Quantum Mechanics

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UNIT 2 : GENERAL FORMULATION IN WAVE MECHANICS <u>HEISENBERG'S UNCERTAINTY PRINCIPLE</u>

STATEMENT:

Heisenberg's uncertainty principle states that is impossible to determine precisely and simultaneously the values of both the numbers of a pair of physical variables which the motion of atomic system. Such pairs of variables are called canonically conjugate variables.

EXAMPLE:

According to this principle, consider the particle such as an electron, its position and momentum cannot be determined simultaneously to any desired degree of accuracy. Taking Δx as the error in determining its momentum at the same instant, these quantities are related as follows:

$$\Delta \mathbf{x} \cdot \Delta \mathbf{p} = \frac{\mathbf{h}}{2\pi}$$

The product of the two errors is approximately of the order of planck's constant. If Δx is small. Δp will be large and vice versa. It means that if one quantity measured accurately the other quantity becomes less accurate. Thus any instrument cannot measure the quantities more accurately than predicted by Heisenberg's uncertainty or indeterminacy. The same relation holds for the energy and time related to any given event.

$$\Delta \mathbf{E} \cdot \Delta \mathbf{t} = \frac{\mathbf{h}}{2\pi}$$

According to classical ideas, it is possible for a particle to occupy a fixed position and have a definite momentum ad we can predict exactly its position and momentum at any time later. But according to the uncertainly principle, it is not possible to determine accurately the simultaneous values of position and momentum of a particle at any time. Heisenberg's principle implies that a physical measurements probability takes the place of exactness and as such phenomena which are impossible according to classical ideas may find a small but finite probability of occurrence.

Applications of Heisenberg's uncertainty principle:

Suppose we try to measure the position and linear of an electron using an imaginary microscope with a very high resolving power. The electron can be observed if atleast one photon

is scattered by it into the microscope lens. The resolving power of the microscope is given by the relation

$$\Delta \mathbf{x} = \frac{\lambda}{2 \sin \theta}$$

Where Δx is the distance between two points which can be just revolved by microscope. This is the range in which the electron would be visible when disturbed by the photon. Hence Δx is the uncertainty involved in the position measurement of the electron.

However, the incoming photon will interact with the electron through the Compton Effect. To be able to see this electron, the scattered photon should enter the microscope within the angle 2θ . The momentum imparted by the photon should enter during the impact is of the order of $\frac{h}{\lambda}$. The component of this momentum along OA is $-\frac{h}{\lambda} \sin \theta$ and that along OB is $\frac{h}{\lambda} \sin \theta$.



Hence the uncertainty in the momentum measurement in the x-direction is

$$\Delta \mathbf{P}_{\mathbf{x}} = \frac{h}{\lambda} \sin \theta - \left(-\frac{h}{\lambda} \sin \theta\right)$$
$$= \frac{2h}{\lambda} \sin \theta$$
$$\Delta \mathbf{x} \cdot \Delta \mathbf{P}_{\mathbf{x}} = \frac{\lambda}{2\sin\theta} \times \frac{2h}{\lambda} \sin \theta = \mathbf{h}$$

A more sophisticated approach will show that $\Delta \mathbf{x} \cdot \Delta \mathbf{P}_{\mathbf{x}} \geq \frac{\mathbf{h}}{2\pi}$.

It is clear that the process of measurement itself perturbs the particle whose properties being measured.

Non-existence of electrons in the nucleus

we will prove that electrons cannot exist inside the nucleus using Heisenberg's uncertainty principle.

But to prove it, let us assume that electrons exist in the nucleus. As the radius of the nucleus in approximately 10^{-14} m. If electron is to exist inside the nucleus, then uncertainty in the position of the electron is given by

$$\Delta x = 10^{-14} \,\mathrm{m}.$$

According to uncertainty principle,

$$\Delta \mathbf{x} \cdot \Delta \mathbf{p}_{\mathbf{x}} = \frac{\mathbf{h}}{2\pi}.$$
Thus $\Delta \mathbf{p}_{\mathbf{x}} = \frac{\mathbf{h}}{2\pi\Delta \mathbf{x}}$
Or $\Delta p_{\mathbf{x}} = 6.62 \times 10^{-34} / 2 \times 3.14 \times 10^{-14}$
 $\Delta p_{\mathbf{x}} = 1.05 \times 10^{-20} \text{kg m/ sec}$

If this is p the uncertainty in the momentum of electron, then the momentum of electron should be at least of this order, that is $p=1.05*10^{-20}$ kg m/sec. An electron having this much high momentum must have a velocity comparable to the velocity of light. Thus, its energy should be calculated by the following relativistic formula

$$E = \sqrt{m_0^2 c^4 + p^2 c^2}$$

$$E = \sqrt{(9.1*10^{-31})^2 (3*10^8)^4 + (1.05*10^{-20})^2 (3*10^8)^2}$$

$$= \sqrt{(6707.61*10^{-30}) + (9.92*10^{-24})}$$

$$= (0.006707*10^{-24}) + (9.92*10^{-24})$$

$$= \sqrt{9.9267*10^{-24}}$$

$$E = 3.15*10^{-12} J$$
Or $E = 3.15*10^{-12}/1.6*10^{-19} eV$

$$E = 19.6*10^6 eV$$

$$E = 19.6 MeV$$

Therefore, if the electron exists in the nucleus, it should have an energy of the order of 19.6 MeV. However, it is observed that beta-particles (electrons) ejected from the nucleus during b -decay have energies of approximately 3 Me V, which is quite different from the calculated value of 19.6 MeV. Second reason that electron can not exist inside the nucleus is that experimental results show that no electron or particle in the atom possess energy greater than 4 MeV. Therefore, it is confirmed that electrons do not exist inside the nucleus.

HEISENBERG PICTURES:

In this picture, in contrast to the schroedinger picture, the operators are chosen timedependent whereas the wavefunctions are time-independent. This picture can be obtained from the schroedinger picture through a unitary transformation as shown below:

$$-(i/\hbar)H|\Psi(t)\rangle = \frac{d|\Psi(t)\rangle}{dt}$$

or

$$\frac{\mathrm{d}|\Psi(t)>}{\Psi(t)} = -\left(\frac{i}{\hbar}\right)Hdt$$

Integrating above, we get

$$log_{e|\Psi(t)>=-\frac{i}{\hbar}Ht+C_1}$$
 (H is independent of time)

When,

 $t = 0, \Psi(t) = \Psi(0),$ $C_{1=log_e | \Psi(0) >}$ $log_{e}|\Psi(t)\rangle = -i\hbar Ht + log_{e}|\Psi(0)\rangle$

Where
$$log_e |\Psi(0)\rangle$$
 is the constant of integration ; $|\Psi(0)\rangle$ defines the state at t=0. $|\Psi(0)\rangle$ actually defines the state vector in Heisenberg picture, which does not change with time and retains its initial value as time progresses.

$$log_e \frac{|\Psi(t)>}{|\Psi(0)>} = -\frac{i}{\hbar} Ht$$

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$$|\Psi(t)\rangle = e^{-\frac{(i)Ht}{\hbar}} |\Psi(0)\rangle$$
$$= e^{-\frac{(i)Ht}{\hbar}} |\Psi H\rangle$$

 $|\Psi(0)\rangle \equiv \Psi H$, in Heisenberg picture as explained. We have thus proved that

$$|\Psi H\rangle = e^{-\frac{(i)Ht}{\hbar}} |\Psi(t)\rangle = e^{-\frac{(i)Ht}{\hbar}} |\Psi s|$$

i.e., the state vector in the Heisenberg picture is obtained from the state vector in the schrodinger picture through a unitary transformation by the operator

$$U=e^{-\frac{(i)Ht}{\hbar}}$$

Now, we shall obtain the relationship between any operator Qs(time-independent) of the schrodinger picture and the operator QH(time-dependent) of the Heisenberg picture, using the transformation. Since the expectation value of the two pictures should be identical,

$$\langle \Psi s | Qs | \Psi s \rangle = \langle \Psi H | QH | \Psi H \rangle,$$

Or

 $<\!\!\Psi s|Qs|\Psi s\!\!>=<\!\!\Psi s|e^{-(\frac{i}{\hbar})Ht\ QH}\ e^{(\frac{i}{\hbar})Ht}|\Psi s\!\!>$

From which we have

$$Qs = e^{-\frac{(i)Ht}{\hbar}} QH e^{-\frac{(i)Ht}{\hbar}}$$
$$Qs = U^{\dagger}QHU$$

Hence the heisenberg operators are obtained by a unitary transformation of the schrodinger operators:

QH=UQsU[†]=
$$e^{(\frac{i}{\hbar})Ht}$$
Qs e⁻ $(\frac{i}{\hbar})Ht$

It follows that the Hamiltonian operator does not change with time even in the Heisenberg picture. This can be seen as follows:

Hh=
$$e^{(\frac{i}{\hbar})Ht}$$
 Hs $e^{-(\frac{i}{\hbar})Ht}$ =Hs $e^{(\frac{i}{\hbar})Ht}e^{-(\frac{i}{\hbar})Ht}$ =Hs

The Heisenberg picture is closer to the classical description, since here the operators, just like the dynamical quantities in classical mechanics , change in time.

EQUATION OF MOTION IN HEISENBERG PICTURE

The defining equation for the operator in the Heisenberg picture with respect to time,

$$\frac{d}{dt} QH = \frac{d}{dt} (UQsU^{\dagger}) = \frac{\partial U}{\partial t} QsU^{\dagger} + UQs\frac{\partial U}{\partial t} + U\frac{\partial Qs}{\partial t}U^{\dagger}$$

Now since

$$\frac{\partial U}{\partial t} = e^{\left(\frac{i}{\hbar}\right)Ht} \left(\frac{i}{\hbar}\right) H = \left(\frac{i}{\hbar}\right) UH$$
$$\frac{\partial U^{\dagger}}{\partial t} = \left(\frac{\partial U}{\partial t}\right)^{\dagger} = -\left(\frac{i}{\hbar}\right) H^{\dagger}U^{\dagger} = -\left(\frac{i}{\hbar}\right) HU^{\dagger}, [H \text{ is hermition}].$$

We obtain the time rate of change of the operator in Heisenberg picture as,

$$\frac{d}{dt}QH = \left(\frac{i}{\hbar}\right) (UHQsU^{\dagger} UQsHU^{\dagger}) + U\frac{\partial Qs}{\partial t}U^{\dagger} = \left(\frac{i}{\hbar}\right) U(HQs - QsH)U^{\dagger} + U\frac{\partial Qs}{\partial t}U^{\dagger}$$

Here use has been made of the fact that [H,Qs] is the commutator bracket is Schrodinger picture and goes over to [H,Qs] in the Heisenberg picture, as H is independent of time in the latter picture. The equation of motion in the Heisenberg picture and has a close resemblance to the corresponding equation of motion in classical mechanics of a dynamic variable Q:

$$\frac{dQ}{dt} = \{Q,H\} + \frac{dQ}{dt},$$

Where, $\{Q,H\}$ is the Poisson bracket of Q with the Hamaltonian. Thus according to the matrix form of the operator has a time dependence such that it obeys the classical equation of motion, with the correspondence.

$$-1/i\hbar[Q,H] \rightarrow \{Q,H\}$$

If the operator Q does not depend on the time explicity,

$$\frac{\partial Qs}{\partial t} = \frac{d}{dt} QH = 0$$
$$\frac{d}{dt} QH = i/\hbar [H,Qh]$$

And therefore,

Further, if $Qh \equiv H$, $\frac{dH}{dt} = i/\hbar[H,H] = 0$

i.e., Hamiltonian H is a constant of motion, if H does not depend on time explicitly.

SCHROEDINGER PICTURE

The formulation of quantum dynamics in which the wave functions are time dependent and the operators are time independent is known as the Schrodinger picture

Ĥ is the time independent Hamiltonian operator

 $\partial/\partial t=0$

MATRIX FORM OF SCHROEDINGER EQUATION

Let Ψ i represent a complete set of time independent orthonormal set of basis function and let us expand Ψ (r,t) in terms of these

 $\Psi(\mathbf{r},t)=\Sigma ci(t)\Psi i(\mathbf{r})$

$$\Sigma \hat{H}ci(t)\Psi i(r) = i\hbar\Sigma d/dt ci(t)\Psi i(r)$$

Multiply by $\Psi j^*(r)$ and integrate over all space

 $\Sigma ci(t) \int \Psi j^{*}(r) \hat{H} \psi i(r) d\tau = i \hbar \Sigma d/dt ci(t) X \int \Psi j^{*}(r) \Psi i(r) d\tau$

 Σ hjici(t)=iTh Σ d/dt cj(t)

Interchanging I and j

 Σ hijcj(t)=iThd/dt ci(t)

These equations form a matrix equation

 $H|\Psi(t)\rangle = i Th d/dt |\Psi(t)\rangle$

 $|\Psi(t)$ is the state vector

 $|\Psi(t)>= c1(t)$

EQUATION OF MOTION IN SCHROEDINGER PICTURE

The expectation value of an operator As in state Ψ s is given by,

 $<\!\!As\!\!>=\!\!<\!\!\Psi s|As|\Psi s\!>$

Taking differential equation

$$d/dt < As > = <\partial \Psi s / \partial t |As| \Psi s > + < \Psi s |As| \partial \Psi s / \partial t >$$

According to schrodinger equation

 $Hs\Psi s=i\hbar\partial\Psi s/\partial t$ so $Hs^{*}\Psi s^{*}=-i\hbar\partial\Psi s^{*}/\partial t$

 $\partial \Psi s / \partial t = -1/i h H s \Psi s$ and $\partial \Psi s^* / \partial t = -1/i h H s^* \Psi s^*$

Hence $d/dt < As > = <-1/i\hbar Hs\Psi s |As|\Psi s > + <\Psi s |As|1/i\hbar Hs\Psi s >$

iThd/dt<As>=<\Ps|AsHs-HsAs|\Ps>

In matrix form iThd/dt<As>=<AsHs-HsAs>=<[As,Hs]>

In presence of external field,

If ∂As/∂t=0,As=Hs

<Hs> = constant of motion

The total energy remains constant, if the Hamiltonian of the system does not depends on time.

UNIT 3: APPROXIMATE METHODS

Degenerate perturbation theory

If the unperturbed states are degenerate, then the denominator

$$E_{n}^{\circ} - E_{m}^{\circ}$$

in the second order expression is zero, and, unless the numerator

is zero as well in this case, the perturbation theory in the way we formulated it fails. First, we consider a case of a two-fold degeneracy, i.e. when there are two states for each energy.

Two - fold degeneracy

We have two states $\begin{array}{c} & & & \\ &$

$$H^{\circ} \Psi_{a}^{\circ} = E^{\circ} \Psi_{a}^{\circ}, \quad H^{\circ} \Psi_{b}^{\circ} = E^{\circ} \Psi_{b}^{\circ}, \quad \langle \Psi_{a}^{\circ} | \Psi_{b}^{\circ} \rangle = 0,$$

 $\langle \Psi_{a}^{\circ} | \Psi_{a}^{\circ} \rangle = \langle \Psi_{b}^{\circ} | \Psi_{b}^{\circ} \rangle = 1.$

Linear combination of these states

is also an eigenstate of H with eigenvalue ξ .

We want to solve,

$$H \Psi = E \Psi, \quad H = H^{\circ} + H'.$$

$$E = E^{\circ} + E' + ...$$

$$\Psi = \Psi^{\circ} + \Psi' + ...$$

$$H^{\circ} \Psi' + H' \Psi^{\circ} = E^{\circ} \Psi' + E^{\circ} \Psi^{\circ} \qquad (5)$$

This time we multiply this equation from the left by $\int a$ and integrate, i.e. take inner

0

product with
$$\psi^{\circ}$$
.
 $< \psi^{\circ}_{\alpha} + \psi^{\circ}_{\gamma} + < \psi^{\circ}_{\alpha} + \psi^{\circ}_{\gamma} = E^{\circ} < \psi^{\circ}_{\alpha} + \psi^{\circ}_{\gamma} + E^{\dagger} < \psi^{\circ}_{\alpha} + \psi^{\circ}_{\gamma} + \psi^{\circ}_{\alpha} + \psi^{\circ}_{\alpha} + \psi^{\circ}_{\gamma} + \psi^{\circ}_{\alpha} + \psi$

N

We now plug

Ξ

$$d < \psi_{a}^{\circ} | H' \psi_{a}^{\circ} 7 + \beta < \psi_{a}^{\circ} | H' \psi_{b}^{\circ} 7$$

$$= dE' < \psi_{a}^{\circ} | \psi_{a}^{\circ} 7 + \beta E' < \psi_{a}^{\circ} | \psi_{b}^{\circ} 7$$

$$dE' = d < \psi_{a}^{\circ} | H' \psi_{a}^{\circ} 7 + \beta < \psi_{a}^{\circ} | H' \psi_{b}^{\circ} 7$$

$$\lim_{\|I\|} \qquad \lim_{dWaa} \qquad B \leq \psi_{a}^{\circ} | H' \psi_{b}^{\circ} 7$$

)

$$W_{ij} \equiv \langle \psi_i^{\circ} | H' | \psi_j^{\circ} 7, \quad (i, j = a, b)$$

$$d E^{I} = d Waa + \beta Wab \qquad (6)$$

$$\psi_i^{\circ} = 7$$

i

 $W_{ij} \, are \, known \, since \, we \, know \, we \, can \, calculate \, them.$

If we take inner product of equation (5) with γ_{b}° we get

$$\beta E^{1} = \Delta W_{ba} + \beta W_{bb}$$
 17)

We now solve this system of equations (6), (7) for E^1 .

$$dE^{1} = dWaa + \beta Wab = 7 \qquad \beta Wab = dE^{1} - dW_{aa}$$

$$\left(\beta E^{1} = dW_{ba} + \beta W_{bb}\right) \times W_{ab}$$

$$E^{1}\beta W_{ab} = dW_{ab} W_{ba} + \beta W_{ab} W_{bb}$$

$$E^{1}(dE^{1} - dW_{aa}) = dW_{ab} W_{ba} + W_{ab}(dE^{1} - dW_{aa})$$

$$d(E^{1} - dW_{aa})(E^{1} - W_{bb}) = dW_{ab} W_{ba}$$

$$If d\neq 0$$

$$\left(E^{1}\right)^{2} - E^{1}(W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$$

$$W_{ba} = W_{ab}^{*} \qquad bg definition = 7$$

$$E^{1} = \frac{1}{2} \left[W_{aa} + W_{ab} \pm \sqrt{(W_{aa} - W_{ab})^{2} + 4|W_{ab}|^{2}}\right]$$

Fundamental result of degenerate perturbation theory: two roots correspond to two perturbed energies (degeneracy is lifted).

If
$$d=0=7$$
 Wab = 0 and $E^{1} = W_{bb}$
If $p=0=7$
 $E_{\pm}^{1} = \begin{cases} Waa = c \gamma_{a}^{a} |H'| \gamma_{a}^{a} \\ W_{bb} = c \gamma_{b}^{a} |H'| \gamma_{b}^{b} \\ H'| \gamma_{b}^{b} \end{cases}$, i.e.

If we could guess some good linear combinations Ψ and Ψ , then we can just use nondegenerate perturbation theory.

Theorem: let A be a hermitian operator that commutes with H^0 and H'. If \mathcal{V}_0 and \mathcal{V}_t that are degenerate eigenfunctions of H^0 , are also eigenfunctions of A with distinct

eigenvalues, $A \gamma_{a}^{\circ} = \mu \gamma_{a}^{\circ}$, $A \gamma_{b}^{\circ} = \nu \gamma_{b}^{\circ}$, $\mu \neq \nu$

then Wab=0 and we can use degenerate perturbation theory.

Higher-order degeneracy: if we rewrite our equations

$$dE^{1} = dW_{aa} + \beta W_{ab} \qquad \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} d \\ \beta \end{pmatrix} = E^{4} \begin{pmatrix} d \\ \beta \end{pmatrix}$$

we see that E^1 are eigenvalues of the matrix

$$W = \begin{pmatrix} Waa & Wab \\ Wba & Wbb \end{pmatrix}.$$

In the case of n-fold degeneracy, E^1 are eigenvalues of n x n matrix

$$W_{ij} = \langle \Psi_i^{\circ} | H' | \Psi_j^{\circ} \rangle$$

"Good" linear combinations of unperturbed states are eigenvectors of W.

Degeneracy of Hydrogen atom

In quantum mechanics, an energy level is said to be degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be **degenerate** if they give the same value of energy upon measurement. The number of different states corresponding to a particular energy level is known as the degree of degeneracy of the level. It is represented mathematically by the Hamiltonian for the system having more than one linearly independent eigenstate with the same eigenvalue.

In classical mechanics, this can be understood in terms of different possible trajectories corresponding to the same energy. Take for instance, in projectile motion, we can project the particle in different trajectories each having the same total energy as the particle travel through its parabolic path.

Thus, for the degree of degeneracy of Hydrogen atom, we need to calculate how many possible linearly independent energy eigenstates

| the same total | 8 |
|-------------------|---|
| ugh its parabolic | |
| deconcrease of | Non-degenerate (ground state) |
| degeneracy of | |
| sulate how many | |
| y eigenstates | Figure showing Degenerate Energy Levels |

Degeneracy=5

Degeneracy=3

corresponds to energy of the atom. We knew that for hydrogen atom, its energy eigenstates are given by Ψ where:

Principal quantum number n = 1, 2, 3...

Azimuthal or Orbital Angular momentum quantum number l = 0, 1, 2, ..., n-1 i.e. *n* choices of them.

Magnetic Quantum number $m = 0, \pm 1, \pm 2, ..., \pm l$ i.e. 2l + 1 choices of them.

Hence for a given *n*,

Total number of possible energy eigenstate (n/m)

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

Therefore, the degree of degeneracy of Hydrogen atom = n^2 . We know that electrons have two different types of spins (spin up and spin down). Putting that into our degeneracy result, we have The *n*th shell of Hydrogen atom can hold up to $2n^2$ electrons

- The first shell (K) can hold up to two electrons.
- The second shell (L) can hold up to eight 8 electrons.
- The third shell (M) can hold up to 18 electrons.

THE NORMAL HELIUM ATOM

Now we shall consider the normal state of helium atom which contains a nucleus of charge Ze and two electrons each having a charge –e. The potential energy of such a system is given by,

$$V = (-Ze^{2}/r_{1} - Ze^{2}/r_{2} + e^{2}/r_{12})1/4\pi\varepsilon_{0} \qquad \dots \dots (1)$$

In which r_1 and r_2 are the distance of electron 1 and 2, respectively from nucleus, and r_{12} is the separation of the electron.

Considering the nucleus at rest, the wave equation for the two electrons becomes,

$$(\partial^{2}\psi/\partial x_{1}^{2} + \partial^{2}\psi/\partial y_{1}^{2} + \partial^{2}\psi/\partial z_{1}^{2} + \partial^{2}\psi/\partial x_{2}^{2} + \partial^{2}\psi/\partial y_{2}^{2} + \partial^{2}\psi/\partial z_{2}^{2}) + 2m/\hbar^{2}[E + 1/4\pi\epsilon_{0}(Ze^{2}/r_{1} + Ze^{2}/r_{2} - e^{2}/r_{12})]\psi = 0$$

the variables $x_{1,y_{1,}z_{1}}$ are Cartesian coordinates of one electrons and $x_{2,y_{2},z_{2}}$ those of other. If the term $e^{2}/4\pi\epsilon_{0}r_{12}$ is omitted, the wave equation can be solved exactly; hence this may be regarded as perturbation term,

$$H^{(1)} = e^2 / r_{12} 1 / 4\pi \varepsilon_0 \qquad \dots (2)$$

The unperturbed wave equation can be separated into two equations by substituting

$$\Psi^{(1)}(x_1y_1z_1,x_2y_2z_2) = u_1^{(0)}(x_1y_1z_1)u_2^{(0)}(x_2y_2z_2) \qquad \dots (3)$$

Considering the wave functions in polar coordinates r_1, θ_1, ϕ_1 and r_2, θ_2, ϕ_2 and in normal state, and corresponding eigen value is

$$E^{(0)}{}_{100,100} = E_1{}^{(0)} + E_2{}^{(0)} = -2Z^2 E_H \qquad \dots \dots (4)$$

The first order perturbed energy $E^{(1)}$ is the average value value of the perturbation function

$$H^{(1)} = e^2/4\pi\epsilon_0$$
(5)

Over the unperturbed state of the system. Hence,

$$E^{(1)} = \int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)} d\tau = 1/4\pi\varepsilon_0 \int e^2/r_{12} \psi^{(0)}{}_{100,100} d\tau \qquad \dots (6)$$

We know that,

$$u_{1s}^{(0)} = \psi^{(0)} = \sqrt{(Z^3/\pi a_0^3)}e^{-\ell/2}$$
(7)

in which $\ell = 2Zr/a_0$ and $a_0 = \hbar/me^2(4\pi\epsilon_0)$

$$\psi^{(0)}_{100,100} = \text{Ze}^{3}/\pi a_{0}^{3} \exp(-\ell_{1}/2) \exp(-\ell_{2}/2)$$
(8)

the volume element is

$$d\tau = r_1^2 dr_1 \sin\theta_1 d\theta_1 d\phi_1 r_2^2 \sin\theta_2 d\theta_2 d\phi_2 \qquad \dots \dots (9)$$

So, that the integral for $E^{(1)}$ becomes

$$E^{(1)} = Ze^{2} / (4\pi\epsilon_{0})2^{5}\pi^{2}a_{0} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} exp(-\ell_{1}-\ell_{2})/\ell_{12}$$

$$\ell_{1}^{2}d\ell_{1}\sin\theta_{1}d\theta_{1}d\phi_{1}\ell_{2}^{2}d\ell_{2}\sin\theta_{2}d\theta_{2}d\phi_{2} \qquad \dots \dots \dots (10)$$

in which $\ell_{12} = 2Zr_{12}/a_{0.}$

The value of the integral can be calculated by considering the electrostatic interaction energy of two spherically distribution of electricity, with density functions $\exp(-\ell_1)$ and $\exp(-\ell_2)$, respectively. Solving the integral, we have

$$E^{(1)} = (5/4) Z E_H$$
(11)

Thus, the total energy of the system is

$$E = -(2Z^2 - 5/4.Z)E_H$$
(12)

Thus, we can calculate the energy of He,Li⁺,Be⁺⁺,etc with Z = 2,3,4 etc., respectively.

Stark Effect

The Stark effect is the shift in atomic energy levels caused by an external electric field. There are various regimes to consider. The one treated here is the so-called strong field case, where the shift

in energy levels due to the external electric field is large compared to fine structure (although still small compared to the spacings between the unperturbed atomic levels.) In the strong field limit, the Stark effect is independent of electron spin.

We start with the ordinary hydrogen Hamiltonian,

$$H_{0=\frac{p^2}{2m}-\frac{e^2}{r}}$$

and add a term arising from a uniform electric field along the z axis.

$$H' = e\varepsilon z.$$

Note the + sign on this term. It is easily checked by remembering that the force on the electron due to this term would be obtained by taking ∂_{z} , which gives a force along the z axis, as it should for an electron. To understand the matrix elements that are non-zero, it is useful to temporarily give the external electric field an arbitrary direction,

$$\mathbf{H}' = e \vec{\varepsilon}. \vec{x}$$

The selection rules on the matrix elements of \vec{x} are

$$<$$
n',1',m'/ \vec{x} /n,1,m> \neq 0,1'=1±1.

These follow from angular momentum conservation (\vec{x} has angular momentum 1), and parity (\vec{x} is odd under parity). Returning to the case of the electric field along the z axis, we have an additional selection rule on m,

$$< n', 1', m'/z/n, l, m > \neq 0, l' = l \pm 1, m' = m$$

From these selection rules we see that non-zero matrix elements require different values of 1. Now for n = 1 there is only l = 0, so

 $n = 1, 1 = 0 \rightarrow no$ first order Stark Effect.

However, for n = 2, we have two l values, so

$$n = 2, l = 0, 1, \rightarrow l = 0 \leftrightarrow l = 1$$

Listing the states for n = 2, we have

$$\Psi_{200}, \Psi_{211}, \Psi_{210}, \Psi_{21-1}$$

.

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However, l = 0 has only m = 0, so the selection rule on m says we only have non-zero matrix elements

$$l = 0 \leftrightarrow l = 1 \rightarrow \Psi_{200} \leftrightarrow \Psi_{210}$$

Without the electric field these states have the same energy, so we have a 2 2_{\times} problem in degenerate perturbation theory. The matrix element we need is proportional to

We label the two degenerate states as follows:

$$200 \rightarrow 1\ 210 \rightarrow 2$$

Using this notation, we need to find new linear combinations of these degenerate states, and along the way we find values for the perturbed energy eigenvalues. The equations which accomplish both of these tasks are

$$\begin{pmatrix} E^{(1)} & 0 \\ 0 & E^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_1 \end{pmatrix} = \begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_1 \end{pmatrix}$$

By our selection rules, the diagonal matrix elements vanish,

$$H_{11} = H_{22} = 0$$

and

$$H_{12} = H_{21} = e\varepsilon < 200/z/210 >.$$

The wave functions of our states are

$$\varphi_{200} = N_{20} \left(1 - \frac{1}{2a_0}\right) exp\left(-\frac{1}{2a}\right) \frac{1}{\sqrt{4\pi}}$$
$$\varphi_{210} = N_{21} \left(-\frac{r}{2a}\right) \sqrt{\frac{3}{4\pi}} \cos \theta$$

Where the N 's are normalization factors, given below. It is useful at this point to go over to atomic units,

$$z \to a_0 r' \cos \theta, \varepsilon \to \frac{e}{a_0^2} \varepsilon'$$

and we subsequently drop the on atomic unit quantities. The matrix element we need is an exercise in elementary integrations. We have

$$|rcos\theta|210 >= N_{20}N_{21}\int d\Omega \int r^2 dr \frac{r}{2} (1 - \exp(-r/2) r(rexp(-r/2))) \frac{\sqrt{3}}{4\pi} \cos^2 \theta = -3$$

Moving the matrix elements of H' to the left side of our equation, we have

$$\begin{pmatrix} E^{(1)} & 3\varepsilon \\ 3\varepsilon & E^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_1 \end{pmatrix} = 0$$

(E⁽¹⁾)² - (3\varepsilon)² = 0.
E⁽¹⁾ = ±3 \varepsilon .

This gives the two eigenvalues

These two values determine the amounts by which the n = 2 level is split by the external electric field. To determine the corresponding wave functions, we go back to the equations, with E ⁽¹⁾ set equal to one of the eigenvalues. Taking first the lower eigenvalue, we have

$$E^{1} = -3\varepsilon, \begin{pmatrix} -3\varepsilon & 3\varepsilon \\ 3\varepsilon & -3\varepsilon \end{pmatrix} \begin{pmatrix} c_{1} \\ c_{1} \end{pmatrix} = 0$$

This gives,

$$c_1 = c_2, \varphi_- = \frac{1}{\sqrt{2}} [\varphi_{200} + \varphi_{210}]$$

where Ψ - is now the correct unperturbed wave function corresponding to the lower eigenvalue. Said another way, the perturbing Hamiltonian has matrix element -3ε in the state Ψ -. Doing the same for the upper eigenvalue, we have

$$E^{1} = 3\varepsilon, \begin{pmatrix} 3\varepsilon & 3\varepsilon \\ 3\varepsilon & 3\varepsilon \end{pmatrix} \begin{pmatrix} c_{1} \\ c_{1} \end{pmatrix} = 0$$
$$c_{1} = -c_{2}, \varphi_{+} = \frac{1}{\sqrt{2}} [\varphi_{200} - \varphi_{210}]$$

and Ψ_{+} has +3E for the matrix element of the perturbed Hamiltonian. In writing Ψ_{+}

and Ψ -, we have supplied the normalization factor $1/\sqrt{2}$,

and Ψ_{210} with normalization factors supplied are

$$\varphi_{200} = R_{20}Y_0^1 = \frac{1}{\sqrt{2}}\left(1 - \frac{1}{2}\right)exp\left(-\frac{r}{2}\right)\frac{1}{\sqrt{4\pi}}$$

and

$$\varphi_{210} = R_{21}Y_0^1 = \frac{1}{2\sqrt{6}}rexp\left(-\frac{r}{2}\right)\sqrt{\frac{3}{4\pi}\cos\theta}$$

In atomic units, the states Ψ_{200} with these formulas the wave functions Ψ_+ and Ψ_- are easily constructed and them properties explored. This is done in more detail in Homework Set 2. The basic qualitative feature is that Ψ_- favors an increased electron density for z < 0 and a decreased electron density for z > 0 as expected for the effect of a force directed along the negative z axis.

The Variation Principle (Rayleigh-Ritz Approximation)

As the ground state has the lowest possible energy, we can vary a test wave function, minimizing the energy, to get a good estimate of the ground state energy.

$$H\psi_E = E\psi_E$$

 $\Psi_{\rm E}$, for the ground state

$$E = \frac{\int \psi_E^* H \psi_E dx}{\int \psi_E^* \psi_E dx}$$

 Ψ , for any trial wave function,

$$E' = \frac{\int \psi^* H \psi dx}{\int \psi^* \psi dx} = \frac{\langle \psi^* | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

We wish to show that E' errors are second order in $\delta \Psi$

$$\Rightarrow \qquad \frac{\partial E}{\partial \psi} = 0$$

At Eigen energies,

To do this, we will add a variable amount of an arbitrary function φ to the energy Eigen state.

$$E' = \frac{\langle \psi_E + \alpha \phi | H | \psi_E + \alpha \phi \rangle}{\langle \psi_E + \alpha \phi | \psi_E + \alpha \phi \rangle}$$

Assume α is real since we do this for any arbitrary function. Now we differentiate with respect to α and evaluate at zero.

$$\frac{dE'}{d\alpha}\Big|_{\alpha=0} = \frac{\langle\psi_E|\psi_E\rangle\left(\langle\phi|H|\psi_E\rangle + \langle\psi_E|H|\phi\rangle\right) - \langle\psi_E|H|\psi_E\rangle\left(\langle\phi|\psi_E\rangle + \langle\psi_E|\phi\rangle\right)}{\langle\psi_E|\psi_E\rangle^2}$$

$$= E \langle \phi | \psi_E \rangle + E \langle \psi_E | \phi \rangle - E \langle \phi | \psi_E \rangle - E \langle \psi_E | \phi \rangle = 0$$

We find that the derivative is zero around any Eigen function, proving that variations of the energy are second order in variations in the wave function. That is, E' is stationary (2nd order changes only) with respect to variation in Ψ . Conversely, it can be shown that E' is only stationary for Eigen functions Ψ_E . We can use the **variation principle** to approximately find and Ψ_E to find an upper bound on E_0 .

$$\psi = \sum_{E} c_E \psi_E$$
$$E' = \sum_{E} |c_E|^2 E \ge E_0$$

For higher states this also works if trial Ψ is automatically orthogonal to all lower states due to some symmetry.

WKB approximation:

The WKB approximation, named after Wentzel, Kramers, and Brillouin, is a method for obtaining an approximate solution to a time-independent one-dimensional differential equation, in this case the Schrodinger equation. Its principal applications for us will be in calculating bound-state energies and tunneling rates through potential barriers. Note that both examples involve what is called the `classical turning point', the point at which the potential energy V is approximately equal to the total energy E. This is the point at which the kinetic energy equals zero, and marks the boundaries

$$\lambda = \frac{h}{p} = \frac{h}{[2m (E-V)^{1/2}]} \quad \dots \quad (1)$$
$$\frac{1}{2} m v^2 = E - V$$
$$m^2 v^2 = 2m (E - V)$$
$$p = mv = \sqrt{2m (E - V)^{1/2}}$$
$$k = \frac{2\pi}{\lambda} = \frac{[2m (E-V)^{1/2}]}{h} \dots \quad (2)$$

Mathematically slowly varying potential can be expressed as by conditions,

between regions where a classical particle is allowed and regions where it is not.

$$\left|\frac{1}{k^2}\frac{\partial k}{dx}\right| < 1.$$

Substituting the value of k from (1), we get

$$\frac{\hbar m \left| \frac{\partial V}{dx} \right|}{\left[2m \left(E - V \right)^{3/2} \right]} < 1 \text{ or } \frac{\lambda \frac{\partial V}{dx}}{2\pi \left(E - V \right)} < 1 \quad -----(3)$$

This equation gives the validity of W.K.B. approximation.

Principle of the Method:

W.K.B. method consists in introducing an expression in the powers of \hbar .The schrodiger equation (at least in some regions of space) is reduced in its classical limit. However, the method has a wider range of applicability than the classical approximation, because this produce can be carried out even in region of space where classical interpretation in meaningless (region E < V is inaccessible to classical particle).

Let $\Psi(x)$ be the wavefunction satisfying schrodinger's equation

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} \left[E - V(x) \right] \Psi = 0 \quad \dots \quad (4)$$

Let the solution of equation (4) be the form

$$\Psi = C e^{i\phi x/\hbar} \quad \dots \quad (5)$$

Where C is a constant, $\phi(x)$ is yet an undetermined function of x,

We have,
$$\frac{\partial \Psi}{\partial x^2} = C \frac{i}{\hbar} e^{i\phi x/\hbar} \cdot \frac{\partial \phi}{\partial x}$$

 $\frac{\partial^2 \Psi}{\partial x^2} = \frac{c}{\hbar^2} e^{i\phi x/\hbar} \cdot \left(\frac{\partial \phi}{\partial x}\right)^2 + C \frac{i}{\hbar} e^{i\phi x/\hbar} \cdot \frac{\partial^2 \phi}{\partial x^2} - \cdots - (6)$

Now substituting $\frac{\partial \phi}{\partial x} = \phi'$ and $\frac{\partial^2 \phi}{\partial x^2} = \phi''$, equation (6) takes the form

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{c}{\hbar^2} e^{i\phi x/\hbar} \cdot (\phi')^2 + C \frac{i}{\hbar} e^{i\phi x/\hbar} \cdot \phi'' \qquad \dots (7)$$

Substituting values of Ψ and $\frac{\partial^2 \Psi}{\partial x^2}$ from (5) and (7) in (4), we get

$$-\frac{c}{\hbar^{2}}e^{i\phi x/\hbar} \cdot (\phi')^{2} + C \cdot \frac{i}{\hbar}e^{i\phi x/\hbar} \cdot \phi'' + \frac{2m}{\hbar^{2}}[E - V(x)] C e^{i\phi x/\hbar} = 0$$

Or
$$-\frac{c}{\hbar^{2}}e^{i\phi x/\hbar} [-\phi'^{2} + i\hbar\phi'' + 2m[E - V(x)]] = 0$$

As $\Psi = C e^{i\phi x/\hbar} \neq 0$; therefore above equation fields

$$[i\hbar\phi'' - {\phi'}^2 + 2m[E - V(x)] = 0 \quad -----(8)$$

To get approximate solution of (8), we apply W.K.B. method and hence expand $\phi(x)$ in powers of \hbar i.e.

$$\phi'(x) = \phi_0'^{(x)} + \hbar \phi_1'(x) + \frac{\hbar^2}{2} \phi_2(x) + \dots$$
$$\phi''(x) = \phi_0''^{(x)} + \hbar \phi_1''(x) + \frac{\hbar^2}{2} \phi_2''(x) + \dots$$
$$i\hbar \left[\phi_0''^{(x)} + \hbar \phi_1''(x) + \frac{\hbar^2}{2} \phi_2''(x) + \dots\right] - \left[\phi_0'^{(x)} + \hbar \phi_1'(x) + \frac{\hbar^2}{2} \phi_2(x) + \dots\right]^2$$
$$2m[E - V(x)] = 0$$

Collecting coefficients of various powers of \hbar . We see that up to second order in \hbar , the result is

$$[2m(E-V) - \phi_0'^2] + \hbar [i\phi_0'' - 2\phi_0'\phi_1'] + \hbar^2 [i\phi_1'' - {\phi'}^2 - 2\phi_0'\phi_2'] = 0 \dots (11)$$

In order that equation (11) may hold identically in \hbar , the coefficient of each power of \hbar must vanish separately. The requirement leads to the following series of equations.

$$2m(E - V) - \phi_0'^2 = 0 \qquad \dots \dots \dots (a)$$

$$i\phi_0'' - 2\phi_0'\phi_1' = 0 \qquad \dots \dots \dots (b)$$

$$i\phi_1'' - \phi_1'^2 - 2\phi_0'\phi_2' = 0 \qquad \dots \dots \dots (c)$$

And so on. These equations may be solved successively. That is, the first equation defines ϕ_0 . In terms of |(E - V)|, the second equation defines ϕ_1 In terms of ϕ_0 , the third defines ϕ_1 and ϕ_0 etc.

From equation (12a), we obtain

$$\phi_0' = \pm \sqrt{2m(E-V)}$$
(13)

Integration of above yields

Where x_0 is an arbitrary fixed value of x.

From equation (12b), we obtain

$$\phi_0' = \frac{i\phi_0''}{2\phi_0'}$$

Integration of above equation yields

$$\phi_1 = \frac{i}{2} \log \phi_0' + C_1 \quad ----- (15)$$

Where C_1 is a constant of integration. This result is inconvenient if ϕ'_0 is negative. Therefore keeping in mind that the logarithm of a negative function differs only by an Imaginary constant from the logarithm

$$\phi_1 = \frac{i}{2} \log |\phi_0'| + C_2$$
 ------ (16)

Where C_2 is an arbitrary constant.

Similarly,

$$\phi_2 = \frac{m\left(\frac{\partial V}{\partial x}\right)}{\left[2m\left(E-V\right)^{3/2}\right]} - \int_{x_0}^x \frac{m^2\left(\frac{\partial V}{\partial x}\right)}{\left[2m\left(E-V\right)^{5/2}\right]}$$
(17)

From equation (16) we see that ϕ_1 is represented as a logarithm of $|\phi_0'|$. Therefore it is not, in general, small compared with ϕ_0 and ϕ_1 both must be retained. On the other hand from equation

(17) we see that ϕ_2 will be small whenever $\frac{\partial v}{\partial x}$ is small and (E-V) is not too close to zero. Further it can be seen easily that the smallness of the higher approximations ($\phi_3, \phi_4 \dots etc$) requires the smallness of all derivatives of V. Thus the W.K.B. approximation will be suitable in cases where V is a sufficiently smooth and slowly varying function of position.

$$\phi = \phi_0(x) + \frac{1}{2}i\hbar \log |\phi_0'|$$
 ------ (18)

Assuming constant C_2 is absorbed in $\phi_0(x)$.

Substituting value of $\phi(x)$ from (18) in equation (5) and rearranging the result, we finally get the approximate solution Ψ_{app} of equation (4) in the form

$$\Psi_{\rm app} = C \left\{ 2m|E - V(x)| \right\}^{-1/4} \exp\left[\pm \frac{i}{\hbar} \int_{x_0}^x \sqrt{2m[(E - V(x))]} dx \right] \dots (19)$$

Application in Quantum Mechanics:

In quantum mechanics it is useful in

- 1. Calculating the bond energies(whenever the particle cannot move to infinity)
- 2. Transmission property through potential barriers.

UNIT 4: SCATTERING THEORY & MATRICES IN QUANTUM MECHANICS

GREEN'S FUNCTION

$$G(r,r') = \frac{\exp(ik|r-r'|)}{|r-r'|}$$

Green's function is a solution of the scattering problem for a source of unit strength at point r'. To prove this it must be shown this the equation,

$$(\nabla^2 + k^2)G(r - r') = -4\pi\delta(r - r')$$

is satisfied and the solution has proper asymptotic form.

General formulation of the scattering theory:

The schroedinger equation for central potential V(r) is written as

The complete time-dependent solution of above equation can be written as

$$\Psi(r,t) = \Psi(r)e^{-i\frac{Et}{\hbar}}$$
$$= [e^{-tk.r} + \Psi_S(r)]e^{-i\frac{Et}{\hbar}}...(2)$$
Where,
$$\Psi_S(r) = f(\theta,\phi)\frac{e^{-ikr}}{r} + g(\theta,\phi)\frac{e^{-ikr}}{r}...(3)$$

The first term in bracket of equation (2) represents the incident; while the second term Ψ_S , the *Scattered wave*. The first term in Ψ_S represents outgoing scattered wave, while the second term represents the incoming scattered wave which does not exist in most of the physical problems. The stationary state solution of Schroedinger equation (1) is

Comparing equation (1) with $(H^0 + H')\Psi = E\Psi$, we note that the perturbation operator is V(r) which is very-very less than E; here H⁰ is the unperturbed Hamiltonian. The unperturbed Schoredinger equation is therefore written as

So, that the Schroedinger equation is now written as,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)\Psi_S = -V(r)\left[e^{-ik.r} + \Psi_S\right]$$
$$= -V(r)\Psi(r) \quad \dots\dots\dots(6)$$

This equation may be written as

Where $K^2 = \frac{2m}{\hbar^2} E$

Further substituting

$$\frac{2m}{\hbar^2}V(r)\Psi(r) = -4\pi\rho(r) \quad \dots \dots \dots (8)$$

Equation (7) takes the form

$$(\nabla^2 + K^2)\Psi_S = -4\pi\rho(r) \qquad \dots \dots \dots \dots \dots \dots (9)$$

The quantity $\rho(r)$ may be regarded as a source density for spherical waves. Equation (9) may be solved by using principle of superposition. Accordingly if Ψ_{S1} and Ψ_{S2} are solutions of equation (9) belonging to density functions $\rho 1(r)$ and $\rho 2(r)$ and satisfying

$$\Psi_{S1} = f \frac{e^{-ikr}}{r}, \Psi_{S2} = f \frac{e^{-ikr}}{r}$$
(10)

Then the function $\Psi_S = \Psi_{S1} + \Psi_{S2}$ is a solution of equation (9) belonging to $\rho(r) = \rho 1(r) + \rho 2(r)$ such that

$$\Psi_S = f \frac{e^{-ikr}}{r}$$

where,
$$f = f_1 + f_2$$
(11)

By means of the principle of superposition a solution of equation (9) can be found by adding solutions for simple point sources of unit strength. The identity

Represents the arbitrary density $\rho(r)$ as a sum of point sources $\delta(r - r')$ at the point r'.

Now in order to express Ψ_s as a function of $\rho(r)$ we make use of the following *theorem*.

$$(\nabla^2 + K^2)G(r - r') = -4\pi\delta(r - r')$$
(13)

Where,

$$G(r,r') = \frac{\exp(ik|r-r'|)}{|r-r'|}$$

is called *Green's function*.

If G(r,r') is asymptotic to a function of r of the form (11), then the solution of the scattering problem for the density $\rho(r)$ is given by

$$\Psi_S = \int G(r,r') \rho(r') dr' \qquad (14)$$

Green's function: It may be noted that green's fuction

$$G(r,r') = \frac{\exp(ik|r-r'|)}{|r-r'|}$$

This is a solution of the scattering problem for a source of unit strength at point r'. To prove this it must be shown this the equation (13) is satisfied and the solution has proper asymptotic form.

For simplicity we first change the origin of coordinates to point r', so that equation (13) takes the form

Being the radial distance in new coordinates.

We notice by direct differentiation that if $r \neq 0$

$$(\nabla^2 + k^2) \frac{e^{ikr}}{r} = 0$$
(18)

Therefore equation (16) is satisfied in every region which does not contain the source point. To prove that the singularly at r=0 is properly represented by G, it must be established that the function

$$\delta(r) = \frac{1}{4\pi} (\nabla^2 + k^2) G(r)$$
(19)

must satisfy the condition of a *delta function*. From equations (16) and (18) we note that if $\delta(r)=0$ if $r \neq 0$. Thus $\delta(r)$ satisfies the first requirement of a delta function, namely that it is zero everywhere except at r = 0. The another condition of a delta function is that

Where F(r) is any continuous function of r which has value F(0) at the origin and τ represents thus region of integration which is any finite volume containing the origin. Let us therefore choose for our range of integration a small sphere of radius \in . Consider the identity

$$\int_{\tau} \left[(\nabla^2 G + k^2 G)F - (\nabla^2 F - k^2 F)G \right] d\tau = \int_{S} \left[\frac{\partial G}{\partial r} F - \frac{\partial F}{\partial r} G \right] dS \quad \dots \dots (21)$$

Where S represents the surface of the sphere τ , then we may assume positive numbers M and N such that

$$|\nabla^2 F + k^2 F| < M$$
$$\left|\frac{\partial F}{\partial r}\right| < N(r \le \varepsilon) \quad \dots (22)$$

In other words the above functions are bounded in τ . Now it follows that

Therefore if we take the limit $\in \rightarrow 0$, we find

$$\int_{\tau} (\nabla^2 F + k^2 F) G d\tau \to 0$$
$$\int_{S} \frac{\partial F}{\partial r} G dS \to 0$$

In view of above relations equation (21) in the limit $\in \rightarrow 0$ yields

$$\lim_{\epsilon \to 0} \int_{\tau} (\nabla^2 G + k^2 G) F d\tau = \lim_{\epsilon \to 0} \int_{S} \frac{\partial G}{\partial r} F dS$$

Because of relation (18) the only contribution to the internal (20) must be the singularity of $\delta(r)at r = 0$ and by equation (25),

$$\frac{1}{4\pi} \int_{\tau} (\nabla^2 + k^2) GF(r) d\tau = F(0)$$
$$\int_{\tau} \delta(r) F(r) d\tau = F(0)$$

Hence $\delta(r)$ is a delta function. Returning to the original coordinate system by the substitution $r \rightarrow r + r'$, we obtain equation (13) instead of (16).



The asymptotic form of G(r, r') is easily found by referring to above figure.

If |r| is large compared to |r'|, then it is clear that

The error involved in this approximation can be made arbitrarily small by choosing |r| sufficiently large. Substituting the value of |r - r'| from equation (26) in (15), we get

$$G(r,r') = \frac{\exp(ik|r-r'|)}{|r-r'|}$$
$$= \frac{\exp(ik\left(r-\frac{r.r'}{rr'}\right))}{\left(r-\frac{r.r'}{rr'}\right)}$$
$$= \frac{\exp(ik\left(r-\frac{r.r'}{rr'}\right))}{r} \left[1+\frac{r.r'}{r^2}+\cdots\dots\right]$$

Thus as $r \rightarrow \propto$, we obtain

$$G(r,r') \approx \exp\left(-ik\frac{r'.r}{r}\right) \cdot \frac{e^{ikr}}{r}$$

Writing $k' = \frac{kr}{r}$, we obtain

$$G(r,r') \approx e^{-ik'.r'} \cdot \frac{e^{ikr}}{r}$$

The first term in this expression depends upon the orientation of k' relative to vector r', i.e. it is of the form $f(\theta, \phi)$. thus equation (27) represents the asymptotic form of green's function and represents an outgoing wave. Thus the green's function represents the solution of the scattering problem of unit intensity at point r'. Setting

$$\rho(r') = -\frac{1}{4\pi} \frac{2m}{\hbar^2} V(r') \Psi(r')$$

From equation (8) and the value of G(r, r') from equation (15), equation (14) gives

This is a part of the wave function produced by the scattering potential, Ψ_S in an integral involving the function $\frac{e^{ik(r-r')}}{|r-r'|}$ which represents just a spherical wave that spreads out from point r', with a wavelength $\lambda = \frac{2\pi}{k}$. The amplitude of the spherical wave is proportional to the product $V(r')\Psi(r')$ i.e. jointly to the strength of the interaction and amplitude of the wave function at r'. All these spherical waves are compounded at the point r which is then added to the incident wave to produce the total wave function Ψ of r [i.e. $\Psi(r)$].

 $\Psi(r) = e^{ik' \cdot r'} + \Psi_S$

...

If the potential energy function is confined to a limited region of space, then the asymptotic form of green's function form (27) can be substituted in equation (14)

$$\Psi_{S} = -\frac{1}{2\pi} \frac{m}{\hbar^{2}} \int G(r, r') V(r') \Psi(r') d\tau'$$

Then, we obtain,

Therefore scattering amplitude $f(\theta, \phi)$

This yields for the scattering cross section

$$\sigma(\theta,\phi) = |f(\theta-\phi)|^2 = \left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\int e^{-ik'\cdot r'} V(r')\Psi(r')d\tau'\right|^2....(32)$$

THE BORN APPROXIMATION:

The born approximation, named after physicist max born, was first developed for scattering theory in quantum mechanics. If the scattering takes place in a system from the scattering centres which are localized but are weak then the scattering doesn't takes place for a long distance. Therefore the scattered waves are weak in amplitude. Born approximation can be used to find the scattering amplitude. We restrict our attention to the potential energy of interaction between the coloiding particles to carry the first order calculation. Born approximation is therefore suitable for which the kinetic energy of the particle is large when compared to the interaction energy.

Perturbation Approximation:

To solve the wave equation for a relative motion

$$-\hbar^2/2\mu \nabla^2 \Psi + V(r)\Psi = E\Psi$$

where, $\mu = m1m2/m1 + m2$.

Asymptotic form of solution is given by,

$$\Psi(\mathbf{r},\theta,\emptyset) \to e^{i\mathbf{k}\mathbf{z}} + \mathbf{f}(\theta,\emptyset) e^{i\mathbf{k}\mathbf{r}}/\mathbf{r},$$

 e^{ikz} represents particles moving in Z- direction and second term represents the particle are moving radially outward.

Applying perturbation approach

$$\Psi(\mathbf{r}) = e^{\mathbf{i}\mathbf{k}\mathbf{z}} + \mathbf{v}(\mathbf{r})$$

v(r) is regarded as small addition to the unperturbed plane wave e^{ikz} . Born approximation becomes tedious for higher orders.

$$\nabla^2 \Psi + \mathbf{K}^2 \Psi = \mathbf{U} (\mathbf{r}) \Psi$$

Where,

$$K^2=2\mu E/\hbar^2$$
 and U(r)= $2\mu V(r)/\hbar^2$

We have,

$$\nabla^{2}[e^{ikz}+v(r)]+K^{2}[e^{ikz}+v(r)] = U(r) [e^{ikz}+v(r)]$$
$$\nabla^{2}[e^{ikz}+v(r)]+K^{2}[e^{ikz}+v(r)] = U(r) e^{ikz} +U(r) v(r)$$

According to our assumption that v(r) is small in comparison with e^{ikz} or roughly that U(r) is small as compared with K^2 lead us to neglect the term U(r)v(r) in above equation. It becomes,

$$\nabla^2 e^{ikz} + \nabla^2 v(r) + K^2 e^{ikz} + K^2 v(r) = U(r) e^{ikz}$$
$$\nabla^2 e^{ikz} = -K^2 e^{ikz}$$
$$\therefore \nabla 2 v(r) + K^2 v(r) = U(r) e^{ikz}$$

A sufficient criterion for the validity of our solution is

$$|v(r)| \ll |e^{ikz}| = 1$$
 for all r

This condition is necessary for born approximation to provide useful results.

Applications:

1. In neutron scattering, the first – order born approximatin is almost always adequate, except for neutron optical phenomena like internal total reflection in a neutron guide.

- 2. It is also used to calculate conductivity in bilayer graphene.
- 3. To approximate the propagation of long-wavelength waves in elastic media.

OPERATORS AS MATRICES

According to Heisenberg a wave function can be represented as a vector in Hilbert space. When an operator \hat{A} operates on some function f(q), it is transformed into another function g(q) i.e

$$\hat{A} f(q) = g(q)$$
(1)

Now we pass from one representation to the other viz. q representation to p representation (say). For the purpose let us expand the eigen function f(g) and g(q) in terms of the eigen function $\psi_m(q)$ of the operator \hat{A} as follows

Substituting (2) in (1), we get

$$\hat{A} \Sigma_{m} a_{m} \psi_{m} (q) = \Sigma_{n} b_{n} \psi_{n} (q) \qquad \dots \dots \dots \dots (3)$$

Multiplying above equation by ψ_1^* and integrating over entire space, we get

 $\Sigma_{m} a_{m} \int \psi_{l}^{*} \hat{A} \psi_{m} d\upsilon = \Sigma_{n} b_{n} \int \psi_{l}^{*} \psi_{n} d\upsilon$ Therefore, $b_{l} = \Sigma_{m} a_{m} \int \psi_{l}^{*} \hat{A} \psi_{m} d\upsilon = \Sigma_{n} a_{m} A_{lm} \qquad \dots \dots (4a)$ Where $A_{lm} = \int \psi_{l}^{*} \hat{A} \psi_{m} d\upsilon \qquad \dots \dots (4b)$

Equation (4a) determines the transformation of the function f(q) into g(q) in prepresentation under the action of operator Å. The operator Å in the representation is given by equ. (4b) in the form of a matrix. Thus the definition of matrix (A) is equivalent to the operator Å itself. The matrix element A_{ij} is generally called the matrix element corresponding to transition from ith state with the assumption that the initial state of the system is ith state i.e. $f(q) = \psi_i(q)$.

Using (2) and (4a) and keeping in mind that in the given case $a_m = \delta_{mi}$, $b_n = A_{ni}$, we obtain

$$g(q) = \hat{A} f(q) = \sum_{n} b_{n} \psi_{n}(q) = \sum_{n} A_{ni} \psi_{n}(q) \qquad \dots \dots \dots \dots (5)$$

So the square of the matrix element A_{ni} determines the probability of finding the system in the ith state.

If the matrix corresponding to operator A is known, we can determine the expectation (or mean value) of observable A in certain state f i.e.

$$\langle A \rangle = \int f^* \hat{A} f dv$$
(6)

Substituting expansion (2

) in place of f, we obtain

$$\langle A \rangle = \Sigma_m \Sigma_n a_m^* a_n \int \psi_{m^*} \hat{A} \psi_n d\tau = \Sigma_m \Sigma_n a_m^* a_n A_{mn} \qquad \dots \dots (7)$$

If the operator À is Hermitian, then it may be represented as a diagonal matrix.

As Hermitian operator has real eigen values i.e.

$$\hat{A} \psi_m = \alpha_m \psi_m \qquad \dots \dots \dots (8)$$

Where α_m is real number.

From equation (4b)

$$A_{lm} = \int \psi_{l}^{*} \hat{A} \psi_{m} d\sigma = \int \psi_{l}^{*} \alpha_{m} \psi_{m} d\sigma \qquad (using (8))$$
$$= \alpha_{m} \int \psi_{l}^{*} \psi_{m} d\sigma = \alpha_{m} \delta_{lm} \qquad \dots \dots (9)$$

Obviously the matrix elements with m = l are non – zero; while the elements with $m \neq l$ are zero i.e. matrix is diagonal.

Thus we see that each Hermitian operator has a representation as a diagonal matrix, provided that the wave function is expanded in terms of its eigen functions.

Summarising we can say the definition of operator \hat{A} is equivalent to the matrix , [A]. The matrix representation of operator enables us to determine the eigen values and eigen function of the corresponding operator. If the operator \hat{A} is known, then the matrix elements A_{lm} can be determined. If the operator A is Hermitian then it can be represented as a diagonal matrix as

EIGEN – VALUE PROBLEM

Let us consider eigen – value problem in n- dimensional vector space R_n . As Hamiltoian H is Hermitian operator, it can be represented as a diagonal matrix, the diagonal terms being its eigen values. Let E_1 , E_2 , E_3 ,, E_n be the distinct eigen values corresponding to a complete orthogonal set of eigen functions ψ_1 , ψ_2 , ψ_3 ,, ψ_n so that eigen value equation is

$$H^{a} \psi_{n} = E_{n} \psi_{n}$$

The elements of matrix corresponding to operator H are expressed as

$$H^{d}_{mn} = (\psi_{m}, H^{d}\psi_{n}) = E_{n}(\psi_{m}, \psi_{n}) = E_{n}\delta_{mn} \qquad \dots \dots (1)$$

In some arbitrary representation ψ_n matrix H_{mn} is given by

$$H_{mn} = (\Phi_m, H\Phi_n) \qquad \dots \dots (2)$$

Let us now find a unitary transformation which transforms this arbitrary basis Φ_1 , Φ_2 , Φ_3 ,, Φ_n into the set of eigen function ψ_1 , ψ_2 , ψ_3 ,, ψ_n (eigen function of H^d), i.e.

$$\Psi_n = U\Phi_n (n = 1, 2, 3, ..., n)$$
(3)

Then, H_{mn} is transformed into the diagonal matrix A^{d}_{mn} , i.e.

$$U^{\dagger} H U = H^{d} \qquad \dots \dots (4a)$$

$$HU = UH^d$$
 (4b)

In terms of matrix elements above equation may be expressed as

$$\begin{split} \Sigma^{n}{}_{i=1} & H_{mi} Uin = \Sigma^{n}{}_{i=1} & U_{mi} H^{d}{}_{in} \\ & = & \Sigma^{n}{}_{i=1} & U_{mi} E_{n} \delta_{in} & [using (1)] \\ & = & U_{mn} E_{n} = & \Sigma^{n}{}_{i=1} & \delta_{mi} U_{in} E_{n} (m, n, =1, 2, 3, ..., n) \end{split}$$

So that $\Sigma^{n}_{i=1}$

Or

$$\Sigma^{n}_{i=1}$$
 (H_{mi} - $\delta_{mi} E_{n}$) U_{in} = 0(5)

It is obvious that equ. (5) is equivalent to the problem of diagonalisation of matrix. The secular equation being $det (H_{mi} - \delta_{mi} E_n) = 0$ (6)

Which is equation of n-degree in E_n , having n distinct solutions E_1 , E_2 ,, E_n which are required eigen values of H. Equation (5) then determines the transformation matrix U. It is obvious that equ. (4b) i.e. $HU = UH^d$ is matrix form of eigen value equation $H\psi_n = E_n \ \psi_n$ where U is a $n \times n$ matrix having n columns ψ_i and H^d is a $n \times n$ diagonal matrix with elements $H^d{}_{mn} = E_m \ \delta_{mn}$. Thus the problem of solving Schrodinger equation is reduced to diagonalise the Hamiltonian by suitable unitary transformation if Hamiltonian in some arbitrary representation Φ_n is provided. Then the basic set obtained (to which ψ_n is transformed) represents the solution of the Schroedinger equation $H\psi_n = E_n\psi_n$. As already pointed out in the diagonalised Hamiltonian matrix, the non-vanishing diagonal elements give eigen values.

UNIT 5: THEORY OF RADIATION (SEMI CLASSICAL TREATMENT) Einstein co-efficients, spontaneous and induced emission:

Spontaneous Emission:

An atom cannot be stay in the excited state for a longer time. In a time of about 10^{-8} s the atom reverts to the lower energy state by releasing a photon of energy hv, where hv = (E₂-E₁). The emission of photon occurs on its own and without any external impetus given to the excited atom. Emission of a photon by an atom without any external impetus is called spontaneous emission. We may be write the process as,

$$A^* \rightarrow A + hv$$

The number of spontaneous transitions depends only on the number of atoms N_2 at the excited state E_2 . Therefore, the rate of spontaneous transitions is given by

$$R_{sp} = A_{mn} N_b$$

Where, A_{mn} is the proportionality constant and is called the Einstein co-efficients for spontaneous emission. A_{mn} represents the probability of a spontaneous transition from level $2\rightarrow 1$. It is to be noted that the process of spontaneous emission is independent of the incident light energy.

It follows from quantum mechanical considerations that spontaneous transition takes place from a given state to states lying lower in energy. Thus, spontaneous emission is not possible from level E_1 to E_2 . Therefore, the probability of spontaneous transition from E_1 to E_2 is zero.

$$A_{mn} = 0$$

Einstein theory of Stimulated Emission:

An atom in the excited state need not "wait" for spontaneous emission of photon. Well before the atom can make a spontaneous transition it may interact with a photon with energy $hv = (E_2-E_1)$, and make a downward transition. The photon is said to stimulate or induce the excited atom to emit a photon of energy $hv = (E_2-E_1)$. The passing photon does not disappear and in addition to it there is a second photon which is emitted by the excited atom. The phenomenon of forced photon emission in an excited atom due to the action of external agency is called induced emission or stimulated emission. This process may be expressed as

$$A^* + jhv \rightarrow A + khv$$

The rate of stimulated emission of photons is given by

$$\mathbf{R}_{\mathrm{st}} = \mathrm{Bop} \ \varrho \ (\upsilon) \ \mathbf{N}_{\mathrm{b}}$$

Where Bop is the Einstein co-efficient for stimulated emission and represents the probability for induced transition from level $2\rightarrow 1$. In stimulated emission each incident photon encounters a previously excited atom, and the optical field of the photon interacts with the electron. The result of the interaction is a kind of resonance effect, which induces each atom to emit a second photon with the same frequency, direction, phase and polarization as the incident photon.

Einstein co-efficients:

Under thermal equilibrium, the mean population N_a and N_b in the lower and upper energy levels respectively must remain constant. This condition requires that the number of transitions from E_2 to E_1 must be equal to the number of transitions from E_1 to E_2 .

The number of atom emitting photons emitting photons per second per unit volume

$$= A_{mn} N_b + B_{op} \varrho (v) N_b$$

As the number of transitions from E_1 to E_2 must be equal to the number of transitions from E_2 to E_1 .

$$\begin{split} B_{cd} \ \varrho \ (\upsilon) \ N_a &= A_{mn} \ N_b + B_{op} \ \varrho \ (\upsilon) \ N_b \\ \\ \varrho \ (\upsilon) \ [B_{cd} \ N_a - B_{op} \ N_b] &= A_{mn} \ N_b \\ \\ \varrho \ (\upsilon) &= \frac{Amn \ Nb}{[Bcd \ Na - Bop \ Nb]} \end{split}$$

By dividing both the numerator and denominator on the right hand side of the above equation with $B_{cd} N_b$, we obtain

$$\varrho(\upsilon) = \frac{\operatorname{Amn}/\operatorname{Bcd}}{\left(\frac{\operatorname{Na}}{Nb} - \frac{\operatorname{Bop}}{\operatorname{Bcd}}\right)}$$
$$\frac{\operatorname{Na}}{Nb} = e^{-(\operatorname{E}_2 - \operatorname{E}_1)/\operatorname{k} \mathrm{T}}$$
$$\frac{\operatorname{Na}}{Nb} = e^{-(\operatorname{hu})/\operatorname{k} \mathrm{T}}$$

$$\varrho\left(\upsilon\right) = \frac{Amn}{Bcd} \frac{1}{e^{-\frac{h\upsilon}{kT}} - \frac{Bop}{Bcd}}$$

To maintain thermal equilibrium, the system, must release energy in the form of electromagnetic relation. It is required that the radiation be identical with black body radiation and be consistent with Planck's radiation law for any value of T. According to Planck's law

$$\varrho\left(\upsilon\right) = \frac{8 \, \Pi h \upsilon^3 \mu^3}{c^3} \, \frac{1}{e^{-\frac{h\upsilon}{kT}} - 1}$$

where, μ is the refractive index of the medium and c is the velocity of light in free space. Energy density $\rho(v)$ will be consistent Planck's law

$$\frac{Amn}{Bcd} = \frac{8 \Pi h v^3 \mu^3}{c^3}$$

and $\frac{Bop}{Bcd} = 1 \text{ or } B_{op} = B_{cd}$

The above equations are known as the Einstein relations. The co-efficients B_{op} , B_{cd} and A_{21} are known as Einstein co-efficients. It follows that the co-efficientes are related through

$$\mathbf{B}_{\rm cd} = \mathbf{B}_{\rm op} = \frac{c^3}{8 \, \Pi h \upsilon^3 \mu^3} \, \mathbf{A}_{\rm mm}$$

The above relation shows that the co-efficients for both absorption and stimulated emission are numerically equal. The equality implies that when an atom with two energy levels is placed in the radiation field, the probability for an upward transition is equal to the probability for a downward transition. The ratio of co-efficients of spontaneous versus stimulated emission is proportional to the third power of frequency of the radiation.

Radiation field as an assembly oscillators:

The subject of interaction of electromagnetic wave on an atom is of great importance. The theory will be semi-classical due to the fact that we shall treat the motion of the atoms to be quantized and the electromagnetic field to be classical represented by continuous potentials A and Ψ .

From the knowledge of classical electrodynamics it is known that for transverse electromagnetic waves the vector potential A satisfies the questions.

$$\nabla^2 A - \frac{1}{C^2} \frac{\partial A}{\partial t} = 0 - \dots - (1)$$

$$A(\mathbf{r},\mathbf{t}) = Ao e^{i(\mathbf{k}.\mathbf{r}\cdot\omega\mathbf{t})} + Ao^* e^{-i(\mathbf{k}.\mathbf{r}\cdot\omega\mathbf{t})} - \dots - (2a)$$
$$= 2|Ao|COS (\mathbf{k}.\mathbf{r}\cdot\omega\mathbf{t}+\alpha); Ao = |Ao|e^{i\alpha} - \dots - (2b)$$

Equation(2a) is satisfied if ω =kc,k being magnitude of propagation vector k and (2b) is satisfied a constant complex vector Ao is perpendicular to k.

The electric field associated with vector potential A (equation $(1)^{\phi}=0$) is

$$E = -1/C \frac{\partial A}{\partial t} = -2\omega/C |Ao| \sin (k.r \cdot \omega t + \alpha) - \cdots + (4)$$

The intensity of radiation i.e, flow of energy per unit area per second is given by well known poynting's vector

$$I=C/4\Pi (E \times B) \qquad (C.G.S.System) -----(5)$$

In free space |E|=|B| and E is normal to B. Thus in free space $(E \times B)$ is a vector of magnitude $|E^2|$ and direction k. i.e.,

$$I=C/4\Pi.4\omega^2/c^2|Ao|^2Sin^2(k.r-\omega t+\alpha)$$

Mean pointing vector

 $I=\omega^2/2\Pi C |Ao|^2$

[Since time averaged magnitude of $\sin^2(k.r-\omega t+\alpha)$ is 1/2]

| m | n |
|--------------|-----------------------|
| Absorption ↑ | Emission \downarrow |
| Em- En=ħω | Em- En=-ħω |
| n | m |

From the preceding section, the first order correction to Hamiltonian for a charged particle interaction with electromagnetic field is given by,

H' int=
$$-\frac{e}{mc}(A.P) = \frac{ie\hbar}{mc} A \nabla$$

$$=ie\hbar/mc \ [Ao \ e^{i(k.r-\omega t)} + Ao^* e^{-i(k.r-\omega t)}].\nabla -----(6)$$

Assuming nth state as initial state, equation (12) of section 8-1, for a final state m becomes

$$i\hbar am^{(1)}(t) = (H' \text{ int }) \text{ mn } e^{i\omega mnt} \text{ where } \omega_{mn} = [\frac{Em - En}{\hbar}]$$
$$= H'_{mn} e^{i(\omega mn - \omega)t} + H''_{mn} e^{i(\omega mn + \omega)t} - \dots - (7)$$

Where,

$$H'_{mn} = ie\hbar/mc \int \varphi_m^{o^*} e^{i(k.r)} (Ao.\nabla) \varphi_n^{o} d\tau$$
$$H'_{mn} = ie\hbar/mc \int \varphi_m^{o^*} e^{-i(k.r)} (Ao^*.\nabla) \varphi_n^{o} d\tau \qquad -----(8)$$

If harmonic perturbation of frequency ω is switched on at t=0, then equation (+) on integration with respect to t gives,

The consider Quantum approximation methods and semiclassical theory of radiation,

$$a_{m}^{(1)}(t) = \frac{1}{i\hbar} \left[\int_{0}^{t} H'_{mn} e^{i(\omega mn-\omega)t} dt + \int_{0}^{t} H''_{mn} e^{i(\omega mn+\omega)t} dt \right]$$
$$= H'_{mn} 1 - e^{i(\omega mn-\omega)t} / \hbar(\omega_{mn-\omega}) + H''_{mn} 1 - e^{i(\omega mn+\omega)t} / \hbar(\omega_{mn+\omega}) - \dots (9a)$$

Using $\omega_{mn} = \frac{Em - En}{\hbar}$, we get

$$a_{m}^{(1)}(t) = H'_{mn} [1 - e^{i(Em - En - \hbar\omega)t/\hbar} / E_{m} - E_{n} - \hbar\omega] + H''_{mn} [1 - e^{i(Em - En + \hbar\omega)t/\hbar} / E_{m} - E_{n} + \hbar\omega] - \dots (9b)$$

Out of the two terms in (9) only one term at a time is to be considered. If $E_m-E_n-\hbar\omega=0$ or $E_m-E_n-\hbar\omega$ the first term will be very large compared with the second; but if

$$E_m - E_n - \hbar\omega = 0$$
 (or) $E_m - E_n = -\hbar\omega$

The second term will be large compared to first, while if neither of these condition is satisfied, the probability of transition is vanishingly small this means that the transitions are probable only if,

$$E_{\rm m}-E_{\rm n}=\pm\hbar\omega$$
 -----(10)

For Absorption:

$$|a_{m}^{(1)}(t)|^{2} = |H'_{mn}|^{2} \frac{4Sin^{2}\frac{1}{2}(\omega mn - \omega)t}{\hbar^{2}(\omega mn - \omega)^{2}} \qquad -----(12)$$

For Emission:

$$\frac{1}{t} |a_{m}^{(1)}(t)|^{2} = \frac{4\pi^{2} e^{2}}{m'^{2} e \omega^{2} m n'} I(\omega_{mn}) |\int \varphi_{m'} e^{-ik \cdot r} \operatorname{grad}_{A} \varphi_{n}^{o} d\tau|^{2} - --(16)$$

DENSITY OPERATOR AND DENSITY MATRIX

- A pure quantum state of a system is represented by a single Eigen vector ψ_{α} or $|\alpha\rangle$; but if the knowledge of the system is described by non-negative probabilities p_{α} , p_{β} ,..., for being in states $|\alpha\rangle$, $|\beta\rangle$...; a statistical approach is necessary if the theory of pure states is inadequate. This can be developed in close analogy with the classical situation. A pure classical state is one that is represented by a single moving point in phase space: that have definite values of coordinates $q_1, q_2,...q_f$ and canonical momenta $p_1, p_2,..., p_f$ at each instant of time.
- ♦ On the other hand a statistical state can be described by a non-negative density function

$$f_{(q_{1,...}, q_{f}, p_{1,...}, p_{f}, t)}$$

such that the probability that a system is found in the interval dq1...dqf dp1...dpf at time t is

$$\rho(dq_1,...dq_f dp_1...dp_f)$$

- The quantum analogy of the classical density function is known as the **density operator** and its representation in the matrix form is known as the **density matrix**.
- Consider an ensemble consisting of N system in the normalised states ψ_α : α =1,3,2... N.
 The expectation value of an observable f in this representation is given by

$$\langle f \rangle = \int \psi_{\alpha}^{*} \dot{f} \psi_{\alpha} dq \dots (1)$$

- ✤ f being operator associated with observable f.
- If ϕ_n 's represent the orthonormal eigen functions, then a pure state ψ_{α} may be represented by the coefficients of expansion of ψ_{α} into Eigen vectors ϕ_n , i.e.,

$$\Psi_{\alpha} = \sum_{n} C_{n} \phi_{n}$$
;

$$\psi_{\alpha}^{*} = \sum_{n} C_{m}^{*} \phi_{m}^{*}; ...(2)$$

 \clubsuit so that equation (1) takes the form

$$< f > = \sum_{m} \sum_{n} C_{m}^{*} C_{n}^{*} \int \phi_{m}^{*} \dot{f} \phi_{n} dq$$
$$= \sum_{m} \sum_{n} C_{m}^{*} C_{n} < m \mid f \mid n > \dots (3)$$

If the state is not specified completely: it may be represented by incoherent specified superposition of a number of pure states ψ with statistical weight p, to each pure state there corresponds a mean value <f>; and the mean value of f for the incoherent superposition is given by the grand (or ensemble) average given by

$$< f > = \sum_{\alpha} p^{(\alpha)} < f >_{\alpha} = \sum_{\alpha} p^{(\alpha)} \sum \sum_{\alpha} C_{m}^{*(\alpha)} C_{n}^{(\alpha)} < m \mid f \mid n >$$
$$= \sum_{m} \sum_{n} < m \mid f \mid n > \sum_{\alpha} p^{(\alpha)} C_{m}^{(\alpha)} C_{n}^{(\alpha)} \dots (4)$$
$$0 < p^{(\alpha)} < 1 \text{ and } \sum p^{(\alpha)} = 1 \dots (5)$$

Where, $p^{(\alpha)}$ represent the probability of finding the system in the state $|\alpha\rangle$: when a measurement is made at random on the system.

✤ For brevity let us write

$$\sum p^{(\alpha)} C_m^{*(\alpha)} = \rho_{nm}; \dots (6)$$

then equation (5) takes the form

$$< f > = \sum_{n} \sum_{m} \rho_{mn} < m \mid f \mid n > = \sum_{m} \sum_{n} \rho_{mn} f_{mn} \dots (7)$$

 \diamond The ensemble average of f is also represented by the equation

$$f = \int \int P_{(q, p)} f_{(q, p)} dq dp \dots (8)$$

Where, P is termed as the normalised density of distribution.

- A comparison of equation (7) and (8) shows that the integration over q and p has been replaced by a double sum over the quantum states.
- Thus the matrix ρ_{mn} plays a role analogous to that of the probability density $P_{(q, p)}$.
- Therefore ρ is termed as the density matrix, whose matrix element can be defined by equation (6) as

$$\rho_{mn} = \sum p^{(\alpha)} C_m^{*(\alpha)} C_n^{(\alpha)}$$

✤ So that equation (7) gives

$$< f \ge \sum_{m} \sum_{n} \rho_{nm} f_{mn} = \sum_{n} (\rho f)_{nm}$$
$$= Trace (\rho f) \dots (9)$$

Where, Trace stands for the sum of the diagonal elements of the matrix (ρ f). It is a convenient to regard the density matrix as defined by equation (9) rather than by equation (6).

Limitation on density matrix:

The condition that the expectation value of f is real for every Hermitian operator f, requires ρ must be also be Hermitian.

$$\rho_{\rm mn} = \rho^{\dagger}_{\rm (mn)} \ldots (10)$$

> The condition that the unit operator I has the expectation value I, require that

Trace (
$$\rho f$$
) = Trace (ρl) = Trace (ρ) = $\sum_{n} \rho_{n} = 1 \dots (11)$

The condition that every operator with negative Eigen values has a non-negative mean value requires that ρ must be definitely positive. This means

$$\rho_{nm} \ge 0 \dots (12)$$

The hermitian matrix ρ by means of unitary transformations mat be reduced to diagonal form

$$\rho_j \delta_{jj} = \sum_n \sum_m U_{jn} \rho_{nm} U_{mj}^{-1}$$

The conditions given by (11) and (12) require that

$$\sum_{j} \rho_{j}^{2} \rho_{j} (\sum_{j} \rho_{j})^{2} = [\text{Trace } (\rho)^{2} = 1]$$

Thus we have in general, Trace $(\rho)^2 = \sum_n \sum_m |\rho_{nm}| \le 1$. In this limit the value of every single element of the density matrix.