p = mv = \sqrt{[2m(E - V)]}.$$

The propagation constant

$$k = \frac{2\pi}{\lambda} = \frac{[2m(E-V)]^{1/2}}{\hbar} \qquad ...(2)$$

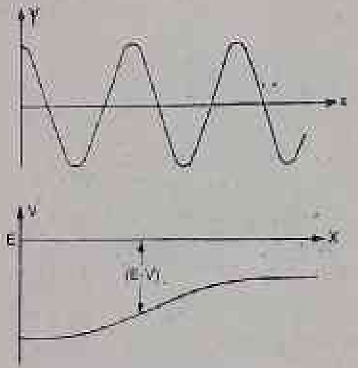

Fig. 11·7. "Slowly changing" one-dimensional potential and its associated wavefunction.

Mathematically slowly varying potential can be expressed by conditions

$$\left|\frac{1}{k^2}\frac{dk}{dx}\right| < 1,$$

Substituting value of k from (1), we get

$$\frac{\hbar m\left|\frac{\partial V}{dx}\right|}{[2m(E-V)]^{3/2}} < 1 \quad \text{or} \quad \frac{\lambda\frac{\partial V}{dx}}{4\pi(E-V)} < 1, \qquad ...(3)$$

This equation gives the validity of W.K.B. approximation.

Principle of the Method : W.K.B. method consists in introducing an expansion in the powers of ħ neglecting the terms in higher order of ħ. The Schrodinger equation (at least in some regions of space) educed in its classical limit. However, the method has a wider range of applicability than the classical roximation, because this procedure can be carried out even in regions of space where classical rpretation is meaningless (region $E < V$ is inaccessible to classical particle).

Let $\psi(x)$ be the wavefunction satisfying Schroedinger's equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0. \qquad ...(4)$$

Let the solution of eqn. (4) be of the form

$$\psi = Ce^{i\phi(x)/\hbar} \qquad ...(5)$$

where C is a constant, $\phi(x)$ is yet an undetermined function of x.

We have

$$\frac{\partial\psi}{\partial x} = C\frac{i}{\hbar}e^{i\phi(x)/\hbar}\frac{\partial\phi}{\partial x}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}\left(\frac{\partial\phi}{\partial x}\right)^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}\frac{\partial^2\phi}{\partial x^2} \qquad ...(6)$$

Now substituting $\frac{\partial\phi}{\partial x} = \phi'$ and $\frac{\partial^2\phi}{\partial x^2} = \phi''$, equation (6) takes the form

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}\phi'^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}\phi'' \qquad ...(7)$$

Substituting values of ψ and $\frac{\partial^2\psi}{\partial x^2}$ from (5) and (7) in (4), we get

$$-\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}\phi'^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}\phi'' + \frac{2m}{\hbar^2}[E - V(x)]Ce^{i\phi(x)/\hbar} = 0$$

or

$$\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}[-\phi'^2 + i\hbar\phi'' + 2m\{E - V(x)\}] = 0$$

As $\psi = Ce^{i\phi(x)/\hbar} \neq 0$; therefore above equation yields

$$i\hbar\phi'' - \phi'^2 + 2m[E - V(x)] = 0 \qquad ...(8)$$

To get an approximate solution of (8), we apply W.K.B. method and hence expand $\phi(x)$ in powers of $\hbar$ i.e.

$$\phi(x) = \phi_0(x) + \hbar\phi_1(x) + \frac{\hbar^2}{2!}\phi_2(x) + \qquad ...(9)$$

where the subscripts ϕ's are independent of $\hbar$. Let us assume that on account of the smallness of $\hbar$, the first two terms in equation (9) give a sufficiently good approximation of ϕ.

Differentiating equation (6), we obtain

$$\left.\begin{aligned}\phi'(x) &= \phi_0'(x) + \hbar\phi_1'(x) + \frac{\hbar^2}{2}\phi_2'(x) + \dots\\ \phi''(x) &= \phi_0''(x) + \hbar\phi_1''(x) + \frac{\hbar^2}{2}\phi_2''(x) + \dots\end{aligned}\right\} \qquad ...(10)$$

Substituting values of ϕ' and ϕ'' from (10) in equation (8), we get

$$i\hbar\left[\phi_0''(x) + \hbar\phi_1''(x) + \frac{\hbar^2}{2}\phi_2''(x) + \dots\right] - \left[\phi_0'(x) + \hbar\phi_1'(x) + \frac{\hbar^2}{2}\phi_2'(x) + \dots\right]^2 + 2m[E - V(x)] = 0.$$

Collecting coefficients of various powers of $\hbar$ we see that upto second order in $\hbar$, the result is

$$[2m(E - V) - \phi_0'^2] + \hbar[i\phi_0'' - 2\phi_0'\phi_1'] + \hbar^2[i\phi_1'' - \phi_1'^2 - \phi_0'\phi_2'] = 0. \qquad ...(11)$$

In order that equation (11) may hold identically in $\hbar$, the coefficient of each power of $\hbar$ must vanish separately. This requirement leads to the following series of equations

$$\left.\begin{aligned}2m(E - V) - \phi_0'^2 &= 0 && (a)\\ i\phi_0'' - 2\phi_0'\phi_1' &= 0 && (b)\\ i\phi_1'' - \phi_1'^2 - \phi_0'\phi_2' &= 0 && (c)\end{aligned}\right\} \qquad ...(12)$$

and so on

These equations may be solved successively. That is, the first equation defines ϕ_0 in terms of $|(E - V)|$, the second equation defines ϕ_1 in terms of ϕ_0, the third defines ϕ_2 in terms of ϕ_1 and ϕ_0 etc.

---

m equation (12a), we obtain

$$\phi_0' = \pm\sqrt{[2m(E - V)]} \qquad ...(13)$$

egration of above equation yields

$$\phi_0 = \pm\int_{x_0}^{x}\sqrt{[2m(E - V)]}\,dx \qquad ...(14)$$

x_0 is an arbitrary fixed value of x.

m equation (12b) we obtain

$$\phi_1' = \frac{i\phi_0''}{2\phi_0'}$$

egration of above equation yields

$$\phi_1 = \frac{i}{2}\log\phi_0' + C_1 \qquad ...(15)$$

C_1 is a constant of integration. This result is inconvenient if ϕ_0' is negative. Therefore keeping in at the logarithm of a negative function differs only by an imaginary constant from the logarithm bsolute value of the function, we replace equation (15) by

$$\phi_1 = \frac{i}{2}\log|\phi_0'| + C_2 \qquad ...(16)$$

C_2 is an arbitrary constant.

milarly

$$\phi_2 = \frac{i}{4}\frac{m\left(\frac{\partial V}{\partial x}\right)}{[2m(E - V)]^{3/2}} - \frac{i}{4}\int_{x_0}^{x}\frac{m^2\left(\frac{\partial V}{\partial x}\right)dx}{[2m(E - V)]^{5/2}} \qquad ...(17)$$

om equation (16) we see that ϕ_1 is represented as a logarithm of $|\phi_0'|$, therefore it is not, in l, small compared with ϕ_0. Consequently ϕ_0 and ϕ_1 both must be retained. On the other hand from m (17) we see that ϕ_2 will be small whenever $\partial V/\partial x$ is small and $(E - V)$ is not too close to zero. it can be seen easily that the smallness of the higher approximations (ϕ_3, ϕ_4... etc) requires the ess of all derivatives of V. Thus the W.K.B. aproximation will be suitable in cases where V is a ntly smooth and slowly varying function of position.

us the approximation W.K.B. solution of equation (8) may be expressed in the form

$$\phi = \phi_0(x) + \frac{1}{2}i\hbar\log|\phi_0'| \qquad ...(18)$$

ng constant C_2 is absorbed in $\phi_0(x)$.

bstituting value of $\phi(x)$ from (18) in equation (5) and rearranging the result, we finally get the imate solution ψ_{app} of equation (4) in the form

$$\psi_{app} = C\{2m|E - V(x)|\}^{-1/4}\exp\left[\pm\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[2m\{E - V(x)\}]}\,dx\right] \qquad ...(19)$$

C remains arbitrary. The two solutions contained in (19) and differing in sign of the exponent are y independent, and hence the approximate general solution, according to W.K.B. approximation, is

$$\psi_{app} = \{2m|E - V(x)|\}^{-1/4}\left[A\exp\left(\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[\{2m\{E - V(x)\}]}\,dx\right) + B\exp\left(-\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[\{2m\{E - V(x)\}]}\,dx\right)\right] \qquad ...(20)$$

where A and B are arbitrary constants. The positive exponential corresponds to a wave moving in the positive direction and the negative exponential corresponds to a wave moving in the negative direction. For the special case when $V(x)$ is a constant, these reduce respectively to the plane waves

$$\exp\,(ipx/\hbar) \quad \text{and} \quad \exp\,(-ipx/\hbar).$$

The alternative form of equation (20) may be expressed as

$$\psi_{app} = C\,(2m\,|(E-V)|)^{-1/4}\cos\left(\frac{1}{\hbar}\int_{x_0}^{x}\sqrt{[2m\,[E-V(x)]]}\,dx+\theta\right) \qquad ...(21)$$

where C and θ are arbitrary constants.

The approximate solutions (20) and (21) of the Schroedinger equation are usually called W.K.B. ψ-functions.

11.9 CONNECTION FORMULAS FOR PENETRATION OF A BARRIER

W.K.B. method is applicable to the problems only where the potential function does not change too rapidly ; because in the regions approximations considered do not apply. In the problems where the potential function vary slowly in some regions, so that W.K.B. method holds and the potential function varies rapidly in only regions, so that W.K.B. method is inapplicable ; we find the solution in the regions of inapplicability of W.K.B. method by some other methods and carry it to the regions where W.K.B. method is applicable. In order to connect these two solutions : we need the connection formulas.

Fig. represents potential function $V(x)$ as a function of x.

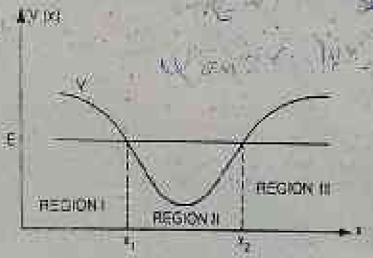

Fig. 11.8.

Let a particle has energy E. Then the whole region may be divided into three regions

Region I where $V > E$

Region II where $E > V$

Region III where $V > E$

There are two varieties of turning points, specified by points x_1 and x_2

When we pass from region I to region II, then at the turning point x_1 the barrier is to the left. But if pass from region II to region III, the barrier is to the right.

In region I, the wave-function decreases exponentially, for $x \to -\infty$ and $p_1 = \sqrt{2m\,(V-E)}$, then ψ is approximated as

$$\psi_1 = \frac{A}{\sqrt{p_1}}\exp\left(\int_{x_1}^{x'}\frac{p_1 dx}{\hbar}\right) \qquad ...(1)$$

In region II, the wave function ψ is oscillatory given by

Time Dependent Perturbation Theory and Semiclassical Theory of Radiation

NTRODUCTION

hen the Hamiltonian of a system depends on the time, there are no stationary state solutions of dinger's equation. Thus the identification of a bound state with discrete energy levels and stationary unctions must be modified. In this chapter we shall discuss three ways in which this modification made, named below :

Time dependent perturbation theory or method of variation of constants : In this method tonian is divided into two parts as usual

$$H = H_0 + H'$$

H_0 is simple unperturbed hamiltonian and H' is small time dependent perturbation term and has the of causing transitions between eigen-states of H_0 that would be stationary in the absence of H'.

Adiabatic Approximation : This method assumes that the Hamiltonian of the system (H) contains rameter that change very slowly with time. Thus the system is expected to be described approximate- means of stationary eigenfunctions of the instantaneous Hamiltonian.

Sudden Approximation : This method assumes that the Hamiltonian of the system (H) is constant e except for a very short time interval in which it changes from one form to another.

TIME DEPENDENT PERTURTATION THEORY : TIME DEVELOPMENT OF STATES

When a system is isolated and the Hamiltonian is independent of time, then the eigen states of the are true stationary states. If the system is in a particular state ψ_n which is an eigen state of ltonian H_0, then the system will always stay is that state. The time dependence of wave-function of the form

$$\psi_n(t) = \psi_n(0)\, e^{-iE_nt/\hbar}$$

where E_n is the eigen value for the state ψ_n ...(1)

$$H_0\psi_n = E_n\,\psi_n \quad ...(2)$$

If however the Hamiltonian of system depends on time, the energy of system is no longer constant. In such a case the behaviour of the systems described by solving the time-dependent schroedinger's equation

$$H(t)\,\psi = i\hbar\frac{\partial\psi}{\partial t} \quad ...(3)$$

In most of the cases the exact solution of such an equation can not be obtained.

In many physical problems the time dependence of Hamiltonian arises due to external agency. An atom exposed to light radiations is such an example.

In such a case the Hamiltonian is supposed to be formed of two parts

(i) Hamiltonian of isolated system H_0 and (ii) $H'(t)$, the interaction term H' due to interaction of external agency on system.

i.e., Hamiltonian of system $\qquad H = H^0 + H'$. ...(4)

As direct solution of equation (3) can not be obtained, we deal the problem in a different manner.

At a particular instant assumed initial instant, the Hamiltonian is regarded in same initial state (ψ_i), which is approximately an eigen state of H_0. We then attempt to calculate the probability of finding the system in some other state ψ_f at a later time t which is a also the state of H_0.

Under these circumstances we suppose the states to be *quasi-static*.

Probability of Final State

Let ϕ_n denote the complete set of eigen functions of H_0 then $H_0\phi_n = E_n\phi_n$ ...(5)

where $E_n = \hbar\omega$ represent the corresponding eigen values

The time dependent Schroedinger equation for state ψ is

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \quad ...(6)$$

The energy eigen-states of such a system are stationary; the time enters only in the phases according to

$$\psi(t) = \sum a_n(t)\,\phi_n(r)\,e^{(-iE_nt/\hbar)} \quad ...(7)$$

where a_n's are time-dependent constants and $\phi(r)$ is time-independent.

This equation represents solution of (6), therefore substituting value of ψ and H from (7) and (4) in (6), we get

$$i\hbar\frac{\partial}{\partial t}\Big[\sum_n a_n(t)\,\phi_n(r)\,e^{-iE_nt/\hbar}\Big] = (H_0 + H')\Big[\sum_n a_n(t)\,\phi(r)\,e^{-iE_nt/\hbar}\Big]$$

or

$$\Big[\sum_n i\hbar\,\dot a_n(t)\,\phi_n(r)\,e^{(-iE_nt)/\hbar} + \sum_n a_nE_n\,\phi_n(r)\,e^{(-iE_nt)/\hbar}$$

$$= \sum_n a_n H_0\phi_n(r)\,e^{(-iE_nt)/\hbar} + \sum a_n H'\phi_n(r)\,e^{(-iE_nt)/\hbar}$$

where $\qquad \frac{d}{dt}a_n(t) = \dot a_n$

Using (5) i.e. $H_0\phi_n = E_n\phi_n$, we get

$$\sum_n i\hbar\,\dot a_n\,\phi_n(r)\,e^{-iE_nt/\hbar} + \sum_n a_nE_n\phi_n(r)\,e^{-iE_nt/\hbar} = \sum_n a_nE_n\phi_n(r)\,e^{-iE_nt/\hbar} + \sum_n a_nH'\phi_n(r)\,e^{-iE_nt/\hbar}$$

$$\sum i\hbar\,\dot a_n\,\phi_n(r)\,e^{(-iE_nt)/\hbar} = \sum a_nH'\phi_n(r)\,e^{(-iE_nt)/\hbar} \quad ...(8)$$

plying both sides by ϕ_k^* and integrating over configuration space, we get

$$\sum i\hbar\,\dot a_n\,e^{-iE_nt/\hbar}\int\phi_k^*\,\phi_n^*\,d\tau = \sum_n a_n\,e^{-iE_nt/\hbar}\int\phi_k^*\,H'\,\phi_n\,d\tau$$

using orthonormality condition of ϕ's, i.e.

$$\int\phi_k^*\,\phi_n\,d\tau = \delta_{kn}\quad\begin{cases} = 0 \text{ for } n \neq k\\ = 1 \text{ for } n = k\end{cases}$$

$$i\hbar\,\dot a_n\,e^{(-iE_nt)/\hbar}\,\delta_{kn} = \sum_n a_n\,e^{(-iE_n)t/\hbar}\int\phi_k^*\,H'\,\phi_n\,d\tau.$$

wise in L.H.S. all terms will be zero except kth term due to the properties of Kronecker delta

ave

$$i\hbar\,\dot a_k\,e^{-iE_kt/\hbar} = \sum_n a_n\,e^{-iE_nt/\hbar}\int\phi_k^*\,H'\,\phi_n\,d\tau \quad ...(9)$$

integral $\int\phi_k^*\,H'\,\phi_n\,d\tau$ at right hand side is a matrix

$$<k\,|\,H'\,|\,n> = H'_{kn}$$

$$i\hbar\,\dot a_k = \sum_n a_n\,e^{i(E_k-E_n)t/\hbar}\,H'_{kn} \quad ...(10)$$

$$\frac{E_k - E_n}{\hbar} = \omega_{kn} \quad ...(11)$$

is the Bohr's angular frequency.

e dependent constants a_n's are given by

$$\left.\begin{aligned}\dot a_k &= (i\hbar)^{-1}\sum_n a_n H'_{kn}\,e^{i\omega_{kn}t}\\ &= (i\hbar)^{-1}\sum_n a_n <k\,|\,H'\,|\,n>\,e^{i\omega_{kn}t}\end{aligned}\right\} \quad ...(12)$$

e assume that at time t, there is no appreciable change in amplitudes from their values at if we replace $a_n(t)$ by $a_n(0)$ on R.H.S. of equation (12), so

$$\dot a_k(t) = (i\hbar)^{-1}\sum_n a_n(0) <k\,|\,H'\,|\,n>\,e^{i\omega_{kn}t}$$

$$\Big[a_k(t)\Big]_{t=0}^{t=t} = (i\hbar)^{-1}\sum_n a_n(0)\int_0^t <k\,|\,H'\,|\,n>\,e^{i\omega_{kn}t}\,dt$$

$$a_k(t) - a_k(0) = (i\hbar)^{-1}\sum_n a_n(0)\int_0^t <k\,|\,H'\,|\,n>\,e^{i\omega_{kn}t}\,dt \quad ...(13)$$

r convenience without any loss in generality, we can assume that the system is any particular state = 0

as

$$\left.\begin{aligned}a_k(0) &= 1 \text{ for } k = m\\ &= 0 \text{ for } k \neq m\end{aligned}\right\}$$

so

$$a_k(t) = (i\hbar)^{-1}\int_0^t <k\,|\,H'\,|\,m>\,e^{i\omega_{kn}t}\,dt \quad ...(14)$$

Equation (14) gives the probability amplitude at later times of states other than the initial one.

Perturbation Constant in Time

Suppose that perturbation is applied at $t = 0$ and for $t > 0$, it is constant independnet of time, then equation (12) may be expressed as

$$a_k(t) = (i\hbar)^{-1} \langle k | H' | m \rangle \int_0^t e^{i\omega_{km}t}\, dt$$

$$= (i\hbar)^{-1} \langle k | H' | m \rangle \left[\frac{e^{i\omega_{km}t}}{i\omega_{km}} \right]_0^t$$

$$= (i\hbar)^{-1} \langle k | H' | m \rangle \frac{e^{i\omega_{km}t} - 1}{i\omega_{km}}$$

$$= -\frac{\langle k | H' | m \rangle}{\hbar\omega_{km}} \{ e^{i\omega_{km}t} - 1 \} \qquad \ldots(15)$$

Thus, the probability of the system from mth state to kth state is given by

$$P_k(t) = |a_k^{(1)}(t)|^2 = \frac{|\langle k | H' | m \rangle|^2}{\hbar^2 \omega_{km}^2} |(e^{i\omega_{km}t} - 1)|^2 \qquad \ldots(16)$$

Using the relation

$$\lim_{x \to 0} (e^{ix} - 1) = 2ie^{ix/2} \sin\frac{x}{2} = 2i \sin\frac{x}{2}$$

or

$$|(e^{ix} - 1)|^2 = 4 \sin^2\frac{x}{2}$$

i.e.

$$|(e^{i\omega_{km}t} - 1)|^2 = 4 \sin^2\left(\frac{\omega_{km}t}{2}\right)$$

equation (16) takes the form

$$|a_k^{(1)}(t)|^2 = \frac{4|\langle k | H' | m \rangle|^2}{\hbar^2 \omega_{km}^2} \sin^2\left(\frac{\omega_{km}t}{2}\right) \qquad \ldots(17)$$

Physical Interpretation : In order to interpret equation (17) physically, we plot $\frac{\sin^2(\omega_{km}t/2)}{\omega_{km}^2}$ as a function of ω_{km} and find the curve as shown is fig. 12.1.

The major maxima of probability curve occurs at $\omega_{km} = 0$ i.e. for $E_k = E_m$. If we substitute $\omega_{km} = x$ in $\frac{\sin^2\frac{\omega_{km}t}{2}}{\omega_{km}^2}$ we note that

$$\frac{\sin^2\frac{\omega_{km}t}{2}}{\omega_{km}^2} = \frac{\sin^2(xt/2)}{x^2} = \frac{1}{x^2}\left[\frac{xt}{2} - \frac{(xt/2)^3}{3!} + \frac{(xt/2)^5}{5!} - \ldots\right]^2$$

$$= \frac{1}{x^2}\left(\frac{xt}{2}\right)^2 \text{ if higher powers of } \left(\frac{xt}{2}\right) \text{ are neglected due to their smaller values}$$

$$= \frac{t^2}{4}$$

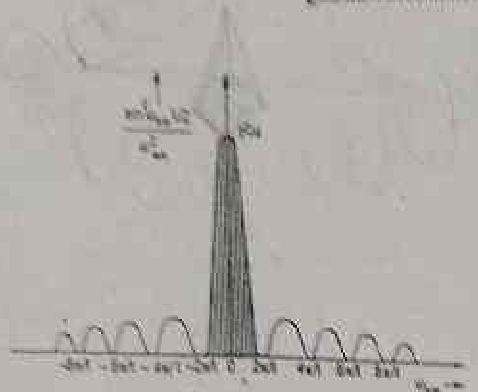

Fig. 12.1.

hus the height of the main peak is proportional $t^2/4$ and the intensity of probability curve touches axis at points where $\frac{\sin^2(xt/2)}{x^2} = 0$.

his occurs at points where

$$\frac{xt}{2} = \pm r\pi \text{ or } x = \pm\frac{2\pi r}{t}$$

where r is an integer (i.e. $r = 0, 1, 2, 3, \ldots$)

hus $x = \omega_{km} = \pm\frac{2\pi r}{t} = 0, \pm\frac{2\pi}{t}, \pm\frac{4\pi}{t}, \pm\frac{6\pi}{t}, \ldots$ i.e. width of the peak is proportional to he area under the curve is proportional to t i.e. time of application of the perturbation. These results d under constant perturbation for a definite time are analogous to single slit diffraction experiment re applicable to problems of excitation and emission of radiation in elementary systems.

ow we seek the physical interpretation from the figure : For sufficiently large t, the area under the l peak is much greater than that under the neighbouring peaks and hence most transitions take place ies under the main peak.

f we have a system with the Hamiltonian H_0 and if this system interacts with an external agency n interaction Hamiltonian H', then there are transitions in the system and it is observed that there efinite transition rate from a fixed initial state to a final state.

sition Probability : Fermi – Golden Rule

et us suppose that unperturbed Hamiltonian H_0 has continuous spectrum and the transitions are e place to the state in the continuum. This is the situation in most of physical problems e.g. in ring problems the scattered states belong to the continuum eigen values of the Hamiltonian. f the transition takes place to state k of energy between E_k and $E_k + dE_k$ and the energy density of s given by $\rho(k)$ at this stage, then the transition *probability per unit time* is defined as

$$\omega = \frac{1}{t}\int |a_k^{(1)}(t)|^2 \rho(k)\, dE_k \qquad \ldots(18)$$

e $\rho(k)$ gives the number of final states in the energy interval from E_k to $E_k + dE_k$. If t is large gh, the central peak in the probability curve is sharp and then the quantities $\langle k | H' | m \rangle$ and

$\rho(k)$ may be regarded as sufficiently independent of E_k, so that they may be taken out the integral, therefore

$$\omega = \frac{1}{t}\int_{-\infty}^{+\infty} \frac{4\,|<k\,|H'|\,m>|^2}{\omega_{km}^2\hbar^2}\sin^2(\omega_{km}t/2)\,\rho(k)\,dE_k$$

$$= \frac{|<k\,|H'|\,m>|^2\,\rho(k)}{\hbar^2 t}\int_{-\infty}^{+\infty}\frac{4\sin^2(\omega_{km}t/2)\,\hbar\,d\omega_{km}}{\omega_{km}^2}$$

[Since $dE_k = E_k - E_m = \hbar\, d\omega_{km}$]

i.e.

$$\omega = \frac{|<k\,|H'|\,m>|^2\,\rho(k)}{\hbar t}\int_{-\infty}^{+\infty}\frac{\sin^2(\omega_{km}t/2)}{(\omega_{km}/2)^2}\,d\omega_{km} \qquad ...(19)$$

we have the standard integral

$$\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}\,dx = \pi$$

Substituting

$$\frac{\omega_{km}t}{2} = x, \text{ i.e. } \omega_{km} = \frac{2x}{t}, \text{ so } d\omega_{km} = \frac{2}{t}\,dx$$

$$\int_{-\infty}^{+\infty}\frac{\sin^2(\omega_{km}t/2)}{(\omega_{km}/2)^2}\,d\omega_{km} = \int_{-\infty}^{+\infty}\frac{\sin^2 x}{\left(\frac{x}{t}\right)^2}\left(\frac{2}{t}\,dx\right)$$

$$= 2t\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}\,dx = 2\pi t \qquad ...(20)$$

Substituting this in (19), we get

$$\omega = \frac{|<k\,|H'|\,m>|^2\,\rho(k)}{\hbar t}\cdot 2\pi t = \frac{2\pi}{\hbar}\rho(k)\,|<k\,|H'|\,m>|^2 \qquad ...(21)$$

This in an important result of time dependent perturbation theory and is called the ***Fermi Golden Rule***. This relation has been successsfully employed to calculate the transition probabilities between two states and their corresponding life times. In perticular in β-decay it has given the results actually observed experimentally.

There may be several different groups of final states $k_1, k_2, k_3, \ldots$ all of which possess nearly the same energy $E_k = E_m + \hbar\omega$ for which the perturbation matrix elements $<k_j\,|H'|\,m>$ and density of states $\rho(k_j)$ although nearly constant within each group, differ from one group to another. Then the transition probability per unit time for jth group (replacing k) by k_j in (21) is given by

$$\omega = \frac{2\pi}{\hbar}\rho(k_j)\,|<k_j\,|H'|\,m>|^2;\ j = 1, 2, \ldots \qquad ...(22)$$

The spread of energy of final state to which transitions occur is connected with uncertainty relation $\Delta E\cdot\Delta t \approx \hbar$ in the following manner :

We can regard the perturbation H' as a device that measures the final energy of the system by transferring it to one of the state k. The time available for the measurement in t so that the uncertainty in

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gy predicted by the relation is $\Delta E \approx \hbar/t$ and this is in agreement with the width of the main peak. s there is no need to insert separate assumption for it.

monic Perturbation

Let us now consider a different but physically important case when the perturbation is harmonic of uency ω, *i.e.*

$$<k\,|H'(t')|\,m> \text{ or } H'_{km}(t') = \begin{cases} 0 \text{ for } -\infty < t' < 0 \\ 2<k\,|H'_0|\,m>\sin\omega t' \text{ for } 0 \le t' \le t \\ 0 \text{ for } t' > t \end{cases} \qquad ...(23)$$

re $<k\,|H'_0|\,m>$ is independent of time.

The first order amplitude $a_k^{(1)}(t')$ at time t', would then be given as

$$a_k^{(1)}(t' \ge t) = (i\hbar)^{-1}\int_0^t <k\,|H'|\,m>\,e^{i\omega_{km}t'}\,dt'$$

$$= (i\hbar)^{-1}\int_0^t 2<k\,|H'_0|\,m>\sin\omega t'\,e^{i\omega_{km}t'}\,dt'$$

$$= \frac{2<k\,|H'_0|\,m>}{i\hbar}\int_0^t\frac{e^{i\omega t'} - e^{-i\omega t'}}{2i}\,e^{i\omega_{km}t'}\,dt'$$

$$= -\frac{<k\,|H'_0|\,m>}{\hbar}\int_0^t\left[e^{i(\omega_{km}+\omega)t'} - e^{i(\omega_{km}-\omega)t'}\right]dt'$$

$$= -\frac{<k\,|H'_0|\,m>}{\hbar}\left[\frac{e^{i(\omega_{km}+\omega)t'}}{i(\omega_{km}+\omega)} - \frac{e^{i(\omega_{km}-\omega)t'}}{i(\omega_{km}-\omega)}\right]_0^t$$

$$a_k^{(1)}(t) = -\frac{<k\,|H'_0|\,m>}{i\hbar}\left[\frac{e^{i(\omega_{km}+\omega)t}-1}{\omega_{km}+\omega} - \frac{e^{i(\omega_{km}-\omega)t}-1}{\omega_{km}-\omega}\right] \qquad ...(24)$$

The form of this equation suggests that

(i) The first order amplitude depends on perturbation duration t and not on instantaneous time t'.

(ii) The amplitude is appreciable only when the denominator of the one or the other terms is actically zero.

The first term is important when $\omega_{km} = -\omega$ or $E_k = E_m - \hbar\omega$ and the second term is important hen $\omega_{km} = \omega$ or $E_k = E_m + \hbar\omega$. Thus the first order fect of a harmonic perturbation (*i.e.* perturbation that aries sinusoidally with time) with angular frequency ω is transfer or to receive from the system on which it acts the lanck's energy quantum $\hbar\omega$.

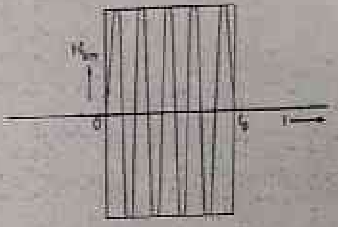

Fig. 12.2

In the special case in which the initial state m is a screte bound state and the final state k is one of the ntinuous set of dissociated states. Then $E_k > E_m$ and only e second term in (24) need be considered. In this case the st order probability of finding the system in k th state after e perturbation is removed is given by

$$|a_k^{(1)}(t \geq t)|^2 = \frac{4\,|\langle k|H_0'|m\rangle|^2 \sin^2 \frac{(\omega_{km}-\omega)\,t}{2}}{\hbar^2\,(\omega_{km}-\omega)^2} \qquad \text{...(25)}$$

12.2 ADIABATIC APPROXIMATION

In adiabatic approximation the perturbation is turned on very slowly. In this approximation we expect on physical grounds that solution of the Schroedinger equation can be approximated by means of stationary eigen functions of the instantaneous Hamiltonian, so that a particular eigen function at one time goes over continuously into corresponding eigen function at a later time.

Let us try to solve Schroedinger's equations

$$i\hbar\,\frac{\partial \psi}{\partial t} = H(t)\,\psi \qquad \text{...(1)}$$

where $H(t)$ varies slowly with time. Under this condition we may expect that a good approximation should be given by solving equation (1) at each instant of time under the assumption that H is constant and is equal to the instantaneous value $H'(t')$ where t' is the time at which H is required. The stationary state wave function is obtained by setting $t' = t$ = constant and would satisfy the equation

$$H(t')\,\psi_n(\mathbf{r}, t') = E_n(t')\,\psi_n(\mathbf{r}, t') \qquad \text{...(2)}$$

The approximate solution is

$$\psi_n = \phi_n(t)\,\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\} \qquad \text{...(3)}$$

In general

$$\psi = \sum_n a_n(t)\,\phi(t)\,\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\} \qquad \text{...(4)}$$

Substituting this value in (1), we get

$$i\hbar\left[\sum_n\left(\dot{a}_n(t)\,\phi_n(t) + a_n\,\frac{\partial \phi_n}{\partial t}\right)\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\} + \sum_n a_n\,\phi_n\,E_n\,\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\}\right]$$

$$= H\sum_n a_n\,\phi_n\,\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\}$$

$$= \sum_n a_n\,\phi_n\,E_n\,\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\}$$

or

$$i\hbar\sum_n\left(\dot{a}_n\,\phi_n + a_n\,\frac{\partial \phi_n}{\partial t}\right)\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\} = 0$$

or

$$\sum_n\left(\dot{a}_n\,\phi_n + a_n\,\frac{\partial \phi_n}{\partial t}\right)\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right\} = 0 \qquad \text{...(5)}$$

Multiplying by $\phi_f^*\,\exp\left\{\frac{i}{\hbar}\int_0^t E_f(t')\,dt'\right\}$ and integrating over all space, we get

$$\int\sum_n \dot{a}_n\,\phi_n\,\phi_f^*\,\exp\left\{-\frac{i}{\hbar}\int_0^t (E_n - E_f)\,dt'\right\}d\tau + \sum_n a_n\int \phi_f^*\,\frac{\partial \phi_n}{\partial t}$$

$$\exp\left\{-\frac{i}{\hbar}\int_0^t (E_n - E_f)\,dt'\right\}d\tau = 0$$

$$a_f = \int_0^{t_0}\frac{\left\langle f\left|\frac{\partial H}{\partial t}\right|k\right\rangle}{(E_k - E_f)}\exp\left\{-\frac{i}{\hbar}(E_k - E_f)\,t\right\}dt$$

$$= \left\{\frac{\langle f|H(t)|k\rangle}{(E_k - E_f)}\exp\left(-\frac{i}{\hbar}(E_k - E_f)\,t\right)\right\}_0^{t_0}$$

$$- \int_0^{t_0}\frac{\langle f|H(t)|k\rangle}{(E_k - E_f)}\exp\left(-\frac{i}{\hbar}(E_k - E_f)\,t\right)\left\{-\frac{i}{\hbar}(E_k - E_f)\,t\right\}dt \qquad \text{...(2)}$$

The condition of sudden approximation, by the help of uncertainly relation $\Delta E\,\Delta t = \hbar$, is expressed (since $\Delta t = t_0$ is very small) as ...(3)

$$\frac{\hbar}{\Delta E} >> t_0$$

The physical interpretation of this condition is that of the energy of the system changes by an amount ΔE. In a time t_0 which is much less than the characteristic time associated with this energy change, then the state of the system remains unaltered (*i.e.* there is no transition) and so $\langle f|H(t)|k\rangle = 0$; so equation (2) becomes

$$a_f = \frac{i}{\hbar}\int_0^{t_0}\langle f|H(t)|k\rangle.\ \exp\left(-\frac{i}{\hbar}(E_k - E_f)\,t\right)dt \qquad \text{...(4)}$$

If ω_{fk} is the angular frequency of the transition from initial state k to a final state f, then

$$\omega_{fk} = \frac{E_f - E_k}{\hbar}\text{; so that we may write}$$

$$a_f = \frac{i}{\hbar}\int_0^{t_0}\langle f|H(t)|k\rangle\,e^{i\omega_{fk}t}\,dt \qquad \text{...(5)}$$

when perturbation is switched on suddenly, $H(t)$ changes instantaneously in time Δt which is small compared to period $(\omega_{fk})^{-1}$ so that the factor $e^{i\omega_{fk}t}$ in the above integral changes a little and hence can be taken outside the integral, then we get

$$a_f = \frac{i}{\hbar}\,e^{i\omega_{fk}t}\int_0^{t_0}\langle f|H(t)|k\rangle\,dt$$

$$= \frac{i}{\hbar}\,e^{i\omega_{fk}t}\,\langle f|H(t_0) - H(0)|k\rangle\,t_0$$

$$= \frac{i\,t_0}{\hbar}\,e^{i\omega_{fk}t}\,\langle f|H'|k\rangle \qquad \text{...(6)}$$

where $H' = (H(t_0) - H(0))$ and may be taken as the maximum value of interaction during its sudden switch on.

Therefore sudden probability of transition from state k to state f will be given by

$$|a_f|^2 = \frac{t_0^2}{\hbar^2}\,|\langle f|H'|k\rangle|^2 = \frac{|\langle f|H'|k\rangle|^2}{\hbar^2\,\omega_{fk}^2} \qquad \text{...(7)}$$

This equation may be used to evaluate the probability for transition under the influence of sudden perturbation which are sufficiently small, so that the perturbation theory may be applied.

Ex. 1. *Calculate the probability that an electron in an atom is excited when the nuclear charge is suddenly changed from Z to Z ± 1 i.e. electron and positron decay of nucleus.*

Solution. For convenience let us suppose that an atom consists of only one electron in field of charge (+ Ze). Then the initial state of atom is determined by the wavefunction

$$\phi_{100} = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a_0} Y_0^0, \qquad ...(1)$$

with

$$a_0 = \frac{\hbar^2}{me^2}$$

After the sudden change of nuclear charge, the wave functions of stationary state will correspond to H-like wavefunctions.

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi)$$

of a nuclear charge Z ± 1 Using expression for probability amplitude for sudden change

$$a_{nl,10} = \int \psi_{nlm}^* \phi_{100}\, d\tau \qquad ...(2)$$

This is non zero only for transition to s-state in view of equation (1). Using radial function for H-like atoms, we have

$$R_{20}(r) = \left(\frac{Z+1}{2a_0}\right)^{3/2}\left[2 - \frac{(Z \pm 1)\,r}{a_0}\right] e^{-(Z+1)\,r/2a_0} \qquad ...(3)$$

Then equation (2) becomes

$$a_{20,10} = 2\left(\frac{Z}{a_0}\right)^{3/2} \int R_{20}(r)\, e^{-Zr/a_0} r^2\, dr$$

$$= \pm \frac{2\,(2^3 Z (Z+1))^{3/2}}{(3Z \pm 1)^4} \qquad ...(4)$$

Thus the probability of transition 1s → 2s, when nuclear charge suddenly changes from Z to Z ± 1, is given by

$$P(1s \to 2s) = |a_{20,10}|^2 = 2^{11} \frac{Z^3 (Z \pm 1)^3}{(3Z \pm 1)^8} \qquad ...(5)$$

For large values Z, it takes the form

$$P(1s \to 2s) = 2^{11} \frac{Z^6}{(3Z)^8}$$

$$= 0.3112\, Z^{-2}$$

12.4 A CHARGED PARTICLE IN AN ELECTROMAGNETIC FIELD

In order to apply the time-dependent perturbation theory of the *charged particle*, the effect of electric and magnetic fields on the particle must be investigated

The electromagnetic force on a particle of charge *e*, and mass *m* moving with velocity v in an electromagnetic field characteristised by electric field **E** and magnetic field **B** (or scalar potential ϕ and vector potential A) is

$$\mathbf{F} = e\mathbf{E} + e\frac{\mathbf{v} \times \mathbf{B}}{c} \qquad ...(1)$$

c being speed of electromagnetic waves.

The electric and magnetic fields can be expressed in terms of scalar and vector potential as

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi \quad \text{and} \quad \mathbf{B} = \nabla \times \mathbf{A} \qquad ...(2)$$

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k. bayu Q.M – unit – IV, V

Note : If sometimes the factors of ħ are omitted; then it means that quantum mechanical definition (3) of angular momentum has been used instead of classical definition.

$$\mathbf{J} = \mathbf{r} \times \mathbf{p}.$$

10.5 COMMUTATION RELATIONS OF TOTAL ANGULAR MOMENTUM WITH COMPONENTS

The total angular momentum is defined by the relation

$$J^2 = J_x^2 + J_y^2 + J_z^2 \qquad ...(1)$$

We can derive the commutation relation of J^2 with components J_x, J_y, J_z. Let us take

$$[J^2, J_x] = [J_x^2 + J_y^2 + J_z^2, J_x] = [J_x^2, J_x] + [J_y^2, J_x] + [J_z^2, J_x] \qquad ...(2)$$

We know that

$$[ab, c] = a[b, c] + [a, c]\, b.$$

So

$$[J_x^2, J_x] = [J_x J_x, J_x]$$

$$= J_x [J_x, J_x] + [J_x, J_x] J_x = 0$$

$$[J^2, J_x] = [J_y^2, J_x] + [J_z^2, J_x]$$

$$= [J_y J_y, J_x] + [J_z J_z, J_x]$$

$$= J_y [J_y, J_x] + [J_y, J_x] J_y + J_z [J_z, J_x] + [J_z, J_x] J_z$$

$$= J_y(-i\hbar J_z) + (-i\hbar J_z) J_y + J_z (i\hbar J_y) + (i\hbar J_y) J_z$$

$$= 0, \qquad ...(3)$$

$$[J^2, J_x] = 0$$

Similarly,

$$[J^2, J_y] = 0, \qquad ...(4)$$

$$[J^2, J_z] = 0, \qquad ...(5)$$

Ladder Operators J_+ and J_- Now let us define the new operators,

$$\left.\begin{aligned} J_+ &= J_x + iJ_y \\ J_- &= J_x - iJ_y \end{aligned}\right\} \qquad ...(6)$$

Commutation relation of J_z with J_+ an J_-.

$$[J_z, J_+] = [J_z, J_x + iJ_y]$$

$$= [J_z, J_x] + i[J_z, J_y] = [J_z, J_x] - i[J_y, J_z]$$

$$= i\hbar J_y - i(i\hbar J_x), \qquad [\text{since } [J_z, J_x] = i\hbar J_y \text{ and } [J_y, J_z] = i\hbar J_x]$$

$$= i\hbar J_y + \hbar J_x = \hbar(J_x + iJ_y),$$

$$= \hbar J_+ \qquad ...(7)$$

And similarly,

$$[J_z, J_-] = [J_z, J_x - iJ_y]$$

$$= [J_z, J_x] - i[J_z, J_y]$$

$$= i\hbar J_y - i(-i\hbar J_x)$$

$$= i\hbar J_y - \hbar J_x$$

$$= -\hbar\,(J_x - i\,J_y) = -\hbar\,J_- \qquad \text{...(8)}$$

or we can write (7) and (8) in compact form as

$$[J_z, J_\pm] = \hbar\,J_\pm \qquad \text{...(9)}$$

Commutation Relation of J_+ and J_- Mutually.

$$\begin{aligned}[J_+, J_-] &= [J_x + i\,J_y, J_x - i\,J_y]\\ &= [J_x, J_x] - [J_x, J_y] - i\,[J_y, J_x] + [J_y, J_y]\\ &= 0 - i\,[J_x, J_y] - i\,[J_x, J_y] + 0\\ &= -\,2i\,[J_x, J_y] = -2i\,(i\,\hbar\,J_z)\\ &= 2\,\hbar\,J_z \qquad \text{...(10)}\end{aligned}$$

Commutation Relations of J^2 with J_+ and J_-. Let us take $[J^2, J_+]$ first.

$$\begin{aligned}[J^2, J_+] &= [J^2, J_x + i\,J_y]\\ &= [J^2, J_x] + i\,[J^2, J_y]\end{aligned}$$

Using (3) and (4), we get

$$[J^2, J_+] = 0 + 0 = 0 \qquad \text{...(11)}$$

Similarly,

$$\begin{aligned}[J^2, J_-] &= [J^2, J_x - i\,J_y]\\ &= [J^2, J_x] - i\,[J^2, J_y] = 0 \qquad \text{...(12)}\end{aligned}$$

[using (3) and (4)]

Combining (11) and (12), we have

$$[J^2, J_\pm] = 0. \qquad \text{...(13)}$$

20.3 EIGEN VALUES OF J^2 AND J_z

As J^2 and J_z commute, they possess simultaneous eigen functions. If a and b are eigen values of operators J^2 and J_z in the state $|\psi>$, then eigen value equations of J^2 and J_z in the state $|\psi>$, are

$$J^2\,|\psi> = a\,|\psi> \qquad \text{...(1)}$$

$$J_z\,|\psi> = b\,|\psi> \qquad \text{...(2)}$$

Now let us operate by ladder operators $J_+ = J_x + i\,J_y$ and $J_- = J_x - iJ_y$, then we have

$$J_z J_+ |\psi> = \left\{[J_z, J_+] + J_+ J_z\right\} |\psi>$$

{since $[J_z, J_+] = J_z J_+ - J_+ J_z$}

$$\begin{aligned}&= [J_z, J_+]\,|\psi> + J_+ J_z\,|\psi>\\ &= \hbar\,J_+\,|\psi> + J_+\,b\,|\psi>\end{aligned}$$

{since $[J_z, J_+] = \hbar\,J_+$ and $J_z|\psi> = b\,|\psi>$}

i.e.

$$J_z J_+\,|\psi> = (b + \hbar)\,J_+\,|\psi> \qquad \text{...(3)}$$

This equation shows that J_z has eigen value $(b + \hbar)$ in the state $J_+|\psi>$. Thus the operation of J_+ on ψ increases the eigen value of J_+ by an amount $\hbar$.

Operating again by J_+ on $J_+|\psi>$, then we have

$$J_+ J_+\,|\psi> = J_+^2\,|\psi>$$

So that

$$\begin{aligned}J_z J_+^2\,\psi> &= J_z J_+\,(J_+\,\psi)\\ &= \left\{[J_z, J_+] + J_+ J_z\right\} J_+\,|\psi>\\ &= (\hbar\,J_+ + J_+\,J_z)\,J_+\,|\psi>\\ &= \hbar\,J_+^2\,|\psi> + J_+\,J_z\,J_+\,|\psi>\\ &= \hbar\,J_+^2\,|\psi> + J_+\,(b + \hbar)\,J_+\,|\psi> \qquad \text{using (3)}\\ &= (b + 2\,\hbar)\,J_+^2\,|\psi> \qquad \text{...(4)}\end{aligned}$$

This equation shows that J_z has eigen value $(b + 2\hbar)$ in the state $J_+^2\,|\psi>$. Thus the operation of J_+ on $|\psi>$ each time simply means the increase in eigen value of J_z by $\hbar$ each time. Hence in general we may write

$$J_z\,J_+^n\,|\psi> = (b + n\,\hbar)\,J_+^n\,|\psi> \qquad \text{...(5)}$$

And similarly for J_- operator, we have

$$J_z\,J_-^n\,|\psi> = (b - n\,\hbar)\,J_-^n\,|\psi>. \qquad \text{...(6)}$$

These two equations show that there is a discrete spectrum for the eigen values of J_z depending on the integer n. The eigen values are

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

$$(b - n\,\hbar), \dots (b - 2\,\hbar), (b - \hbar), b, (b + \hbar), (b + \hbar) \dots, (b + n\,\hbar).$$

Thus we see that as n tends from $-\infty$ to $+\infty$, the eigen values of J_z tend from $-\infty$ to $+\infty$.

As angular momentum of a system is finite, therefore eigen value of J^2 is finite i.e. a is finite.

$$J^2 = J_x^2 + J_y^2 + J_z^2$$

Also since

i.e. $J_z^2 \leq J^2$ therefore the eigen values of J_z must be finite and hence terminated after certain terms so that inequality $J_z^2 \leq J^2$ may hold good. Hence we terminate this series of eigen values like

$$J_z\,J_+^{l+1}\,|\psi> = 0 \text{ and } J_z\,J_-^{k+1}\,|\psi> 0 \qquad \text{...(7)}$$

i.e., maximum and minimum values of integers are l and k respectively defined by (7)

Therefore the eigen values of J_z are restricted to the region

$$n = -k, \dots n = -1, n = 0, n = 1, \dots n = l,$$

$$(b - k\,\hbar) \dots (b - \hbar), b, (b + \hbar) \dots (b + l\,\hbar).$$

Now we have

$$J_+ = J_x + i\,J_y, J_- = J_x - i\,J_y$$

$$J_- J_+ = (J_x - i\,J_y)(J_x + i\,J_y) = J_x^2 + J_y^2 + i\,[J_x, J_y]$$

or

$$J_x^2 + J_y^2 = J_- J_+ - i\,(i\,\hbar\,J_z), \qquad \text{...(5a)}$$

$$J_x^2 + J_y^2 = J_- J_+ + \hbar\,J_z.$$

Similarly if we start with $J_+ J_-$ we get

$$J_x^2 + J_y^2 = J_+ J_- - \hbar J_z \qquad \text{...(8b)}$$

$$J^2 = J_x^2 + J_y^2 + J_z^2 = (J_x^2 + J_y^2) + J_z^2$$

$$= J_z^2 + J_- J_+ + \hbar J_z, \quad \text{using (8a)} \qquad \text{...(9a)}$$

Also

$$J^2 = J_z^2 + J_+ J_- - \hbar J_z \quad \text{using (8b)} \qquad \text{...(9b)}$$

Now let us find *eigen values* of J^2 in terms of J_z.

Since $[J_z, J^2] = 0$. Therefore J_z and J^2 have the same eigen function, *i.e.* if $J_+^l|\psi>$ is an eigen ction of J_z, it will be also for J^2.

Hence

$$J^2 J_+^l|\psi> = (J_z^2 + J_- J_+ + \hbar J_z) J_+^l|\psi>$$

$$= J_z^2 J_+^l|\psi> + J_- J_+ J_+^l|\psi> + \hbar J_z J_+^l|\psi>.$$

Using equations (5) and (7)

$$J^2 J_+^l|\psi> = J_z J_z J_+^l|\psi> + J_- J_+^{l+1}\psi> + \hbar J_z J_+^l|\psi>.$$

$$= J_z (b + l\hbar) J_+^l|\psi> + 0 + \hbar (b + l\hbar) J_+^l \psi>$$

$$= \{(b + l\hbar)(b + l\hbar) + \hbar (b + l\hbar)\} J_+^l|\psi>$$

$$= (b + l\hbar)(b + l\hbar + \hbar) J_+^l|\psi>. \qquad \text{...(10)}$$

This equation gives the eigen values for J^2.

Again

$$J^2 J_-^k|\psi> = (J_z^2 + J_+ J_- - \hbar J_z) J_-^k|\psi>$$

$$= \{(b - k\hbar)^2 + 0 - \hbar (b - k\hbar)\} J_-^k|\psi>$$

$$= (b - k\hbar)(b - k\hbar - \hbar) J_-^k|\psi> \qquad \text{...(11)}$$

Equating these two eigen values given by (10) and (11) of J^2, which represent eigen values of 'a', have

$$a = (b + l\hbar)(b + l\hbar + \hbar) = (b - l\hbar)(b - k\hbar - \hbar). \qquad \text{...(12)}$$

Solving for b, we get

$$b = \frac{\hbar}{2}(k - l) \qquad \text{...(13)}$$

And therefore from (12), we have

$$a = \hbar^2 \left(\frac{k+l}{2}\right)\left\{\frac{(k+l)}{2} + 1\right\}$$

Now we substitute $\frac{k+l}{2} = j$ where $\left(\frac{k+l}{2}\right)$ and $\left(\frac{k-l}{2}\right)$ are necessarily integers. Hence

$$\left.\begin{aligned} a &= j(j+1)\hbar^2 \\ b &= \frac{\hbar}{2}(k - l), \end{aligned}\right\} \qquad \text{...(14)}$$

Now since

$$j = \frac{k+l}{2}, \text{ hence}$$

2

$$\left.\begin{aligned} k_{\max} &= 2j : k_{\min} = 0 \\ l_{\max} &= 2j : l_{\min} = 0 \end{aligned}\right\}$$

Therefore when $\quad k = k_{\max} = 2j, \quad l = l_{\min} = 0 \quad$ we have $\quad j_{\max} = j$

and when $\quad k = k_{\min} = 0, \quad l = l_{\max} = 2j, \quad$ we have $\quad j_{\min} = -j$

Thus eigen values b may be expressed as

$$-j\hbar, (-j+1)\hbar, \ldots, -2\hbar, -\hbar, 0, \hbar, 2\hbar, \ldots, (j-1)\hbar, j\hbar. \qquad \text{...(15)}$$

Therefore J_z have eigen values from $-j\hbar$ to $+j\hbar$ *i.e.* the total values are $(2j+1)$. Thus we define $b = m_z$ when m_z have these all $(2j+1)$ values and it is called *magnetic quantum number*.

$$\left.\begin{aligned} &\text{Hence eigen values of } J^2 \text{ are } j(j+1)\hbar^2 \\ &\text{and of } J_z \text{ are} \qquad\qquad m_z\hbar \end{aligned}\right\} \qquad \text{...(16)}$$

Equation (16) represents the eigen values of J^2 and J_z. The matrix elements of J_z which is diagonal in above representation are determined by equation $J_z\psi(jm) = m_z\psi(jm)$ whence if $\psi(jm)$ are normalized

$$(\psi(j'm'), J_z\psi(jm)) = <j'm'|J_z|jm> = m_z\hbar\,\delta_{mm'}\delta_{jj'}$$

10.7 EIGEN VALUES OF J+ AND J−

If we represent a state function $\psi(r, j, m)$ where j and m are angular and magnetic quantum numbers respectively, then eigen value equation of operators $J_\pm$ is

$$J_\pm\psi(r, j, m) = N_\pm\psi(r, j, m \pm 1) \qquad \text{...(1)}$$

where $N_\pm$ is eigen value of $J_\pm$, J_+ being is raising operator and J_- the lowering operator.

We have

$$J_\pm^*\psi^*(r, j, m) = N_\pm^*\psi^*(r, j, m \pm 1)$$

So that

$$\psi^*(r, j, m \pm 1)\psi(r, j, m \pm 1) = \frac{1}{N_\pm^* N_\pm} J_\pm^*\psi^*(r, j, m) J_\pm\psi(r, j, m)$$

$$= \frac{1}{|N_\pm|^2} J_\mp J_\pm \psi^*(r, j, m)\psi(r, j, m)$$

$$= \frac{1}{|N_\pm|^2}[J^2 - J_z(J_z \pm \hbar)]\psi^*(r, j, m) \times \psi(r, j, m)$$

Now applying normalization condition

$$\int \psi^*\psi\, d\tau = 1$$

we get

$$1 = \frac{1}{|N_\pm|^2}[j(j+1)\hbar^2 - m_z\hbar(m_z\hbar \pm \hbar)]$$

or

$$N_\pm = \hbar\sqrt{[j(j+1) - m_z(m_z \pm 1)]}\, e^{i\delta} \qquad \text{...(2)}$$

where δ is arbitrary real number and is phase factor. Thus we have some useful derivation from (1) and (2) by taking $e^{i\delta} = 1$.

From (1) $\quad J_\pm\psi(r, j, m) = N_\pm\psi^*(r, j, m \pm 1)$.

Then equation (1) becomes

$$J_+\,\psi(r,j,m) = \hbar\sqrt{[j(j+1)-m_z(m_z+1)]}\,.\psi(r,j,m+1), \qquad \text{...(3)}$$

$$J_-\,\psi(r,j,m) = \hbar\sqrt{[j(j+1)-m_z(m_z-1)]}\,\psi(r,j,m-1), \qquad \text{...(4)}$$

or in more simplified from (3) and (4) can be written as

$$J_+\,\psi(jm) = \hbar\sqrt{[(j-m)(j+m+1)]}\,\psi(j,m+1), \qquad \text{...(5)}$$

$$J_-\,\psi(jm) = \hbar\sqrt{[(j+m)(j-m+1)]}\,\psi(j,m-1), \qquad \text{...(6)}$$

The matrix elements of J_+ and J_- are

$$<j'm'\,|\,J_+\,|\,jm> \;=\; <j'm'\,|\,jm+1>\hbar\sqrt{[(j-m)(j+m+1)]}$$

or

$$<j'm'\,|\,J_+\,|\,jm> = \hbar\sqrt{\{(j-m)(j+m+1)\}}\;\delta_{j,j'}\,\delta_{m',m+1}. \qquad \text{...(7)}$$

Similarly,

$$<j'm'\,|\,J_-\,|\,jm> = \hbar\sqrt{\{(j+m)(j-m+1)\}}\;\delta_{j,j'}\,\delta_{m',m-1}. \qquad \text{...(8)}$$

10.8 EIGEN VALUES OF J_x AND J_y

The matrix elements or eigen values of J_x and J_y can be determined by the following equation

$$\left.\begin{aligned} J_+ &= J_x + i\,J_y,\\ J_- &= J_x - i\,J_y.\end{aligned}\right\}$$

Hence

$$\left.\begin{aligned} J_x &= \tfrac{1}{2}(J_+ + J_-)\\ J_y &= \tfrac{1}{2i}(J_+ - J_-) = -\tfrac{1}{2}i\,(J_+ - J_-)\end{aligned}\right\} \qquad \text{...(1)}$$

and also

$$J_1^{\,\dagger} = J$$

$$<j'm'\,|\,J_x\,|\,jm> \;=\; <j'm'\,|\,\tfrac{1}{2}(J_+ + J_-)\,|\,jm> = \tfrac{1}{2}<j'm'\,|\,(J_+ + J_-)\,|\,jm>$$

$$= \tfrac{1}{2}<j'm'\,|\,J_+\,|\,jm> + \tfrac{1}{2}<j'm'\,|\,J_-\,|\,jm>$$

From equations (7) and (8) of section 10·7 we get

$$<j'm'\,|\,J_x\,|\,jm> = \tfrac{1}{2}\hbar\sqrt{[(j-m)(j+m+1)]}\;\delta_{j',j}\,\delta_{m',m+1}$$

$$+\tfrac{1}{2}\hbar\sqrt{[(j+m)(j-m+1)]}\;\delta_{j',j}\,\delta_{m',m-1} \qquad \text{...(2)}$$

in another form

$$J_x\,\psi(jm) = \tfrac{1}{2}\hbar\sqrt{[(j-m)(j+m+1)]}\,\psi(j,m+1)$$

$$+\tfrac{1}{2}\hbar\sqrt{[(j+m)(j-m+1)]}\,\psi(j,m-1) \qquad \text{...(3)}$$

Similarly matrix elements of J_y are as follows :

$$<j'm'\,|\,J_y\,|\,jm> \;=\; <j'm'\,|\,-\tfrac{1}{2}i\,(J_+ - J_-)\,|\,jm>$$

$$= -\tfrac{1}{2}i<j'm'\,|\,J_+\,|\,jm> + \tfrac{1}{2}i<j'm'\,|\,J_-\,|\,jm>$$

$$= -\frac{i\hbar}{2}\sqrt{[(j-m)(j+m+1)]}\;\delta_{j',j}\,\delta_{m',m+1} + \frac{i\hbar}{2}\sqrt{[(j+m)(j-m+1)]}\;\delta_{j',j}\,\delta_{m',m-1} \qquad \text{...(4)}$$

or in more simplified form

$$J_y\,\psi(jm) = -\frac{i}{2}\hbar\sqrt{[(j-m)(j+m+1)]}\,\psi(j,m+1) + \frac{i\hbar}{2}\sqrt{[(j+m)(j-m+1)]}\,\psi(j,m-1)$$

If we consider $j' = j$, then equations (2) and (4) will reduce to

$$<jm'\,|\,J_x\,|\,jm> = \tfrac{1}{2}\hbar\sqrt{[(j-m)(j+m+1)]}\;\delta_{jj}\,\delta_{m',m+1} + \tfrac{1}{2}\hbar\sqrt{[(j+m)(j-m+1)]}\;\delta_{jj}\,\delta_{m',m-1} \qquad \text{...(5)}$$

and

$$<jm'\,|\,J_y\,|\,jm> = -\frac{i\hbar}{2}\sqrt{[(j-m)(j+m+1)]}\;\delta_{m',m+1}\,\delta_{jj} + \frac{i\hbar}{2}\sqrt{[(j+m)(j-m+1)]}\;\delta_{m',m-1}\,\delta_{jj}$$

But $\delta_{jj} = 1$; then

$$<jm'\,|\,J_x\,|\,jm> = \tfrac{1}{2}\hbar\sqrt{[(j-m)(j+m+1)]}\;\delta_{m',m+1} + \tfrac{1}{2}\hbar\sqrt{[(j+m)(j-m+1)]}\;\delta_{m',m-1} \qquad \text{...(6)}$$

If $\qquad m' = m+1,\ \delta_{m',m+1} = 1,$

and $\qquad m' = m-1,\ \delta_{m',m-1} = 1,$

the matrix element of J_x will be finite.

But if $\qquad m' \neq m+1,\ \delta_{m',m+1} = 0,$

$\qquad m' \neq m-1,\ \delta_{m',m-1} = 0,$

the matrix elements of J_x will be zero.

Similarly,

$$<jm'\,|\,J_y\,|\,jm> = -\frac{i}{2}\hbar\sqrt{[(j-m)(j+m+1)]}\;\delta_{m',m+1} + \frac{i}{2}\hbar\sqrt{[(j+m)(j-m+1)]}\;\delta_{m',m-1} \qquad \text{...(7)}$$

If $m' \neq m \pm 1$, the matrix element of J_y will be zero and if $m' = m \pm 1$, elements will be finite.

Hence if $m' = m+1$, we get

$$<j,m+1\,|\,J_x\,|\,jm> = \tfrac{1}{2}\hbar\sqrt{[(j-m)(j+m+1)]} \qquad \text{...(8i)}$$

If $m' = m-1$,

$$<j,m-1\,|\,J_x\,|\,jm> = \tfrac{1}{2}\hbar\sqrt{[(j+m)(j-m+1)]} \qquad \text{...(8ii)}$$

All other elements for which $m' \neq m \pm 1$ will be zero.

Similarly the matrix elements of J_y can be written as

If $m' = m+1$, we get

$$<j,m+1\,|\,J_y\,|\,jm> = -\frac{i\hbar}{2}\sqrt{[(j-m)(j+m+1)]}, \qquad \text{...(9i)}$$

and if $m' = m-1$

$$<j,m-1\,|\,J_y\,|\,jm> = +\frac{i\hbar}{2}\sqrt{[(j+m)(j-m+1)]}. \qquad \text{...(9ii)}$$

10.9 EXPLICIT FORM OF THE ANGULAR MOMENTUM MATRICES

The matrices J^2 and J_z are diagonal

$$J_z = m_z\hbar$$

and

$$J^2 = j(j+1)\hbar^2$$

The value of magnetic quantum number m_z varies from $-j$ to $+j$ and total values of m_z will be $(2j+1)$. Hence the dimensions of these diagonal matrices will be $(2j+1)\times(2j+1)$, *i.e.* $(2j+1)$ rows and $(2j+1)$ columns

$$\frac{\delta p}{\Delta p} < 1 \text{ or } \frac{\Delta p}{\delta p} > 1.$$

i.e.
$$\frac{\Delta p}{\hbar/2b} = \frac{2b^2}{\hbar v}\int_{-\infty}^{+\infty}\frac{F(r)}{r}\,dx > 1 \qquad \textit{(for small deflections)}$$

13.3 DEFINITIONS OF CROSS-SECTIONS

The probability that a particle will be scattered as it traverses a given thickness of matter dx can be expressed in terms of a quantity called the scattering cross-section. To do this let us note that each molecule presents to the on-coming particle a target area πd^2, d being diameter of the molecule. This target area is just a cross-section of the region within which a collision can take place as viewed along the direction of motion of the beam. This is where the name scattering cross-section comes from. The results of the collision experiments are expressed by means of cross section and are directly related to the asymptotic behaviour of the stationary solutions of the Schroedinger's equation.

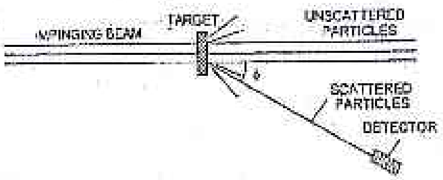

Fig. 13.2

To define the cross-section consider a typical experiment in which a target is struck by a beam of mono-energetic particles and the scattered particles are counted with the aid of a detector (fig. 13.2). Let J be the magnitude of the incident flux i.e. the number of incident particles crossing per unit time a unit surface area placed perpendicular to the direction of incident beam and at rest respect to the target. If ρ is the number of particles per unit volume in the incident beam and v is the velocity of the incident particles, then

$$J = \rho v$$

Fig. 13.3

If ρ is small (under the conditions of the experiment) that the mutual interaction of the incident particles can be neglected, then they undergo their collisions independently of each other. If n is the number of particles scattered per unit time into a solid angle $d\omega$ located in the direction (θ, ϕ) (polar coordinates), then n is directly proportional to the incident current i.e.

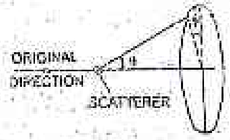

Fig. 13.4

$$n \propto J\,d\omega$$

or
$$n = \Sigma(\omega)\,J\,d\omega$$

where $\Sigma(\omega)$ is a constant of proportionality which has dimensions of surface area and is characteristic parameter of the collision of particle with target. It is known as *Scattering cross-section of the particle and the target in the direction* $\omega(\theta, \phi)$.

3

Differential Scattering Cross-section : Let us now consider the target to be made up of a large number N of atomic or nuclear scattering centres and the distances between these atoms or nuclei are sufficiently large with respect to the wavelength of the incident particles as is observed in most practical cases. Then each scattering centre acts as it were alone. Moreover, if the target is sufficiently thin, so that one may neglect multiple scattering; then n is directly proportional to N also i.e. $n \propto N$; so in this case

$$n \propto N\,J\,d\omega$$
$$= \sigma(\omega)\,N\,J\,d\omega$$

Again $\sigma(\omega)$, the constant of proportionality, has the dimensions of surface area and is called the *scattering cross-section* of the particle by the scattering centre in the direction $\omega(\theta, \phi)$ or briefly the *differential scattering cross-section*.

Total Scattering Cross-section : The total number of particles scattered in unit time is obtained by integrating n over all angles. It is equal to

$$N_{total} = \int \sigma(\omega)\,N\,J\,d\omega = NJ\,\sigma_{total}$$

where
$$\sigma_{total} = \int \sigma(\omega)\,d\omega$$

is the *total scattering cross section*.

In the cases of nuclear physics the scattering centres have linear dimensions of the order of 10^{-13} to 10^{-12} cm. and the cross-sections are usually measured in barns or millibarns where

$$1 \text{ barn} = 10^{-24} \text{ cm}^2$$

and
$$1 \text{ millibarn} = 10^{-27} \text{ cm}^2$$

we have assumed *explicitly* that the only possible collisions are elastic collisions i.e. where there is no energy transfer to the *internal degrees of freedom* of the scatterer. We shall confine ourselves to this type of collision for the moment. Moreover rather than treating the scatterer atom or nucleus in all its complexity, we shall represent by static potential $V(r)$ depending upon coordinate r of the particle.

13.4 LABORATORY AND CENTRE OF MASS REFERENCE SYSTEMS

Fig. 13.5

The scattering of particles can be visualised in two kinds of coordinates :

1. *Laboratory frame or system* **(L-system) :** It is that co-ordinate system in which the bombarded particle (or target) is initially at rest.

2. *Centre of mass co-ordinate system* **(C-system) :** It is that coordinate system in which the centre of mass of two colliding particles is at rest (initially and always).

It is easy to calculate the result of collision experiment in the centre of mass system than the laboratory system since there are three degrees of freedom in centre of mass system (C-system) as compared to six degrees of freedom in laboratory system *(L-system)*. Generally calculations are made in C system and observations are *made* in L-system. In C-system the reduced mass of two particles of masses m_1 and m_2 is

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

So μ must remain at rest before and after collision in C system.

The Kinetic energy of the system : We take **p** to be the momentum of the beam in the co-ordinate frame in which the total momentum of the system is zero. Since in this co-ordinates system the centre of mass is at rest, it is called the centre of mass (C.M.) frame. But experiment is actually carried out in the laboratory, where the beam of particles have momentum **q**, say, and target is at rest. This is called the laboratory frame.

Fig. 13.8

The kinetic energy of the system in the laboratory system is

$$T_L = \frac{q^2}{2m_1}$$

In the C.M. system it is

$$T_C = \frac{p^2}{2m_1} + \frac{p^2}{2m_2} = \frac{p^2}{2\mu}$$

In laboratory frame the total momentum of the system is **q**.

$$v = \frac{q}{m_1 + m_2}$$

The relation between the magnitudes of the moments in the two frames is

$$p = q - m_1 v = q - m_1\left(\frac{q}{m_1+m_2}\right) = \frac{m_2 q}{m_1+m_2}$$

After squaring, we get

$$p^2 = \left(\frac{m_2}{m_1+m_2}\right)^2 q^2.$$

On substituting $p^2 = 2\mu T_C$ and $q^2 = 2m_1 T_L$ we have

$$T_C = \frac{m_2}{m_1+m_2} T_L \qquad \text{...(5)}$$

13.5 STATIONARY SCATTERING WAVE : SCATTERING AMPLITUDE

In wave mechanics, an incident beam of particles is represented by a plane wave in incident channel. Let us consider the scattering of a particle of mass m by a central potential $V(\mathbf{r})$ such that $V(\mathbf{r})$ tends to zero more rapidly than $1/r$ as $r \to \infty$.

Let E be the energy and $\mathbf{p} = \hbar \mathbf{k}$ the initial momentum of the particle where $\mathbf{k}$ is the wave-vector. The Scroedinger equation for the central potential $V(\mathbf{r})$ is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_k(\mathbf{r}) = E\,\psi_k(\mathbf{r}) \qquad \text{...(1)}$$

The wave-function ψ_k may be written as a function of θ, ϕ and radial distance r between the two articles, i.e.

$$\psi_k = \psi_k(r, \theta, \phi)$$

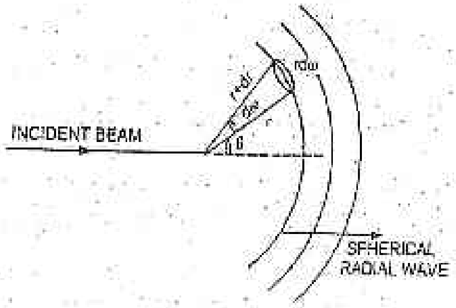

Fig. 13.9

The scattering is determined by the asymptotic form of $\psi_k(r, \theta, \phi)$ in the region where $V = 0$, when the colliding particles are far apart (or $r \to \infty$). We want to represent it into two parts, one representing an incident wave and the other representing a scattered radially outgoing wave i.e.

$$\psi_k(r, \theta, \phi) = \lim_{r\to\infty} e^{i\mathbf{k}.\mathbf{r}} + f(\omega)\frac{e^{ikr}}{r} \qquad \text{...(2)}$$

Let us assume that one and only one solution of this type exists for each value of k. We shall call this solution, the stationary scattering wave-vector k. The two terms of the asymptotic form are easily interpreted if we remember the definition of current density vector

$$J = \frac{\hbar}{2im}(\psi^* \nabla \psi - \psi \nabla \psi^*) \qquad \text{...(3)}$$

The plane wave term $e^{i\mathbf{k}.\mathbf{r}}$ represents a wave of unit density and of current density $\frac{\hbar k}{m}$. Retaining only the lowest order in r, the term $\frac{f(\omega)}{r}e^{ikr}$ represents a wave of *density* $\frac{|f(\omega)|^2}{r^2}$ *and of current density* $\frac{|f(\omega)|^2}{r^2}\frac{\hbar k}{m}$ *directed along the direction ω towards increasing r* (outgoing-wave). In fact, since the effect of the potential $V(r)$ can be neglected in the asymptotic region, therefore according to classical approximation we can interpret the term $e^{i\mathbf{k}.\mathbf{r}}$ as a beam of monoenergetic particles of momentum ħ k and of density 1, representing the incident beam and the term $\frac{f(\omega)}{r}e^{ikr}$ is interpreted as a beam of particles emitted radially from the scattering centre and represents a beam of the scattered particles.

In accordance with this interpretation we can calculate the number of particles emitted per unit time into the solid angle $d\omega$ located in the direction ω.

The scattering wave-function is $f(\omega)\frac{e^{ikr}}{r}$; hence density of scattered particles

$$\rho_s = \left|f(\omega)\frac{e^{ikr}}{r}\right|^2 = \frac{1}{r^2}|f(\omega)|^2$$

From fig. 13.9, small elementary area $= r \,.\, r d\omega = r^2 d\omega$

The volume element between r and $r+dr$ is $= r^2\, d\omega\,.\, dr$.

As ρ_s in the number of scattered particles per unit volume, hence the number of particles in this elementary volume

$$N_s = \rho_s\, r^2\, d\omega\, dr.$$

Substituting value of ρ_s from equation (4), we get

$$N_s = \frac{|f(\omega)|^2}{r^2}\cdot r^2\, d\omega\, dr = |f(\omega)|^2\, dr\, d\omega \qquad ...(5)$$

∴ The number of scattered particles per unit time

$$\frac{dN_s}{dt} = |f(\omega)|^2\, d\omega\, \frac{dr}{dt} = |f(\omega)|^2\, d\omega\, v = |f(\omega)|^2\, d\omega\, \frac{\hbar k}{m}$$

$$= |f(\omega)|^2\, \frac{\hbar k}{m}\, d\omega. \qquad ...(6)$$

If J is the current density, then $\qquad J = \rho v. \qquad ...(7)$

Since beam of particles is travelling in the same direction with velocity v. The flux of the beam is the number of particles crossing unit area (perpendicular to the beam) per unit time. These are number of particles in a volume of unit cross-section and length v.

But $\rho = 1$ for incident particles.

$$J = v = \frac{\hbar k}{m} \qquad ...(8)$$

Also if $\sigma(\omega)$ is the scattering cross-section, then number of particles scattered in solid angle $d\omega$ per unit time

$$= J\,\sigma(\omega)\, d\omega = \frac{\hbar k}{m}\cdot\sigma(\omega)\, d\omega \qquad [\text{using (8)}] \qquad ...(9)$$

Comparing equations (6) and (9) we get

$$\frac{\hbar k}{m}\,\sigma(\omega)\, d\omega = |f(\omega)|^2\, \frac{\hbar k}{m}\, d\omega$$

∴
$$\sigma(\omega) = |f(\omega)|^2. \qquad ...(10)$$

Here $f(\omega)$ is called the *scattering amplitude*.

Hence the *total* scattering cross-section is

$$\sigma_{total} = \int |f(\omega)|^2\, d\omega. \qquad ...(11)$$

The wave-function ψ_k may be normalised by making

$$\int \psi_k^*\, \psi_k\, d\tau = 1$$

or
$$\int |\psi_k|^2\, d\tau = 1 \qquad ...(12)$$

over a large box that have periodic boundary conditions.

Therefore for finding out the normalisation constant A, we must take the wave function as

$$\psi_k = \lim_{r\to\infty} A\left[e^{i\mathbf{k}.\mathbf{r}} + f(\omega)\,\frac{e^{ikr}}{r}\right] \qquad ...(13)$$

The wave-function may be normalised to unit incident flux by choosing

---

⑪

$$A = \frac{1}{v^{1/2}} = \left(\frac{m}{\hbar k}\right)^{1/2};$$

but for simplicity we often choose A equal to unity.

The argument given above is incorrect for two reasons :

(i) The current density vector is not simply the sum of the current of the incident plane wave and that of the scattered wave. We must add to these contributions, the interaction term

$$e^{i\mathbf{k}.\mathbf{r}} \text{ and } f(\omega)\,\frac{e^{ikr}}{r}$$

in the foregoing treatment. The interferences between incident and scattered waves have been deliberately ignored.

(ii) The representation of the physical situation by the stationary wave

$$\psi_1(r)\, e^{-iEt/\hbar} \qquad ...(14)$$

in an idealisation. In reality each particle participating in the scattering process must be represented by a wave-packet formed by superposition of the stationary waves of the type (14) corresponding to wave-vectors of magnitude and direction slightly different from k. This packet is constructed so as to correctly fulfil the initial conditions. Therefore the scattering phenomenon must be represented by suitable wave-packets.

13.6 GENERAL FORMULATION OF THE SCATTERING THEORY

The Schroedinger equation for central potential $V(r)$ is written as

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi = E\psi \qquad ...(1)$$

The complete time-dependent solution of above equation can be written as

$$\psi(r,t) = \psi(r)\, e^{-iEt/\hbar}$$

$$= [e^{i\mathbf{k}.\mathbf{r}} + \psi_s(r)]\, e^{-iEt/\hbar} \qquad ...(2)$$

where
$$\psi_s(r) = f(\theta,\phi)\,\frac{e^{ikr}}{r} + g(\theta,\phi)\,\frac{e^{-ikr}}{r} \qquad ...(3)$$

The first term in bracket of (2) represents the incident wave : while the second term ψ_s, the *scattered wave*. The first term in ψ_s represents outgoing scattered wave, while the second term represents the incoming scattered wave which does not exist in most of the physical problems. The stationary state solution of Schroedinger equation (1) is

$$\psi(r) = e^{i\mathbf{k}.\mathbf{r}} + \psi_s \qquad ...(4)$$

Comparing equation (1) with $(H^0 + H')\psi = E\psi$, we note that the perturbation operator is $V(r)$ which is very-very less than E ; here H^0 is the unperturbed Hamiltonian. The unperturbed Schroedinger equation is therefore written as

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)e^{i\mathbf{k}.\mathbf{r}} = 0 \qquad ...(5)$$

So that the Schroedinger equation is now written as

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)\psi_s = -V(r)\,[e^{i\mathbf{k}.\mathbf{r}} + \psi_s]$$

$$= -V(r)\,\psi(r). \qquad ...(6)$$

This equation may be written as

$$(\nabla^2 + k^2)\,\psi_s = \frac{2m}{\hbar^2} V(r)\,\psi(r) \qquad ...(7)$$

where $k^2 = \frac{2mE}{\hbar^2}$

Further substituting

$$\frac{2m}{\hbar^2} V(r)\,\psi(r) = -4\pi\,\rho(r) \qquad ...(8)$$

equation (7) takes the form

$$(\nabla^2 + k^2)\,\psi_s = -4\pi\,\rho(r). \qquad ...(9)$$

The quantity $\rho(r)$ may be regarded as a source density for divergent spherical waves. Equation (9) may be solved by using principle of superposition. Accordingly if ψ_{s1} and ψ_{s2} are solutions of equation (9) belonging to density functions $\rho_1(r)$ and $\rho_2(r)$ and satisfying

$$\psi_{s1} = f_1\frac{e^{ikr}}{r},\ \psi_{s2} = f_2\frac{e^{ikr}}{r} \qquad ...(10)$$

then the function $\psi_s = \psi_{s1} + \psi_{s2}$ is a solution of equation (9) belonging to $\rho(r) = \rho_1(r) + \rho_2(r)$ such that

$$\psi_s = f\frac{e^{ikr}}{r} \qquad \text{where } f = f_1 + f_2 \qquad ...(11)$$

By means of the principle of superposition a solution of equation (9) can be found by adding solutions for simple point sources of unit strength. The identity

$$\rho(r) = \int \delta(\mathbf{r} - \mathbf{r}')\,\rho(\mathbf{r}')\,d\tau' \qquad ...(12)$$

represents the arbitrary density $\rho(r)$ as a sum of point sources $\delta(\mathbf{r} - \mathbf{r}')$ at the point $\mathbf{r}'$.

Now in order to express ψ_s as a function of $\rho(r)$ we make use of the following *theorem*.

$$(\nabla^2 + k^2)\,G(\mathbf{r}, \mathbf{r}') = -4\pi\,\delta(\mathbf{r} - \mathbf{r}') \qquad ...(13)$$

where

$$G(\mathbf{r}, \mathbf{r}') = \frac{\exp(ik\,|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}$$

; called **Green's function.**

If $G(\mathbf{r}, \mathbf{r}')$ is asymptotic to a function of r of the form (11), then the solution of the scattering problem r the density $\rho(r)$ is given by

$$\psi_s = \int G(\mathbf{r}, \mathbf{r}')\,\rho(\mathbf{r}')\,d\tau' \qquad ...(14)$$

Green's function: It may be noted that *Green's function*

$$G(\mathbf{r}, \mathbf{r}') = \frac{\exp(ik\,|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \qquad ...(15)$$

is a solution of the scattering problem for a source of unit strength at point $\mathbf{r}'$. To prove this it must shown that the equation (13) is satisfied and the solution has proper asymptotic form.

For simplicity we first change the origin of coordinates to point $\mathbf{r}'$, so that equation (13) takes the rm

$$(\nabla^2 + k^2)\,G(r) = -4\pi\,\delta(\mathbf{r}) \qquad ...(16)$$

where

$$G(\mathbf{r}) = \frac{e^{ikr}}{r} \qquad ...(17)$$

r being the radial distance in new coordinates.

We notice by direct differentiation that if $r \neq 0$

$$(\nabla^2 + k^2)\frac{e^{ikr}}{r} = 0 \qquad ...(18)$$

Therefore equation (16) is satisfied in every region which does not contain the source point. To prove that the singularity at $\mathbf{r} = 0$ is properly represented by G, it must be established that the function

$$\delta(r) = -\frac{1}{4\pi}(\nabla^2 + k^2)\,G(r) \qquad ...(19)$$

must satisfy the condition of a *delta function*. From equations (16) and (18) we note that if $\delta(r) = 0$ if $r \neq 0$. Thus $\delta(\mathbf{r})$ satisfies the first requirement of a delta function, namely that it is zero everywhere except at $r = 0$. The another condition of a delta function is that

$$\int_\tau \delta(\mathbf{r})\,F(\mathbf{r})\,d\tau = F(0) \qquad ...(20)$$

where $F(\mathbf{r})$ is any continuous function of $\mathbf{r}$ which has value $F(0)$ at the origin and τ represents thus region of integration which is any finite volume containing the origin. Let us therefore choose for our range of integration a small sphere of radius ϵ. Consider the identity

$$\int_\tau [(\nabla^2 G + k^2 G)\,F - (\nabla^2 F + k^2 F)\,G]\,d\tau = \int_S \left[\frac{\partial G}{\partial r}F - \frac{\partial F}{\partial r}G\right] dS \qquad ...(21)$$

where S represents the surface of the sphere τ. If $F(r)$ is sufficiently regular within the sphere τ, then we may assume positive numbers M and N such that

$$|\nabla^2 F + k^2 F| \le M$$

and

$$\left|\frac{\partial F}{\partial r}\right| \le N\ (r \le \epsilon) \qquad ...(22)$$

In other words the above functions are bounded in τ. Now is follows that

$$\left|\int_\tau (\nabla^2 F + k^2 F)\,G\,d\tau\right| \le M\int_\tau |G|\,d\tau$$

$$= M\int_0^{\epsilon}\frac{1}{r}\,4\pi r^2\,dr = 2\pi M\epsilon^2 \qquad ...(23)$$

and

$$\left|\int_S \frac{\partial F}{\partial r}G\,dS\right| \le N\int_S |G|\,dS = N\left[\frac{1}{r}\,4\pi r^2\right]_0^{\epsilon} = 4\pi N\epsilon \qquad ...(24)$$

Therefore if we take the limit $\epsilon \to 0$, we find

$$\int_\tau (\nabla^2 F + k^2 F)\,G\,d\tau \to 0$$

and

$$\int_S \frac{\partial F}{\partial r}\,G\,dS \to 0$$

In view of above relations equation (21) in the limit $\epsilon \to 0$ yields

$$\lim_{\epsilon \to 0}\int_\tau (\nabla^2 G + k^2 G)\,F\,d\tau = \lim_{\epsilon \to 0}\int_S \frac{\partial G}{\partial r}\,F\,dS$$

$$= \lim_{\epsilon \to 0}\int_S \left(ik\frac{e^{ikr}}{r} - \frac{e^{ikr}}{r^2}\right)F\,dS$$

$$= \lim_{\epsilon \to 0} 4\pi\epsilon^2 F(0) \left[ik\frac{e^{ik\epsilon}}{\epsilon} - \frac{e^{ik\epsilon}}{\epsilon^2} \right]$$

$$= -4\pi F(0) \qquad \text{...(25)}$$

Because of relation (18) the only contribution to the integral (20) must be noted to the singularity of (r) at $r = 0$ and by equation (25)

$$\frac{1}{4\pi}\int_\tau (\nabla^2 + k^2)\, GF(r)\, d\tau = F(0)$$

$$\int_\tau \delta(r)\, F(r)\, d\tau = F(0)$$

Hence $\delta(\mathbf{r})$ is a delta function. Returning to the original co-ordinate system by the substitution $\mathbf{r} + \mathbf{r}'$, we obtain equation (13) instead of (16).

The asymptotic form of $G(\mathbf{r}, \mathbf{r}')$ is easily found by ring to fig. 13.10.

If $|\mathbf{r}|$ is large compared to $|\mathbf{r}'|$, then it is clear that

$$|r - r'| = r - r'\cos\theta = r - r' \frac{\mathbf{r}\cdot\mathbf{r}'}{rr'}$$

$$= r - \frac{\mathbf{r}\cdot\mathbf{r}'}{r}$$

$$-r'| = |r| - \frac{\mathbf{r}'\cdot\mathbf{r}}{|r|}$$

$$= r - \frac{\mathbf{r}'\cdot\mathbf{r}}{r} \qquad \text{...(26)}$$

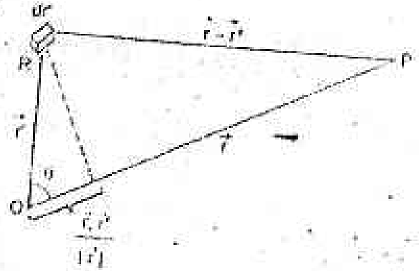

Fig. 13.10. The vectors r and r'

error involved in this approximation can be made arbitrarily small by choosing $|r|$ sufficiently

stituting value of $|(r - r')|$ from equation (26) in (15), we get

$$G(\mathbf{r}, \mathbf{r}') = \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}$$

$$= \frac{\exp\left[ik\left(r - \frac{\mathbf{r}'\cdot\mathbf{r}}{r}\right)\right]}{\left(r - \frac{\mathbf{r}'\cdot\mathbf{r}}{r}\right)}$$

$$= \frac{\exp\left[ik\left(r - \frac{\mathbf{r}'\cdot\mathbf{r}}{r}\right)\right]}{r}\left[1 + \frac{\mathbf{r}'\cdot\mathbf{r}}{r^2} + \dots\right]$$

∞, we obtain

$$G(\mathbf{r}, \mathbf{r}') = \exp\left(-ik\frac{\mathbf{r}'\cdot\mathbf{r}}{r}\right)\cdot\frac{e^{ikr}}{r}$$

$\frac{k\mathbf{r}}{r}$, we obtain

$$G(\mathbf{r}, \mathbf{r}') = e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,\frac{e^{ikr}}{r} \qquad \text{...(27)}$$

⑨

The first term in this expression depends upon the orientation of $\mathbf{k}'$ relative to vector $\mathbf{r}'$, *i.e.* it is of the form $f(\theta, \phi)$. Thus equation (27) represents the asymptotic form of Green's function and represents an outgoing wave. Thus the Green's function represents the solution of the scattering problem of unit intensity at point $\mathbf{r}'$. Setting

$$\rho(\mathbf{r}') = -\frac{1}{4\pi}\frac{2m}{\hbar^2} V(\mathbf{r}')\,\psi(\mathbf{r}')$$

from equation (8) and the value of $G(\mathbf{r}, \mathbf{r}')$ from equation (15), equation (14) gives

$$\psi_s = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int V(\mathbf{r}')\,\psi(\mathbf{r}')\,\frac{e^{ik(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|}\,d\tau' \qquad \text{...(28)}$$

This is a part of the wave-function produced by the scattering potential, ψ_s in an integral involving the function $\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$ which represents just a spherical wave that spreads out from point $\mathbf{r}'$, with a wavelength $\lambda = 2\pi/k$. The amplitude of the spherical wave is proportional to the product $V(\mathbf{r}')\,\psi(\mathbf{r}')$ *i.e.* jointly to the strength of the interaction and the amplitude of the wave-function at $\mathbf{r}'$. All these spherical waves are compounded at the point $\mathbf{r}$ which is then added to the incident wave to produce the total wave-function ψ of $\mathbf{r}$ [*i.e.* $\psi(\mathbf{r})$].

Thus

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \psi_s$$

$$= e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int V(\mathbf{r}')\,\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\,d\tau' \qquad \text{...(29)}$$

If the potential energy function is confined to a limited region of space, then the asymptotic form of Green's function form (27) can be substituted in equation (14) *i.e.*

$$\psi_s = -\frac{m}{2\pi\hbar^2}\int G(\mathbf{r}, \mathbf{r}')\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau'$$

then, we obtain,

$$\underset{(r\to\infty)}{\psi_s} = -\frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau' \qquad \text{...(30)}$$

But

$$\psi_s = f(\theta, \phi)\,\frac{e^{ikr}}{r}$$

∴ Scattering amplitude $f(\theta, \phi)$

$$= -\frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau' \qquad \text{...(31)}$$

This yields for the *scattering cross-section*

$$\sigma(\theta, \phi) = |f(\theta, \phi)|^2 = \left(\frac{m}{2\pi\hbar^2}\right)^2\left|\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau'\right|^2 \qquad \text{...(32)}$$

13.7 BORN APPROXIMATION

If the scattering takes place from the scattering centres which are localised but are weak such that the scattering does not take place at large distances from the scatterer and scattered wave is weak in amplitude, then Born-approximation can be used to evaluate the scattering amplitude $f(\theta, \phi)$ and hence the differential cross section $\sigma(\theta, \phi) = |f(\theta, \phi)|^2$.

The Born approximation is applicable whenever potential function V is fairly small. The idea is simply that of successive approximations. ***The Born approximation simply accounts neglecting the rescattering of the scattered waves provided the scattered wave is small compared with the incident wave.***

The total wave-function of the scattering problem with source point at $\mathbf{r}''$ is given by

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}'')\,V(\mathbf{r}'')\,\psi(\mathbf{r}'')\,d\tau'' \qquad \text{...(33)}$$

Replacing $\mathbf{r}$ by $\mathbf{r}'$ in above equation, we get

$$\psi(\mathbf{r}') = e^{i\mathbf{k}\cdot\mathbf{r}'} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r}',\mathbf{r}'')\,V(\mathbf{r}'')\,\psi(\mathbf{r}'')\,d\tau''$$

Substituting this value of $\psi(\mathbf{r}')$ in the integral of equation representing the total wave-function with source point at $\mathbf{r}'$ viz.

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau' \qquad \text{...(34)}$$

we get,

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\tau'$$

$$+\left(\frac{-m}{2\pi\hbar^2}\right)^2\int\!\!\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,G(\mathbf{r}',\mathbf{r}'')\,V(\mathbf{r}'')\,d\tau''\,d\tau' \qquad \text{...(35)}$$

This equation obtained by the process of *iteration* is called the first iterated form of equation (34). This process can be repeated indefinitely resulting in an infinite (Neumann) series which can be expected to represent a solution provided the series converges. The series has the following meaning.

The first term $e^{i\mathbf{k}\cdot\mathbf{r}}$ represents the incident wave-function, while the remaining terms correspond to scattered wave-function. The first term in the scattered wave represents single scattering of the incident wave $\exp(i\mathbf{k}\cdot\mathbf{r}')$ by the interaction $V(\mathbf{r}')$ in the volume element $d\tau'$. This produces a wave which travels from $\mathbf{r}'$ to the point of observation $\mathbf{r}$, and the total wave arising from single scattering is obtained by integration over the region in which the force is effective. In the second term, the incident wave $e^{i\mathbf{k}\cdot\mathbf{r}''}$ is scattered at the point $\mathbf{r}''$, $[V(\mathbf{r}'')\,e^{i\mathbf{k}\cdot\mathbf{r}''}]$, travels to the point $\mathbf{r}'$, $[G(\mathbf{r}',\mathbf{r}'')\,V(\mathbf{r}'')\,e^{i\mathbf{k}\cdot\mathbf{r}''}]$, where it is again scattered and the travels from $\mathbf{r}'$ to $\mathbf{r}$. The total effect of all such scattering is obtained by integration over $\mathbf{r}''$ and $\mathbf{r}'$. Accordingly *n*th term represents the contribution of waves which have been scattered *n*-times in the region of interaction before travelling to the point $\mathbf{r}$, where their total contribution is observed.

If the interaction is weak, so that the scattered wave is not too large, it can be expected that the Neumann series will converge rapidly and that the first term in the series will provide an approximation to ψ. This is called the ***first Born approximation***

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\tau' \qquad \text{...(36)}$$

The equation by cutting off the Neumann series at the *n*th term is called the *n*th *Born approximation*. Obviously *n*th Born approximation amounts to neglecting multiply scattered waves which have been scattered more than *n*-times by the interaction.

Substituting asymptotic form of Green's function from (27) in (36), we get

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\,\frac{e^{ikr}}{r}\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,V(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\tau' \qquad \text{...(37)}$$

But

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta,\phi)\,\frac{e^{ikr}}{r} \qquad \text{...(38)}$$

Therefore according to *first Born approximation scattering amplitude*

$$f(\theta,\phi) = -\frac{m}{2\pi\hbar^2}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}\,V(\mathbf{r}')\,d\tau' \qquad \text{...(39)}$$

Hence the scattering cross-section

$$\sigma(\theta,\phi) = \left(\frac{m}{2\pi\hbar^2}\right)^2\left|\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}\,V(\mathbf{r}')\,d\tau'\right|^2 \qquad \text{...(40)}$$

13.8 CONDITION FOR VALIDITY OF BORN APPROXIMATION

The Born approximation will be valid only whenever the total wave function is not greatly different from the incident wave function $e^{i\mathbf{k}\cdot\mathbf{r}}$. It will, therefore be valid whenever the scattered wave $\psi_s(\mathbf{r})$ is small compared to $e^{i\mathbf{k}\cdot\mathbf{r}}$ in the region where $V(\mathbf{r})$ is large. In most cases both $V(\mathbf{r})$ and $\psi_s(\mathbf{r})$ are largest near the origin, so that a rough criterion for the validity of Born approximation is

$$|\psi_s(\mathbf{r})|^2 < 1 \qquad \text{for small values of } r. \qquad \text{...(41)}$$

In case in which $\psi_s(\mathbf{r})$ is small when r is small but large for intermediate values of r, such that $V(r)$ is still appreciable, we must carefully apply this criterion. Further it may happen that Born approximation holds when the criterion is not satisfied. *Having $\psi_s(\mathbf{r})$ small everywhere provides a sufficient condition for validity of the Born approximation; but not a necessary condition.*

If we recall that a change of potential acts like a change in refractive index in optics, we can derive another criterion for the validity of Born approximation. Consequently the change of potential produces a change in the phase of the wave function. The total wave function will not differ greatly from the initial wave function if the phase of the incident wave is not much altered as it passes through the region in which it is influenced by the perturbing potential. At great distance the magnitude of wave vector is $k = \frac{\sqrt{(2mE)}}{\hbar}$ and near the centre of force it is $\frac{\sqrt{[2m(E-V)]}}{\hbar}$.

The change of phase due to the potential is then given by

$$\Delta\phi = \int_0^\infty \sqrt{\left(\frac{2m}{\hbar^2}\right)}\,[\sqrt{(E-V)} - \sqrt{E}]\,dr \qquad \text{...(42)}$$

If this difference is small compared with unity, we may take it as an indication that the wave function is not very different from that in the absence of the potential. Thus the first order Born approximation will be valid if

$$|\Delta\phi| = \left|\sqrt{\left(\frac{2m}{\hbar^2}\right)}\int_0^\infty [\sqrt{(E-V)} - \sqrt{E}]\,dr\right| << 1 \qquad \text{...(43)}$$

If $V << E$ the criterion may be simplified by expressing equation (43) as a function of the ratio V/E and expanding the square root. Then the criterion becomes

$$\sqrt{\left(\frac{2mE}{\hbar^2}\right)}\left|\int_0^\infty \left\{\left(1-\frac{V}{E}\right)^{1/2} - 1\right\}dr\right| << 1 \qquad \text{...(44)}$$

Then
$$f(\theta) = -\frac{m}{2\pi\hbar^2}\cdot\frac{4\pi}{K}\int_0^\infty V(r')\sin Kr'\, r'\, dr'. \qquad \text{...(2)}$$

We shall find the differential scattering cross-section when $V(r)$ is the screened Coulomb potential

$$V(r) = \frac{Zze^2}{4\pi\varepsilon_0 r}e^{-r/r_0} \quad \text{(S.I. system)} \qquad \text{...(3)}$$

Ze and ze being the charges of target and scattered particle respectively and r_0 being called the screening radius.

On substituting the value of $V(r)$ in equation (2), we get

$$f(\theta) = -\frac{2m}{\hbar^2 K}\left(\frac{Zze^2}{4\pi\varepsilon_0}\right)\int_0^\infty r'\sin Kr'\,\frac{e^{-r'/r_0}}{r'}\,dr'$$

$$= -\frac{2m}{\hbar^2 K}\left(\frac{Zze^2}{4\pi\varepsilon_0}\right)\int_0^\infty e^{-r'/r_0}\sin Kr'\,dr'.$$

But
$$\int_0^\infty e^{-r'/r_0}\sin Kr'\,dr' = \frac{Kr_0^2}{K^2r_0^2+1}$$

$$f(\theta) = -\frac{2m}{\hbar^2 K}\left(\frac{Zze^2}{4\pi\varepsilon_0}\right)\frac{Kr_0^2}{K^2r_0^2+1}$$

$$= -\left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{K^2+\frac{1}{r_0^2}}$$

But
$$\mathbf{K} = \mathbf{k} - \mathbf{k}'$$
$$\mathbf{K}\cdot\mathbf{K} = (\mathbf{k}-\mathbf{k}')\cdot(\mathbf{k}-\mathbf{k}')$$
$$K^2 = k^2 + k'^2 - 2\mathbf{k}\cdot\mathbf{k}'$$

As
$$k = k'$$
$$K^2 = k^2 + k^2 - 2kk\cos\theta$$
$$= 2k^2(1-\cos\theta)$$
$$= 2k^2\cdot 2\sin^2\frac{\theta}{2} = 4k^2\sin^2\frac{\theta}{2}$$

$$K = 2k\sin\theta/2$$

$$f(\theta) = -\left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{4k^2\sin^2\frac{\theta}{2}+\frac{1}{r_0^2}}$$

$$\sigma(\theta) = |f(\theta)|^2 = \left(\frac{2m\,Zze^2}{4\pi\varepsilon_0\hbar^2}\right)^2\frac{1}{\left(4k^2\sin^2\theta+\frac{1}{r_0^2}\right)^2}$$

For Coulomb Potential

As $r_0\to\infty$, $V(r)$ becomes the ordinary Coulomb potential

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{Zze^2}{r}$$

Hence
$$f(\theta) = -\left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{4k^2\sin^2\theta/2}$$

and scattering cross-section

$$\sigma(\theta) = |f(\theta)|^2 = \left(\frac{2mzZe^2}{4\pi\varepsilon_0}\right)^2\frac{1}{(4h^2k^2\sin^2\frac{1}{2}\theta)^2}$$

But
$$\hbar k = p,$$
$$\sigma(\theta) = \frac{m^2}{4p^4}\left(\frac{zZe^2}{4\pi\varepsilon_0}\right)^2\operatorname{cosec}^4\frac{\theta}{2}$$

Using $p^2 = 2mE$, we get

$$\sigma(\theta) = \frac{1}{16E^2}\left(\frac{zZe^2}{4\pi\varepsilon_0}\right)^2\operatorname{cosec}^4\frac{\theta}{2}. \qquad \text{...(5)}$$

It is in agreement with the classical Rutherford's formula of α-scattering with Coulomb field of nuclei.

The total cross-section calculated from (4) by integrating over all angles is

$$\sigma_{total} = \int_0^\pi \sigma(\theta)\,2\pi\sin\theta\,d\theta = \left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)^2\frac{4\pi r_0^4}{(4k^2r_0^2+1)^2}$$

13.10 SCATTERING BY SQUARE-WELL POTENTIAL IN BORN APPROXIMATION

Let the square well potential be defined as

$$V(r) = -V_0 \text{ for } r<a$$
$$= 0 \text{ for } r>a$$

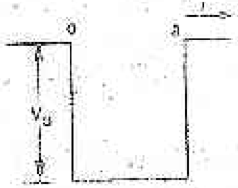

Fig. 13.12

The scattering amplitude by Born approximation is given by

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int e^{i\mathbf{K}\cdot\mathbf{r}'}V(r')\,d\tau'$$

Taking $\mathbf{K}$ as the polar axis of new set of coordinates, so that vector $\mathbf{r}'$ has rectangular components $r'\sin\theta\cos\phi$, $r'\sin\theta\sin\phi$, $r'\cos\theta$

$$\mathbf{K}\cdot\mathbf{r}' = Kr'\cos\theta,\ d\tau' = r'^2\,dr'\sin\theta\,d\theta\,d\phi$$

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\int_0^{2\pi}d\phi\int_0^\pi e^{iKr'\cos\theta}\sin\theta\,d\theta$$

Putting $\cos\theta = t$ in last integral, we have

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\cdot 2\pi\int_{-1}^{+1}e^{iKr't}\,dt$$

$$= -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\left[\frac{e^{iKr't}}{iKr'}\right]_{-1}^{+1}$$

$$\sqrt{\left(\frac{2mE}{\hbar^2}\right)}\left|\int_0^{\infty}\left\{\left(1-\frac{V}{2E}+\ldots\right)-1\right\}dr\right|<<1$$

$$\sqrt{\left(\frac{2mE}{\hbar^2}\right)}\left|\int_0^{\infty}\frac{V}{2E}\,dr\right|<<1 \text{ since } \frac{V}{E}<<1$$

$$\sqrt{\left(\frac{m}{2\hbar^2 E}\right)}\left|\int_0^{\infty}V\,dr\right|<<1$$

$$\sqrt{\left(\frac{m}{2\hbar^2 E}\right)}\,\overline{V}\,\overline{r}<<1 \qquad \ldots(45)$$

re $\overline{V}$ is the average potential and $\overline{r}$ is the mean range.

In the case of the *scattering of high-energy particles by the square potential well* of radius a and h V_0, $V_0<<E$, this condition gives

$$\sqrt{\left(\frac{m}{2\hbar^2 E}\right)}V_0\,a<<1 \qquad \ldots(46a)$$

$$\Rightarrow \quad E<<\frac{m}{2}\left(\frac{V_0\,a}{\hbar}\right)^2 \qquad \ldots(46b)$$

ter

Validity of Born Approximation : The criterion of the validity of Born approximation is that the nered wave should be much smaller as compared to the incident wave *i.e.*

$$|\psi_{sc}(\mathbf{r})|<<|\psi_{in}| \quad i.e. \ |\psi_{sc}(\mathbf{r})|<<|e^{i\mathbf{k}\cdot\mathbf{r}}|=1$$

$$|\psi_{sc}(\mathbf{r})|^2<<1$$

But

$$\psi_{sc}(\mathbf{r})=f(\theta,\phi)\frac{e^{ikr}}{r}$$

ere

$$f(\theta,\phi)=-\frac{m}{2\pi\hbar^2}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}V(\mathbf{r}')\,d\tau'$$

$$\mathbf{k}-\mathbf{k}'=\mathbf{K}$$

But

$$\psi_{sc}(\mathbf{r})=-\frac{m}{2\pi\hbar^2}\int e^{i\mathbf{K}\cdot\mathbf{r}'}V(\mathbf{r}')\frac{e^{ikr'}}{r'}\,d\tau'$$

The scattered waves are in general spherical waves and their intensity decreases with increase of eir distance from the scattering centre; therefore intensity of scattered wave will be maximum near/at = 0

$$|\psi_{sc}(0)|=\left|-\frac{m}{2\pi\hbar^2}\int e^{i\mathbf{K}\cdot\mathbf{r}'}V(\mathbf{r}')\,d\tau'\frac{e^{ikr'}}{r'}\,d\tau'\right|$$

Thus the condition of validity of Born approximation is

$$|\psi_{sc}(0)|^2=\left|\frac{m}{2\pi\hbar^2}\int\frac{e^{i(\mathbf{K}\cdot\mathbf{r}'+kr')}V(r')\,d\tau'}{r'}\right|^2<<1$$

If $V(r)$ is spherically symmetric, then choosing $\mathbf{K}$ as polar axis, we can write

$$d\tau'=dr'\,r'\,d\theta'\,r'\sin\theta'\,d\phi'$$

$$|\psi_{sc}(0)|^2=\left(\frac{m}{2\pi\hbar^2}\right)^2\left|\int_0^{a}\int_0^{\pi}\int_0^{2\pi}e^{i(\mathbf{K}\cdot\mathbf{r}'+kr')}\frac{V(r')}{r'}\,r'^2\sin\theta'\,d\theta'\,d\phi'\right|<<1$$

But

$$\mathbf{K}\cdot\mathbf{r}'=Kr'\cos\theta'$$

$$\int_0^{\pi}e^{iKr'\cos\theta'}\sin\theta'\,d\theta'=\int_{-1}^{+1}e^{iKr'p}\,dp=\left\{\frac{e^{iKr'p}}{iKr'}\right\}_{-1}^{+1}$$

$$=\frac{e^{iKr'}-e^{-iKr'}}{iKr'}$$

and

$$\int_0^{2\pi}d\phi=2\pi$$

$$|\psi_{sc}(0)|^2=\left(\frac{m}{2\pi\hbar^2}\right)^2\left|\int_0^{a}e^{ikr'}V(r')\frac{e^{iKr'}-e^{-iKr'}}{iK}(2\pi)\,dr'\right|^2<<1$$

Near scattering centre, the propagation vectors K and k of scattered and incident waves are equal, so that

$$|\psi_{sc}(0)|^2=\left(\frac{m}{\hbar^2 k}\right)^2\left|\int_0^{a}(e^{2ikr'}-1)\,V(r')\,dr'\right|^2<<1$$

13.5 SCATTERING BY A SCREENED COULOMB POTENTIAL. RUTHERFORD'S SCATTERING FORMULA FROM BORN APPROXIMATION

We know the scattering amplitude from Born approximation

$$f(\theta)=-\frac{m}{2\pi\hbar^2}\int V(r')\,e^{i\mathbf{K}\cdot\mathbf{r}'}\,d\tau' \qquad \text{(from 39)} \qquad \ldots(1)$$

where

$$\mathbf{K}=\mathbf{k}-\mathbf{k}'$$

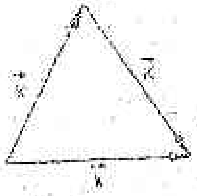

Fig. 13.11

The integral is solved by taking polar angles θ, ϕ about the direction of K.

$$\int V(r')\,e^{i\mathbf{K}\cdot\mathbf{r}'}\,d\tau'=\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}V(r')e^{iKr'\cos\theta}\,d\phi\,\sin\theta\,d\theta\,r'^2\,dr'$$

$$=2\pi\int_0^{\infty}\int_0^{\pi}V(r')\,e^{iKr'\cos\theta}\sin\theta\,d\theta\,r'^2\,dr'$$

Let $\cos\theta=t$, $-\sin\theta\,d\theta=dt$

$$\int_0^{\pi}e^{-Kr'\cos\theta}\sin\theta\,d\theta=-\int_{1}^{-1}e^{iKr't}\,dt=\left[\frac{e^{iKr't}}{iKr'}\right]_{-1}^{+1}=\frac{e^{iKr'}-e^{-iKr'}}{iKr'}$$

$$\int V(r')\,e^{i\mathbf{K}\cdot\mathbf{r}'}\,d\tau'=\frac{2\pi}{iK}\int_0^{\infty}V(r')\,(e^{iKr'}-e^{-iKr'})\,r'\,dr'$$

$$=\frac{4\pi}{K}\int_0^{\infty}V(r')\sin Kr'\,r'\,dr'$$

14

Relativistic Quantum Mechanics

14.0 INTRODUCTION

So far we have considered non-relativistic quantum mechanics and it is not applicable to the phenomena involving particles moving with relativistic velocities. Therefore it is desirable to include the requirements imposed on our theory by the relativistic theory, at least required by special theory of relativity which deals with inertial systems. Since the use of general theory is not essential due to negligible gravitational field in atomic systems. The idea of relativity may be introduced in two ways :

(1) taking into account the concepts only.

(2) formulation of quantum theory in Lorentz invariant form.

Here we shall include only the concepts of special theory of relativity.

14.1 KLEIN GORDAN EQUATION

The *Schroedinger equation in operator from* is

$$\hat{H}\,\psi = i\hbar\,\frac{\partial\psi}{\partial t} \qquad \text{...(1)}$$

The *non-relativistic Hamiltonian for a free particle* is

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2\nabla^2}{2m} \qquad \text{...(2)}$$

$$\left(\text{since } \hat{p} = \frac{\hbar}{i}\nabla = -i\hbar\nabla\right)$$

Substituting this in (1), we obtain

$$-\frac{\hbar^2}{2m}\nabla^2\,\psi\,(\mathbf{r}, t) = i\hbar\,\frac{\partial\psi}{\partial t}\,(\mathbf{r}, t)\,. \qquad \text{...(3)}$$

Let us now discuss the general situation in cartesian co-ordinates. This means that the transformations (under which the requirements of special theory of relativity are invariant) to be considered are the linear transformation

$$\bar{x}^{\mu} = a^{\mu}_{\nu}\,.\,x^{\nu} \qquad \text{...(4)}$$

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⑦

These transformations leaves the metric tensor $g_{\mu\nu}$ invariant, where

$$g_{\mu\nu} = \begin{cases} 1 & \text{for } \mu = \nu \\ 0 & \text{for } \mu \neq \nu \end{cases}$$

i.e. $$g_{11} = g_{22} = g_{33} = g_{44} = 1 \text{ and } g_{\mu\nu} = 0 \text{ for } \mu \neq \nu$$

As special theory of relativity treats spatial and temporal (time) variables on equal footings in Minkowski four-dimensional space, a co-ordinate representation must necessarily be cast into Schroedinger picture. In tensor notations equation (3) may be written as

$$\left.\begin{aligned} -\frac{\hbar^2}{2m}\,g^{\mu\nu}\,\frac{\partial}{\partial x^{\mu}}\,\frac{\partial}{\partial x^{\nu}}\,\psi\,(x^{\alpha}) &= -\hbar c g^{44}\,\frac{\partial}{dx^4}\,\psi\,(x^{\alpha}) \\ \text{where} \qquad x^4 &= ict \end{aligned}\right\} \qquad \text{...(5)}$$

This equation while invariant under linear transformations of space co-ordinates alone, is not invariant under more general transformations known as Lorentz transformations in special relativity. Under these transformations this equation can become of second order in new time co-ordinates $\bar{x}^4$ and mixed space time second order partial derivatives will appear. Such a result is not surprising since the Hamiltonian used here was non-relativistic. But if we consider the relativistic Hamiltonian more serious difficulties arise. The relativistic *Hamiltonian for a free particle* is

$$\hat{H} = E = \pm\sqrt{(\hat{p}^2c^2 + m^2c^4)} = \pm\,[\hat{\vec{p}}^2c^2 + m^2c^4]^{1/2} \qquad \text{...(6)}$$

The *Schroedinger's equation* would then become

$$\pm\,[\hat{p}^2c^2 + m^2c^4]^{1/2}\,\psi = i\hbar\,\frac{\partial\psi}{\partial t} \qquad \text{...(7)}$$

There are two **difficulties in the interpretation** of above equation.

The first *difficulty* is to interpret the positive and negative signs. In classical theory this was no problem; since in classical theory the energy changes continuously with a gap of $2mc^2$ between the minimum positive and the maximum negative value, a particle whose energy at one instant is known to be positive will always have a positive energy. Under such conditions the negative energies could be ignored. But in quantum mechanics the energy of the particle can change discontinuously and either we must show that the negative energies are spurious or we must take them into account.

The second *difficulty* is even more serious. If we write the equation (7) as

$$[-\hbar^2c^2\nabla^2 + m^2c^4]^{1/2}\,\psi = i\hbar\,\frac{\partial\psi}{\partial t} \qquad \text{...(8a)}$$

i.e. $$\left[-\hbar^2c^2g^{\mu\nu}\,\frac{\partial}{\partial x^{\mu}}\,\frac{\partial}{\partial x^{\nu}} + m^2c^4\right]^{1/2}\psi\,(x^{\alpha}) = -\hbar c\,\frac{\partial\psi\,(x^{\alpha})}{\partial x^4} \qquad \text{...(8b)}$$

where μ, $\nu = 1, 2, 3$

We are unable to interpret the square root of an operator. However if we get rid of square root of an operator by expanding it in terms of power series, the expansion will cause the space and time derivatives in unsymmetrical form and thereby would make impossible the formulation of a convariant theory. Moreover the left hand side will contain a large number of terms involving various powers of operator ∇, making it difficult to be solved.

Obviously equation (8) still lacks the necessary invariance under Lorenz transformations. Hence some further modification is required. This was done by *Klein-Gordan*. He operated the entire equation $\hat{H}\,\psi = i\hbar\,\frac{\partial\psi}{\partial t}$ by $\hat{H}$ and obtained

$$\hat{H}^2\psi = \hat{H}\left(i\hbar\frac{\partial\psi}{\partial t}\right)$$

$$= i\hbar\frac{\partial(\hat{H}\psi)}{\partial t} \qquad \text{(since the operations of } \hat{H} \text{ and } \frac{\partial}{\partial t} \text{ are interchangeable)}$$

$$= i\hbar\frac{\partial}{\partial t}\left(i\hbar\frac{\partial\psi}{\partial t}\right) \qquad \text{using (1)}$$

i.e.
$$\hat{H}^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial t^2} \qquad \text{...(9)}$$

This equation is called the *Klein-Gordan equation* or *relativistic Schroedinger equation*.

For a free particle
$$\hat{H}^2 = \hat{p}^2c^2 + m^2c^4$$

$$= \left(\frac{\hbar}{i}\nabla\right)^2c^2 + m^2c^4$$

i.e.
$$\hat{H}^2 = -\hbar^2c^2\nabla^2 + m^2c^4 \qquad \text{...(10)}$$

Therefore *Klein-Gordan equation for a free particle* takes the form

$$(-\hbar^2c^2\nabla^2 + m^2c^4)\psi = -\hbar^2\frac{\partial^2\psi}{\partial t^2}$$

This equation may be written as

$$\left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right]\psi = 0 \qquad \text{...(11a)}$$

or
$$\left[\Box^2 - \frac{m^2c^2}{\hbar^2}\right]\psi = 0 \qquad \text{...(11b)}$$

where
$$\Box^2 = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \frac{\partial}{\partial x^\mu}\frac{\partial}{\partial x^\nu},$$

is called the *D' Alembertian operator.*

In co-ordinate representation equation (11) takes the form

$$\left(g^{\mu\nu}\frac{\partial}{\partial x^\mu}\frac{\partial}{\partial x^\nu} - k^2\right)\psi(x^\alpha) = 0 \qquad \text{...(12)}$$

where $k = \frac{mc}{\hbar}$. In this form the invariance of Klein-Gordan equation is obvious.

(a) Charge and Current Densities : The Klein-Gordan equation for a free particle is

$$\left(\Box^2 - \frac{m^2c^2}{\hbar^2}\right)\psi = 0$$

or
$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right)\psi = 0$$

or
$$\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi = 0. \qquad \text{...(13)}$$

Taking complex conjugate of above equation, we get

$$\nabla^2\psi^* - \frac{1}{c^2}\frac{\partial^2\psi^*}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi^* = 0. \qquad \text{...(14)}$$

Multiplying equations (13) and (14) by ψ^* and ψ respectively, we obtain

$$\psi^*\nabla^2\psi - \frac{1}{c^2}\psi^*\frac{\partial^2\psi}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi^*\psi = 0 \qquad \text{...(15)}$$

and
$$\psi\nabla^2\psi^* - \frac{1}{c^2}\psi\frac{\partial^2\psi^*}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi^*\psi = 0. \qquad \text{...(16)}$$

Substracting (16) from (15), we get

$$\psi^*\nabla^2\psi - \psi\nabla^2\psi^* - \frac{1}{c^2}\left(\psi^*\frac{\partial^2\psi}{\partial t^2} - \psi\frac{\partial^2\psi^*}{\partial t^2}\right) = 0$$

or
$$\nabla\cdot[\psi^*\nabla\psi - \psi\nabla\psi^*] - \frac{1}{c^2}\frac{\partial}{\partial t}\left[\psi^*\frac{\partial\psi}{\partial t} - \frac{\partial\psi^*}{\partial t}\psi\right] = 0.$$

Multiplying throughout by $\frac{\hbar}{2im}$, we get

$$\nabla\cdot\left[\frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*)\right] + \frac{\partial}{\partial t}\left[\frac{\hbar}{2imc^2}\left(\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\psi t}\right)\right] = 0 \qquad \text{...(17)}$$

Substituting

$$\left.\begin{aligned} P(\mathbf{r}, t) &= \frac{\hbar}{2imc^2}\left(\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right) && \text{...}(a) \\ \text{and} \quad S(\mathbf{r}, t) &= \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*) && \text{...}(b) \end{aligned}\right\} \qquad \text{...(18)}$$

equation (17) takes the form

$$\nabla\cdot S(\mathbf{r}, t) + \frac{\partial P}{\partial t}(\mathbf{r}, t) = 0, \qquad \text{...(19)}$$

which is *well known equation of continuity*. The current density expression $\mathbf{S}(\mathbf{r}, t)$ has the same form as in non-relativistic case, but the inspection of expression $P(\mathbf{r}, t)$ indicates that it can not be interpreted as *position probability density* in analogy with non-relativistic case in which $P(\mathbf{r}, t) = \psi^*\psi$ due to following reason, :

The expression $P(\mathbf{r}, t)$ may be expressed as

$$P(\mathbf{r}, t) = \frac{\hbar}{2imc^2}\left(\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right)$$

$$= \frac{1}{2mc^2}\left[\left(-i\hbar\frac{\partial\psi^*}{\partial t}\right)\psi + \psi^*\left(i\hbar\frac{\partial\psi}{\partial t}\right)\right] \qquad \text{...(20)}$$

Now using Schroedinger equation in operator form and keeping in mind that the Hamiltonian operator associated with dynamic observable energy E is Hermitian, we have

$$H\psi = i\hbar\frac{\partial\psi}{\partial t} \quad i.e. \quad i\hbar\frac{\partial\psi}{\partial t} = E\psi.$$

and
$$H^*\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t} \quad i.e. \quad -i\hbar\frac{\partial\psi^*}{\partial t} = E\psi^*.$$

So equation (20) may be expressed as

$$P(\mathbf{r}, t) = \frac{1}{2mc^2} [(E\psi^*) \psi + \psi^* (E\psi)]$$

$$= \frac{1}{2mc^2} [2E\psi^* \psi]$$

i.e.,

$$P(\mathbf{r}, t) = \frac{E}{mc^2} [\psi^* \psi]. \qquad ...(21)$$

From expression $E = \pm \sqrt{(p^2c^2 + m^2c^4)}$, we note that the energy of a particle can be either positive or negative. Thus it follows that the expression for $P(\mathbf{r}, t)$ is not definitely positive and hence it can not be regarded as conventional *position probability density*. Thus it is necessary to reinterpret ψ if Klein-Gordan equation is to be used. This was done by Pauli and Wesskopf in 1934 (after about 7 years the Klein-Gordan equation was proposed); according to them P multiplied by e *i.e.* $(e\,P)$ can be interpreted as *charge density* which may be positive and negative since charge can have either sign ; then eS will be corresponding *current density*.

Remarks. 1. Klein-Gordan equation with new interpretation of charge and current densities would inherently represent many particle theory, since it would have to encompass particles of both signs of charge.

2. The wavefunction ψ in Klein-Gordan equation has only one component (scalar). If the wavefunction has more than one component as Pauli wavefunction, then more degress of freedom than those required to describe translatory motion are available. The additional degrees of freedom describe *spin motion*. Thus in the absence of other components, the Klein-Gordan equation will describe *particles of zero spin* like π-mesons.

3. The *probability density expression in Klein-Gordan equation reduces to correct non-relativistic expression as may be seen as follows.*

Substituting

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-iEt/\hbar} \qquad ...(22)$$

If E' is non-relativistic energy, then total energy E may be expressed as $E = E' + mc^2$; mc^2 being rest energy.

∴

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-i(E' + mc^2)t/\hbar}$$

$$= \psi(\mathbf{r})\, e^{-iE't/\hbar} \cdot e^{-imc^2t/\hbar}$$

$$= \psi'(\mathbf{r}, t)\, e^{-imc^2t/\hbar} \qquad ...(23)$$

where *non-relativistic wavefunction*

$$\psi'(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-iE't/\hbar} \qquad ...(24)$$

Differentiating (23) with respect to t, we get

$$\frac{\partial\psi}{\partial t} = \left(\frac{\partial\psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right) e^{-imc^2t/\hbar} \qquad ...(25)$$

Taking complex conjugates of (23) and (25), we get

$$\psi^*(\mathbf{r}, t) = \psi'^*(\mathbf{r}, t)\, e^{imc^2t/\hbar}$$

and

$$\frac{\partial\psi^*}{\partial t} = \left(\frac{\partial\psi'^*}{\partial t} + \frac{imc^2}{\hbar}\psi'^*\right) e^{imc^2t/\hbar}. \qquad ...(27)$$

Substituting these values in (18a), we get

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$$P(\mathbf{r}, t) = \frac{\hbar}{2imc^2} \left[\psi'(\mathbf{r}, t)\, e^{-imc^2t/\hbar} \left\{\left(\frac{\partial\psi'^*}{\partial t} + \frac{imc^2}{\hbar}\psi'^*\right) e^{imc^2t/\hbar}\right\}\right.$$

$$\left. - \psi'^*(\mathbf{r}, t)\, e^{imc^2t/\hbar} \left\{\left(\frac{\partial\psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right) e^{-imc^2t/\hbar}\right\}\right]$$

$$= \frac{\hbar}{2imc^2}\left[\psi'(\mathbf{r}, t)\left(\frac{\partial\psi'^*}{\partial t} + \frac{imc^2}{\hbar}\psi'^*\right) - \psi'^*(\mathbf{r}, t)\left(\frac{\partial\psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right)\right]$$

$$= \frac{1}{2mc^2}\left[\psi'(\mathbf{r}, t)\left(\frac{\hbar}{i}\frac{\partial\psi'^*}{\partial t}\right) + \psi'^*\left(i\hbar\frac{\partial\psi'}{\partial t}\right)\right] + \psi'^*\psi'$$

$$= \frac{1}{2mc^2}\left[\psi'(\mathbf{r}, t)\left(-i\hbar\frac{\partial\psi'^*}{\partial t}\right) + \psi'^*\left(i\hbar\frac{\partial\psi'}{\partial t}\right)\right] + \psi'^*\psi'$$

$$= \frac{E'}{mc^2}\psi'^*\psi' + \psi'^*\psi' \qquad \text{(Since } E'^* = E'\text{, eigen-value of } H \text{ being real)}$$

$$= \psi'^*\psi'. \qquad ...(28)$$

(Since non-relativistic energy $E' << mc^2$)

which is correct non-relativistic expression for *probability density*.

14.2 KLEIN-GORDAN EQUATION IN ELECTROMAGNETIC FIELD

An electromagnetic field can be uniquely represented by a vector potential **A** and a scalar potential ϕ. These potentials form a four vector A_μ whose components are A_1, A_2, A_3 and $A_4 = i\phi$ and transform like momentum-energy four vector p_μ having components $p_1, p_2, p_3, p_4 = \frac{iE}{c}$. Therefore the potentials **A** and ϕ should be included in Klein Gordan equation with momentum and energy.

If e is the charge on the particle, then in analogy with non-relativistic expression $\mathbf{p}$ and E are replaced by $\mathbf{p} - \frac{e\mathbf{A}}{c}$ and $E - e\phi$ respectively *i.e.*

$$\left.\begin{aligned} \mathbf{p} &\rightarrow \mathbf{p} - \frac{e\mathbf{A}}{c} \\ E &\rightarrow E - e\phi \end{aligned}\right\} \qquad ...(29)$$

So the relativistic expression between momentum and energy of a particle of charge e in electromagnetic field becomes,

$$(E - e\phi)^2 = c^2\left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right)^2 + m^2c^4$$

i.e.

$$(E - e\phi)^2 = (c\mathbf{p} - e\mathbf{A})^2 + m^2c^4. \qquad ...(30)$$

Replacing operators E and $\mathbf{p}$ by $i\hbar\frac{\partial}{\partial t}$ and $-i\hbar\nabla$ respectively we get *Klein Gordan equation* as

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2 \psi = [(-i\hbar c\nabla - e\mathbf{A})^2 + m^2c^4]\,\psi. \qquad ...(31)$$

$$\frac{2E\gamma}{\hbar c\alpha} = \lambda = n' + 1 - \frac{1}{2} + \frac{1}{2}\left[\{(2l+1)\}^2 - 4r^2\right]^{1/2}.$$

$$\frac{4E^2}{\hbar^2 c^2 \alpha} = \frac{\lambda^2}{r^2} \quad \text{or} \quad \frac{E^2}{m^2c^4 - E^2} = \frac{\lambda^2}{r^2}$$

or

$$E = mc^2\left(1 + \frac{r^2}{\lambda^2}\right)^{-1/2} \qquad \ldots(13)$$

If Z is so large that $(2l+1)^2 - 4r^2$ is negative, there is no integer satisfying equation and the series does not terminate. Hence the solutiions are not bounded and square integrable.

Fine structure. Expanding the energy eigen value in a series in r^2.

$$\lambda = n' + \frac{1}{2} + \frac{(2l+1)}{2}\left[1 - \frac{4r^2}{(2l+1)^2}\right]^{1/2}$$

$$= n' + \frac{1}{2} + \left(l + \frac{1}{2}\right)\left[1 - \frac{2r^2}{(2l+1)^2} - \frac{1}{8}\frac{16r^4}{(2l+1)^4} + \ldots\right]$$

$$= n' + \frac{1}{2} + \left(l + \frac{1}{2}\right)\left[1 - \frac{1}{2}\frac{r^2}{\left(l+\frac{1}{2}\right)^2} - \frac{1}{8}\frac{r^4}{\left(l+\frac{1}{2}\right)^4} + \ldots\right]$$

$$= n' + \frac{1}{2} + \left(l + \frac{1}{2}\right) - \frac{1}{2}\frac{r^2}{\left(l+\frac{1}{2}\right)} - \frac{1}{8}\frac{r^4}{\left(l+\frac{1}{2}\right)^3} \ldots$$

$$\cong n' + l + 1 - \frac{1}{2}\frac{r^2}{l+\frac{1}{2}} - \frac{1}{8}\frac{r^4}{\left(l+\frac{1}{2}\right)^3}$$

$$\cong n - \frac{1}{2}\frac{r^2}{l+\frac{1}{2}} - \frac{1}{8}\frac{r^4}{\left(l+\frac{1}{2}\right)^3} \qquad \ldots(14)$$

where $n = n' + l + 1 \cong$ principal quantum number.

$$E = mc^2\left[1 - \frac{1}{2}\frac{r^2}{\left(n - \frac{r^2}{2l+1}\right)^2} - \frac{3}{8}\frac{r^4}{\left(n - \frac{r^2}{2l+1}\right)^4}\right]$$

$$= mc^2\left[1 - \frac{r^2}{2n^2} - \frac{r^2}{2n^3}\frac{2r^2}{(2l+1)} - \frac{3r^4}{8n^4}\right]$$

$$= mc^2\left[1 - \frac{r^2}{2n^2} - \frac{r^4}{2n^4}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right)\right] \qquad \ldots(15)$$

This equation represents an expression for binding energy of Klein Gordan particle

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The first term is the rest energy; the second term

$$\frac{-mc^2\gamma^2}{2n^2} = \frac{-mc^2Z^2e^4}{2n^2\hbar^2c^2} = \frac{-mZ^2e^4}{2n^2\hbar}$$

in the non-relativistic Rydberg term. This third term removes the degeneracy of states with the same n but different l; this is the fine structure. The fine structure obtained here does not agree with the experimentally observed fine structure of the hydrogen atom. Therefore the Klein-Gordan particle cannot be an electron. The spin is absent in this solution. It is valid for spin zero particle orbiting about a nucleus.

14.4 DIRAC'S RELATIVISTIC EQUATION

In 1962, Dirac formulated an equation to avoid the difficulties arising in Klein Gordan equation on the basis of requirements of Lorentz invariance which demand that an equation which is linear in H and hence in E must also be linear in **p**. This is because both E and **p** enter linearly in four momentum p^μ given by $\left(\mathbf{p}, i\frac{E}{c}\right)$

Dirac approached the problem of finding a relativistic wave equation from

$$\hat{H}\,\psi(\mathbf{r}, t) = i\hbar\frac{\partial\psi(\mathbf{r}, t)}{\partial t} \qquad \ldots(1)$$

Linearization of Hamiltonian H : Dirac took a bolder approach by assuming that the Hamiltonian H is linear in energy and momentum. The simplest linearized Hamiltonian for a free particle is

$$H = c\,\vec{\alpha}\cdot\mathbf{p} + \beta\, mc^2 \qquad \ldots(2)$$

Here β and the components of $\vec{\alpha}$ are yet undetermined except that we postulate them to be independent of **p**. This implies that they commute with **r**. We can also require that they must be independent of **r** and t, since otherwise the energy of a particle in empty space would depend on the position of the particle and the instant of observation. Thus they also commute with **p**.

Substituting H from (2) in (1), we get the wave equation

$$(c\,\vec{\alpha}\cdot\mathbf{p} + \beta\, mc^2)\,\psi(\mathbf{r}, t) = i\hbar\frac{\partial\psi(\mathbf{r}, t)}{\partial t} \qquad \ldots(3)$$

Substituting operator for **p** viz $\mathbf{p} \to -i\hbar\nabla$, we obtain

$$[c\,\vec{\alpha}\cdot(-i\hbar\nabla) + \beta mc^2]\,\psi(\mathbf{r}, t) = i\hbar\frac{\partial\psi(\mathbf{r}, t)}{\partial t}$$

or

$$\left(i\hbar\frac{\partial}{\partial t} + i\hbar c\,\vec{\alpha}\cdot\nabla - \beta mc^2\right)\psi(\mathbf{r}, t) = 0. \qquad \ldots(4)$$

As already indicated if this equation is to describe a free particle, there can be no term in the Hamiltonian that depend upon the space and time coordinates. Consequently $\vec{\alpha}$ and β are independent of **r**, t, **p** and E and hence commute with all of them. This does not necessarily mean that $\vec{\alpha}$ and β are numbers, since they need not commute with each other.

For simplicity writing again E for $i\hbar\,(\partial/\partial t)$ and **p** for $-i\hbar\nabla$, equation (11) may be expressed as

or

$$(E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2)\,\psi(\mathbf{r}, t) = 0 \qquad \ldots(5)$$

Operating above equation by $(E + c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)$, from left we get

$$(E + c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)\,(E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2)\,\psi = 0$$

or

$$[E^2 - (c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)^2]\,\psi = 0$$

or
$$(E^2 - c^2 (\vec{\alpha} \cdot \mathbf{p})^2 - \beta^2 m^2 c^4 - mc^3 (\vec{\alpha} \cdot \mathbf{p})\, \beta - mc^3\, \beta \vec{\alpha} \cdot \mathbf{p})\ \psi = 0 \qquad ...(6)$$

But
$$\vec{\alpha} = \mathbf{i}\, \alpha_x + \mathbf{j}\, \alpha_y + \mathbf{k}\, \alpha_z,\ \mathbf{p} = \mathbf{i}\, p_x + \mathbf{j}\, p_y + \mathbf{k} p_z$$

$\therefore$
$$\vec{\alpha} \cdot \mathbf{p} = \alpha_x p_x + \alpha_y p_y + \alpha_z p_z$$

Therefore equation (6) becomes
$$\Big[E^2 - c^2 (\alpha_x p_x + \alpha_y p_y + \alpha_z p_z)^2 - \beta^2 m^2 c^4 - mc^3 (\alpha_x p_x + \alpha_y p_y + \alpha_z p_z)\, \beta - mc^3\, \beta\, (\alpha_x p_x + \alpha_y p_y + \alpha_z p_z)\Big]\ \psi = 0 \qquad ...(7)$$

or
$$\Big[E^2 - c^2 \{\alpha_x^2 p_x^2 + \alpha_y^2 p_y^2 + \alpha_z^2 p_z^2 + (\alpha_x \alpha_y + \alpha_y \alpha_x)\, p_x p_y + (\alpha_y \alpha_z + \alpha_z \alpha_y)\, p_y p_z + (\alpha_z \alpha_x + \alpha_x \alpha_z)\, p_z p_x\} - \beta^2 m^2 c^4 - mc^3 \{(\alpha_x \beta + \beta \alpha_x)\, p_x + (\alpha_y \beta + \beta \alpha_y)\, p_y + (\alpha_z \beta + \beta \alpha_z)\, p_z\Big]\ \psi = 0. \qquad ...(8)$$

where the substitutions $i\hbar\ (\partial/\partial t)$ for E and $- i\hbar \nabla$ for $\mathbf{p}$ are implied. Klein-Gordan equation is
$$\Big[E^2 - c^2\ (p_x^2 + p_y^2 + p_z^2) - m^2 c^4\Big]\ \psi = 0. \qquad ...(9)$$

Comparing equations (8) and (9), we obtain
$$\left.\begin{aligned} &\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1 \\ \text{and}\quad &\alpha_x \alpha_y + \alpha_y \alpha_x = 0;\ (\alpha_y \alpha_z + \alpha_z \alpha_y) = 0;\ (\alpha_z \alpha_x + \alpha_x \alpha_z) = 0 \\ &\alpha_x \beta + \beta \alpha_x = 0\ ;\ (\alpha_y \beta + \beta \alpha_y) = 0;\ (\alpha_z \beta + \beta \alpha_z) = 0 \end{aligned}\right\} \qquad ...(10)$$

That is the four quantities α_x, α_y, α_z and β have the following properties :

(i) their squares are unity and ;

(ii) They anticommute with one another in pairs.

Since $\vec{\alpha}$ and β anticommute rather than commute with each other, they connot be numbers. Moreover the quantities of this type can be expressed in terms of matrices and it is convenient to find a matrix representation of them.

Matrices for $\vec{\alpha}$ and β

The squares of all the four matrices are unity; so that their eigen-values are + 1 and – 1. Let us arbitrarily choose β as the matrix that is to be diagonal and we rearrange its rows and columns so that all the + 1 eigen values are grouped together in the matrix of rank n and all the – 1 eigen values are grouped together in a matrix of rank m.

The matrix β can be expressed as
$$\beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad ...(10a)$$

which is an abbreviation of
$$\beta = \begin{bmatrix} 1 & 0 & & 0 & 0 \\ 0 & 1 & & 0 & 0 \\ \cdots & & & & \\ 0 & 0 & & -1 & 0 \\ 0 & 0 & & 0 & -1 \end{bmatrix} \qquad ...(10b)$$

All the four matrices α_x, α_y, α_z and β are such that their squares are unity and they anticommute with one another in pairs. We already have three well known 2 × 2 matrices σ_x, σ_y and *σ_z called Pauli spin matrices;* which satisfy the above properties, given by
$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},\ \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix},\ \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad ...(11)$$

Since a 2 × 2 matrix has four elements, there are four and only four, independent 2 × 2 matrices. three of these are σ_x, σ_y, σ_z. The only other matrix linearly independent of these three is
$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad ...(12)$$

which is a unit matrix and therefore commutes rather than anticommutes with every σ. Hence we can not have fourth 2 × 2 matrix which satisfies both properties of Dirac Matrices. Now we show that ***the Dirac Matrices must be even-dimensional.***

Let us choose a representation in which β is diagonal $N \times N$ matrix *i.e.*
$$\beta = \begin{bmatrix} b_1 & & O \\ & b_i & \\ O & & b_N \end{bmatrix} \qquad ...(13)$$

As $\beta^2 = 1$, $b_i^2 = 1$ and $b_i = \pm 1$ $(i = 1, 2, \ldots N)$

Also since $\beta^2 = \alpha_k^2 = 1$ $(k = x, y, z)$; det α_k or det $\beta \neq 0$.

This implies that matrices α_k $(k = x, y, z)$ and β has an inverse*

Since β anticommutes with each component of $\vec{\alpha}$ we have
$$\alpha_k \beta + \beta \alpha_k = 0\ (k = x, y, z)$$

This relation may be expressed as
$$\beta \alpha_k = - \alpha_k \beta$$

or
$$\alpha_k^{-1} \beta \alpha_k = - \alpha_k^{-1} \alpha_k \beta$$

As $\alpha_k^{-1}\ \alpha_k = 1$; we have
$$\alpha_k^{-1}\ \beta\, \alpha_k = - \beta \qquad ...(14)$$

Taking trace of both sides, we get
$$\text{Trace}\ (\alpha_k^{-1}\ \beta\, \alpha_k) = - \text{Trace}\ \beta$$

or
$$\text{Trace}\ (\alpha_k\ \alpha_k^{-1}\ \beta) = - \text{Trace}\ \beta\ \ [\text{Since Trace (ABC)} = \text{Trace (CAB)}]$$

or
$$\text{Trace}\ (\beta) = - \text{Trace}\ (\beta) \qquad (\text{Since}\ \alpha_k\ \alpha_k^{-1} = I)$$

This gives 2 (Trace β) = or Trace (β) = 0

Similarly Trace (α_k) = 0

Thus
$$\text{Trace}\ (\beta) = \text{Trace}\ (\alpha_k) = 0 \qquad ...(15)$$

This equation *shows that the trace of each of the matrices α_k and β must be zero :*

In matrix (13) let r of the b_i's are + 1 and the rest s of b_i's are – 1 *i.e.*
$$b_1 = b_2 = \ = b_r = 1$$

and
$$b_{r+1} = b_{r+2} = \ldots = b_N = -1$$

so that
$$r + s = N \qquad ...(16)$$

But the condition that Trace (β) = 0 requires that
$$\sum_{i=1}^{N} b_i = r - s = 0\ \ i.e.\ \ r = s$$

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*The necessary and sufficient condition for a matrix A to possess inverse in that det $A \neq 0$.

In view of this equation (16) shows

$$N = 2r \qquad ...(17)$$

Thus Dirac matrices $\vec{\alpha}$ and β must be even dimensional. Therefore we can not use 3 × 3 matrices. The next simplest choice is 4 × 4 matrices.

As eigen values of all the four matrices are +1 and −1. Let us arbitrarily choose β as the matrix which is to be diagonal and we arrange its rows and columns so that all the +1 eigen values are grouped together and all the −1 eigen values are grouped together in a matrix as

$$\beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \qquad ...(18a)$$

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad ...(18b)$$

As β anticommutes with each component of $\vec{\alpha}$ we have

$$\alpha_k \beta + \beta \alpha_k = 0.$$

the jl element of which is $(\alpha_k)_{jl} (\beta_j + \beta_l) = 0$.

Here β_j and β_l are the two eigen values of β, which are arranged in accordance with equation (18). If $\beta_j = \beta_l$ then $(\beta_j + \beta_l) \neq 0$ and so $(\alpha_k)_{jl} = 0$; whereas if β_j and β_l have opposite signs, then $\beta_j + \beta_l = 0$; so $(\alpha_k)_{jl}$ need not be zero. Therefore the matrix for α_k may be expressed as

$$\alpha_k = \begin{bmatrix} 0 & \alpha_{x1} \\ \alpha_{x2} & 0 \end{bmatrix} \qquad ...(19)$$

where α_{x1} has n rows and m columns and α_{x2} has m rows and n columns. Since the square of (19) is a unit matrix, we note that

$$\alpha_{x1}\,\alpha_{x2} = 1 \qquad ...(20a)$$

$$\alpha_{x2}\,\alpha_{x1} = 1 \qquad ...(20b)$$

The unit matrix appearing on R.H.S. of (20) has n rows and m columns while the unit matrix on R.H.S. of (20b) has m rows and n columns.

But no two matrices exist that satisfy (20a) and (20b) simultaneoulsy if $m \neq n$. Therefore we must have $m = n = 2$ for 4 × 4 matrices. It is apparent that α_y and α_z can be put in a form similar to (19).

Using Pauli spin matrices σ_x, σ_y and σ_z and choosing

$$\alpha_{x1} = \alpha_{x2} = \sigma_x;\ \text{then}$$

$$\alpha_x = \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \qquad ...(21a)$$

Similarly

$$\alpha_y = \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \qquad ...(21b)$$

$$\alpha_z = \begin{bmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \qquad ...(21c)$$

We already have

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad ...(21d)$$

These 4 × 4 matrices are evidently Hermitian and in abbreviated form may be expressed as

$$\beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix};\ \vec{\alpha} = \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix} \qquad ...(22)$$

where each element is a matrix with two rows and two columns.

The four components of ψ's : If the Dirac operators are to involve 4 by 4 matrices, then the Dirac operands must have the four components, that is Dirac ψ function, must have the form

$$\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \qquad ...(23)$$

where each of four components is an ordinary function of x, y, z and t. Then ψ^* or $\overline{\psi}$'s corresponding to above equation are denoted by the row symbol

$$\overline{\psi} = [\overline{\psi}_1, \overline{\psi}_2, \overline{\psi}_3, \overline{\psi}_4] \qquad ...(24)$$

and the corresponding Dirac $\overline{\psi}\,\psi$ is the following orbinary function,

$$\overline{\psi}\,\psi = \overline{\psi}_1 \psi_1 + \overline{\psi}_2 \psi_2 + \overline{\psi}_3 \psi_3 + \overline{\psi}_4 \psi_4 \qquad ...(25)$$

Two Dirac ψ's ψ_I and ψ_{II} are said to be orthogonal to each other if

$$\int \overline{\psi}_I \psi_{II}\, d\tau = 0. \qquad ...(26)$$

this is, if

$$\int (\overline{\psi}_{1I} \psi_{1II} + \overline{\psi}_{2I} \psi_{2II} + \overline{\psi}_{3I} \psi_{3II} + \overline{\psi}_{4I} \psi_{4II})\, d\tau = 0. \qquad ...(27)$$

The time dependence of a Dirac pertaining to a system whose Hamiltonian is H is determined through the equation

$$H\psi = i\hbar \frac{\partial \psi}{\partial t}$$

where

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial t} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} \partial \psi_1/\partial t \\ \partial \psi_2/\partial t \\ \partial \psi_3/\partial t \\ \partial \psi_4/\partial t \end{bmatrix}$$

The Dirac Equation

The equation $H\psi = E\psi$ with H given by (2) that is, equation

$$(c\vec{\alpha} \cdot \mathbf{p} + \beta mc^2)\, \psi = E\psi \qquad ...(29a)$$

or

$$(c\alpha_x p_x + c\,\alpha_y p_y + c\,\alpha_z p_z + \beta mc^2)\, \psi = E\psi \qquad ...(29b)$$

with $p_x = -i\hbar\,\partial/\partial x$ and so on, is called the *Dirac equation for free particle.*

To write it in more explicit form we replace α's and β by specific matrices and replace ψ by four-component column symbol.

$$\begin{bmatrix} mc^2 & 0 & cp_z & c(p_x - ip_y) \\ 0 & mc^2 & c(p_x + ip_y) & -cp_z \\ cp_z & c(p_x - ip_y) & -mc^2 & 0 \\ c(p_x + ip_y) & -cp_z & 0 & -mc^2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

so that this equation reduces to the four simultaneous equations

$$\left.\begin{aligned} (mc^2)\,\psi_1 + cp_z\psi_3 + c(p_x - ip_y)\,\psi_4 &= E\psi_1 \\ (mc^2)\,\psi_2 + cp_z\psi_4 + c(p_x + ip_y)\,\psi_3 &= E\psi_2 \\ (-mc^2)\,\psi_3 + cp_z\psi_1 + c(p_x + ip_y)\,\psi_2 &= E\psi_3 \\ (-mc^2)\,\psi_4 + cp_z\psi_2 + c(p_x + ip_y)\,\psi_1 &= E\psi_4 \end{aligned}\right\}$$

These equations may be expressed as

$$\left.\begin{aligned} (E - mc^2)\,\psi_1 - cp_z\psi_3 - c(p_x - ip_y)\,\psi_4 &= 0 \\ (E - mc^2)\,\psi_2 - c(p_x + ip_y)\,\psi_3 + cp_z\,\psi_4 &= 0 \\ (E + mc^2)\,\psi_3 - cp_z\psi_1 - c(p_x - ip_y)\,\psi_2 &= 0 \\ (E + mc^2)\,\psi_4 - c(p_x + ip_y)\,\psi_1 + cp_z\,\psi_2 &= 0 \end{aligned}\right\} \qquad \ldots(30)$$

Finally we replace p_x by $-i\hbar\dfrac{\partial}{\partial x}$ etc. and get

$$\left.\begin{aligned} (E - mc^2)\,\psi_1 + i\hbar c\,\frac{\partial\psi_3}{\partial z} + i\hbar c\left(\frac{\partial}{\partial x} - i\,\frac{\partial}{\partial y}\right)\psi_4 &= 0 \\ (E - mc^2)\,\psi_2 + i\hbar c\left(\frac{\partial}{\partial x} + i\,\frac{\partial}{\partial y}\right)\psi_3 - i\hbar c\,\frac{\partial\psi_4}{\partial z} &= 0 \\ (E + mc^2)\,\psi_3 + i\hbar c\,\frac{\partial\psi_1}{\partial z} + i\hbar c\left(\frac{\partial}{\partial x} - i\,\frac{\partial}{\partial y}\right)\psi_2 &= 0 \\ (E + mc^2)\,\psi_4 + i\hbar c\left(\frac{\partial}{\partial x} + i\,\frac{\partial}{\partial y}\right)\psi_1 - i\hbar c\,\frac{\partial\psi_2}{\partial z} &= 0 \end{aligned}\right] \qquad \ldots(31)$$

Ex. 1. *If $\vec{\alpha}$ represents three Dirac matrices $\alpha_x, \alpha_y, \alpha_z$ and* **B** *and* **C** *are usual three dimensional vectors, then show that*

$$(\vec{\alpha}\cdot\mathbf{B})\,(\vec{\alpha}\cdot\mathbf{C}) = \mathbf{B}\cdot\mathbf{C} + i\,\vec{\sigma}'\cdot\mathbf{B}\times\mathbf{C}$$

where $\vec{\sigma}' = \begin{bmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{bmatrix}$ *is a 4 × 4 matrix.* ***(Meerut 1992)***

$\vec{\sigma}$ being 2 × 2 Pauli spin matrices.

Solution.

$$(\vec{\alpha}\cdot B)\,(\vec{\alpha}\cdot C) = (\alpha_x B_x + \alpha_y B_y + \alpha_z B_z)\,(\alpha_x C_x + \alpha_y C_y + \alpha_z C_z)$$

$$= \alpha_x^2 B_x C_x + \alpha_y^2 B_y C_y + \alpha_z^2 B_z C_z + \alpha_x\alpha_y\,(B_x C_y - B_y C_x) + \alpha_y\alpha_z\,(B_y C_z - B_z C_y) + \alpha_z\alpha_x\,(B_z C_x - B_x C_z)$$

$$[\text{Since } \alpha_x\alpha_y = -\alpha_y\alpha_x \text{ etc.}]$$

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$$= B_x C_x + B_y C_y + B_z C_z + \alpha_x\alpha_y\,(B_x C_y - B_y C_x) + \alpha_y\alpha_z\,(B_y C_z - B_z C_y) + \alpha_z\alpha_x\,(B_z C_x - B_x C_z)$$

$$(\text{Since } \alpha_x^2 = \alpha_y^2 = \alpha_z^2 = 1)$$

But

$$\alpha_x\alpha_y = \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} = \begin{bmatrix} \sigma_x\sigma_y & 0 \\ 0 & \sigma_x\sigma_y \end{bmatrix}$$

$$= \begin{bmatrix} i\sigma_z & 0 \\ 0 & i\sigma_z \end{bmatrix} = i\begin{bmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{bmatrix} = i\sigma_z'$$

Similarly

$$\alpha_y\alpha_z = i\,\sigma_x' \quad\text{and}\quad \alpha_z\alpha_x = i\,\sigma_y'$$

$$\therefore\ (\vec{\alpha}\cdot B)\,(\vec{\alpha}\cdot C) = (B\cdot C) + i\,\sigma_z'\,(B_x C_y - B_y C_x) + i\,\sigma_x'\,(B_y C_z - B_z C_y) + i\,\sigma_y'\,(B_z C_x - B_x C_z)$$

$$= \mathbf{B}\cdot\mathbf{C} + i\begin{vmatrix} \sigma_x' & \sigma_y' & \sigma_z' \\ B_x & B_y & B_z \\ C_x & C_y & C_z \end{vmatrix} = \mathbf{B}\cdot\mathbf{C} + i\,\vec{\sigma}'\cdot\mathbf{B}\times\mathbf{C}$$

Ex. 2. *If $\vec{\alpha}$ and β are Dirac matrices, prove that*

(i) $\alpha_x = \frac{1}{2}\,[\alpha_x\,\alpha_y,\ \alpha_y]$

(ii) $\alpha_x\alpha_y\alpha_z = \frac{1}{2}\,[\alpha_x\alpha_y\alpha_z\,\beta,\ \beta]$

(iii) Trace $(\vec{\alpha}\cdot\mathbf{B})\,(\vec{\alpha}\cdot\mathbf{C}) = 4\,\mathbf{B}\cdot\mathbf{C}$

where **B** *and* **C** *are three dimensional vectors.* ***(Meerut 1997; Rohilkhand 1984)***

Solution. *If $\vec{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are Dirac matrices, then we have the following properties :*

1. The squares of all matrices are unity

i.e. $$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1$$

2. All four matrices anticommute in pairs i.e.

$$\alpha_\mu\alpha_\nu = -\alpha_\nu\alpha_\mu \qquad (\mu,\ \nu = x,\ y,\ z)$$

(i) We have

$$[\alpha_x\alpha_y,\ \alpha_y] = \alpha_x\alpha_y\alpha_y - \alpha_y\alpha_x\alpha_y$$

$$= \alpha_x\alpha_y^2 + \alpha_x\alpha_y\alpha_y = \alpha_x\alpha_y^2 + \alpha_x\alpha_y^2 = \alpha_x + \alpha_x$$

$$\therefore\quad \alpha_x = \tfrac{1}{2}\,[\alpha_x\alpha_y,\ \alpha_y]$$

(ii) $[\alpha_x\alpha_y\alpha_z\,\beta,\ \beta] = \alpha_x\alpha_y\alpha_z\,\beta\beta - \beta\,\alpha_x\alpha_y\alpha_z\,\beta$

$$= \alpha_x\alpha_y\alpha_z\,\beta^2 + \alpha_x\beta\alpha_y\alpha_z\,\beta = \alpha_x\alpha_y\alpha_z - \alpha_x\alpha_y\beta\alpha_z\,\beta$$

$$= \alpha_x\alpha_y\alpha_z + \alpha_x\alpha_y\alpha_z\,\beta^2 = 2\,\alpha_x\alpha_y\alpha_z$$

$$\alpha_x\alpha_y\alpha_z = \tfrac{1}{2}\,[\alpha_x\alpha_y\alpha_z\,\beta,\ \beta]$$

(iii) If $\alpha_x, \alpha_y, \alpha_z$ are cartesian components of $\vec{\alpha}$,

$$(B_x, B_y, B_z) \quad\text{and}\quad (C_x, C_y, C_z)$$

are cartesian components of three dimensional vectors **B** and **C**, then we have

$$(\vec{\alpha}\cdot\mathbf{B}) = (\mathbf{i}\,\alpha_x + \mathbf{j}\,\alpha_y + \mathbf{k}\,\alpha_z)\cdot(\mathbf{i}\,B_x + \mathbf{j}\,B_y + \mathbf{k}\,B_z)$$

$$= \alpha_x B_x + \alpha_y B_y + \alpha_z B_z$$

Similarly $$(\vec{\alpha}\cdot\mathbf{C}) = \alpha_x C_x + \alpha_y C_y + \alpha_z C_z$$

$$(\vec{\alpha}\cdot\mathbf{B})\,(\vec{\alpha}\cdot\mathbf{C}) = (\alpha_x B_x + \alpha_y B_y + \alpha_z B_z)\,(\alpha_x C_x + \alpha_y C_y + \alpha_z C_z)$$

$$= \alpha_x^2 B_x C_x + \alpha_x\alpha_y B_x C_y + \alpha_x\alpha_z B_x C_z + \alpha_y\alpha_x B_y C_x + \alpha_y^2 B_y C_y + \alpha_y\alpha_z B_y C_z$$
$$+ \alpha_z\alpha_x B_z C_x + \alpha_z\alpha_y B_z C_y + \alpha_z^2 B_z C_z$$

$$= \alpha_x^2 B_x C_x + \alpha_y^2 B_y C_y + \alpha_z^2 B_z C_z + \alpha_x \alpha_y B_x C_y + \alpha_y \alpha_x B_y C_x + \alpha_x \alpha_z B_x C_z + \alpha_z \alpha_x B_z C_x$$
$$+ \alpha_y \alpha_z B_y C_z + \alpha_z \alpha_y B_z C_y$$
$$= \alpha_x^2 B_x C_x + \alpha_y^2 B_y C_y + \alpha_z^2 B_z C_z + \alpha_x \alpha_y (B_x C_y - B_y C_x) + \alpha_z \alpha_x (B_z C_x - B_x C_z)$$
$$+ \alpha_y \alpha_z (B_y C_z - B_z C_y) \qquad \text{...(1)}$$

Now α_x, α_y and α_z are 4×4 matrices having squares unity i.e.

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Also $$\alpha_x \alpha_y = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{bmatrix}$$

$$\alpha_z \alpha_x = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix}$$

and $$\alpha_y \alpha_z = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \end{bmatrix}$$

Substituting these values in (1), we get

$$(\vec{\alpha} \cdot \mathbf{B})\,(\vec{\alpha} \cdot \mathbf{C}) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} (B_x C_x + B_y C_y + B_z C_z)$$
$$+ \begin{bmatrix} i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{bmatrix} (B_x C_y - B_y C_x) + \begin{bmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix} (B_z C_x - B_x C_z)$$
$$+ \begin{bmatrix} 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \end{bmatrix} (B_y C_z - B_z C_y)$$

As the trace of a matrix is the sum of its diagonal terms, we have

$$\text{Trace} \quad (\vec{\alpha} \cdot \mathbf{B})\,(\vec{\alpha} \cdot \mathbf{C}) = 4\,(B_x C_x + B_y C_y + B_z C_z) + 0 + 0 + 0$$
$$= 4\,(\mathbf{B} \cdot \mathbf{C})$$

14.5 DIRAC FREE PARTICLE SOLUTIONS OR PLANE WAVE SOLUTIONS

The wave function ψ has 4 components and the Dirac equation is exactly a set of 4 first order linear partial differential equations. The plane wave solutions of these component wave-functions will have the form

$$\psi_j\,(\mathbf{r}, t) = u_j\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \qquad \text{...(1)}$$

where $j = 1, 2, 3, 4$.

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u_j are numbers, $\psi_j\,(\mathbf{r}, t)$ are eigen functions of the energy and momentum operators with eigen values $E = \hbar\,\omega$ and $\mathbf{p} = \hbar\,k$ respectively. After substitution, we get

$$\left.\begin{aligned} (E - mc^2)\, u_1 - cp_z u_3 - c\,(p_x - ip_y)\, u_4 &= 0 \\ (E - mc^2)\, u_2 - c\,(p_x + ip_y)\, u_3 + cp_z\, u_4 &= 0 \\ (E + mc^2)\, u_3 - cp_z u_1 - c\,(p_x - ip_y)\, u_2 &= 0 \\ (E + mc^2)\, u_4 - c\,(p_x + ip_y)\, u_1 + cp_z\, u_2 &= 0 \end{aligned}\right\} \qquad \text{...(2)}$$

These equations being homogeneous will have non-trivial solution only if the determinant of the coefficients of u_1, u_2, u_3, u_4 is zero or

$$\begin{bmatrix} (E - mc^2) & 0 & -cp_z & -c\,(p_x - ip_y) \\ 0 & (E - mc^2) & -c\,(p_x + ip_y) & cp_z \\ -cp_z & -c\,(p_x - ip_y) & (E + mc^2) & 0 \\ -c\,(p_x + ip_y) & cp_z & 0 & (E + mc^2) \end{bmatrix} = 0$$

or $$(E^2 - m^2c^4 - c^2\mathbf{p}^2)^2 = 0 \qquad \text{...(3)}$$

This is an agreement with momentum energy-relation for a free particle.

Explicit solutions can be found for any momentum $\mathbf{p}$ by choosing a sign for energy, say

$$E_+ = +\,[c^2\mathbf{p}^2 + m^2c^4]^{1/2}$$

The determinant (3) is of rank 2. To show this we replace it by Δ,

$$\Delta = (E - mc^2) \cdot \begin{vmatrix} (E - mc^2) & -c\,(p_x + ip_y) & cp_z \\ -c\,(p_x - ip_y) & (E + mc^2) & 0 \\ -cp_z & 0 & (E + mc^2) \end{vmatrix}$$
$$- cp_z \begin{vmatrix} 0 & (E - mc^2) & cp_z \\ -cp_z & -c\,(p_x - ip_y) & 0 \\ -c\,(p_x + ip_y) & cp_z & (E + mc^2) \end{vmatrix}$$
$$- c\,(p_x - ip_y) \begin{vmatrix} 0 & (E - mc^2) & -c\,(p_x + ip_y) \\ -cp_z & -c\,(p_x - ip_y) & (E + mc^2) \\ -c\,(p_x + ip_y) & cp_z & 0 \end{vmatrix}$$

After solving we obtain

$$\Delta = (E^2 - m^2c^4 - c^2p^2)\,(E^2 - m^2c^4 - c^2\mathbf{p}^2) = 0$$

so each cofactor is zero and so on.

From (3) we obtain

$$E = \pm\,(p^2c^2 + m^2c^4)^{1/2}$$

i.e. the relation between E and p is in agreement with Schroedinger picture.

Hence we can assign numerical values to two of u's. We choose terms conveniently and obtain linearly independent solutions.

Taking first

$$E_+ = +\,(p^2c^2 + m^2c^4)^{1/2},$$

there are two linearly independent solutions, which are conveniently written as [from last two of (2)]

$$\left.\begin{aligned} u_1 = 1,\ u_2 = 0,\ u_3 = \frac{cp_z}{E_+ + mc^2},\ u_4 = \frac{c\,(p_x + ip_y)}{E_+ + mc^2} \\ u_1 = 0,\ u_2 = 1,\ u_3 = \frac{c\,(p_x - ip_y)}{E_+ + mc^2},\ u_4 = \frac{-cp_z}{E_+ + mc^2} \end{aligned}\right\} \quad \ldots(4)$$

Similarly if we choose the negative square root

$$E_- = -(c^2p^2 + m^2c^4)^{1/2},$$

we obtain two new solutions from first two of (2)

$$\left.\begin{aligned} u_1 = \frac{cp_z}{E_- - mc^2},\ u_2 = \frac{c\,(p_x - ip_y)}{E_- - mc^2},\ u_3 = 1,\ u_4 = 0 \\ u_1 = \frac{c\,(p_x - ip_y)}{E_- - mc^2},\ u_2 = \frac{-cp_z}{E_- - mc^2},\ u_3 = 0,\ u_4 = 1 \end{aligned}\right\} \quad \ldots(5)$$

Each of these solutions can be normalised by multiplying it by N in the sense

$$\psi^*\psi = 1,$$

i.e.

$$u_1^*u_1 + u_2^*u_2 + u_3^*u_3 + u_4^*u_4 = 1$$

or

$$N^2\left[1 + 0 + \frac{c^2p_z^2}{(E_+ + mc^2)^2} + \frac{c^2\,(p_x^2 + p_y^2)}{(E_+ + mc^2)^2}\right] = 1$$

or

$$N^2 = \frac{1}{1 + \dfrac{c^2\,(p_x^2 + p_y^2 + p_z^2)}{(E_+ + mc^2)^2}} = \frac{1}{1 + \dfrac{c^2p^2}{(E_+ + mc^2)^2}}$$

$$\therefore \quad N = \left[1 + \frac{c^2p^2}{(E_+ + mc^2)^2}\right]^{-1/2} \quad \ldots(6)$$

14.6 PROBABILITY DENSITY AND CURRENT DENSITY

Let us check whether the Dirac equation leads to the correct probability density.

The Dirac equation for a free particle is

$$[E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2]\,\psi = 0,$$

where E and $\mathbf{p}$ are operators given by

$$E \to i\hbar\frac{\partial}{\partial t},$$

$$\mathbf{p} \to -i\hbar\nabla.$$

So

$$i\hbar\frac{\partial\psi}{\partial t} + i\hbar c\,\vec{\alpha}\cdot\nabla\psi - \beta mc^2\psi = 0; \quad \ldots(1)$$

A Hermitian conjugate equation gives (Hermitian conjugate is denoted by dagger †)

$$-i\hbar\frac{\partial\psi^\dagger}{\partial t} - i\hbar c\,\nabla\psi^\dagger\cdot\vec{\alpha} - \psi^\dagger\beta mc^2 = 0 \quad \ldots(2)$$

Recall $\vec{\alpha}$ and β are Hermitian. Multiply (1) on the left by $\psi^\dagger$ and (2) on the right side by ψ.

$$i\hbar\psi^\dagger\frac{\partial\psi}{\partial t} + i\hbar c\,\psi^\dagger\vec{\alpha}\cdot\nabla\psi - mc^2\psi^\dagger\beta\psi = 0$$

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$$-i\hbar\frac{\partial\psi^\dagger}{\partial t}\psi - i\hbar c\,\nabla\psi^\dagger\cdot\vec{\alpha}\psi - mc^2\psi^\dagger\beta\psi = 0$$

On subtracting,

$$i\hbar\frac{\partial}{\partial t}(\psi^\dagger\psi) + i\hbar c\,\nabla\cdot(\psi^\dagger\vec{\alpha}\psi) = 0.$$

This equation may be expressed as

$$\frac{\partial}{\partial t}(\psi^\dagger\psi) + \nabla\cdot(\psi^\dagger c\,\vec{\alpha}\psi) = 0 \quad \ldots(3)$$

comparing this equation with equation of continuity $\frac{\partial P}{\partial t} + \nabla\cdot S = 0$,

we identify the probability density and current density as

$$\left.\begin{aligned} P(\mathbf{r}, t) &= \psi^\dagger\psi \\ S(\mathbf{r}, t) &= \psi^\dagger c\,\vec{\alpha}\psi \end{aligned}\right\} \quad \ldots(4)$$

The expression for probability density is familiar. The current density expression looks more plausible if we note $c\vec{\alpha}$ is the velocity of the particle in the usual sense

$$i\hbar\frac{\partial x}{\partial t} = [x, H] = [x, c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2] = i\hbar c\,\vec{\alpha} \qquad \text{since } [x, \vec{p}] = i\hbar$$

$$\frac{dx}{dt} = c\,\vec{\alpha} \quad \ldots(5)$$

This implies however, that the eigen values of the velocity operator (in the usual sense) are $c\vec{\alpha}$. This result is often attributed to Zitterbewegung and interpreted by uncertainly principle. A very precise measurement of instantaneous velocity (which is distinct from momentum in the relativity theory) requires the accurate measurement of the position of the particle at two slightly different times. Such accurate position measurements imply that the momentum of the particle is completely unknown, so that very large momenta of the particle become possible and large velocities result. In a rigorous sense (5) is not quite correct, because the position operator and the velocity operator have to be defined properly. This requires the Foldy-Wouthuysen transformation.

14.7 ELECTROMAGNETIC POTENTIALS : MAGNETIC MOMENT OF THE ELECTRON

In order to introduce electromagnetic potentials, we make the usual changes. If A and ϕ are electromagnetic vector and scalar potentials, then

$$\mathbf{p} \to \mathbf{p} - \frac{e\mathbf{A}}{c} \text{ or } c\mathbf{p} \to c\mathbf{p} - e\mathbf{A}$$

$$E \to E - e\phi$$

where e represents charge on the particle.

So that the Dirac equation

$$(E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2)\,\psi = 0$$

in electromagnetic field takes the form

$$[E - e\phi - \vec{\alpha}\cdot(c\mathbf{p} - e\mathbf{A}) - \beta mc^2]\,\psi = 0 \quad \ldots(1)$$

Here E and $\mathbf{p}$ stand for corresponding operators, viz

$$E \to i\hbar\frac{\partial}{\partial t},\ \mathbf{p} = -i\hbar\nabla.$$

operating equation (1) by

$$[E - e\phi + \vec{\alpha}\cdot(c\mathbf{p} - e\mathbf{A}) + \beta mc^2]$$

$$i\hbar\frac{dL_x}{dt} + i\hbar\frac{d}{dt}\left(\frac{1}{2}\hbar\sigma_x'\right) = 0$$

or

$$\frac{d}{dt}\left(L_x + \frac{1}{2}\hbar\sigma_x'\right) = 0$$

or

$$L_x + \frac{1}{2}\hbar\sigma_x' = \text{constant} \qquad \text{...(11)}$$

Hence the quantity $\mathbf{J} = (\mathbf{L} + \frac{1}{2}\hbar\vec{\sigma}')$ commutes with H and therefore can be taken as the *total angular momentum.*

We refer to the operator

$$\mathbf{S} = \frac{1}{2}\hbar\vec{\sigma}' \qquad \text{...(12)}$$

as the *spin angular momentum of the electron.*

Hence Dirac's theory automatically endows the electron with properties that account for the phenomenon previously ascribed to a hypothetically spinning motion of the electron.

14.9 SPIN-ORBIT ENERGY

The spin orbit coupling energy follows as a result to Dirac equation in a central field. The term is however of order v^2/c^2 and in order to obtain a consistent approximation we proceed by two-component reduction of Dirac equation in the central field $V(r)$.

The Dirac equation for the central field is

$$[c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2 + V(r)]\,\psi = E\,\psi.$$

Writing $\psi = \begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}$ which represent the first and the last two components of ψ respectively.

i.e.

$$\left\{c\begin{bmatrix}0 & \vec{\sigma}\\ \vec{\sigma} & 0\end{bmatrix}\cdot\mathbf{p} + \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}mc^2 + V(r)\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\right\}\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix} = E\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}$$

i.e.

$$\begin{bmatrix}c & \vec{\sigma}\cdot\mathbf{p} & \psi_2\\ c & \vec{\sigma}\cdot\mathbf{p} & \psi_1\end{bmatrix} + \begin{bmatrix}mc^2\psi_1\\ -mc^2\psi_2\end{bmatrix} + \begin{bmatrix}V\psi_1\\ V\psi_2\end{bmatrix} = \begin{bmatrix}E\psi_1\\ E\psi_2\end{bmatrix}$$

This equation is equivalent to following two equations

$$c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_2 + mc^2\psi_1 + V\psi_1 = E\psi_1$$

and

$$c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1 - mc^2\psi_2 + V\psi_2 = E\psi_2$$

or

$$\left.\begin{aligned}(E - V - mc^2)\,\psi_1 - c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_2 &= 0\\ (E - V + mc^2)\,\psi_2 - c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1 &= 0\end{aligned}\right] \qquad \text{...(1)}$$

Assuming that ψ_1 and ψ_2 together constitute a non-relativistic energy eigen-function, which means that

$$E = E' + mc^2$$

is regarded as a number rather than an operator; the non-relativistic energy E' and V are assumed to be smaller in comparison with mc^2.

The wave equations (1) then become

$$\left.\begin{aligned}[E' - V(r)]\,\psi_1 - c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_2 &= 0 \quad \text{...(a)}\\ [E' + 2mc^2 - V(r)]\,\psi_2 - c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1 &= 0 \quad \text{...(b)}\end{aligned}\right] \qquad \text{...(3)}$$

From (3b), we have

$$\psi_2 = \frac{c\,\vec{\sigma}\cdot\mathbf{p}}{E' + 2mc^2 - V(r)}\,\psi_1 \qquad \text{...(4)}$$

Substituting this value of ψ_2 in (3a), we get

$$\begin{aligned}[E' - V(r)]\,\psi_1 &= c^2(\vec{\sigma}\cdot\mathbf{p})\,[E' + 2mc^2 - V(r)]^{-1}\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1\\ &= \frac{\vec{\sigma}\cdot\mathbf{p}}{2m}\left[1 + \frac{E' - V(r)}{2mc^2}\right]^{-1}\vec{\sigma}\cdot\mathbf{p}\,\psi_1\\ &= \frac{\vec{\sigma}\cdot\mathbf{p}}{2m}\left[1 - \frac{E' - V}{2mc^2}\right]\vec{\sigma}\cdot\mathbf{p}\,\psi_1\\ &= \frac{1}{2m}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p})\,\psi_1 - (\vec{\sigma}\cdot\mathbf{p})\frac{(E' - V)}{4m^2c^2}\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1 \qquad \text{...(5)}\end{aligned}$$

Using the identity

$$(\vec{\sigma}\cdot\mathbf{B})(\vec{\sigma}\cdot\mathbf{C}) = \mathbf{B}\cdot\mathbf{C} + i\,\vec{\sigma}\cdot\mathbf{B}\times\mathbf{C}$$

we have

$$(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) = \mathbf{p}\cdot\mathbf{p} + i\,\vec{\sigma}\cdot\mathbf{p}\times\mathbf{p} = p^2$$

Also if u is any function

$$\begin{aligned}[\mathbf{p}, V]\,u &= (\mathbf{p}\,V - V\,\mathbf{p})\,u = \mathbf{p}\,V\,u - V\,\mathbf{p}\,u \qquad \text{...(6)}\\ &= \frac{\hbar}{i}\nabla(Vu) - V\frac{\hbar}{i}\nabla u\\ &= \frac{\hbar}{i}[V\nabla u + u\nabla V] - V\frac{\hbar}{i}\nabla u\\ &= \frac{\hbar}{i}u\nabla V = \left(\frac{\hbar}{i}\nabla V\right)u\end{aligned}$$

i.e.

$$(\mathbf{p}\,V - V\,\mathbf{p})\,u = (-i\hbar\nabla V)\,u$$

$$(\mathbf{p}V - V\mathbf{p}) = -i\hbar\nabla V$$

or

$$\mathbf{p}\,V = V\mathbf{p} - i\hbar\nabla V \qquad \text{...(7)}$$

∴

$$(\vec{\sigma}\cdot\mathbf{p})\,V = V(\vec{\sigma}\cdot\mathbf{p}) - \vec{\sigma}\cdot i\hbar\nabla V \qquad \text{...(8)}$$

∴

∴

$$\begin{aligned}(\vec{\sigma}\cdot\mathbf{p})\frac{(E' - V)}{4m^2c^2}\,\vec{\sigma}\cdot\mathbf{p} &= \frac{E'}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \frac{1}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})\,V(\vec{\sigma}\cdot\mathbf{p})\\ &= \frac{E'}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \frac{1}{4m^2c^2}\{V(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \vec{\sigma}\cdot(i\hbar\nabla V)(\vec{\sigma}\cdot\mathbf{p})\}\\ &= \frac{E'}{4m^2c^2}p^2 - \frac{1}{4m^2c^2}Vp^2 + \frac{i\hbar}{4m^2c^2}(\vec{\sigma}\cdot\nabla V)(\vec{\sigma}\cdot\mathbf{p})\\ &= \left(\frac{E' - V}{4m^2c^2}\right)p^2 + \frac{i\hbar}{4m^2c^2}\{\nabla V\cdot\mathbf{p} + i\,\vec{\sigma}\cdot\nabla V\times\mathbf{p}\} \qquad \text{...(9)}\end{aligned}$$

Using (6) and (9), equation (5) gives

$$(E' - V)\,\psi_1 = \frac{1}{2m}p^2\psi_1 - \left\{\left(\frac{E - V}{4m^2c^2}\right)p^2 + \frac{i\hbar}{4m^2c^2}(\nabla V\cdot\mathbf{p} + i\,\vec{\sigma}\cdot\nabla V\times\mathbf{p})\right\}\psi_1$$

$$\therefore \quad E'\psi_1 = \left\{\left(1 - \frac{E'-V}{2mc^2}\right)\frac{p^2}{2m} + V\right\}\psi_1 - \frac{\hbar^2}{4m^2c^2}\nabla V \cdot \nabla\psi_1 + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\nabla V \times \mathbf{p}\,\psi_1 \qquad ...(10)$$

Now if V is spherically symmetric, we have

$$\nabla V = \frac{1}{r}\frac{dV}{dr}\mathbf{r}$$

and

$$(\nabla V)\cdot\nabla = \frac{dV}{dr}\frac{\partial}{\partial r}.$$

$$\therefore \quad \nabla V \times \mathbf{p} = \left(\frac{1}{r}\frac{dV}{dr}\mathbf{r}\right)\times\mathbf{p} = \frac{1}{r}\frac{dV}{dr}(\mathbf{r}\times\mathbf{p})$$

and noting that $E' - V = \frac{p^2}{2m}$, equation (10) gives

$$E'\psi_1 = \left\{\left(1 - \frac{(p^2/2m)}{2mc^2}\right)\frac{p^2}{2m} + V\right\}\psi_1 - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial\psi_1}{\partial r} + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\frac{1}{r}\frac{dV}{dr}\mathbf{r}\times\mathbf{p}\,\psi_1$$

Now using $\frac{1}{2}\hbar\,\vec{\sigma} = \mathbf{S}$ and $\mathbf{r}\times\mathbf{p} = \mathbf{L}$, we have

$$E'\psi_1 = \left(\frac{p^2}{2m} + V - \frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S.L}\right)\psi_1 \qquad ...(11)$$

The first and second terms on right hand side of above equation give the non-relativistic Schroedinger equation. The third term is the classical relativistic mass correction term which can be obtained by the expression

$$\begin{aligned} E' &= E - mc^2 = (p^2c^2 + m^2c^4)^{1/2} - mc^2 \\ &= mc^2\left(1 + \frac{p^2c^2}{m^2c^4}\right)^{1/2} - mc^2 = mc^2\left(1 + \frac{p^2}{m^2c^2}\right)^{1/2} - mc^2 \\ &= mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \ldots\ldots\right) - mc^2 \\ &= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}. \end{aligned} \qquad ...(12)$$

The fourth term is a similar relativistic correction to the potential energy, which does not have a classical analogue and the last term is the **spin orbit coupling energy** which appears as an automatic consequence of the Dirac equation.

Thus the spin-orbit coupling energy is

$$U_{s-0} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S}\cdot\mathbf{L}, \qquad ...(13)$$

where $\mathbf{S}$ is spin angular momentum and $\mathbf{L}$ is orbital angular momentum.

14.10 ZITTERBEWEGUNG

Let us consider the motion of an electron according to Dirac equation in Heisenberg representation where the Hamiltonian becomes time dependent.

The relativistic linearised Hamiltonian in electromagnetic field described by vector and scalar potentials ϕ and $\mathbf{A}$ is

$$H = \vec{\alpha}\cdot(c\mathbf{p} - e\mathbf{A}) + \beta mc^2 + e\phi \qquad ...(1)$$

Now according to Heisenberg representation, the equation of motion for operator x

$$\dot{x} = \frac{1}{i\hbar}[x, H] = \frac{1}{i\hbar}[x, \vec{\alpha}\cdot(c\,\mathbf{p} - e\mathbf{A}) + \beta mc^2 + e\phi] \qquad ...(2)$$

Omitting the terms which commute with x, we get

$$\dot{x} = \frac{1}{i\hbar}[x, \alpha_x cp_x] = \frac{c}{i\hbar}\alpha_x[x, p_x] = \frac{c}{i\hbar}\alpha_x i\hbar = c\alpha_x. \qquad ...(3)$$

In general the velocity operator $\dot{\mathbf{r}} = \mathbf{v}$ is given by

$$\mathbf{v} = c\,\vec{\alpha} \qquad ...(4)$$

The probability density function according to Dirac equation is $\psi^\dagger\psi$; thereby giving momentum density for Dirac particle as $\psi^\dagger\,\mathbf{p}\,\psi$ and the *velocity density* for Dirac particle appears to be

$$\psi^\dagger\,\mathbf{v}\,\psi = \psi^\dagger\,(c\vec{\alpha})\,\psi = c\,\psi^\dagger\cdot\vec{\alpha}\psi$$

The eigen-values of each α are ± 1 therefore the observed value of any component of velocity is $\pm c$ this is peculiar result, since according to relativistic mechanics speed of light is the upper limit for the speed of material particle.

To find the significance of the this result let us investigate the motion of an electron under no field (*i.e.* $\mathbf{A} = 0$ and $\phi = 0$). The Hamiltonian then is expressed as

$$H = c\vec{\alpha}\cdot\mathbf{p} + \beta\,mc^2. \qquad ...(5)$$

Writting the equation of motion for operator α_x, we have

$$\dot{\alpha}_x = \frac{1}{i\hbar}[\alpha_x, H] = \frac{1}{i\hbar}(\alpha_x H - H\alpha_x) \qquad ...(6)$$

But

$$\begin{aligned} \alpha_x H + H\alpha_x &= \alpha_x(c\,\vec{\alpha}\cdot\mathbf{p} + \beta\,mc^2) + (c\,\vec{\alpha}\cdot\mathbf{p} + \beta\,mc^2)\,\alpha_x \\ &= c\alpha_x(\alpha_x p_x + \alpha_y p_z + \alpha_z p_z + \beta\,mc) + c\,(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z + \beta\,mc)\,\alpha_x = 2\,cp_x. \\ H\alpha_x &= 2\,cp_x - \alpha_x H. \end{aligned} \qquad ...(7)$$

In view of this equation (6) gives

$$\dot{\alpha}_x = \frac{1}{i\hbar}(2\alpha_x H - 2cp_x) \qquad ...(8)$$

As for a free particle the energy and momentum are conserved, we have

$$i\hbar\,\dot{p}_x = [p_x, H] = 0 \text{ and } i\hbar\,\dot{H} = [H, H] = 0$$

therefore H and p_x are independent of time. Keeping this in mind, the differential of equation (8) with respect to time gives

$$\ddot{\alpha}_x = \frac{1}{i\hbar}(2\,\dot{\alpha}_x H) \qquad ...(9)$$

This may be expressed as

$$\frac{\ddot{\alpha}_x}{\dot{\alpha}_x} = -\frac{2i}{\hbar}H$$

Integrating w.r. to time t, we get

$$\log(\dot{\alpha}_x) = -\frac{2i}{\hbar}Ht + K \qquad ...(10)$$

K being a constant of integration.

If at $t = 0$, $\dot{\alpha}_x = (\dot{\alpha}_x)_{t=0}$; we have

$$K = \log(\dot{\alpha}_x)_{t=0}$$

$\therefore$ Equation (10) gives

$$\log\dot{\alpha}_x = -\frac{2i}{\hbar}Ht + \log(\dot{\alpha}_x)_{t=0}$$

i.e.

$$\log\left\{\frac{\dot{\alpha}_x}{(\dot{\alpha}_x)_{t=0}}\right\} = -\frac{2i}{\hbar}Ht$$

or

$$\dot{\alpha}_x = (\dot{\alpha}_x)_{t=0}\exp\left\{\left(-\frac{2i}{\hbar}\right)Ht\right\} \qquad ...(11)$$

Substituting this in (8), we get

$$(\dot{\alpha}_x)_{t=0}\exp\left(-\frac{2i}{\hbar}Ht\right) = \frac{1}{i\hbar}(2\alpha_x H - 2cp_x) \qquad ...(12)$$

We have $H^2 = p^2c^2 + m^2c^4 = E^2$, therefore

$$H = (p^2c^2 + m^2c^4)H^{-1}$$

This implies that H is the reciprocal of H^{-1} with eigen value E^{-1}

From equation (12), we have

$$\alpha_x = cp_x H^{-1} + \tfrac{1}{2}i\hbar(\dot{\alpha}_x)_{t=0}\exp\left(-\frac{2i}{\hbar}Ht\right)H^{-1} \qquad ...(13)$$

Therefore

$$\dot{x} = c\alpha_x = c^2p_xH^{-1} + \tfrac{1}{2}i\hbar c(\dot{\alpha}_x)_{t=0}\exp\left(-\frac{2i}{\hbar}Ht\right)H^{-1} \qquad ...(14)$$

Integration of above equation gives

$$x = c^2p_xH^{-1}t - \tfrac{1}{4}c\hbar^2(\dot{\alpha}_x)_{t=0}\exp\left(-\frac{2i}{\hbar}Ht\right)H^{-2} + x_0 \qquad ...(15)$$

when x_0 is constant of integration

Since

$$\dot{\alpha}_x^{\dagger} = \left\{\frac{1}{i\hbar}[\alpha_x, H]\right\}^{\dagger} = -\frac{1}{i\hbar}[H, \alpha_x] = \frac{1}{i\hbar}[\alpha_x, H] = \dot{\alpha}_x$$

Also p_x and H are Hermitian, therefore right hand side of (15) is Hermitian if we ignore the constant of integration which would obviously represent the initial position of particle. Then x would be an observable quantity and its expectation value is given by

$$<x> = \frac{c^2p_xt}{E} - \frac{1}{4}\frac{c\hbar^2}{E^2}<(\dot{\alpha}_x)_{t=0}>\exp\left(-\frac{2i}{\hbar}Et\right) \qquad ...(16)$$

where $<(\dot{\alpha}_x)_{t=0}>$ is the eigen value of α_x at $t = 0$.

Now we have

$$E = (p^2c^2 + m^2c^4)^{1/2} = mc^2$$

and writing $\frac{2E}{\hbar} = \omega$, equation (16) may be expressed as

$$<x> = \frac{c^2p_xt}{E} - \frac{1}{4}\frac{c\hbar^2}{E^2}<(\dot{\alpha}_x)_{t=0}>e^{i\omega t} \qquad ...(17)$$

In this equation the first term represents usual term

$$\left(\frac{c^2p_xt}{E} = \frac{c^2p_xt}{mc^2} = \frac{mv_xt}{m} = \right)v_xt$$

of classical mechanics and the second term because of the exponential factor represents the motion of particle, oscillating with angular frequency ω. This trembling motion of the electron was first observed by Schroedinger and is called the *Zitterbewgung* and it imparts the value to the velocity of electron. That is the electron's motion is something like the superposition of classical motion and electromagnetic wave motion.

However the frequency

$$\omega = \frac{2E}{\hbar} \geq \frac{2mc^2}{\hbar}$$

is so high that the departure from the classical mechanics term v_xt is undetectable. The Zitterbewgung did not appear in our nonrelativistic theory, the reason that this phenomenon is due to the rest energy of the electron which remains unaccounted in classical mechanics.

14.11 DIRAC'S EQUATION OF A CENTRAL FIELD FORCE (H-ATOM)

The Dirac equation for central field force is given by

$$H\psi = E\psi$$

or

$$[c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2 + V(r)]\psi = E\psi \qquad ...(1)$$

with

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

i.e. Dirac equation for an electron in a Coulomb's field of a nucleus is

$$H\psi = \left(c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2 - \frac{ze^2}{r}\right)\psi$$

The Hamiltonian takes the form

$$H = \left(c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2 - \frac{ze^2}{r}\right) \qquad ...(2)$$

For central field force the vector and scalar potentials will be

$$\mathbf{A} = 0, \phi(r) = \phi(r)$$

Now (1) reduces to

$$[(E - e\phi) - \vec{\alpha}\cdot(c\mathbf{p} - e\mathbf{A}) - \beta mc^2]\psi = 0 \qquad ...($$

We write in equation (3)

$$\psi = \begin{pmatrix}\psi_A \\ \psi_B\end{pmatrix}, \qquad ...($$

$$= (l+\tfrac{1}{2})(l+\tfrac{3}{2}) - l(l+1) + \tfrac{1}{4} \qquad \text{if } j = l+\tfrac{1}{2}$$

$$= (l^2+2l+\tfrac{3}{4}-l^2-l+\tfrac{1}{4}) = l+1$$

and

$$= (l-\tfrac{1}{2})(l+\tfrac{1}{2}) - l(l+1) - \tfrac{1}{4} = -l \qquad \text{if } j = l-\tfrac{1}{2},$$

and thus

$$k = \begin{cases} l+1 & \text{if } \; j = l+\tfrac{1}{2} \\ -l & \text{if } \; j = l-\tfrac{1}{2} \end{cases} \qquad \text{...(42)}$$

Consider $n = 1$; the ground state; n' can be zero or one, but $k \neq 0$. So $n' = 0$. In that case $k = +1$. From (42) it follows that in the non-relativistic case, the state is $S_{1/2}$.

For $\quad n' = 2,$

$n' = 0, |k| = 2; k = 2$ so the state is $P_{3/2}$.

$n' = 1, |k| = 1, \quad \begin{cases} k = +1, & \text{the state is } S_{1/2}. \\ k = -1 & \text{the state is } P_{1/2}. \end{cases}$

The last two states are degenerate and determined by $|k|$ only.

For $\quad n' = 3,$

$n' = 0, |k| = 3,$ we get $\quad D_{5/2},$

$n' = 1, |k| = 2, \quad \begin{cases} k = 2, & P_{3/2}; \\ k = -2, & D_{3/2}, \end{cases}$

$n' = 2, |k| = 1, \quad \begin{cases} k = +1, & S_{1/2}; \\ k = -1. & P_{1/2}. \end{cases}$

Hence the energy spectrum is.

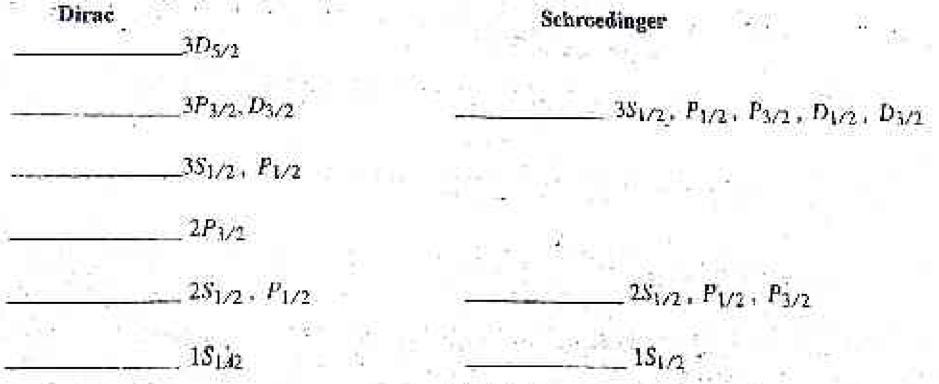

Fig. 14.1

In 1947 W.E. Lamb and R.C. Rutherford observed a splitting between $2S_{1/2}$ and $2P_{1/2}$ states of hydrogen atom not accounted by equation (40). The shift is well known **Lamb-shift** and can be accounted satisfactorily if we consider the *interaction of electron with the quantised radiation field.*

14.13 NEGATIVE ENERGY STATE OF ELECTRON ; THEORY OF POSITRON

We have Dirac equation in electromagnetic field as :

$$[E - e\,\phi - \vec{\alpha}\cdot(cp - eA) - \beta mc^2]\,\psi = 0$$

This equation may be written as four equivalent equations, two corresponding to positive energy and the remaining two corresponding to negative energy states of the particle. According to classical mechanics negative energy states can be excluded on physical grounds ; but according to quantum mechanics, it is not so because energy changes take place discontinuously and the transition from positive to negative energy states and vice-versa are possible.

If equation (1) is expressed as a matrix equation assuming all the elements of matrices representing $\alpha_x, \alpha_y, \alpha_z$ to be real and all those of matrix representing β to be purely imaginary or zero, then if we take complex conjugate of (1) remembering

$$E = i\hbar\frac{\partial}{\partial t} \text{ and } p = -i\hbar\nabla,$$

we get

$$[(-E - e\,\phi) - \vec{\alpha}\cdot(-cp - eA) + \beta mc^2]\,\psi^* = 0$$

or

$$[E + e\phi] - \vec{\alpha}\cdot(c\,\vec{p} + e\,\vec{A}) - \beta mc^2]\,\psi^* = 0 \qquad \text{...(2)}$$

Thus each solution of the wave-equation (1) has for its complex conjugate a solution of (2). Further if the solution ψ of (1) belongs to a negative value for $(E - e\phi)$ the corresponding solution ψ^* of equation (2) will belong to a positive energy for $(E + e\,\phi)$. But the operator in equation (2) is just what one would get if one substitutes $-e$ for e in the operator of (1). It follows that each negative energy solution of the wave-equation is obtained from (1) by substitution of $-e$ for e. Thus latter solution represents an electron of charge $+e$ (instead of $-ve$ as we had upto the present) moving through the given electromagnetic field.

Thus the unwanted solution of (1) is connected with the motion of an electron of charge $+e$. [It is not possible, of course with an arbitrary electromagnetic field, to separate the solution of (1) definitely into those referring to positive and those referring to negative values for $(E - e\phi)$, as such a separation would imply the transitions from one kind to the other do not occur. The preceding discussion is therefore only a rough one, applying to the case when such a separation is approximately possible].

In this way we are led to infer that the negative energy solutions of (1) refer to the motion of a new kind of particle having the mass of an electron and opposite charge. Such particles have been observed experimentally and are called *positrons*. We cannot however assert that the negative energy solutions represent positrons, as this would make the dynamical relations all wrong. For instance is it certainly not true that a positron has a negative kinetic energy. We must therefore establish the theory of positron on a somewhat different footing.

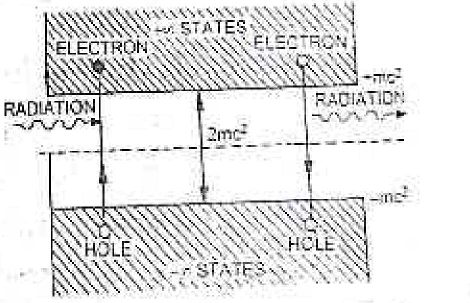

Fig. 14.2. Dirac picture of positive and nagative energy states of an electron ($h\nu = e^+ + e^-$)

Dirac proposed that nearly all the negative energy states are occupied with one electron in each state in accordance with Pauli exclusion principle and there are no positive energy electrons ; so that electrons can no longer reduce in their energy as all the negative energy states are full. This explains the ground state definition of a field to be vacuum state in the new definition. Thus the normal state of vacuum consists of an infinite density of negative energy electrons. It is assumed that there are no electromagnetic or gravitational effects of these electrons but the deviations from the normal state produced by emptying one or of more the negative energy states can be observed.

Evidently Dirac relativistic equation gives two regions of the continuous energy spectrum of a free electron

$$E = \pm \sqrt{(p^2c^2 + m^2c^4)}$$

For minimum energy of electron $p = 0$; therefore when these Dirac electrons are at rest, the energy differnce between positive and negative energy states is separated by a gap = $2mc^2$. Both in the positive and negative energy states, the electrons can take continuous values of energy states, upto infinity. The positive branch of energy is similar to the classical relativistic energy; but the negative energy states of a free electron has no classical analogue.

Now the transition from negative energy states to positive energy state will create an unoccupied negative energy state. Physically this unoccupied negative energy state will now appear as something with a positive energy, since to make it disappear or to fill it up, we should have to add to it an electron with negative energy. ***These unoccupied negative energy states are called holes or positrons.***

The assumptions require there to be a distribution of electrons of infinite density everywhere in the well. A perfect vacuum is a region where all the states of positive energy are unoccupied and all those of negative energy are occupied. In a perfect vacuum, Maxwell's equation

$$\nabla \cdot \mathbf{E} = 0$$

must, of course, be valid. This means that the infinite distribution of negative energy electrons does not contribute to the electron field. Only departure from the disrtibution in a vacuum will contribute to the electric density ρ_0 in Maxwell equation.

$$\nabla \cdot \mathbf{E} = 4\pi \rho_0$$

Thus there will be a contribution $-e$ for each occupied state of positive energy and a contribution of e for each unoccupied state of negative energy.

The exclusion principle will operate to prevent a positive energy electron ordinarily from making transitions to states of negative energy. It will be still possible for such an electron to drop into an occupied state of negative energy. In this case we should have an electron and positron disappearing simultaneously, their energy being emitted in the form of radiation. The reverse process would consist in the creation of an electron and a positron from electromagnetic radiation.

It is possible for a negative energy electron to absorb radiation and be excited into a positive-energy state as shown in Fig. 14.2. In this process we observe an electron of charge $-|e|$ and energy $+E$ and in addition a hole in the negative energy sea. The hole shows the absence of an electron of charge $-|e|$ and energy $+E$; that is the positron. It is called pair production on the basis of the hole theory. Correspondingly electron jumps in the negative energy sea with emission of radiation and leads to electron-positron annihilation.

Dirac equation predicts the correct hydrogen-atom energy spectrum and g value of the electron to high accuracy. Moreover positron predicted by the theory has been experimentally observed. This theory gives the existence of antiparticles as well as particles. The particles are described by positive energy solution for Dirac equation and in the present case are electrons of mass m and charge $-|e|$, the antiparticles are described by negative energy solution , and in the present instance are positrons of mass m and charge $+|e|$.

Thus the hole theory results to a new fundamental symmetry in nature *"To each particle there is an antiparticle and in particular the existence of electrons implies the existence of positrons."*

13.14 COVARIANT FORMULATION OF DIRAC EQUATION

It has already been pointed out that the relativistic formulation of equation of motion requires linearization of energy E and momentum $\mathbf{p}$ though this requirement is fulfilled by Dirac equation

$$(c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)\,\psi(\mathbf{r}, t) = i\hbar\frac{\partial\psi}{\partial t}(\mathbf{r}, t) \qquad ...(1)$$

but it does not appear in convariant form. Here we proceed to find its covariant form.

Replacing p_k by $-i\hbar\dfrac{\partial}{\partial x^k}$, equation (1) may be expressed as

$$\left(-i\hbar c\sum_{k=1}^{3}\alpha^k\frac{\partial}{\partial x^k} - i\hbar\frac{\partial}{\partial t}\right)\psi(x^k, t) + \beta mc\,\psi(x^k, t) = 0$$

or

$$-i\hbar\left[\frac{1}{c}\frac{\partial}{\partial t} + \sum_{k=1}^{3}\alpha^k\frac{\partial}{\partial x^k}\right]\psi(x^k, t) + \beta mc\,\psi(x^k, t) = 0.$$

Using $ct = x^0$ and multiplying on the left by β, we get

$$-i\hbar\left[\beta\frac{\partial}{\partial x^0} + \sum_{k=1}^{3}\beta\alpha^k\frac{\partial}{\partial x^k}\right]\psi(x^0, x^k) + mc\,\psi(x^0, x^k) = 0. \qquad ...(2)$$

This equation is now symetrical in x^k and $ct\,(x^0)$. Let us now define a set of four matrices called Westein Dirac's Γ–matrices γ^μ ($\mu = 0, 1, 2, 3$) matrices as follows

$$\gamma^0 = \beta,\ \gamma^k = \beta\alpha^k\ (k = 1, 2, 3). \qquad ...(3)$$

Then equation (2) may be expressed as

$$\left(-i\gamma^\mu\frac{\partial}{\partial x^\mu} + \frac{mc}{\hbar}\right)\psi(x^\mu) = 0. \qquad ...(4)$$

This equation appears in a covariant form because here space and time derivatives are treated on equal footing.

From known form of matrices $\vec{\alpha}$ and β and equation (3), the γ-matrices have representation

$$\gamma^0 = \beta = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix};\ \gamma^k = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}\begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \qquad ...(5)$$

This representation is due to Feynman, known as *Feynman representation of matrices*. From these definitions, we obtain

$$(\gamma^k)^\dagger = (\beta\alpha^k)^\dagger\beta^\dagger = \alpha^k\beta = -\beta\alpha^k = -\gamma^k \qquad ...(6)$$

and

$$(\gamma^0)^2 = \beta^2 = 1,\ (\gamma^k)^2 = -1$$

That is γ^0 is hermitian and γ^ks, are antihermitian. It then follows that the γ-matrices obey the anticommutation relations

$$\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2g^{\mu\nu}I \qquad ...(7)$$

where $g^{\mu\nu}$ is the metric given by

$$g_{00} = 1,\ g_{11} = g_{22} = g_{33} = -1,\ g_{\mu\nu} = 0 \text{ for } \mu \neq \nu$$

and I is the identity matrix. It may also be noted that γ-matrices are *unitary*.