QUANTUM MECHANICS

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Syllabus

QUANTUM MECHANICS

UNIT I: The Schrodinger equation and Stationary states

Physical basis of quantum mechanics- wave particle duality- The Schrodinger equation (time-dependent and time independent)- Physical interpretation and conditions on the wave function- Expectation values and Ehrenfest theorem- Stationary states and energy spectra-Particle in a Square well potential.

General formulation: The fundamental postulates of wave mechanics- Dirac notation: BRA and KET-Hilbert space- Hermitian operators and their properties- commutator relation and Heisenberg uncertainty principle

UNIT II: Exactly Solvable systems

Linear Harmonic oscillator- Solving the one dimensional Schrodinger equation- Abstract operator method-Particle in a box- Square well potential- Rectangular barrier potential-Rigid rotator- Hydrogen atom

UNIT III: Approximation Methods

Time independent problems: Nondegenerate case: First and second order perturbations-Degenerate case: Zeeman effect- Stark effect- Variation method- WKB quantization rule-Methods for time dependent problems: Time dependent perturbation theory- First order perturbation- Harmonic perturbation- Transition probability- Fermi's Golden rule- Adiabatic approximation- Sudden approximation

UNIT IV: Angular, Spin angular Momentum and Scattering theory

Matrix representation of angular momentum and spin angular momentum- Commutation relations- Eigen values- Addition of angular momenta- Clebsch-Gordan coefficients (basic ideas only) -Identical particle with spin-Pauli's exclusion principle- Spin statistics- Stern Gerlach experiment and electron spin

Scattreing theory: The Scattering cross section- Born approximation- Partial wave analysis- Differential and total cross sections- Phase shift

UNIT V: Relativistic Quantum Mechanics

Klein Gordan equation for a free particle and in an electro magnetic field- Dirac equation for a free particle-Charge and current densities

Dirac matrices- Plane wave solution- Negative energy states- Zitterbewegung- Spin angular momentum-Spin-orbit coupling- Fine structure

Books for study and reference:

1. *L. Schiff,Quantum Mechanics (Tata McGraw Hill, New Delhi, 1968)*
2. *P.M. Mathews and K. Venkatesan, A text Book of Quantum Mechanics (Tata McGraw Hill,New Delhi, 1987)*
3. *V.K. Thankappan, Quantum Mecahnics (Wiley-Eastern, New Delhi, 1985)*
4. *J. Singh, Quantum Mechanics- Fundamentals and Applications in Technology (John Wiley, Newyork,1997)*
5. *Goswami, Quantum Mecahnics (W.C.Brown, Dubuque,1992)*
6. *Y.R. Waghmare, Foundations of Quantum Mecahnics (Wheeler, New Delhi, 1996)*
7. *S. Devanarayanan, Quantum Mecahnics (Sci. Tech Publications Pvt. Ltd. Chennai,2005)*

UNIT I

1.1 Matter Waves

According to Debroglie, the wavelength λ associated with a moving particle having momentum p is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{where } h \text{ is Planck's constant}$$

This wave associated with a particle is called matter waves.

Consider a particle possessing wave length λ. The value of ψ at any point x at time t is given by

$$\psi = \psi_0 \sin \omega t$$
$$or \quad \psi = \psi_0 \sin 2\pi \nu t$$

where ν is the frequency of the particle. Let the particle moves with velocity v along positive x-direction. Using Lorentz transformation theory, we can write

$$t = \frac{t' + \frac{vx'}{c^2}}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}}$$

$$\therefore \psi = \psi_0 \sin \frac{2\pi\nu\left(t' + \frac{vx'}{c2}\right)}{\sqrt{\left(1 - \frac{v2}{c2}\right)}} \tag{1.1}$$

But the standard equation of wave motion is

$$\psi = \psi_0 \sin\left\{\frac{2\pi}{T'}\left(t' + \frac{x'}{u'}\right)\right\} \tag{1.1A}$$

where ψ_0 is the amplitude, T' is the period and u' is the phase velocity

Comparing eqns. (1.1) and (1.1A)

$$u' = \frac{c^2}{v} \quad \text{and} \quad \frac{1}{T'} = \nu' = \frac{\nu}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}} \tag{1.2}$$

According to Einstein's mass-energy relation

$$E = m_0 c^2 = h\nu \quad \text{or} \quad \nu = \frac{m_0 c^2}{h}$$

Substituting this in eqn. (1.2)

$$\nu' = \frac{m_0 c^2/h}{\sqrt{\left(1-\frac{v^2}{c^2}\right)}} = \frac{mc^2}{h}$$

The wavelength of the particle

$$\lambda = \frac{\text{velocity}}{\text{frequency}} = \frac{u'}{\nu'} = \frac{c^2/v}{mc^2/h}$$

or $$\lambda = \frac{h}{mv} \tag{1.3}$$

This is the expression for the de-Broglie wavelength for a particle of mass *m* moving with velocity *v*

1.2 Schroedinger time-independent wave equation.

The classical wave equation is written as,

$$\nabla^2 \Psi = \frac{1}{v^2}\frac{\partial^2 \Psi}{dt^2} \tag{1.4}$$

where Ψ is the displacement and v is the velocity of the wave. Let the wave amplitude is periodic in time t as

$$\Psi \text{ (r, t)} = \psi \text{ (r)} e^{-i\omega t} \tag{1.5}$$

Substituting eq. (1.5) in eq. (1.4), we get

$$\nabla^2 \psi = -\frac{\omega^2}{v^2}\psi$$

Or $$\nabla^2 \psi + \frac{\omega^2}{v^2}\psi = 0$$

or $$\nabla^2 \Psi + \frac{4\pi^2}{\lambda^2}\Psi = 0 \text{ since } \frac{\omega}{v} = \frac{2\pi}{\lambda}$$

ν and λ being the frequency and wavelength of the de-Broglie waves. Rearranging the terms, we get the wave equation in the form

$$\nabla^2\psi + (4\pi^2/\lambda^2)\psi = 0. \tag{1.6}$$

From the expression for de-Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{mv}$,

$$\nabla^2\psi \quad + \frac{4\pi^2 m^2 v^2 \psi}{h^2} = 0.$$

Now, $E - V = \frac{1}{2}mv^2$ where E is the total energy and V is the potential energy of the system from which,

$mv = \sqrt{2m(E-V)}$ and the wave equation becomes

$$\nabla^2 \Psi + \frac{2m}{\hbar^2}(E-V)\Psi = 0 \tag{1.7}$$

This equation is known as Schroedinger time-independent wave equation.

1.3 Schroedinger Time-dependent equation

Schrodinger time independent wave equation can be written as

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

Mulktiplying on the right by $e^{-i\omega t}$ and rearranging we get,

$$-\nabla^2\psi(r)e^{-i\omega t} + \frac{8\pi^2 m}{h^2}V\psi\, \mathrm{e}^{-i\omega t} = \frac{8\pi^2 m}{h^2}E\psi\, \mathrm{e}^{-i\omega t} \tag{1.8}$$

The right hand side can be written as

$$\frac{8\pi^2 m}{h^2}E\Psi(r,t) = \frac{8\pi^2 m}{h^2}\,\frac{E}{(\text{-i}\omega)}\,\frac{\partial}{\partial t}\left[\Psi(r,t)\right]$$

$$= \frac{8\pi^2 m}{h^2}\,\frac{ih}{2\pi}\,\frac{\partial\Psi(\mathbf{r},t)}{\partial t} \qquad \text{since} \quad \text{E}=\hbar\omega$$

$$= \frac{2m}{\hbar}\,\frac{i}{\ }\,\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

Substituting this in eqn. (1.8), we get

$$\text{or} \quad \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

This is the required Schoedinger time – dependent wave equation

(a) Solution of the Time dependent Schroedinger equation

The Schroedinger Time-dependent wave equation is written as,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}\,V(x)\Psi(x,t)=-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} \tag{1.9}$$

Now $\Psi(x,t)$ can be expressed as the product of two functions, one involving the time coordinate alone and the other position coordinate alone. That is,

$$\Psi(x,\mathrm{t}) = \psi(x)\,\phi(\mathrm{t})$$

Substituting this in the eqn. (1.9) and simplifying we get,

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)\right]=-\frac{\hbar}{i}\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

The left hand side is a function of *x* while the right hand side is a function of *t* only. But *x* and *t* are independent coordinates. This is possible only when they are separately equal to a constant (E)

Hence, $$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)\right]=E$$

and $$-\frac{\hbar}{i}\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}=E \tag{1.9A}$$

From the first of equations (1.9A) ,

$$\frac{d^2\psi(x)}{dx^2}+\frac{2m}{\hbar^2}\{E-V(x)\}\psi(x)=0, \tag{1.10}$$

which is Schroedinger time independent wave equation whose solution is given by $\psi(x)$. Considering the second of equations (1.9A), we have

$$\frac{d\phi(t)}{dt}=-\frac{i}{\hbar}E\,\phi(t)$$

or $$\frac{d\phi(t)}{\phi(t)}=-\frac{i}{\hbar}E\,dt.$$

Integrating, $$\log\ \phi(t)=-\frac{iEt}{\hbar}$$

or $$\phi(t)=\exp\left[\frac{-i\,E_n t}{\hbar}\right]$$

or in general for the n^th^ state, $$\phi_n(t)=\exp\left[\frac{-i\,E_n t}{\hbar}\right]$$

Hence the general solution is

$$\Psi(\mathrm{x,t}) = \sum_n a_n\,\Psi_n(x,t) = \sum_n a_n\,\psi_n(x)\exp\left[\frac{-iE_n t}{\hbar}\right] \tag{1.11}$$

(b) Stationary State Solutions

Consider the probability distribution function ΨΨ* for a system in the state represented by the wave function

$$\Psi\,(x, y, z, t) \quad = \sum_{n=1}^{\infty} a_n\, \psi_n\,(x, y, z) \exp\left[\frac{-iE_n t}{\hbar}\right] \tag{1.12}$$

Taking the complex conjugate

$$\Psi^*\,(x, y, z\,, t) \quad = \sum_{m} a_m{}^*\, \psi_m{}^*(x, y, z) \exp\left[\frac{iE_m t}{\hbar}\right] \tag{1.13}$$

Multiplying eqns. (1.12) and (1.13),

$$\Psi\Psi^* = \sum a_n\, a_m{}^* \psi_n(x,y,z)\psi_m{}^*(x,y,z) + \sum_m \sum_n{}' a_n a_m{}^* \psi_n(x,y,z)\psi_m{}^*(x,y,z) \exp\left\{\frac{i(E_m - E_n)t}{\hbar}\right\}$$

$\sum{}'$ indicates $m \neq n$

If a_n values are zero for all values except for one value of E_n then ΨΨ* will be independent of time and the state represented by wave function Ψ would be stationary. In this case the wave function is represented by

$$\Psi_n(x, y, z, t) = a_n \psi_n(x, y, z) \exp\left\{\frac{-i\,E_n\,t}{\hbar}\right\} \tag{1.14}$$

1.4 Physical significance of Ψ

The wave function is large where the particle is most likely to be and small elsewhere. The finite region in which the wave function ψ is appreciably different from zero is called a wave packet. According to Max Born, the absolute square of ψ(**r**,t), that is $|\Psi|^2$ gives the probability per unit volume of finding the particle at some position r at any time t. The probability of finding the particle in a volume element $d\tau$ is P(**r**,t) $d\tau$ = $|\psi(\mathbf{r},t)|^2\, d\tau$. The total probability of finding the particle in the whole region is unity.

$$\text{ie. } \iiint |\psi|^2\, d\tau = 1 \tag{1.15}$$

ψ satisfying this condition is said to be a normalised wave function.

(a) Limitations on ψ :

a) ψ must be finite for all values of x, y, z of the region

b) ψ must be single valued

c) ψ must be continuous in all regions

d) ψ is analytical i.e. it possesses continuous first order derivative

e) ψ vanishes at infinity space

1.5 Orthogonal, Normalised and Orthonormal wave functions

For any two wave function, ψ_1 (x) and ψ_2 (x) in the limit a to b, if the condition

$$\int_b^a \psi_2^*(x)\psi_1(x)\,dx = 0.$$

is satisfied then, then $\psi_1(x)$ and $\psi_2(x)$ are said to be mutually orthogonal wave functions

We know that the probability of finding a particle in the volume element dτ is given by ψψ* dτ or $|\psi|^2$ dτ. The total probability of finding the particle in the entire space is unity.

$$\text{i.e., } \int |\psi(r,t)|^2 d\tau = 1$$

where the integration extends over the entire space.

This can also be written as,

$$\int \psi(\mathbf{r},t)\psi^*(\mathbf{r},t)\,d\tau = 1$$

Any wave function satisfying the above condition is said to be normalized to unity or simply normalised. If ψ is not a normalised wave function, then it can be made normalised by multiplying it with a constant called normalisation constant (A).

To find the normalisation constant,

$$(A\psi)^* A\psi d\tau = |A|^2 \int \psi\psi^* d\tau = 1 \quad \text{or} \quad |A|^2 = \frac{1}{\int \psi\psi^* d\tau} \tag{1.16}$$

The functions which are orthogonal as well as normalised are called ortho-normal functions.

1.6 Pobability current density

If P(r) is the probability of finding a particle at a given point, then the probability of finding the particle in a volume V bounded by the surface area A is

$$\begin{aligned} P &= \int_V P(r)d\tau = \int_V \psi^*\psi d\tau \\ ie. \frac{dP}{dt} &= \frac{d}{dt}\int_V \psi^*\psi d\tau = \int_V \left(\psi\frac{d\psi^*}{dt} + \frac{d\psi}{dt}\psi^*\right)d\tau \end{aligned} \tag{1.17}$$

From Time dependent Schrodinger eqn.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{1.18}$$

The complex conjugate of the above eqn. is (1.19)

$$-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t}$$

Multiplying equations (1.18) by ψ^* and (1.19) by ψ and subtracting the two we get

$$\psi\frac{d\psi^*}{dt} + \frac{d\psi}{dt}\psi^* = -\frac{\hbar}{2im}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*)$$

Using this eqn. (1.17) can be written as

$$\frac{dP}{dt} = -\frac{\hbar}{2im}\int_V(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*)d\tau$$

ie. $\frac{dP}{dt} = -\frac{\hbar}{2im}\int_A(\psi^*\nabla\psi - \psi\nabla\psi^*)dA$ (volume integral is changed into surface integral)

If we define a new vector S such that,

$S(r,t) = \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*)$, then we can write

$$\begin{aligned} \frac{dP}{dt} &= -\int_A S.dA = -\text{div } S \\ or \quad \frac{dP}{dt} &+ \text{div } S = 0 \end{aligned} \tag{1.20}$$

This is analogous to the equation of continuity in hydrodynamics $\frac{\partial\rho}{\partial t} + div\ j = 0$. Here ρ is the fluid density and j is the current density. Thus we can define S is the probability current density

1.7 Expectation values of dynamical quantities

The average value or the expected value of any function *f(x)* is given by

$$< f >= \int \psi^* f(x) \psi dx \qquad (1.21)$$

Thus the expectation value is the mathematical expectation for the result of a single measurement or it is the average of the large number of measurements on independent systems. The expectation value of position vector **r** is given by

$$< \mathrm{r} > \int \psi^*(\mathrm{r},t)\, \mathrm{r}\, \psi(\mathrm{r},t)\, d\tau \qquad (1.22)$$

The expectation value of potential energy (V) is

$$< \mathrm{V} > \; = \int \psi^*(\mathrm{r},t)\, \mathrm{V}\, \psi(\mathrm{r},t)\, d\tau \qquad (1.23)$$

We can prove the classical equations are valid for the expectation values of the dynamical quantities, For example, consider the classical equation,

$$\mathrm{E} = \frac{p^2}{2m} + V$$

Considering expectation values throughout we get,

$$< \mathrm{E} > \; = < \frac{p^2}{2m} > + < V >$$

Operating on a wave function ψ gives

$$< \mathrm{E} > \psi \; = < \frac{p^2}{2m} > \psi \; + < V > \psi$$

Using the operator formalism

$\hat{E} \rightarrow i\hbar \frac{\partial}{\partial t}, \; \hat{p} \rightarrow -i\hbar\nabla$, we can write the above eqn. as

$$< i\hbar \frac{\partial}{\partial t} > \psi = < \frac{-\hbar^2}{2m} \nabla^2 > \psi + < V > \psi \qquad (1.24)$$

Multiply eqn. (1.24) on the left by ψ^*,

$$\psi^* < i\hbar \frac{\partial}{\partial t} > \psi = \psi^* < -\frac{\hbar^2}{2m} \nabla^2 > \psi + \psi^* < V > \psi \qquad (1.25)$$

This means the expectation value is obtained by corresponding operator acting on ψ and multiplied on the left by ψ^*. Therefore

$$< \mathrm{E} > \; = \int \psi^* i\hbar \frac{\partial \psi}{\partial t} d\tau ; \quad < p >= \int \psi^* (\, -i\hbar\nabla) \psi \;\; d\tau \qquad (1.26)$$

1.8 Ehrenfest Theorem (Newton's Law of motion)

Statement:

The average motion of a wave packet described by a wave function ψ agrees with the corresponding classical motion of the particle. That is,

$$\text{(a)} \qquad \frac{dr}{dt}=\frac{p}{m}$$

$$\text{(b)} \qquad \frac{dp}{dt}=-\nabla V \tag{1.27}$$

Proof:

The Schroedinger time dependent wave equation is written as

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi$$

$$or \qquad \frac{\partial\psi}{\partial t}=-\frac{\hbar}{2mi}\left[\nabla^2\psi-\frac{2m}{\hbar^2}V\psi\right] \tag{1.28}$$

Taking its complex conjugate,

$$\frac{\partial\psi*}{\partial t}=\frac{\hbar}{2mi}\left[\nabla^2\psi^*-\frac{2m}{\hbar^2}V\psi*\right] \tag{1.29}$$

For a normalized wave function, the expectation value of *x* is given by

$$<x>=\int_{-\infty}^{+\infty}\psi*x\psi\,d\tau \tag{1.30}$$

Differentiating w.r.t. *t*,

$$\frac{d<x>}{dt}=\int_{-\infty}^{+\infty}\frac{\partial\psi*}{\partial t}x\psi\,d\tau+\int_{-\infty}^{+\infty}\psi*x\frac{\partial\psi}{\partial t}d\tau \tag{1.31}$$

since dx/dt=0.

Substituting the value of $\frac{\partial\psi*}{\partial t}$ and $\frac{\partial\psi}{\partial t}$ from equation (1.28) and (1.29) into equation (1.31), we get,

$$\frac{d<x>}{dt}=\int_{-\infty}^{+\infty}\frac{\hbar}{2mi}\left(\nabla^2\psi*-\frac{2m}{\hbar^2}V\psi^*\right)x\psi\,d\tau-\int_{-\infty}^{+\infty}\psi^*x\frac{\hbar}{2mi}\left(\nabla^2\psi-\frac{2m}{\hbar^2}V\psi\right)d\tau$$

$$=\frac{\hbar}{2mi}\int_{-\infty}^{+\infty}\left(\nabla^2\psi^*\right)x\psi\,d\tau-\frac{\hbar}{2mi}\int_{-\infty}^{+\infty}\psi^*x\left(\nabla^2\psi\right)d\tau \tag{1.32}$$

The first integral on R.H.S. can be integrated by parts by taking $u=x\psi$ and $dv=\nabla^2\psi^*$

$$\int_{-\infty}^{+\infty}\left(\nabla^2\psi*\right)x\psi d\tau = \int_{-\infty}^{+\infty}\nabla.[(x\psi)(\nabla\psi*)]d\tau - \int_{-\infty}^{+\infty}\left(\nabla^2\psi*\right)\nabla(x\psi)d\tau \tag{1.33}$$

Using Gauss divergence theorem, the first term of the integral of R.H.S can be transformed to an integral over a surface at infinity and since the wave function vanishes at infinity, we have

$$\int_{-\infty}^{+\infty}\nabla.[(x\psi)(\nabla\psi*)]d\tau - \int_{-\infty}^{+\infty}(x\psi\nabla\psi*)dA = 0 \tag{1.34}$$

Thus from equation (1.33), we get

$$\int_{-\infty}^{+\infty}\left(\nabla^2\psi*\right)x\psi d\tau = \int_{-\infty}^{+\infty}\left(\nabla^2\psi*\right)\cdot\nabla(x\psi)d\tau \tag{1.35}$$

Integrating again equation (1.35) by parts and again the surface integral vanishes at infinity, we have

$$\int_{-\infty}^{+\infty}\left(\nabla^2\psi*\right)x\psi d\tau = \int_{-\infty}^{+\infty}\psi*\nabla^2(x\psi)d\tau \tag{1.36}$$

Using equation (1.36), equation (1.32) becomes

$$\begin{aligned}
\frac{d<x>}{dt} &= \frac{\hbar}{2mi}\int_{-\infty}^{+\infty}\psi*\nabla^2(x\psi)\,d\tau - \frac{\hbar}{2mi}\int_{-\infty}^{+\infty}\psi*x(\nabla^2\psi)\,d\tau \\
&= \frac{\hbar}{2mi}\int_{-\infty}^{+\infty}\psi*[\nabla^2(x\psi) - x\nabla^2\psi]\,d\tau \\
&= \frac{\hbar}{mi}\int_{-\infty}^{+\infty}\psi*\left[\frac{\partial\psi}{\partial x}\right]d\tau \qquad (1.37) \\
&= \frac{1}{m}\int_{-\infty}^{+\infty}\psi*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,d\tau \\
&= \frac{1}{m}<p_x>
\end{aligned}$$

Considering y and z components, we have

$$\frac{d<\mathbf{r}>}{dt} = \frac{1}{m}<p> \tag{1.38}$$

Differentiating once again the eqn. (1.37) and multiplying by *m*,

$$\frac{d<p_x>}{dt} = \frac{\hbar}{i}\frac{d}{dt}\int_{-\infty}^{+\infty}\psi*\frac{\partial\psi}{\partial x}d\tau = \frac{\hbar}{i}\int_{-\infty}^{+\infty}\frac{\partial\psi*}{\partial t}\frac{\partial\psi}{\partial x}d\tau + \frac{\hbar}{i}\int_{-\infty}^{+\infty}\psi^*\frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial t}\right)d\tau$$

$$=\frac{\hbar}{i}\int_{-\infty}^{+\infty}\frac{\hbar}{2mi}\left(\nabla^2\psi *-\frac{2m}{\hbar^2}V\psi *\right)\frac{\partial\psi}{\partial x}d\tau-\frac{\hbar}{i}\int_{-\infty}^{+\infty}\psi^*\frac{\hbar}{2mi}\left[\frac{\partial}{\partial x}\nabla^2\psi-\frac{2m}{\hbar^2}\frac{\partial}{\partial x}(V\psi)\right]d\tau$$

$$=\frac{-\hbar^2}{2m}\int_{-\infty}^{+\infty}\left[(\nabla^2\psi *)\frac{\partial\psi}{\partial x}-\psi *\nabla^2\left(\frac{\partial\psi}{\partial x}\right)+\psi *\frac{2m}{\hbar^2}\frac{\partial V}{\partial x}\psi\right]d\tau \qquad (1.39)$$

The first two terms cancel out and we get

$$\frac{d<p_x>}{dt}=-\int_{-\infty}^{+\infty}\psi *\left(\frac{\partial V}{\partial x}\right)\psi d\tau=<-\frac{\partial V}{\partial x}> \qquad (1.40)$$

Considering all other components, we get

$$\frac{d<p>}{dt}=-<\nabla V>=\text{F (force acting on the system)} \qquad (1.41)$$

This eqn. shows that the rate of change of momentum is equal to force, which is Newton's second law of motion.

1.9 Postulates of wave mechanics

Postulate:1

Quantum system is characterised by a wave function $\psi(r,t)$. It is a complex function of space and time and contains all possible informations about the system.

Postulate:2

The probability of observing a particle at time t within volume dτ is

$$dP(r,t)=\frac{1}{N}|\psi(r,t)|^2 d\tau \qquad (1.42)$$

Postulate:3

Any wave function $\psi(r,t)$ can be expanded interms of complete set of orthonormal functions as

$$\psi(r,t)=\sum_a C_a(t)\varphi_a(r) \qquad (1.43)$$

Postulate:4

Time evolution of a system described by the wave function $\psi(r,t)$ is given by the Schrodinger equation

$$i\hbar\frac{\partial\psi}{\partial t}=\frac{-\hbar^2}{2m}\nabla^2\psi+V\psi \tag{1.44}$$

1.10 Dirac's 'BRA' and 'KET' vectors : Dual Space

The quatum matrix theory can be put into compact form by making use of notations invented by Dirac. Accordingly each dynamical state may be represented by a certain type of vector known as ket vector or simply ket represented by the symbol $|>$, In order to distinguish the kets from each other, we complete each symbol by inserting a particular letter in the middle. For example $|a>$ denotes the ket vector corresponding to state a of the system (ψ_a in old notation)

The kets form a linear vector space and any linear combination of several ket vectors is also a ket vector. For example let us consider two kets $|a>$ and $|b>$ and two arbitrary complex numbers c_1 *and* c_2 the linear combination.

$$|v>=c_1\,|a>+c_2\,|b> \tag{1.45}$$

is also a vector of ket space.

Accordingly ket vectors may be multiplied by complex numbers and added together to give other ket vectors. The vectors of dual space are called bra vectors or simply bras and denote in general one of them by the symbol $<|$, the mirror image of the symbol for a ket vector. If one wants to specify a particular one of them by a label b, (say), it is written in the middle as $<b|$.

There exists one to one correspondence between the vectors of bra and ket spaces. Bra and ket thus associated by this one to one correspondence are said to be conjugate of each other and are labelled by the same indices. Thus the bra conjugate to ket $|a>$ is represented by the symbol $<a|$; subject to the conditions

$$|a>+|b>\longleftrightarrow<a|+<b|$$

and

$$c|a>\longleftrightarrow c^*<a|$$

The connection between dual spaces is given by defining the scalar product of a bra vector and a ket vector such that

$$< a \| b > = \left(\psi_a , \psi_b \right) = \int \psi_a^{\ *} \, \psi_b \, dq \Big)$$

We have the rules that any complete bracket expression denotes a number and any incomplete bracket expression denotes a vector of the bra or ket space according to whether it contains the first or second part of bracket. The first three (bra) and the last three (ket) letters of bracket provide the names for the two kinds of state vectors (bra and ket). The bra vector $<|$ is analogous to the complex conjugate (or hermitian adjoint) of the wave function of the system. Evidently we have

$$< a | b > = < b | a >^{*}$$

$$< a | \left\{ | b > + | b' > | \right\} = < a | b > + < a | b' >$$

$$< a | \left\{ c | b > \right\} = c < a | b >$$

where c is any number.

The bra conjugate to ket $| \upsilon > = c_1 | a > + | c_2 | b >$ is

$$< \upsilon | = c_1^{\ *} < a | + c_2^{\ *} | < b |$$

Thus the correspondence between the kets and bras is analogous to the correspondence between the wave functions of wave mechanics and their complex conjugates. We further note that if a ket vanishes, its conjugate bra also vanishes and vice – versa. A bra and a ket vectors are said to be orthogonal if their scalar product is zero. The length of a bra vector $< a |$ or of its conjugate imaginary ket vector $| a >$ is defined as the square root of the possible number $< a | a >$.

1.11 Hilbert Space

A set of n vectors a_i is said to be linearly independent if there exists no relation between them of the form

$$\sum_{i=1}^{n} c_i \, a_i = 0$$

except for $c_1 = c_2 = ... = c_n = 0.$ Otherwise such a relation will reduce the number of independent terms. If a_i and a_j are mutually orthogonal i.e., their scalar product denoted by (a_i, a_j) vanishes for $i \neq j,$ then a_i and a_j are linearly independent. In three dimensional space the maximum number of linearly independent vectors is obviously three. In general, any set of n-linearly independent vectors spans an n-dimensional linear space denoted by R_n. This purely abstract concept of n-dimensional space (n a finite real positive integer) indeed becomes essential in many problems in modern physics. A linear operator $\hat{P}$ of R_n transforms one vector u of R_n into another vector $\mathbf{v}$ of R_n

i.e., $$\hat{P}\,\mathbf{u} = \mathrm{v}.$$

A vector u_i which is carried over by a given operator $\hat{P}$. An operator of n-dimensional space R_n has in general n eigen values. If some of them coincide, the system is said to have degeneracy. All these notions can be carried out into a (complex) space with (countable) infinitely many dimensions $(n \to \infty)$. If one imposes restriction that the scalar product

$$|\left|\mathrm{u}\right|^2 = (\mathbf{u}, \mathbf{u}) = \sum_{i=1}^{\infty} u_i{}^2$$

exists, where $\mathbf{u} = (\mathrm{u}_1, \mathrm{u}_2 \ldots)$ is a sequence of real or complex scalars and is called a vector i.e., if all infinite series which occur and convergent, then the space is said to be Hilbert space.

In brief the vector space is said to be Hilbert space if it is complex and of countable infinite dimensions such that all infinite series occurring in it are convergent. In Quantum Mechanics we often deal with complex functions and the corresponding Hilbert space is that of quadratically integrable (complex) function in i variables $(q_1, q_2, \ldots . q_i)$

Let us now consider some properties of Hilbert space and some operations in it. The scalar product of two functions viz., $f(q_1, q_2, \ldots . q_i)$ and $g(q_1, q_2, \ldots . q_i)$ is defined by $(f(q_1, q_2, \ldots . q_i)\; g(q_1, q_2, \ldots . q_i)$

$$\int f^*(q_1, q_2, \ldots . q_i)\, g\; (q_1, q_2, \ldots . q_i)\, d\,q_1,\, dq_2, \ldots . dq_i$$

The condition (1.69) then becomes

$$\int |\;f\;|^2\, dq_1\;\; dq_2\;\; \ldots . dq_i\; = C \text{ exists}$$

which is true for wave function

Now the wave function are orthogonal when

$$\int f^*(q_1, q_2\;\; \ldots . q_i)\; g\; (q_1, q_2\;\; \ldots . q_i)\; dq_1\; dq_2\;\; \ldots . dq_i = 0$$

In Quantum Mechanics a state function ψ contains all the physically relevant information about a physical system at a given instant of time and is represented by a vector along a direction in the Hilbert space. If ψ represents a physical state, then ψ and a constant multiple of ψ both represent this state. Therefore the arbitrary representative vector of the ray is usually normalised to one.

The states specified by different functions, ψ_i (forming complete basic set) and represented by vectors along mutually perpendicular axes form a complete orthogonal system of coordinates axes in the Hilbert space. The completeness of the system means that any wave function associated with vector Ω in the Hilbert space can be represented as the vector-sum of its components along these axes i.e.,

$$\Omega = \sum_i b_i \, \psi_i$$

there being an axis for each ψ_i. Thus each b_i corresponds to the (complex) component of arbitrary vector along i-axis.

The multiplication of two finite matrices is defined as

$$(AB)_{mn} = \sum_i A_{mi} B_{in}$$

where m denotes the row and i the column of matrix A. This law may be extended to the matrices having infinite number of rows and columns in the Hilbert space. Then this multiplication is same as that obeyed by two operators. Hence any operator $\hat{A}$ can be associated a matrix A whose matrix elements are defined as

$$A\psi_m = \sum_n A_{mnm}\psi_n = \sum_n \psi_n \, A_{nm}$$

$$\text{where} \quad A_{nm} = \int \psi_n * A\psi_m \, dq = (\psi_n, \, A\psi_m)$$

with respect to a basic set of eigen functions ψ_n. As each integral has a certain numerical value, therefore

$$A_{nm} = \int \psi_n * A\psi_m \, dq = (\psi_n, \, A\psi_m)$$

gives a doubly infinite array of number i.e. a matrix. Now a matrix operating on a wave function (vectors) can be represented as a linear transformation in the Hilbert space .For example in the equation.

$$Af = g.$$

‘A’ transforms f into g where f and g are two wave functions (vectors) in the Hilbert space. Unless specified we consider only those eigen functions which are located in the Hilbert space. This imposes a restriction to discrete spectrum.

1.12 Hermitian operator

Operator A is said to be Hermitian if for two square integrable functions Φ and Ψ the following condition is satisfied.

$$<\Phi \,|\, A\Psi> = <A\Phi \,|\, \Psi>$$

Adjoint or Hermitian conjugate of an operator:

For an orbitrary operator A, we can define another operator A+ such that $<\Phi \,|\, A^{+}\Psi> = <A\Phi \,|\, \Psi>$. Then A^{+} is called the adjoint or Hermitian conjugate of A

(a) Properties of Hermitian operators:

(i) Product of two Hermitian operators is Hermitian, if and only if, they commute

Consider two Hermitian operators A and B. If they commute then we will show AB is hermitian. Let $\psi(x)$ and $\phi(x)$ are two functions. If A is hermitian, then we can write,

$$<\psi \,|\, AB \,|\, \phi> = \int <A\psi \,|\, B \,|\, \phi>$$

If B is also hermitian ,

$$<A\psi \,|\, B \,|\, \phi> = <BA\psi \,|\, \phi>$$

$$\therefore \quad <\psi \,|\, AB \,|\, \phi> = <BA\psi \,|\, \phi> \tag{1.46}$$

IF C=AB is hermitian then,

$$<\psi \,|\, AB \,|\, \phi> = <\psi \,|\, C \,|\, \phi> = <C\psi \,|\, \phi> = <AB\psi \,|\, \phi> \tag{1.47}$$

From eqns.(1.46) and (1.47), AB=BA. Thus AB is hermitian only if they commute.

(ii) Eigen values of hermitian operator are real:

Let $A|\psi_n> = a_n|\psi_n>$

Now, $<\psi_n|A|\psi_n> = a_n<\psi_n|\psi_n>$ (1.48)

Also $<A\psi_n|\psi_n> = a_n^*<\psi_n|\psi_n>$ (1.49)

If A is hermitian then $<\psi_n|A|\psi_n> = <A\psi_n|\psi_n>$. Using (1.48) and (1.49), we get

$$a_n = a_n^* \qquad (1.50)$$

Hence the eigen values of hermitian operators are real

(iii) Eigen functions of a hermitian operator corresponding to different eigen values are orthogonal to each other.

Let P be any Hermitian operator and ψ_1 *and* ψ_2 be any two eigen functions of P. If A and B are the two distinct eigen values of P corresponding to ψ_1 *and* ψ_2, then we can write

$$\begin{array}{l} P\psi_1 = A\psi_1 \\ P\psi_2 = B\psi_2 \end{array} \quad \text{or} \quad \begin{array}{l} P^*\psi_1^* = A^*\psi_1^* = A\psi_1^* \\ P^*\psi_2^* = B^*\psi_2^* = B\psi_2^* \end{array} \quad \text{since A and B are real.} \qquad (1.51)$$

From the general characteristics of the Hermitian operator P,

$$\int \psi_2^* P\psi_1 d\tau = \int P^*\psi_2^*\psi_1 d\tau \qquad (1.52)$$

Using eqn. (1.51),

$$\int \psi_2^* A\psi_1 d\tau = \int B\psi_2^*\psi_1 d\tau \quad \text{or} \quad A\int \psi_2^*\psi_1 d\tau = B\int \psi_2^*\psi_1 d\tau$$

or $(A-B)\int \psi_2^*\psi_1 d\tau = 0$

or $\int \psi_2^*\psi_1 d\tau = 0$ since $A \neq B$. Hence proved. (1.53)

1.13 Proof of Uncertainty principle for one-dimension Wave packet

The uncertainty in position along X - axis, by analogy with the standard deviation of statistics, may be defined as

$$\nabla x = \sqrt{<\{x - <x>\}^2>} \tag{1.54}$$

where $<x>$ is the expectation value of x. The probability of finding the particle between co-ordinates x and $x+dx$ is given by $\psi*(x)\psi(x)\,dx,$ so that expectation of average value of $x,$ for normalised function $\psi(x)$, is written as

$$<x> = \int \psi*(x)\; x\psi(x)\,dx, \tag{1.55}$$

Similarly the uncertainty in momentum is represented as

$$\nabla p = \sqrt{<\{p - <p>\}^2>} \tag{1.56}$$

where $<p>$ is the expectation value of momentum defined as

$$<p> = \int \psi*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx$$

$$-i\hbar\int \psi*\;\frac{\partial\psi}{\partial x}\psi\,dx \tag{1.57}$$

Let us choose $<x> = <p> = 0.$

Now consider the integral

$$i\hbar\int\psi*\frac{d}{dx}(x\psi)dx$$

Integrating by pars,

$$i\hbar\int\psi*\frac{d}{dx}(x\psi)dx \;=\; i\hbar[\psi x\psi*]_{-\infty}^{+\infty} - i\hbar\int_{-\infty}^{+\infty}x\psi\frac{d\psi*}{dx}dx$$

$$= \;0 - i\hbar\int_{-\infty}^{+\infty}x\psi\frac{d\psi*}{dx}dx$$ since ψ vanishes at infinity.

But $\int\psi*\psi\,dx = 1$ for normalised wave function.

$$\therefore\;\int i\hbar\,\frac{d\psi*}{dx}x\psi\,dx = -\,i\hbar\int\psi*\;\frac{d\psi}{dx}x\,dx - i\hbar$$

or $$i\hbar\int\;\frac{d\psi*}{dx}x\psi\,dx + \;i\hbar\int\psi*\;\frac{d\psi}{dx}x\,dx = -i\hbar$$

As the right hand side is imaginary, therefore it must be equal to the imaginary part of left hand side i.e., $2i$ imaginary part of $\int i\hbar \ \frac{d\psi *}{dx} x\psi \, dx = -i\hbar$ (1.58)

Taking modulus of both sides and then squaring we get

$$4\left|\text{Imaginary Part of } \int i\hbar \ \frac{d\psi *}{dx} x\psi \, dx\right|^2 = \hbar^2 \tag{1.59}$$

But we have

$$\left|\int i\hbar \ \frac{d\psi *}{dx} x\psi \, dx \geq \text{imaginary part of } \int i\hbar \ \frac{d\psi *}{dx} x\psi \, dx\right|$$

Equation (1.59) can now be written as

$$4\left|\int i\hbar \ \frac{d\psi *}{dx} x\psi \, dx\right|^2 \geq \hbar^2 \tag{1.60}$$

According to Schwarz inequality, we have

$$\left|\int f * \varphi \, dx\right|^2 \leq \int f * f \, dx \int \varphi\varphi * dx \tag{1.61}$$

So that the left hand side of equation (1.59) (using $f * = i\hbar(d\psi */dx)$ and $\phi = x\psi$ can be written as

$$4\left|\int i\hbar \ \frac{d\psi *}{dx} x\psi \, dx\right|^2 \leq 4\int i\hbar \ \frac{d\psi *}{dx}\left(-i\hbar\frac{d\psi}{dx}\right)dx \int x\psi \, x\psi * dx.$$

Therefore equation (1.59) itself can be written as

$$4\int i\hbar \ \frac{d\psi *}{dx}\left(-i\hbar\frac{d\psi}{dx}\right)dx \int \psi * x^2 \psi \, dx \geq \hbar^2.$$

or $$\left|\int -i\hbar \ \frac{d\psi}{dx}\right|^2 \int \psi * x^2 \psi \, dx \geq \frac{\hbar^2}{4}.$$

or $$< p^2 > \ < x^2 > \ \geq \frac{\hbar^2}{4}. \tag{1.62}$$

Since $< x^2 > = \psi * x^2 \psi \, dx$

and $< p^2 > = \int \left|-i\hbar\frac{d\psi}{dx}\right|^2 dx.$

Applying conditions expressed by (1.58) to equations (1.54) and (1.56), we get

and
$$\left.\begin{aligned}(\Delta x)^{2} &= <x^{2}> \\ (\Delta p)^{2} &= <p^{2}>,\end{aligned}\right\} \tag{1.63}$$

Using (1.63), equation (1.62) becomes

$$(\Delta x)^{2}(\Delta p)^{2} \geq \hbar^{2}\big/4$$

or
$$\Delta x\Delta p \geq \frac{\hbar}{2} \tag{1.64}$$

(a) Commutation Relation between Position and Momentum :

(i) Let us find the commutation relation between x and p_x.

In operator formalism

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

Consider the operation of $[x, p_x]$ on a function $\psi(x,)$

i.e.,
$$[\hat{x}\ \hat{p}_x]\psi(x) = (\hat{x}\ \hat{p}_x - \ \hat{p}_x\hat{x})\psi(x) \tag{1.65}$$

We have
$$\hat{x}\ p_x\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x}$$

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

$\therefore$ Equation (1.65) gives

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

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

i.e.
$$[\hat{x}\ \hat{p}_x] = i\hbar \tag{1.66}$$

UNIT II

2.1 Linear Harmonic oscillator

In the case of a liner harmonic oscillator the force F = - $K\,x$ can be represented by the potential energy function $V(x)=1/2Kx^2$

From the Schroedinger equation,

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left(E-\frac{1}{2}Kx^2\right)\psi=0. \qquad (2.1)$$

Introducing a variable ξ = $\alpha\,x$, where α is constant, we can write,

$$\frac{d\psi}{dx}=\frac{d\psi}{d\xi}\frac{d\xi}{dx}=\frac{d\psi}{d\xi}\alpha$$

and
$$\frac{d^2\psi}{dx^2}=\frac{d}{dx}\left(\frac{d\psi}{d\xi}.\alpha\right)=\frac{d}{d\xi}.\frac{d\xi}{dx}\left(\frac{d\psi}{d\xi}.\alpha\right)=\alpha^2\frac{d^2\psi}{d\xi^2}$$

Therefore eq. (2.1) becomes

$$\alpha^2\frac{d^2\psi}{d\xi^2}+\left[\frac{2mE}{\hbar^2}-\frac{mK}{\hbar^2}\frac{\xi^2}{\alpha^2}\right]\psi=0. \qquad (2.2)$$

or
$$\frac{d^2\psi}{d\xi^2}=\left[\frac{2mE}{\hbar^2\alpha^2}-\frac{mK\xi^2}{\alpha^4\hbar^2}\right]\psi=0. \qquad (2.3)$$

Let us choose α such that $\frac{mK}{\hbar^2\alpha^4}=1$ and $\lambda=\frac{2mE}{\hbar^2\alpha^2}$

Therefore equation (2.3) assumes the dimensionless form

$$\frac{d^2\psi}{d\xi^2}=+(\lambda-\xi^2)\psi=0. \qquad (2.4)$$

Let the solution is of the form

$$\psi(\xi)=H(\xi)e^{-\xi^2/2} \qquad (2.5)$$

where H(ξ) is a polynomial of finite order in ξ. If we consider the positive sign in the exponent, then ψ will diverge as $\xi\to\infty$. From eqn. (2.5)

$$\frac{d\psi}{d\xi}=H'(\xi)\exp\left[\frac{-\xi^2}{2}\right]-H(\xi)\,\xi\exp\left[\frac{-\xi^2}{2}\right]$$

and
$$\frac{d^2\psi}{d\xi^2}=H''(\xi)\exp\left[\frac{-\xi^2}{2}\right]-H'(\xi)\,\xi\exp\left[\frac{-\xi^2}{2}\right]$$

$$-H(\xi)\exp\left[\frac{-\xi^2}{2}\right]-\xi H'(\xi)\exp\left[\frac{-\xi^2}{2}\right]+\xi^2H(\xi)\exp\left[\frac{-\xi^2}{2}\right]$$

$$= -H''(\xi)\exp\left[\frac{-\xi^2}{2}\right] - 2\xi H'(\xi)\exp\left[\frac{-\xi^2}{2}\right] + (\xi^2 - 1)H(\xi)\exp\left[\frac{-\xi^2}{2}\right]$$

Substituting the value of $\psi(\xi)$ and $\frac{d^2\psi}{d\xi^2}$ in equation (2.4) we get

$$\exp\left[\frac{-\xi^2}{2}\right]\left\{H''(\xi) - 2\xi H'(\xi) + \xi^2 H(\xi) - H(\xi) + (\lambda - \xi^2)H(\xi)\right\} = 0$$

or

$$H''(\xi) - 2\xi H'(\xi) + (\lambda - 1)H(\xi) = 0 \qquad (2.6)$$

Energy Levels.

Using power series, we can solve equation (2.6)

Let

$$H(\xi) = \xi^s(a_0 + a_1\xi + a_2\xi^2 + ...),$$

$a_0 \neq 0$, $s \geq 0$

$$= \xi^s \sum_{v=0}^{\infty} a_v\, \xi^v = \sum_{v=0}^{\infty} a_v\, \xi^{s+v}$$

On differentiation, $\frac{dH}{d\xi} = \sum_v a_v(s+v)\,\xi^{s+v-1}$

and $\frac{d^2H}{d\xi^2} = \sum_v a_v(s+v)(s+v-1)\,\xi^{s+v-2}$

Substituting these values in equation (2.6), we get,

$$\sum_v a_v(s+v)(s+v-1)\,\xi^{s+v-2} - 2\xi\sum_v a_v(s+v)\,\xi^{s+v-1} + (\lambda - 1)\sum_v a_v\,\xi^{s+v} = 0$$

or

$$\sum_v a_v(s+v)(s+v-1)\,\xi^{s+v-2} - 2\sum_v a_v(s+v)\,\xi^{s+v} + (\lambda - 1)\sum_v a_v\,\xi^{s+v} = 0 \qquad (2.7)$$

For H(ξ) to be a solution for all values of ξ, the coefficient of the individual powers of ξ must vanish separately, i.e., equating to zero the coefficients of various powers of ξ we get

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

$$(s+1)\,(s)\,a_1 = 0$$

$$(s+2)\,(s+1)\,a_2 - (2s + 1 - \lambda)\,a_0 = 0$$

$$(s+3)\,(s+2)\,a_3 - (2s + 3 - \lambda)\,a_1 = 0$$

... ...

... ...

$$(s+v+2)\,(s+v+1)\,a_{v+2} - (2s + 2v + 1 - \lambda)\,a_v = 0 \qquad (2.8)$$

From these expressions we can write,

$$a_{v+2} = \frac{2s + 2v + 1 - \lambda}{(s+v+1)(s+v+2)}\,a_v$$

(2.9)

where v is an integer. Since a_0 cannot be equal to zero, from the first of equations (2.8), $s = 0$ or 1. If a_0 is equal to zero, only odd powers appear. With a_1 equals to zero, the series contains even powers only. If we examine the convergence of the power series solution defined by equation (2.9), we find that as $\nu \rightarrow \infty$, $(a_{v+2})/a_v \rightarrow 2/v$, so that the series converges for all finite values of ξ.

Considering the series expansion of $e^{+\xi^2}$, we have

$$e^{+\xi^2} = 1+\xi^2+\frac{\xi^4}{2!}+\frac{\xi^6}{3!}+...+\frac{\xi^v}{(v/2)!}+\frac{\xi^{v+2}}{(v/2+1)!}+..$$

$$= b_0 + b_2\,\xi^2 + b_4\,\xi^4 + b_v\,\xi^v + b_{v+2}\xi^{v+2} + ...$$

$$\frac{b_{v+2}}{b_v}=\frac{\frac{1}{(v/2+1)!}}{\frac{1}{(v/2\ )!}}=\frac{2}{2+v} \quad \text{or} \quad \lim_{v\rightarrow\infty}\ \frac{b_{v+2}}{b_v}=\frac{2}{v}$$

This shows that H(ξ) diverges approximately as $e^{\xi 2}$ and the product $H(\xi)e^{-\xi^2/2}$ will behave like $e^{+\xi^{2/2}}$ in this region which tends to $\infty, \quad as\ \xi \rightarrow \infty$.So this is not an acceptable solution. This situation can be avoided by coosing λ in such a way that the power series for H(ξ) cuts off at some term, making H (ξ) a polynomial.

From eqn (2.9), by making

$$\lambda = 2s + 2v + 1.$$

we can make the series cut off. The index s can still be either 0 or 1, and corresponding to these values, λ is equal to $2v + 1$ or $2v+3$ where $2v$ is an even integer. Or,

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

Then $$\frac{2E_n}{\hbar}\sqrt{\frac{m}{K}} = (2n+1)$$

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

n = 0,1,2... ...(2.9A)

where $\omega_c = \sqrt{\frac{K}{m}}$ is the classical angular frequency of the oscillator.

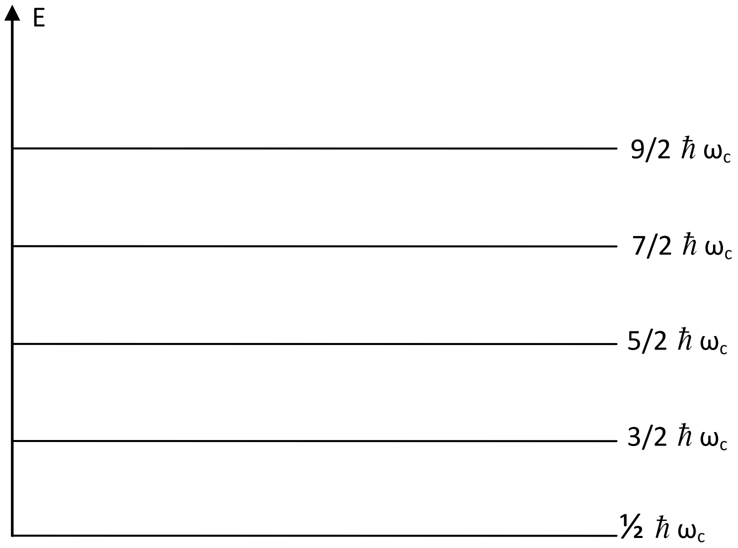

Fig. 2.5

Zero point energy. The energy levels given by equations (2.9A) are discrete and have equal spacings. When n=0, the finite value of lowest energy or ground state energy is (1/2) $\hbar\omega_c$. Hence zero point energy is given by,

$$E_0 = \frac{1}{2}\hbar\omega_c$$

and all higher energy levels are separated by an amount equal to $\hbar\omega_c$. Zero point energy is characteristic of quantum mechanics and is related to the uncertainty principle.

2.2 Infinitely deep potential well or particle in one-dimensional box

Consider a square potential well with infinitely high sides, as indicated in figure (2.1). The particle is bounded by impenetrable rigid walls of width 2a as shown.The potential of the well is represented by,

$V(x) = 0$ for $-a < x < a$ and

$V(x) = \pm\infty$, for $|x| \geq a$

The boundary condition on the wavefunction is, it vanishes at the wall. That is

$$\psi_{x=a} = \psi_{x=-a} = 0$$

The wave equation for $|x| < a$ is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \qquad [\because V = 0]$$

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \quad where \quad \alpha^2 = \frac{2mE}{\hbar^2}$$

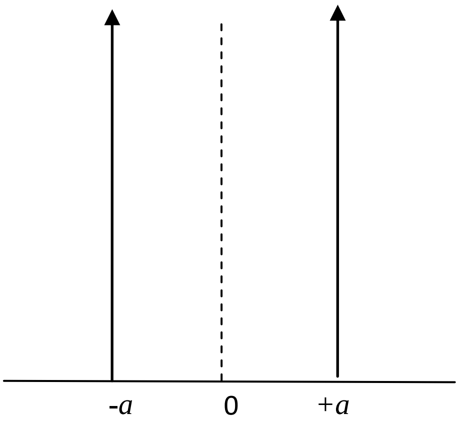

Fig.2.1

The general solution of this eqn can be written as,

$$\psi = A\cos\alpha x + B\sin\alpha x. \quad (2.10)$$

Applying the boundary conditions,

$\psi = 0$ at $x = a$ and $\psi = 0$ at $x = -a$

We get, $A\cos\alpha a + B\sin\alpha a = 0.$ (2.11)

and $A\cos\alpha a - B\sin\alpha a = 0.$ (2.12)

Adding and subtracting equations (2.11) and (2.12), we get,

$$2A\cos\alpha a = 0 \qquad \text{and} \qquad 2B\sin\alpha a = 0.$$

There are two possible solutions namely,

(i) A = 0 or cos α*a* = 0.

(ii) B = 0 or sin α*a* = 0.

For sin α*a* = 0, α*a* = π, 2π, 3π .... n π/2 where n is even

And for cos α*a* =0, α*a* = π/2, 3π/2, ...= nπ/2, where *n* is an odd integer.

We have, $$\alpha^2 = \frac{2mE}{\hbar^2} \quad \text{or} \quad E = \frac{\alpha^2\hbar^2}{2m} \qquad (2.13)$$

or in general, $$E_n = \frac{n^2\pi^2\hbar^2}{8ma^2} \quad \text{since, } \alpha = n\pi/2a. \qquad (2.14)$$

There are an infinite sequence of discrete energy levels that correspond to all positive integral values of *n*.

Wave function. The general form of wave functions may be written as

$$\psi_n = A\cos\frac{n\pi x}{2a} \qquad \text{when } n \text{ is odd} \qquad (2.15)$$

$$\psi_n = B\sin\frac{n\pi x}{2a} \qquad \text{when } n \text{ is even} \qquad (2.16)$$

To normalise the wave function ψ_n :

From eqn (2.15),

$$|\psi_n|^2 = \int_{-a}^{a} A^2\cos^2\frac{n\pi x}{2a}\,dx = 1$$

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

On simplifying the above integral we get,

$$A^2 = \frac{1}{a} \quad or \quad A = \sqrt{(1/a)}.$$

Similarly we can show, $$B = \sqrt{(1/a)}.$$

Hence the normalized wavefunctions are,

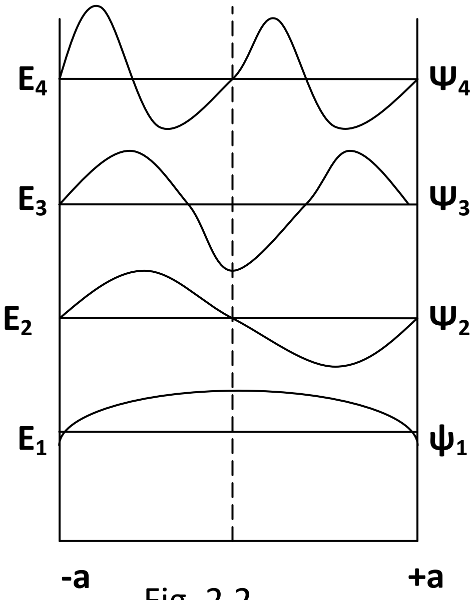

Fig. 2.2

$$\psi_n = \frac{1}{\sqrt{a}} \cos \frac{n\pi x}{2a} \qquad (n = 1, 3, 5,...). \qquad (2.17)$$

$$\psi_n = \frac{1}{\sqrt{a}} \sin \frac{n\pi x}{2a} \qquad (n = 2, 4, 6,...). \qquad (2.18)$$

The energy levels and wavefunctions are shown in fig. (2.2) The successive energy states differ by half wavelength. The lowest energy level has only half wavelength. The points between $a \leq x \leq -a$, where the wave function vanishes are called a *node.* For a particular energy state, characterised by the quantum number *n*, the number of intermediate nodes is *(n*-1). Wavefunctions $\psi_n(x)$ for odd *n* are even functions of *x*. Such functions are said to have an even parity (symmetric). Similiary $\psi_n(x)$ for even n are odd functions (antisymmetric) and have an odd parity.

2.3 Energy levels for One – Dimensional Square Well Potential of finite depth (bound states)

-Let us consider a simple one – dimensional well of finite depth. Let, the potential be equal to zero within a distance *a* on either side of the origin, and equal to +V elsewhere, a shown in Fig. (2.3).

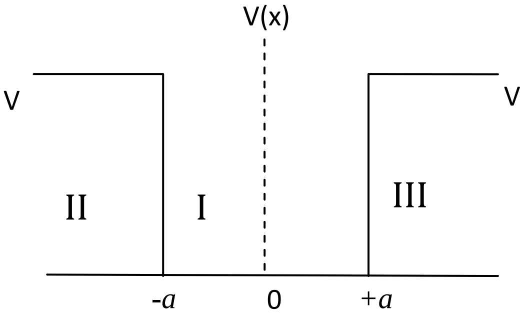

Fig. 2.3

$$V = \begin{cases} 0 & \text{for} -a < x < a \\ V & \text{for} \ |x| > a \end{cases}$$

In the region where $|x| < a$, the Schrodinger wave equation is

$$\frac{d^2\psi_1}{dx^2} + \frac{2m}{\hbar^2} E\psi_1 = 0 \qquad (\because V = 0)$$

or

$$\frac{d^2\psi_1}{dx^2} + \alpha^2\psi_1 = 0$$

where $\alpha^2 = \left(\frac{2mE}{\hbar^2}\right)$

The general solution of this equation is,

$$\psi_1 = A \cos \alpha x + B \sin \alpha x$$

Similarly, the wave equation outside this region is

$$\frac{d^2\psi_2}{dx^2} - \frac{2m}{\hbar^2}(V-E)\psi_2 = 0$$

or $$\frac{d^2\psi_2}{dx^2} - \beta^2\psi_2 = 0.$$ Where $\beta^2 = \left[\frac{2m}{\hbar^2}(V-E)\right]$

This has the general solution

$$\psi_2 = C\, e^{\beta x} + D\, e^{-\beta x}$$

The boundary conditions at $x = +\infty$ requires that

for $x>a$, $C = 0$

and for $x<-a$ $D= 0$

Thus we have wave functions in the three regions as,

$$\psi_1 = A\cos\alpha x + B\sin\alpha x \qquad -a < x < a, \qquad (2.19)$$

$$\psi_2 = C\, e^{\beta x} \qquad x < -a \qquad (2.20)$$

$$\psi_3 = D\, e^{-\beta x} \qquad x > a \qquad (2.21)$$

Considering the equations (2.19) and (2.21) and applying the boundary condition $(\psi_1)_{x=a} = (\psi_3)_{x=a}$

We have

$$A\cos\alpha a + B\sin\alpha a = D\, e^{-\beta a} \qquad (2.22)$$

and applying the other boundary condition

$$\left(\frac{d\psi_1}{dx}\right)_{x=a} = \left(\frac{d\psi_3}{dx}\right)_{x=a}$$

$$-A\,\alpha\sin\alpha a + B\,\alpha\cos\alpha a = -\beta D\, e^{-\beta a} \qquad (2.23)$$

Again at $x = -a$ and by applying $(\psi_1)_{x=-a} = (\psi_2)_{x=-a}$ we have

$$A\cos\alpha a - B\sin\alpha a = C\, e^{-\beta a} \qquad (2.24)$$

And by applying $\left(\frac{d\psi_1}{dx}\right)_{x=-a} = \left(\frac{d\psi_2}{dx}\right)_{x=-a}$ we have,

$$A\alpha\sin\alpha a + B\alpha\cos\alpha a = C\beta e^{-\beta a} \qquad (2.24A)$$

Adding equations (2.22) and (2.24) we have,

$$2\,A\ \cos \alpha a = (C + D)\, e^{-\beta a} \tag{2.25}$$

And subtracting eqns. (2.22) and (2.24) we have

$$2\,B\ \sin \alpha a = (D - C)\, e^{-\beta a} \tag{2.26}$$

Similarly from equation (2.23) and (2.24A) we have,

$$2\,B\,\alpha\ \cos \alpha a = (C - D)\, \beta e^{-\beta a} \tag{2.27}$$

$$2\,A\,\alpha \sin \alpha a = (C + D)\, \beta e^{-\beta a} \tag{2.28}$$

Dividing eqn. (2.28) by (2.25) gives

$$\alpha \tan \alpha a = \beta\ , \tag{2.29}$$

and from eqns. (2.27) and (2.26)

$$\alpha \cot \alpha a = -\beta\ , \tag{2.30}$$

A solution of the equations (2.29) and (2.30) is obtained graphically.

Now consider equation (2.29) and let $\xi = \alpha a$ and $\eta = \beta a$, then

$$\xi \tan \xi = \eta$$

and $\xi^2 + \eta^2 = \alpha^2 a^2 + \beta^2 a^2 = a^2 [\alpha^2 + \beta^2] = \frac{2mVa^2}{\hbar^2}$ = constant for a given system.

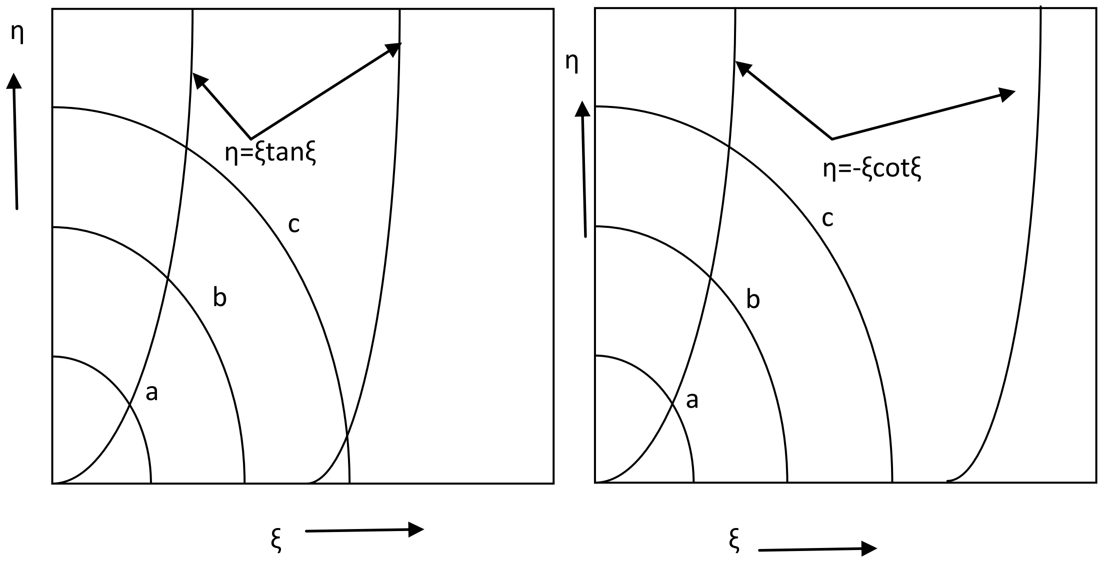

Fig. 2.4

Since ξ and η are positive values, the energy levels are found from the intersection in the first quadrant of the curve of ξ tan ξ against η with the circle of known radius $\left\{\frac{2mVa^2}{\hbar^2}\right\}^{1/2}$

Curves for three values of Va^2 are shown in figure (2.4).

The product Va^2 is a measure of the strength of the potential well – which binds the particle to the well. In other words, the greater the depth (V) and breath (a) of a well, the greater the number of bound states and greater the probability of retaining a particle in the well.

The first three increasing values of Va^2 give altogether one, two and three energy levels, respectively. As a special case let V approaches infinity. For the first group of solutions,

$$\tan \alpha a = \beta/\alpha \to \infty$$

$$\alpha a = (2n + 1)\, \pi/2$$

The characteristic energy values are

$$E_n = \frac{(2n+1)^2\, \pi^2 \hbar^2}{8ma^2} \qquad \text{with n = 0,1,2 ...} \qquad (2.31)$$

For the second group of solutions,

$$\tan \alpha a = -\ \frac{\alpha}{\beta} \to 0.$$

or

$$\alpha a = n\pi$$

The characteristic energy values are

$$E_n = \frac{(2n)^2\, \pi^2 \hbar^2}{8ma^2} \qquad \text{n = 0, 1, 2...} \qquad (2.31A)$$

2.4 Rectangular potential barrier

Let us consider the one-dimensional problem where the potential is defined as in fig.2.5.

$$\left\{ \begin{aligned} V(x) &= 0 \quad for \quad x < 0 \\ &= V_0 \, for \; 0 < x < a \\ &= 0 \; for \; x > a \end{aligned} \right\} \qquad (2.31)$$

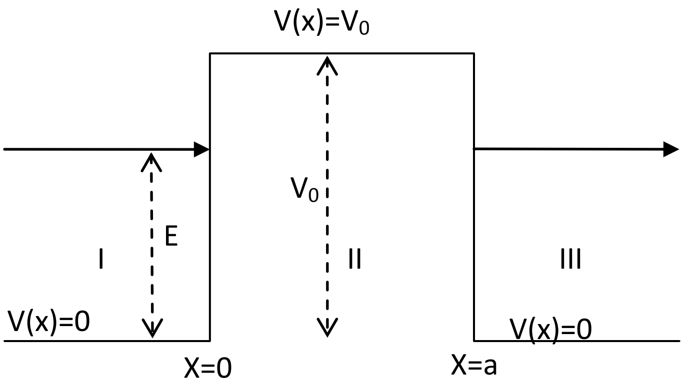

Fig. 2.5

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 $E > V_0$ classical mechanics predicts 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.

The Schroedinger equation for region-I is

$$\frac{\partial^2 \psi_1}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_1 = 0 \text{ (since } V = 0). \tag{2.32}$$

The Schroedinger equation for II region is

$$\frac{\partial^2 \psi_2}{\partial x^2} + \frac{2m}{\hbar^2} (E - V_0)\psi_2 = 0. \tag{2.33}$$

The Schroedinger equation for III region is

$$\frac{\partial^2 \psi_3}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_3 = 0. \tag{2.34}$$

Here ψ_1, ψ_2 and ψ_3 are the wave-functions for I, II and III regions respectively.

The general solutions of equations (2.32) (2.33) and (2.34) may be written as

$$\psi_1 = A_1 e^{ip_1 x/\hbar} + B_1 e^{-ip_1 x/\hbar} \tag{2.35}$$

$$\psi_2 = A_2 e^{ip_2 x/\hbar} + B_2 e^{-ip_2 x/\hbar} \tag{2.36}$$

$$\psi_3 = A_3 e^{ip_1 x/\hbar} + B_3 e^{-ip_1 x/\hbar} \tag{2.37}$$

where p_1 and p_2,are the momenta of particle in the corresponding regions, which are given by

$$\left\{ \begin{array}{c} P_1 = \sqrt{2mE} \\ p_2 = \sqrt{2m(E - v_0)} \end{array} \right\} \tag{2.38}$$

A_1, B_1, A_2, B_2 and B_3 are constants to be determined by boundary conditions.

In equation (2.35) 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 (2.36), the first term represents the wave travelling along (+) ve X-axis in the II region, i.e., the wave transmitted at $x = 0$ and second term represents the wave travelling along (-) ve X-axis in the II region, i.e., the wave reflected at $x = a$.

In equation (2.37) the first term represents the wave travelling along (+)ve X-axis in the III region, i.e., the wave transmitted $x = a$ and the second term represents the wave travelling along (-)ve X-axis in the III region; but no wave travels back from infinity in III region. Consequently $B_3 = 0$, so that the solution of equation (2.34), i.e., equation (2.37) can be written as

$$\psi_3 = A_3 e^{ip_1 x/\hbar} \tag{2.39}$$

For the 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.,

$$\left\{\begin{array}{l} \psi_1 = \psi_2 \quad at \;\; x=0 \quad ....(\;A\;) \\ \psi_2 = \psi_3 \quad at \;\; x=a \quad ....(\;B \end{array}\right\} \tag{2.40}$$

The other condition is $\partial\psi/\partial x$ must be continuous at the boundaries i.e.,

$$\left\{\begin{array}{l} \dfrac{\partial\psi_1}{\partial x} = \dfrac{\partial\psi_2}{\partial x} at\, x=0 \quad ....(A) \\ \dfrac{\partial\psi_2}{\partial x} = \dfrac{\partial\psi_3}{\partial x} at\, x=a \quad ....(B) \end{array}\right\} \tag{2.41}$$

Applying boundary condition (2.40A) to equations (2.35) and (2.36), we have

$$A_1 + B_1 = A_2 + B_2 \tag{2.42}$$

Applying boundary condition (2.40B) to equations (2.36) and (2.39), we get

$$A_2 e^{ip_2 a/\hbar} + B_2 e^{-ip_2 a/\hbar} = A_3 e^{ip_1 a/\hbar} \tag{2.43}$$

Differentiating equations (2.35), (2.36) and (2.39), we get

$$\frac{\partial \psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[A_1 e^{ip_1 x/\hbar} + B_1 e^{-ip_1 x/\hbar}\right] \tag{2.44}$$

$$\frac{\partial \psi_2}{\partial x} = \frac{ip_2}{\hbar}\left[A_2 e^{ip_2 x/\hbar} + B_2 e^{-ip_2 x/\hbar}\right] \tag{2.45}$$

$$\frac{\partial \psi_3}{\partial x} = \frac{ip_1}{\hbar} A_3 e^{ip_1 x/\hbar} \tag{2.46}$$

Applying boundary conditions (2.41) to these equations, we get

$$p_1[A_1 - B_1] = p_2[A_2 - B_2]$$

and $$p_2\left[A_2 e^{ip_2 a/\hbar} - B_2 e^{-ip_2 a/\hbar}\right] = p_1\left[A_3 e^{ip_1 a/\hbar}\right]$$

or $$A_1 - B_1 = \frac{p_2}{p_1}(A_2 - B_2) \tag{2.47}$$

$$\left[A_2 e^{ip_2 a/\hbar} - B_2 e^{-ip_2 a/\hbar}\right] = \frac{p_1}{p_2} A_3 e^{ip_1 a/\hbar} \tag{2.48}$$

Solving (2.42) and (2.47) for A_1 and B_1, we get

$$A_1 = \frac{A_2}{2}\left(1 + \frac{p_2}{p_1}\right) + \frac{B_2}{2}\left(1 - \frac{p_2}{p_1}\right) \tag{2.49}$$

$$B_1 = \frac{A_2}{2}\left(1 - \frac{p_2}{p_1}\right) + \frac{B_2}{2}\left(1 + \frac{p_2}{p_1}\right) \tag{2.50}$$

Solving (2.43) and (2.48) for A_2 and B_2, we get

$$A_2 = \frac{A_3}{2}\left(1 + \frac{p_1}{p_2}\right) e^{i(p_1 - p_2)a/\hbar} \tag{2.51}$$

$$B_2 = \frac{A_3}{2}\left(1 - \frac{p_1}{p_2}\right) e^{i(p_1 + p_2)a/\hbar} \tag{2.52}$$

Substituting values of A_2 and B_2 from these equations in (2.49) and (2.50), we get

$$A_1 = \frac{A_3}{4} e^{ip_1 a/\hbar}\left[\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{-p_2 a/\hbar}\right] \qquad (2.53A)$$

$$B_1 = \frac{A_3}{4} e^{ip_1 a/\hbar}\left[\left(1-\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1+\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{-p_2 a/\hbar}\right] \qquad (2.53B)$$

Equation (2.53A) may be written as

$$\frac{A_3}{A_1} = \frac{4e^{-ip_1 a/\hbar}}{\left\{\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2 a/\hbar}\right\}}$$

$$= \frac{4p_1 p_2 e^{-ip_1 a/\hbar}}{(p_1+p_2)^2 e^{-ip_2 a/\hbar} - (p_1-p_2)^2 e^{-ip_2 a/\hbar}}$$

$$= \frac{4p_1 p_2 e^{-ip_1 a/\hbar}}{(p_1^2 + p_2^2)(e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar}) + 2p_1 p_2 (e^{-ip_2 a/\hbar} + e^{ip_2 a/\hbar})}$$

$$= \frac{2p_1 p_2 e^{-ip_1 a/\hbar}}{(p_1^2 + p_2^2)(\frac{e^{-ip_2 a/\hbar} - e^{-ip_2 a/\hbar}}{2}) + 2p_1 p_2 \frac{(e^{-ip_2 a/\hbar} + e^{-ip_2 a/\hbar})}{2}}$$

Dividing equation (2.53B) by (2.53A), we get,

$$\frac{B_1}{A_1} = \frac{\left(1-\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1+\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2 a/\hbar}}{\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2 a/\hbar}}$$

$$= \frac{(p_1^2 - p_2^2)(e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar})}{(p_1 + p_2)^2 (e^{-ip_2 a/\hbar} - (p_1 - p_2)^2 e^{ip_2 a/\hbar}}$$

$$= \frac{(p_1^2 - p_2^2)(e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar})}{(p_1^2 + p_2^2)(e^{ip_2 a/\hbar} - e^{ip_2 a/\hbar}) + 2p_1 p_2 (e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar})}$$

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

$$\frac{A_3}{A_1} = \frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1^2+p_2^2)\left\{-2i\sin\frac{p_2a}{\hbar}\right\}+2p_1p_2\left(-2\cos\frac{p_2a}{\hbar}\right)}$$

$$= \frac{2p_1p_2 \quad e^{-ip_1a/\hbar}}{i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}+2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$$\frac{A_3*}{A_1*} = \frac{2p_1p_2e^{\mathbf{ip_1}a/\hbar}}{-i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}+2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$\therefore$ Transmission coefficient $\mathrm{T} = \dfrac{\text{Transmitted flux}}{\text{Incident flux}}$

$$= \frac{A_3A_3^*p_1/m}{A_1A_1^*p_1/m} = \left(\frac{A_3}{A_1}\right)\left(\frac{A_3^*}{A_1^*}\right)$$

$$= \frac{4p_1^2+p_2^2}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\cos^2\frac{p_2a}{\hbar}}$$

$$= \frac{4p_1^2p_2^2}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\left(1-\sin^2\frac{p_2a}{\hbar}\right)}$$

$$= \frac{4p_1^2+p_2^2}{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2}$$

Reflection Coefficient

$$\frac{B_1}{A_1}=\frac{(p_1^2-p_2^2)\left(-2i\sin\frac{p_2a}{\hbar}\right)}{(p_1^2+p_2^2)\left(-2i\sin\frac{p_2a}{\hbar}\right)+2p_1p_2\left(2\cos\frac{p_2a}{\hbar}\right)}$$

$$=\frac{i(p_1^2-p_2^2)\sin\frac{p_2a}{\hbar}}{i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}-2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$$\frac{B_1*}{A_1*}=\frac{-i(p_1^2-p_2^2)\sin\frac{p_2a}{\hbar}}{-i(p_1^2+p_2^2)\sin\frac{p_2a}{\hbar}-2p_1p_2\cos\frac{p_2a}{\hbar}}$$

$$R=\frac{\text{Reflected flux}}{\text{Incident flux}}=\frac{B_1B_1*\frac{p_1}{m}}{A_1A_1*\frac{p_1}{m}}=\frac{B_1B_1*}{A_1A_1*}$$

or $$R=\frac{B_1}{A_1}\left(\frac{B_1*}{A_1*}\right)=\frac{(p_1^2-p_2^2)\sin^2\frac{p_2a}{\hbar}}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\cos^2\frac{p_2a}{\hbar}}$$

$$=\frac{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}}{(p_1^2+p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2\left(1-\sin^2\frac{p_2a}{\hbar}\right)}$$

$$=\frac{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}}{(p_1^2-p_2^2)^2\sin^2\frac{p_2a}{\hbar}+4p_1^2p_2^2} \qquad (2.54)$$

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.

The transmittance or the transmission coefficient is given by

$$T = \frac{-4p_1^2 p_2^2 \operatorname{sech}^2(ip_2 a/\hbar)}{(p_1^2+p_2^2)^2 \tanh^2(ip_2 a/\hbar) - 4p_1^2 p_2^2} \tag{2.55}$$

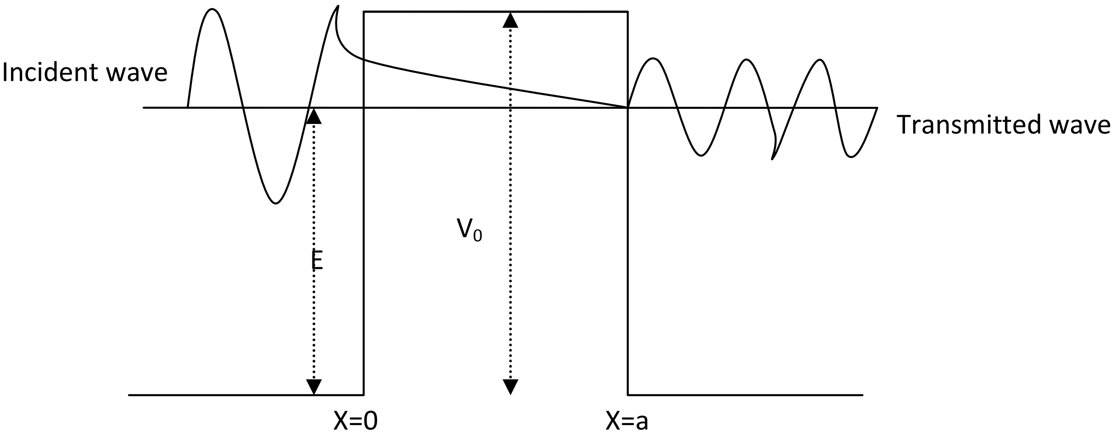

Fig. 2.7

And reflection coefficient is given by,

$$R = \frac{(p_1^2 - p_2^2)\tanh^2(ip_2 a/\hbar)}{(p_1^2+p_2^2)^2 \tanh^2(ip_2 a/\hbar) - 4p_1^2 p_2^2} \tag{2.56}$$

2.5 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

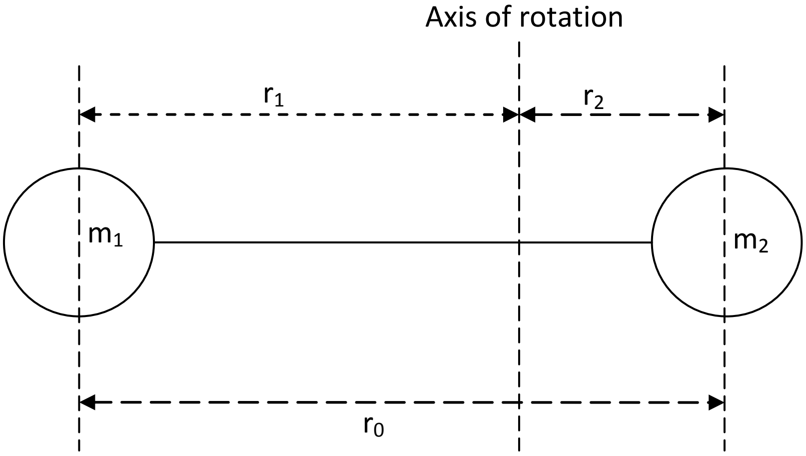

Fig. 2.7

rigid; how ever; it may be treated, at least as a first approximation, as a rigid rotator with free axis.

Energy for the rotator

The kinetic energy of a particle of mass m can be expressed as

$$T = \frac{1}{2} m(\dot{x}^{2} + \dot{y}^{2} + \dot{z}^{2}) \tag{2.57}$$

where $\dot{x}, \dot{y}, \dot{z}$ are the components of the velocity of a particle along X, Y and z axes respectively. The transformation between Cartesian co-ordinates (x, y, z) and spherical co-ordinates $(\mathrm{r}, \Theta, \varphi)$ are given by

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned} \tag{2.58}$$

so that the kinetic energy in spherical co-ordinates is expressed as

$$T = \frac{1}{2} m(\dot{r}^{2} + r^{2}\,\dot{\theta}^{2} + r^{2}\,\sin^{2}\theta\,\dot{\phi}^{2}) \tag{2.59}$$

If the distance r of the particle from the origin is fixed, its derivative $\dot{r}$ will be zero ; then from equation (2.59) the kinetic energy would be

$$T = \frac{1}{2} mr^{2}\,(\dot{\theta}^{2} + \sin^{2}\theta\,\dot{\phi}^{2}) \tag{2.60}$$

Taking O, the centre of mass of the rotator, as origin, the K.E. of the particle of mass m_1 is given by

$$T_1 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

Similarly the K.E of the particle of mass m_2 is

$$T_2 = \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

Hence the total kinetic energy of the rotator will be

$$T = T_1 + T_2 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2) + \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2\right)(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2) \qquad (2.61)$$

As there is no potential energy of the rotator, total energy is given by

$$E = T + V = T \qquad \text{(since } V = 0\text{)}$$

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2\right)(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2) \quad (2.62)$$

But $m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 = I$, the moment of interia of the system about the axis passing through the centre of mass and perpendicular to the line joining the two masses.

$$E = T = \frac{1}{2}\, I\, (\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2) \qquad (2.63)$$

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

$$0 = \frac{-m_1 r_1 + m_2 r_2}{m_1 + m_2} \quad ie.\ m_1 r_1 = m_2 r_2 \qquad (2.64)$$

But $\qquad r_0 = r_1 + r_2 \quad$ or $\quad r_2 = r_0 - r_1$

Substituting this in eqn. (2.64) we get

$$m_1 r_1 = m_2 \left(r_0 - r_1 \right)$$

$\therefore$
$$r_1 = \frac{m_2}{m_1 + m_2} r_0 \tag{2.65}$$

Similarly
$$r_2 = \frac{m_1}{m_1 + m_2} r_0 \tag{2.66}$$

Then the moment of intertia of the rotator may be expressed as

$$I = m_1 r_1^{\,2} + \frac{1}{2} m_2 r_2^{\,2} = m_1 \left(\frac{m_2}{m_1 + m_2} r_0 \right)^2 + m_2 \left(\frac{m_1}{m_1 + m_2} r_0 \right)^2$$

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2 \qquad \text{since, } I = \mu r_0^2 \tag{2.67}$$

$$\text{where} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.68}$$

is called the reduced mass of the system.

From equations (2.60) and (2.63) it is evident that the rigid rotator behaves like a single particle of mass μ given by eqn. (2.68) 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

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \tag{2.69}$$

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

$$\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin\theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2I}{\hbar^2} E \psi = 0. \tag{2.70}$$

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 (2.70) may be solved by the method of separation of variables, i.e., the wave-function $\psi(\theta,\phi)$ may be represented by

$$\psi(\theta,\phi)=\Theta(\theta)\,\Phi(\phi) \qquad (2.71)$$

Where $\Theta(\theta)$ is function θ alone and $\Phi(\phi)$ is the function of ϕ alone.

Substituting in equation (2.70) and dividing throughout by $\Theta\Phi$, we get

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\phi\sin^2\theta}\cdot\frac{\partial^2\Theta}{\partial\phi^2}+\frac{2IE}{\hbar^2}=0. \qquad (2.72)$$

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 $$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2IE}{\hbar^2}\sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad (2.73)$$

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.,

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2IE}{\hbar^2}\sin^2\theta=-m^2 \qquad (2.74)$$

and $$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

Equation (2.74) may be rewritten as

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi=0 \qquad (2.75)$$

The solution of above equation may be written as

$$\Phi=Ae^{im\,\Phi} \qquad \text{where} \qquad m=0,\pm1,\pm2,\pm3\,\text{etc.} \qquad (2.76)$$

A is any arbitrary constant which may be chosen in such a way that the function is normalised,

i.e., $\int_0^{2\pi} \Phi_m \Phi_m * d\phi = 1$ 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 $A^2 2\pi = 1$ (2.77)

i.e. $A = \frac{1}{\sqrt{(2\pi)}}$

Thus the normalised function is

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

Multiplying equation (2.74) by $\frac{\Theta}{\sin^2\theta}$, we get

$$\frac{1}{\sin\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\frac{2IE}{\hbar^2} - \frac{m^2}{\sin^2\theta}\right)\Theta = 0. \quad (2.78)$$

Let us introduce a new variable x such that $x = \cos\theta$

so that $\sin\theta = \sqrt{(1-x^2)}$ (2.79)

Then $$\frac{\partial\Theta}{\partial\theta} = \frac{\partial\Theta}{\partial x}\cdot\frac{\partial x}{\partial\theta} = -\sin\theta\,\frac{\partial\Theta}{\partial x} \quad (2.80)$$

and in general, $$\frac{\partial}{\partial\theta} = -\sin\theta\,\frac{\partial}{\partial x} \quad (2.81)$$

$$\therefore \quad \sin\theta\frac{\partial\Theta}{\partial\theta} = -\sin^2\theta\cdot\frac{\partial\Theta}{\partial x} = -(1-x^2)\frac{\partial\Theta}{\partial x} \quad (2.82)$$

Using equation (2.80) and (2.81) and (2.82), equation (2.78) can be written in terms of x as

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\} + \left(\beta - \frac{m^2}{1-x^2}\right)\Theta = 0. \quad (2.83)$$

where $$\beta = \frac{2IE}{\hbar^2} \quad (2.84)$$

Equation (2.83) 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 $\cos\theta$.

$$\Theta(\theta)=(1-x^2)^{m/2}X(x) \qquad (2.85)$$

Where $X(x)$ is the function of X only.

Equation (2.85) yields

$$\frac{\partial\Theta}{\partial x}=-mx\,(1-x2)^{(m/2)-1}X+(1-x^2)^{(m/2)}\frac{dX}{dx} \qquad (2.86)$$

$$\therefore \qquad \frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\}=\frac{\partial}{\partial x}\left\{-mx\,(1-x^2)^{m/2}X+(1-x^2)^{(m/2)+1}+\frac{dX}{dx}\right\}$$

$$=\left\{-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{(m/2)-1}\right\}X$$

$$-\left\{2x(m+1)(1-x^2)^{m/2}\right\}X'+(1-x^2)^{(m/2)+1}X'' \qquad (2.86a)$$

where we have assumed $X'=\dfrac{dX}{dx}$ and $X''=\dfrac{d^2X}{dx^2}$ (2.87)

Using equations (2.85) and (2.86a), equation (2.83) can be written as

$$\left\{-m\,(1-x^2)^{m/2}+m^2x^2\;(1-x^2)^{(m/2)-1}X-\{2x(m+1)(1-x^2)^{m/2}\right\}X'$$

$$+(1-x^2)^{(m/2)-1}X''+\left(\beta-\frac{m2}{1-x^2}\right)(1-x^2)^{m/2}\;X=0.$$

Dividing throughout by $(1-x^2)^{m/2}$, we get

$$(1-x^2)\,X''-2(m+1)xX'+\{\beta-m(m+1)\}X=0$$

or $$(1-x^2)\,X''-2\alpha xX'+\lambda X=0 \qquad (2.88)$$

$$\left.\begin{array}{l}\text{where }\alpha=m\\ \text{and}\quad\lambda=\beta-m(m+1)\end{array}\right\} \qquad (2.89)$$

Now let us assume that $X(x)$ may be expressed as a power series, as,

$$X=a_0+a_1x=\alpha_2x^2+a_3x^3+.................. \qquad (2.90)$$

or $$X'=a_1+2a_2x+3a_3x^2+.........\,........$$

and $$X'' = 2a_2 + 6a_3x + 12a_4x^2 + ... \qquad (2.91)$$

substituting these values in equation (2.88) and simplifying, we get

$$(2a_2 + \lambda a_0) + \left\{6a_3 + (\lambda - 2\alpha)a_4\right\}x + \left\{12a_4(\lambda - 4\alpha - 2)a_2\right\}x^2 + \left\{20a_5 + (\lambda - 4\alpha - 6)a_3\right\}x^3 + ...$$
$$+ \left[(n+1)(n+2)a_{n+2} + \left\{\lambda - 2n\alpha - n(n-1)\right\}a_n\right]x^n + ... = 0$$

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

$$(n+1)(n+2)a_{n+2} + \left\{\lambda - 2n\alpha - n(n-1)\right\}a_n = 0$$

Where $n = 0, 1, 2, 3, ...$

$$a_{n+2} = \frac{2n\alpha + n(n-1) - \lambda}{(n+1)(n+2)} a_n$$

Substituting values of α and λ in above equation, we get

$$\frac{a_{n+2}}{a_n} = \frac{(n+m)(n+m+1) - \beta}{(n+1)(n+2)} \qquad (2.92)$$

This is called recursion formula for the coefficients in power series for $X(x)$.

In order to obain 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 numerator of equation (2.92) is zero

i.e. $$(n+m)(n+m+1) - \beta = 0$$

$$\beta = (n+m)(n+m+1) \qquad (2.93)$$

Therefore, the sum $(n+m)$ may be replaced by l, where l is also zero or an integer.

$$\beta = l(l+1), \qquad l = m + n = 0,1,2,3,... \qquad (2.94)$$

Substituting this value of β in equation (2.83), we get

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial \Theta}{\partial x}\right\} + \left\{l(l+1) - \frac{m^2}{1-x_2}\right\}\Theta = 0. \qquad (2.95)$$

The solution of above equation contains the factor called the associated Legendre function $P_i^m(x)$ which may be defined as

$$P_i^m(x) = (1-x^2)^{m/2}\frac{d^m P_l(x)}{dx^m}$$

where $P_l(x)$ is Legendre polynomial of degree l.

The solution of equation (2.95) is written as

$$\Theta = BP_l^m(x) = BP_l^m(\cos\theta) \tag{2.96}$$

$[\text{since } x = \cos\theta]$

Where B is normalizing constant.

From orthogonal properties of associated Legendre's Polynomials,

and
$$\left.\begin{aligned} &\int_{-1}^{+1} P_k^m(x)P_l^m(x)dx = 0 \\ &\int_{-1}^{+1} P_k^m(x)P_l^m(x)dx = \frac{2}{(2l+1)}\frac{(l+m)!}{(l-m)!}\end{aligned}\right\} \quad \begin{aligned}&for\ k \neq l \\ &for k = l\end{aligned} \tag{2.97}$$

According to normalizing condition,

$$\int \Theta_{ml}\Theta_{ml}{}^{*}d\Theta = 1$$

i.e.,
$$B^2\int_{-1}^{+1} P_l^m(x)P_l^m dx = 1$$

$$B^2\cdot\frac{2}{2l+1}\frac{(l+m)!}{(l-m)!} = 1$$

or
$$B = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)} \tag{2.98}$$

Substituting the value of B in (2.96) the normalized wave function Θ is given by

$$\Theta(\theta) = \left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)P_l^m(\cos\theta) \tag{2.99}$$

The complete wave-function or eigen-function for the rigid rotator is given by

$$\Psi = \Theta(\theta)\Phi(\phi) = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)}P_l^m(\cos\theta)\cdot\frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}m\phi} \tag{2.100}$$

or $$\Psi_{ml} = (\theta,\phi) = \frac{1}{\sqrt{(2\pi)}}\sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)} P_l^m\,(\cos\theta)\mathrm{e}^{\mathrm{i}m\phi}$$ (2.101)

Eigen values or energy levels of the rigid rotator.

From equations (2.84) and (2.94), we have

$$\frac{2IE}{\hbar^2} = l(l+1)$$

or $$E = E_l = \frac{l(l+1)\hbar^2}{2I} \qquad l = 0,1,2,3....$$ (2.102)

This equation gives allowed values for the energy (i.e. eigen values) of a rigid rotator with free axis.

2.6 Rigid Rotator in a Fixed Plane

If we consider the rotator to be only in XY plane, then $\theta = 90°$ and hence the Schroedinger's equation, in this case may be written as

$$\frac{\partial^2\psi}{\partial\phi^2} + \frac{2IE}{\hbar^2}\psi = 0$$ (2.103)

In this case $\psi = \Phi_m(\phi)$, so that,

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} - \frac{2IE}{\hbar^2} = \text{constant} = -m^2$$

So that we have

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} + m^2 = 0$$

i.e. $$\frac{\partial^2\Phi}{\partial\phi^2} + m^2\,\Phi = 0$$

(2.104)

where $$\frac{2IE}{\hbar^2} = m^2$$ (2.105)

Eigen functions: The solution of equation (2.104) can be written as

$$\Phi_m = Ae^{im\Phi} \tag{2.106}$$

where A is arbitrary constant and $m = 0, \pm 1, \pm 2, ...$

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 $A^2\, 2\pi = 1$ or $A = \frac{1}{\sqrt{(2\pi)}}$

$\therefore$ The eigen functions are given by

$$\psi = \Phi_m(\phi) = Ae^{im\phi} \tag{2.107}$$

$$= \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad m = 0, \pm 1, \pm 2, ...$$

Eigen values : From equation (2.105), we have

$$E = E_m = \frac{m^2 \hbar^2}{2I}$$

2.7 The Hydrogen atom

The Schroedinger wave equation is written as

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2}[E - V]\psi = 0.$$

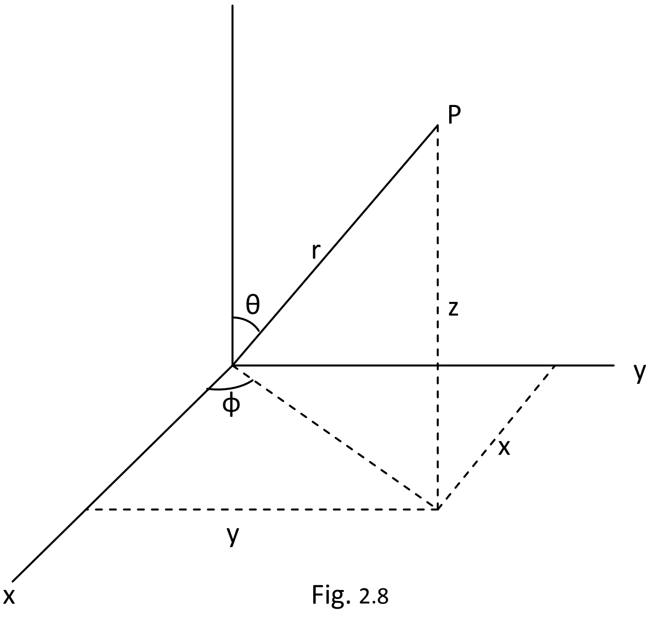

Fig. 2.8

In spherical polar coordinates (fig 2.8)

x = r sin θ cos ϕ

y = r sin θ sin ϕ

z = r cos θ

The expression for ∇^2 in spherical polar coordinates is expressed as,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Hence the Schroedinger wave equation in a spherically symmetric potential may be written in the spherical coordinates as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}[E - V(r)]\psi = 0.$$

The solution of the above equation can be separated in different variables of r, θ *and* ϕ by writing.

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

and differentiating, dividing throughout by $\psi = R\ \Theta\ \Phi$ and multiplying by $r^2 \sin{}^2\theta$ we get,

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta} + \right) + \frac{2\mu r^2\sin^2\theta}{\hbar^2}\{E - V(r)\} = 0.$$

(2.107A)

The second term of this equation depends only on ϕ and the rest is independent of ϕ. Hence the second term should be equal to a constant . Let the constant is equal to $-m^2$

That is, $$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

$$\frac{d^2\Phi}{d\phi^2} = +m^2\Phi = 0. \qquad (2.108)$$

With this value for the second term, equation (2.107a) now can be written as,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\sin\theta}\frac{1}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta} + \right) - \frac{m^2}{\sin^2\theta} + \frac{2\mu r^2}{\hbar^2}\{E - V(r)\} = 0. \qquad (2.109)$$

The I and IV terms of this equation depend only on *r* and the II and III terms only on θ; therefore each part must be equal to a constant, (say) λ.

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(E - V) = \frac{m^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = \lambda.$$

so that we have

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0. \qquad (2.110)$$

and $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2\mu}{\hbar^2}\{E - V(r)\} - \frac{\lambda}{r^2}\right]R = 0. \qquad (2.111)$$

Equation (2.108), (2.110) and (2.111) are known as φ, θ and r equations respectively.

(b) Solution of φ equation :

The φ equation is $$\frac{d^2\Phi}{d\phi^2} = +m^2\Phi = 0$$

This is a second order differential equation whose solution is given by

$$\Phi = A\, e^{\pm i m \phi,} \qquad (2.112)$$

where A is an arbitrary constant. The constant may be evaluated by normalizing Φ, *i.e.*,

$$\int_0^{2\pi} \Phi * \Phi \, d\phi = 1$$

$$\int_0^{2\pi} A^2 d\phi = 1$$

or $$A = \frac{1}{\sqrt{2\pi}} \qquad (2.113)$$

therefore the solution becomes

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{\pm i m \phi} \qquad (2.114)$$

The single valuedness of the function Φ indicates that it should have the same value at φ = 0 and φ = 2π; hence

$$\Phi = A = A e^{\pm 2\pi i m}$$

$$e^{\pm 2\pi i m} = \cos 2\pi m \pm i \sin 2\,\pi m = 1$$

or (2.115)

This is true only when *m* is zero or an integer (positive or negative). Thus we write

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{i m \phi}, \qquad m = 0, \pm 1, \pm 2, \ldots\ldots. \qquad (2.116)$$

The quantity m is called the magnetic quantum number .

Solution for θ equation :

In the θ-equation $$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0.$$

Let $x = \cos\theta$,

we have

$$\frac{d\Theta}{d\theta} = \frac{dx}{d\theta}\frac{d\Theta}{dx} = -\sin\theta \frac{d\Theta}{dx}$$

$$\frac{d}{d\theta} = -\sin\theta\frac{d}{dx}$$

or $$\sin\theta\frac{d\Theta}{d\theta} = -\sin^2\theta\frac{d\Theta}{dx} \qquad (2.117)$$

$$\sin\theta\frac{d\Theta}{d\theta} = -(1-x^2)\frac{d\Theta}{dx}$$

or $$(2.118)$$

Using equations (2.117) and (2.118), the θ equation becomes

$$\frac{d}{dx}\left\{(1-x^2)\frac{d\Theta}{dx}\right\} + \left(\lambda - \frac{m^2}{1-x^2}\right)\Theta = 0. \qquad (2.119)$$

If λ = *l* (*l* + 1), then

$$\frac{d}{dx}\left\{(1-x^2)\frac{d\Theta}{dx}\right\} + \left(l(l+1) - \frac{m^2}{1-x^2}\right)\Theta = 0. \qquad (2.120)$$

Comparing this with associated Legendre equation

$$\frac{d}{dx}\left\{(1-x^2)\frac{d}{dx}p_l^m(x)\right\} + \left(l(l+1) - \frac{m^2}{1-x^2}\right)p_l^m(x) = 0.$$

gives the solution of equation (20) as

$$\Theta = B\, p_l^m(x) = B\, p_l^m(\cos\theta) \qquad |m| < l. \qquad (2.121)$$

B is normalization constant which is evaluated by normalising Θ in the following way.

$$\int_0^{\pi}\Theta^*\Theta\sin\theta\, d\theta = 1$$

$$\int_{-1}^{+1} B^2 P_l^{m*}(x)P_l^m(x)dx = 1$$

Hence $$B = \sqrt{\left[\left\{\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right\}\right]} \qquad (2.122)$$

Thus the solution is

$$\Theta(\theta) = \sqrt{\left[\left\{\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right\}\right]}\; p_l^m(\cos\theta), \qquad (2.123)$$

with $$p_l^m(x) = (1-x^2)^{m/2}\frac{d^m}{dx^m}p_l(x)$$

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

where $x = \cos\theta$

Solution of r-equation (radial equation)

In this problem V(r) = $-\frac{Ze^2}{r}$, where Z is the atomic number. Consider this problem to one – electron or hydrogen – like atom.

Equation for radial part can be written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E+\frac{Ze^2}{r}-\frac{l(l+1)\hbar^2}{2\mu r^2}\right]R=0.$$

Let

ρ = αr or r = ρ/α ;

Then r-equation becomes

$$\alpha^2\frac{1}{\rho^2}\alpha\frac{d}{d\rho}\left[\frac{\rho^2}{\alpha^2}\alpha\frac{dR}{d\rho}\right]+\frac{2\mu}{\hbar^2}\left[E+\frac{Ze^2\alpha}{\rho}-\frac{\alpha^2 l(l+1)\hbar^2}{2\mu\rho^2}\right]R=0. \qquad (2.124)$$

For bound states, ie. E < 0,

$$\alpha^2\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR}{d\rho}\right]+\frac{2\mu}{\hbar^2}\left[-|E|+\frac{Ze^2\alpha}{\rho}-\frac{\alpha^2 l(l+1)\hbar^2}{2\rho^2\mu}\right]R=0.$$

or

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR}{d\rho}\right]+\left[-\frac{2\mu|E|}{\hbar^2\alpha^2}+\frac{2\mu Ze^2}{\hbar^2\alpha\rho}-\frac{l(l+1)}{\rho^2}\right]R=0. \qquad (2.125)$$

Choosing α such that

$$\frac{2\mu|E|}{\alpha^2\hbar^2}=\frac{1}{4}, \qquad \text{and} \qquad \lambda'=\frac{2\mu Ze^2 a}{\alpha\hbar^2}$$

The equation (2.125) can be written as

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR}{d\rho}\right]+\left[\frac{\lambda'}{\rho}-\frac{1}{4}\frac{l(l+1)}{\rho^2}\right]R=0. \qquad (2.126)$$

where the particular choice of the number (1/4) for the eigen value term $\frac{2\mu|E|}{\alpha^2\hbar^2}$ is arbitrary .

For large ρ, the equation (2.126) has the form

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)-\frac{1}{4}R=0. \qquad (2.127)$$

The solutions of equation (2.127) are

$$R=e^{+\rho/2} \quad \text{and} \quad R=e^{-\rho/2} \qquad (2.128)$$

Only the second solution is satisfactory (vanishing for ρ → ∞). The exact solution of equation (2.126) is of the form

$$R(\rho) = F(\rho)e^{-\rho/2}$$

Substituting this value in equation (2.127), we have

$$\left[\rho^2 F''(\rho)+(2-\rho)\rho F'(\rho)+\left\{\frac{1}{4}\rho^2-\rho-\frac{\rho^2}{4}+\lambda'\rho-l(l+1\right\}F(\rho)\right]e^{-\rho/2}=0. \qquad (2.129)$$

As $e^{-\rho/2}$ is not zero, the expression within the square brackets is zero :

$$\left[\rho^2 F''(\rho)+(2-\rho)\rho F'(\rho)+[(\lambda'-1)\rho-l(l+1)]\;\; F(\rho)\right]=0. \tag{2.130}$$

Let $F(\rho) = \rho^s L(\rho)$

$F'(\rho) = s\rho^{s-1} L + \rho^s L'$

$F''(\rho) = s(s-1)\rho^{s-2} L + 2s\rho^{s-1} L' + \rho^s L''$

Substituting these values in equation (2.130),

$$\rho^2 L''+(2s\rho+2\rho+\rho^2)\; L'+\{s(s-1)+2s-s\rho+((\lambda'-1)\rho-l(l+1)\}\; L=0. \tag{2.131}$$

Let $L(\rho) = \sum_{r=0}^{\infty} a_r \rho^r$

i.e., $F(\rho) = \sum_{r=0}^{\infty} a_r \rho^{s+r}$ (2.132)

Substituting the values of F(ρ), F′(ρ), and F″(ρ) in eq. (2.130) we have

$$\rho 2\sum_{r=0}^{\infty} a_r(s+r)(s+r-1)\rho^{s+r-2}+(2-\rho)\rho\sum_{r=0}^{\infty} a_r\;(s+r)\rho^{s+r-1} +[(\lambda'-1)\rho-l(l+1)]\sum_{r=0}^{\infty} a_r\rho^{s+r}=0$$

or $\sum_{r=0}^{\infty} a_r(s+r)(s+r-1)\rho^{s+r}+2\sum_{r=0}^{\infty} a_r(s+r)\rho^{s+r}$

$$-\sum_{r=0}^{\infty} a_r(s+r)\rho^{s+r+1}+(\lambda'-1)\sum_{r=0}^{\infty} a_r\rho^{s+r+1}-l(l+1)\sum_{r=0}^{\infty} a_r\rho^{s+r}=0$$

or
$$\sum_{r=0}^{\infty}\{(s+r)(s+r-1)+2(s+r)-l(l+1)\}\;a_r\rho^{s+r} -[(s+r)-(\lambda'-1)]\sum_{r=0}^{\infty} a_r\rho^{s+r+1}=0. \tag{2.132a}$$

Equating the coefficients of ρ^s in eq. (2.132a), we have

$$\{s(s-l)+2s-l(l+1)\}a_0=0$$

$$\{s(s+l)-l(l+1)\}=0 \quad \text{since}, a_0\neq 0$$

It means that either $s = l$ or $s = -(l+1)$; the value $s=-(l+1)$ does not satisfy the condition of well – behaved function and so, the only accepted value of s is l. Comparing now the coefficients of ρ^{s+r+1} we can write,

$$[(s+r+1)(s+r)+2(s+r+1)-l(l+1)]a_{r+1}=(s+r+1-\lambda')a_r$$

or
$$\frac{a_{r+1}}{a_r}=\frac{s+r+1-\lambda'}{(s+r+1)(s+r+2)-l(l+1)} \tag{2.133}$$

The series (2.132) represented by coefficients (2.133) behaves like e^{ρ} for large ρ and therefore R = $e^{-\rho/2}$ F(ρ) will diverge as $e^{+\rho/2,}$ which is not an acceptable solution.. Therefore the series must break off after certain number of terms. From eq (2.133) let,

$l + n_r + 1 - \lambda' = 0$ (putting $s = l$)

or $$\lambda' = n_r + l + 1. \qquad (2.134)$$

Replacing λ' by integer n, $$n = n_r + l + 1. \qquad (2.135)$$

It is seen that n is a positive integer and is identified as total quantum number. Eq. (2.131) may now be written as (putting $s = l$ and replacing λ' by n):

$$\rho L'' + \{(2l+1) + 1 + \rho\} L' + (n - l - 1)\, L = 0 \qquad (2.136)$$

Comparing it with the associated Laguerre equation

$$\rho L''^{\,p}_{\,q} + (p+1+\rho)\; L'^{\,p}_{\,q} + (q-p)\, L^{\,p}_{\,q} = 0,$$

We obtain, $p = 2l + 1$, $q = n+l$ and so we get the solution of r-equation as

$$R(r) = Ce^{-\rho/2}\, \rho^{l}\; L^{2l+1}_{n+l}(\rho);$$

Here, C is the normalisation constant given by,

$$C = \sqrt{\left[(\alpha)^{3} \cdot \frac{(n-l-1)!}{2n\{(n+l)!\}^{3}} \right]}$$

(e) Energy of atomic levels and degeneracy.

We have assumed that $$\lambda' = \frac{Ze^2}{\hbar} \left[\frac{\mu}{2|E|} \right]^{1/2}$$

or $$\lambda'^{2} = \frac{Z^2 e^4}{\hbar^2}\, \frac{\mu}{2|E|}$$

Replacing λ' by n

$$E_n = -|E_n| = -\frac{\mu Z^2 e^4}{2\hbar^2\, n^2} \qquad (2.137)$$

Equation (2.137) is the expression for energy of an atomic state of a hydrogen – like atom defined by the principal quantum number n.

Now consider the equation

$$n = n_r + l + 1$$

can be satisfied for a given n for several combinations of n_r and l. This implies that there are several possible wave functions for a given energy value (n fixed). When this happens the state is said to be degenerate. This holds good for every value of $n > 1$.

To determine the degeneracy

From equation (2.137) it is clear that energy eigen –values depend upon n and so are degenerate with respect to both *l* and m. Thus for each value of *n, l* can vary from 0 to *n – 1* and for each of these *l* values, *m* can vary from – *l* to +*l*. So, the total degeneracy is

$$\sum_{l=0}^{n-1}(2l+1)=\frac{2(n)(n-1)}{2}+n=n^2 \qquad (2.138)$$

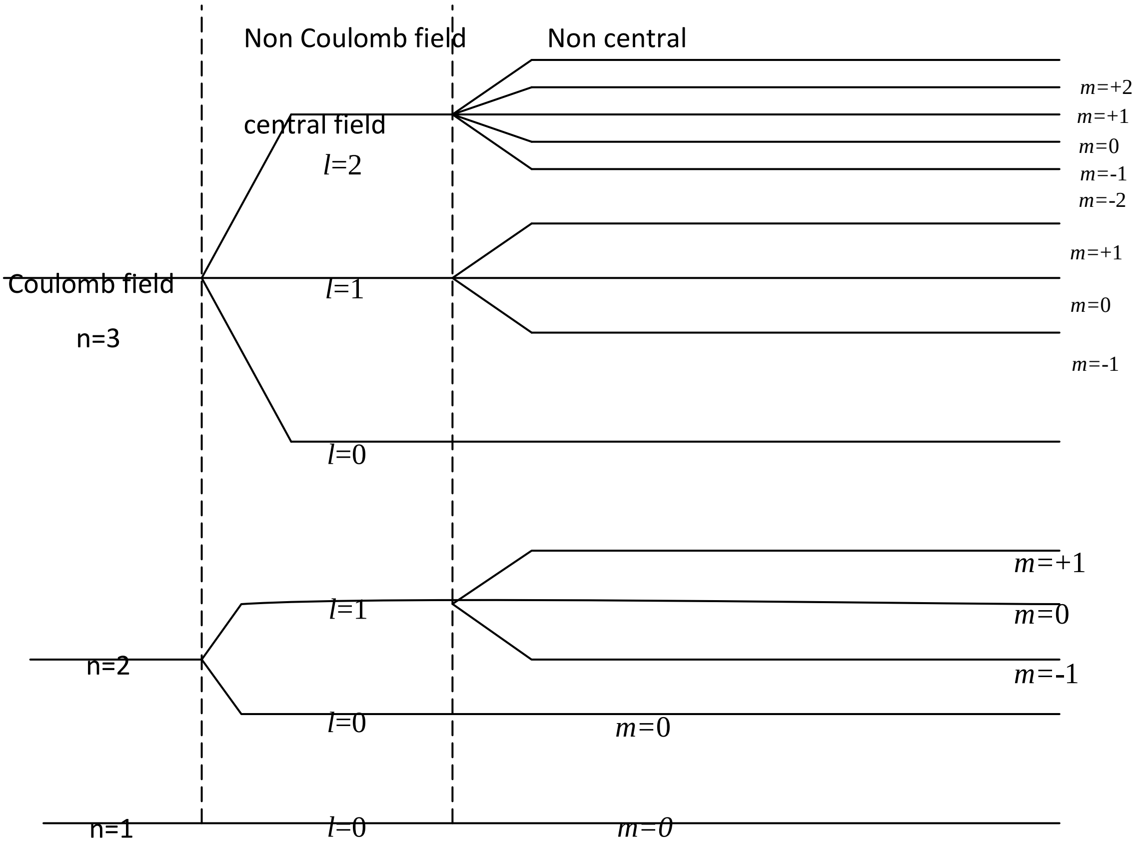

Fig. 2.9

In particular

$$m = 0, \pm 1, \pm 2, \ldots\ldots \pm l$$

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

so that for n=2, we have l=0, m=0, and l=1, m=0,+1,-1 giving four wave functions or quantum states etc. Fig. (2.10) shows the different eigen – states in case of hydrogen – like atom.

The solution for radial wave function is found as

$$R(r)=\sqrt{\left[\left(\frac{2z}{na_0}\right)^3\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}\exp\left(-\frac{zr}{na_0}\right)\left(\frac{2zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2zr}{na_0}\right)$$

The complete solution for the problem of hydrogen atom is obtained by multiplying the solutions $R(r),\Theta(\theta)\,and\,\Phi(\phi)$

2.8 Normal or Ground state of Hydrogen Atom

For the ground state of the atom,

n = 1, l=0, m=0, and hence the wave-function is

$$\psi_{100}=\sqrt{\left(\frac{1}{\pi a_0{}^3}\right)}\,e^{-\rho/2}\text{ where } a_0 \text{ is the radius of Bohr's first orbit} \qquad (2.139)$$

But $$\rho=\alpha r=\frac{2Zr}{na_0}=\frac{2r}{a_0}\left[\text{because } n=1, Z=1 \text{ and } a_0=\frac{\hbar^2}{\mu e^2}\right]$$

$$\text{Hence, } \psi_{100}=\sqrt{\left(\frac{1}{\pi a_0{}^3}\right)}\exp\left[\frac{-r}{a_0}\right] \qquad (2.140)$$

and $$\psi_{100}\psi_{100}{}^*=\frac{1}{\pi a_0{}^3}\exp\left[\frac{-2r}{a_0}\right] \qquad (2.141)$$

since this expression for probability density is independent of θ and ϕ, the normal hydrogen atom is spherically symmetric. Consider a small value $dV = r^2 \sin\theta\, dr\, d\theta\, d\phi$, then the probability of finding the electron in this volume is given by

$$\psi_{100}\psi_{100}{}^* r^2 dr\sin\theta d\theta d\phi=\frac{1}{\pi a_0{}^3}\exp\left[\frac{-2r}{a_0}\right]r^2 dr\sin\theta d\theta d\phi \qquad (2.142)$$

For a spherical shell between radii r and $r + dr$, this value becomes

$$=\frac{1}{\pi a_0{}^3}\exp\left[\frac{-2r}{a_0}\right]r^2\,dr\int_0^{\pi}\sin\theta\,d\theta\int_0^{2\pi}d\phi=\frac{4}{a_0{}^3}\exp\left[\frac{-2r}{a_0}\right]r^2 dr$$

Thus the probability of finding the electron between the distance r and $r + dr$ from the nucleus is $$P(r)dr=\frac{4}{a_0{}^3}\exp\left[\frac{-2r}{a_0}\right]r^2 dr$$

The radial distribution function $P(r)$ is given by

$$P(r) = \frac{4}{a_0^{\,3}} \exp\left[\frac{-2r}{a_0}\right] r^2$$

The probability is maximum when *dP/dr* = 0.

or $$\frac{dP}{dr} = \frac{4}{a_0^{\,3}}\left[r^2\left(\frac{-2}{a_0}\right)\exp\left(\frac{-2r}{a_0}\right) + 2r\exp\left(\frac{-2r}{a_0}\right)\right] = 0$$

or $$\frac{4}{a_0^{\,3}}\exp\left(\frac{-2r}{a_0}\right)\left[2r - \left(\frac{2r^2}{a_0}\right)\right] = 0$$

or $$2r - \left(\frac{2r^2}{a_0}\right) = 0$$

or $$r = a_0 \qquad (2.143)$$

Thus in the normal state, the maximum probability of finding the electron is at a distance equal to the radius of the first Bohr's orbit.

UNIT III

31 Perturbation theory

Perturbation theory is of two types.

1. Time independent perturbation theory
2. Time dependent perturbation theory

In time independent or stationary perturbation theory, the Hamiltonian is separated into two parts, one represents the characteristics of the system which can be solved exactly and the other due to perturbation.

Perturbed Hamiltonian $H = H^{(0)} + H^{'}$ where $H^{(0)}$ represents the unperturbed part and $H^{'}$ the perturbed part.

Time independent perturbation theory for nondegenerate case

The schrodinger eqn. is written as

$$H\psi = E\psi$$

The Hamiltonian $H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V \right)$

Expanding H interms of some parameter λ as,

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + ... \qquad (3.1)$$

Let the energy eigen values are $E_1^{(0)}, E_2^{(0)} ... E_n^{(0)}$ and the eigen functions are $\psi_1^{(0)}, \psi_2^{(0)} ... \psi_n^{(0)}$. It is possible to expand the eigen functions and eigen values as power series in λ as

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + ... \qquad (3.2)$$

Substituting these E_n and ψ_n values in the schrodinger eqn. $H\psi_n = E_n\psi_n$ we get

$$(H^{(0)} + \lambda H^{(1)})(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + ...) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + ...)$$

Collecting the like coefficients of λ,

$$H^{(0)}\psi_n^{(0)} + \lambda(H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)}) + \lambda^2(H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)} + ...) + ...$$

$$+\lambda(E_n^{(0)}\psi_n^{(1)} + E^{n(1)}\psi_n^{(0)}) + \lambda^2(E_n^{(0)}\psi_n^{(2)} + E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)}) + ... == E_n^{(0)}\psi_n^{(0)}$$

For this eqn. to be valid for all values of λ, the coefficient of equal powers of λ on both sides must be equal.

Comparing the coefficient of λ^0,

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

Comparing the coefficient of λ^1,

$$H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \qquad (3.3)$$

Comparison of coefficient of λ^2 gives

$$H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)}) \text{ etc.} \qquad (3.3A)$$

These eqns. represent unperturbed, first order, second order etc. perturbation equations.

First order perturbation theory:

To find the first order correction to energy En$^{(1)}$

Consider the first order eqn $H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)} = E^{n(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$

$\psi_n^{(1)}$ can be expanded as a series by using expansion theorem as

$$\psi_n^{(1)} = \sum_{m=0}^{\infty} C_m \psi_m^{(0)} \qquad (3.3B)$$

Substituting this eqn in (3.3) we get,

$$\sum_m C_m H^{(0)}\psi_m^{(0)} + H^{(1)}\psi_n^{(0)} = C_m E_n^{(0)}\psi_m^{(0)} + E_n^{(1)}\psi_n^{(0)} \quad \text{by using } H^{(0)}\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}$$

or $C_m\left(E_m^{(0)} - E_n^{(0)}\right)\psi_m^{(0)} + H^{(1)}\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)}$ (3.4A)

Multiply the above on the left by $\psi_n^{(0)^*}$ and integrating we get,

$$\int\sum_m \psi_n^{(0)^*} C_m[E_m^{(0)} - E_n^{(0)}]\psi_m^{(0)}\, d\tau + \int\psi_n^{0*}H^{(1)}\psi_n^{(0)}\, d\tau = \int E_n^{(1)}\psi_n^{(0)*}\psi_n^{(0)} d\tau \qquad (3.4B)$$

Here we have used the kronecker delta function

$$\int \psi_i^{(0)*}\psi_j^{(0)}d\tau = \delta_{ij} = 0 \quad if\ i \neq j \qquad (3.4C)$$
$$= 1 \quad if\ i = j$$

Therefore,

$$E_n^{(1)} = \int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)} d\tau = < n \,|\, H^1 \,|\, n > = H_{nn}^1$$

To find the first order correction to wave function $\psi_n^{(1)}$:

Multiplying eqn (3.4A) by $\psi_m^{(0)*}$ and integrating,

$$\int \sum_m C_m [E_m^{(0)} - E_n^{(0)}] \psi_m^{(0)*} \psi_n^{(0)} d\tau + \int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} d\tau = E_n^{(1)} \psi_m^{(0)*} \psi_n^{(0)} d\tau$$

Applying the condition (3.4C),

$$C_m = -\frac{\int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} d\tau}{E_m^{(0)} - E_n^{(0)}}, m \neq n$$

Substituting this value of C$_m$ in eqn (3.3B) we get the first order correction for the wave function.

To find the second order correction to energy E$_n$$^{(2)}$

The second order correction to wave function $\psi_n^{(2)}$ can be expressed as

$$\psi_n^{(2)} = \sum_m g_m \psi_m^{(0)} \qquad (3.5)$$

Substituting (3.5) and (3.3B) in (3.3A), we get

$$\sum g_m H_{(0)} \psi_m^{(0)} + C_m H^{(1)} \psi_m^{(0)} = g_m E_n^{(0)} \psi_m^{(0)} + \sum C_m E_n^{(1)} \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}$$

or $\sum_m g_m [E_m^{(0)} - E_n^{(0)}] \psi_m^{(0)} = \sum C_m [E_n^{(1)} - H^{(1)}] \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}$ (3.6)

Here we have used $H^{(0)} \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$

Multiplying this eqn with $\psi_n^{(0)*}$ and integrating over the space variables and applying the kronecker delta function we get,

$$E_n^{(2)} = \sum_m C_m \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)} d\tau$$

Substituting the value of C_m we have,

$$E_n^{(2)} = -\sum_m \frac{\int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} d\tau \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)} d\tau}{E_m^{(0)} - E_n^{(0)}}, \quad m \neq n$$

or $E_n^{(2)} = \sum_n{}' \frac{(< m | H^{(1)} | n >)^2}{E_n^{(0)} - E_m^{(0)}} \quad m \neq n$ if $H^{(1)}$ is Hermitian.

To find the second order correction to wave function $\psi_n^{(2)}$:

Multiplying the eqn (3.6) by $\psi_m^{(0)*}$ and integrating,

$$\int \sum_m g_m \int [E_m^{(0)} - E_n^{(0)}] \psi_m^{(0)*} \psi_m^{(0)} d\tau$$

$$= \sum_m C_m \int \psi_m^{(0)*} [E_n^1 - H^{(1)}] \psi_m^{(0)} d\tau + \int E_n^{(20} \psi_m^{(0)*} \psi_n^{(0)} d\tau$$

or $$g_m = \sum_m \frac{C_m}{E_m^{(0)} - E_n^{(0)}} \left(E_n^{(1)} - \int \psi_m^{(0)*} H^{(1)} \psi_m^{(0)} d\tau \right) \quad m \neq n$$

Substituting this value of g_m in eqn. (3.5) we get the second order perturbed wave function.

3.2 Zeeman Effect (without electron spin)

The change in the energy levels of an atom when it is placed in uniform external magnetic field, is called the Zeeman effect. Let us consider that the field strength **B** is applied on a hydrogen atom, so that an electron of reduced mass μ carrying the charge $'-e'$ is moving in a field whose vector potential is **A**. The magnetic induction **B** in terms of vector potential **A** can be written as

$$\mathbf{B} = \text{curl}\, \mathbf{A} = \nabla \times \mathbf{A}$$

Then the constant magnetic potential A in terms of magnetic induction B can be expressed as

$$\mathbf{A} = \frac{1}{2} (\mathbf{B} \times \mathbf{r}).$$

[since $\mathbf{B} \times \mathbf{r} \;=\; \nabla \times \mathbf{A} \times \mathbf{r}$ (for $\mathbf{B} = \nabla \times \mathbf{A}$)

$$= (\nabla .\, \mathbf{r})\, \mathbf{A} - (\mathbf{A}.\nabla)\mathbf{r} = 3\mathbf{A} - \mathbf{A} = 2\mathbf{A}$$

$$\therefore \quad \mathbf{A} = \frac{1}{2} (\mathbf{B} \times \mathbf{r})$$

The classical Hamiltonian of a particle of mass μ carrying charge $-e$ and moving in field of vector potential **A** may be expressed as

$$H(\mathbf{P},\mathbf{r}) = \frac{1}{2\mu}(p+e\mathbf{A})^2 + V(\mathbf{r})$$

$$= \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r}) + \frac{e}{2\mu}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2\mu}\mathbf{A}^2$$

$$= H^0 + H' + H''$$

where $H^0 = \frac{\mathbf{P}^2}{2\mu} + V(\mathbf{r}),$ is the unperturbed Hamiltonian

$$H' = \frac{e}{2\mu}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p})$$

and $H'' = \frac{e^2}{2\mu}\mathbf{A}^2$

Ist Order Zeeman effect :

For weak fields and second order perturbation term H'' containing $\mathbf{A}^2$ may be neglected and hence the perturbed Hamiltonian takes the form

$$H = H^0 + H' = \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r}) + \frac{e}{2\mu}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p})$$

$P \to \hat{P} = \frac{\hbar}{i}\nabla$ and keeping in mind the vector identity

$$\text{div }(\mathbf{A}\psi) = \psi\,\text{div }\mathbf{A} + \mathbf{A}\cdot\nabla\psi$$

or $\nabla\cdot(\mathbf{A}\,\psi) = (\nabla\cdot A)\psi + \mathbf{A}\cdot\nabla\psi$

We note $(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) = \left(\frac{\hbar}{i}\nabla\cdot\mathbf{A} + \mathbf{A}\cdot\frac{\hbar}{i}\nabla\right)\psi$

$$= \frac{\hbar}{i}\nabla\cdot(\mathbf{A}\psi) + \frac{\hbar}{i}\mathbf{A}\cdot\nabla\psi$$

$$= \frac{\hbar}{i}\{(\nabla\cdot\mathbf{A})\psi + \mathbf{A}\cdot\nabla\psi\} + \frac{\hbar}{i}\mathbf{A}\cdot\nabla\psi$$

$$= \frac{\hbar}{i}\left[(\nabla \cdot \mathbf{A})\psi + 2\mathbf{A}\cdot\nabla\psi\right] \tag{3.7}$$

$$\nabla\cdot\mathbf{A} = \nabla\cdot[\frac{1}{2}(\mathbf{B}\times r)] = \frac{1}{2}\nabla\cdot(\mathbf{B}\times r)$$

Using the vector identity

$$\text{div } (A \times B) = B\cdot \text{ curl } A - A\cdot \text{ curl } B, \text{we get}$$

$$\nabla \times \mathbf{B} = 0 \text{ and } \nabla \times \mathbf{r} = 0 \tag{3.8}$$

and
$$\mathrm{A}\cdot\nabla\psi = \frac{1}{2}(\mathbf{B}\times\mathbf{r})\cdot\nabla\psi = \frac{1}{2}\mathbf{B}\cdot(\mathrm{r}\times\nabla)\psi \tag{3.9}$$

using (3.8) and (3.9) equation (3.7) gives

$$(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p})\psi = \frac{\hbar}{i}\left[0 + 2\cdot\frac{1}{2}\mathbf{B}\cdot(r\times\nabla)\psi\right]$$

$$= \mathbf{B}\cdot\left(r\times\frac{\hbar}{i}\nabla\right)\psi = \mathbf{B}\cdot(\mathrm{r}\times p)\psi$$

$$= \mathbf{B}\cdot\mathbf{L}\ \psi. \tag{3.10}$$

$$\therefore \quad \text{or} \quad \mathrm{p}\cdot\mathrm{A} + \mathrm{A}\cdot\mathrm{p} = \mathrm{B.L} \tag{3.11}$$

The energy eigen functions of the unperturbed $H-$atom are usually chosen to be eigen state of L_z with eigen values $m\hbar$, m being magnetic quantum number. It is customary for convenience to choose magnetic field along $Z-$axis then $\mathbf{B}\cdot\mathbf{L} = \mathbf{BL}_z$

First order energy correction

$$E' = <n|H'|n> = <n|\frac{e}{2\mu}BL_z|n>$$

$$\frac{e}{2\mu}Bm\hbar<n|n> = m\frac{e\hbar}{2\mu}B \tag{3.12}$$

can take for $(2l+1)$ values since m varies form $-l$ to $+l$

with a difference of unity

The selection rule permits only those transitions in which magnetic quantum number m changes by 0 or ± 1. This selection rule coupled with expression (3.12) is sufficient to explain the spectrum of normal Zeeman effect. For an example we consider the transitions between two states with $l=2$ and $l=1$, (*i.e.* between d and $p-$states). The transitions are shown in the fig. 3.1

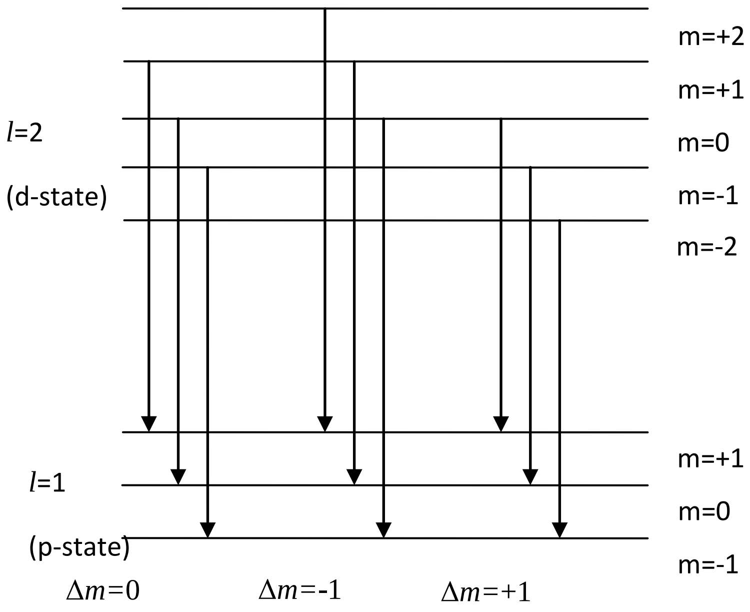

Fig. 3.1

3.3 First Order stark effect in Hydrogen atom

The effect of change in energy levels of an atom in the presence of an electric field is called stark effect. The unperturbed Hamiltonian of Hydrogen is given by,

$H^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$ where r is the distance between the nucleus and the electron of an hydrogen atom and μ-the reduced mass

Due to an external electric field of strength E, the perturbed Hamiltonian term is given as

$H' = -Ee\,r\cos\theta$, where e is the charge of the electron (3.13)

For the ground state of the atom, n=1, l=0, m=0

The non-degenerate wave function is

$$\psi_{nlm} = \psi_{100} = R_{10}(r)Y_{00}(\theta,\phi) = R_{10}(r)\frac{1}{\sqrt{4\pi}}$$

for the ground state of hydrogen, the first order energy correction due to perturbation is

$H'_{100,100} = \int_{-\infty}^{\infty} \psi^{*}_{100} H' \psi_{100} d\tau = 0$ since H' is having odd parity

Thus there is no first order stark effect in hydrogen atom

First Excited State

Consider the first excited state of hydrogen. Here n=2, l=0, 1 and m=1, 0, -1. The corresponding wave functions are,

$$\begin{aligned}
\psi_{200} &= R_{20}(r)Y_{00}(\theta,\phi) = R_{20}(r)\frac{1}{\sqrt{4\pi}} \qquad \textit{even} \quad \textit{parity} \\
\psi_{210} &= R_{21}(r)Y_{10}(\theta,\phi) = R_{21}(r)\frac{3}{\sqrt{4\pi}}\cos\theta \qquad \textit{odd} \quad \textit{parity} \\
\psi_{211} &= R_{21}(r)Y_{11}(\theta,\phi) = R_{21}(r)\frac{3}{\sqrt{8\pi}}\sin\theta e^{i\phi} \qquad \textit{odd} \quad \textit{parity} \\
\psi_{21,-1} &= R_{21}(r)Y_{1,-1}(\theta,\phi) = R_{21}(r)\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \qquad \textit{odd} \quad \textit{parity}
\end{aligned} \tag{3.14}$$

Out of the four wave functions ψ_{200} is of even parity and all other wave functions are of odd parity. The secular determinant is given as

$$\begin{vmatrix}
H'_{200,200} - E^{(1)} & H'_{200,211} & H'_{200,210} & H'_{200,21,-1} \\
H'_{211,200} & H'_{211,211} - E^{(1)} & H'_{211,210} & H'_{211,21-1} \\
H'_{210,200} & H'_{210,211} & H'_{210,210} - E^{(1)} & H'_{210,21,-1} \\
H'_{21,-1,200} & H'_{21,-1,211} & H'_{21,-1,210} & H'_{21,-1,21,-1} - E^{(1)}
\end{vmatrix} = 0 \tag{3.15}$$

If the integrand value is of odd parity, then the integral value is zero. Hence, $H'_{200,200} = \int_{-\infty}^{\infty} \psi^{*}_{200} H^{(1)} \psi_{200} d\tau = 0$ since ψ_{200}- even parity and $H^{(1)}$ is odd parity and the net integrand is odd parity. In the same manner we can show

$H^{(1)}_{211,211}, H^{(1)}_{210,210}, H^{(1)}_{21-1,21-1}, H^{(1)}_{211,210}, H^{(1)}_{211,21-1}, H^{(1)}_{210,211}, H^{(1)}_{210,21-1}, H^{(1)}_{21-1,211}, H^{(1)}_{21-1,210}$ are all zeros

Consider

$$H^{(1)}_{200,211} = -\iiint \frac{1}{\sqrt{4\pi}} R_{20}(r)\, r\cos\theta \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} R_{21}(r)\, r^2 dr \sin\theta d\theta d\phi$$

But, $\int_0^{2\pi} e^{i\phi} d\phi = 0$. Hence $H^{(1)}_{200,211} = 0$

On the same ground, $H^{(1)}_{211,200}, H^{(1)}_{200,21-1}, H^{(1)}_{21-1,200}$ are zero

So we are left with two elements namely $H^{(1)}_{200,210}$ and $H^{(1)}_{210,200}$

First, let us evaluate $H^{(1)}_{200,210}$:

$$H^{(1)}_{200,210} = \int \psi^*_{200} H^{(1)} \psi_{210} d\tau$$

Here, $$\psi_{200} = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$$ where a_0 is the Bohr's first orbit radius $$\psi_{210} = \sqrt{\frac{3}{4\pi}} \cos\theta \left(\frac{1}{2a_0}\right)^{3/2} \frac{r}{\sqrt{3}a_0} \exp\left(-\frac{r}{2a_0}\right)$$

Using these values and $H^{(1)} = -r\cos\theta$ and assuming $\frac{r}{a_0} = \eta$, we get the r-integral value as,

$$= \frac{1}{8} \frac{a_0^5}{\sqrt{3}a_0^4} \left[2\int_0^\infty \eta^4 e^{-\eta} d\eta - \int_0^\infty \eta^5 e^{-\eta} d\eta \right]$$

$$= \frac{a_0}{8\sqrt{3}} [2\Gamma 5 - \Gamma 6] = -3\sqrt{3} a_0$$

The Θ-integral gives the value as 2/3 and φ-integral gives 2π

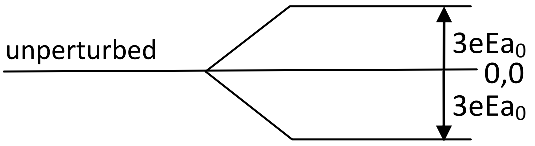

Fig.3.2

Therefore,

$$H^{(1)}_{200,210} = -\frac{1}{\sqrt{4\pi}} \sqrt{\frac{3}{4\pi}} (-3\sqrt{3}a_0) \times \frac{2}{3} \times 2\pi = 3a_0$$

Similarly we get $H^{(1)}_{210,200} = 3a_0 \mathrm{eE}$

Substituting these values the secular determinant becomes

$$\begin{vmatrix} -E_{(1)} & 0 & 3a_0 & 0 \\ 0 & -E_{(1)} & 0 & 0 \\ 3a_0 & & -E_{(1)} & 0 \\ 0 & 0 & 0 & -E_{(1)} \end{vmatrix} = 0$$

There are four roots for this determinant as $E^{(1)} = 0, 0, 3a_0, -3a_0$

The corresponding perturbed energy values are

$$E^{(1)} = 0, 0, 3eEa_0, -3eEa_0 \qquad (3.16)$$

Thus for the first excited state of hydrogen atom, one energy level is raised by $3eEa_0$, and one is decreased by the same amount. The other two levels remain unchanged.

3.4 The Variation Method

The expectation value of energy in normalized state Ψ is given by

$$< E >= \int \Psi^* H\psi \, d\tau \qquad (3.17)$$

If we choose the wave function Ψ as variable function, then the integral (3.17) is known as variation 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.

$$< E >= \int \psi_0^* H\psi_0 \, d\tau = E_0 \qquad (3.18)$$

If $\psi \neq \psi_0$, they by expansion theorem ψ may be expanded in terms of a complete set of orthonormal functions $\phi_0, \phi_1, \phi_2 \ldots$obtaining

$$\psi = \sum_n a_n \phi_n \; with \sum_n a_n a_n^* = 1 \; and \; H\phi_n = E_n \phi_n \qquad (3.19)$$

Substituting this in equation (3.17), we get

$$< E >= \sum_n a_n {}^* a_m \int \phi_n {}^* H\phi_m d\tau \qquad (3.20)$$

But $\qquad H\phi_m = E_m \phi_m$

we have

$$< E >= \sum_n a_n {}^* a_m \int \phi_n {}^* E_m \phi_m d\tau$$

$$= \sum_n a_n {}^* a_m E_m \int \phi_n {}^* \phi_m d\tau$$

$$= \sum_n a_n {}^* a_m E_m \delta_{nm}$$

Therefore $< E >= \sum_n a_n {}^* a_n E_n$ $\begin{bmatrix} Since\ \delta_{mn} = 1\ for\ m = n \\ = 0\ for\ m \neq n \end{bmatrix}$

$$= \sum_n | a_n |^2 E_n$$

Substracting the ground state energy E_0 from both sides, we get

$$< E > - E_0 = \sum_n | a_n |^2 \left(E_n - E_0 \right) \qquad (3.21)$$

As $|a_n|^2$ is positive and $E_n \geq E_0$ (always) for all values of n; therefore right hand side is positive or zero. Thus we have proved that < E > is always an upper limit to E_0, i.e.

$$< \mathrm{E} > \ \geq \ \mathrm{E}_0 \qquad (3.22)$$

This theorem is the basis of the variation method for the calculation of the approximate eigen value of the system. If we choose a number of wave-functions Ψ_1, Ψ_2,Ψ_3… and calculate the E_1, E_2, E_3... coresponding to them, then each of these values of E is greater than the energy E_0, So that the lowest one is the nearest to E_0. Often the functions Ψ_1, Ψ_2,Ψ_3…are only distinguished by having different values of some parameter λ the process of minimising E with respect to this parameter may then be carried out in order to obtain the best approximation to E_0. Which from the trial function Ψ will follow.

3.5 Physical applications of Variation method

Ground State of Helium : We use the variation method with a simple trial function to obtain an upper limit for the energy of the ground state of the helium atom. The helium atom consists of a nucleus of charge + 2*e* and two electrons each of charge '- *e*' If we consider the nucleus at rest, the Hamiltonian will be

$$\mathrm{H}=-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)-2e^2\left(\frac{1}{\mathrm{r}_1}+\frac{1}{\mathrm{r}_2}\right)+\frac{e^2}{\mathrm{r}_{12}} \tag{3.23}$$

where ∇_1^2 and ∇_2^2 and Laplacian operators for the first and second electrons at a distance r_1 and r_2 from the nucleus, $\mathrm{r}_{12}=|\mathrm{r}_2-\mathrm{r}_1|$ is the distance between two electrons. If the interaction energy $\frac{e^2}{\mathrm{r}_{12}}$ between two electrons were not present, the ground state eigenfunction of He would be product of two normalized hydrogen like wavefunctions $u_{100}(\mathrm{r}_1)u_{100}(\mathrm{r}_2)$ given by

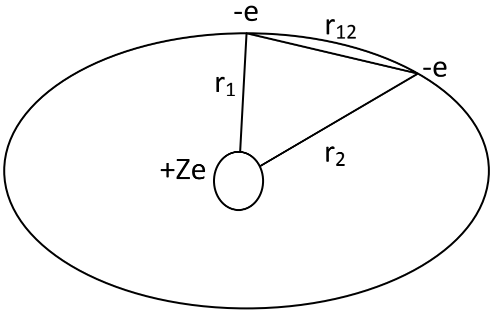

Fig. 3.3

$$\psi(r_1\, r_2)=\mathbf{u}_{100}(r_1)\mathbf{u}_{100}(r_2)=\frac{z^3}{\pi a_0^3}e^{-(\mathbf{z}/a_0)(r_1+r_2)}$$

with $z=2$ and $\mathrm{a}_0=\frac{\hbar^2}{me^2}$

We shall use (r$_1$, r$_2$) as a trial function and treat z to be the variation parameter, so that it is not necessarily equal to 2. The expectation value of Hamiltonian H is the sum of expectation values of kinetic energy and potential energy individually.

H = K.E. + P.E.

= T + V + interaction energy $\left(\frac{\mathbf{e}^2}{\mathbf{r}_{12}}\right)$ of electrons.

then $<H> = <T> + <V> + <\frac{e^2}{\mathrm{r}_{12}}>$

Now the expectation values of hydrogen-like atoms (having one electron) with z atomic number in general are

$$<T>=\frac{\mathbf{z}^2\mathbf{e}^2}{2a_0},<V>=-\frac{2\mathbf{z}\mathbf{e}^2}{a_0}.\ \text{Since}\frac{1}{r_1}=\frac{\mathbf{z}}{a_0}.$$

But helium atom in ground state has two electrons, so it will be twice of hydrogen-like atom,

i.e. $$<\mathrm{T}> = \frac{2\mathbf{z}^2\mathbf{e}^2}{2a_0}=\frac{\mathbf{z}^2\mathbf{e}^2}{2a_0} \tag{3.24}$$

and $$< V > = -2 \times \frac{2\mathbf{ze}^2}{a_0} = -\frac{4\mathbf{ze}^2}{a_0} \tag{3.25}$$

Hence $$< H > = \frac{\mathbf{z}^2\mathbf{e}^2}{2a_0} - \frac{4\mathbf{ze}^2}{a_0} + < \frac{e^2}{r_{12}} > \tag{3.26}$$

Electron Interaction Energy : The expectation value of the interaction energy between the electron is

$$< \frac{e^2}{r_{12}} > = \iint \psi^*(r_1 r_2)\frac{e^2}{r_{12}}\psi(r_1 r_2) d^3 r_1 d^3 r_2$$

$$= \left(\frac{z^3}{\pi a_0^3}\right)^2 e^2 \iint \frac{1}{r_{12}} e^{-(2z/a_0)(r_1+r_2)} d^3 r_1 d^3 r_2$$

Substituting,

$$\frac{2z}{a_o} r_1 = \rho_1 \text{ and } \frac{2z}{a_0} r_2 = \rho_2, \frac{2z}{a_0} r_{12} = \rho_{12}$$

we get $$< \frac{e^2}{r_{12}} > = \frac{ze^2}{32\pi^2 a_0} \iint \frac{e^{-(\rho_1+\rho_2)}}{\rho_{12}} d^3\rho_1 d^3\rho_2$$

Solving the spherically symmetric integral by knowledge of electrostatics as in perturbation theory, we get

$$\therefore \quad < \frac{e^2}{r_{12}} > = \frac{ze^2}{32\pi^2 a_0} 20\pi^2$$

$$= \frac{5ze^2}{8a_0} \tag{3.27}$$

The expectation value of Hamiltonian (3.26) for the trial function is

$$< H > = \frac{e^2 z^2}{a_0} - \frac{4e^2 z}{a_0} + \frac{5e^2 z}{8a_0} = \frac{e^2}{a_0}\left(z^2 - \frac{27}{8} z\right)$$

Differentiating with respect to z and for minimum <H>, equating the differential to zero,

$$\frac{\partial < H >}{\partial z} = \frac{\partial}{\partial z}\left\{\frac{e^2}{a_0}\left(z^2 - \frac{27}{8} z\right)\right\} = 0,$$

This gives $z = \frac{27}{16} = 1.69$. Thus the lowest upper limit for the ground state energy of helium atom obtained with trial function

$$= \frac{e^2}{a_0}\left[\left\{\frac{27}{16}\right\}^2 - \frac{27}{8}.\frac{27}{16}\right] = -\left\{\frac{27}{16}\right\}^2 \frac{e^2}{a_0} = -2.85\frac{e^2}{a_0} \qquad (3.28)$$

By the help of perturbation method, the ground state energy of helium atom comes out $-2.85\frac{e^2}{a_0}$, where $a_0 = \frac{\hbar^2}{m_0 e^2}$.

The hydrogenetic wavefunctions give the best energy value when $z = \frac{27}{16}$ rather than 2. It indicates that each electron screens the nucleus from the other electron, therefore the effective nuclear charge being reduced $\left(i.e.\ 2 - \frac{27}{16} = \frac{5}{16}\right)$ by of an electronic charge.

Hence "effective charge" in the nucleus is less than 2.

3.6 Connection formulas for penetration of a barrier

Figure (3.4) represents potential function *V(x)* as a function of *x*. Let a particle has energy E. Then the whole region is divided into three regions

Region I where $V > E$

Region II where $E > V$

Region III where $V > E$

There are two types of turning points, specified by points x_1 and x_2. When we pass from region I to 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

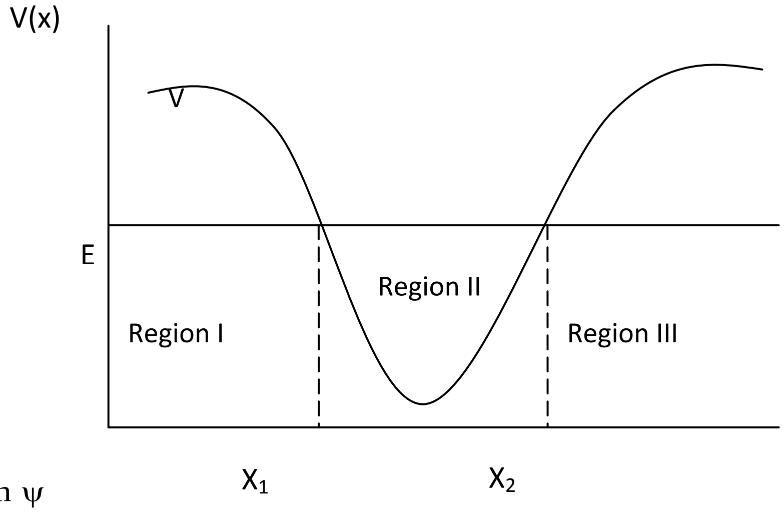

Fig. 3.4

$$\psi_1 = \frac{A}{\sqrt{p_1}} \exp\left(\int_{x_1}^{x} \frac{p_1 dx}{\hbar}\right) \tag{3.28a}$$

In region II, the wave function ψ is oscillatory given by

$$\psi_2 = \frac{B}{\sqrt{p_2}} \exp\left(i\int^{x} \frac{p\,dx}{\hbar}\right) + \frac{C}{\sqrt{p_2}} \exp\left(-i\int^{x} \frac{p\,dx}{\hbar}\right) \tag{3.29}$$

In region III, the wave-function decreases exponentially for $x \to -\infty$

$$\psi_3 = \frac{D}{\sqrt{p_1}} \exp\left(-\int_{x_2}^{x} \frac{p_1\,dx}{\hbar}\right) \tag{3.30}$$

The regions of validity of these wave-forms of wave-functions are separated by the classical turning points near which W.K.B. approximation fails. As ψ_1, ψ_2, ψ_3 are all the approximations of the same function ψ, therefore the constants A, B, C and D cannot all be arbitrary.

To connect the wave-functions at the turning points we assume that the potential energy function is approximately linear in the neighbourhood of turning points x_1 and x_2. Thus at x_1 and x_2, we write

$$\left.\begin{array}{l} E - V(x) = C_1(x - x_1) \\ V(x) - E = C_2(x - x_2) \end{array}\right\} \text{ or } \left.\begin{array}{l} E - V(x) = C_1(x - x_1) \\ E - V(x) = -C_2(x - x_2) \end{array}\right\} \tag{3.31}$$

The schroedinger wave-equation

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

In the neighbourhood of $x = x_1$ and $x = x_2$, this eqn. takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mC_1}{\hbar^2}(x - x_1)\psi = 0 \qquad \text{(near } x_1\text{)} \tag{3.32}$$

and
$$\frac{d^2\psi}{dx^2} - \frac{2mC_2}{\hbar^2}(x - x_2)\psi = 0 \qquad \text{(near } x_2\text{)} \tag{3.33}$$

Now we change the variable in equation (3.32) by substituting

$$z = -\left(\frac{2mC_1}{\hbar^2}\right)^{1/3}(x - x_1) \tag{3.34}$$

$$\Rightarrow \qquad \frac{d\psi}{dx} = \frac{d\psi}{dz}\frac{dz}{dx}$$

$$= -\frac{\mathrm{d}\psi}{\mathrm{dz}}\left(\frac{2m\mathrm{C}_1}{\hbar^2}\right)^{1/3} 1$$

and
$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = \frac{\mathrm{d}}{\mathrm{dz}}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)\frac{\mathrm{dz}}{\mathrm{d}x}$$

$$= \frac{d}{d\mathbf{z}}\left\{-\frac{d\psi}{d\mathbf{z}}\left(\frac{2\mathbf{m}C_1}{\hbar^{\ 2}}\right)\right\}^{1/3}\left\{-\left(\frac{2\mathbf{m}C_1}{\hbar^{\ 2}}\right)^{1/3}\right\}$$

$$= \left(\frac{2m\mathrm{C}_1}{\hbar^2}\right)^{2/3}\frac{\mathrm{d}^2\psi}{\mathrm{dz}^2}$$

Making these substitutions in (3.32), we get

$$\frac{\mathrm{d}^2\psi}{\mathrm{dz}^2} - \mathrm{z}\psi = 0 \tag{3.35}$$

Similarly by substituting $z = \left[\frac{2mC_2}{\hbar^2}\right]^{\frac{1}{3}}(\mathbf{x} - \mathbf{x}_2)$

equation (3.33) becomes $\frac{\mathrm{d}^2\psi}{\mathrm{dz}^2} - \mathrm{z}\psi = 0$ (3.36)

Equation (3.35) and (3.36) are Airy functions. We require a function which vanishes asymptotically for large positive z (z > 0) corresponds to $x < x_1$ and $x > x_2$) such a function is

$$\mathrm{Ai(z)} = \frac{1}{\pi}\int_0^\infty \cos\left[\frac{s^{\ 3}}{3} + sz\right]ds \tag{3.37}$$

For Large (z) it has asytnptotic form

$$Ai(z) - \frac{1}{2\sqrt{\pi}\, z^{\frac{1}{4}}}\exp\left[-\frac{2}{3}z^{\frac{3}{2}}\right] \qquad (z > 0) \tag{3.38}$$

$$Ai(z) - \frac{1}{2\sqrt{\pi}\,(-z)^{\frac{1}{4}}}\sin\left[\frac{2}{3}(-z)^{\frac{3}{2}} + \frac{\pi}{4}\right] \qquad (z > 0) \tag{3.39}$$

If the energy E is sufficiently large, the de-Broglie wavelength associated with the particle is extremely small so the regions of validity of linear approximations contain many wavelengths. The function Ai(z) which passes smoothly through the turning point provides the required connections among the approximate forms equations (3.28a), (3.29) and (3.30).

In the neighbourhood of x_1, we have

$$p_1{}^2 = 2mC_1(\mathbf{x} - \mathbf{x}_1) = -(2mC_1\hbar)^{\frac{2}{3}}\, z$$

$$\text{and } \int_{\mathbf{x}1}^{\mathbf{x}} \frac{p_1 d\mathbf{x}}{\hbar} = \left[\frac{2mC_1}{\hbar^{\;2}}\right]^{\frac{1}{3}} \int_{\mathbf{x}1}^{\mathbf{x}} \sqrt{z}\, dx$$

$$= \int_0^z \sqrt{-z}\, dz = \frac{-2}{3}(z)^{\frac{3}{2}} \qquad (3.40)$$

$$\text{Similarly } \int_{\mathbf{x}1}^{\mathbf{x}} \frac{p_2 d\mathbf{x}}{\hbar} = \left[\frac{2mC_1}{\hbar^2}\right]^{\frac{1}{3}} \int_{\mathbf{x}1}^{\mathbf{x}} \sqrt{-z}\, dz = \int_0^{\tau} \sqrt{-z}\, dz = \frac{2}{3}(-z)^{\frac{3}{2}} \qquad (3.41)$$

Comparison of (3.40) and (3.41) with equations (3.38) and (3.39) shows that the functions approximated to the left of x_1 by

$$\psi_1 = \frac{1}{\sqrt{p_1}} \exp\left[\int_{\mathbf{x}_1}^{\mathbf{x}} \frac{p_1 d\mathbf{x}}{\hbar}\right]; \qquad \mathbf{x} < \mathbf{x}_1 \qquad (3.42)$$

has on the right the approximation

$$\psi = \frac{2}{\sqrt{p_2}} \sin\left(\int_{x1}^{x} \frac{p_2 dx}{\hbar} + \frac{\pi}{4}\right); \; x > x_1 \qquad (3.43)$$

A similar analysis in the neighbourhood of points x_2 shows that the function approximated to the right of x_2 by

$$\psi_3 = \frac{1}{\sqrt{p_1}} \exp\left(-\int_{x2}^{x} \frac{p_1 dx}{\hbar}\right); \qquad (x > x_2) \qquad (3.44)$$

is approximated in region II by

$$\psi = \frac{2}{\sqrt{p_2}} \sin\left(\int_{x}^{x2} \frac{p_2 dx}{\hbar} + \frac{\pi}{4}\right); \; (x < x_2) \qquad (3.45)$$

$$\psi_{WKB} = \begin{cases} \dfrac{1}{\sqrt{p_1}} \exp\left(-\displaystyle\int_{x2}^{x} \frac{p_1 dx}{\hbar}\right); & x > x_2 \\ \dfrac{2}{\sqrt{p_2}} \sin\left(\displaystyle\int_{x}^{x2} \frac{p_2 dx}{\hbar} + \frac{\pi}{4}\right); & x < x_2 \end{cases}$$

Again the solution of equation (3.33) is the Airy function

$$\mathrm{B_i(z)} = \frac{1}{\pi}\int_0^{\infty}\left[e^{-sz-\frac{s^3}{3}} + \sin\left(\frac{s^3}{3}+sz\right)\right]ds \tag{3.46}$$

This has asymptotic forms

$$\mathrm{B_i(z)} \sim \frac{1}{\sqrt{\pi}\mathrm{z}^{1/4}}\exp\left(\frac{2}{3}\mathrm{z}^{3/2}\right)\ (\mathrm{z}>0) \tag{3.47}$$

$$\mathrm{B_i(z)} \sim \frac{1}{\sqrt{\pi}(-\mathrm{z})^{1/4}}\cos\left[\frac{2}{3}(-\mathrm{z})^{3/2}+\frac{\pi}{4}\right]\ (\mathrm{z}<0) \tag{3.48}$$

A similar argument leads to the connection formulae

$$\psi_{\mathrm{WKB}} \approx \begin{cases} \dfrac{1}{\sqrt{\mathrm{p}_1}}\exp\left(\displaystyle\int_{\mathrm{x}}^{\mathrm{x}_1}\frac{\mathrm{p}_1\mathrm{dx}}{\hbar}\right);\ (\mathrm{x}<\mathrm{x}_1) \\ \dfrac{1}{\sqrt{\mathrm{p}_2}}\cos\left(\displaystyle\int_{\mathrm{x}_1}^{\mathrm{x}}\frac{\mathrm{p}_2\mathrm{dx}}{\hbar}+\frac{\pi}{4}\right);\ (\mathrm{x}>\mathrm{x}_1) \end{cases} \tag{3.49}$$

Hence, the connection formulae at turning point x = a may be expressed in terms of Barrier to the right and Barrier to the left as follows.

Barrier to the Right : Let V > E to the right of x = a.

For decreasing exponential

$$\frac{1}{\sqrt{p_1}}\exp\left(-\int_a^x\frac{p_1dx}{\hbar}\right) \approx \frac{2}{\sqrt{p_2}}\sin\left(\int_a^x\frac{p_2dx}{\hbar}+\frac{\pi}{4}\right)$$

$$\frac{1}{\sqrt{\mathrm{p}_1}}\exp\left(-\int_{\mathrm{a}}^{\mathrm{x}}\frac{\mathrm{p}_1\mathrm{dx}}{\hbar}\right) \approx \frac{-2}{\sqrt{\mathrm{p}_2}}\cos\left(\int_{\mathrm{a}}^{\mathrm{x}}\frac{\mathrm{p}_2\mathrm{dx}}{\hbar}-\frac{\pi}{4}\right)$$

(3.50)

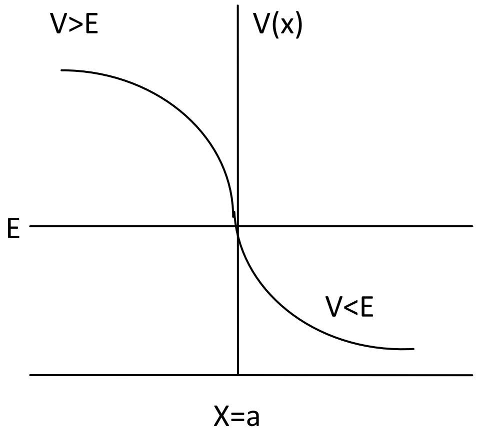

Fig.3.5

For increasing exponential

$$\frac{1}{\sqrt{p_1}}\exp\left(\int_a^x \frac{p_1 dx}{\hbar}\right) = \frac{1}{\sqrt{p_2}}\cos\left(\int_a^x \frac{p_2 dx}{\hbar} + \frac{\pi}{4}\right)$$
$$\frac{1}{\sqrt{p_1}}\exp\left(\int_a^x \frac{p_1 dx}{\hbar}\right) = -\frac{1}{\sqrt{p_2}}\sin\left(\int_a^x \frac{p_2 dx}{\hbar} - \frac{\pi}{4}\right) \qquad (3.51)$$

Barrier to the left: Let V > E to the left of x = a.

For decreasing exponential

$$\frac{1}{\sqrt{p_1}}\exp\left(-\int_x^a \frac{p_1 dx}{\hbar}\right) = \frac{2}{\sqrt{p_2}}\sin\left(\int_a^x \frac{p_2 dx}{\hbar} + \frac{\pi}{4}\right) \qquad (3.52)$$

or $$\frac{1}{\sqrt{p_1}}\exp\left(-\int_x^a \frac{p_1 dx}{\hbar}\right) \approx \frac{2}{\sqrt{p_2}}\cos\left(\int_a^x \frac{p_2 dx}{\hbar} - \frac{\pi}{4}\right) \qquad (3.53)$$

For increasing exponential

$$\frac{1}{\sqrt{p_1}}\exp\left(\int_x^a \frac{p_1 dx}{\hbar}\right) \approx \frac{1}{\sqrt{p_2}}\cos\left(\int_a^x \frac{p_2 dx}{\hbar} + \frac{\pi}{4}\right) \qquad (3.54)$$

or $$\frac{1}{\sqrt{p_1}}\exp\left(\int_x^a \frac{p_1 dx}{\hbar}\right) \approx -\frac{1}{\sqrt{p_2}}\sin\left(\int_a^x \frac{p_2 dx}{\hbar} - \frac{\pi}{4}\right) \qquad (3.54A)$$

It may be noted that the connection formulae enable us only to obtain the relation between the solutions in a region at some distance to the right of the turning point x = a, with those in a region some distance to the left. In order to obtain the form of the wave-function in the intermediate region, we should consider the exact, solution, which involves Bessel functions of order $\frac{1}{3}$.

For applying W.K.B. approximation, the following requirements must be satisfied.

1. On either side of the turning point, there exist regions when the potential function changes slowly so that W.K.B. approximation is applicable.
2. In the region near the turning point x = a, where W.K.B. method becomes inapplicable, the kinetic energy can be represented approximately by a straight line (E – V) = C (x – a). In other words the potential should not undergo a large fractional

change in slope within this region. Inside the barrier W.K.B. approximation begins to hold after

$$\int_{a}^{x} \sqrt{[2m(V-E)]}\ \frac{dx}{\hbar}$$

becomes appreciably greater than unity.

3.7 Time Dependent Perturbation Theory

Consider the wave eqn,

$$H^{(0)}\Psi^{(0)} = i\hbar\frac{\partial\Psi^{(0)}}{\partial t}$$

The general solution of the above eqn is

$$\Psi^{(0)} = \sum_{n=0}^{\infty} a_n^{(0)} e^{\frac{-i}{\hbar}E_n^{(0)}t}\psi_n^{(0)} \qquad (3.55)$$

Consider the Hamiltonian $H = \left(H^{(0)} \ + \lambda H^{(1)}\right)$

$H^{(0)}$ is the unperturbed Hamiltonian and $H^{(1)}$ is a small perturbation varying very slowly w.r.t. time

Substituting H in the perturbed eqn $H\Psi = E\Psi$ we get

$$(H^{(0)} + \lambda H^{(1)})\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

The general solution of this eqn is

$$\Psi(r,t) = \sum_n a_n(t)\Psi_n^{(0)}(r,t) \qquad (3.56)$$

Substituting (3.56) and using $H^{(0)}\Psi_n^{(0)} = i\hbar\frac{\partial\Psi_n^{(0)}}{\partial t}$ we get

$$\lambda\sum_n a_n(t)H^{(1)}\Psi_n^{(0)} = i\hbar\sum \Psi_n^{(0)}\frac{\partial a_n(t)}{\partial t}$$

Multiply by $\Psi_m^{(0)*}$ and integrating

$$\lambda\sum_n\int a_n(t)\Psi_m^{(0)*}H^{(1)}\Psi_n^{(0)}d\tau = i\hbar\sum_n\int\frac{\partial a_n(t)}{\partial t}\Psi_m^{(0)*}\Psi_n^{(0)}d\tau$$

or $$\frac{\partial a_m(t)}{\partial t} = \dot{a}_m(t) = \frac{1}{i\hbar}\lambda\sum_n a_n(t)\int\ \Psi_m^{(0)*}H_{(1)}\Psi_n^{(0)}d\tau, \quad m = 0,1,2...$$

multiplying and dividing by $\exp\left(\frac{i}{\hbar}E_m(t)\right)$ and using $\omega_{mn} = \frac{E_m - E_n}{\hbar}$ we get

$$\dot{a}_m(t) = \frac{1}{i\hbar}\lambda\sum_n a_n(t)H'_{mn}\exp(i\omega_{mn}t) \tag{3.57}$$

where $H_{mn}^{(1)} = \int\psi_m^{(0)*}H^{(1)}\psi_n^{(0)}d\tau$

the perturbation is so small such that $a_n(t)$ does not vary very much with time.to find the value of an(t)

Let $a_n(t) = a_n^{(0)} + \lambda a_n^1(t) + \lambda^2 a_n^{(2)}(t) + ...$ (3.58)

Substituting (3.58) in (3.57) we get

$$\dot{a}_m(t) = -\frac{i}{\hbar}\lambda\sum_n(a_n{}^{(0)} + \lambda a_n^1 + \lambda^2 a_n^2 + ...)H_{mn}^{(1)}\exp(i\omega_{mn}t) \tag{3.58a}$$

Zereo Order Calculation:

Equating the coefficient of λ^0 we get the zero order calculation as

$$\frac{\partial a_m^{(0)}(t)}{\partial t} = 0 \quad \text{or} \quad a_m^{(0)}(t) = \text{constant t} \tag{3.59}$$

This gives the initial state of the system. Let us assume the system is in particular state '*l*' at t=0. That is $a_l^{(0)}(0) = 0$ or $a_i^{(0)} = \delta_{il}$

First order calculation:

Equating the coefficients of λ in eqn (3.58a),

$$\frac{\partial}{\partial t}a_m^{(1)}(t) = -\frac{i}{\hbar}\sum_n a_n^{(0)}(t)H_{mn}^{(1)}\exp(i\omega_{mn}t)$$

or
$$a_m^{(1)}(t) = -\frac{i}{\hbar}\int_{-\infty}^{t}\left[\sum_n a_n^{(0)}(t)H_{mn}^{(1)}\exp(i\omega_{mn}t)\right]dt$$

$$= -\frac{i}{\hbar}\int_{-\infty}^{t}\left[\sum_n \delta_{nl}H_{mn}^{(1)}\exp(i\omega_{ml}t)\right]dt$$

$$= -\frac{i}{\hbar}\int_{-\infty}^{t}\left[H_{ml}^{(1)}\exp(i\omega_{ml}t)\right]dt$$

Let the perturbation is turned on at time *t*=0 and turned off at time *t*=*t*. Now we can write

$$a_m^{(1)}(t) = -\frac{i}{\hbar}H_{ml}^{(1)}\int_0^t \exp(i\omega_{ml}t)dt$$

$$= -\frac{i}{\hbar}H_{ml}^{(1)}\left[\frac{e^{i\omega_{ml}t}-1}{\omega_{ml}}\right] \tag{3.60}$$

Probability of finding a particle in mth state:

$$\text{Probability } P = a_m^{(1)}(t)a_m^{(1)*}(t) = \frac{1}{\hbar^2}\left|H_{ml}^{(1)}\right|^2\frac{1}{\omega_{ml}{}^2}(e^{i\omega_{ml}t}-1)(e^{-i\omega_{ml}t}-1)$$

$$\text{P}= \frac{1}{\omega_{ml}^2}2(1-\cos\omega_{ml}t)\frac{\left|H_{ml}^{(1)}\right|^2}{\hbar^2} \tag{3.61}$$

$$= \frac{4}{\omega_{ml}^2}\sin^2(\omega_{ml}t/2)\frac{\left|H_{ml}^{(1)}\right|^2}{\hbar^2} == \frac{4\left|H_{ml}^{(1)}\right|^2\sin^2(\omega_{ml}t/2)}{\hbar^2\omega_{ml}^2}$$

The fig.(3.6) shows the plot of $\frac{\sin^2(\omega_{ml}t/2)}{\omega_{ml}^2}$ against ω_{ml}

Physical interpretation of the curve:

The maximum value of $\frac{\sin^2(\omega_{ml}t/2)}{\omega_{ml}^2}$ occurs when $\omega_{ml} = 0$. Let $\omega_{ml} = x$

$$\frac{\sin^2(xt/2)}{x^2} = \frac{1}{x^2}\left[\left(\frac{xt}{2}\right) - \frac{(xt)^3}{3.2^3} + \dots\right]^2$$

$$= \frac{1}{x^2}\left[\frac{xt}{2}\right]^2$$

$$= \frac{t^2}{4}$$

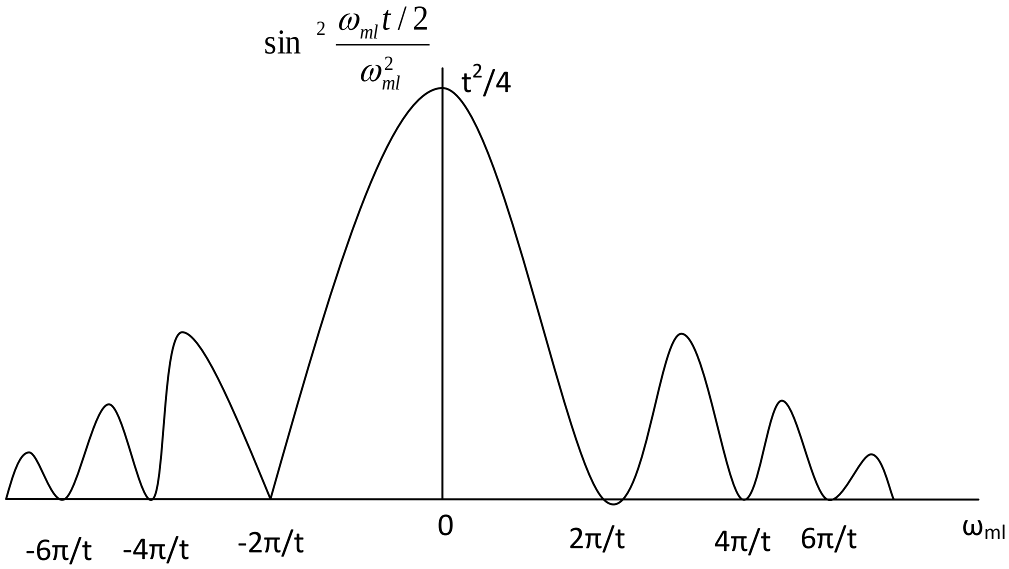

Fig. 3.6

This is the highest value on the y-axis of the graph. The value of $\frac{\sin^2(xt/2)}{x^2}$ is zero when

$$\frac{xt}{2} = \pm n\pi \quad \text{or} \quad x = \omega_{ml} = \pm\frac{2\pi n}{t}$$

$$\omega_{ml} = \pm\frac{2\pi}{t}, \pm\frac{4\pi}{t}, \pm\frac{6\pi}{t}\, etc. \quad for \quad n = 1,2,3\, etc.\ \text{respectively.}$$

From the figure the main peak is proportional to t^2 and the breadth is inversely proportional to t. Therefore the area under the curve is proportional to t. This indicates that the transition probability per unit time is proportional to the 'ON' time of perturbation.

Fermi Golden Rule(Transition to continuum):

The probability of transition l^{th} state to mth state is given by

$$W = \left|a_m^2(t)\right|^2 = \frac{1}{\hbar^2}\left|H_{ml}^{(1)}\right|^2 \frac{4\sin^2(\omega_{ml}t/2)}{\omega_{ml}^2} \qquad (3.62)$$

Since ω_{ml} appears in the denominator, transition probability is maximum when ω_{ml} is small or E_m and E_l are closer. If the energy levels are closer, they form a cluster or continuum states.

Now, the total probability of transition $= \sum |a_m(t)|^2$. If $\rho(m)$ is the density of final states then $\rho(m)dE$ will be the number of such states in the energy interval E_m and $E_m + dE$

The total probability of transition to these states $= \sum |a_m(t)|^2 = \int |a_m(t)|^2 \rho(m)dE$

The main contribution for transition comes from the peak

Therefore transition probability $T = \frac{1}{\hbar^2}\left|H_{ml}^{(1)}\right|^2 \rho(m) \int_{-\infty}^{\infty} \frac{4\sin^2(\omega_{ml}t/2)}{\omega_{ml}^2} dE$

But $dE = \hbar d\omega$ since $E = \hbar\omega$

$$\therefore T = \frac{1}{\hbar}\left|H_{ml}^{(1)}\right|^2 \rho(m) \int_{-\infty}^{\infty} \frac{4\sin^2 \omega_{ml}t/2)}{\omega_{ml}^2} d\omega$$

The integral value is $2t\pi$. Therefore $T = \frac{1}{\hbar}\left|H_{ml}^{(1)}\right|^2 \rho(m)2t\pi$

or transition probability per unit time is $T = \frac{2\pi}{\hbar}\left|H_{ml}^{(1)}\right|^2 \rho(m)$

(3.63)

This is Fermi Golden Rule. It states that,

The transition probability per unit time to states of continuum is

i. Non-zero between continuum states

ii. Proportional to $\left|H_{ml}^{(1)}\right|^2$ perturbation

iii. Proportional to density of final states

3.8 Harmonic perturbation

Let us consider a perturbation is harmonic of frequency ω as

$$< k \,|\, H'(t') \,|\, m >$$

$$>$$

or

$$H'_{km}(t') = \begin{cases} 0 \quad for\ -\infty < t' < 0 \\ 2 < k \,|\, H_0' \,|\, m > \sin\omega t' \quad for\ \ 0 \le t' \le t \\ 0 \qquad for \qquad t' > t \end{cases} \tag{3.64}$$

where $< k \,|\, H_0' \,|\, m >$ is independent of time.

The first order amplitude $a^{(1)}{}_k(t')$ at t' is

$$a_k^{(1)}(t' \le t) = (i\hbar)^{-1} \int_0^t < k \,|\, H' \,|\, m > e^{i\omega_{km} t'} dt'$$

$$= (i\hbar)^{-1} \int_0^t 2 < k \,|\, H_0' \,|\, m > \sin\omega t' e^{i\omega_{km} t'} dt'$$

$$= \frac{2 < k \,|\, H_0' \,|\, m >}{i\hbar} \int_0^t \frac{e^{i\omega t'} - e^{-i\omega t'}}{2i} e^{i\omega_{km} t'} dt'$$

$$= -\frac{< k \,|\, H_0' \,|\, m >}{\hbar} \int_0^t \left\{ e^{i(\omega_{km}+\omega)t'} - e^{i(\omega_{km}-\omega)t'} \right\} dt'$$

$$a_k^{(1)}(t') = -\frac{< k \,|\, H'_0 \,|\, m >}{i\hbar} \left[\frac{\exp(i(\omega_{km}+\omega)t - 1}{\omega_{km}+\omega} - \frac{\exp(i(\omega_{km}-\omega)t - 1}{\omega_{km}-\omega} \right]$$

This reveals the amplitude depends on perturbation duration interval *t* and independent of instantaneous time *t'*.The amplitude is appreciable when one of the terms in the denominator is zero.Thus the effect of harmonic perturbation is either transfer or receive energy from the system.

The probability of finding the system in kth state is given by

$$\left| a_k^{(1)}(t' \ge t) \right|^2 = \frac{4 \left| < k \,|\, H'_0 \,|\, m > \right|^2 \sin^2 \dfrac{(\omega_{km} - \omega)t}{2}}{\hbar^2 (\omega_{km} - \omega)^2} \tag{3.65}$$

3.9 Adiabatic approximation:

This method is used to find approximate solutions to time dependent Schrodinger eqn for the systems where the Hamiltonian changes slowly in comparison eith the internal frequency of wave functions.

Consider the schrodinger eqn $i\hbar\frac{\partial\Psi}{\partial t}=H(t)\Psi$. (3.65A)

Here $H(t)$ varies slowly such that a good approximation is obtained by solving sch eqn at each instant of time.We assume H is constant and equal to instantaneous value $H(t^{'})$ where $t^{'}$ is the value of t at which we calculate H.Then the stationary state wave functionobtained by setting t=t'=const would satisfy

$$H(t')\psi_n(x,t')=E_n(t')\psi_n(x,t')$$

Since H is a slowly varying fn of time t',the approximate soln can be written as

$$\Psi_n=\psi_n(x,t)\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right) \tag{3.66}$$

When this wave functionis known at zero time then at later times we can write

$$\Psi=\sum_n a_n(t)\psi_n(x,t)\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right) \tag{3.66A}$$

Substituting (3.66A) in (3.65A)

$$\begin{aligned}&i\hbar\sum_n\left(\dot{a}_n\psi_n+a_n\frac{\partial\psi_n}{\partial t}\right)\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right)+\sum_n a_n\psi_n E_n\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right)\\&=H(t)\sum_n a_n\psi_n E_n\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right)\end{aligned}$$

Here we have used $H(t)\psi_n=E_n\psi_n$

or $i\hbar\sum_n\left(\dot{a}_n\psi_n+a_n\frac{\partial\psi_n}{\partial t}\right)\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right)=0$

Multiplying the above eqn by $\psi_m * \exp\left(\frac{i}{\hbar}\int_0^t E_m(t')dt'\right)$ and integrating over all space we get

$$\int\sum \dot{a}_n\psi_n\psi_m * \exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right)\exp\left(\frac{i}{\hbar}\int_0^t E_m(t')dt'\right)d\tau + \sum_n a_n\int\psi_m * \frac{\partial\psi_n}{\partial t}\exp\left(-\frac{i}{\hbar}\int_0^t (E_n - E_m)dt'\right)d\tau = 0$$

Using orthonormal conditions

$$\dot{a}_m = -\sum_n a_n\int\psi_m * \frac{\partial\psi_n}{\partial t}d\tau \quad \left\{\exp\left(-\frac{i}{\hbar}\int_0^t (E_n - E_m)dt'\right)\right\}d\tau \qquad (3.67)$$

To solve the integral of the above expression we know $H(t)\psi_n(t) = E_n(t)\psi_n(t)$

Differentiating w.r.t. *t*, $\quad \frac{\partial H}{\partial t}\psi_n + H\frac{\partial\psi_n}{\partial t} = \frac{\partial E_n}{\partial t}\psi_n + E_n\frac{\partial\psi_n}{\partial t}$

Multiply this equation by ψ_m^* and integrating,

$$\int\psi_m * \frac{\partial H}{\partial t}\psi_n d\tau + \int\psi_m * H\frac{\partial\psi_n}{\partial t}d\tau = \frac{\partial E_n}{\partial t}\underbrace{\int\psi_m^*\psi_n d\tau}_{0} + E_n\int\psi_m^*\frac{\partial\psi_n}{\partial t}d\tau \qquad (3.67\text{A})$$

or $\quad \int\psi_m * H\frac{\partial\psi_n}{\partial t}d\tau = \int(H\psi_m)^*\frac{\partial\psi_n}{\partial t}d\tau = E_m\int\psi_m^*\frac{\partial\psi_n}{\partial t}d\tau$ since, H is Hermitian.

Substituting in (3.67A) and simplifying,

$$\int\psi_m * \frac{\partial\psi_n}{\partial t}d\tau = -\frac{\int\psi *_m\left(\frac{\partial H}{\partial t}\psi_n d\tau\right)}{E_m - E_n}, \quad m \neq n$$

Substituting in (3.67)

$$\dot{a}_m + \sum_{m\neq n}\frac{\int \psi_m^*\frac{\partial H}{\partial t}\psi_n d\tau \exp\left(-\frac{i}{\hbar}\int_0^t (E_n - E_m)dt'\right)}{E_n - E_m} = 0 \qquad (3.68)$$

Now, let us suppose that the system starts with $a_s = 1 \quad and \quad a_n = 0 \quad for\, n \neq s$.

By successive approximation we can solve for a_m.

$$\dot{a}_{ms} + \frac{\left(\frac{\partial H}{\partial t}\right)_{ms}}{(E_s - E_m)} \exp\left[-\frac{i}{\hbar}\int_o^t (E_s - E_m)dt'\right] = 0, \qquad \text{where } \left(\frac{\partial H}{\partial t}\right)_{ms} = \int \psi_m^* \frac{\partial H}{\partial t} \psi_s d\tau$$

Neglecting the slow variation of $\left(\frac{\partial H}{\partial t}\right)_{ms}$,

$$a_{ms} = \frac{\hbar}{i(E_s - E_m)^2}\left(\frac{\partial H}{\partial t}\right)_{ms}\left[\exp\left(-\frac{i}{\hbar}(E_s - E_m)t\right) - \exp\left(-\frac{i}{\hbar}(E_s - E_m)t_0\right)\right] \tag{3.69}$$

where we have neglected the slow change of $\left(\frac{\partial H}{\partial t}\right)_{ms}$ and the exponential factor is of the order of unity.

Total probability of transmission to m^{th} state is

$$|a_m|^2 = \frac{4\hbar^2}{(E_m - E_s)^4}\left|\left(\frac{\partial H}{\partial t}\right)_{ms}\right|^2 \tag{3.70}$$

3.10 Sudden Approximation

The sudden approximation occurs when the Hamiltonian changes appreciably during a very short but finite interval of time t_0. The sudden approximation consists of the change in Hamiltonian discontinuous on different times. Let t_0 to be duration and to consider sudden approximations, we consider the equation

$$\dot{a}_f = -\frac{< f\left|\frac{\partial H}{\partial t}\right|k >}{E_k - E_f}\exp\left\{-\frac{i}{\hbar}(E_k - E_f)t\right\} \tag{3.71}$$

In sudden approximation the variation of $\frac{\partial H}{\partial t}$ can not be neglected ; so

$$a_f = \int_0^{t0} \frac{< f\left|\frac{\partial H}{\partial t}\right|k >}{(E_k - E_f)}\exp\left\{-\frac{i}{\hbar}(E_k - E_f)t\right\}dt$$

$$= \left\{\frac{< f\,|H(t)|\,k >}{(E_k - E_f)}\exp\left(-\frac{i}{\hbar}(E_k - E_f)t\right)\right\}_0^{t0}$$

$$-\int_0^{t0}\left\{\frac{< f\,|H(t)|\,k >}{(E_k - E_f)}\exp\left(-\frac{i}{\hbar}(E_k - E_f)t\right)\cdot\left(-\frac{i}{\hbar}(E_k - E_f)t\right)\right\}dt \tag{3.72}$$

The condition of sudden approximation, by the help of uncertainly relation $\Delta E\,\Delta t \approx \hbar,$ is expressed (since $\Delta t = t_0$ is very small) as

$$\frac{\hbar}{\Delta E} >> t_0 \qquad (3.73)$$

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 $< f|H(t)|k> = 0;$ so equation (3.72) becomes

$$a_f = \frac{i}{\hbar}\int_0^{t0} < f'|H(t)|k> \cdot \exp\left\{-\frac{i}{\hbar}(E_k - E_f)t\right\}dt \qquad (3.74)$$

If ω_{fk} is the angular frequency of the transition from initial state k to a final state f, then

$$\omega_{fk} = \frac{E_f - E_k}{\hbar};$$ so that we may write

$$a_f = \frac{i}{\hbar}\int_0^{t0} < f|H(t)|k> e^{\,i\omega jkt}\,dt \qquad (3.75)$$

When perturbation is switched on suddenly, $H(t)$ changes instantaneously in time Δt which is small compared to period $(\omega_{jk})^{-1}$ so that the factor $e^{i\omega_{jk}t}$ in the above integral changes a little and hence can be taken outside the integral, then we get

$$a_f = \frac{i}{\hbar}\, e^{i\omega jkt}\int_0^{t0} < f|H(t)|k> dt$$

$$= \frac{i}{\hbar}\, e^{\,i\omega_{fk}t} < f|H(t_0) - H(0)\,|k> t_0$$

$$= \frac{it_0}{\hbar}\, e^{i\omega_{jk}t} < f|H'\,|k> \qquad (3.76)$$

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

$$|\,a_f\,|^2 = \frac{t_0^2}{\hbar^2}\,|< f|H'|k >|^2 \approx \frac{|< f|H'|k>|^2}{\hbar^2\omega_{fk}^{2}} \qquad (3.77)$$

This is used to calculate the transition probability under the influence of sudden perturbation.

UNIT IV

4.1 Addition of angular momenta

Consider two non interacting systems (1) and (2) with angular momenta J_1 and J_2 respectively. Now, the total angular momentum $J=J_1+J_2$. The components as well as the total angular momenta satisfy the fundamental commutation relations

$$j_1 \times j_1 = ij_1; \qquad j_2 \times j_2 = ij_2; \qquad j \times j = ij \tag{4.1}$$

Let $\psi_1(j_1, m_1)$ is the simultaneous eigen vector of J_1^2 and J_{1z} and J_2 has no effect on them. Similarly $\psi_2(j_2, m_2)$ is the simultaneous eigen vector of J_2^2 and J_{2z} and J_1 has no effect on them. Hence we can write,

$$\begin{aligned} J_1^2\psi_1(j_1, m_1) &= j_1(j_1+1)\psi_1(j_1m_1) \\ J_{1z}\psi_1(j_1, m_1) &= m_1\psi_1(j_1, m_1) \\ J_2^2\psi_2(j_2, m_2) &= j_2(j_2+1)\psi_2(j_2m_2) \\ J_{2z}\psi_2(j_2, m_2) &= m_2\psi_2(j_2, m_2) \end{aligned} \tag{4.2}$$

And the products $\psi(j_1j_2m_1m_2) = \psi_1(j_1, m_1)\psi_2(j_2, m_2)$ form a complete set of simultaneous eigen vectors of mutually commuting set of operators J_1^2, J_{1z}, J_2^2 *and* J_{2z}. Using unitary transformation, vector form of (j_1, j_2, m_1, m_2) can be transformed into (j_1, j_2, j, m). Let $j_1 > j_2$ and $\psi(j_1, j_2, m_1, m_2)$ be the eigen vector of J_z belonging to eigen value (m_1+m_2)

$$\begin{aligned} J_z\psi(j_1, j_2, m_1, m_2) &= (J_{1z}+J_{2z})\psi_1(j_1m_1)\psi_2(j_2m_2) \\ &= (m_1+m_2)\psi_1(j_1m_1)\psi_2(j_2m_2) \\ &= (m_1+m_2)\psi(j_1, j_2, m_1, m_2) \end{aligned} \tag{4.3}$$

Since $|m_1| \le j_1, |m_2| \le j_2$ then $|m| \le j_1 + j_2$. That is the largest value of m is $(j_1+j_2) = j$ because j_1 *and* j_2 are the largest values of m_1 *and* m_2 respectively.

For a given value of j_1 *and* j_2 let us find the possible values of j. Let $j_1 = 1$ *and* $j_2 = \frac{1}{2}$

There will be three possible values for m_1 and two possible values for m_2. Thus there will be six possible ψ values. They are of the form $\psi(j_1, j_2, m_1, m_2)$ as

$$
\begin{aligned}
&\psi\left(1,\frac{1}{2},1,\frac{1}{2}\right) \quad \text{corresponding to } m_1 = 1, m_2 = \frac{1}{2} \\
&\psi\left(1,\frac{1}{2},1,-\frac{1}{2}\right) \quad \text{corresponding to } m_1 = 1, m_2 = -\frac{1}{2} \\
&\psi\left(1,\frac{1}{2},0,\frac{1}{2}\right) \quad \text{corresponding to } m_1 = 0, m_2 = \frac{1}{2} \\
&\psi\left(1,\frac{1}{2},0,-\frac{1}{2}\right) \quad \text{corresponding to } m_1 = 0, m_2 = -\frac{1}{2} \qquad (4.4) \\
&\psi\left(1,\frac{1}{2},-1,\frac{1}{2}\right) \quad \text{corresponding to } m_1 = -1, m_2 = \frac{1}{2} \\
&\psi\left(1,\frac{1}{2},-1,-\frac{1}{2}\right) \quad \text{corresponding to } m_1 = -1, m_2 = -\frac{1}{2}
\end{aligned}
$$

The corresponding $m = m_1 + m_2$ values are $\frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2},$

We can say that there are four states with $m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ corresponding to the total angular momentum $j = \frac{3}{2}$ and two states with $m = \frac{1}{2}, -\frac{1}{2}$ corresponding to $j = \frac{1}{2}$. Thus there are two possible values for j as 3/2 and ½. It is possible to define six angular momentum vectors of the form $\phi(j_1, j_2, j, m)$ as

$$\begin{aligned}
&\phi\left(1,\frac{1}{2},\frac{3}{2},\frac{3}{2}\right) \text{corresponding to} \quad j=\frac{3}{2}, m=\frac{3}{2}\\
&\phi\left(1,\frac{1}{2},\frac{3}{2},\frac{1}{2}\right) \text{corresponding to} \quad j=\frac{3}{2}, m=\frac{1}{2}\\
&\phi\left(1,\frac{1}{2},\frac{3}{2},-\frac{1}{2}\right) \text{corresponding to} \quad j=\frac{3}{2}, m=-\frac{1}{2}\\
&\phi\left(1,\frac{1}{2},\frac{3}{2},-\frac{3}{2}\right) \text{corresponding to} \quad j=\frac{3}{2}, m=-\frac{3}{2}\\
&\phi\left(1,\frac{1}{2},\frac{1}{2},\frac{1}{2}\right) \text{corresponding to} \quad j=\frac{1}{2}, m=\frac{1}{2}\\
&\phi\left(1,\frac{1}{2},\frac{1}{2},-\frac{1}{2}\right) \text{corresponding to} \quad j=\frac{1}{2}, m=-\frac{1}{2}
\end{aligned} \tag{4.5}$$

j_1 *and* j_2 are the largest values of m_1 *and* m_2. Hence the largest value of $m = m_1 + m_2 = j_1 + j_2$

For this value of m we can write one function as

$$\phi(j_1, j_2, j_1 + j_2, j_1 + j_2) = \psi(j_1, j_2, j_1, j_2) \tag{4.6}$$

The next value of m is $j_1 + j_2 - 1$ which has two possible values for m_1 and m_2 as
$m_1 = j_1 \quad and \quad m_2 = j_2 - 1$
$m_1 = j_1 - 1 \quad and \quad m_2 = j_2$. That is $\psi(j_1, j_2, j_1, j_2 - 1), \psi(j_1, j_2, j_1 - 1, j_2)$

Correspondingly we have two ϕ-values as,
$\phi(j_1, j_2, j_1 + j_2, j_1 + j_2 - 1), \phi(j_1, j_2, j_1 + j_2 - 1, j_1 + j_2 - 1)$

Extending the discussion for $m = j_1 + j_2 - n$, we get a set of vectors for ϕ corresponding to ψ -vectors as

$$\begin{array}{lcl}
\psi(j_1, j_2, j_1 - n, j_2), & & \phi(j_1, j_2, j_1 + j_2, j_1 + j_2 - n) \\
\psi(j_1, j_2, j_1 - n + 1, j_2 - 1) & \text{and} & \phi(j_1, j_2, j_1 + j_2 - 1, j_1 + j_2 - n) \\
\cdots\cdots\cdots & & \cdots\cdots\cdots\cdots\cdots \\
\psi(j_1, j_2, j_1, j_2 - n) & & \phi(j_1, j_2, j_1 + j_2 - n, j_1 + j_2 - n)
\end{array} \tag{4.7}$$

The smallest value of j will occur corresponding to

$j_2 - n = -j_2 \quad or \quad n = 2j_2$. So the smallest value of m is $j_1 - j_2$. So, the total number of eigen states are given by,

$\sum_{j_1-j_2}^{j_1+j_2}(2j+1) = (2j_1+1)(2j_2+1)$. It is very clear to express the vector $\phi(j_1, j_2, j, m)$ as a linear combination of the vector $\psi(j_1, j_2, m_1, m_2)$

$$\phi(j_1, j_2, j, m) = \sum_{m_1}\sum_{m_2} C^{j_1 j_2}_{j,m,m_1,m_2}\psi(j_1, j_2, m_1, m_2) \tag{4.8}$$

The coefficient $C^{j_1j_2}_{j,m,m_1,m_2}$ represents the unitary transformation between two angular momentum representations known as Clebsch-Gordon coefficients. In Dirac notation it is represented as $C^{j_1j_2}_{j,m,m_1,m_2} < j_1 j_2 m_1 m_2 \mid j_1 j_2 jm >$

Problem: Find the C.G. coefficient for the coupling of two angular momenta $j_1 = 1\, and\;\, j_2 = \frac{1}{2}$

Solution:

For simplicity let us use the notations

$$\phi(j_1 j_2 jm) = \phi_{jm};\psi(j_1 j_2 m_1 m_2) = \psi_{m_1 m_2}$$

The six independent vectors are

$$\begin{array}{l}\psi_{1,1/2};\psi_{1,-1/2};\psi_{0,1/2};\psi_{0,-1/2};\psi_{-1,1/2};\psi_{-1,-1/2} \quad and \\ \phi_{3/2,3/2};\phi_{3/2,1/2};\phi_{3/2,-1/2};\phi_{3/2,-3/2};\phi_{1/2,1/2};\phi_{1/2,-1/2}\end{array}$$

Obviously,
$$\begin{array}{l}\phi_{3/2,3/2} = \psi_{1,1/2} \\ \phi_{3/2,-3/2} = \psi_{-1,-1/2}\end{array} \tag{4.9}$$

Similarly, for the remaining vectors we have

$$\phi_{3/2,1/2} = a_1\psi_{1,-1/2} + a_2\psi_{0,1/2}$$
$$\phi_{3/2,-1/2} = a_3\psi_{0,-1/2} + a_4\psi_{-1,1/2}$$
$$\phi_{1/2,1/2} = a_5\psi_{1,-1/2} + a_6\psi_{0,1/2}$$
$$\phi_{3/2,-1/2} = a_7\psi_{0,-1/2} + a_8\psi_{-1,1/2}$$

The coefficients *a* gives the unitary transformation matrix.

We know,

$J_-\phi_{jm} = \sqrt{(j+m)(j-m+1)}\phi_{j,m-1}$ where $J_- = J_x - iJ_y = (J_1)_- + (J_2)_-$

Also,

$$(J_1)_-\psi_{m1,m2} = \begin{cases} \{\sqrt{(1+m_1)(2-m_1)}\psi_{m1-1,m2} & if\ m_1 - 1 \geq -j_1 \\ 0 \quad if\ m_1 - 1 < -j_1 \end{cases}$$
$$(J_2)_-\psi_{m1,m2} = \begin{cases} \sqrt{(1/2+m_2)(3/2-m_2)}\psi_{m_1,m2-1} & if\ m_2 - 1 \geq -j_2 \\ 0 \quad f\ m_2 - 1 < -j_2 \end{cases} \tag{4.10}$$

Thus $J_-\phi_{3/2,3/2} = \sqrt{\left(\frac{3}{2}+\frac{3}{2}\right)\left(\frac{3}{2}-\frac{3}{2}+1\right)}\phi_{3/2,1/2}$ by using eqn4

$\phi_{3/2,1/2} = \frac{1}{\sqrt{3}}J_-\psi_{1,1/2}$ by using eq(4.70a)

$= \frac{1}{\sqrt{3}}\left\{\sqrt{(1+1)(2-1)}\psi_{0,1/2} + \sqrt{(1/2+1/2)(3/2-1/2)}\right\}\psi_{1,-1/2}$ by using (4.70b)

$= \frac{1}{\sqrt{3}}\psi_{1,-1/2} + \sqrt{\frac{2}{3}}\psi_{0,1/2}$ .which gives $a_1 = \frac{1}{\sqrt{3}}; a_2 = \sqrt{\frac{2}{3}}$

Applying the lowering operator again on $\phi_{3/2,1/2}$

$$J_{-}\phi_{3/2,1/2} = \sqrt{2\times 2}\phi_{3/2,-1/2}$$

$$or \quad \phi_{3/2,-1/2} = \frac{1}{2}\left\{(J_1)_- + (J_2)_-\right\}\left[\frac{1}{\sqrt{3}}\psi_{1,-1/2} + \sqrt{\frac{2}{3}}\psi_{0,1/2}\right]$$

$$= \frac{1}{2}\left[\frac{1}{\sqrt{3}}\left\{\sqrt{[(1+1)(2-1)]}\psi_{0,-1/2} + 0\right\} + \sqrt{\frac{2}{3}}\left\{[(1+0)(2-0)]\psi_{-1,1/2}\right\} + \sqrt{\{(1/2+1/2)(3/2-1/2)\}}\psi_{0,1/2}\right]$$

or

$$\phi_{3/2,-1/2} = \sqrt{2/3}\psi_{0,-1/2} + \sqrt{1/3}\psi_{-1,1/2} \quad and \quad \phi_{3/2,3/2} = \psi_{-1,-1/2}$$

$\phi_{1/2,1/2}$ is a linear combination of $\psi_{1,-1/2}$ and $\psi_{0,1/2}$ which is orthogonal to $\phi_{3/2,1/2}$. This demands

$$a_1^* a_5 + a_2^* a_6 = 0$$

$$or \quad \frac{a_6}{a_5} = -\frac{a_1^*}{a_2^*} = -\frac{1/\sqrt{3}}{\sqrt{2}/3} = -\frac{1}{\sqrt{2}}$$

$$hence, \phi_{1/2,1/2} = a_5\left[\psi_{1,-1/2} - \frac{1}{\sqrt{2}}\psi_{0,1/2}\right]$$

From the condition for normalisation

$$\phi_{1/2,1/2} = \frac{1}{\sqrt{3}}\left[\sqrt{2}\psi_{1,-1/2} - \psi_{0,1/2}\right]$$

If the lowering operator J₋ is applied we get

$$\phi_{1/2,-1/2} = \frac{1}{\sqrt{3}}[\psi_{0,-1/2} - \sqrt{2}\psi_{-1,1/2}]$$

Thus we have

$$\begin{pmatrix} \phi_{3/2,3/2} \\ \phi_{3/2,-3/2} \\ \phi_{3/2,1/2} \\ \phi_{3/2,-1/2} \\ \phi_{1/2,1/2} \\ \phi_{1/2,-1/2} \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & \sqrt{1/3} & \sqrt{2/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2/3} & \sqrt{1/3} & 0 \\ 0 & \sqrt{2/3} & -\sqrt{1/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{1/3} & -\sqrt{2/3} & 0 \end{pmatrix}}_{C.G.coefficient} \begin{pmatrix} \psi_{1,1/2} \\ \psi_{1,-1/2} \\ \psi_{0,1/2} \\ \psi_{0,-1/2} \\ \psi_{-1,1/2} \\ \psi_{-1,-1/2} \end{pmatrix}$$

Problem: Find the C.G. coefficient for the coupling of $j_1 = \frac{1}{2}\ and\ j_2 = \frac{1}{2}$**.**

For the given problem, the four independent ψ -states are:

$\psi_{m_1,m_2} = \psi_{1/2,1/2}; \psi_{1/2,-1/2}; \psi_{-1/2,1/2}; \psi_{-1/2,-1/2}$ and the possible values of j are 1 and 0.

Hence the possible ϕ-states are

$$\phi_{jm} = \phi_{11};\ \phi_{10};\ \phi_{00};\ \phi_{1,-1}$$

Obviously

$$\phi_{11} = \psi_{1/2,1/2}$$
$$\phi_{1,-1} = \psi_{-1/2,-1/2}$$

The remaining states can be written as

$$\phi_{10} = a_1\psi_{1/2,-1/2} + a_2\psi_{-1/2,1/2}$$

$$J_-\phi_{1,1} = \sqrt{2}\phi_{1,0}$$

$$\text{hence}, \phi_{10} = \frac{1}{\sqrt{2}}[(J_1)_- + (J_2)_-]\psi_{1/2,1/2}$$

Since ϕ_{00} is orthogonal to ϕ_{10} we have

$$\phi_{00} = \frac{1}{\sqrt{2}}[\psi_{1/2,-1/2} - \psi_{-1/2,1/2}]$$

The matrix transformation is

$$\begin{pmatrix} \phi_{11} \\ \phi_{10} \\ \phi_{00} \\ \phi_{1,-1} \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}}_{C.G.coefficient} \begin{pmatrix} \psi_{1/2,1/2} \\ \psi_{1/2,-1/2} \\ \psi_{-1/2,1/2} \\ \psi_{-1/2,-1/2} \end{pmatrix}$$

4.2 Commutation rules for angular momentum:

The commutation rules can be combined symbolically as,

$$L \times L = i\hbar L. \tag{4.11}$$

Two different components of the angular momentum do not commute. It will not be possible, in general, to measure $L_x, L_y,$ and L_z simultaneously, because product of the uncertainties of two quantities is proportional to the mean value of their commutator. It is of interest to obtain the commutation relations of L with the components, L_x, L_y, L_z. Let us consider, for example,

$$[L^2, L_z] = [(L_x{}^2 + L_y{}^2 + L_z{}^2), L_z]$$

$$= (L_x{}^2 L_z - L_z L_x{}^2) + L_y{}^2 L_z - L_z L_x{}^2) + (L_z{}^2 L_z - L_z L_z{}^2)$$

$$\text{as} \qquad [L_z{}^2 L_z - L_z L_z{}^2] = 0,$$

hence $[L^2, L_z] = (L_x L_x L_z - L_z L_x L_x) + (L_y L_y L_z - L_z L_y L_y).$

Adding and subtracting $L_x L_z L_x$ and $L_y L_z L_y$ on R.H.S, we get

$$= (L_x L_x L_z - L_x L_z L_x + L_x L_z L_x - L_z L_x L_x) + (L_y L_y L_z - L_y L_z L_y + L_y L_z L_y - L_z L_y L_y)$$

$$= L_x (L_x L_z - L_z L_x) + (L_x L_z - L_z L_x) L_x + L_y (L_y L_z - L_z L_y) + (L_y L_z - L_z L_y) L_y$$

$$= -i\hbar L_x L_y - i\hbar L_y L_x + i\hbar L_y L_x + i\hbar L_x L_y = 0. \qquad (4.12)$$

Thus we conclude that L^2 commute with L_z. By symmetry, we conclude that it also commutes with L_x and L_y. In other words it is possible to measure simultaneously L^2 and any single component of L.

Eigenvalues of L_Z

We now try to find the eigenfunctions of L_Z that is, we want to satisfy the equation,

$$L_Z \psi = c\psi. \qquad (4.13)$$

or

$$\frac{\hbar}{i} \frac{\partial \psi}{\partial \phi} = c\psi.$$

The solution of eq. (4.13) is

$$\psi = f(r, \theta) \exp(i c \phi / \hbar), \qquad (4.14)$$

where $f(r, \theta)$ is an arbitrary function of r and θ.

Now ψ must be a single valued function of x, y, z. In this case increase in the angle ϕ by 2π should not change the wavefunction, so that

$$f(r, \theta) \exp(i c \phi / \hbar) = f(r, \theta) \exp[i c (\phi + 2\pi) / \hbar]$$

or

$$\exp(i c 2\pi / \hbar) = 1$$

$$\frac{2\pi c}{\hbar} = 2m\pi$$

$$c = m\hbar,$$

where m is an integer. Thus eigenvalues of L_z are

$$L_z = m\hbar \tag{4.15}$$

The eigenfunction are

$$\psi = e^{im\phi} f(r, \theta). \tag{4.16}$$

4.3 Angular momentum in General

The total angular momentum can be written as a sum of the orbital and spin angular momenta:

$$J = L + S \tag{4.17}$$

where **J** has the components

$$J_x = L_x + S_x \qquad J_y = L_y + S_y \qquad J_z = L_z + S_z$$

J follows the same commutation rules as orbital angular momentum does, i.e.,

$$\lfloor J_x, J_y \rfloor = i\hbar J_z \qquad \lfloor J_y, J_z \rfloor = i\hbar J_x \qquad [J_z, J_x] = i\hbar J_y \tag{4.18}$$

or equivalently

$$J \times J = i\hbar J$$

and

$$[J_x, J_x] = \lfloor J_y, J_y \rfloor = [J_z, J_z] = 0. \tag{4.19}$$

Further
$$[J_x, J^2] = \lfloor J_x, J_x{}^2 + J_y{}^2 + J_z{}^2 \rfloor$$

$$= \lfloor J_x, J_y \rfloor J_y + J_y \lfloor J_x, J_y \rfloor + [J_x, J_z] J_z + J_z \lfloor J_x J_y \rfloor$$

$$= i\hbar \lfloor J_z J_y + J_y J_z - J_y J_z - J_z J_y \rfloor = 0.$$

Thus the operator

$J^2 = J_x{}^2 + J_y{}^2 + J_z{}^2$ commutes with J_x, J_y and J_z.

Commutation relation of J_z with ladder operators $J_+ = (J_x + i J_y)$ *and* $J_- = (J_x - i J_y)$.

$$\lfloor J_{z,} J_+ \rfloor = J_z J_+ - J_+ J_z = J_z (J_x + iJ_y) - (J_x + iJ_y) J_z = J_z J_x - J_x J_z - i(J_y J_z - J_z J_y)$$

$$= \lfloor J_{z,} J_x \rfloor - i \lfloor J_{y,} J_z \rfloor = i\hbar J_{y,} - i(i\hbar J_x) = i\hbar J_y + \hbar J_{x,} = \hbar (J_x + iJ_y) = \hbar J_+$$

Similarly $\lfloor J_{z,} J - \rfloor = -\hbar J_-$

Commutation relation of $J+$ and $J-$

$$[J_+, J_-] = J_+ J_- - J_- J_+ = (J_x + iJ_y)(J_x - iJ_y) - (J_x - iJ_y)(J_x + iJ_y)$$

$$= J_x\,(J_x - iJ_y) + iJ_y(J_x - iJ_y) - J_x\,(J_x + iJ_y) + iJ_y\,(J_x + iJ_y)$$

On simplification, we get

$$= 2i(J_y J_x - J_x J_y) = 2i[J_y, J_x] = 2i(-i\hbar J_z) = 2\hbar J_z$$

Commutation of J^2 with J_+ and J_-

$$[J^2, J_+] = [J_x^2, J_y^2 + J_z^2, J_+]$$

Now $\quad J_+ J_- = J_x^2 + J_y^2 - i(J_x J_y - J_y J_x)$

and $\quad J_- J_+ = J_x^2 + J_y^2 + i(J_x J_y - J_y J_x)$

$\therefore \quad \frac{1}{2}(J_+ J_- + J_- J_+) = J_x^2 + J_y^2$

or $\quad J_x^2 + J_y^2 + J_z^2 = \frac{1}{2}(J_+ J_- + J_- J_+) + J_z^2$

So, $\quad \left[J^2\ , J_+\right] = \left[\left[\left\{\frac{1}{2}(J_+ J_- + J_- J_+) + J_z^2\right\}\right], J_+\right]$

$$= \frac{1}{2}[J_+ J_-, J_+] + \frac{1}{2}[J_-, J_+, J_+] + [J_z^2\ J_+]$$

We known that $\quad [a,b,c] = a[b,c] + [a,c]b.$

Applying this we get

$$[J^2, J_+] = \frac{1}{2}J_+[J_-, J_+] + \frac{1}{2}[J_+, J_+]J_- + \frac{1}{2}J_-[J_+, J_+] + \frac{1}{2}[J_-, J_+]\,J_+ + J_z[J_z, J_+] + [J_z, J_+]J_z$$

$$= \frac{1}{2}J_+(-2\hbar J_z) + 0 + 0 + \frac{1}{2}(-2\hbar J_z)J_+ + J_z(\hbar J_+) + \hbar J_+ J_z = 0.$$

Similarly $[J^2, J_-] = 0.$

Allowed values of Total angular momentum : J

Since J_z and J^2 commute, they will have a set of simultaneous eigen vectors and therefore can be simultaneously diagonalized. Let the basic vectors in the representation in which J^2 and J_z are simultaneously diagonal be $\psi(\lambda m)$. This will satisfy

$$J^2\,\psi(\lambda m) = \lambda\hbar^2\psi(\lambda m) \qquad (4.20A)$$

and

$$J_z\,\psi(\lambda m) = m\hbar\,\psi(\lambda m) \qquad (4.20B)$$

where λ and m are real numbers (J^2 and J_z are hermitian).. We will use commutation relations to determine the eigenvalue λ and m. Let,

$$J_+ = J_x + iJ_y \qquad (4.21)$$

$$J_- = J_x + iJ_y \tag{4.22}$$

$$(J_+ \dagger = J_-) \tag{4.23}$$

which satisfy the commutation rules :

$$\lfloor J_+, J_z \rfloor = -\hbar J_+ \tag{4.24}$$

Similarly $\quad \lfloor J_-, J_z \rfloor = +\hbar J_-$

and $\quad \lfloor J_+, J_- \rfloor = -2\hbar J_z \quad (4.25)$

and the identities $J_+ J_- = (J_x + iJ_y)\,(J_x - iJ_y) = J_x{}^2 + J_y{}^2 - i\left[J_x, J_y\right], = J^2 - J_z{}^2 + \hbar J_z$

and $\quad J_- J_+ = J^2 - J_z{}^2 - \hbar J_z \quad (4.26)$

Now consider the scalar product

$$(\psi, J^2\psi) = (\psi, J_x{}^2\psi) + (\psi, J_y{}^2\psi) + (\psi, J_z{}^2\psi) = (J_x\psi, J_x\psi) + (J_y\psi, J_y\psi) + (J_z\psi, J_z\psi)$$

(because J_x, J_y *and* J_z are hermitian)

$$\geq (J_z\psi, J_z\psi) \qquad \left[because\ for\ any\ vector\ X, (X, X) \geq 0\right]$$

Substituting $\psi = \psi(\lambda m)$, we have

$$\left\{\psi(\lambda m), J^2\psi(\lambda m)\right\} \geq \left\{J_z\psi(\lambda m), J_z\psi(\lambda m)\right\}.$$

Using equations (4.20A) and (4.20B) We have

$$\left\{\psi(\lambda m),\ \lambda\hbar^2\psi(\lambda m)\right\} \geq \left\{m\hbar\psi(\lambda m),\ m\hbar\psi(\lambda m)\right\}.$$

or $\quad \lambda \geq m^2 \quad (4.27)$

Now from equation (4.24)

$$\left[J_+, J_z\right] = (J_+, J_z - J_z, J_+) = -\hbar J_+$$

Operating on the function $\psi(\lambda m)$, we have

$$J_+, J_z\psi(\lambda m) - J_z, J_+\psi(\lambda m) = -\hbar J_+\psi(\lambda m)$$

or $\quad J_z J_+\psi(\lambda m) = J_+ J_z\psi(\lambda m) + \hbar J_+\psi(\lambda m)$

$$= J_+ m\hbar\psi(\lambda m) + \hbar J_+\psi(\lambda m) = (m+1)\hbar J_+\psi(\lambda m) \tag{4.27A}$$

or $\quad J_z J_+\psi(\lambda m) = J_+ J_z\psi(\lambda m) + \hbar J_+\psi(\lambda m)$

Since $\left[J_+, J_z\right] = 0$

$\therefore \quad J^2 J_+\psi(\lambda m) = J_+ J^2\psi(\lambda m) + \lambda\hbar^2 J_+\psi(\lambda m)$

or $\quad J^2 J_+\psi(\lambda m) = \lambda\hbar^2 J_+\psi(\lambda m)$

It is clear that the vector $J_+\psi(\lambda m)$ is an eigenvector of J_z belonging to the eigenvalue $(m+1)\hbar$ and of J^2 belonging to the same eigenvalue $\lambda\hbar^2$ of J^2. Similarly, $J_+ J_+\psi(\lambda m)$ is an eigenvector of eigenvalue $(m+2)\hbar$ and belonging to the same eigenvalue $\lambda\hbar^2$ of J^2. This process cannot continue indentfinitely otherwise it will contradict equation (4.27). Let μ be the greatest eigenvalue of J_z for the given eigenvalue $\lambda\hbar^2$ of J^2, and $\psi(\lambda\mu)$ be the corresponding eigenvector. Now from equation (4.27A)

$$J_z J_+ \psi(\lambda\mu) = (\mu+1)\hbar J_+ \ \psi(\lambda\mu$$

hence $$J_+\psi(\lambda\mu) = 0,$$

Since $(\mu+1)$ cannot be an eigenvalue of J_x. Thus

$$J_- J_+ \psi(\lambda\mu) = 0,$$

or $$(J^2 - J_z{}^2 - \hbar J_z)\psi(\lambda\mu) = 0$$

or $$(\lambda - \mu^2 - \mu)\hbar^2\psi(\lambda\mu) = 0$$

But $\psi(\lambda\mu)$ is not identically zero, hence μ is the root of a quadratic equation. The larger root of this equation is

$$\mu = -\frac{1}{2} + \frac{1}{2}(1+4\lambda)$$

In a similar way

$$J_z\{J - \psi(\lambda m)\} = J_- J_z \psi(\lambda m) - J_- \psi(\lambda m) = (m-1)\hbar\{(J_- \psi(\lambda m)\} \qquad (4.28)$$

and hence $\left[J^2, J_-\right] = 0$

$$\therefore \qquad J^2\{J - \psi(\lambda m)\} = J_- J^2 \psi(\lambda m) = \lambda\hbar^2\{J_- \psi(\lambda m\} \qquad (4.29)$$

It is clear from equations (4.28) and (4.29), that the vector $J_-\psi(\lambda m)$ is an eigenvector of J_z belonging to the eigenvalue $(m-1)\hbar\, J^2$ belonging to the same eigenvalues $\lambda\hbar^2$ *of* J^2, unless, of course, if $J_-\psi(\lambda m) = 0$. Repeated application shows that $J_- J_- \psi(\lambda m)$ is an eigenvector of J_z belonging to the eigenvalue $(m-2)\hbar$. This cannot continue indefinitely otherwise it will again contradict equation (4.27). If μ_1 is the least eigenvalue of J_z then

$$J_+ J_- \psi(\lambda\mu_1) = 0$$

or $$(J^2 - J_z{}^2 + \hbar J_z)\psi(\lambda\mu_1) = 0$$

or $$(\lambda - \mu_1{}^2 + \mu_1)\hbar^2\psi(\lambda\mu_1) = 0$$

or $$\mu_1{}^2 - \mu_1 - \lambda = 0$$

The smaller root of the above equation would be

$$\mu_1 = -\frac{1}{2} + \frac{1}{2}(1+4\lambda)$$

Thus $\mu_1 = -\mu$

and the eigenvalues of J_z are

$$-\mu\hbar, (-\mu+1)\hbar, ...(\mu-1)\hbar, \mu\hbar$$

It follows that 2μ must be an integer, i.e.,

or $$\frac{1}{2}n = -\frac{1}{2} + \frac{1}{2}(1+4\lambda).$$

Rearranging, we obtain

$$\lambda = \frac{n}{2}\left(\frac{n}{2}+1\right)$$

Thus $\lambda = j(j+1)$ with $j = 0, \frac{1}{2}, 1, \frac{1}{2}, ...$

We may therefore infer that the eigenvalues of the operator J^2 are the number $j(j+1)\hbar^2$

where $j = 0, \frac{1}{2}, 1, \frac{1}{2}, ...$

and each of these is $(2j+1)$ fold degenerate, the eigenvalues of J_z for a given value of j being

$$m = -j\hbar, (-j+1)\hbar, ...(j-1), \hbar\, j\hbar$$

4.4 Angular momentum matrices

The matrices of J^2 and J_z are given

$$J_z = m\hbar$$

and $$J^2 = j(j+1)\hbar^2$$

We know that m (magnetic quantum number) varies from $-j$ to $+j$ i.e., it has $(2j+1)$ values. Hence the dimensions of these diagonal matrices will be $(2j+1)$ *i.e.*, $(2j+1)$ rows and $(2j+1)$ columns. The explicit forms of angular momentum matrices are shown below :

$$J_Z = \hbar \begin{vmatrix} j & 0 & ... & ... & 0 \\ 0 & j-1 & ... & ... & 0 \\ ... & ... & ... & ... & ... \\ ... & ... & ... & ... & ... \\ 0 & 0 & ... & ... & -j \end{vmatrix} \tag{4.30}$$

$$J^2 = \hbar^2 \begin{vmatrix} j(j+1) & \ldots & \ldots\ \ldots & 0 \\ 0 & j(j+1) & \ldots\ \ldots & 0 \\ \ldots & \ldots & \ldots\ \ldots & \ldots \\ \ldots & \ldots & \ldots\ \ldots\ \ldots & \\ 0 & \ldots & \ldots\ \ldots & j(j+1) \end{vmatrix} \tag{4.31}$$

Examples : Here we shall consider the following examples :

(i) For $j=0, J^2$ and J_z are represented by null matrices of unit rank: (0)

(ii) $J=\frac{1}{2}$. In this case $m=\frac{1}{2},-\frac{1}{2}$

Dimension of J^2 matrix $=(2j+1)=\{2X(1/2)+1\}=2$

i.e., there will be two rows and two columns.

Now $$J^2=\hbar^2 j(j+1)=\hbar^2\frac{1}{2}\left(\frac{1}{2}+1\right)=(3/4)\hbar^2$$

$\therefore$ $$J^2=\hbar^2\begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix}$$

Further $J_z=m\hbar=\frac{1}{2}\hbar$ for $m=\frac{1}{2}$ and $-\frac{1}{2}\hbar$ for $m=-\frac{1}{2}$

$\therefore$ $$J_z=\hbar^2\begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

Also $$J_+=\hbar\{(j-m)(j+m+1)\}$$

Only upper diagonal appears and rest of elements are zero.

$$J_+=\hbar\left\{\left(\frac{1}{2}-\frac{1}{2}\right)\left(\frac{1}{2}+\frac{1}{2}+1\right)\right\}=0 \qquad \text{for } j=\frac{1}{2} \text{ and } m=\frac{1}{2}$$

$$J_+=\hbar\left\{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)\right\}=\hbar \qquad \text{for } j=\frac{1}{2} \text{ and } m=-\frac{1}{2}$$

$\therefore$ $$J_+=\hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$J_-=\hbar\{(j+m)(j-m+1)\}$$

Only lower diagonal appears and rest of elements are zero.

For $j=\frac{1}{2}$, and $m=\frac{1}{2}$, $J_-=\hbar$

and for $j=\frac{1}{2}$, and $m=-\frac{1}{2}$, $J_-=0$

$\therefore$ $$J_-=\hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

(iii) $j=1$. In this case $m=1,\upsilon,-1$

Dimension of J^2 matrix $=(2j+1)=3$

i.e., there will be three rows and three columns.

Now $$J^2=\hbar^2 j(j+1)=\hbar^2\cdot 1\cdot(1+1)2\hbar^2$$

$$J^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \qquad (4.32)$$

Further $J_z = m\hbar = \hbar, 0, -$ according to the values of m as $1, 0, -1$.

$$J_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad (4.33)$$

Now $\qquad J_+ = \hbar\{(j-m)(j+m+1)\}$

$= 0 \qquad$ for $j = 1$ and $m = 1$

$= \sqrt{2}\,\hbar \qquad$ for $j = 1$ and $m = 0$

$= \sqrt{2}\,\hbar \qquad$ for $j = 1$ and $m = -1$

4.5 Physical meaning of Identity

The word identical in quantum mechanics is to describe the particles that can be substituted for each other under the most general possible circumstances with no change in physical situation of the system.

Symmetrical and anti symmetric wave functions

i) Symmetric wave function Ψ_s : A wave function is symmetric if the interchange of any pair of particles among its arguments leave the wave function unchanged.

ii) Antisymmetric wave function Ψ_A : Δ wave function is antisymmetric if the interchange of any pair of particles among its arguments changes the sign of the wave function.

If *P* is an exchange operator, then we must have

$$P\Psi_s(1,2) = \Psi_s(2, 1)$$

$$P\Psi_A(1,2) = \Psi_A(2, 1)$$

This symmetry property of the wave function has relationship with the spin of the particle. This relationship is listed here in the following postulates.

1. The identical particles having an integral spin quantum number are described by symmetric wave function, i.e.,

$$P\Psi_s(1,2,3,..r,\ldots s..n) = +\Psi_s(1,2,3,...s,...r,...n)$$

This class of particles, i.e. the particles described by symmetric wave functions are known as Bosons and obey Bose-Einstein Statistics. The examples of Bosons are photons (spin 1), netural helium atoms in normal state (s = 0) etc.

2. The identical particles having half odd integral spin quantum number are described by antisymmetric wave functions, i.e.

$$P\Psi_A(1,2,3,..r,\ldots s..n) = -\Psi_A(1,2,3,...s,...r,...n)$$

This class of particles i.e. the particles described by antisymmetric wave function obey Fermi-Dirac statistics and the particles are known as Fermi-particles or Fermions. The examples of Fermions are electrons, protons, neutrons, muons (all spin $\frac{1}{2}$)

4.6 Construction of Symmetric and antisymmetric wave functions

An antisymmetric unnormalised wave function can be constructed by adding togather all the perumated wave functions that arise from the original solution by means of an even number of interchanges of pairs of particles and subtracting the sum of all the permuted wave functions that arise by means of an odd number of interchanges of pairs of particles in the original solution.

In the case where the Hamiltonian does not depend upon time, stationary state solutions

$$\psi(1,2,..n) = \phi(1,2,..n)\, e^{-iE_n t/\hbar} \qquad (4.34)$$

can be found and the time independent Schroedinger's eqn. can be written as

$$H(1,2,......n)\,\phi(1,2..n) = E\phi(1,2,..n) \qquad (4.35)$$

There are n ! solutions of the eqn. (eigen functions) derived from ϕ (1,2..n) by means of permutations of its arguments belonging to the same eigen value E. Any linear combination of these eigen functions is also an eigen function belonging to eigen value E. Hence the system is degenerate and this type of degeneracy is called exchange degeneracy.

$$H(1,2)\,\Psi(1,2) = E\,\Psi(1,2)$$

The 2 ! = 2 solutions of this equation are Ψ (1, 2) and Ψ (2,1). The solutions correspond to a single energy state E.

The symmetric wave function can be written as

$$\Psi_s = \Psi(1,2) + \Psi(2,1) \tag{4.36}$$

and the antisymmetric wave functions is written as

$$\Psi_A = \Psi(1,2) - \Psi(2,1) \tag{4.37}$$

Similarly for a system of 3 particles, the Schroedinger's equation is

$$H(1,2,3)\,\Psi(1,2,3) = E\,\Psi(1,2,3) \tag{4.38}$$

This equation has 3! = 6 solutions corresponding to the same eigen values E. The six possible functions obtained by exchanging the indices of the particles are

$$\Psi(1,2,3),\ \Psi(2,3,1),\ \Psi(3,2,1),\ \Psi(1,3,2),\ \Psi(2,1,3),\ \Psi(3,1,2)$$

Out of these six functions, those arising by an even number of interchanges of the pairs of particles in original wave function $\Psi(1,2,3)$, are

$$\Psi(1,2,3),\ \Psi(2,3,1),\ \Psi(3,1,2)$$

and the functions arising by an odd number of interchanges of pairs of particles in original function $\Psi(1,2,3)$ are

$$\Psi(1,3,2),\ \Psi(2,1,3),\ \Psi(3,2,1)$$

So the symmetric wave function can be written as

$$\Psi_s = \Psi(1,2,3) + \Psi(2,3,1) + \Psi(3,1,2) + \Psi(1,3,2) + \Psi(2,1,3) + \Psi(3,2,1) \tag{4.39}$$

and the antisymmetric wave function is

$$\Psi_A = \Psi(1,2,3) + \Psi(2,3,1) + \Psi(3,1,2) - \{\Psi(1,3,2) + \Psi(2,1,3) + \Psi(3,2,1)\} \tag{4.40}$$

Here Ψ_s and Ψ_A are unnormalised wave functions.

4.7 Distinguishability of identical particles

The two identical particles can be distinguishable from each other if the sum of the probabilities of the individual wave functions in two states is equal to the probability derived by the symmetrised wave function i.e, if

$$\begin{aligned} |\psi(1,2)|^2 + |\psi(2,1)|^2 &= |\{\psi(1,2) \pm \psi(2,1)\}|^2 \\ &= |\psi(1,2)|^2 + |\psi(2,1)|^2 \pm 2\,\mathrm{Re}\,\psi\left[(1,2)\psi^*(2,1)\right] \end{aligned} \tag{4.41}$$

where Re denotes the real part of $\{\psi(1,2)\psi^*(2,1)\}$

It is possible only when overlap of wave-functions Ψ (1,2) and Ψ (2,1) is zero or 2 Re $\{\psi(1,2)\psi^*(2,1)\}$ = 0. Thus when the co-ordinates (space and spin) of two particles are not the same between exchange degenerate functions, the interference term, *i.e.* 2 Re $\Psi(1,2)\,\Psi^*(2,1)$ becomes zero and particle co-ordinates do not overlap.

4.8 The Palui's Exclusion principle:

A particle, during its motion in space reflects the properties of the statistics which it obeys. Consider two particle system which contains electrons in indistinguishable positions. Electrons are $\frac{1}{2}$ spin particles and obey Fermi Dirac statistics. If they occupy the same position in space and have the same z-component of spin, it can be seen that the eigen function of exchange operator for a case will be

$$P_{12}\,\Psi_A(r_1,s_1;\,r_2,s_2) = -\Psi_A(r_2,s_2,\,r_1,s_1)$$

$$= \Psi_A(r_1,s_1;\,r_2,s_2) \qquad (4.42)$$

$$= 0\, if \begin{cases} r_1 = r_2 \\ s_1 = s_2 \end{cases} \qquad (4.43)$$

The non existence of the wave-function under these conditions implies that there is zero probability that the particle will occupy the same point in space and have identical spin orientations. Pauli exculsion principle which states that no two particles obeying Fermi Statistics can exist in the same quantum state.

4.9 Pauli Spin Matrices for electron

Like orbital angular momentum operators L_x, L_y, L_z, the spin operators, S_x, S_y and S_z to be associated with the components of spin angular momentum satisfy the commutation relations.

$$\left.\begin{array}{l} [S_{x,}S_y] = S_xS_y - S_yS_x = i\hbar S_z \\ [S_{y,}S_z] = S_yS_z - S_zS_y = i\hbar S_x \\ [S_{z,}S_x] = S_zS_x - S_xS_z = i\hbar S_z \end{array}\right] \qquad (4.44)$$

If we consider the case with spin $=\frac{1}{2}$ *i.e.* electron, then according the Unlenbeck and Goudsmit hypothesis each of operators S_x, S_y and S_z must have just two eigen values $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. Now we introduce new auxiliary operators σ_x, σ_y and σ_z such that

$$\left.\begin{aligned} S_x &= \frac{1}{2}\hbar\,\sigma_x \\ S_y &= \frac{1}{2}\hbar\,\sigma_y \\ S_z &= \frac{1}{2}\hbar\,\sigma_z \end{aligned}\right] \tag{4.45}$$

The following properties of σ's may be noted:

Since the eigen values of each S are to be just $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, the eigen values of each σ must be +1 and −1. Each of the operators $\sigma_x^2, \sigma_y^2, \sigma_z^2$ must therefore have only the eigen value 1 and such operator is only unit operator, therefore.

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1. \tag{4.46}$$

According to (4.45) and (4.46), the commutation rules satisfied by σ s must be

$$\left.\begin{aligned} [\sigma_x, \sigma_y] &= \sigma_x\sigma_y - \sigma_y\sigma_x = 2i\sigma_z \\ [\sigma_y, \sigma_z] &= \sigma_y\sigma_z - \sigma_z\sigma_y = 2i\sigma_x \\ [\sigma_z, \sigma_x] &= \sigma_z\sigma_x - \sigma_x\sigma_z = 2i\sigma_y \end{aligned}\right\} \tag{4.47}$$

Now $2i\left(\sigma_x\sigma_y + \sigma_y\sigma_x\right) = \left(2i\,\sigma_x\right)\sigma_y + \sigma_y\left(2i\sigma_x\right)$

$$= \left(\sigma_y\sigma_z - \sigma_z\sigma_y\right)\sigma_y + \sigma_y\left(\sigma_y\sigma_z - \sigma_z\sigma_y\right)$$

Hence $\sigma_x\sigma_y = -\sigma_y\sigma_x$, so that σ_x and σ_y anticommute.

Similarly any two of the σ's anticommute in pairs

$$\left.\begin{aligned} \sigma_x\sigma_y + \sigma_y\sigma_x &= 0 \\ \sigma_y\sigma_z + \sigma_z\sigma_y &= 0 \\ \sigma_z\sigma_x - \sigma_x\sigma_z &= 0 \end{aligned}\right\} \tag{4.48}$$

Finally from (4.47) and (4.48) we have

$$\left.\begin{aligned}\sigma_x\sigma_y &= i\,\sigma_z\\ \sigma_y\sigma_z &= i\,\sigma_x\\ \sigma_z\sigma_x &= i\,\sigma_y\end{aligned}\right\}$$

Since each σ has two eigen values, so (2 x 2) matrix may be expected to fulfil the purpose and we begin by associating with σ_z, the simplest (2 x 2) matrix having the eigen values 1 and −1.

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{4.49}$$

Now we have

$$\sigma_x\sigma_z \equiv \begin{bmatrix} a & b \\ c & d \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} a & -b \\ c & -d \end{bmatrix} \tag{4.50}$$

and
$$\sigma_z\sigma_x \equiv \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} a & -b \\ -c & -d \end{bmatrix} \tag{4.51}$$

But σ_x and σ_z anticommute, we must have

$$\sigma_x\sigma_z + \sigma_z\sigma_x = \begin{bmatrix} a & -b \\ c & -d \end{bmatrix} + \begin{bmatrix} a & b \\ -c & -d \end{bmatrix} = 0$$

$$\begin{bmatrix} 2a & 0 \\ 0 & -2d \end{bmatrix} = 0$$

This yields $a = d = 0$

So that every matrix that anticommutes with (4.49) as σ_x and σ_y do, accordingly σ_x must have the form

$$\sigma_x = \begin{bmatrix} 0 & b \\ c & 0 \end{bmatrix} \tag{4.52}$$

The eigen values of (4.52) are ± √(bc) so that if they are to be 1 and −1, we must set bc = 1. And simple possibility is to take b =c =1, so $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$

It then follows form (4.48) that the matrix to be associated with σ_y is $\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$ and hence complete list of σ's becomes

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \ \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{4.53}$$

These matrices σ_x, σ_y and σ_z are called Pauli spin matrices associated with the components of spin angular momentum.

$$S_x = \frac{1}{2}\hbar\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ S_y = \frac{1}{2}\hbar\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, S_z = \frac{1}{2}\hbar\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{4.54}$$

These are same as J_x, J_y and J_z in total angular momenta (Angular Momentum chapter) when $j = \frac{1}{2}$

Thus we have $\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3$

and $S^2 = S_x^2 + S_y^2 + S_z^2$

$$= \frac{\hbar^2}{4}\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right) = \frac{3}{4}\hbar^2$$

4.10 Electron spin hypothesis : Stern -Gerlach experiment

The spin phenomenon has no classical analogue and approaching its theory we shall begin the recounting an empirical clue. In 1925, Uhlenbeck and Goudsmit proposed that each electron spins while revolving about nucleus and has a quantized spin angular momentum and being an electrically charged body possesses a spin magnetic moment. This proposal was successful in correlating spectral data for both unpertubed and perturbed complex atoms and in interpreting the results of the Stern-Gerlackh experiment concerned with the deflection of atoms projected into an inhomogeneous magnetic field.

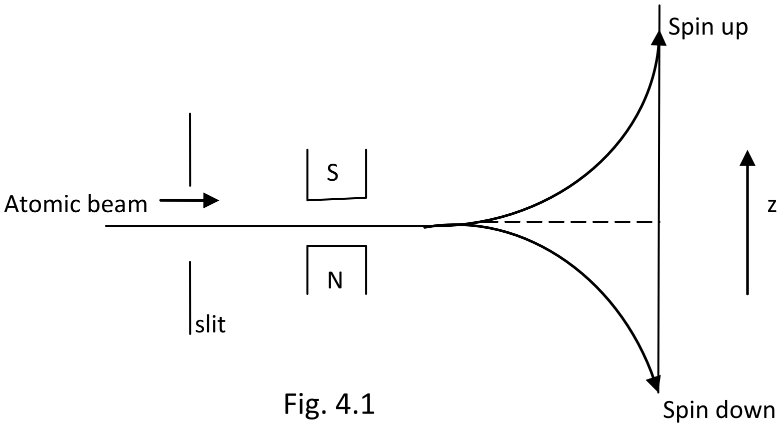

Fig. 4.1

A beam of neutral atoms or molecules, collimated by slits S_1 and S_2 is allowed to pass through a non-uniform magnetic field B. The atoms or molecules are defected by a force which according to classical physics, is given by

$$\mathbf{F} = \nabla(\mathbf{m.B}) \qquad (4.55)$$

Where **m** is magnetic moment vector.

The arrangement is such that in the region through which the beam of atoms passes, the direction of **B** varies slowly, but the magnitude of **B** is strongly dependent on position, thus if thus if the projection of **m** along the direction of **B** is denoted by $m_{\mathbf{B}}$, then we have approximately.

$$\mathbf{F} = \mathbf{m}_{\mathbf{B}}\ \nabla \mathbf{B}$$

By measuring the deflection on the screen, the force **F** and hence the magnetic moment along **B** may be determined. Classically $m_{\mathbf{B}}$ can have any value ranging from $-m$ to $+m$ i.e. we would expect a single continuous trace on the screen; but experimentally, instead of a continuous trace, discrete equidistant traces were observed, giving clear proof of quantisation (discrete values) of the magnetic moment. Since the magnetic moment vector **m** appeared to assume certain discrete directions in space, it is said to have undergone space quantisation.

Stem and Gerlach also measured allowed values of $m_{\mathbf{B}}$ to moderate accuracy and found that the values of $m_{\mathbf{B}}$ appeared in the range from minimum $-m$ to maximum $+m$. The value of maximum projection of **m** (i.e.m) is conventionally regarded as the magnetic moment of the particle. Now the magnetic moment of charged particle **m** is related to angular momentum **L** by the classical relation.

$$\mathbf{m} = -\frac{\mathrm{e}}{2\mathrm{m}_0}\mathbf{L} \tag{4.56}$$

Where m_0= mass of electron, e its charge. This relation, being a simple proportionality between **m** and **L** is expected to be true in quantum mechanics also. Since any component of L has $(2l+1)$ eigen values, we may expect the projection of **m** in a fixed direction, such as on **B**, to possess also $(2l+1)$ distinct eigen values and to be expressible as

$$mB = -\frac{e\hbar}{2m_0}m = -\mu_B m$$

(4.57)

where $\mu_B = \frac{e\hbar}{2m_0} = 9.2032\,\mathrm{x}\,10^{-20}\ J/Tesla$

is called Bohr magneton and m can assume the values from $-l$ to $+l$ with steps of unity, i.e., $(2l+1)$ values. Since l is an integer, $(2l+1)$ is an odd number, therefore we expect an old number of traces $(2l+1)$ in Stern Gerlach experiment. But a beam of silver atom yielded two traces in this experiment; which is an even number and a value of m equal of

$$m = \frac{e\hbar}{2m_0}m = \mu B \tag{4.58}$$

The extra-ordinary implications of this experiment could not be explained immediately. Later Goudsmit and Uhlenbeck hypothesis of existence of electron spin and intrinsic magnetic moment provided an explanation for this. On the basis of this theory the silver atom in an S-state has two projections possible in space, namely.

$$m = \pm\frac{e\hbar}{2m_0}m = \pm\,\mu_B \tag{4.59}$$

The positive and negative signs signify the orientations of the magnetic moment in space, i.e., up or down. Goudsmit and Uhlenbeck also assumed that the electron has an intrinsic (or spin) angular momentum, but this is not easy to measure directly as the magnetic moment.

The existence of intrinsic angular momentum of electron seems correct by the following arguments :

(i) Electron has a magnetic moment which may be assumed to be due to some internal circulating currents of charged matter, then the appearance of an intrinsic angular momentum is expected together with a magnetic moment.

(ii) Conservation of angular momentum for an isolated system such as an atom can not be maintained unless the electron moving in an electric field of nucleus consists of an intrinsic momentum.

Dirac's relativistic theory given a deeper understanding of intrinsic angular momentum and magnetic moment of the electron. It is conventional to associate spin S with the magnetic moment as

$$\left.\begin{array}{l} S=+\frac{\hbar}{2}, \quad m=-\frac{e\hbar}{2m_0} \\ S=-\frac{\hbar}{2}, \quad m=+\frac{e\hbar}{2m_0} \end{array}\right\} \tag{4.60}$$

Theory of Stern Gerlach Experiment : The separation of beam of silver atoms into two components in Stern-Gerlach experiment may be explained as follows : Let an atom of magnetic moment m enter a non-uniform slowly varying magnetic field **B.** Then the force acting on the atom, according to classical physics, is given by

$$\mathbf{F}=\nabla(\mathbf{m.B})$$

If magnetic field **B** is assumed along Z-direction and θ is the angle between **m** and **B**, then the force on atom,

$$F=m\cos\theta\frac{\partial B}{\partial z} \tag{4.61}$$

Classically θ can have all possible values ; but quantum mechanically, according to property of space quantization, it can have only two discrete values. When atom enters the non-uniforms field, it experiences an acceleration along z - direction given by

$$a_z=\frac{F}{M_0}$$

where M_0 is the mass of atom. If L the length of magnetic field and v the velocity of atom along the directions of beam, then time taken by atom in magnetic field.

$$t = \frac{L}{v}$$

If we assume the acceleration along z - direction to be constant, then displacement of atom along z - direction is given by

$$z = \frac{1}{2} a_z t^2 = \frac{1}{2} \frac{F}{M_0} \left(\frac{L}{v} \right)^2$$

$$= \frac{1}{2} \frac{\left(m \cos\theta \left(\frac{\partial B}{\partial z} \right) \right)}{M_0} \left(\frac{L}{v} \right)^2 = \frac{1}{2} m \cos\theta \left(\frac{L2}{M_o v^2} \right) \left(\frac{\partial B}{\partial z} \right) \qquad (4.62)$$

This is classical expression for the displacement of atom in an non-uniform field. Quantum mechanically, due to space quantization cos $\theta = \pm 1$, therefore for spin half particles, we have

$$z = \pm \frac{1}{2} \frac{mL^2}{M_0 v^2} \frac{\partial B}{\partial z} \qquad (4.63)$$

This expression gives two directions for spin half particles, which is actually observed in Stern – Gerlach experiment. Thus Stern – Gerlach experiment provides a satisfactory experimental evidence of the Goudsmit and Uhlenbeck hypothesis of space quantization.

Limitations of Stern-Gerlach Experiment

1. The experiment can be carried out only for neutral atoms or molecules ; it can not be carried out for changed particles.
2. The Stern-Gerlach experiment can not be performed even for those neutral atoms or molecules which remain in the field for a duration shorter than $\frac{\hbar}{\mathbf{mB_z}}$.

4.11 Scattering Cross – Section

The effective area presented by the target to the incident beam of particles in the process of scattering is called scattering cross section. Let a beam of particular of flux *N is* incident on a scattering centre; particles are scattered in all directions. If *dN* is the number of particles scattered per unit time into the solid angle $d\omega$ located in the direction θ and ϕ with respect to the bombarding direction , then dN will be proportional to the incident flux and the solid angle taken. Thus we can write,

$$dN = \sigma(\theta,\phi)\, N\, d\omega \tag{4.63A}$$

where $\sigma(\theta,\phi)$ is the proportionality constant. $\sigma(\theta,\phi)$ has the dimensions of an area. This can be regarded as the cross – section of the incident beam scattered into the solid angle dω about θ and ϕ. The proportionality constant is known as the differential scattering cross – section.

The total scattering cross section (σ_t) is obtained by integrating eqn. (4.63A) over the entire solid angle.

$$N_{scatt} = \int dN = \int \sigma(\theta,\phi) N d\omega = N \int \sigma(\theta,\phi)\, d\omega$$

$$= N\,\sigma_t \qquad \text{since, } \sigma_t = \int \sigma(\theta,\phi)\, d\omega$$

Thus $\sigma_t = \dfrac{N_{scatt}}{N}$

The cross – sections are usually measured in barns (1barn = 10^{-24} cm^2) or millibrans

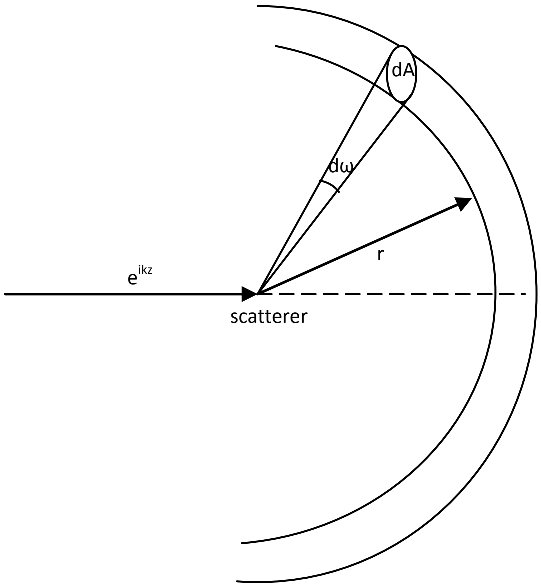

Fig. 4.2

4.12 Quantum mechanical discription of scattering process:

a scattering experiment, a beam of particles impinges on a target which scatters them in a sphere around the scattering centre. Figure (4.2) explains the general behaviour of the particles scattering. In the quantum mechanical description of scattering, the total wavefunction can be regarded as consisting, of two parts, one representing the incoming part and the other, representing the scattered part.

The complete wavefunction is given by

$$\psi = e^{ikz} + f(\theta,\phi)\frac{e^{ikr}}{r} \qquad (4.64)$$

The first term represents a particle moving in the positive z-direction. The second term represents a particle moving radially outward; its amplitude depends upon θ and ϕ and is inversely proportional to r.

The magnitude of the incident flux density along z-axis is

$$v|\psi_{inc}|^2 = v|e^{ikz}|^2 \text{ where } v \text{ is the velocity.} \qquad (4.65)$$

$$= v$$

the magnitude of scattered flux is

$$v|\psi_{scat}|^2 = v\left|f(\theta)\frac{e^{ikr}}{r}\right|^2 = \frac{v}{r^2}|f(\theta)|^2 \qquad (4.66)$$

Let the scattered particles are intercepted by a detector of area *dA* which is placed at a distance *r* from the scatterer. The solid angle subtended by the detector at the scattering centre is

$$d\omega = \frac{dA}{r^2} \quad \text{or} \quad dA = d\omega\, r^2 \qquad (4.67)$$

Therefore, the number of particles crossing the area dA per sec. is

$$\frac{\upsilon}{r^2}\,|\,f(\theta)|^2\,dA = \upsilon|\,f(\theta)|^2\frac{dA}{r^2} = \upsilon|\,f(\theta)|^2\,d\omega \qquad (4.68)$$

Now the differential scattering cross – section σ(θ) is defined by

$\sigma(\theta)\, d\omega$ = (no. of particles scattered into $d\omega$ per unit time) / (no. of particles incident per unit time)

$$= \frac{v|f(\theta)|^2 d\omega}{v}$$

or σ(θ) $= |f(\theta)|^2$

(4.69)

This is the expression for differential scattering cross – section.

The Born approximation

When the kinetic energy of colliding particles is large compared to the interaction energy, then Born approximation is best applied.

4.13 Perturbation approximation We wish to solve the wave equation for a relative motion, i.e.,

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi+V(r)\psi=E\psi, \qquad \text{where } \mu = \frac{m_1 m_2}{m_1+m_2} \tag{4.70}$$

Its solution in asymptotic form is given by

$$\psi(r,\theta,\phi)\longrightarrow e^{ikz}+f(\theta,\phi)\frac{e^{ikr}}{r} \tag{4.71}$$

Where e^{ikz} represents the part of the particles moving in the z- direction and the second term represents the part which is moving radially outward after scattering.

Equation (4.70) can be written as

$$\nabla^2\psi+k^2\psi=U(\mathbf{r})\psi,$$

$$\text{where} \quad k^2=\frac{2\mu E}{\hbar^2} \quad \text{and} \quad U(r)=\frac{2\mu V(r)}{\hbar^2}$$

Substituting $\psi=e^{ikz}+v(r)$ where $v(r)$ represents scattered wave part which is a small perturbation . We have,

$$\nabla^2\left[e^{ikz}+v(\mathbf{r})\right]+k^2\left[e^{ikz}+v(\mathbf{r})\right]=U(\mathbf{r})\left[e^{ikz}+v(\mathbf{r})\right]$$

or

$$\nabla^2\left[e^{ikz}+v(\mathbf{r})\right]+k^2\left[e^{ikz}+v(\mathbf{r})\right]=U(\mathbf{r})e^{ikz}+U(\mathbf{r})v(\mathbf{r})$$

since $v(\mathbf{r})$ is small in comparison with e^{ikz} we can neglect the term $U(\mathbf{r})\, v(\mathbf{r})$

Hence ,

$$\nabla^2 e^{ikz}+\nabla^2\upsilon(\mathbf{r})+k^2e^{ikz}+k^2\upsilon(\mathbf{r})=U(\mathbf{r})\,e^{ikz}$$

$$\text{or } \nabla^2\upsilon(\mathbf{r})+k^2\upsilon(\mathbf{r})=U(\mathbf{r})\,e^{ikz} \qquad \text{since} \qquad \nabla^2 e^{ikz}=-k^2e^{ikz} \tag{4.72}$$

Therefore we have to solve the inhomogeneous wave equation the right hand side is known. Sufficient criterion for the validity of our solution is

$$|\nu(\mathbf{r})| \ll |e^{ikz}| = 1, \quad \text{for all } \mathbf{r}. \tag{4.73}$$

Scattering cross – section :

The solution of inhomogeneous equations (4.72) can be expressed as

$$\upsilon(\mathbf{r}) = \int G_{k'}(\mathbf{r},\mathbf{r'})\, F(\mathbf{r'})\, d\mathbf{r'}$$

where $G_{k'}$ is the Green's function.

For a free particle, Green's function is expressed as,

$$\int G_{k'}(\mathbf{r},\mathbf{r'}) = \frac{1}{4\pi|\mathbf{r}-\mathbf{r'}|} e^{ik|\mathbf{r}-\mathbf{r'}|}$$

$$\upsilon(\mathbf{r}) = \int \frac{e^{ik|(\mathbf{r}-\mathbf{r'})|}}{4\pi|\mathbf{r}-\mathbf{r'}|} F(\mathbf{r'})\, d\mathbf{r'}$$

$$\upsilon(\mathbf{r}) = -\int \frac{e^{ik|(\mathbf{r}-\mathbf{r'})|}}{4\pi|\mathbf{r}-\mathbf{r'}|} U(\mathbf{r'})\, e^{ikz'}\, d\mathbf{r'} \tag{4.74}$$

We assume that U($\mathbf{r}'$) falls off rapidly for large $\mathbf{r}'$ so that there is an asymptotic region in which r is large in comparison with those values of *r'* For r → ∞,

$$(r-r')^2 = r^2 + r'^2 - 2rr'\cos\Theta$$

$$= r^2 + r'^2 - 2rr'\omega \quad where\ \omega = \cos\Theta$$

$$= r^2\left[1 + \frac{r'^2}{r^2} - \frac{2rr'\omega}{r^2}\right]$$

$$= r^2\left(1 - \frac{2r'\omega}{r}\right) \quad as\ r \to \infty$$

or

$$|(r-r')|_{r\to\infty} = r\left(1 - \frac{2r'\omega}{r}\right)^{1/2} = r - r'\omega$$

$$=$$

Similarly,

Now eqn (4.74) becomes

$$v(r) = -\frac{1}{4\pi}\int\left(\frac{1}{r} + \frac{\omega r'}{r^2}\right) e^{ikr} e^{-ik\omega r'} U(r') e^{ikz'} dr'$$

$$v(r)|_{r\to\infty} = -\frac{1}{4\pi r} e^{ikr} \int U(r') e^{ik(z'-\omega r')} dr'$$

Now, $\psi(r) = e^{ikz} + v(r) = e^{ikz} - \frac{1}{4\pi r} e^{ikr} \int U(r') e^{ik(z'-\omega r')} dr'$

Comparing this with $\psi(r)=e^{ikz}+\frac{e^{ikr}}{r}f(\theta,\phi)$,we have

$$f(\theta,\phi)=-\frac{1}{4\pi}\int U(r')e^{\,ik(z-\omega r')}dr'$$

Denoting the incoming wave by the vector K_0 and the scattered wave by K, we can write

$$Kz'=Kn_0.r'=K_0.r'$$

Therefore, $f(\theta,\phi)=\frac{1}{4\pi}\int U(r')e^{[i(k_0-k)]r'dr'}$

Let us define a vector Ƙ as Ƙ=K_0-K

Now, $f(\theta,\phi)=-\frac{1}{4\pi}\int U(r')e^{[i\kappa.r']dr'}$

The scattering cross section

$$\sigma(\theta,\phi)=|f(\theta,\phi)|^2=\frac{1}{16\pi^2}\left|\int U(r')e^{[i\kappa.r']}dr'\right|^2$$

$$=\left(\frac{\mu}{2\pi\hbar^2}\right)^2\int\left|V(r')e^{[i\kappa.r']}dr'\right|^2$$

(4.75)

This gives the total scattering cross section.

4.14 Scattering by Spherically Symmetric potentials : Partial wave analysis

Consider a particle of energy E which moves in a central, spherically symmetric force field . Let the wave function ψ is the solution of the Schroedinger equation

$$\nabla^2\psi+\frac{2m}{\hbar^2}[E-V(r)]\psi=0, \qquad (4.76)$$

We have assumed that *V* is a function of *r* only. In a special case of symmetric problem, let the wave function is independent of the angle ϕ. Therefore the general solution of eq.(4.37) is

$$\psi = R_l(r)\,P_l(\cos\theta), \qquad (4.77)$$

where $R_l(r) = \frac{\chi_l(r)}{r}$ and P_l (cos θ) is the Legendre polynomial of order *l*. χ_l satisfies the equation

$$\frac{d^2\chi_l}{dr^2}+\left[k^2-U(r)-\frac{l(l+1)}{r^2}\right]\chi_l=0 \tag{4.78}$$

where $k=\left[\frac{2mE}{\hbar^2}\right]^{1/2}$ and $U(r)=\frac{2mV(r)}{\hbar^2}$

To study the nature of asymptotic behaviour, we consider *r* to be so large that the *U* and *l* terms in equation (4.78) can be neglected. Then the solution of equation (4.78) is of the form $e^{\pm ikr}$. Hence the solution is

$$\psi=\sum_l p_l(\cos\theta)\frac{\chi_l}{r}=\sum_l p_l(\cos\theta)\frac{e^{\pm ikr}}{r} \tag{4.79}$$

Therefore, the general solution is

$$\psi=\sum_l p_l(\cos\theta)\left[C_l\frac{e^{+ikr}}{r}+D_l\frac{e^{-ikr}}{r}\right] \tag{4.80}$$

Here C_l and D_l are constants.

From the quantum mechanical description of scattering,

$$\psi=e^{ikz}+f(\theta)\frac{e^{ikz}}{r} \tag{4.81}$$

From eqns. (4.80) and (4.81) we have

$$e_{ikz}+f(\theta)\frac{e^{ikr}}{r}=\sum_l P_l(\cos\theta)\left[C_l\frac{e^{+ikr}}{r}+D_l\frac{e^{-ikr}}{r}\right]$$

or

$$e_{ikz}+f(\theta)\frac{e^{ikr}}{r}=\sum_l P_l(\cos\theta)\left[b_l\right]\left[\frac{\sin\left[\zeta-l\pi/2+\delta_l\right]}{\zeta}\right]. \tag{4.82}$$

where *l*π/2 has been written for convenience in place of π/2. Other constants have been generalised into the new constant b_l. The quantity δ_l is the phase shift of the l^{th} partial wave. It measures the amount by which the regular function sin (ζ - (1/2) *l* π+δ_l) is displaced in ζ, relative to the free particle function $f_l(\zeta)$. Thus the effect of the scattering potential is to shift the phase of each outgoing partial wave.

To evaluate the constant b_l:

From Bauer's formula, substituting the value of e^{ikr} in eq. (4.82) we get,

$$\sum i^l(2l+1)P_l(\cos\theta)\frac{\sin\left[\zeta-l\pi/2\right]}{\zeta}+k\,f(\theta)\frac{e^{i\zeta}}{\zeta}=\sum b_lP_l(\cos\theta)\frac{\sin(\zeta-(1/2)l\pi+\delta_l}{\zeta} \tag{4.83}$$

or $$\sum_l i^l (2l+1) P_l(\cos\theta)\sin(\zeta-(1/2)l\pi)+kf(\theta)e^{i\zeta}=\sum_i b_l\, P_l(\cos\theta)\sin(\zeta-(1/2)l\pi)+\delta_l$$

or $$\sum_l i^l (2l+1) P_l(\cos\theta)\ \frac{e^{i(\zeta-l\pi/2)}-e^{-i(\zeta-1\pi/2)}}{2i}+kf(\theta)e^{i\zeta}$$

$$=\sum b_l P_l(\cos\theta)\quad \frac{e^{i(\zeta-(1/2)l\pi+\delta l)}-e^{-i(\zeta-(1/2\ )l\pi+\delta l})}{2i}$$

or $$e^{i\zeta}\left[\left\{\sum_l i^l (2l+1)\, p_l(\cos\theta)e^{-il\pi/2}\right\}-\left\{\sum_l b_l\ p_l(\cos\theta)\, e^{-(1/2)il\pi+i\delta_l}\right\}+2ikf(\theta)\right]$$

$$=e^{-i\zeta}\left[\left\{\sum_l i^l (2l+1)e^{il\pi/2}\ p_l(\cos\theta\right\}-\left\{\sum b_l P_l(\cos\theta)\ \ e^{(1/2)il\pi-i\delta_l}\right\}\right] \tag{4.84}$$

Since e$^{+i\zeta}$ and e$^{-i\zeta}$ are linearly independent, each of the quantities in square brackets must vanish. Therefore from the coefficient of e$^{+i\zeta}$, we have

$$\sum_i \left\{(i^l)(2l+1)-b_l e^{-i\delta l}\right\}P_l(\cos\theta)\, e^{il\pi/2} \ =0$$

or $$b_l=i^l(2l+1)e^{i\delta_l} \tag{4.85}$$

Using eqn. (4.85) into equation (4.84) and equating the coefficients of $e^{i\zeta}$ to zero.

$$2ikf(\theta)=\sum i^l(2l+1)e^{2i\delta_l}\ e^{-il\pi/2}\ P_l(\cos\theta)-\sum_l i^l(2l+1)P_l(\cos\theta)e^{-il\pi/2}$$

$$=\sum_l(2l+1)P_l(\cos\theta)\left[e^{2i\delta}-l\right], \qquad \because e^{-il\pi/2}=i^{-1} \tag{4.86}$$

$$=-\sum_l(2l+1)P_l(\cos\theta)e^{i\delta^l}\left[e^{i\delta_l}-e^{-i\delta_l}\ \right]$$

$$\therefore \qquad f(\theta)=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)e^{\ i\delta_l}\ \left[\frac{e^{\ i\delta l}-e^{\ -i\delta_l}}{2i}\right]$$

or $$f(\theta)=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)e^{\ i\delta_l}\ \sin\delta_l, \tag{4.87}$$

The differential cross –section is then $\sigma(\theta)=|\,f(\theta)\,|^2$

$$=\ \frac{1}{k_2}\sum_{l=0}^{\infty}[\,2l+1)P_l(\cos\theta)e_{i\delta_l}\sin\delta_l\,]^{\ 2}$$

$$\sigma(\theta)\ =\ \sum_{l=0}^{\infty}\ \frac{(2l+1)^2 P_l^{\ 2}(\cos\theta)\sin^2\delta_l}{k^2} \tag{4.88}$$

The total scattering cross – section is the integral of the above eqn.

ie. $$\sigma_t = \int_\omega \sigma(\theta)\,d\omega = 2\pi\int_{-1}^{+1} |f(\theta)|^2 d(\cos\theta). \tag{4.89}$$

$$\sigma_t = 2\pi \int_{-1}^{+1} |\sigma(\theta)|\, d(\cos\theta).$$

$$= \frac{2\pi}{k^2}\sum_l \int_{-1}^{+1} (2l+1)^2 P_1^2(\cos\theta)\sin^2\delta_l d\,(\cos\theta)$$

$$= \frac{2\pi}{k^2}\sum_l (2l+1)^2 \sin^2\delta_l \int_{-1}^{+1} P_l^2(\cos\theta)\,d\,(\cos\theta)$$

$$= \frac{2\pi}{k^2}\sum (2l+1)\sin^2\delta_l \;\frac{2}{2l+1}$$

from the orthogonality relation

$$\int_{-1}^{+1} P_l^2(\cos\theta)\; d\,(\cos\theta) = \frac{2}{2l+1}$$

Hence, $$\sigma_t = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\delta_l \tag{4.90}$$

The eqn. (4.90) shows that different partial waves contribute independently to the total cross – section. Thus the phase shifts completely determine the scattering, and scattering cross – section vanishes when each of the δ_l is 0° or 180°. Cross section is maximum when $\delta_1 = \pm \pi/2, \; \pm 3\pi/2, ...$

Phase shifts are related to the potential energy function by the relation

$$\text{Sin } \delta_l = - \int_0^a \frac{V}{E} F_l(\zeta)\, f_l(\zeta) d\zeta \tag{4.91}$$

Where $f_l(\zeta)$ and $F_l(\zeta)$ are the functions in the differential equations

$$\frac{d^2 f_l}{d\zeta^2} + \left\{1 - \frac{l(l+1)}{\zeta^2}\right\} f_l = 0 \tag{4.92}$$

and $$\frac{d^{\,2}F_l}{d\zeta^{\,2}} + \left\{1 - \frac{V}{E} - \frac{l(l+1)}{\zeta^{\,2}}\right\} F_l = 0 \tag{4.93}$$

To find the Phase shifts (δ_l):

Multiplying equation (4.93) by f_l and equation (4.92) by F_l and subtracting, we get

$$\frac{d}{d\zeta}\left[f_l' F_l - f_l F_l'\right] + \frac{V}{E} F_l f_l = 0 \tag{4.94}$$

When $\zeta \to \infty$

$$[f_l' F_l - f_l F_l'] = \cos\left(\zeta - \frac{1}{2}l\pi\right)\sin\left(\zeta - \frac{1}{2}l\pi + \delta_l\right)$$

$$-\sin\left(\zeta - \frac{1}{2}l\pi\right)\cos\left(\zeta - \frac{1}{2}l\pi + \delta_l\right) = \sin\delta_l$$

Hence from equation (4.94), we get

$$\frac{d}{d\zeta}\sin\delta_l + \frac{V}{E}F_l f_l = 0$$

or $$\sin\delta_l = -\int \frac{V}{E}F_l f_l d\zeta$$

when the phase shifts are small, *i.e.*, $F_l(\zeta) \rightarrow f_l(\zeta)$.

$$\delta_l = -\int_o^a \frac{V}{E} |f_l(\zeta)|^2 \, d\zeta \tag{4.95}$$

where *a* is the range of potential energy function.

At low energies approaching zero, only phase shift for $l=0$ partial waves are important and scattering becomes isotropic.

4.15 Optical theorem. The optical theorem relates the total scattering cross – section to the scattering amplitude in the forward direction (the scattering amplitude for θ = 0). Substituting θ = 0 in eqN. (4.87) we get,

$$f(0) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)P_l(\cos(0))e^{i\delta_l}\sin\delta_l$$

But $$P_l(\cos\ 0) = P_l(1) = 1$$

$$f(0) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)(\cos\delta_l + i\sin\delta_l)\sin\delta_l$$

The imaginary part of *f*(0) *i.e.*, Im *f*(0) is given by

$$\text{Im } f(0) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l \tag{4.96}$$

According to eq. (4.90), we have

$$\sigma_t = \frac{4\pi}{\mathrm{k}^2}\sum_{\mathrm{l}=0}^{\infty}(2l+1)\sin^2\delta_{\mathrm{l}} = \frac{4\pi}{k}.\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l$$

or $$\sigma_{\mathrm{t}} = \frac{4\pi}{k}.\text{Im } f(0) \tag{4.97}$$

Thus the imaginary part of fprward scattering amplitude measures the suffering in intensity of incident beam due to scattering.

UNIT V

5.1 Schrodinger relativistic equation (K.G.Equation)

Classical Hamiltonian function is given by

$$H=\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+V \tag{5.1}$$

Schrodinger equation in Hamiltonian form is

$$i\hbar\frac{\partial\psi(r,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi(r,t)+V\psi(r,t) \tag{5.2}$$

Let the particle of rest mass m_0 is moving in free space (V=0)

Now, the velocity of the particle is given by,

$$v^2=\dot{x}^2+\dot{y}^2+\dot{z}^2 \tag{5.3}$$

Energy $E=mc^2=\frac{m_0c^2}{\sqrt{(1-\beta^2}}$, where $\beta=\frac{v}{c}$ (5.4)

$$p_x^2+p_y^2+p_z^2=\frac{m_0^2(\dot{x}^2+\dot{y}^2+\dot{z})^2}{(1-\beta^2)}=\frac{m_0^2v^2}{(1-\beta^2)}=\frac{m_0^2\beta^2c^2}{(1-\beta^2)}=m_0^2c^2\left(\frac{1}{1-\beta^2}-1\right)$$

$$=\frac{E^2}{c^2}-m_0{}^2c^2 \qquad \text{BY using eqn.(5.4)}$$

$$p_x^2+p_y^2+p_z^2+m_0{}^2c^2-\frac{E^2}{c^2}=0 \tag{5.5}$$

Using the operators,

$E=i\hbar\frac{\partial}{\partial t}$, $p_x=\frac{h}{2\pi i}\frac{\partial}{\partial x}$ etc., we get

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\frac{4\pi^2}{h^2}m_0^2c^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}=0$$

or $$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\frac{4\pi^2}{h^2}m_0^2c^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi=0$$

or $$\left(\nabla^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi=\frac{m_0^2c^2}{\hbar^2}\psi \tag{5.6}$$

$\square^2\psi=\dfrac{m_0^2c^2}{\hbar^2}\psi$ where $\square^2=\left(\nabla^2-\dfrac{1}{c^2}\dfrac{\partial^2}{\partial t^2}\right)$ is called D'Alembertian operator (5.7)

The above equation is called Klein-Gordan equation for free particle.

5.2 K.G.equation in the presence of electromagnetic field

Consider a particle of charge *'-e'* with rest mass m_0 in an e.m. field.

The equation of motion is written as

$$\frac{d}{dt}\left(\frac{m_0v}{\sqrt{(1-v^2/c^2)}}\right)=-eE-\frac{e}{c}(v\times H) \tag{5.8}$$

where, *v*-velocity of the particle, *c*-velocity of light, E-electric field intensity, H-magnetic field. E and H can be expressed as

$$E=-\nabla\phi-\frac{1}{c}\frac{\partial A}{\partial t} \quad \text{and} \quad H=\nabla\times A. \tag{5.9}$$

Here, A and ϕ are the vector and scalar potentials.

Substituting in eqn. (5.8) we have

$$\frac{d}{dt}\left(\frac{m_0v}{\sqrt{(1-v^2/c^2)}}\right)=-e\nabla\phi+\frac{e}{c}\frac{\partial A}{\partial t}-\frac{e}{c}[v\times(\nabla\times A)]$$

Consider the *x*-component value,

$$\frac{d}{dt}\left(\frac{m_0v_x}{\sqrt{(1-v_x{}^2/c^2)}}\right)=e\frac{\partial\phi}{\partial x}+\frac{e}{c}\frac{\partial A_x}{\partial t}-\frac{e}{c}[v_y(curl\ A)_z-v_z(curl\ A)_y]$$

$$= e\frac{\partial \phi}{\partial x} + \frac{e}{c}\left(\frac{dA_x}{dt} - \frac{\partial A_x}{\partial x}v_x - \frac{\partial A_x}{\partial y}v_y - \frac{\partial A_x}{\partial z}v_z\right) - \frac{e}{c}\left[v_y\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) + v_z\left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z}\right)\frac{\partial A_x}{\partial t}\right]$$

$$= e\frac{\partial \phi}{\partial x} + \frac{e}{c}\frac{dA_x}{dt} - \frac{e}{c}\left[\frac{\partial A_x}{\partial x}v_x + \frac{\partial A_y}{\partial x}v_y + \frac{\partial A_z}{\partial x}v_z\right]$$

$$= e\frac{\partial \phi}{\partial x} + \frac{e}{c}\frac{dA_x}{dt} - \frac{e}{c}\frac{\partial}{\partial x}\left[A_x v_x + A_y v_y + A_z v_z\right]$$

$$= e\frac{\partial \phi}{\partial x} + \frac{e}{c}\frac{dA_x}{dt} - \frac{e}{c}\frac{\partial}{\partial x}\left[A.v\right]$$

or $$\frac{d}{dt}\left(\frac{m_0 v_x}{\sqrt{(1-{v_x}^2/c^{\,2})}} - \frac{e}{c}A_x\right) = \frac{\partial}{\partial x}\left[e\phi - \frac{e}{c}(A.v)\right] \qquad (5.10)$$

This eqn. can also be written as

$$\frac{d}{dt}\left[\frac{\partial}{\partial v_x}\left\{-m_0c^2\sqrt{(1-v^2/c^2} + e\phi - \frac{e}{c}(A.v)\right\}\right] = \frac{\partial}{\partial x}\left[\left\{-m_0c^2\sqrt{(1-v^2/c^2} + e\phi - \frac{e}{c}(A.v)\right\}\right] \quad (5.11)$$

This is the Lagrangean equation

ie. $\frac{d}{dt}\left(\frac{\partial L}{\partial v_x}\right) = \frac{\partial L}{\partial x}$, where we have assumed L= $-m_0c^2\sqrt{(1-v^2/c^2} + e\phi - \frac{e}{c}(A.v)$

Canonical momentum $p_x = \frac{\partial L}{\partial v_x} = \frac{1}{2}\frac{m_0c^2}{\sqrt{(1-v^2/c^2)}}\frac{2v_x}{c^2} - \frac{e}{c}A_x$

or in general,

$$p = \frac{m_0 v}{\sqrt{(1-v^2/c^2)}} - \frac{e}{c}A \qquad (5.12)$$

Total energy $E = \sum p_j \dot{q}_j - L = p.v - L$

$$= \frac{m_0 v^2}{\sqrt{(1-v^2/c^2)}} - \frac{e}{c}(A.v) + m_0c^2\sqrt{(1-v^2/c^2} - e\phi + \frac{e}{c}(A.v)$$

$$=\frac{m_0}{\sqrt{(1-v^2/c^2)}}\left[v^2+c^2(1-v^2/c^2)\right]-e\phi$$

$$\text{E}=\frac{m_0\ c^2}{\sqrt{(1-v^2/c^2)}}-e\phi \qquad (5.13)$$

From eqn. (5.12)

$$p+\frac{e}{c}A=\frac{m_0v}{\sqrt{(1-v^2/c^2)}}$$

or $$(p+\frac{e}{c}A)^{\ 2}+m_0^2c^{\ 2}=\frac{{m_0}^2v^{\ 2}}{(1-v^{\ 2}/c^{\ 2})}$$

$$=(p+\frac{e}{c}A)^2+\frac{m_0^2c^2}{(1-v^2/c^2)}=\frac{1}{c^{\ 2}}\left(\frac{m_0c^{\ 2}}{\sqrt{(1-v^{\ 2}/c^{\ 2})}}\right)^2=\frac{1}{c^2}(E+e\phi)^2,$$

since $\text{E}=\frac{m_0\ c^2}{\sqrt{(1-v^2/c^2)}}-e\phi$

$$c^2(p+\frac{e}{c}A)^2+m_0^2c^4-(E+e\phi)^2=0$$

or $$(cp+eA)^2+m_0^2c^4-(E+e\phi)^2=0 \qquad (5.14)$$

5.3 Dirac’s relativistic equation for a free electron

Dirac modified the Hamiltonian which is linear in momentum and mass as

$$H=c\alpha.p+\beta m_0c^2 \qquad (5.15)$$

We know the eigen value eqn. $H\psi=E\psi$ which can be written as

$$(E-c\alpha.p-\beta m_0c^2)\psi=0 \qquad (5.16)$$

Using operators for E and p

$$(i\hbar\frac{\partial}{\partial t}+i\hbar c\alpha.\nabla-\beta m_0c^2)\psi=0$$

Any solution of the above eqn. must be the solution of Schrodinger relativistic eqn

$$(E^2 - p^2c^2 - m_0^2c^4)\psi = 0 \qquad (5.17)$$

Multiplying eqn (5.16) by $(E + c\alpha.p + \beta m_0 c^2)$ (keeping $p_{x,}p_y and\ p_z$ commute; $\alpha \quad and \quad \beta$ commute with $E \quad and \quad p$, while $\alpha\ and\ \beta$ do not commute), we can show that this agrees with schrodinger relativistic eqn (5.17) if $\alpha\ and\ \beta$ satisfy the following relations

$$\begin{aligned}
&\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = 1 \\
&\alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0 \\
&\beta^2 = 1 \\
&\alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0
\end{aligned} \qquad (5.18)$$

$\alpha\ and\ \beta$ can be represented as

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \text{ with } \alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \text{ etc.} \qquad (5.19)$$

Here $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ (5.20)

All $\alpha \quad and \quad \beta$ matrices called Dirac operators are of 4X4 dimension

5.4 Dirac's Free particle solution or plane wave solution

From the equation

$$H\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad (5.20a)$$

Hamiltonian $H = c(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z) + \beta m_0 c^2$

and

$\alpha_x p_x = \begin{pmatrix} 0 & 0 & 0 & p_x \\ 0 & 0 & p_x & 0 \\ 0 & p_x & 0 & 0 \\ p_x & 0 & 0 & 0 \end{pmatrix}$ etc. Substituting these $\alpha_x p_x$; $\alpha_y p_y$; $\alpha_Z p_Z$ values in eq.(5.20a) we get

$$\begin{aligned} & m_0c^2\psi_1 + 0 + cp_z\psi_3 + c(p_x - ip_y)\psi_4 = i\hbar\frac{\partial\psi_1}{\partial t} \\ & 0 + m_0c^2\psi_2 + c(p_x + ip_y)\psi_3 - cp_z\psi_4 = i\hbar\frac{\partial\psi_2}{\partial t} \\ & cp_z\psi_1 + c(p_x - ip_y)\psi_2 - m_0c^2\psi_3 + 0 = i\hbar\frac{\partial\psi_3}{\partial t} \\ & c(p_x + ip_y)\psi_1 - cp_z\psi_2 + 0 - m_0c^2 p_z\psi_4 = i\hbar\frac{\partial\psi_4}{\partial t} \end{aligned} \tag{5.21}$$

Using the operator forms, the above eqn becomes

$$\begin{aligned} & (E - m_0c^2)\psi_1 - cp_z\psi_3 - c(p_x - ip_y)\psi_4 = 0 \\ & (E - m_0c^2)\psi_2 - c(p_x + ip_y)\psi_3 + cp_z\psi_4 = 0 \\ & (E + m_0c^2)\psi_3 - cp_z\psi_1 - c(p_x - ip_y)\psi_2 = 0 \\ & (E + m_0c^2)\psi_4 - c(p_x + ip_y)\psi_1 + cp_z\psi_3 = 0 \end{aligned} \tag{5.22}$$

The above set of eqns have solutions if the determinant of the coefficients of ψ is zero.

$$\begin{vmatrix} E - m_0c^2 & 0 & -cp_z & -c(p_x - ip_y) \\ 0 & E - m_0c^2 & -c(p_x + ip_y) & cp_z \\ -cp_z & -c(p_x - ip_y) & E + m_0c^2 & 0 \\ -c(p_x + ip_y) & cp_z & 0 & E + m_0c^2 \end{vmatrix} = 0 \tag{5.23}$$

The determinant value gives

$$\begin{aligned} & (E^2 - m_0^2c^4 - c^2p^2)^2 = 0 \\ & or \quad E = \pm\sqrt{(p^2c^2 + m_0^2c^4} \end{aligned} \tag{5.24}$$

Taking $\psi_1=1$, $\psi_2=0$ we get, $\psi_3=\frac{cp_z}{E_+ + m_0c^2}$, $\psi_4=\frac{c(p_x+ip_y)}{E_+ + m_0c^2}$ (5.25)

Taking $\psi_1=0$, $\psi_2=1$ we get, $\psi_3=\frac{c(p_x-ip_y)}{E_+ + m_0c^2}$, $\psi_4=-\frac{cp_z}{E_+ + m_0c^2}$. (5.26)

If we consider the negative roots E_-,we get two more solutions as

$$\psi_1=\frac{cp_z}{E_- - m_0c^2} \qquad \psi_2=\frac{c(p_x+ip_y)}{E_- - m_0c^2} \qquad \psi_3=1 \qquad \psi_4=0 \tag{5.27}$$

$$\psi_1=\frac{c(p_x-ip_y)}{E_- - m_0c^2} \qquad \psi_2=-\frac{cp_z}{E_- - m_0c^2} \qquad \psi_3=0 \qquad \psi_4=1 \tag{5.28}$$

If we write $\psi_j(r,t)=u_je^{i(k.r-\omega t)}$ with j=1,2,3... where u_j are numbers, we can rewrite the solution as

$$u^1(p)=\begin{pmatrix} 1 \\ 0 \\ \frac{cp_z}{E_+ + m_0c^2} \\ \frac{c(p_x+ip_y)}{E_+ + m_0c^2} \end{pmatrix}; \qquad u^2(p)=\begin{pmatrix} 0 \\ 1 \\ \frac{c(p_x-ip_y)}{E_+ + m_0c^2} \\ \frac{-cp_z}{E_+ + m_0c^2} \end{pmatrix};$$

$$v^1(p)=\begin{pmatrix} \frac{cp_z}{E_- - m_0c^2} \\ 1 \\ \frac{c(p_x+ip_y)}{E_- - m_0c^2} \\ 1 \\ 0 \end{pmatrix}; \qquad v^2(p)=\begin{pmatrix} \frac{c(p_x-ip_y)}{E_- - m_0c^2} \\ -\frac{cp_z}{E_- - m_0c^2} \\ 0 \\ 1 \end{pmatrix} \tag{5.29}$$

u's and v's are called Dirac spinors. u represents positive energy spinors with spin up and v represents negative energy spinors with spin down. Solution for Dirac equation for a free particle is thus obtained as the product of Dirac spinors multiplied by $e^{i(k.r)-\omega t}$.

5.5 Charge and current densities:

$$\nabla \cdot \mathbf{S}(\mathbf{r},t)+\frac{\partial P}{\partial t}(\mathbf{r},t)=0, \tag{5.30}$$

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 $\mathrm{P}(\mathbf{r},t)$ indicates that it can not be interoperated as position probability density in analogy with non-relativistic case in which $\mathrm{P}(\mathbf{r},t)=\psi * \psi$ due to following reason, :

The expression $\mathrm{P}(\mathbf{r},t)$ may be expressed as

$$\mathrm{P}(\mathbf{r},t)=\frac{\hbar}{2imc^2}\left(\psi\frac{\partial \psi^*}{\partial t}-\psi *\frac{\partial \psi}{\partial t}\right)$$

$$=\frac{1}{2mc^2}\left[\left(-i\hbar\frac{\partial \psi^*}{\partial t}\right)\psi+\psi *\left(\;i\hbar\frac{\partial \psi}{\partial t}\right)\right] \tag{5.31}$$

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

$$H\psi=-i\hbar\frac{\partial \psi}{\partial t}\; i.e., i\hbar\frac{\partial \psi}{\partial t}=E\psi$$

and

$$H^*\psi^*=-i\hbar\frac{\partial \psi^*}{\partial t}\; i.e., -i\hbar\frac{\partial \psi^*}{\partial t}=E\psi^*$$

So equation (5.31) may be expressed as

$$\mathrm{P}(\mathbf{r},t)=\frac{1}{2mc^{2}}\left[(E\psi*)\psi+\psi*\;\right]$$

$$=\frac{1}{2mc^{2}}\left[2E\psi*\psi\right]$$

i.e.,
$$\mathrm{P}(\mathbf{r},t)=\frac{E}{mc^2}\left[\psi^*\psi\;\right] \tag{5.32}$$

From the expression $E=\pm\sqrt{(p^2c^2+m^2c^4)}$, e note that the energy of a particle can be either positive or negative. Thus it follows that the expression for $\mathrm{P}(\mathbf{r},t)$ is not definitely positive an 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. According to them P multiplied by (eP) 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.

5.6 Matrics for α and β

The squares of all the four matrics are unity; so that their eigen-values are +1 and −1. Let us arbitratily 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

$$\beta = \begin{bmatrix} 1 & 0 \\ 1 & -1 \end{bmatrix} \tag{5.33}$$

which is an abbreviation of

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{5.34}$$

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

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{5.35}$$

Since a 2 × 2 matrix has four elements, there are four and only four, independent 2 × 2 matrices, three of these σ_x, σ_y, σ_z. The only other matrix linearly independent of these three is

$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

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 × N matrix i.e.

$$\beta = \begin{bmatrix} b_1 & & O \\ & b_i & \\ O & & b_N \end{bmatrix} \tag{5.36}$$

As $\beta_2 = 1$, $b_i^2 = 1$ and $b_i = \pm 1$ (I = 1, 2, . . . N)

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

$$\beta\alpha_k = -\alpha_k\beta$$

$$\alpha_k^{-1}\beta\alpha_k = -\alpha_k^{-1}\alpha_k\beta$$

or $\alpha_k^{-1}\beta\alpha_k = -\beta$, as $\alpha_k^{-1}\alpha_k = 1$; we have

Taking trace of both sides, we get

$$\text{Trace}\,(\alpha_k^{-1}\beta\alpha_k) = -\text{Trace}\,\beta$$

or $\text{Trace}\,(\alpha_k\alpha_k^{-1}\beta) = -\text{Trace}\,\beta$ [Since Trace (ABC) = Trace (CAB)]

$$\text{Trace}\,(\beta) = -\text{Trace}\,(\beta) \qquad (\text{Since } \alpha_k\alpha_k^{-1} = I) \tag{5.37}$$

This gives 2(Trace β) = or Trace (β) = 0

Similarly Trace (α_k) = 0

Thus $$\text{Trace}\,(\beta) = \text{Trace}\,(\alpha_k) = 0 \tag{5.38}$$

This equation shows that the trace of each of 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

$b_{r+1} = b_{r+2} = \ldots = b_3 = -1$

so that r + s = N (5.39)

But the condition that Trace (β) = 0 requires that

$$\sum_{i=l}^{N} b_i = r - s = 0 \text{ i.e., } r = s$$

In view of this equation (16) shows

$$N = 2r \qquad (540)$$

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

$$\beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \quad \text{or} \quad \beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

Therefore the matrix for α_k may be expressed as

$$\alpha_k = \begin{bmatrix} 0 & \alpha_{x1} \\ \alpha_{x2} & 0 \end{bmatrix} \qquad (5.41)$$

where α_{x1} has n rows and columns and α_{x2} has m rows and columns. Since the square of (5.41) is a unit matrix, we note that

$$\alpha_{x1}\,\alpha_{x2} = (1)_{n \times n} \qquad (5.42)$$

$$\alpha_{x2}\,\alpha_{x1} = (1)_{m \times m} \qquad (5.42A)$$

The unit matrix appearing on R.H.S of (5.42) has n rows and n columns while the unit matrix on R.H.S. of (5.42A) has m rows and m columns. But no two matrices exist that satisfy (5.42) and (5.742A) simultaneously 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 (5.41).

Using Pauli spin matrices σ_x, σ_y and σ_z and choosing

$\alpha_{x1} = \alpha_{x2} = \sigma_x$; then

$$\alpha_x = \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

Similarly

$$\alpha_y = \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$$

$$\alpha_z = \begin{bmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \tag{5.43}$$

We already have

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

These 4×4 matrices are evidently Hermitian and in abbreviated form may be expressed as

$$\beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}; \; \vec{\alpha} = \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix} \tag{5.44}$$

where each element is a matrix with two rows and two columns.

Negative Energy states

Now it is evident that there are two continuous energy spectrum $E_{+} = \sqrt{m_0^2 c^4 + c^2 p^2}$ and $E_{-} = \sqrt{m_0^2 c^4 + c^2 p^2}$ .When the Dirac electrons are at rest (p=0) then E_{+} and E_{-} are separated by an amount of $2m_0 c^2$. Dirac suggested that all negative energy states are completely filled. When electron from negative energy state picks up some energy and goes to positive state, a vacancy called Dirac hole is created in negative energy states. This Dirac hole has all similarities with an ordinary electron except a charge of '+*e*'. This is the antiparticle of electron called positron.

5.7 Zitterbewegung Method

Consider the motion of an electron according to Dirac equation in Heisenberg representation. TheHamiltonian is time dependent. The relativistic Hamiltonian in electromagnetic field described by scalar potentials ϕ and vector potential **A** is

$$\mathrm{H} = \vec{\alpha} \cdot (\mathrm{c}\mathbf{p} - \mathrm{e}\mathbf{A}) + \beta \mathrm{mc}^{2} + \mathrm{e}\varphi \qquad (5.45)$$

Now according to Heisenberg representation, the equation of motion for operator x

$$\dot{x} = \frac{1}{i\hbar}[x, H] = \frac{1}{i\hbar}\left[x, \vec{\alpha} \cdot (\mathrm{c}\mathbf{p} - \mathrm{e}\mathbf{A}) + \beta \mathrm{mc}^{2} + \mathrm{e}\varphi\right] \qquad (5.46)$$

Omitting the terms which commute with x, we get

$$\dot{x} = \frac{1}{i\hbar}[x, \alpha_x c p_x] = \frac{c}{i\hbar}\alpha_x [x, p_x] = \frac{c}{i\hbar}\alpha_x i\hbar = c\alpha_x \qquad (5.47)$$

But the velocity operator $\dot{\mathrm{r}} = \mathbf{v}$ is given by

$$v = c\,\vec{\alpha} \qquad (5.48)$$

The probability density function according to Dirac equation is $\psi^{\dagger}\psi$; thereby given momentum density for Dirac particle as $\psi^{\dagger}\mathbf{p}\psi$ and he velocity density for Dirac particle appears to be

$$\psi^{\dagger} v \psi = \psi^{\dagger}(\mathrm{c}\vec{\alpha})\psi = \mathrm{c}\psi^{\dagger} \cdot \vec{\alpha}\psi \qquad (5.49)$$

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.* **A** = 0 and $\phi = 0$). the Hamiltonian then is expressed as

$$H = c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2 \tag{5.50}$$

Writing the equation of motion for operator α_x, we have

$$\dot{\alpha}_x = \frac{1}{i\hbar}[\alpha_x, H] = \frac{1}{i\hbar}(\alpha_x, H - H\alpha_x) \tag{5.51}$$

But $$\alpha_x H + H\alpha_x = \alpha_x(c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2) + (c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)\alpha_x$$

$$= c\alpha_x(\alpha_x p_x + \alpha_y p_z + \alpha_z p_z + \beta mc) + c\,(\alpha_x p_x + \alpha_y p_z + \alpha_z p_z + \beta mc)\,\alpha_x = 2cp_x$$

$$H\alpha_x = 2cp_x H - \alpha_x H. \tag{5.52}$$

In view of this equation (5.51) gives

$$\dot{\alpha}_x = \frac{1}{i\hbar}(2\alpha_x H - 2cp_x) \tag{5.53}$$

As for a free particle the energy and momentum are conserved, we have

$$i\hbar\dot{p}_x = [p_x H] = 0 \quad \text{and} \quad i\hbar\dot{H} = [H, H] = 0 \tag{5.54}$$

Therefore H and p_x are independent of time. Keeping this in mind, the differential of equation (5.53) with respect to time gives

$$\ddot{\alpha}_x = \frac{1}{i\hbar}(2\dot{\alpha}_x H) \tag{5.55}$$

which may be expressed as

$$\frac{\ddot{\alpha}_x}{\dot{\alpha}_x} = -\frac{2i}{\hbar}H \tag{5.56}$$

Integrating w.r.t. time t, we get,

$$\log(\dot{\alpha}_x) = -\frac{2i}{\hbar}Ht + K \tag{5.57}$$

K being a constant of integration.

If at $t=0, \dot{\alpha}_x = (\dot{\alpha}_x)_{t=0}$; we have

$$K = \log\ (\dot{\alpha}_x)_{t=0} \tag{5.58}$$

$\therefore$ Equation (5.57) 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

$$\dot{\alpha}_x = (\dot{\alpha}_x)_{t=0} \exp\left\{\left(-\frac{2i}{\hbar}\right)Ht\right\} \tag{5.59}$$

Substituting this in (5.53), we get

$$(\dot{\alpha}_x)_{t=0} \exp\left(-\frac{2i}{\hbar}Ht\right) = \frac{1}{i\hbar}(2\alpha_x H - 2cp_x) \tag{5.59A}$$

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 (5.59A), we have

$$\alpha_x = cp_x H^{-1} + \frac{1}{2}i\hbar\ (\dot{\alpha}_x)_{t=0} \exp\left(-\frac{2i}{\hbar}Ht\right)H^{-1} \tag{5.60}$$

Therefore

$$\dot{x} = c\alpha_x = c^2p_x H^{-1} + \frac{1}{2}i\hbar c(\dot{\alpha}_x)_{t=0} \exp\left(-\frac{2i}{\hbar}Ht\right)H^{-1}$$

Integrating,

$$x = c^2 p_x H^{-1} t - \frac{1}{4} c\hbar^2 \, (\dot{\alpha}_x)_{t=0} \exp\left(-\frac{2i}{\hbar} Ht\right) H^{-2} + x_0 \qquad (5.60A)$$

where x_0 is constant of integration

Since $\dot{\alpha}_x \dagger = \left\{\frac{1}{\mathrm{i}\hbar}[\alpha_x, H]\right\}\dagger = \frac{1}{\mathrm{i}\hbar}[H, \alpha_x] = \frac{1}{\mathrm{i}\hbar}[\alpha, H] = \dot{\alpha}_x$

Also p_x and H are Hermitian, therefore right hand side of (5.60A) 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

$$< x > = \frac{c^2 p_x t}{E} - \frac{1}{4} \frac{c\hbar^2}{E^2} < (\dot{\alpha}_x)_{t=0} > \exp\left(-\frac{2i}{\hbar} Et\right) \qquad (5.61)$$

Where $<(\dot{\alpha}_x)_{t=0}>$ is the eigen value of α_x at $t=0$.

Now we have

$$E = (p^2 c^2 + m^2 c^4)^{1/2} = mc^2$$

and writing $\frac{2E}{\hbar} = \omega$, equation (5.61) may be expressed as

$$< x > = \frac{c^2 p_x t}{E} - \frac{1}{4} \frac{c\hbar^2}{E^2} < (\dot{\alpha}_x)_{t=0} > e^{i\omega t} \qquad (5.62)$$

In this equation the first term represents usual term

$$\left(\frac{c^2 p_x t}{E} \approx \frac{c^2 p_x t}{mc^2} = \frac{m\upsilon_x t}{m}\right) = \upsilon_x t \qquad (5.63)$$

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 $\upsilon_x t$ is undetectable. The Zitterbewgung did not appear in out no relativistic theory, the reason that this phenomenon is due to the rest energy of the electron which remains unaccounted in classical mechanics.

5.8 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 $V(r)$.

$$[c\vec{\alpha}\cdot p + \beta mc^2 + V(r)]\psi = E\psi. \tag{5.64}$$

Writing $\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$ which represent the first and the last two components of ψ respectively.

i.e.
$$\left\{ c\begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix}\cdot \mathrm{p} + \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} mc^2 + V(r)\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right\} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = E\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

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

$$c\,\vec{\sigma}\cdot\mathbf{p}\psi_1 + mc^2\,\psi_1 + V\psi_1 = E\psi_1$$

and
$$c\,\vec{\sigma}\cdot\mathbf{p}\psi_1 - mc^2\,\psi_2 + V\psi_2 = E\psi_2$$

$$\left.\begin{array}{l} (E - V - mc^2)\,\psi_1 - c\,\vec{\sigma}\cdot\mathbf{p}\psi_2 = 0 \\ (E - V + mc^2)\,\psi_{21} - c\,\vec{\sigma}\cdot\mathbf{p}\psi_1 = 0 \end{array}\right] \tag{5.65}$$

Assuming the 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 (5.65) then become

$$\left.\begin{array}{r}\{E'-V(r)\}\,\psi_1-c\,\vec{\sigma}\cdot\mathbf{p}\psi_2=0\ \ldots(a)\\ \{E'+2mc^2-V(r)\}\,\psi_2-c\,\vec{\sigma}\cdot\mathbf{p}\psi_1=0\ \ldots(b)\end{array}\right] \tag{5.66}$$

From (5.66b), we have

$$\psi_2=\frac{c\,\vec{\sigma}\cdot\mathbf{p}}{E'+2mc^2-V(r)}\ \psi_1$$

Substituting this value of ψ_2 in (5.66b), we get

$$[E'-V(r)]\,\psi_1 = c^2\,(\vec{\sigma}\cdot\mathbf{p})[E'+2mc^2-V(r)]^{-1}\vec{\sigma}\cdot\mathbf{p}\ \psi_1$$

$$= \frac{\vec{\sigma}\cdot\mathbf{p}}{2m}\left[1+\frac{E'-V(r)}{2mc^2}\right]^{-1}\vec{\sigma}\cdot\mathbf{p}\ \psi_1$$

$$= \frac{\vec{\sigma}\cdot\mathbf{p}}{2m}\left[1-\frac{E'-V}{2mc^2}\right]\vec{\sigma}\cdot\mathbf{p}\ \psi_1$$

$$= \frac{1}{2m}(\vec{\sigma}\cdot\mathbf{p})\,((\vec{\sigma}\cdot\mathbf{p})\ \psi_1-(\vec{\sigma}\cdot\mathbf{p})\,\frac{(E'-V)}{4m^2c^2}\,\vec{\sigma}\cdot\mathbf{p}\ \psi_1 \tag{5.67}$$

Using the identity

$$(\vec{\sigma}\cdot\mathbf{B})(\vec{\sigma}\cdot\mathbf{C})=\mathbf{B}\cdot\mathbf{C}+i\vec{\sigma}\cdot\mathbf{B}\mathrm{x}\mathbf{C}$$

we have $(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p})=\mathbf{p}\cdot\mathbf{p}+i\vec{\sigma}\cdot\mathbf{p}\mathrm{x}\mathbf{p}=\mathrm{p}^{2}$ (5.67A)

For any any function u,

$$[\mathbf{p},\mathrm{V}]\mathrm{u}=(\mathbf{p}\mathrm{V}-\mathrm{V}\mathbf{p})\mathrm{u}=\mathbf{p}\mathrm{V}\mathrm{u}-\mathrm{V}\mathbf{p}\mathrm{u}$$

$$= \frac{\hbar}{i}\nabla(Vu)-V\frac{\hbar}{i}\nabla u$$

$$= \frac{\hbar}{i}\left[V\nabla u + u\nabla V\right] - V\frac{\hbar}{i}\nabla u$$

$$= \frac{\hbar}{i}u\nabla V = \left(\frac{\hbar}{i}\nabla V\right)u$$

i.e. $$(\mathbf{p}\mathrm{V} - \mathrm{V}\mathbf{p})\mathrm{u} = (-\mathrm{i}\hbar\nabla\mathrm{V})\,\mathrm{u}$$

or $$(\mathbf{p}\mathrm{V} - \mathrm{V}\mathbf{p})\mathrm{u} = -\mathrm{i}\hbar\nabla\mathrm{V}$$

$\therefore$ $$\mathbf{p}\mathrm{V} = V\mathbf{p} - \mathrm{i}\hbar\nabla\mathrm{V}$$

$\therefore$ $$(\vec{\sigma}\cdot\mathbf{p})\mathrm{V} = V(\vec{\sigma}\cdot\mathbf{p}) - \vec{\sigma}\cdot\mathrm{i}\hbar\nabla\mathrm{V} \qquad (5.68)$$

$\therefore$ $$(\vec{\sigma}\cdot\mathbf{p})\frac{(E'-V)}{4m^2c^2}\vec{\sigma}\cdot\mathbf{p} = \frac{E'}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \frac{1}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p})$$

$$= \frac{E'}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \frac{1}{4m^2c^2}\left\{V(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \vec{\sigma}\cdot(i\hbar\nabla V)(\vec{\sigma}\cdot\mathbf{p}))\right\}$$

using eqn. (5.68)

$$= \frac{E'}{4m^2c^2}p^2 - \frac{1}{4m^2c^2}Vp^2 + \frac{i\hbar}{4m^2c^2}(\vec{\sigma}\cdot\nabla V)\,(\vec{\sigma}\cdot\mathbf{p})$$ using eqn.(5.67a)

$$= \left(\frac{E'-V}{4m^2c^2}\right)p^2 + \frac{i\hbar}{4m^2c^2}\left\{\nabla V\cdot\mathbf{p} + \vec{\sigma}\cdot\nabla V \,\mathrm{x}\,\mathbf{p}\right\}$$

(5.69)

Using (5.67A) and (5.69), equation (5.67) gives

$$(E'-V)\psi_1 = \frac{1}{2m}p^2\psi_1 - \left\{\left(\frac{E'-V}{4m^2c^2}\right)p^2 + \frac{i\hbar}{4m^2c^2}(\nabla V\cdot\mathbf{p} + i\vec{\sigma}\cdot\nabla V \,\mathrm{x}\,\mathbf{p}\right\}\psi_1 .$$

$$E'\psi_1 = \left\{\left(1 - \frac{E'-V}{2mc^2}\right)\frac{p^2}{2m} + V\right\}\psi_1 - \frac{\hbar^2}{4m^2c^2}\nabla V\cdot\nabla\psi_1 + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\nabla V \,\mathrm{x}\,\mathbf{p}\psi_1 \qquad (5.70)$$

Now if V is spherically symmetric, we have

$$\nabla V = \frac{1}{r}\frac{dV}{dr}\mathbf{r}$$

and $$(\nabla V)\cdot\nabla = \frac{dV}{dr}\frac{\partial}{\partial r}\cdot$$

$$\therefore \qquad \nabla V \text{ x } p = \left(\frac{1}{r}\frac{dV}{dr}\mathbf{r} \right) \text{x } p = \frac{1}{r}\frac{dV}{dr}(\mathbf{r} \text{ x } p)$$

and noting that $E' - V \approx \frac{p^2}{2m}$, equation (5.70) gives

$$E'\psi_1 = \left\{ \left(1 - \frac{(p^2/2m)}{2mc^2} \right) \frac{p^2}{2m} + V \right\} \psi_1 - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial \psi_1}{\partial r} + \frac{\hbar}{4m^2c^2}\vec{\sigma} \cdot \frac{1}{r}\frac{dV}{dr} r \text{ x } \mathbf{p}\psi_1$$

Using $\frac{1}{2}\hbar\vec{\sigma} = \mathbf{S}$ and $\mathbf{r} \text{ x } \mathbf{p} = \mathbf{L}$, we have

$$E'\psi_1 = \left(\frac{p^2}{2m} + V - \frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S}.\mathbf{L} \right)\psi_1 \qquad (5.71)$$

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.

$$E' = E - mc^2 = (p^2c^2 + m^2c^4)^{1/2} - mc^2$$

$$= mc^2 \left(1 + \frac{p^2c^2}{m^2c^4} \right)^{1/2} - mc^2 = mc^2 \left(1 + \frac{p^2}{m^2c^2} \right)^{1/2} - mc^2$$

$$= mc^2 \left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \ldots\ldots\ldots \right) - mc^2$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \qquad (5.72)$$

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

$$U_{s-0} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S}.\mathbf{L}, \qquad (5.73)$$