M.Sc. PHYSICS
SEMESTER - III
CORE XI - QUANTUM MECHANICS – II

UNIT I : Systems of identical particles Indistinguishability of identical particles – Symmetric and anti Symmetric wave function – Exchange operator – Distinguishability of identical particles – Bosons and Fermions – Pauli's Exclusion principles – Collision of identical particles – Ensemble of identical particle systems– Density operator – Density matrix – Properties – Symmetric and Anti symmetric wave function of hydrogen molecule. .

UNIT II : Scattering Theory Differential and Total cross-section – Scattering amplitude – Green's function: formal expression for scattering amplitude – Born approximation and its validity – scattering by coulomb and Screened coulomb potentials – Square-well potential – Exponential – Gaussian potential – Partial wave analysis – Phase Shifts – Scattering amplitude in terms of phase shift– Low energy scattering: Scattering length and effective rangescattering by a perfectly rigid sphere.

UNIT III : Emission and absorption of radiation Semi – Classical theory of radiation: Einstein coefficients – atom field interaction –Transition probabilities for stimulated emission and absorption and spontaneous emission of radiation – Electric dipole transition – Selection rules and polarizability – Quantum theory of radiation: Radiation field Hamiltonian – Radiation field as an assembly of oscillators – emission and absorption rates.

UNIT IV : Atomic and molecular Structure Approximations in atomic structure – Central field approximation – Thomas Fermi Statistical model – Hartree - Fock Equation – The method of self consistent field – Residual electrostatic and spin orbit interaction – Alkali atoms – Doublet separation – Coupling schemes – Hydrogen molecule – Covalent bond.

UNIT V : Relativistic Wave equation The Klein – Gordon Equation – Charge and current densities in four vector – KG equation in electromagnetic field – The Dirac relativistic equation: The Dirac matrices – Free particle solutions – Meaning of negative energy states– Electromagnetic potential: magnetic moment of the electron – Existence of electron spin - Spin orbit energy.

BOOKS FOR STUDY AND REFERENCE:

1. Quantum Mechanics, Satyaprakash, Kedar Nath Ram Nath.
2. Quantum Mechanics, Ajay Ghatak and S.Loganathan, Macmillan India Ltd.
3. Quantum Mechanics, P.M. Mathews and K. Venkatesan, Tata McGraw Hill.
4. Quantum Mechanics, Leonard I. Schiff, McGraw Hill.
5. Quantum Chemistry, R.K. Prasad, New Age International Pvt. Ltd.
6. Quantum Mechanics, Gupta, Kumar, Sharma, Jai Prakash Nath and Co.
7. Quantum Mechanics, Third Edition, E. Merzbacher, John Wiley Interscience Publications.
8. Quantum mechanics, Franz Schwabl, Narosa Publications.
9. Molecular Quantum mechanics, Third Edition, P.W.Atkins and R.S.Friedman, Oxford University

UNIT I : Systems of identical particles

Indistinguishability of identical particles – Symmetric and anti Symmetric wavefunction – Exchange operator – Distinguishability of identical particles – Bosons and Fermions – Pauli's Exclusion principles – Collision of identical particles – Ensemble of identical particle systems– Density operator – Density matrix – Properties – Symmetric and Anti symmetric wave function of hydrogen molecule. .

Topics

1. Indistinguishability of identical particles
2. Symmetric and anti Symmetric wavefunction
3. Particle Exchange Operator
4. Distinguishability of identical particles
5. Bosons and Fermions
6. The Pauli exclusion principle
7. Collision of identical particles
8. Ensemble of identical particle systems
9. Density operator and Density matrix – Properties
10. Symmetric and antisymmetric wave functions of a hydrogen molecule

UNIT – I

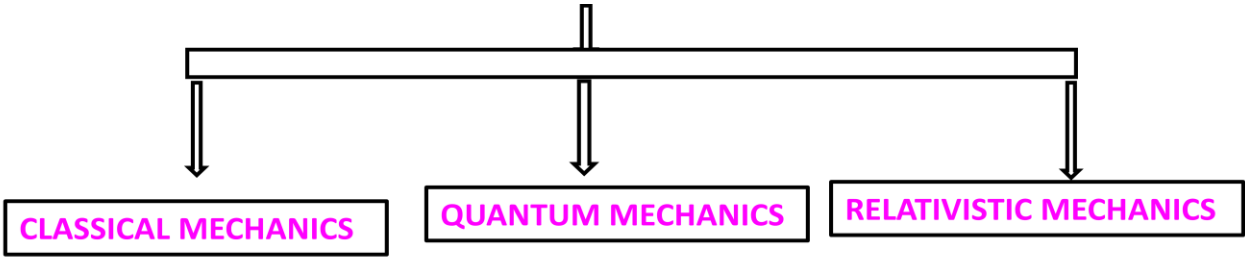
1.1 INDISTINGUISHABILITY OF IDENTICAL PARTICLES

MECHANICS is the science that deals with

- study of motion of a system
- cause of motion of a system.

- It describes the average properties of the molecules, atoms, or elementary particles in random motion in a system of many such particles
- It relates these properties to the thermodynamic and other macroscopic properties of the system.

CLASSIFICATION OF MECHANICS



Identical Particles

i. **Identical Particles** means the particle which cannot be distinguished by means of any inherent (intrinsic) property.
ii. There are many systems in nature that are made of several particles of the same species.
iii. All these particles have the same mass, charge, and spin.
iv. For instance the electrons in an atom are identical particles.
v. An electron is not identical to a proton or to a positron; etc.
vi. If a system consists of two or more identical particles there should be no change in its properties. (or) no change in its evolution if the roles of any two particles are exchanged.

There are two general categories of particles.

1. Classical particles which are identical and distinguishable
2. Quantum particles which are identical and indistinguishable.

Classical mechanics

i. **In Classical mechanics** the existence and the physical properties of the identical particles can be sharply defined and followed during the course of an experiment.
ii. we can always follow the trajectory of each individual particle, i.e. their time evolution in space.
iii. The trajectories identify each particle in classical mechanics, making identical particles distinguishable.
iv. Hence the molecules (classical particles) are distinguishable in classical mechanics

Quantum mechanics

i. **In Quantum mechanics,** a particle can be described by a wave packet of finite size and spread over the volume.
ii. The existence and physical properties of the identical particles cannot be defined and track during the course of experiment.
iii. According to quantum theory, the particles do not possess definite positions during the periods between measurements.
iv. Instead, they are governed by wave functions that give the probability of finding a particle at each position.
v. As time passes, the wavefunctions tend to spread out and overlap.
vi. Once this happens, it becomes impossible to determine, in a subsequent measurement, which of the particle positions correspond to those measured earlier.
vii. In quantum mechanics the concept of trajectory does not exist and identical particles are indistinguishable
viii. Hence the indentical particles cannot be distinguished by quantum mechanics cannot be distinguished. The particles are then said to be indistinguishable.

Physical Meaning of Identity in Quantum Mechanics

- Identical particles are those particles in a system for which the system remains unaltered by interchanging the particles.
- As each particle is described by a wave packet, these particles can be distinguished from one another, only if their wavepackets do not overlap.
- According to spin considerations, the particles can be distinguished from one another if they have different spin components.
- The component of spin along some particular axis remain unchanged during elastic collision.

REVIEW - Distinguishing between particles

Two particles having the same physical attributes are equivalent.

They behave the same way if subjected to the same treatment

CM: Equivalent particles are distinguishable since one can keep track of each particle all the time.

QM: Equivalent particles are indistinguishable since one cannot keep track of each particle all the time due to the uncertainty principle.

1.2 SYMMETRIC AND ANTI SYMMETRIC WAVE FUNCTIONS:

The Schroedinger eqn for n identical particles is written as

$$H(1,2,\dots n)\Psi(1,2,\dots n,t) = i\hbar\frac{\partial}{\partial t}\,\Psi(1,2,\dots..n,t) - - - -1$$

where each of the numbers represent the position and spin of a particle (say i)

In equation 1 the Hamiltonian H is symmetrical with respect to identity of particles. So they can be substituted for each other without changing (H) or any other observable.

There are two kinds of solutions of wave function Ψ of eqn 1.

1. Symmetric wave equation (Ψ_S)
2. Anti Symmetric wave equation (Ψ_A)

Symmetric wave equation ($\boldsymbol{\Psi_S}$)

A wave function is symmetric if the interchange of any pair of particles leave the wave function remains unchanged.

Anti Symmetric wave equation ($\boldsymbol{\Psi_A}$)

A wave function is symmetric if the interchange of any pair of particles among its arguments changes the sign of the wave function.

Note:

1. The symmetry character of a wave function does not change with time.
2. If $\boldsymbol{\Psi_A}$ is antisymmetric wave function at any time t, then H $\boldsymbol{\Psi_A}$ is **antisymmetric.**
3. **So** $\boldsymbol{\frac{\partial \Psi_A}{\partial t}}$ also anti symmetric.

1.2.1 CONSTRUCTION OF SYMMETRIC AND ANTI SYMMETRIC WAVE FUNCTION FROM EXCHANGE DEGENERACY

In case, where the Hamiltonian does not depend upon time, the solution of stationary state can be written as,

$$\Psi(1,2,\dots n) = \phi(1,2,\dots\dots n) - - - -2$$

So eqn 1 becomes

$$H(1,2,\dots n)\phi(1,2,\dots\dots n) = E\,\phi(1,2,\dots\dots n) - - - -3$$

There are n! solutions for this equation 3 by means of permutations of its arguments belonging to same eigen value E.

Hence this system is degenerate. This type of degeneracy is called Exchange Degeneracy.

Consider a two particle wave function, the time independent schroedinger's eqn is

$$H(1,2)\phi(1,2) = E\,\phi(1,2) - - - -4$$

There are 2! (=2) solutions for this eqn 4.

$$\boldsymbol{\Psi(1,2)\ and\ \Psi(2,1)}$$

These solutions correspond to single energy state E.

The symmetric wave function is written as

$$\boldsymbol{\Psi_S = \Psi(1,2) + \Psi(2,1)}$$

The anti symmetric wave function is written as

$$\boldsymbol{\Psi_A = \Psi(1,2) - \Psi(2,1)}$$

Similarly for a 3 particle system there are 3! (=6) solutions

They are $\boldsymbol{\Psi(1,2,3), \Psi(2,3,1), \Psi(3,2,1), \Psi(1,3,2), \Psi(2,1,3), \Psi(3,1,2)}$

The wave functions arising from even no of interchanges of the pair of particles are

$$\Psi(1,2,3), \Psi(2,3,1), \Psi(3,2,1)$$

The wave functions arising from odd no of interchanges of the pair of particles are

$$\Psi(1,3,2), \Psi(2,1,3), \Psi(3,1,2)$$

So the symmetric wave function can be written as

$$\boldsymbol{\Psi_S = \Psi(1,2,3) + \Psi(2,3,1) + \Psi(3,2,1) + \Psi(1,3,2) + \Psi(2,1,3) + \Psi(3,1,2)}$$

And the anti symmetric wave function can be written as

$$\boldsymbol{\Psi_A = \Psi(1,2,3) + \Psi(2,3,1) + \Psi(3,2,1) - \Psi(1,3,2) - \Psi(2,1,3) - \Psi(3,1,2)}$$

1.3 EXCHANGE OPERATOR

1.3.1 Define Particle exchange operator and show that its eigen values are ±1.

The **particle exchange operator P_{12}** is defined by equation

$$P_{12}\,\psi\,(r_1s_1 : r_2s_2) = \psi\,(r_2s_2 : r_1s_1) \text{ ---------1.}$$

The effect of this operator is to interchange the subscripts of the spin and position variables of the wave function for particles 1 and 2.

If two particles are identical, then the Hamiltonian must be symmetric with respect to position and spin of identical particles.

Hence energy of the system will remain same if we relabel the particles.

Eigen Values of Particle exchange operator:

Eigen value equation of particle exchange operator is

$P_{12}\ \psi\ (1, 2) = \alpha\ \psi\ (1, 2)$ --------------------2.

Where α is the Eigen value of operator P_{12} in state $\psi\ (1, 2)$

Operating again

$$P_{12}^2\ \psi\ (1, 2) = P_{12}\ P_{12}\ \psi\ (1, 2) = P_{12}\ \alpha\ \psi\ (1, 2)$$

$$= \alpha\ P_{12}\ \psi\ (1, 2)$$

$$= \alpha\ [\alpha\ \psi\ (1, 2)]$$

$$P_{12}^2\ \psi\ (1, 2) = \alpha^2\ \psi\ (1, 2) \text{ ----------------------3.}$$

From the definition of particle exchange operator

$P_{12}\ \psi\ (1, 2) = \psi\ (2, 1)$ -------------------------------4.

Operating again

$$P_{12}^2\ \psi\ (1, 2) = P_{12}\ P_{12}\ \psi\ (1, 2) = P_{12}\ \psi\ (2, 1)$$

$$P_{12}^2\ \psi\ (1, 2) = \psi\ (1, 2) \text{ -----------------------5.}$$

Comparing 3 & 5 we get,

$\alpha^2 = 1$ or $\alpha = \pm 1$

i.e., **the eigen values of particle exchange operator are ± 1** just like parity operator.

1.3.2 Show that the eigen functions of particle exchange operator are symmetric and antisymmetric.

Eigen function of particle exchange operator corresponding to **eigen value +1** is **symmetric** and

Eigen function of particle exchange operator corresponding to **eigen value – 1** is **Antisymmetric.**

i.e., $P_{12}\ \psi_S = \psi_S$ and $P_{12}\ \psi_A = -\ \psi_A$

This may be explained as follows.

$$\psi_S = \psi(1, 2) + \psi(2, 1)$$

$$P_{12}\,\psi_S = P_{12}\,[\psi(1, 2) + \psi(2, 1)]$$

$$= \psi(2, 1) + \psi(1, 2)$$

$$P_{12}\,\psi_S = \psi_S$$

Also $\psi_A = \psi(1, 2) - \psi(2, 1)$

$$P_{12}\,\psi_A = P_{12}\,[\psi(1, 2) - \psi(2, 1)]$$

$$= \psi(2, 1) - \psi(1, 2)$$

$$= -[\psi(1, 2) - \psi(2, 1)]$$

$$P_{12}\,\psi_A = -\psi_A$$

1.3. 3. Particle exchange operator commutes with Hamiltonian.

From the definition of particle exchange operator

$P_{12}\,\psi(1, 2) = \psi(2, 1)$

$P_{12}\,H(1, 2)\,\psi(1, 2) = H(2, 1)\,\psi(2, 1)$

Since Hamiltonian H is symmetric $H(1, 2) = H(2, 1)$

$P_{12}\,H(1, 2)\,\psi(1, 2) = H(1, 2)\,P_{12}\,\psi(1, 2)$

$[P_{12}\,H(1, 2) - H(1, 2)\,P_{12}]\,\psi(1, 2) = 0$

As $\psi(1, 2)$ is non zero

$P_{12}\,H(1, 2) - H(1, 2)\,P_{12} = 0$

$\therefore [P_{12}, H] = 0$

Thus the Particle exchange operator commutes with Hamiltonian

1. 4. Discuss about the Distinguishability of identical particles.

- Two identical particles can be distinguished when they are in different orbits. i.e., when they do not overlap.
- For example, two electrons in an atom are well – differentiated when two electrons are in different orbits.
- The electrons of the same orbit cannot be distinguished.
- In terms of quantum mechanical concept, two electrons are distinguished when their wave functions do not overlap.
- When two wave functions do not overlap, the overlap terms $\Psi\,(1,2) + \Psi\,(2,1)$and $\Psi\,(1,2) - \Psi\,(2,1)$ are zero.
- If the wave functions of these two particles overlap, we can't detect a particle which one is it?
- Quantum mechanics can only tell us the probability of finding a particle in a given region.
- It further means that,
- $|\Psi\,(1,2)|^2 + |\Psi\,(2,1)|^2 = |\{\Psi\,(1,2) \pm \Psi\,(2,1)\}|^2$

The two identical particles can be distinguished from each other **when the sum of the probabilities of the individual wave functions in two states is equal to the probability derived by the symmetrised wave functions.**

i.e., $|\Psi\,(1,2)|^2 + |\Psi\,(2,1)|^2 = |\{\Psi\,(1,2) \pm \Psi\,(2,1)\}|^2$

$= |\Psi\,(1,2)|^2 + |\Psi\,(2,1)|^2 \pm 2\mathrm{Re}[\Psi\,(1,2)\Psi(2,1)]$ --------1

This is possible when the overlap terms $\Psi\,(1,2)\ and\ \ \Psi\,(2,1)$ is zero or $2\mathrm{Re}[\Psi\,(1,2)\Psi(2,1)]$ = 0.

In this way when the co - ordinates (space and spin) of two particles are not the same between exchange degenerate functions, the interference term $2\mathrm{Re}[\Psi\,(1,2)\Psi(2,1)]$ becomes zero and particle co-ordinates do not overlap.

1. 5. What do you mean by Bosons and Fermions?

Pauli demonstrated that quantum particles are classified as

1. **Bosons**
2. **Fermions**

Bosons:

1. Systems of identical particles with integer spins (S = 0,1,2,----) are described by symmetric wave functions.
2. They do not follow Pauli's exclusion principle
3. Such particles obey Bose – Einstein Statistics
4. They are called Bosons.
5. Examples : $\pi - mesons,\ photons$

Fermions:

1. Systems of identical particles with half – odd integer spins ($S = \frac{1}{2}$, $\frac{3}{2}$, …) are described by antisymmetric wave functions
2. They follow Pauli's exclusion principle.
3. Such particles obey Fermi – Dirac Statistics.
4. They are called Fermions.
5. Examples : electron, proton, neutrons

1.6. Write short notes on Pauli's Exclusion Principle.

Pauli's Exclusion Principle:

Pauli's exclusion principle states that **"No two particles obeying Fermi Dirac Statistics can exist in the same quantum state"**.

1. Consider two particle system which contains electrons in indistinguishable positions.
2. Electrons are $\frac{1}{2}$ spin particles and obey Fermi Dirac Statistics.
3. If they occupy the same position in space and have the same z – component of spin , then the eigen function of exchange operator will be

$$P_{12}\,\psi_A(r_1s_1 : r_2s_2) = -\,\psi_A(r_2s_2 : r_1s_1) \text{ ------------------1}$$

$$= \psi_A(r_1s_1 : r_2s_2)$$

$$= 0 \text{ if } \begin{cases} r_1 = r_2 \\ s_1 = s_2 \end{cases} \text{ --------------------2}$$

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.

Eqn 2 is called **Pauli exclusion principle which states that**

"No two particles obeying Fermi Dirac Statistics can exist in the same quantum state".

(This means that if there are two electrons in one atomic orbit, they cannot have the same spin orientations. Their spins have to be oppositely directed.)

1.6.1. What is Pauli's theory? Show that antisymmetric wave function for 2 electrons would vanish if both occupy the same position with identical spin.

Or) Show that the antisymmetric wave function obeys Pauli's exclusion principle.

(a) Pauli' s theory:

"No two particles obeying Fermi Dirac Statistics can exist in the same quantum state".

(This means that if there are two electrons in one atomic orbit, they cannot have the same spin orientations. Their spins have to be oppositely directed.)

(b) Show that antisymmetric wave function for 2 electrons would vanish if both occupy the same position with identical spin.

Consider a system of **non interacting indistinguishable particles**.

The Hamiltonian of such a system can be written as

H_0 (1,2,…..n) = H_0'(1) + H_0'(2) + …….+ H_0'(n) -----------------1

The approximate **Energy - Eigen function** will be a simple product of one particle eigen functions. ϕ

If $\phi_a(1), \phi_b(2), \dots\dots\dots\dots\, \phi_k(n)$ are the n – one particle eigen functions, then

ψ (1, 2 ………..n) = $\phi_a(1)\ \phi_b(2)\ \dots\dots\dots\dots\, \phi_k(n)$ --------------2.

Eigen value will be

E = E_a +E_b +………..E_k --------------------------------3

Hence, comparing 1,2 & 3

$$\left.\begin{aligned} &\mathbf{H_0'(1)\ \phi_a(1) = E_a\ \phi_a(1)} \\ &\mathbf{H_0'(2)\ \phi_a(2) = E_b\ \phi_b(2)} \quad \text{etc.,} \end{aligned}\right\} \text{----------------------------4.}$$

Since the particles are **indistinguishable**, our assumption that **ϕ_a is occupied by particle 1 and ϕ_b is occupied by particle 2 is incorrect.**

Under exchange of two particles, to distinguish them, we have to take probability distribution.

∴ The possible eigen functions are

$$\left.\begin{aligned} &\psi(1, 2) = \phi_a(1)\ \phi_b(2) \ \text{ and} \\ &\psi(2, 1) = \phi_a(2)\ \phi_b(1) \end{aligned}\right\} \text{-----------------------5.}$$

The symmetric and antisymmetric combinations are

$\psi_S = \phi_a(1)\,\phi_b(2) + \phi_a(2)\,\phi_b(1)$ --------------------------------6.

$\psi_A = \phi_a(1)\,\phi_b(2) - \phi_a(2)\,\phi_b(1)$ -------------------------------7.

$= \begin{vmatrix} \phi_a(1) & \phi_a(2) \\ \phi_b(1) & \phi_b(2) \end{vmatrix}$ ----------------------------------8.

If both the particles are put in the same state say ϕ_a then,

$\psi_S = \phi_a(1)\,\phi_a(2) + \phi_a(2)\,\phi_a(1)$

$\boxed{\psi_S = 2\,\phi_a(1)\,\phi_a(2)}$ -------------------------------9. and

$\psi_A = \phi_a(1)\,\phi_a(2) - \phi_a(2)\,\phi_a(1)$

$\boxed{\psi_A = 0}$ ----------------------------------10.

Eqn 10 shows that the antisymmetric wave function vanishes, when two identical particles have the same set of co – ordintates.

It concludes that two identical fermions cannot occupy the same state.

1.6.2 Explain Pauli's exclusion principle using slater's determinant. (optional)

The antisymmetric wave function can be expressed as determinant of the ϕ's known as slater's determinant.

$$\psi_A\,(1.2.\,\ldots.n) = \frac{1}{\sqrt{n}} \begin{bmatrix} \phi_a(1) & \phi_a(2) & \cdots & \phi_a(n) \\ \phi_b(1) & \phi_b(2) & \ldots & \phi_b(n) \\ \vdots & \vdots & \ldots & \vdots \\ \phi_k(1) & \phi_k(2) & \cdots & \phi_k(n) \end{bmatrix} \text{ -------------1}$$

The factor $\frac{1}{\sqrt{n}}$ is called normalization constant and the determinant is called **Slater's determinant.**

If two or more ϕ's are same (i.e.,) $\phi_a(1) = \phi_b(1)$, the determinant will vanish.

∴ The antisymmetric wave function can not be constructed by the interchange of any pair of particles.

Hence Pauli's exclusion principle states that "***no two particles described by antisymmetric wave functions (or obeying Fermi Dirac Statistics) can exist in the same quantum state."***

PAULI SPIN MARICES.

Assume that components of spin angular momentum (S_x, S_y and S_z) satisfy same commutation relations observed by the components of orbital angular momentum L_x, L_y and L_z.

$$\left.\begin{array}{l}[S_x, S_y] = i\hbar S_z \\ [S_y, S_z] = i\hbar S_x \\ [S_z, S_x] = i\hbar S_y .\end{array}\right\} \longrightarrow ①$$

Now we introduce a new vector operater $\vec{\sigma}$, known as Pauli spin operator, such that

$$S = \frac{1}{2} \hbar \vec{\sigma} .$$

$$\therefore \left.\begin{array}{l} S_x = \frac{1}{2} \hbar \sigma_x \\ S_y = \frac{1}{2} \hbar \sigma_y \\ S_z = \frac{1}{2} \hbar \sigma_z \end{array}\right] \longrightarrow ②$$

$S_x = -\frac{1}{2} \hbar \sigma_x$

$S_y = -\frac{1}{2} \hbar \sigma_y$

$S_z = -\frac{1}{2} \hbar \sigma_z$.

Since the eigen values of each S are to be just $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, the eigen value of each σ must be $+1$ and -1.

~~The Square~~ $\therefore \sigma = \pm 1$

The square of the operator $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$. ~~[illegible]~~ ~~[illegible]~~

(i.e) $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$ (the unit operater I) $\rightarrow$ ③

Comparing ①, ②, & ③.

$$[\sigma_x \sigma_y] = \sigma_x \sigma_y - \sigma_y \sigma_x = 2i\sigma_z \longrightarrow ④$$

$$\left.\begin{aligned}[\sigma_y, \sigma_z] &= 2i\sigma_x \\ [\sigma_z, \sigma_x] &= 2i\sigma_y\end{aligned}\right\} \longrightarrow ④$$

Collectively $\sigma \times \sigma = 2i\vec{\sigma} \longrightarrow$ ⑤

Also σ_x and σ_y anticommute with each other

$\therefore \sigma_x \sigma_y = -\sigma_y \sigma_x \longrightarrow$ ⑥

$$\left.\begin{aligned}\therefore \sigma_x\sigma_y + \sigma_y\sigma_x &= 0 \\ \sigma_y\sigma_z + \sigma_z\sigma_y &= 0 \\ \sigma_z\sigma_x + \sigma_x\sigma_z &= 0\end{aligned}\right\} \longrightarrow ⑦$$

from ④ we get

$$\left.\begin{aligned}\sigma_x\sigma_y &= -\sigma_y\sigma_x = i\sigma_z \\ \sigma_y\sigma_z &= -\sigma_z\sigma_y = i\sigma_x \\ \sigma_z\sigma_x &= -\sigma_x\sigma_z = i\sigma_y\end{aligned}\right\} \longrightarrow ⑧ Ⓧ$$

Also we have $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I \longrightarrow$ ⑨ Ⓧ

I is a unit operator or unit matrix

Now we start by assuming σ_z as a 2×2 matrix with eigen values ± 1 (ie) $+1$ and -1

$$\therefore \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Let $\sigma_x = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$ and

$$\sigma_y = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$$

Let
~~We know that~~ $\sigma_z \sigma_x + \sigma_x \sigma_z = 0$

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} + \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 0$$

$$2\begin{pmatrix} a_{11} & 0 \\ 0 & -a_{22} \end{pmatrix} = 0 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\therefore a_{11} = a_{22} = 0$$

$$\therefore \sigma_x = \begin{pmatrix} 0 & a_{12} \\ a_{21} & 0 \end{pmatrix}$$

$$\therefore \sigma_y \sigma_z + \sigma_z \sigma_y = 2\begin{pmatrix} b_{11} & 0 \\ 0 & -b_{22} \end{pmatrix} = 0 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$ ③

$$\therefore b_{11} = -b_{22} = 0$$

$$\therefore \sigma_y = \begin{pmatrix} 0 & b_{12} \\ b_{21} & 0 \end{pmatrix}$$

$$\sigma_x^2 = \begin{pmatrix} a_{12}a_{21} & 0 \\ 0 & a_{21}a_{12} \end{pmatrix} = I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\therefore a_{12}a_{21} = 1$$

|||ly

$$\sigma_y^2 = \begin{pmatrix} b_{12}b_{21} & 0 \\ 0 & b_{21}b_{12} \end{pmatrix} = I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\therefore b_{12}b_{21} = 1$$

From eqn ⑧

$$\sigma_z \sigma_x = -\sigma_x \sigma_z = i\sigma_y$$

$$\therefore \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & a_{12} \\ a_{21} & 0 \end{pmatrix} = \begin{pmatrix} 0 & a_{12} \\ -a_{21} & 0 \end{pmatrix} = i\begin{pmatrix} 0 & b_{12} \\ b_{21} & 0 \end{pmatrix}$$

It means

$$a_{12} = i b_{12} \Rightarrow b_{12} = -i a_{12}$$

$$-a_{21} = i b_{21}$$

$$\therefore b_{21} = i a_{21}$$

Sub

$$a_{12} = a_{21} = I = 1$$

$$\left.\begin{aligned} \therefore b_{21} &= i \\ \text{and } b_{12} &= -i \end{aligned}\right\} \longrightarrow ⑨$$

As a result, we get

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These are known as Pauli spin matrices.

same spin [illegible] ground state

The Pauli's principle with the help of [illegible] forms what it is known as Aufbau principle. The principle [illegible] up entire periodic table, explaining of course the ground state of each element. The repetition of ground state configuration gives an explanation for the periodicity in the properties of element.

The exclusion principle governs the group behaviour of all elementary particles possessing spin $\hbar/2$ including the electron, proton, neutron etc. One of the most important consequences of the principle is that in the interaction of identical particles of spin $\hbar/2$, new forces of non-dynamical character occur. To illustrate this we consider two electrons moving along the same line defined by position and momentum coordinates x_1, p_1 and x_2, p_2, respectively. Then de-Broglie waves associated with them are given by $\exp.(i\,p_1x_1/\hbar)$ and $\exp.(i\,p_2\,x_2/\hbar)$, respectively. When both of them are present, it is not possible to identify them, since they may be interchanged without affecting any physical observable. According to the requirement of Pauli's principle the wavefunction representing a system of several electrons must be antisymmetric. The antisymmetric wavefunction for the system of two electrons considered here reads as

$$\psi_A = \frac{1}{\sqrt{2}}[\exp(i/\hbar\cdot(p_1x_1 + p_2x_2)) - \exp(i/\hbar\cdot(p_1x_2 + p_2x_1))] \quad ...(31)$$

And the probability that first electron will be found at x_1 and second at x_2 is given by

$$\psi_A{}^*\psi_A = 1 - \cos\left\{\frac{1}{\hbar}(p_1 - p_2)(x_1 - x_2)\right\}. \quad ...(32)$$

This result shows that as $x_1 \to x_2$ the quantity $\psi_A{}^*\psi_A$ reduces to zero which is equivalent to a repulsion in addition to the Coulomb repulsion between the two electrons. It is also noticed that repulsion between the electrons is larger for smaller difference in their moments for a given separation.

The principle also predicts that when atoms approach to distances where their electronic structures begin to interpenetrate, then very strong repulsive forces appear which account for very low compressibility of liquid and solids. Further because of this principle, the properties of electron gas are quite different in many respect from those of an ordinary gas.

10.8. COLLISION OF IDENTICAL PARTICLES

In the scattering of identical particles, there are two indistinguishable situations for every scattering angle as shown in fig. (10.1) in which the incident particle (1) and the scatterer (2) have equal and opposite velocities in the centre of mass frame of reference. In fig. (10.1a) particle (1) is observed in the detector *D* while the scatterer (2) in fig. (10.1b). Since the particles are identical and have equal energy, they cannot be distinguished experimentally.

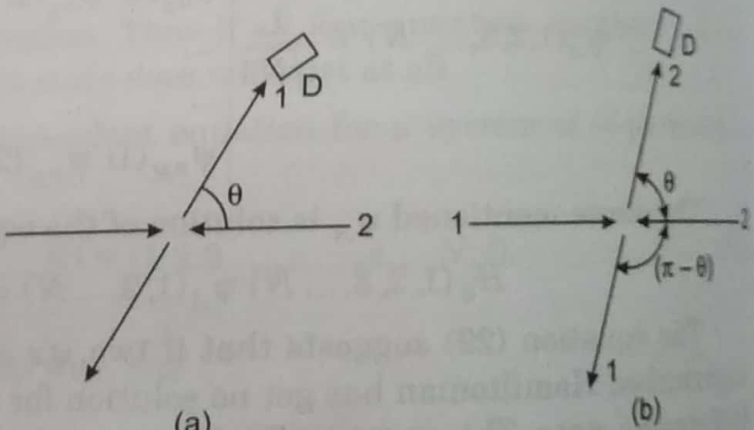


Fig. 10.1. Collision of identical particles.

When the distance between the two particles is very small, the wavefunction must contain a part that represents an incident particle of mass μ moving in a particular direction with velocity υ and another part that represents radially outgoing particle, *i.e.*,

$$\psi(\mathbf{r})_{r\to\infty} = e^{ikz} + \frac{1}{r} f(\theta,\phi)^{e^{ikr}},$$

where

$$k \simeq \frac{\mu \upsilon}{h},\ \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{...(1)}$$

and $\psi(\mathbf{r})$ is the asymptotic form of the scattering wavefunction in the centre of mass coordinate system and (r, θ, ϕ) are the polar coordinates of the relative position vector **r**.

The first term of equation (1) represents a particle moving in positive z-direction or along the polar axis $\theta = 0$. It is an infinite plane wave where propagation vector **k** has the magnitude k and is directed along the polar axis. The second term represents a particle moving radially outward, its amplitude depends on θ and φ and is inversely proportional to r, since radial flux must fall off as the distance increases.

When only forces acting on the two particles result from their mutual interaction, the overall motion can be separated into motion of centre of the mass of the two particles and the motion of the particles relative to centre of mass. It is apparent that the interchange of particles which are identical does not alter the position vector of the centre of mass as,

$$\mathbf{r}_{cm} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_l + m_2} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \quad \text{if } m_1 = m_2 \qquad \text{...(2)}$$

but changes the sign of relative position vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$.

Now neglecting the spin variable, we can examine the effect of symmetry and antisymmetry of the wavefunction on scattering of a particle which collides with an identical particle. For this we reflect first the position vector **r**, to give − **r** which has the polar coordinates $r, (\pi - \theta)$, and $(\pi + \phi)$ with respect to original coordinates. Then the symmetric and antisymmetric wavefunctions will have the form

$$\psi(\mathbf{r}) = (e^{ikz} \pm e^{-ikz}) + 1/r\{f(\theta,\phi) \pm f(\pi-\theta, \pi+\phi)\}e^{ikr}, \qquad \text{...(3)}$$

with upper and lower signs respectively.

The differential scattering cross-section can be written as

$$\sigma(\theta,\phi) = |f(\theta,\phi) \pm f(\pi-\theta,\pi+\phi)|^2$$
$$= |f(\theta,\phi)|^2 + |f(\pi-\theta,\pi+\phi)|^2 \pm 2R_e\{f(\theta,\phi)\, f(\pi-\theta,\pi+\phi)\} \qquad \text{...(4}$$

When the two particles are distinguishable, the last term drops out in the classical case an the differential cross-section becomes just the sum of the two terms, *i.e.*, $|f(\theta,\phi)|^2$ an $|f(\pi-\theta,\pi+\phi)|^2$ which are possibilities of observing the incident particle and the scattered particl If f is independent for φ, then the scattering can be seen to be symmetrical about $\theta = 90°$ in th centre of mass co-ordinates.

The effect of spin on the collision of two identical particles can now be taken into account the interaction between the particles does not involve the spin. Each particle will have $(2s+1)$ sp eigenfunctions and for the pair of two particles there can be $(2s+1)^2$ permutations eigenfunctions which will be the products of single particle functions. These are convenien divided into three categories.

(1) The first group consists of products of one particle functions in which both particles are in the same spin state with S_z values as m , of the form

$$\upsilon_1(m)\,\upsilon_2(m) \quad -s \leq m \leq s$$

where the subscripts specify which of the particles is in which state. There are evidently $(2s + 1)$ such states.

(2) The second group is a sum of the products of the type

$$\upsilon_1(m')\,\upsilon_2(m'') + \upsilon_1(m'')\,\upsilon_2(m').$$

These are $s(2s+1)$ in number. $m' \neq m''$

(3) The third group consists of differences of products

$$\upsilon_1(m')\,\upsilon_2(m'') - \upsilon_1(m'')\,\upsilon_2(m').$$

Again there are $s(2s+1)$ such states.

The first two groups are clearly symmetric in an interchange of the spin coordinates of two particles, and the third group is antisymmetric in such an interchange. Thus the total of $(2s + 1)^2$ states can be divided into $(s+1)(2s+1)$ symmetric and $s(2s + 1)$ antisymmetric states. If all the spin functions $(2s + 1)^2$ are equally probable in collision, then $\left(\frac{s+1}{2s+1}\right)$ of them will appear in equation.

(4) In the collision with the upper (+) sign and a function $\left(\frac{s}{2s+1}\right)$ will appear with lower (–) sign.

On the other hand, the complete wavefunction of a system of two particles must be multiplied by $(-1)^{2s}$ when they are interchanged (*i.e.*, by + 1 for integral s and by – 1 for half integral s). Hence it follows that the symmetry of the coordinate wavefunction with respect to an interchange of particles is given by the factor $(-1)^s$, which depends only on s. Thus we reach the result that the coordinate wavefunction of a system of two identical particles is symmetrical when the total spin is even, antisymmetrical when it is odd.

Thus the modified equation (4) can be written as

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi-\theta)|^2 + \frac{(-1)^{2s}}{(2s-1)}\,2R_e\{f(\theta), f(\pi-\theta)\} \qquad ...(5)$$

where f is assumed to be independent of ϕ.

10.9. ELECTRON SPIN

In the year 1920, in the spectra of alkali atoms some troublesome features were observed which could not be explained on the basis of orbital quantum properties. The spectral lines of the alkali-like atoms appeared as doublets although the members of diffuse and fundamental series were actually triplet. The regularities of the multiple structure of spectra were considered in some detail by Sommerfeld. He introduced an 'inner' quantum number to distinguish the various states of multiplet, and suggested that it may be connected with a property of the electrons in 'inner shells' (the core electrons). The true explanation of the doublet structure of the terms of alkali metal atoms is provided by the concept of electron spin. In 1926, Uhlenbeck and Goudsmidt suggested that an electron has an additional property of intrinsic spin angular momentum. Other observations have led to the conclusion that spin is the property of elementary particles, such as protons and neutrons, as well as electrons. Spin is a vector quantity with the dimensions of

1.8 Write short notes on density operator and density matrix?

Consider a system described by non negative probabilities. Let a classical state is represented by the co-ordinates $q_1, q_2, ---- q_f$, momentum $p_1, p_2, ----------- p_f$ at any instant of time (t).

A statistical state can be described by a non negative density function $f\ (q_1, q_2, ---- q_f, p_1, p_2, ----------- p_{f,}, t\ )$.

Then, the probability of finding the system at time t is

$P\ (dq_1 ----------dq_f, dp_1 ------------dp_f\ )$

The quantum analogue 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 systems of identical particles** in the normalized state ψ_α : where $\alpha = 1,2,3 ----N$.

The expectation value of an observable f is given by

$$< f > = \int \psi_\alpha^* \ \hat{f} \ \psi_\alpha \ dq ------------1$$

$\hat{f}$ is an operator associated with observable f.

If ϕ_n ‘s represent the orthonormal eigen function’s, then a pure state ψ_α may be represented by the coefficients of expansion of ψ_α into eigen vectors ϕ_n. i.e.,

$$\psi_\alpha = \sum_n C_n \phi_n \quad ---------------2$$

$$\psi_\alpha^* = \sum_m C_m^* \phi_m^* \quad ---------------3$$

So that equation (1) takes the form

$$< f > = \sum_m \sum_n C_m^* C_n \int \phi_m^* \hat{f} \phi_n \, dq$$

$$< f > = \sum_m \sum_n C_m^* C_n \langle m|f|n\rangle \text{ ---------- } 4$$

If the state is not specified completely, it may be represented by a superposition of a number of pure states $\psi^{(\alpha)}$ with statistical weight $p^{(\alpha)}$.

So the mean value of f for the incoherent superposition is given by the grand (or ensemble) average given by

$$\langle \bar{f} \rangle = \sum_\alpha p^{(\alpha)} < f > = \sum_\alpha p^{(\alpha)} \sum_m \sum_n C_m^* C_n \langle m|f|n\rangle$$

$$\langle \bar{f} \rangle = \sum_m \sum_n \langle m|f|n\rangle \sum_\alpha p^{(\alpha)} C_m^* C_n \text{ --------------- } 5$$

Where $p^{(\alpha)}$ represents the probability of finding the system in the state$|\alpha >$, where a measurement is made at random on the system.

Let us write, $\sum_\alpha p^{(\alpha)} C_m^* C_n = p_{mn}$ --------------6

$$\langle m|f|n\rangle = f_{mn} \text{ ------------------- } 7$$

Hence the equation 5 takes the form

$$\langle \bar{f} \rangle = \sum_m \sum_n f_{mn} p_{mn} \text{ --------------- } 8$$

$$\langle \bar{f} \rangle = \sum_{mn} (pf)_{mn}$$

$$\langle \bar{f} \rangle = Trace\ (pf) \text{ ------------ } 9$$

Where Trace stands for the sum of the diagonal elements of the matrix (pf). It is convenient to regard the density matrix as defined by equation 9 and then by equation 6.

1.8.1 Limitations on density matrix

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

   $p_{mn} = p_{mn}^{\dagger}$

2. The condition that the unit operator I has the expectation value 1, require that $Trace\ (pf) = Trace\ (p1) = \sum_{mn} p_{mn} = 1$ -------1
3. The condition that every operator with negative eigen values has a non – negative mean value, requires that p must be definitely positive.

   This means $p_{mn} \geq 0$ --------------2
4. The Hermitian matrix p by means of unitary transformations may be reduced to diagonal form

$$p_i \sigma_{jj\prime} = \sum_m \sum_n U_{jm} p_{mn} U_{nj\prime}^{-1}$$

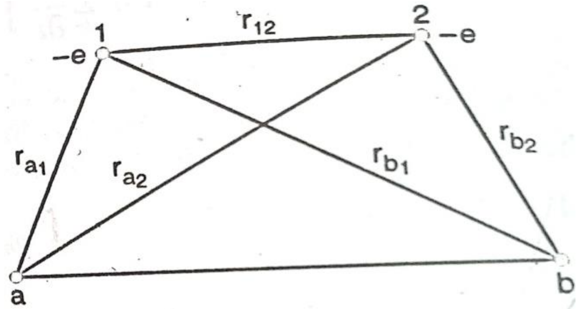
5. The conditions given by 1 and 2 require that

$$[Trace(p)^2] = 1$$

$$[\boldsymbol{Trace}(\boldsymbol{p})^{\boldsymbol{2}}] = \sum_{\boldsymbol{m}} \sum_{\boldsymbol{n}} |\boldsymbol{p}_{\boldsymbol{mn}}|^{\boldsymbol{2}} \leq \boldsymbol{1}$$

This limits the value of every single element of the density matrix.

1.9 Construct symmetric and antisymmetric wave functions of a hydrogen molecule.



When two H atoms meet, a molecule is not always formed.

- The two atoms repel each other if the spins of the two electrons are parallel (⇈)
- The two atoms attract each other if the spins of the two electrons are anti parallel (⇅)

Consider a system consists of two hydrogen nuclei 'a' and 'b', and two electrons whose coordinates are denoted by symbols 1, 2.

Let r_{12} is the distance between the two electrons.

The Schrodinger equation of hydrogen molecule is given as

$$\nabla_1^2\Psi + \nabla_2^2\Psi + \frac{2m}{\hbar^2}\left[E - V_1 - V_2 - \frac{e^2}{r_{12}}\right]\Psi = 0 \text{ --------1}$$

Suppose, neglecting the spinning of electrons, the term $\frac{e^2}{r_{12}}$ may be neglected.

The total energy of the two electrons be $\mathbf{E = E_a + E_b}$ **--------------2**

The solution of equation 1 is given as

$\Psi = \Psi_a(1)\Psi_b(2)$ ------------3

However the two electrons are indistinguishable from each other, we can expect the solution of equation 1 as

$\Psi = \Psi_a(2)\Psi_b(1)$ ------------4

The solution (4) also belongs to the energy E = $\mathbf{E_a + E_b}$

Consequently, for two electron system we have two wave functions belonging to the same energy. This is called degeneracy.

Combining the two solutions 3 & 4, we can build up more **orbital wave functions.**

$\Psi_+ = \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)$ -------------5 (Adding all wave functions)

$\Psi_- = \Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)$ ---------------6 (subtracting all wave functions)

Equations 3, 4 and 5 are symmetrical orbital wave functions and equation 6 is anti symmetrical orbital wave functions.

If we consider spin, we know that each electron has spin $S_1 = S_2 = \frac{1}{2}$. The two spins then combine to give a resultant spin for the total system.

- The spins of same direction (↑↑) produces the resultant spin as S = 1.
- The spins of opposite direction (↑↓) produces the resultant spin as S = 0

For two electrons there will be two positive spin functions say, $\alpha\ (1)\ and\ \alpha\ (2)$ and two negative spin functions $\beta(1) and\ \beta(2)$.

Ultimately for two electrons system we have four spin functions. The total spin wave function is the product of these spins functions.

Two electron system	Electron 1	Electron 2
$\alpha\ (1)\ \alpha\ (2)$	↑	↑
$\beta(1)\ \beta(2)$	↓	↓
$\alpha\ (1)\ \beta(2)$	↑	↓
$\alpha\ (2)\ \beta(1)$	↓	↑

Each α describes the spin $+\frac{1}{2}$ and β describes the spin $-\frac{1}{2}$.

Since the two electrons are identical we can write the linear combination of the spin wave functions as

$S_+ = \alpha\,(1)\,\beta(2) + \alpha\,(2)\,\beta(1)$ ---------------- 7

$S_- = \alpha\,(1)\,\beta(2) - \alpha\,(2)\,\beta(1)$ -------------- 8

Hence the four spin functions will be

1. $\alpha\,(1)\,\alpha\,(2)$
2. $\beta(1)\,\beta(2)$
3. $\alpha\,(1)\,\beta(2) + \alpha\,(2)\,\beta(1)$
4. $\alpha\,(1)\,\beta(2) - \alpha\,(2)\,\beta(1)$

The complete wave function of an electron is the product of the orbital wave function multiplied by one of the spin functions.

According to Pauli Exclusion Principle only two products will be allowed. (i.e.,)

1. $[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)]$ x $[\alpha\,(1)\,\beta(2) - \alpha\,(2)\,\beta(1)]$ ----------9
2. $[\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)]$ x $\begin{bmatrix} \alpha\,(1)\,\alpha\,(2) \\ \beta(1)\beta(2) \\ \alpha\,(1)\,\beta(2) + \alpha\,(2)\,\beta(1) \end{bmatrix}$---------10.

- Hence the total wave function of two electrons system is always anti symmetrical.
- The symmetric orbital wave function is always associated with anti symmetric spin wave function.
- The anti symmetric orbital wave function is always associated with symmetric spin wave function.

Symmetry of Orbital Wave – functions and Spin		
Orbital	Spin	Total S
$\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)$	$\alpha\,(1)\,\beta(2) - \alpha\,(2)\,\beta(1)$	0 (Singlet)
$\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)$	$\alpha\,(1)\,\alpha\,(2)$ $\beta(1)\beta(2)$ $\alpha\,(1)\,\beta(2) + \alpha\,(2)\,\beta(1)$	1 (Triplet)

Definitions of cross section

The probability that a particle will be scattered as it traverses a given thickness of matter dx can be expressed in terms of a quantity called the scattering cross section. To do this let us note that each molecule

presents to the on-coming particle a target area πd^2, d being diameter of the molecule. This target area is just a cross-section of the region within which a collision can take place as viewed along the direction of motion of the beam. This is where the name scattering cross-section comes from. The results of the collision experiments are expressed by means of cross section and are directly related to the asymptotic behaviour of the stationary solutions of the Schroedinger's equation.

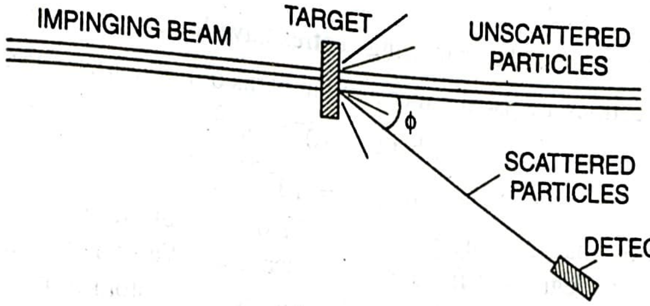


Fig. 11.2

To define the cross-section consider a typical experiment in which a target is struck by a beam of mono-energetic particles and the scattered particles are counted with the aid of a detector (fig. 11.2). Let J bne the magnitude of the incident flux *i.e.* the number of incident particles crossing per unit time a unit surface area placed perpendicular to the direction of incident beam and at rest respect to the target. If ρ is the number of particles per unit volume in the incident beam and v is the velocity of the incident particles, then

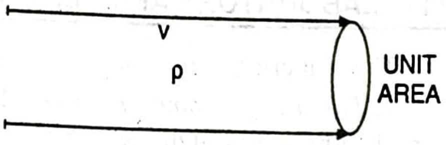


Fig. 11.3

$$J = \rho v$$

If ρ is small (under the conditions of the experiment) that the mutual interaction of the incident particles can be neglected, then they undergo their collisions independently of each other. If n is the number of particles scattered per unit time into a solid angle $d\omega$ located in the direction (θ, ϕ) (polar coordinates), then n is directly proportional to the incident current *i.e.*

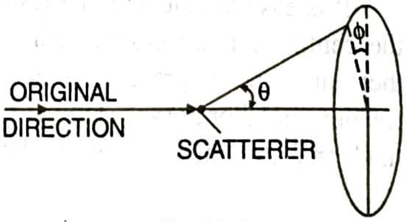


Fig. 11.4

$$n \propto J\,d\omega$$

or

$$n = \Sigma(\omega)\,J\,d\omega$$

where Σ (ω) is a constant of proportionality which has dimension of surface area and is characteristic parameter of the collision of particle with target. It is known as *scattering cross-section of the particle and the target in the direction ω (θ, ϕ).*

Differential Scattering Cross-section : Let us now consider the target to be made up of a large number N of atomic or nuclear scattering centres and the distances between these atoms or nuclei are sufficiently large with respect to the wavelength of the incident particles as is observed in most practical cases. Then each scattering centre acts as it were alone. Moreover, if the target is sufficiently thin, so that one may neglect multiple scattering; then n is directly proportional to N also *i.e.* $n \propto N$; so in this case

$$n \propto N J\,d\omega$$
$$= \sigma(\omega)\,N J\,d\omega$$

Again σ (ω), the constant of proportionality, has the dimensions of surface area and is called the *scattering cross-section* of the particle by the scattering centre in the direction ω (θ, ϕ) or briefly the *differential scattering cross-section.*

Total Scattering Cross-section : The total number of particles scattered in unit time is obtained by integrating n over all angles. It is equal to

$$N_{total} = \int \sigma(\omega) N J \, d\omega = NJ \sigma_{total}$$

where
$$\sigma_{total} = \int \sigma(\omega) \, d\omega$$

is the *total scattering cross section.*

In the cases of nuclear physics the scatterting centres have linear dimensions of the order of 10^{-13} to 10^{-12} cm. and the cross-sections are usually measured in barns or millibarns where

$$1 \text{ barn} = 10^{-24} \text{ cm}^2$$

and
$$1 \text{ millibarn} = 10^{-27} \text{ cm}^2$$

we have assumed explicitly that the only possible collisions are elastic collisions *i.e.* where there is no energy transfer to the internal degrees of freedom of the scatterer. We shall confine ourselves to this type of collision for the moment. Moreover rather than treating the scatterer atom or nucleus in all its complexity. We shall represent by static potential $V(r)$ depending upon coordinate r of the particle.

11·4. LABORATORY AND CENTRE OF MASS REFERENCE SYSTEMS

The scattering of particles can be visualised in two kinds of coordinates :

1. *Laboratory frame or system* **(L-system) :** It is that co-ordinate system in which the bombarded particle (or target) is initially at rest.

2. *Centre of mass co-ordinate system* **(C-system) :** It is that coordinate system in which the centre of mass of two colliding particles is at rest (initially and always).

It is easy to calculate the result of collision experiment in the centre of mass system than the laboratory system, since there are three degrees of freedom in centre of mass system (*C-system*) as compared to six degrees of freedom in laboratory system *(L-system)*. Generally calculations are made in C system and observations are made in L-system. In C-system the reduced mass of two particles of masses m_1 and m_2 is

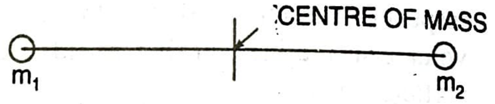


Fig. 11.5

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

So μ must remain at rest before and after collision in C system.

Relation between Angles in L-system and C-system

The relation between the angles in laboratory system (L-system) and C-system can be found by translating the L-system in the direction of the incident particle with sufficient speed to bring the centre of mass to rest.

Let a particle of mass m_1 and initial velocity v strike a relatively heavier particle of mass m_2 at rest in the L-system [Fig. 11.6 (a)].

As particle of mass m_1 moves towards m_2, the centre of mass at the time of collision moves to the right with a velocity V' determined by the conservation of linear momentum.

$$m_1 V = (m_1 + m_2) V'$$

$$\therefore \quad V' = \frac{m_1 V}{m_1 + m_2}. \qquad \text{...(1)}$$

Thus in C-system, the particle approaches the centre of mass with speeds.

$$V'' = (V - V') \text{ and } V'.$$

Total Scattering Cross-section : The total number of particles scattered in unit time is obtained by integrating n over all angles. It is equal to

$$N_{total} = \int \sigma(\omega)\, N J\, d\omega = NJ\, \sigma_{total}$$

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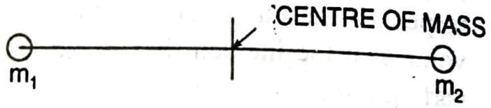

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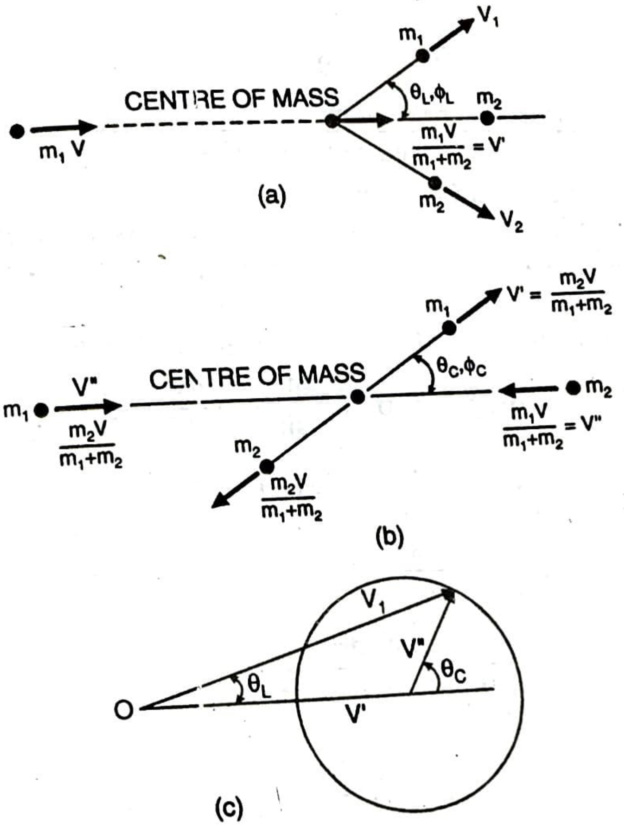


Fig. 11.6 (a) Laboratory co-ordinate system in which the target particle of mass m_1 is initially at rest. (b) Centre of mass co-ordinate system in which the centre of mass is intially and always at rest. (c) Vector addition velocity of centre of mass L-system (V') to velocity of observed particle in C-system (V') to give velocity observed in laboratory system (V_1) : if $V' < V$, θ_L cannot exceed the angle $\sin^{-1}(V'/V)$.

$$V'' = V - V' = V - \frac{m_1 V}{m_1 + m_2}.$$

or

$$V'' = \frac{m_2 V}{m_1 + m_2}$$

If the collision is elastic, the speed will remain same after collision. Now the vector addition of velocity V'' of the observed particle in C-system and velocity V' of the centre of mass in L-system gives the velocity V_1 of the observed particle in the L-system.

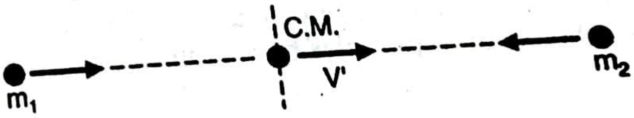


Fig. 11.7

Therefore
$$\left.\begin{aligned} V' + V'' \cos\theta_C &= V_1 \cos\theta_L \\ V'' \sin\theta_C &= V_1 \sin\theta_L \end{aligned}\right\}.$$

As collision is symmetric in ϕ-co-ordinate; then

$$\phi_L = \phi_c$$

Hence from (2)

$$\tan\theta_L = \frac{V'' \sin\theta_C}{V'' \cos\theta_C + V'}$$

$$= \frac{\sin\theta_C}{\cos\theta_C + V'/V''}$$

In the C.M. system it is

$$T_C = \frac{p^2}{2m_1} + \frac{p^2}{2m_2} = \frac{p^2}{2\mu}.$$

In laboratory frame the total momentum of the system is **q**.

$$v = \frac{q}{m_1 + m_2}.$$

The relation between the magnitudes of the momenta in the two frames is

$$p = q - m_1 v = q - m_1\left(\frac{q}{m_1 + m_2}\right) = \frac{m_2 q}{m_1 + m_2}$$

After squaring, we get

$$p^2 = \left(\frac{m_2}{m_1 + m_2}\right)^2 q^2.$$

On substituting $p^2 = 2\mu\, T_C$ and $q^2 = 2m_1 T_L$ we have

$$T_C = \frac{m_2}{m_1 + m_2} T_L. \qquad ...(2)$$

11·5. STATIONARY SCATTERING WAVE : SCATTERING AMPLITUDE

In wave mechanics, an incident beam of particles is represented by a plane wave in incident channel. Let us consider the scattering of a particle of mass m by a central potential $V(\mathbf{r})$ such that $V(\mathbf{r})$ tends to zero more rapidly than $1/\mathbf{r}$ as $r \to \infty$.

Let E be the energy and $\mathbf{p} = \hbar\,\mathbf{k}$ the initial momentum of the particle where **k** is the wave-vector. The Scroedinger equation for the central potential $V(\mathbf{r})$ is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_k(\mathbf{r}) = E\,\psi_k(\mathbf{r}) \qquad ...(1)$$

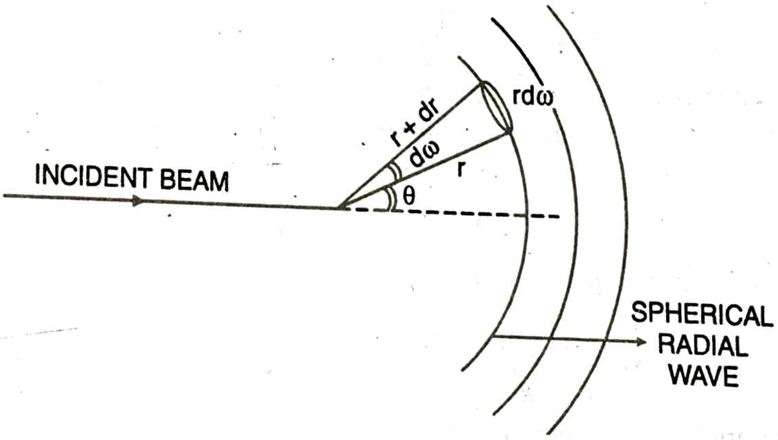


Fig. 11.9

The wave-function ψ_k may be written as a function of θ; ϕ and radial distance r *between the two particles, i.e.*

$$\psi_k = \psi_k(r, \theta, \phi)$$

The scattering is determined by the asymptotic form of $\psi_k(r, \theta, \phi)$ in the region where $V = 0$, when the colliding particles are far apart (or $r \to \infty$). We want to represent such that it contains two parts, one representing an incident wave and the other representing a scattered radially outgoing wave *i.e.*

$$\psi_k(r, \theta, \phi) = \lim_{r \to \infty} e^{i\,\mathbf{k}.\mathbf{r}} + f(\omega)\frac{e^{ikr}}{r} \qquad ...(2)$$

Let us assume that one and only one solution of this type exists for each value of **k**. We shall call this solution, the stationary scattering wave-vector **k**. The two terms of the asymptotic form are easily interpreted if we remember the definition of current density vector

$$\mathbf{J} = \frac{\hbar}{2im}(\psi^* \nabla \psi - \psi \nabla \psi^*) \qquad ...(3)$$

The plane wave term $e^{i\,\mathbf{k}.\mathbf{r}}$ represents a wave of unit density and of current density $\frac{\hbar k}{m}$. Retaining only the lowest order in r, the term $\frac{f(\omega)}{r} e^{ikr}$ represents a wave of *density* $\frac{|f(\omega)|^2}{r^2}$ *and of current density* $\frac{|f(\omega)|^2}{r^2}\frac{\hbar \mathbf{k}}{m}$ *directed along the direction* ω *towards increasing* r (outgoing-wave). In fact, since the effect of the potential $V(r)$ can be neglected in the asymptotic region, therefore according to classical approximation we can interpret the term $e^{i\,\mathbf{k}.\mathbf{r}}$ as a beam of monoenergetic particles of momentum $\hbar\,\mathbf{k}$ and of density 1, representing the incident beam and the term $\frac{f(\omega)}{r} e^{ikr}$ is interpreted as a beam of particles emitted radially from the scattering centre and represents a beam of the scattered particles.

In accordance with this interpretation we can calculate the number of particles emitted per unit time into the solid angle $d\omega$ located in the direction ω.

The scattering wave-function is $f(\omega)\frac{e^{ikr}}{r}$; hence density of scattered particles

$$\rho_s = \left| f(\omega)\frac{e^{ikr}}{r} \right|^2 = \frac{1}{r^2}|f(\omega)|^2$$

From fig. 11.9. small elementary area $= r \,.\, r d\omega = r^2 d\omega$

The volume element between r and $r + dr$ is $= r^2 d\omega \,.\, dr$.

As ρ_s in the number of scattered particles per unit volume, hence the number of particles in this elementary volume

$$N_s = \rho_s r^2 d\omega\, dr.$$

Substituting value of ρ_s from equation (4), we get

$$N_s = \frac{|f(\omega)|^2}{r^2} \cdot r^2 d\omega\, dr = |f(\omega)|^2 dr\, d\omega \qquad ...(5)$$

$\therefore$ The number of scattered particles per unit time

$$\frac{dN_s}{dt} = |f(\omega)|^2 d\omega \frac{dr}{dt} = |f(\omega)|^2 d\omega\, v = |f(\omega)|^2 d\omega \cdot \frac{\hbar k}{m}$$

$$= |f(\omega)|^2 \frac{\hbar k}{m} d\omega. \qquad ...(6)$$

If J is the current density, then $J = \rho v.$ ...(7)

Since beam of particles is travelling in the same direction with velocity v. The flux of the beam is the number of particles crossing unit area (perpendicular to the beam) per unit time. These are number of particles in a volume of unit cross-section and length v.

But $\rho = 1$ for incident particles.

$$\therefore \qquad J = v = \frac{\hbar k}{m} \qquad \text{...(8)}$$

Also if $\sigma(\omega)$ is the scattering cross-section, then number of particles scattered in solid angle $d\omega$ per unit time

$$= J\sigma(\omega)\, d\omega = \frac{\hbar k}{m} \cdot \sigma(\omega)\, d\omega \quad \text{[using (8)]} \qquad \text{...(9)}$$

Comparing equations (6) and (9) we get

$$\frac{\hbar k}{m}\sigma(\omega)\, d\omega = |f(\omega)|^2 \frac{\hbar k}{m} d\omega$$

$$\therefore \qquad \sigma(\omega) = |f(\omega)|^2. \qquad \text{...(10)}$$

Here $f(\omega)$ is called the *scattering amplitude.*

Hence the total scattering cross-section is

$$\sigma_{total} = \int |f(\omega)|^2\, d\omega. \qquad \text{...(11)}$$

The wave-function ψ_k may be normalised by making

$$\int \psi_k^* \psi_k\, d\tau = 1$$

or

$$\int |\psi_k|^2\, d\tau = 1 \qquad \text{...(12)}$$

over a large box that have periodic boundary conditions.

Therefore for finding out the normalisation constant A, we must take the wave function as

$$\psi_k = \lim_{r \to \infty} A\left[e^{i\,\mathbf{k}.\mathbf{r}} + f(\omega)\frac{e^{i\,kr}}{r}\right]. \qquad \text{...(13)}$$

The wave-function may be normalised to unit incident flux by choosing

$$A = \frac{1}{v^{1/2}} = \left(\frac{m}{\hbar k}\right)^{1/2};$$

but for simplicity we often choose A equal to unity.

The argument given above is incorrect for two reasons :

(i) The current density vector is not simply the sum of the current of the incident plane wave and that of the scattered wave. We must add to these contributions, the interaction term

$$e^{i\,\mathbf{k}.\mathbf{r}} \text{ and } f(\omega)\frac{e^{i\,kr}}{r}$$

in the foregoing treatment. The interferences between incident and scattered waves have been deliberately ignored.

(ii) The representation of the physical situation by the stationary wave

$$\psi_k(r)\, e^{i\,Et/\hbar} \qquad \text{...(14)}$$

in an idealisation. In reality each particle participating in the scattering process must be represented by a wave-packet formed by superposition of the stationary waves of the type (14) corresponding to wave-vectors of magnitude and direction slightly different from **k**. This packet is constructed so as to correctly fulfil the initial conditions. Therefore the scattering phenomenon must be represented by suitable wave-packets.

11·6. GENERAL FORMULATION OF THE SCATTERING THEORY

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

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi = E\psi \qquad ...(1)$$

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

$$\begin{aligned}\psi(r, t) &= \psi(r)\, e^{-iEt/\hbar} \\ &= [e^{i\mathbf{k.r}} + \psi_s(r)]\, e^{-iEt/\hbar}\end{aligned} \qquad ...(2)$$

where

$$\psi_s(r) = f(\theta, \phi)\frac{e^{ikr}}{r} + g(\theta, \phi)\frac{e^{-ikr}}{r} \qquad ...(3)$$

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

$$\psi(r) = e^{i\mathbf{k.r}} + \psi_s \qquad ...(4)$$

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

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)e^{i\mathbf{k.r}} = 0 \qquad ...(5)$$

So that the Schroedinger equation is now written as

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)\psi_s &= -V(r)\,[e^{i\mathbf{k.r}} + \psi_s] \\ &= -V(r)\,\psi(\mathbf{r}).\end{aligned} \qquad ...(6)$$

This equation may be written as

$$(\nabla^2 + k^2)\,\psi_s = \frac{2m}{\hbar^2}V(r)\,\psi(r) \qquad ...(7)$$

where $k^2 = \dfrac{2mE}{\hbar^2}$

Further substituting

$$\frac{2m}{\hbar^2}V(r)\,\psi(r) = -\,4\pi\rho(r) \qquad ...(8)$$

equation (7) takes the form

$$(\nabla^2 + k^2)\,\psi_s = -\,4\pi\rho(r). \qquad ...(9)$$

The quantity $\rho(r)$ may be regarded as a source density for divergent spherical waves. Equation (9) may be solved by using principle of superposition. Accordingly if ψ_{s1} and ψ_{s2} are solutions of equation (9) belonging to density functions $\rho_1(r)$ and $\rho_2(\mathbf{r})$ and satisfying

$$\psi_{s1} \approx f_1 \frac{e^{ikr}}{r}, \; \psi_{s2} = f_2 \frac{e^{ikr}}{r} \qquad \text{...(10)}$$

then the function $\psi_s = \psi_{s1} + \psi_{s2}$ is a solution of equation (9) belonging to $\rho(r) = \rho_1(r) + \rho_2(r)$ such that

$$\psi_s = f \frac{e^{ikr}}{r} \qquad \text{where } f = f_1 + f_2. \qquad \text{...(11)}$$

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

$$\rho(r) = \int \delta(r - r')\, \rho(r')\, d\,r' \qquad \text{...(12)}$$

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

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

operator →
$$(\nabla^2 + k^2)\, G(\mathbf{r}, \mathbf{r}') = -\, 4\pi\, \delta(\mathbf{r} - \mathbf{r}') \qquad \text{...(13)}$$

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

is called **Green's function.**

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

$$\psi_s = \int G(\mathbf{r}, \mathbf{r}')\, \rho(\mathbf{r}')\, d\tau' \qquad \text{...(14)}$$

Green's function : It may be noted that *Green's function*

$$G(\mathbf{r}, \mathbf{r}') = \frac{\exp(i\,\mathbf{k}\,|\,\mathbf{r} - \mathbf{r}'\,|)}{|\,\mathbf{r} - \mathbf{r}'\,|} \qquad \text{...(15)}$$

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

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

$$(\nabla^2 + k^2)\, G(r) = -\, 4\pi\, \delta(\mathbf{r}) \qquad \text{...(16)}$$

where
$$G(\mathbf{r}) = \frac{e^{ikr}}{r} \qquad \text{...(17)}$$

r being the radial distance in new coordinates.

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

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

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

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

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

$$\int_\tau \delta(\mathbf{r})\, F(\mathbf{r})\, d\tau = F(0) \qquad \text{...(20)}$$

where $F(\mathbf{r})$ is any continuous function of $\mathbf{r}$ which has value $F(0)$ at the origin and τ represents thue region of integration which is any finite volume containing the origin. Let us therefore choose for our range of integration a small sphere of radius ϵ. Consider the identity

r is the vector from the centre of the co-ordinate System taken at the centre of the scatterer, to the point at Which the Scattered wave is being computed; r' is the Position vector of a pt. in the Scattered potential.

(I)

$$\int_{\tau} [(\nabla^2 G + k^2 G) F - (\nabla^2 F + k^2 F) G]\, d\tau = \int_S \left[\frac{\partial G}{\partial r} F - \frac{\partial F}{\partial r} G\right] dS \qquad ...(21)$$

where S represents the surface of the **sphere** τ. If $F(\mathbf{r})$ is sufficiently regular within the sphere τ, then we may assume positive numbers M and N such that

$$|\nabla^2 F + k^2 F| < M$$

and

$$\left|\frac{\partial F}{\partial r}\right| < N \,(r \le \epsilon) \qquad ...(22)$$

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

$$\left|\int_{\tau} (\nabla^2 F + k^2 F)\, G\, d\tau\right| \le M \int_{\tau} |G|\, d\tau$$

$$= M \int_0^{\epsilon} \frac{1}{r} 4\pi r^2\, dr = 2\pi M \epsilon^2 \qquad ...(23)$$

$\int_0^{\epsilon} \frac{4\pi r^2}{\cancel{r}} = 2\pi r^2$

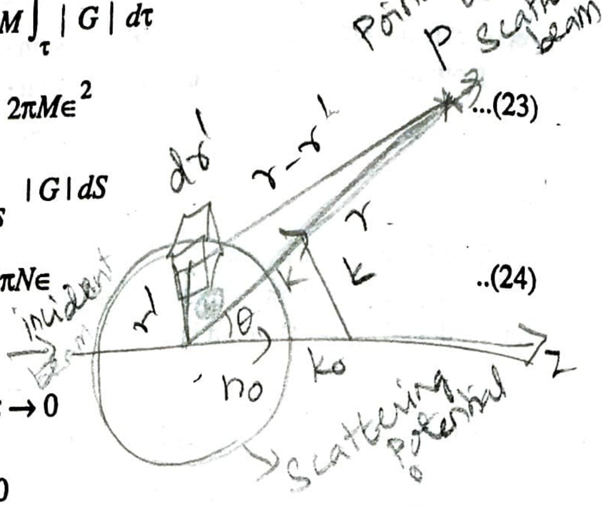
and

$$\left|\int_S \frac{\partial F}{\partial r} G\, dS\right| \le N \int_S |G|\, dS$$

$$= N\left[\frac{1}{r} \cdot 4\pi r^2\right]_0^{\epsilon} = 4\pi N \epsilon \qquad ..(24)$$

$4\pi r\, dr$

$4\pi r\, \delta r$



Therefore if we take the limit $\epsilon \to 0$, we find

$$\int_{\tau} (\nabla^2 F + k^2 F)\, G d\tau \to 0$$

and

$$\int_S \frac{\partial F}{\partial r}\, G\, dS \to 0$$

In view of above relation equation (21) in the limit $\epsilon \to 0$ yields

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

$$= \lim_{\epsilon \to 0} \int_S \left(ik \frac{e^{ikr}}{r} - \frac{e^{ikr}}{r^2}\right) F dS$$

$$= \lim_{\epsilon \to 0} 4\pi\epsilon^2 F(0) \left\{ik \frac{e^{ik\epsilon}}{\epsilon} - \frac{e^{ik\epsilon}}{\epsilon^2}\right\}$$

$$= -4\pi F(0) \qquad ...(25)$$

$4\pi\epsilon^2 F(0)\left(ik\, e^0 - \frac{e^0}{\epsilon}\right)$

$4\pi F(0)(ik\epsilon - 1)$

$-4\pi F(0)$

Because of relation (18) the only contribution to the integral (20) must be noted to the singularity of $\delta(\mathbf{r})$ at $\mathbf{r} = 0$ and by equation (25)

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

or

$$\int_{\tau} \delta(\mathbf{r})\, F(\mathbf{r})\, d\tau = F(0)$$

Hence $\delta(\mathbf{r})$ is a delta function. Returning to the original co-ordinate system by the substitution $\mathbf{r} \to \mathbf{r} + \mathbf{r}'$, we obtain equation (13) instead of (16).

The asymptotic form of $G(\mathbf{r}, \mathbf{r}')$ is easily found by refering to fig. 11.10.

If $|\mathbf{r}|$ is large compared to $|\mathbf{r}'|$, then it is clear that

$$|\mathbf{r} - \mathbf{r}'| = r - r' \cos\theta = r - r' \frac{\mathbf{r} \cdot \mathbf{r}'}{rr'}$$

$$d^3 r'$$

$$\nabla^2 G(r, r') = \delta^3(r - r')$$

$$= r - \frac{\mathbf{r}\cdot\mathbf{r}'}{\mathbf{r}}$$

$$|\mathbf{r}-\mathbf{r}'| \approx |\mathbf{r}| - \frac{\mathbf{r}'\cdot\mathbf{r}}{|\mathbf{r}|}$$

$$= r - \frac{\mathbf{r}'\cdot\mathbf{r}}{\mathbf{r}} \qquad \text{...(26)}$$

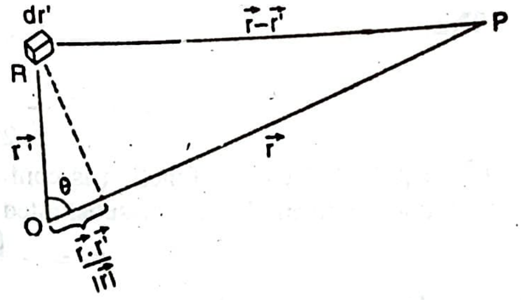


Fig. 11.10. The vectors r and r′

The error involved in this approximation can be made arbitrarily small by choosing $|\mathbf{r}|$ sufficiently large.

Substituting value of $|(\vec{r}-\mathbf{r}')|$ from equation (26) in (15), we get

$$\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(r)$$

Poisson's eqn
from EM.

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

$$= \frac{\exp\left[ik\left(r - \frac{\mathbf{r}'\cdot\mathbf{r}}{\mathbf{r}}\right)\right]}{\left(r - \frac{\mathbf{r}'\cdot\mathbf{r}}{\mathbf{r}}\right)}$$

$$= \frac{\exp\left[ik\left(r - \frac{\mathbf{r}'\cdot\mathbf{r}}{\mathbf{r}}\right)\right]}{r}\left[1 + \frac{\mathbf{r}'\cdot\mathbf{r}}{\mathbf{r}^2} + \dots\right]$$

Thus as $r \to \infty$, we obtain

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

$$e^{-ik\frac{r'\cdot r}{r}} \quad e^{\frac{ikr}{r}}$$

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

$$k = k'\frac{r}{r}$$

$$e^{-\left(\frac{ik' r}{r}\cdot\frac{r' \cdot r}{r}\right)}$$

$$e^{-ik'\cdot r'}$$

$$G(\mathbf{r},\mathbf{r}') \approx e^{-i\mathbf{k}'\cdot\mathbf{r}'}\cdot\frac{e^{ikr}}{r}. \qquad \text{...(27)}$$

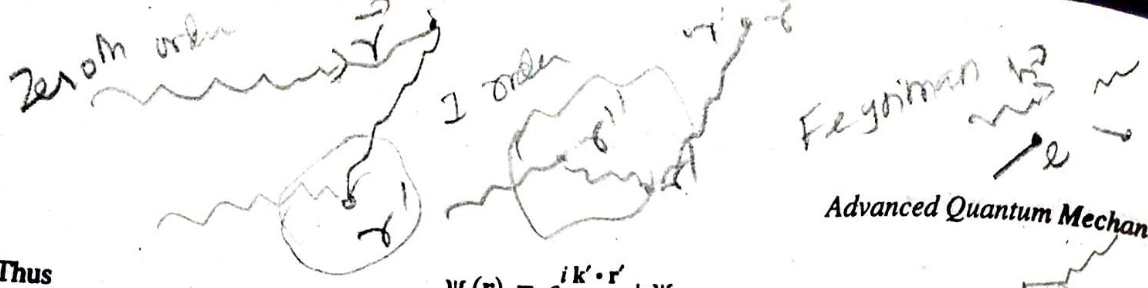
The first term in this expression depends upon the orientation of $\mathbf{k}'$ relative to vector $\mathbf{r}'$, *i.e.* it is of the form $f(\theta, \phi)$. Thus equation (27) represents the asymptotic form of Green's function and represents an outgoing wave. Thus the Green's function represents the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

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

from equation (8) and the value of $G(\mathbf{r},\mathbf{r}']$ from equation (15), equation (14) gives

$$\psi_s = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int V(\mathbf{r}')\,\psi(\mathbf{r}')\frac{e^{ik(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|}\,d\tau' \qquad \text{...(28)}$$

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



Thus

$$\psi(\mathbf{r}) = e^{i\mathbf{k}'\cdot\mathbf{r}'} + \psi_s$$

$$= e^{i\mathbf{k}'.\mathbf{r}'} - \frac{m}{2\pi\hbar^2}\int V(\mathbf{r}')\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}d\tau' \quad ...(29)$$

If the potential energy function is confied to a limited region of space, then the asymptotic form of Green's function form (27) can be substituted in equation (14) *viz.*

$$\psi_s = -\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau'$$

then, we obtain,

$$\underset{(r\to\infty)}{\psi_s} = -\frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-i\mathbf{k}'.\mathbf{r}'}V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau' \quad ...(30)$$

But

$$\psi_s = f(\theta,\phi)\frac{e^{ikr}}{r}$$

∴ Scattering amplitude $f(\theta, \phi)$

$$= -\frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau' \quad ...(31)$$

This yields for the *scattering cross-section*

$$\sigma(\theta,\phi) = |f(\theta,\phi)|^2 = \left(\frac{m}{2\pi\hbar^2}\right)^2\left|\int e^{-i\mathbf{k}'.\mathbf{r}'}V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau'\right|^2 \quad ...(32)$$

11·7. BORN APPROXIMATION

If the scattering takes place from the scattering centres which are localized but are weak such that the scattering does not take place at large distance from the scatterer and scattered wave is weak in amplitude, then Born approximation can be used to evaluate the scattering amplitude $f(\theta, \phi)$, and hence the differential cross section $\sigma(\theta, \phi) = |f(\theta, \phi)|^2$.

The Born approximation is applicable whenever potential function V is fairly small. The idea is simply that of successive approximations. *The Born approximation simply accounts neglecting the rescattering of the scattered waves* provided the scattered wave is small compared with the incident wave.

The total wave-function of the scattering problem with source point at $\mathbf{r}''$ is given by

$$\psi(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}'')\,V(\mathbf{r}'')\,\psi(\mathbf{r}'')\,d\tau'' \quad ...(33)$$

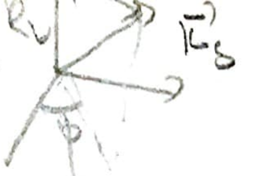
Replacing $\mathbf{r}$ by $\mathbf{r}'$ in above equation, we get

$$\psi(\mathbf{r}') = e^{i\mathbf{k}.\mathbf{r}'} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r}',\mathbf{r}'')\,V(\mathbf{r}'')\,\psi(\mathbf{r}'')\,d\tau''$$

Substituting this value of $\psi(\mathbf{r}')$ in the integral of equation representing the total wave-function with rce point at $\mathbf{r}'$ *viz.*

$$\psi(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\tau' \quad ...(34)$$

ve get,



$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\tau' + \left(\frac{m}{2\pi\hbar^2}\right)^2 \int\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,G(\mathbf{r}',\mathbf{r}'')\,V(\mathbf{r}'')\,d\tau''\,d\tau' \quad ...(35)$$

d^3r' d^3r' $k = 2k\sin\frac{\theta}{2}$

$+\int\int\int$ r', r''

$d^3r'\,d^3r''$

This equation obtained by the process of *iteration* is called the first iterated form of equation (34). This process can be repeated indefinitely resulting is an infinite (Neumann) series which can be expected to represent a solution provided the series converges. The series has the following meaning.

The first term $e^{i\mathbf{k}\cdot\mathbf{r}}$ represents the incident wave-function while the remaining terms correspond to scattered wave--function. The first term in the scattered wave represents single scattering of the incident wave exp $(i\mathbf{k}\cdot\mathbf{r}')$ by the interaction $V(\mathbf{r}')$ in the volume element $d\mathbf{r}'$. This produces a wave which travels from $\mathbf{r}'$ to the point of observation $\mathbf{r}$, and the total wave arising from single scattering is obtained by integration over the region in which the force is effective. In the second term, the incident wave $e^{i\mathbf{k}\cdot\mathbf{r}''}$ is scattered at the point $\mathbf{r}''$, $[V(\mathbf{r}'')\,e^{ik\cdot\mathbf{r}''}]$, travels to the point $\mathbf{r}'$, $[G(\mathbf{r}',\mathbf{r}'')\,V(\mathbf{r}'')\,e^{ik\cdot\mathbf{r}''}]$, where it is again scattered and the travels from $\mathbf{r}'$ to $\mathbf{r}$. The total effect of all such scattering is obtained by integration over $\mathbf{r}''$ and $\mathbf{r}'$. Accordingly *n*th term represents the contribution of waves which have been scattered *n*-times in the region of interaction before travelling to the point $\mathbf{r}$, where their total contribution is observed.

If the interaction is weak, so that the Neumann series will converge rapidly and that the scattered wave is not too large, it can be expected that the first term in the series will provide an approximation to ψ. This is called the first *Born approximation*

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\int G(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\tau' \quad ...(36)$$

The equation by cutting off the Neumann series at the *n*th term is called the *n*th *Born approximation.* Obviously *n*th Born approximation amounts to neglecting multiply scattered waves which have been scattered more than *n*-times by the interaction.

Substituting asymptotic form of Green's function from (27) in (36), we get

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,V(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\tau' \quad ...(37)$$

But

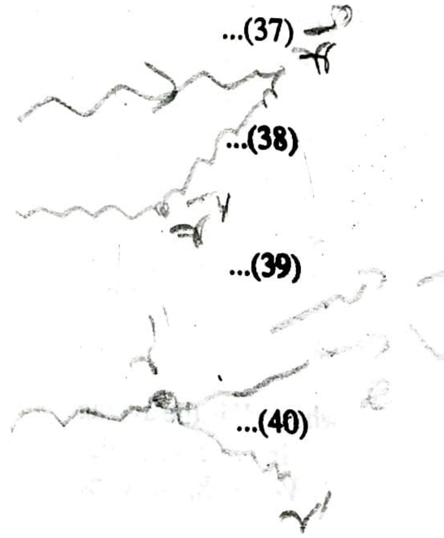
$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta,\phi)\frac{e^{ikr}}{r}. \quad ...(38)$$

Therefore according to *first Born approximation scattering amplitude*

$$f(\theta,\phi) \approx -\frac{m}{2\pi\hbar^2}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}\,V(\mathbf{r}')\,d\tau' \quad ...(39)$$

Hence the scattering cross-section

$$\sigma(\theta,\phi) = \left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}\,V(\mathbf{r}')\,d\tau'\right|^2 \quad ...(40)$$



11·8. CONDITION FOR VALIDITY OF BORN APPROXIMATION

The Born approximation will be valid only whenever the total wave function is not greatly different from the incident wave function $e^{i\mathbf{k}\cdot\mathbf{r}}$. It will, therefore be valid whenever the scattered wave $\psi_s(\mathbf{r})$ is small compared to $e^{i\mathbf{k}\cdot\mathbf{r}}$ in the region where $V(\mathbf{r})$ is large. In most cases both $V(\mathbf{r})$ and $\psi_s(\mathbf{r})$ are largest near the origin, so that a rough criterion for the validity of Born approximation is

$k = \sqrt{2mE}/\hbar$ $E = \frac{\hbar^2 k^2}{2m}$

Target pot. very weak

K.E of incident particle — very high

$$|\psi_S(\mathbf{r})|^2 < 1 \qquad \textit{for small values of } r. \qquad \text{...(41)}$$

In case in which $\psi_s(\mathbf{r})$ is small when r is small but large for intermediate values of r, such that $V(r)$ is still appreciable, we must carefully apply this criterion. Further it may happen that Born approximation holds when the criterion is not satisfied. *Having $\psi_S(\mathbf{r})$ small everywhere provides a sufficient condition for validity of the Born approximation; but not a necessary condition.*

If we recall that a change of potential acts like a change in refractive index in optics, we can derive another criterion for the validity of Born approximation. Consequently the change of potential produces a change in the phase of the wave function. The total wave function will not differ greatly from the initial wave function if the phase of the incident wave is not much altered as it passes through the region in which it is influenced by the perturbing potential. At great distance the magnitude of wave vector is

$k = \dfrac{\sqrt{(2mE)}}{\hbar}$ and near the centre of force it is $\dfrac{\sqrt{[2m(E-V)]}}{\hbar}$.

The change of phase due to the potential is then given by

$$\Delta\phi = \int_0^\infty \sqrt{\left(\frac{2m}{\hbar^2}\right)}[\sqrt{[(E-V)]} - \sqrt{E}]\,dr. \qquad \text{...(42)}$$

It this difference is small compared with unity, we may take it as an indication that the wave function is not very different from that in the absence of the potential. Thus the first order Born approximation will be valid if

$$|\Delta\phi| = \left|\sqrt{\left(\frac{2m}{\hbar^2}\right)}\int_0^\infty [\sqrt{(E-V)} - \sqrt{E}]\,dr\right| << 1 \qquad \text{...(43)}$$

If $V << E$ the criterion may be simplified by expressing equation (43) as a function of the ratio V/E and expanding the square root. Then the criterion becomes

$$\sqrt{\left(\frac{2mE}{\hbar^2}\right)}\left|\int_0^\infty \left\{\left(1-\frac{V}{E}\right)^{1/2} - 1\right\}dr\right| << 1 \qquad \text{...(44)}$$

or

$$\sqrt{\left(\frac{2mE}{\hbar^2}\right)}\left|\int_0^\infty \left\{\left(1-\frac{V}{2E}+ \ldots\ldots\right) - 1\right\}dr\right| << 1$$

or

$$\sqrt{\left(\frac{2mE}{\hbar^2}\right)}\left|\int_0^\infty \frac{V}{2E}\,dr\right| << 1 \quad \text{since } \frac{V}{E} << 1$$

or

$$\sqrt{\left(\frac{m}{2\hbar^2 E}\right)}\left|\int_0^\infty V\,dr\right| << 1$$

or

$$\sqrt{\left(\frac{m}{2\hbar^2 E}\right)}\bar{V}\bar{r} << 1 \qquad \text{...(45)}$$

where $\bar{V}$ is the average potential and $\bar{r}$ is the mean range.

In the case of the *scattering of high-energy particles by the square potential well* of radius a and depth V_0, $V_0 << E$, this condition gives

$$\sqrt{\left(\frac{m}{2\hbar^2 E}\right)}V_0 a < 1 \qquad \text{...(46a)}$$

or

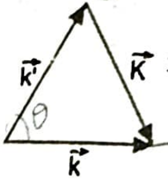
$$E << \frac{m}{2}\left(\frac{V_0 a}{\hbar}\right)^2 \qquad \text{...(46b)}$$

θ integral in spherical coordinate is V cos θ
$e^{ikr\cos\theta}$ length of k and length of r cosine θ times
V(r)

11·9. SCATTERING BY A SCREENED COULOMB POTENTIAL, RUTHERFORD'S SCATTERING FORMULA FROM BORN APPROXIMATION.

combining these 2 exp K

We know the scattering amplitude from Born approximation



$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int V(r')\, e^{i\mathbf{K}.\mathbf{r}'}\, d\tau' \qquad ...(1)$$

where

$$\mathbf{K} = \mathbf{k} - \mathbf{k}' \text{ (from 39)}$$

The integral is solved by taking polar angles θ, φ about the direction of **K**.

$$\int V(r')\, e^{i\mathbf{K}\cdot\mathbf{r}'}\, d\tau' = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} V(r')e^{iKr'\cos\theta}\, d\phi\, \sin\theta\, d\theta\, r'^2\, dr'$$

$$= 2\pi\int_0^{\infty}\int_0^{\pi} V(r')\, e^{iKr'\cos\theta}\sin\theta\, d\theta\, r'^2\, dr'$$

Let $\cos\theta = t,\ -\sin\theta\, d\theta = dt$

$$\int_0^{\pi} e^{-Kr'\cos\theta}\sin\theta\, d\theta = -\int_1^{-1} e^{iKr't}\, dt = \left[\frac{e^{iKr't}}{iKr'}\right]_{-1}^{+1} = \frac{e^{iKr'} - e^{-iKr'}}{iKr'}$$

∴

$$\int V(r')\, e^{i\mathbf{K}.\mathbf{r}'}\, d\tau' = \frac{2\pi}{iK}\int_0^{\infty} V(r')\{e^{iKr'} - e^{-iKr'}\}\, r'\, dr'$$

$$= \frac{4\pi}{K}\int_0^{\infty} V(r')\sin Kr'\, r'\, dr'.$$

$\int d\cos\theta\, e^{ikr\cos\theta} V(r)$ — $\frac{2\sin kr}{kr}$
angular integral is easily doable

volume integral $\int^{2\pi} \phi$
integrate w.r.t K

Then

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\cdot\frac{4\pi}{K}\int_0^{\infty} V(r')\sin Kr'\, r'\, dr'. \qquad ...(2)$$

We shall find the differential scattering cross-section when $V(r)$ is the screened Coulomb potential

$$V(r) = \frac{Zze^2}{4\pi\varepsilon_0 r}\, e^{-r/r_0} \text{ (S.I. system)} \qquad ...(3)$$

$\frac{Z_1 e\, z_2 e}{r} = \frac{z_1 z_2 e^2}{r}$

Ze and *ze* being the charges of target and scatterd particle respectively and r_0 being called the screening radius. On substituting the value of $V(r)$ in equation (2), we get

$$f(\theta) = -\frac{2m}{\hbar^2 K}\left(\frac{Zze^2}{4\pi\varepsilon_0}\right)\int_0^{\infty} r'\sin Kr'\,\frac{e^{-r'/r_0}}{r'}\, dr'$$

$$= -\frac{2m}{\hbar^2 K}\left(\frac{Zze^2}{4\pi\varepsilon_0}\right)\int_0^{\infty} e^{-r'/r_0}\sin Kr'\, dr'.$$

$f(\theta) = \frac{2m}{\hbar^2 k}\int_0^{\infty} r V(r) \sin kr\, dr$

$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$

But

$$\int_0^{\infty} e^{-r'/r_0}\sin Kr'\, dr' = \frac{Kr_0^2}{K^2 r_0^2 + 1}$$

∴

$$f(\theta) = -\frac{2m}{\hbar^2 K}\left(\frac{Zze^2}{4\pi\varepsilon_0}\right)\frac{Kr_0^2}{K^2 r_0^2 + 1}$$

$$= -\left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{K^2 + \frac{1}{r_0^2}}$$

Fourier transform is partially done
K = 2k sin θ/2

K magnitude of momentum or energy

d^3r can be written as
$d\tau = r^2 \sin\theta \, d\theta \, dr \, d\phi$ θ angle

But $\quad \mathbf{K} = \mathbf{k} - \mathbf{k}'$

$\mathbf{K}.\mathbf{K} = (\mathbf{k}-\mathbf{k}').(\mathbf{k}-\mathbf{k}')$

or $\quad \mathbf{K}^2 = \mathbf{k}^2 + \mathbf{k}'^2 - 2\mathbf{k}.\mathbf{k}'$

As $\quad k \approx k'$

$\therefore \quad K^2 = k^2 + k^2 - 2kk\cos\theta$

$= 2k^2(1-\cos\theta)$

$= 2k^2 \cdot 2\sin^2\frac{\theta}{2} = 4k^2\sin^2\frac{\theta}{2}$

$\therefore \quad K = 2k\sin\theta/2$

$\therefore$

$$f(\theta) = -\left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{4k^2\sin^2\frac{\theta}{2}+\frac{1}{r_0^2}} \quad ...(4)$$

$\therefore$

$$\sigma(\theta) = |f(\theta)|^2 = \left(\frac{2m\,Zze^2}{4\pi\varepsilon_0\hbar^2}\right)^2\frac{1}{\left(4k^2\sin^2\theta+\frac{1}{r_0^2}\right)^2}$$

For Coulomb Potential

As $r_0 \to \infty$, $V(r)$ becomes the ordinary Coulomb potential

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{Zze^2}{r}$$

Hence

$$f(\theta) = -\left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{4k^2\sin^2\theta/2}$$

and scattering cross-section

$$\sigma(\theta) = |f(\theta)|^2 = \left(\frac{2mzZe^2}{4\pi\varepsilon_0}\right)^2\frac{1}{(4\hbar^2k^2\sin^2\frac{1}{2}\theta)^2}.$$

But

$$\hbar k = p,$$

$\therefore$

$$\sigma(\theta) = \frac{m^2}{4p^4}\left(\frac{zZe^2}{4\pi\varepsilon_9}\right)^2\operatorname{cosec}^4\frac{\theta}{2}$$

Using $p^2 = 2mE$, we get

$\therefore$

$$\sigma(\theta) = \frac{1}{16E^2}\left(\frac{zZe^2}{4\pi\varepsilon_0}\right)^2\operatorname{cosec}^4\frac{\theta}{2}. \quad ...(5)$$

It is in agreement with the classical Rutherford's formula of α-scattering with Coulomb field of nuclei. The total cross-section calculated from (4) by integrating over all angles is

$$\sigma_{total} = \int_0^{\pi}\sigma(\theta)\,2\pi\sin\theta\,d\theta = \left(\frac{2mzZe^2}{4\pi\varepsilon_0\hbar^2}\right)^2\frac{4\pi r_0^4}{(4k^2r_0^2+1)^2}$$

Yukawa potential → It is the kind of modification of electromagnetic potential

$V(r) = -\frac{\beta}{r}e^{-\mu r}$ in the limit in which the photon would acquire a mass.

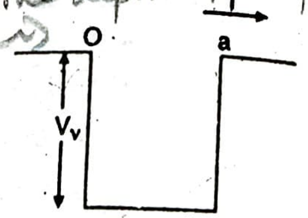
There was reflection and transmission when the energy was higher than the barrier and there was just reflection and a little exponential decay in the forbidden region if the energy was lower than the energy of the barrier. We also observed the packet analysis that a wave packet sent in would have a delay in coming back out. It doesn't come-

11·10. SCATTERING BY SQUARE-WELL POTENTIAL IN BORN APPROXIMATION

V_0 is the depth of the pot.

Let the square well potential be defined as

$$V(r) = -V_0 \text{ for } r<a$$
$$= 0 \text{ for } r>a$$



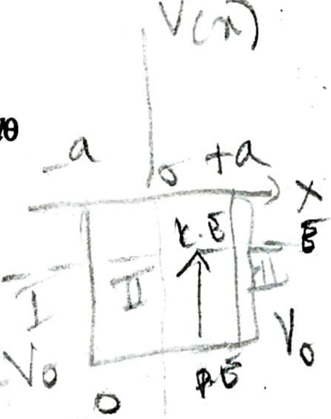
The scattering amplitude by Born approximation is given by

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int e^{i\mathbf{K}.\mathbf{r}'}\,V(r')\,d\tau'$$

Taking **K** as the polar axis of new set of cordinates, so that vector **r′** has rectangular components $r'\sin\theta\cos\phi,\ \ r'\sin\theta\sin\phi,\ \ r'\cos\theta$

$$\mathbf{K}.\mathbf{r}' = Kr'\cos\theta,\ d\tau' = r'^2\,dr'\sin\theta\,d\theta\,d\phi$$

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\int_0^{2\pi}d\phi\int_0^\pi e^{iKr'\cos\theta}\sin\theta\,d\theta$$



Putting $\cos\theta = t$ in last integral, we have

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr.\,2\pi.\int_{-1}^{+1}e^{ikr'\,t}\,dt$$

$$= -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\cdot\left[\frac{e^{iKr't}}{iKr'}\right]_{-1}^{+1}$$

$$= -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\cdot\left(\frac{e^{iKr'}-e^{-iKr'}}{iKr'}\right)$$

$$= -\frac{2m}{\hbar^2}\int_0^\infty\frac{\sin Kr'}{K}\cdot V(r')\,r'\,dr'$$

$= uv - \int u'v$

$v' = \sin kr$

$v = -\frac{\cos kr}{k}$

$V_0 > 0$

$V(x) = 0\ |x| > a$

$= -V_0\ |x| < a$

Substituting $V(r') = -V_0$ for $r<a$ and 0 for $r>a$

We get

$$f(\theta) = +\frac{2mV_0}{\hbar^2K}\int_0^a r'\sin Kr'\,dr'$$

$\frac{\sin kr}{k} + \int r\frac{\cos kr}{k}$

$\psi_I(x) = Ae^{\alpha x}$

$\alpha^2 = \frac{2mE}{\hbar^2},\ \alpha > 0$

Integrating by parts we get

$$f(\theta) = \frac{2mV_0}{\hbar^2K^2}\left\{\frac{\sin Ka}{K} - a\cos Ka\right\}$$

$+\frac{\sin kr}{k^2}$

∴ Scattering cross-section

$$\sigma(\theta) = |f(\theta)|^2$$

$$= \left(\frac{2mV_0}{\hbar^2K^2}\right)^2\left\{\frac{\sin Ka}{K} - a\cos Ka\right\}^2$$

$$= \left(\frac{2mV_0a^3}{\hbar^2}\right)^2 g(Ka)$$

$-\frac{a\cos ka}{k} + \frac{\sin ka}{k^2}$

$\psi_{III}(x) = Be^{-\alpha x}$

$\psi_{II}(x) = C\cos\beta x + D\sin\beta x$

$\beta^2 = \frac{2m(E+V_0)}{\hbar^2}$

$\beta > 0$

$-\frac{\cos kr}{k}$

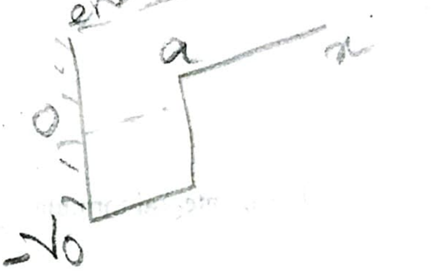
k for bound E < 0, something energy than 0 is bound, you have give some energy to put it at 0 energy and particle would escape.

out immediately and that's the property of those complex nos
that entered into the reflection coefficient. Those comp. nos. were a
phase that had an energy dependence, and when we analyze how

the wave packet is moving, there was a delay

We are producing localized energy eigenfunc here

where
$$g(Ka) = \left(\frac{\sin Ka - Ka\cos Ka}{(Ka)^3}\right)^2$$
or
$$g(x) = \left(\frac{\sin x - x\cos x}{x^3}\right)^2$$



Substituting $K = 2k\sin\frac{\theta}{2}$, we get
$$\sigma(\theta) = \left(\frac{2mV_0a^3}{\hbar^2}\right)^2 g\left(2ka\sin\frac{\theta}{2}\right)$$
This is required expression

The function $\frac{g(x)}{g(0)} = 9\,g(x)$ is 1 at $x = 0$ but falls fairly rapidly for large values of the argument approaching 0 at $x = 4{\cdot}0$ or $\theta = 180°$. Thus large angle scattering is not likely to take place.

11·11. SCATTERING BY AN EXPONENTIAL POTENTIAL

The exponential potential is of the form
$$V(r) = -V_0e^{-r/a}$$
where V_0 and a are constants which determine the strength and the range of the potential and negative sign shows that the potential function is attractive.
$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2}\int e^{i\mathbf{K}.\mathbf{r}'}V(r')\,d\tau'$$
Taking direction of **K** as polar axis of new set of coordinates, we have
$$\mathbf{K}\cdot\mathbf{r}' = Kr'\cos\theta'$$
and volume element $d\tau' = dr'\,r'\,d\theta'\,r'\sin\theta'\,d\phi'$
$$= r'^2\,dr'\sin\theta'\,d\theta'\,d\phi'.$$
we get
$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\int_0^{2\pi}d\phi'\int_0^\pi e^{iKr'\cos\theta'}\sin\theta'\,d\theta'$$
$$= -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\,2\pi\int_0^\pi e^{iKr'\cos\theta'}\sin\theta'\,d\theta'$$
Putting $\cos\theta' = p \Rightarrow -\sin\theta'\,d\theta' = dp$, we get
$$f(\theta) = -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\int_{-1}^{+1}e^{iKr'p}\,dp$$
$$= -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\left[\frac{e^{iKr'p}}{iKr'}\right]^{+1}$$
$$= -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\left[\frac{e^{iKr'} - e^{-iKr'}}{iKr'}\right]$$
$$= -\frac{m}{\hbar^2 iK}\int_0^\infty V(r')\,r'\,(e^{iKr'} - e^{-iKr'})\,dr'$$

what happens
if we send in a
wave? you're sending
in a particle.
will it get reflected
" " " transmitted?
what probabilities for
each

Substituting $V(r') = -\ V_0\, e^{-r'/a}$

$$f(\theta) = +\frac{mV_0}{\hbar^2\, iK}\int_0^\infty e^{-r'/a}\, r'\,(e^{iKr'} - e^{-iKr'})\, dr'$$

$$= \frac{mV_0}{\hbar^2\, iK}\int_0^\infty r'\left\{e^{-r'\left(\frac{1}{a} - iK\right)} - e^{-r'\left(\frac{1}{a} + iK\right)}\right\} dr'$$

Using integral formula

$$\int_0^\infty x^n e^{-\alpha x}\, dx = \frac{n\,!}{\alpha^{n+1}}, \quad \text{we get}$$

$$f(\theta) = \frac{mV_0}{\hbar^2\, iK}\left[\frac{1}{\left(\frac{1}{a} - iK\right)^2} - \frac{1}{\left(\frac{1}{a} + iK\right)^2}\right]$$

$$= \frac{mV_0}{\hbar^2\, iK}\left[\frac{\left(\frac{1}{a} + iK\right)^2 - \left(\frac{1}{a} - iK\right)^2}{\left(\frac{1}{a^2} + K^2\right)^2}\right]$$

$$= \frac{mV_0}{\hbar^2\, iK}\,\frac{(4\, iK/a)}{\left(\frac{1}{a^2} + K^2\right)^2}$$

$$= \frac{4m\, V_0\, a^3}{\hbar^2\,(1 + K^2 a^2)^2} \qquad \text{...(1)}$$

Sin 2x = Sin(x+x)

Sin x cos x + Sin x cos x = 2 sin x cos x

Sin 2α = 2 sin α cos α

But

$$K = 2k \sin\frac{\theta}{2} \qquad \text{...(2)}$$

∴

$$f(\theta) = \frac{4mV_0\, a^3}{\hbar^2\left(1 + 4k^2 a^2 \sin^2\frac{\theta}{2}\right)^2} \qquad \text{...(3)}$$

∴ Differential scattering cross-section

$$\sigma(\theta) = |\, f(\theta)\,|^2 = \frac{16m^2\, V_0^2\, a^6}{\hbar^4\left(1 + 4k^2 a^2 \sin^2\frac{\theta}{2}\right)^4} \qquad \text{...(4)}$$

sin θ dθ = 2 sin θ/2 cos θ/2

Sin 2θ = 2 sin θ cos θ

Sin 2θ/2 = 2 sin θ/2 cos

Total scattering cross-section

$$\sigma_{total} = \iint \sigma(\theta)\, \sin\theta\, d\theta\, d\phi$$

$$= \frac{16m^2 V_0^2 a^6}{\hbar^4}\int_0^\pi \frac{\sin\theta\, d\theta}{\left(1 + 4k^2 a^2 \sin^2\frac{\theta}{2}\right)^4}\int_0^{2\pi} d\phi$$

$$= \frac{16m^2 V_0^2\, a^6}{\hbar^4}\int_0^\pi \left(1 + 4k^2 a^2 \sin^2\frac{\theta}{2}\right)^{-4} \cdot 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\, d\theta\, .\, 2\pi$$

θ = θ/2

sin

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

$\frac{2a^2}{2a^2}$ 2×2 $\frac{2k^2}{2k^2}$

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

$$= \frac{16\,\pi m^2 V_0^2 a^4}{\hbar^4 k^2}\int_0^\pi \left(1+4k^2a^2\sin^2\frac{\theta}{2}\right)^{-4}\cdot 4k^2a^2\cdot 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cdot\left(\frac{1}{2}\,d\theta\right)$$

$$= -\frac{16\pi\, m^2 V_0^2 a^4}{3\hbar^4 k^2}\left[\left(1+4k^2a^2\sin^2\frac{\theta}{2}\right)^{-3}\right]_0^\pi,$$

$$= -\frac{16\pi\, m^2 V_0^2 a^4}{3\,\hbar^4 k^2}\left[(1+4k^2a^2)^{-3}-1\right]$$

$$= \frac{16}{3}\,\frac{\pi m^2 V_0^2 a^4}{\hbar^4 k^2}\left[1-\frac{1}{(1+4k^2a^2)^3}\right]$$

sin cosθ+C

$\frac{1}{(\ )^4}$

$2\sin\theta\cos\theta = \sin 2\theta$

$2\sin\frac{\theta}{2}\cos\frac{\theta}{2} = \sin 2\times\frac{\theta}{2} = \sin\theta$

sin π = 0

sin 0 =

Condition of validity of Born approximation is

$$|\psi_{sc}(0)|^2 = \left(\frac{m}{\hbar^2 k}\right)^2\left|\int_0^\infty V(r')\,(e^{2ikr'}-1)\,dr'\right|^2 << 1$$

$e^{\infty} = \infty$

$e^{-\infty} = 0$

Given $|V(r')| = V_0 e^{-r/a}$

$$\therefore \qquad |\psi_{sc}(0)|^2 = \left(\frac{m}{\hbar^2 k}\right)^2 V_0^2\left|\int_0^\infty e^{-r'/a}\,(e^{2ikr'}-1)\,dr'\right|^2 << 1$$

$$= \left(\frac{mV_0}{\hbar^2 k}\right)^2\left|\int_0^\infty \left(e^{(2ik-\frac{1}{a})r'} - e^{-r'/a}\right)dr'\right|^2 << 1$$

$$= \left(\frac{mV_0}{\hbar^2 k}\right)^2\left|\left\{\frac{e^{-\left(\frac{1}{a}-2ik\right)r'}}{\left(2ik-\frac{1}{a}\right)} - \frac{e^{-r'/a}}{\left(-\frac{1}{a}\right)}\right\}_0^\infty\right|^2 << 1$$

$[0 - (\frac{1}{\ }$

$e^{-\infty} = 0$

I term is 0

II term is 1

$$= \left(\frac{mV_0}{\hbar^2 k}\right)^2\left|-\left\{\frac{1}{\left(2ik-\frac{1}{a}\right)}+\frac{1}{\left(\frac{1}{a}\right)}\right\}\right|^2 << 1$$

$$= \left(\frac{mV_0}{\hbar^2 k}\right)^2\left|\frac{a}{2ika-1}+a\right|^2 << 1$$

$\frac{a + 2ika}{2ika-1}$

$i^2 = -1$

$$= \left(\frac{mV_0 a}{\hbar^2 k}\right)^2\left|\frac{2ika}{2ika-1}\right|^2 << 1$$

$$= \left(\frac{mV_0 a}{\hbar^2 k}\right)^2\frac{4k^2a^2}{1+4k^2a^2} << 1$$

or
$$\left(\frac{2mV_0 a^2}{\hbar^2}\right)^2\left(\frac{1}{1+4k^2a^2}\right) << 1$$

For low energy limit $ka << 1$

∴ $$|\psi_{sc}(0)|^2 = \left(\frac{2mV_0a^2}{\hbar^2}\right)^2 << 1$$

or $$\frac{2mV_0\,a^2}{\hbar^2} << 1$$

For high energy limit $ka >> 1$

$$1 + 4k^2a^2 \approx 4k^2a^2$$

$$|\psi_{sc}(0)|^2 = \left(\frac{2mV_0a^2}{\hbar^2}\right)^2 \cdot \frac{1}{4k^2a^2} << 1$$

or $$|\psi_{sc}(0)| = \frac{mV_0a}{\hbar^2 k} << 1.$$

11·12. SCATTERING BY A GAUSSIAN POTENTIAL

The Gaussian potential is given by

$$V(r) = -\,V_0\,e^{-r^2/a^2}$$

where V_0 and a are constants which determine the strength and the range of potential; negative sign shows that the potential is attractive.

The scattering amplitude in Born approximation is

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2}\int e^{i\mathbf{K}\cdot\mathbf{r}'}\,V(r')\,d\tau'$$

Taking direction of **K** as polar axis of new set of coordinates, we have

$$\mathbf{K}\cdot\mathbf{r}' = Kr'\cos\theta' \text{ and } d\tau' = r'^2\sin\theta'\,dr'\,d\theta'\,d\phi'\,;$$

So $$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2}\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{iKr'\cos\theta'}\,V(r')\,r'^2\sin\theta'\,dr'\,d\theta'\,d\phi'$$

$$= -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\int_0^\pi e^{iKr'\cos\theta'}\sin\theta'\,d\theta'\int_0^{2\pi} d\theta$$

$$= -\frac{m}{2\pi\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\int_{-1}^{+1} e^{iKr'p}\,dp\,.\,(2\pi)$$

$$= -\frac{m}{\hbar^2}\int_0^\infty V(r')\,r'^2\,dr'\left\{\frac{e^{iKr'p}}{iKr'}\right\}_{-1}^{+1}$$

$$= -\frac{m}{\hbar^2 iK}\int_0^\infty V(r')\,r'\,dr'\left\{\frac{e^{iKr'}\;e^{-iKr'}}{iKr}\right\}$$

Substituting $$V(r') = -\,V_0\,e^{-r'^2/a^2},$$ we get

$$f(\theta, \phi) = \frac{mV_0}{\hbar^2 iK}\int_0^\infty e^{-r'^2/a^2}\,r'\,(e^{iKr'} - e^{-iKr'})\,dr'$$

is an even function of r as in case of
Gaussian potential, the scattering amp. can be written as

If we replace r' by $-r'$, the integrand remains unchanged *i.e.* integrand is even function of r; hence we may write

$$f(\theta,\phi) = \frac{mV_0}{\hbar^2 iK}\int_{-\infty}^{+\infty} e^{-r'^2/a^2}\, r'\, e^{iKr'}\, dr'$$

$$= \frac{mV_0}{\hbar^2 iK}\int_{-\infty}^{+\infty} r'\, e^{-\left(\frac{r'}{a}-\frac{iKa}{2}\right)^2}\cdot e^{-K^2a^2/4}\, dr' \qquad \text{...(2)}$$

$\int_{-\infty}^{\infty} dx\, e^{ik_x x-(x/a)^2}$

$\int_{-\infty}^{\infty} dy\, e^{ik_y y-(y/a)^2}$

dz $e^{-k^2 r_0^2/4}\, dr'$

Substituting $\frac{r'}{a} - \frac{iKa}{2} = t$

or

$\frac{dr'}{a} = dt$

$r' = a(t + iKa/2)$

$dr' = a\,dt$

$dr' = a\,dt$

$$r' = a\left(t + \frac{iKa}{2}\right)$$

$$\Rightarrow dr' = a\,dt$$

$$f(\theta,\phi) = \frac{mV_0}{\hbar^2 iK}\int_{-\infty}^{+\infty} a\left(t+\frac{iKa}{2}\right) e^{-t^2}\, e^{-K^2a^2/4}\, a\,dt$$

$$= \frac{mV_0 a^2}{\hbar^2 iK}\, e^{-K^2a^2/4}\left[\int_{-\infty}^{+\infty} t\, e^{-t^2}\, dt + \frac{iKa}{2}\int_{-\infty}^{+\infty} e^{-t^2}\, dt\right]$$

The first integral on R.H.S. vanishes as integrand is an odd function of variable t, while

$$\int_{-\infty}^{+\infty} e^{-t^2}\, dt = \sqrt{\pi}$$

$\therefore$

$$f(\theta,\phi) = \frac{mV_0 a^2}{\hbar^2 iK}\, e^{-K^2a^2/4}\left[0 + \frac{iKa}{2}\cdot\sqrt{\pi}\right]$$

$$= \frac{mV_0 a^3\sqrt{\pi}}{2\hbar^2}\, e^{-K^2a^2/4} \qquad \text{...(3)}$$

As

$$K = 2k\sin\frac{\theta}{2} \qquad \text{...(4)}$$

$\therefore$

$$f(0,\phi) = \frac{mV_0 a^3\sqrt{\pi}}{2\hbar^2}\, e^{-k^2a^2\sin^2(\theta/2)}$$

$\therefore$ Differential scattering cross-section $\sigma(\theta,\phi) = \dfrac{m^2V_0^2a^6\pi}{4\hbar^2}\, e^{-2k^2a^2\sin^2(\theta/2)}$ ...(5)

Condition of validity of Born approximation :

It is given by

$$|\psi_{sc}(0)| = \frac{m}{\hbar^2 k}\left|\int_0^{\infty} V(r)\,(e^{2ikr}-1)\,dr\right| << 1 \qquad \text{...(6)}$$

For low energy $ka << 1$, being range of potential so we may write

$$e^{2ikr} - 1 \approx 1 = 2ikr - 1 \approx 2ikr$$

$\therefore$

$$|\psi_{sc}(0)| = \frac{2m}{\hbar^2}\left|\int_0^{\infty} V(r)\,dr\right| << r$$

For Gaussian potential $V(r) = -V_0 e^{-r^2/a^2}$

$$\therefore \qquad |\psi_{sc}(0)| = \frac{2mV_0}{\hbar^2}\left|\int_0^\infty e^{-r^2/a^2}\,dr\right| << 1$$

Substituting $\frac{r^2}{a^2} = t$, we get $r\,dr = \frac{a^2 dt}{2}$

$$\int_0^\infty e^{-r^2/a^2}\,r\,dr = \frac{a^2}{2}\int_0^\infty e^{-t}\,dt = \frac{a^2}{2}\left[\frac{e^{-t}}{-1}\right]_0^\infty = \frac{a^2}{2}$$

$$\therefore \qquad |\psi_{sc}(0)| = \frac{2mV_0}{\hbar^2}\frac{a^2}{2} << 1 \Rightarrow \frac{mV_0 a^2}{\hbar^2} << 1 \qquad ...(7)$$

This condition is satisfied if the strength of potential V_0 is negligibly small. Thus for low energies Born approximation holds if scattering potential is weak.

For high energy $ka >> 1$, then the contribution due is exponential term may be neglected, so that equation (6) becomes

$$\frac{m}{\hbar^2 k}\left|\int_0^\infty V(r)\,dr\right| << 1 \qquad ...(8)$$

For Gaussian potential $V(r) = -V_0 e^{-r^2/a^2}$, this becomes

$$\frac{mV_0}{\hbar^2 k}\left|\int_0^\infty e^{-r^2/a^2}\,dr\right| << 1$$

or

$$\frac{mV_0}{\hbar k}\left(\frac{a\sqrt{\pi}}{2}\right) << 1 \quad \text{or} \quad \frac{mV_0 a}{2\hbar k}\sqrt{\pi} << 1 \qquad ...(9)$$

Thus for high energy Born approximation holds if incident energy is high and the scattering potential is weak.

11·13. ATOMIC SCATTERING OF ELECTRONS :

To good approximation the scattering of fast electrons by a an atom of atomic number Z can be represented as the scattering in a spherically symmetric field $V(r)$ given by

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} + \frac{1}{4\pi\varepsilon_0}Ze^2\int\frac{\rho(\mathbf{r}')\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \qquad ...(1)$$

where $\mathbf{r}$ is the position vector of the scattered electron and $\rho(\mathbf{r}')$ is the particle density of atomic electrons at the point $\mathbf{r}'$.

The total charge density (nuclear and electronic) of the atom, for convenience, may be expressed as

$$\rho_t(\mathbf{r}') = \delta(\mathbf{r}') - \rho(\mathbf{r}') \qquad ...(2)$$

en

$$V(r) = -\frac{m}{4\pi\varepsilon_0}Ze^2\int\frac{\rho_t(\mathbf{r}')\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \qquad ...(3)$$

The scattering amplitude $f(\theta, \phi)$ at position $\mathbf{r}$ is given by

$$f(\mathbf{k}, \mathbf{k}') = f(\theta, \phi) = -\frac{m}{4\pi\hbar^2}\int e^{i\mathbf{K}.\mathbf{r}}\,V(r)\,d\tau \qquad ...(4)$$

Substituting (3) in (4), are get

The method of Partial wave analysis is applied in Cases where method of Born approx. fails. It is applicable to spherically symmetric potentials. For spherically symmetric potential ang. mom. of scattered particle is a const of motion. When there exists a short range potential only a few eigenfns. of small ang. momenta are affected by this. If the range

$$\left.\begin{aligned}(\mathbf{k}'-\mathbf{k})\cdot\mathbf{a} &= 2\pi\,\alpha\\ (\mathbf{k}'-\mathbf{k})\cdot\mathbf{b} &= 2\pi\,\beta\\ (\mathbf{k}'-\mathbf{k})\cdot\mathbf{c} &= 2\pi\,\gamma\end{aligned}\right\}\qquad\ldots(4)$$

where α, β and γ are integers Equations (4) represent a set of Bragg equation for reflection from a crystal. All real crystals possess a finite number of atoms, however large this number may be. When equation (3) is solved for finite number of terms, we obtain a function that here large peaks at Bragg angles. The width of peak is inversely proportional to the size of the crystal. The function $F(\mathbf{K})$ is called the atomic form factor. It determines the strength of reflection of electrons in any allowed direction. (*i.e.* height of peaks in different orders).

11·15. PARTIAL WAVE ANALYSIS

→ leads to low energy approx.

The working out of the higher perturbation theory is very tedious and when the Born approximation breaks down, it is usual to tackle the scattering and collision problems, by a quite different method known as the *method of partial waves. The method of partial waves is mainly applicable to spherically symmetric potential and consists of the expansion of the wavefunction as a series of spherical harmonics multiplied by a radial wave-function as in the case of hydrogen atom.* This method was originally applied by Rayleigh to the scattering of sound waves and later by Faxen and Holtsmark to the scattering of Schroedinger wave. To discuss scattering we first show that a plane wave is equivalent to a number of spherical waves.

Plane Wave as the sum of spherical waves

The plane wave travelling along z axis given by

$$\psi = e^{ikz}$$

In spherical coordinates (r, θ, ϕ) with $z = r\cos\theta$, it may be expressed as

$$\begin{aligned}\psi &= R(r)\,\Theta(\theta)\,\Phi(\phi)\\ &= e^{ikr\cos\theta}\end{aligned}\qquad\ldots(1)$$

This is a solution of spherical wave equation

$$\nabla^2\psi + k^2\psi = 0,\quad k^2 = \frac{2\mu E}{\hbar^2}\qquad\ldots(2)$$

where μ is reduced mass of particle.

Substituting $\psi = R\Theta\Phi$, we note that R, Θ, Φ are the solutions of separated equations

Two independent solns of

$$r^2\frac{d^2R}{dr^2}+2r\frac{dR}{dr}+k^2r^2-l(l+1)R=0$$

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left\{k^2-\frac{l(l+1)}{r^2}\right\}R=0\qquad\ldots(3)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left\{l(l+1)-\frac{m^2}{\sin^2\theta}\right\}\Theta = 0\qquad\ldots(4)$$

and

$$\frac{d^2\Phi}{d\phi^2}+m^2\Phi = 0\qquad\ldots(5)$$

Every surface of constant phase in the plane wave is symmetrical about the direction of propagation (*i.e.* z axis). Hence $\Phi(\phi) =$ constant. * The wave fn. is independent of angle ϕ in case of

This means that equation (5) has the only solution if $m = 0$. It follows that the solution of (4) are Legendre polynomials $P_l^{(m=0)}(\cos\theta) = P_l(\cos\theta)$ Since the Legendre functions form a complete set in θ space

Thus

$$\psi = R(r)\,P_l(\cos\theta)\qquad\ldots(6)$$

For $l = 0$, equation (3) can be expressed as

of potential is a then in partial wave analysis Problems the Scattering of Particles with ang. momenta satisfying the condition $l \le ka$ is considered. *

Eqns ② & ⑥ can be combined to give

$r^2 \frac{d^2R}{dr^2} + 2r \frac{dR}{dr} + [k^2r^2 - l(l+1)]R_l = 0$

$$\frac{d^2}{dr^2}(r R_0) + k^2 (r R_0) = 0 \qquad \text{...(7)}$$

It has the solutions of the form

$$R_0 = A_0 \frac{\sin kr}{kr} = A_0 j_0 (kr) \qquad \text{...(8)}$$

where $j_0 (kr)$ is the spherical Bessel's function for $l = 0$.

The case $l = 0$ has strong analogy between equation (3) and Bessel's equation. This suggests that if A_l are arbitrary constants, then the general solution of (2), having axial symmetry, may be expressed as

$$\psi = e^{ikz} = e^{ikr\cos\theta} = \sum_l R_l (r) P_l (\cos\theta)$$

$$= \sum_l A_l j_l (kr) P_l (\cos\theta) \qquad \text{...(9)}$$

For large values of (kr), the asymptotic form of $j_l (kr)$ is

$$j_l (kr) \xrightarrow[kr>>1]{} \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right) \qquad \text{...(10)}$$

The value of A_l may be obtained if we multiply both sides of (9) by $P_l (\cos\theta)$ and integrate over all θ Putting $\cos\theta = x$ in (9) and using orthonormality conditions of $P_l (x)$ $(m = 0)$, we get

$$\int_{-1}^{+1} e^{ikrx} P_l (x)\, dx = \sum_m A_m j_m (kr) \int_{-1}^{+1} P_l (x) P_m (x)\, dx$$

$$= \sum_m A_m j_m (kr) \cdot \frac{2}{2m+1} \delta_{ml}$$

$$= \frac{2}{2l+1} A_l j_l (kr)$$

$nx = \frac{e^{ix} - e^{-ix}}{2i}$

i.e. $$\frac{2}{2l+1} A_l j_l (kr) = \frac{1}{ikr}\left[e^{ikrx} P_l (x)\right]_{-1}^{+1} - \left[\frac{1}{ikr}\int_{-1}^{+1} e^{ikrx} \cdot P_l' (x)\, dx\right]$$

The second term of R.H.S. in above equation is the order of $1/r^2$ for large values of r and so negligble. Therefore for large values of r, using $P_l (1) = 1$, $P_l (-1) = (-1)^l = e^{il\pi}$, we get

$$\frac{2}{2l+1} A_l \cdot \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right) \approx \frac{1}{ikr}\left[e^{ikr} - e^{il\pi} \cdot e^{-ikr}\right]$$

$$= \frac{1}{ikr} e^{il\pi/2}\left[e^{i\left(kr - \frac{l\pi}{2}\right)} - e^{-i\left(kr - \frac{l\pi}{2}\right)}\right]$$

$$= 2i^l \cdot \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right)$$

$e^{il\pi/2} = i^l$

$e^{-il\pi/2} = (\pm i)^l$

This implies

$$A_l = (2l+1)\, i^l \qquad \text{...(11)}$$

Hence equation (9) gives

$$\psi = e^{ikz} = \sum_{l=0}^{\infty} (2l+1)\, i^l j_l (kr) P_l (\cos\theta) \qquad \text{...(12)}$$

ere the asymptotic form of $j_l (kr)$ is given by equation (10). Equation (12) suggests that a ***plane wave is ivalent to the superposition of a number of spherical waves.***

The above expn. tells us how to decompose the incident plane-wave into a series of spherical waves. these waves are usually termed Partial waves.

To consider the **scattering problem** let us consider a plane wave incident along z-axis in a region having interaction potential function $V(r)$. Then total wave function may be expressed as

$$\psi(r) = \underbrace{e^{ikz}}_{\substack{\text{incident}\\ \text{wave}}} + \underbrace{f(\theta)\frac{e^{ikr}}{r}}_{\substack{\text{scattered}\\ \text{wave}}} \qquad \text{...(13)}$$

It is a solution of three dimensional Schroedingers equation

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2}[E - V(r)]\,\psi = 0\,. \qquad \text{..(14)}$$

The solution of this may be expressed as

$$\psi(r) = \sum_{l=0}^{\infty} R_l(r)\, Y_{lo}^{(\theta)} \qquad \text{...(15)}$$

This is a superposition of a number of waves. Each term in above equation is called a **partial wave,** corresponding to a particular value of l. the function $R_l(r)$ are called radial wave function.

Let us substitute

$$\frac{2\mu E}{\hbar^2} = k^2 \text{ and } \frac{2\mu V(r)}{\hbar^2} = U(r) \qquad \text{...(16)}$$

Then equation (14) becomes

$$\nabla^2 \psi + [k^2 - U(r)]\,\psi = 0 \qquad \text{...(17)}$$

As there is symmetry about polar axis *i.e.* z-axis ($m = 0$) and potential energy function does not involve ϕ, the solution of (17) may be expressed as

$$\psi(r, \theta, \phi) = \psi(r, \theta) = \sum_l R_l(r)\, P_l(\cos\theta) \qquad \text{...(18)}$$

Setting

$$\chi_l = r R_l(r) \qquad \text{...(19)}$$

This becomes

$$\psi(r, \theta) = \sum_l r^{-1} \chi_l(r)\, P_l(\cos\theta)\,. \qquad \text{...(20)}$$

where $\chi_l(r)$ satisfies the equation

$$\frac{d^2\chi_l}{dr^2} + \left[k^2 - U(r) - \frac{l(l+1)}{r^2}\right]\chi_l = 0 \qquad \text{...(21)}$$

In order to find the general nature of asymptotic behaviour of this equation consider r to be so large tha U and l terms in eq. (21) may be ignored, so (21) becomes

$$\frac{d^2\chi_l}{dr^2} + k^2\chi_l = 0. \qquad \text{...(22}$$

or

$$\chi_l = e^{\pm ikr} \qquad \text{...(2}$$

which gives radial wave only.

For better approximation, we define a distance "a" such that when $r > a$, $V(r) = 0$ and wh $r < a$; $V(r)$ is appreciably finite. Then equation (21) becomes

$$\frac{d^2\chi_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2}\right]\chi_l = 0 \qquad \text{...(}$$

$\cos(\pi/2 + \theta) = -\sin\theta$

$\cos(-\theta) = \cos\theta$

$\cos(x - \pi/2) =$

$\cos(\pi/2 - x) = \sin x$

This is spherical Bessel equation whose solution is given by

$$\chi_l = A\sqrt{(kr)}\, J_{(l+1/2)} + B\sqrt{(kr)}\, J_{-l-1/2} \text{ if } l \neq 0 \text{ and } r \neq \infty$$

and

$$J_{l+1/2} = \left(\frac{2kr}{\pi}\right)^{1/2} J_l(kr)$$

$$J_{-l-1/2} = (-)^{l+1}\left(\frac{2kr}{\pi}\right)^{1/2} \eta_l(kr),$$

where

$$j_l(kr) = \frac{1}{kr}\cos\left\{kr - (l+1)\frac{\pi}{2}\right\}$$

$\cos\theta$

$$= \lim_{kr\to\infty} \frac{1}{kr}\sin\left(kr - \frac{l\pi}{2}\right)$$

$$\eta(kr) = \lim_{kr\to\infty} \frac{1}{kr}\sin\left\{kr - \frac{(l+1)\pi}{2}\right\}$$

Then

$$\chi_l = A' r j_l(kr) + B' r \eta_1(kr), \qquad \text{...(24)}$$

at

$$\frac{\chi_1}{r} = R_l(r) = A' j_l(kr) + B' \eta_l(kr)$$

where A' and B' are new amplitudes which deviate from original amplitudes A and B. Let us take δ as phase angle between these amplitudes and put

$\sin(x - \pi/2) = -\cos x$

$$A' = A_l \cos\delta_l \quad \text{and} \quad B' = -A_l \sin\delta_l$$

or

$$\tan\delta_1 = -\frac{B'}{A'}.$$

So

$$R_l(r) = \frac{A_l}{kr}\left[\cos\delta_1 \sin\left(kr - \frac{l\pi}{2}\right) - \sin\delta_1 \sin\left\{kr - (l+1)\frac{\pi}{2}\right\}\right]$$

$$= \frac{A_l}{kr}\left[\cos\delta_l \sin\left(kr - \frac{l\pi}{2}\right) + \sin\delta_1 \cos\left(kr - \frac{l\pi}{2}\right)\right],$$

or

$$R_l(r) = \frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) \qquad \text{...(25)}$$

In this equation δ_l is called the phase shift of the **partial wave** caused by scattering potential $U(r)$. In view of this equation (18) becomes

$$\psi(r, \theta) = \sum_l \frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) P_l(\cos\theta)$$

$$= \sum_l \frac{A_l}{kr}\left\{\frac{e^{i\left(kr - \frac{l\pi}{2} + \delta_l\right)} - e^{-i\left(kr - \frac{l\pi}{2} + \delta_l\right)}}{2i}\right\} \times P_l(\cos\theta) \qquad \text{...(26)}$$

This equation is identical with asymptotic form of equation (13) *i.e.*

$$\psi = e^{ikz} + f(\theta)\frac{e^{ikr}}{r}$$

$$= \sum_l (2l+1)\, i^l \cdot \frac{1}{kr}\sin\left(kr - \frac{l\pi}{2}\right) P_l(\cos\theta) + f(\theta)\frac{e^{ikr}}{r}$$

i.e =) free particle $\delta_l = 0$

$$= \sum_l (2l+1)\, i^l \cdot \frac{1}{kr}\left(\frac{e^{i\left(kr - \frac{l\pi}{2}\right)} - e^{-i\left(kr - \frac{l\pi}{2}\right)}}{2i}\right\} P_l(\cos\theta) + r^{-1} f(\theta)\, e^{ikr} \qquad \text{...(27)}$$

sin(A−B)
= sin x cos π/2 − cos x sin π/2
0 − cos x
= − cos x

As equations (26) and (27) are the same, therefore comparing coefficients of e^{ikr} and e^{-ikr} from both equation, we get

$$\sum_l A_l \frac{e^{i\left(-\frac{l\pi}{2}+\delta_l\right)}}{2ikr} P_l(\cos\theta) = \sum_l \frac{(2l+1)\, i^l e^{-il\pi/2}}{2ikr} \cdot P_l(\cos\theta) + r^{-1}\cdot f(\theta) \quad \text{...(28)}$$

and

$$\sum_l A_l e^{-i\left(-\frac{l\pi}{2}+\delta_l\right)} \times P_l(\cos\theta) = \sum_l (2l+1)\, i^l e^{il\pi/2} \cdot P_l(\cos\theta) \quad \text{...(29)}$$

Equation (29) suggests that

$$A_l = (2l+1)\, i^l e^{i\delta_l} \quad \text{...(30)}$$

Substituting this value of A_l in (28) we get

$$\sum_l \frac{(2l+1)\, l^l e^{i\left(-\frac{l\pi}{2}+\delta_l\right)}}{2i\,kr} P_l(\cos\theta) = \sum_l \frac{(2l+1)\, i^l e^{-il\pi/2}}{2i\,kr} P_l(\cos\theta) + \frac{1}{r} f(\theta)$$

As $i^l = e^{il\pi/2}$, we get

$$f(\theta) = (2ik)^{-1} \sum_{l=0}^{\infty} (2l+1)\left(e^{2i\delta_l}-1\right) P_l(\cos\theta) \quad \text{...(31a)}$$

$$= \frac{1}{k}\sum_{l=0}^{\infty} (2l+1)\, e^{i\delta_l}\left(\frac{e^{i\delta_l}-e^{-i\delta_l}}{2i}\right) P_l(\cos\theta)$$

$$= \frac{1}{k}\sum_{l=0}^{\infty} (2l+1)\, e^{i\delta_l}\left(\frac{e^{i\delta_l}-e^{-i\delta_l}}{2i}\right) P_l(\cos\theta)$$

$$= \frac{1}{k}\sum_{l=0}^{\infty} (2l+1)\, e^{i\delta_l} \sin\delta_l\, P_l(\cos\theta) \quad \text{...(31b)}$$

This formula was first given by Fexen and Holtsmark and is used quite often.
Hence differential scattering cross-section,

$$\sigma(\theta) = |f(\theta)|^2 = \frac{1}{k^2}\left|\sum_{l=0}^{\infty} (2l+1)\, P_l(\cos\theta)\, e^{i\delta_l}\sin\delta_l\right|^2 \quad \text{...(32)}$$

The total elastic cross-section is the integral of equation (32) over the sphere, *i.e.*

$$\sigma_{total} = 2\pi \int_0^{\pi} \sigma(\theta)\sin\theta\, d\theta$$

$$= \frac{4\pi}{k^2}\sum_{l=0}^{\infty} (2l+1)\sin^2\delta_l \quad \text{...(33)}$$

since $\int |P_l(\cos\theta)|^2 \sin\theta\, d\theta = \frac{2}{(2l+1)}$

Here δ_l the phase shift of lth partial wave is unknown parameter and is to be evaluated.

(a) Optical Theorem :

It may be pointed out that the scattering amplitude $f(\theta)$ jis complex.

For $\theta = 0$, $P_l(\cos\theta) = P_l(\cos 0°) = P_l(1) = 1$ for all values of l.

Then equation (31) for $\theta = 0$ gives

$$f(0) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\,e^{i\delta_l}\sin\delta_l\,P_l(\cos 0)$$

$$= \frac{1}{k}\sum_{l}(2l+1)\,e^{i\delta_l}\sin\delta_l$$

and so

$$I_m f(0) = \frac{1}{k}\sum_{l}(2l+1)\sin^2\delta_l$$

where $I_m f(0)$ denotes thue imaginary part of $f(0)$ or the coefficient of i in $f(0)$.

∴ Equation (33) for total elastic cross-section gives

$$\sigma_{total} = \frac{4\pi}{k}I_m f(0) \qquad \text{...(34)}$$

This relation is a special case of a more general relation (including absorption) called the **optical theorem.** It relates the imaginary part of the forward scattering amplitude (*i.e.* at $\theta = 0°$) to the total scattering cross-section.

(b) Phase Shifts :

We know that total scattering cross-section is given by equation (33) which is cross-section of lth partial wave and δ_l is the phase shift of the l th partial wave.

The scattering cross section vanishes for $\delta_l = 0$ or $180°$ and the cross-section is maximum if the value of $\delta_l = \pm\frac{\pi}{2}, \pm\frac{3\pi}{2}$ etc.

According to equation (25), we have

$$R(r) = \lim_{r\to\infty}\frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)$$

It comes from $R(r) \to A\,j_l(kr)$

So δ_l is the difference in phase between the asympotic form of the actual radial function $R(r)$ and the radial function $j_l(kr)$ in the absence of scattering potential *i.e.*, $V = 0$. $j_l(kr)$ will be maximum when $r \approx l/k$ hence for the value of r (we choose "a") $r \approx a \approx l/k$ we get higher phase difference (since V will vanish beyond 'a' *i.e.* $r > a$).

Small Phase Shift :

The phase shift will be very small if $a << l/k$. Thus the summation $\sum_{l=0}^{\infty}$ involves thue summation of few terms such as $\sum_{l=0}^{l=ak}$.

Calculation of δ_l : δ_l is calculated by applying boundary condition for the continuity of R_l at $r = a$ in he region $r < a$ and $r > a$

$$\left(\frac{1}{R_l}\frac{dR_l}{dr}\right)_{r<a}\Bigg|_{\text{at } r=a} = \left(\frac{1}{R_l}\frac{dR_l}{dr}\right)_{r>a}\Bigg|_{\text{at } r=a}$$

But $R_l = A_l [\cos \delta_l j_i (kr) - \sin \delta_l \eta_l (kr)]$

$$\therefore \qquad \left(\frac{1}{R_l} \frac{dR_l (r)}{dr} \right)_{r>a} \Bigg|_{\text{at } r=a} = k \left[\frac{\cos \delta_l j_l' (ka) - \sin \delta_l n_l' (ka)}{\cos \delta_l j_l (ka) - \sin \delta_l \eta_l (ka)} \right] \Bigg|_{r>a}$$

Let

$$\frac{1}{R_l} \frac{dR_l}{dr}_{r>a} \Bigg|_{\text{at } r=a} = \gamma_l.$$

So

$$\gamma_l = k \frac{[j_l' (ka) - \tan \delta_l \eta_l' (ka)]}{j_l (ka) - \tan \delta_l \eta_l (ka)}$$

or

$$\tan \delta_l = \frac{kj_l' (ka) - \gamma_l j_l (ka)}{k\eta_l' (ka) - \gamma_l \eta_l (ka)} \qquad \text{...(35)}$$

where

$$j_l' (ka) = j_{l-1} (ka) - \frac{l+1}{ka} j_l (ka),$$

and

$$\eta'_l (ka) = \eta_{l-1} (ka) - \frac{l+1}{ka} \eta_l (ka).$$

Here γ_l is the ratio of slope to value of the interior wavefunction. Equation (35) can be used at once to obtain an approximate expression for δ_l when l is large and δ_l is expected to be small. In this case γ_l will differ little from the ratio of slope to value of the solution in the absence of a scattering potential, so that we put

$$\gamma_l = k \left[\frac{j'_l (ka)}{j_l (ka)} + \varepsilon_l \right]$$

as

$$| \varepsilon_l | < \left| \frac{j'_l (ka)}{j_l (ka)} \right| \qquad \text{...(36)}$$

Equation (35) can be written by changing j'_l into j_l so that

$$\tan \delta_l = \frac{\varepsilon_l (ka)^2 j_l^2 (ka)}{\varepsilon_l (ka)^2 j_l (ka) \eta_l (ka) - 1} \qquad \text{...(37)}$$

which is still exact.

If now we make use of the power series equation for j_1 when $l > (ka)^2$ and use the value of j_l in terms of sine and cosine, the inequality (36) becomes

$$| \varepsilon_l | < \frac{1}{ka}$$

and (37) may be approximated as

$$\delta_l = \frac{\varepsilon_l (ka)^{2l+2}}{[(2l+1)\,!\,]^2} = - \frac{\varepsilon_l 2^{2l} (l\,!\,)^2 (ka)^{2l+2}}{[(2l+1)\,!]} \qquad \text{...(38)}$$

By using Stirling's formula, we get

$$\log | \delta_1 | \approx \log | \varepsilon_l | = 2l [\log (ka) + 1 + \log 2] - 2l \log l$$

The following are explanatory remarks concerning δ_l.

(i) From equations (21) and (23) it seen that for an attractive field $\phi (r)$ is shifted outward relative to other function of equations (23),

i.e.

$$\delta_l > \text{ for attractive field,}$$
$$\delta_l < 0 \text{ for repulsive field}$$

(ii) Classically, $l\hbar \approx p\rho$ where p is the momentum of the particle and ρ the impact parameter. The summation of l in equations (31) and (34) for the partial wave $l = 0, 1, \ldots$ in (12) is equivalent to the integration of all values of the impact parameter in the classical theory.

(iii) For large k and l, the phase shift can be calculated by the Born approximation it becomes

$$\delta_l \approx -\frac{1}{2k} U(r_0)\, r_0,$$

where r_0 is the classical distance of closest approach. For large l, r_0, $\rho \approx$ impact parameter. The series for total cross-section behaves like

$$\sigma \propto \Sigma (2l+1)\, \delta_l^2 = \frac{1}{4}\int_0^\infty d\rho \cdot \rho^3\, U^2(\rho),$$

as

$$p\rho = \hbar k \rho.$$

In order that this may converge $U(r)$ must decrease with distance at a rate faster than $1/r^2$.

(iv) For a scattering amplitude in forward direction, $f(0)$ will have the form

$$f(0) \;\alpha\; \Sigma(2l+1)\, \delta_l \to k \int_0^\infty d\rho \,.\, \rho^3\, U(\rho).$$

In order that it may coverge $U(\rho)$ must decrease with distance faster than $1/r^3$.

(v) For low energy scattering by a potential of the asymptotic form c/r^n, the variations of the phase shifts for various l are

$\delta_l \propto k^{2l+1}$ for $2l < n-3$,

$\delta_l \propto k^{2l+2} \log k$ for $2l = n-3$,

$\delta_l \propto k^{n-2}$ for $2l > n-3$,

(c) Phase shifts related to Potential

The phase shift δ_l depends only on the asymptotic form of R_l; however to determine it exactly the radial equation is to be solved completely. This is possible for specific potentials. but in general certain important informations may be deduced regarding δ_l. To express the phase shift in terms of the potential, we compare the function χ_l with the corresponding function $\chi_l^0 \propto r j_l(kr)$; when potential $V = 0$, the corresponding equations are

$$\frac{d^2\chi_l}{dr^2} + \left[k^2 - U(r) - \frac{l(l+1)}{r^2}\right]\chi_l = 0 \qquad \text{...(39)}$$

$$\frac{d^2\chi_l(0)}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2}\right]\chi_l^{(0)} = 0;\ \text{with } \chi_l^{(0)} \propto r j_l(kr) \qquad \text{...(40)}$$

multiplying equation (39) by $\chi_l^{(0)}$ and (40) by χ_l and subtracting, we get

$$\chi_l^{(0)} \frac{d^2\chi_l}{dr^2} - \chi_l \frac{d^2\chi_l^{(0)}}{dr^2} - U(r)\, \chi_l^{(0)} \chi_l = 0$$

or

$$\frac{d}{dr}\left[\chi_l^{(0)} \frac{d\chi_l}{dr} - \chi_l \frac{d\chi_l^{(0)}}{dr}\right] - U(r)\, \chi_l^{(0)} \chi_l = 0 \qquad \text{...(41)}$$

Integrating with respect to r; from limits o to r, and remembering that χ_l and χ_0^0 vanish at the origin $= 0$; we get

$$\left\{\chi_l^0 \frac{d\chi_l}{dr} - \chi_l \frac{d\chi_l^0}{dr}\right\} - \int_0^r U(r')\, \chi_l^0(r')\, \chi_l(r')\, dr' = 0$$

It is obvious that this relation is independent of normalisation of χ and χ_l^0. Let us normalise χ_l and χ_l^0 such that the constant in their asymptotic form is unity). *i.e.* at $r \to \infty$; we have

$$\chi_l \to \sin(kr + \Delta l) \quad \text{and} \quad \chi_l^{(0)} \to \sin\left(kr - \frac{1}{2}\pi\right) \qquad \text{...(43)}$$

This means that $\chi_l^{(0)} = kr\, j_l(kr)$; then the breckétted term in (42) (for $r \to \infty$) may be expressed as

$$k \sin\left(kr - \frac{l\pi}{2}\right)\cos(kr + \Delta l) - \sin(kr + \Delta l)\cos\left(kr - \frac{l\pi}{2}\right)$$

$$= -\, k \sin\left(\frac{l\pi}{2} + \Delta l\right) = -\, k \sin \delta_l$$

Thus at $r \to \infty$, equation (42) becomes

$$k \sin \delta_l = \int_0^\infty V(r')\, \chi_l^0(r')\, \chi_l(r')\, dr'$$

or

$$\sin \delta_l = -\int_0^\infty V(r)\, r\, j_l(kr)\, \chi_l(r)\, dr \qquad \text{...(44)}$$

This expression for the phase shift is exact, but is purely formal since $\chi_l(r)$ for all values of r is not known. However it is important for approximate evaluation. For example suppose χ_l differs very little from $\chi_l^{(0)} = kr\, j_l(kr)$ then

$$\sin \delta_l = -\, k \int_0^\infty U(r)\, r^2 j_l^2(kr)\, dr \qquad \text{...(45)}$$

This is **Born approximation for phase shifts.** For the approximation to be valid, it is necesary that the potential term $U(r)$ in equation (39) is very small. This is only possible if either the kinetic energy term k^2 or the centrifugal potential term dominates over $U(r)$. In the former case δ_l is expected to be small for all l; then we can take $(e^{2i\delta_l} - 1) \to 2i\delta_l \approx 2i \sin \delta_l$

Substituting this in (31) (a); we get

$$f(\theta) = -\sum_{l=0}^{\infty} (2l+l) \int_0^\infty U(r)\, r^2 j_l^2(kr)\, dr\, P_l(\cos\theta) \qquad \text{...(46)}$$

This reduces to Born approximation formula.

11·16. SCATTERING LENGTH AND EFFECTIVE RANGE THERY FOR LOW ENERGY SCATTERING

The method of partial waves is of special interest at low energies if the energy of the incident beam is so low that $ka < 1$ where a is the range of potential, then the only $l = 0$ or s-wave is scattered. All othr partial waves in the region of non-zero potential are so small that they remain unchanged. The scattering amplitude for s-wave is given by

$$f(\theta) = \frac{1}{k} e^{i\delta_0} \sin \delta_0 \qquad \text{...(1)}$$

As the scattering amplitude is independent of θ and ϕ, we note that the scattering is isotropic at the centre of small reference system. Therefore the total scattering cross-section.

$$\rho_{total} = \frac{4\pi}{k^2} \sin^2 \delta_0 \qquad \text{...(2)}$$

In the limit $k \to 0$, $\sigma_{total} \to \sigma_0$ called the *low-energy cross-section.* Then we note that

$$\lim_{k \to 0} k^2 \operatorname{cosec}^2 \delta_0 = \frac{4\pi}{\sigma_0}$$

It is obvious that

$$\lim_{k \to 0} \sin \delta_0 (k) \to 0$$

i.e. $\delta (k)$ approaches o or π in *zero energy limit.*

It is found that low energy cross-section can be described, instead of δ_0, by two quantities that characterize $V(r)$ completely as far as low energy scattering is concerned. These are the "*effective range*" r_0 and the "*scattering length*" 'a' introduced by Fermi both in connection with nucleon-nucleon scattering.

If the system has a bound-state with a small binding energy, the two low energy parameters r_0 and a will be completely determined by the bound state wavefunction and such a relationship exists between the properties of the bound state and low energy scattering is interesting but not unexpected since both are determined by the potential $V(r)$.

Scattering length and effective range for short ranged potential V (r) : For *s*-wave, the Schroedinger equation is

$$\frac{d^2u}{dr^2} + [k^2 - U(r)]\, u = 0,\ U(r) = \frac{2m}{\hbar^2} V(r) \qquad ...(3)$$

Let $u_1 (r)$, $u_2 (r)$ be the solutions for two energies k_1^2, k_2^2. They satisfy

$$u_1 (0) = 0,\ u_2 (0) = 0 \qquad ...(4)$$

and are normalised such that asymptotically they are

$$\left.\begin{aligned} u_1 (r) &\to \frac{1}{\sin \delta_1} \sin (k_1 r + \delta_1), \\ u_2 (r) &\to \frac{1}{\sin \delta_2} \sin (k_2 r + \delta_2), \end{aligned}\right\} \qquad ...(5)$$

From the two equations (3) for $u_1 (r)$, we readily obtain

$$\left[u_2 \frac{du_1}{dr} - u_1 \frac{du_2}{dr} \right]_0^R = (k_2^2 - k_1^2) - \int_0^R u_1\, u_2\, dr, \qquad ...(6)$$

e R is an arbitrary radial distance.

et us take two free-particle solutions

$$\left.\begin{aligned} v_1 (r) &\approx \frac{1}{\sin \delta_1} \sin (k_1 r + \delta_1) \\ v_2 (r) &= \frac{1}{\sin \delta_2} \sin (k_2 r + \delta_2) \end{aligned}\right\} \qquad ...(7)$$

ation obtained by putting $U (r) = 0$ in (3).

the equations for $v_1 (r)$ and $v_2 (r)$ we obtain as in (6)

$$\left[v_2 \frac{dv_1}{dr} - v_1 \frac{dv_2}{dr} \right]_0^R = (k_2^2 - k_1^2) - \int_0^R v_1\, v_2\, dr. \qquad ...(8)$$

action (7) from (8), using (4), (5) and (7) and limiting $R \to \infty$, we get

$$k_2 \cot \delta_2 - k_1 \cot \delta_1 - (k_2^2 - k_1^2) \int_0^\infty (u_1\, v_2 - v_1\, u_2)\, dr. \qquad ...(9)$$

On defining the "*scattering length*" *a* by

$$-\frac{1}{a} = \lim_{k\to 0} [k \cot \delta (k)]. \quad ...(10)$$

We can write (9), on limiting $k_1 \to 0$ and denoting k_2 by *k*,

$$k \cot \delta = -\frac{1}{a} + \frac{b}{2} k^2, \quad ...(11)$$

where
$$b = 2 \int_0^\infty (v_0 v - u_0 u)\, dr. \quad ...(12)$$

The factor 2 in (12) has been introduced so that *b* (or r_0) has the meaning of the range of the potential. From (5) and (7) it is seen that the integrand above differs from zero only in the region where *U*(*r*) is appreciable. In this region the wavefunction *u*(*r*) will not depend very much on the energy k^2 if $|U(r)| >> k^2$.

We shall therefore make the approximation of replacing *u*, *v* by u_0, v_0 (for zero energy) in (12), *i.e.* we shall take the first two terms in power series expansion in k^2 or $k \cot \delta$: It is quadratic in k

taylor exp

$$k \cot \delta = -\frac{1}{a} + \frac{r_0}{2} \{k_2^{2} + 0\} (k^4) \qquad -\frac{1}{a} + \frac{1}{2} r_0 k^2 + r_1 k^4 + \quad ...(11)$$

where
$$r_0 = 2 \int_0^\infty (v_0^2 - u_0^2)\, dr. \quad ...(12)$$

is defined as the "effective range" of the potential *V*(*r*). According to (5), and (10), the zero energy $u_0(r)$ has the asymptotic form

$$u_0(r) \to v(r) = \lim_{k\to 0} (\cos kr + \cot \delta \sin kr) \quad ...(13)$$
$$= 1 - \frac{r}{a}.$$

By the equations (5) and (7) $v_0^2 - u_0^2$ vanishes outside the "range" of *U*(*r*).

So, both r_0 and *a* are determined by *U*(*r*) that they are in sensitive to the exact form of *U*(*r*) but depend only on some integrand of *U*(*r*).

(1) For $k^2 \to 0$, we have from (2) and (10)

$$\sigma = \frac{4\pi}{k^2 (1 + \cot^2 \delta)} \to 4\pi a^2. \quad ...(14)$$

low energy

$$\sin\delta_l \xrightarrow[k\to 0]{} k$$

(2) From thue expression of δ_l, we have δ_0 for $k \to 0$.

$$a = \int_0^\infty r\, U(r)\, u_0(r)\, dr, \quad ...(15)$$

$$\delta_{l=0}(k=0) = \pi/2, 3\pi/2, ...$$

where $u_0(r)$ is normalised by the asymptotic behaviour and is different from (13)

$$u_0(r) \to \lim_{k\to 0} \frac{\sin (kr + \delta)}{k} = (r - a) \cos \delta \quad ...(16)$$

where cos δ has the value between 1 and –1 .

If we apply Born approximation and if it is valid, *i.e.*, u_0 is replaced by the field free solution

$$r\sqrt{(\pi/2kr)}\, J_{1/2}(kr) = (1/k) \sin kr \to r \text{ as } k \to 0$$

Then (15) becomes

$$a \approx \int_0^\infty U(r)\, r^2\, dr. \quad ...(17)$$

$$u_k(0) = 0 \qquad u_k(r \to \infty) \quad \frac{\sin(kr+\delta)}{\sin\delta}$$

(3) The sign of 'a' depends on $U(r)$. We take the following example for variation of 'a' with $U(r)$: Consider a potential well

$$U(r) = \begin{cases} -\beta^2, & r < R \\ 0, & r > R \end{cases} \qquad \text{...(18)}$$

If $E = -\gamma^2$, $\gamma > 0$, is a discrete state, then

$$\left(\frac{d^2}{dr^2} - \gamma^2 + \beta^2\right) u_\gamma(r) = 0; r < R$$

$$\left(\frac{d}{dr^2} - \gamma^2\right) u_\gamma(r) = 0; \; r > R$$

so that

$$u_\gamma(r) = \begin{cases} A \sin\{\sqrt{\beta^2 - \gamma^2})\, r\}\, . & r < R \\ Be^{-\gamma} & r > R \end{cases}$$

The continuity condition at $r = R$ gives that

$$\tan\{\sqrt{(\beta^2 - \gamma^2)}\, R\} = \frac{\sqrt{(\beta^2 - \gamma^2)}}{\gamma} \qquad \text{...(19)}$$

The condition on βR for the existence of 1, 2 or more discrete states is seen to be the following :

For only 1 discrete state, $\frac{1}{2}\pi < \beta R < \frac{3}{2}\pi$.

For only 2 discrete state, $\frac{3}{2}\pi < \beta R < \frac{5}{2}\pi$ etc. ...(20)

Consider now the scattering $U(r)$ in (18), the wave-function u_k can be expressed as :

$$\left(\frac{d^2}{dr^2} + k^2 + \beta^2\right) u_k = 0, r > R,$$

$$\left(\frac{d^2}{dr^2} + k^2\right) u_k = o, \; r > R \qquad \text{...(21)}$$

$$u_\gamma(r) = C \sin\{\sqrt{(\beta^2 + k^2)}\, r\}, r < R$$

$$= D \sin(kr + \delta), r > R \qquad \text{...(21a)}$$

Apply continuity condition at $r = R$

$$k \cot(kR + \delta) = \sqrt{(\beta^2 + k^2)} \cot\{\sqrt{(\beta^2 + k^2)}\, R\} \qquad \text{...(22)}$$

or

$$k \cot \delta = \frac{k \tan\{\sqrt{(\beta^2 + k^2)}\, R\} \tan kR + \sqrt{(\beta^2 + k^2)}}{\tan\{\sqrt{(\beta^2 - k^2)}\, R\} - \frac{1}{k}\sqrt{(\beta^2 + k^2)} \tan kR} \qquad \text{...(22a)}$$

By the equation (10), a comes out to be

$$a = R - \frac{1}{\beta} \tan \beta. \qquad \text{...(23a)}$$

Thus the scattering length a vanishes as $\beta \to 0$. As βR increases from 0, a decreases. As $\beta R \to \pi/2$, a omes negatively infinite. The cross-section σ becomes infinite as $\beta R \to \pi/2$ and has "*resonance*" at energy.

The range r_0 can be calculated for rectangular potential well as follows :

rom (21a) and the $u_k(r)$ for $k \to 0$, $r \to \infty$ in (13), we get

$$u_0 = \left(1 - \frac{R}{a}\right) \frac{\sin \beta r}{\sin \beta R}; 0 < r < R$$

and with (13), for v_0, we have from (12a)

$$r_0 = 2R - 2\frac{R^2}{2} + \frac{3R^{2R^3}}{3a^2} + \left(1 - \frac{R}{a}\right)^2 \left(\frac{1}{\beta \tan \beta R} - \frac{R}{\sin^2 \beta R}\right) \qquad ...(24)$$

If $\beta R = \left(n + \frac{1}{2}\right)\pi$, $n = 0, 1, 2, ...$; a stands to ± ∞ and (24) simplifies and the total cross-section σ in terms of a and r_0 is

$$\sigma = \frac{4\pi a^2}{1 + a(a - r_0)k^2 + \left(\frac{1}{2} a r_0\right)k^4}.$$

11·17. SCATTERING BY A PERFECTLY RIGID SPHERE

A perfectly rigid sphere of radius a is represented by the potential

$$V(r) = \begin{cases} \infty \text{ for } r < a \\ 0 \text{ for } r > a \end{cases}$$

The wave function vanishes for $r \overset{=}{<} a$ $r = a$

The Shoredinger wave equation (radial part) for $r > a$ $[V(r) = 0]$ is

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2} + \frac{2mE}{\hbar^2}\right] u_l(r) = 0$$

Substituting $\xi = kr$ or $r = \frac{\xi}{k}$, we have

$k^2 = \frac{\xi^2}{r^2}$

$$\frac{d}{d\xi}\left(\xi^2 \frac{\partial u_l(\xi)}{\partial \xi}\right) + \left[\xi^2 - l(l+1)\right] u_l(\xi) = 0 \qquad ...(1)$$

Further substituting

$$u_l(\xi) = \frac{v_l(\xi)}{\sqrt{\xi}}. \qquad ..(2)$$

in (1,) we get

$$\xi^2 \frac{d^2 v}{d\xi^2} + \xi \frac{dv}{d\xi} + \left[\xi^2 - \left(l + \frac{1}{2}\right)^2\right] v_l = 0. \qquad ...(3)$$

This is the Bessel's equation of order $\left(l + \frac{1}{2}\right)$. Its general solution is linear combination of Bessels function $J_{l+1/2}(\xi)$ and Neumann's function $N_{l+1/2}(\xi)$. The solution $N_{l+1/2}$ is not satisfactory since it diverges at $\xi = 0$; therefore the solution of (3) is expressed as

$$v_l = \sqrt{\left(\frac{\pi}{2}\right)} J_{l+1/2}(\xi)$$

where $\sqrt{\left(\frac{\pi}{2}\right)}$ is a constant chosen for conveience and it does not affect the solution of the problem.

$$\therefore \qquad u_l(\xi) = \frac{v_l(\xi)}{\sqrt{\xi}} = \sqrt{\left(\frac{\pi}{2}\right)} \frac{J_{l+1/2}(\xi)}{\sqrt{\xi}}$$

Now $u_l(\xi) = j_l(\xi)$ in the spherical Bessel's function, *i.e.*

$$j_l(\xi) = \sqrt{\left(\frac{\pi}{2\xi}\right)} J_{l+1/2}(\xi) \qquad ...(4)$$

The spherical Neumann's functions are defined as

$$n_l(\xi) = (-1)^{l+1}\sqrt{\left(\frac{\pi}{2\xi}\right)}\, J_{-l-1/2}(\xi) \qquad \text{...(5)}$$

Therefore the general solution of (1) is expressed as

$$u_l = A\, j_l(\xi) + B\, n_l(\xi) \qquad \text{...(6)}$$

where A and B are constants.

$$\text{For } \xi \to \infty,\ J_{l+1/2} = \sqrt{\left(\frac{2}{\pi\xi}\right)} \sin\left(\xi - \frac{l\pi}{2}\right)$$

$$\therefore \qquad \underset{\xi\to\infty}{\text{Lim}}\ j_l(\xi) = \sqrt{\left(\frac{\pi}{2\xi}\right)} [J_{l+1/2}(\xi)]_{\xi\to\infty} = \frac{\sin(\xi - l\pi/2)}{\xi} \qquad \text{...(7)}$$

Also

$$\underset{\xi\to 0}{\text{Lim}}\ n_l(\xi) = -\frac{\cos(\xi - l\pi/2)}{\xi} \qquad \text{...(8)}$$

Substituting $A = C\cos\delta_l$ and $B = -C\sin\delta_l$ in (6), we get

$$\begin{aligned} u_l &= C\cos\delta_l\, j_l(\xi) - C\sin\delta_l\, n_l(\xi) \\ &= C[j_l(kr)\cos\delta_l - n_l(kr)\sin\delta_l] \end{aligned} \qquad \text{...(9)}$$

This equation represents the solution of wave equation for $r > a$. When $r = a$, the wave function vanishes,

i.e.

$$u_l(r) = 0 \text{ at } r = a;$$

then equation (9) gives

$$0 = C[j_l(ka)\cos\delta_l - n_l(ka)\sin\delta_l]$$

or

$$\tan\delta_l = \frac{j_l(ka)}{n_l(ka)} \qquad \text{...(10)}$$

This equation gives phase shift δ_l for l^{th} partial wave.

From (10)

$$\sin^2\delta_l = \frac{j_l^2(ka)}{j_l^2(ka) + n_l^2(ka)} \qquad \text{...(11)}$$

∴ *The scattering cross-section for* l^{th} *partial wave* is given by

$$\sigma_l = \frac{4\pi}{k^2}(2l+1)\sin^2\delta_l = \frac{4\pi(2l+1)}{k^2}\,\frac{j_l^2}{j_l^2 + n_l^2} \qquad \text{...(12)}$$

The total scattering cross-section is

$$\sigma_{total} = \frac{4\pi}{k^2}\,\Sigma\,(2l+1)\,\frac{j_l^2}{j_l^2 + n_l^2} \qquad \text{...(13)}$$

From this equation the cross-section at all energies may be evaluated.

Now let us discuss the following two limiting cases :

1) Low Energy Limit : The low energy limit implies the domain of k for which $ka << 1$, we have

$$\underset{\xi\to 0}{\text{Lim}}\ j_l(\xi) \to \frac{\xi^l}{(2l+1)!} \qquad \text{...(14a)}$$

$$\underset{\xi\to 0}{\text{Lim}}\ n_l(\xi) = \frac{(2l-1)!}{\xi^{l+1}} \qquad \text{...(14b)}$$

$$\therefore \qquad \sin^2 \delta_l = \frac{j_l^2(ka)}{j_l^2(ka) + n_l^2(ka)} \approx \frac{j_l^2(ka)}{n_l^2(ka)} \approx \left[\frac{(ka)^{2l+1}}{(2l-1)!\,(2l+1)!} \right]^2 \qquad \text{...(15)}$$

This equation shows that in low energy limit δ_l decreases rapidly with l and consequently the scattering is prominently due to s-wave ($l = 0$) and hence is isotropic.

Equation (10) gives

$$\tan \delta_l = \frac{j_l(ka)}{n_l(ka)} = \frac{\sqrt{\left(\frac{\pi}{2ka}\right)}\, J_{l+\frac{1}{2}}(ka)}{(-1)^{l+1} \sqrt{\left(\frac{\pi}{2\,ka}\right)}\, J_{-l-1/2}(ka)}$$

$$= \frac{J_{l+1/2}(ka)}{(-1)^{l+1} J_{-l-1/2}(ka)}$$

For s-wave ($l = 0$)

$$\tan \delta_0 = -\frac{J_{1/2}(ka)}{J_{-1/2}(ka)} = -\frac{\sqrt{\left(\frac{2}{\pi\,ka}\right)} \sin(ka)}{\sqrt{\left(\frac{2}{\pi\,ka}\right)} \cos ka} = -\tan(ka)$$

Hence

$$\tan \delta_0 = -\tan ka,$$

$$\delta_0 = -ka \qquad \text{...(16)}$$

The total scattering cross-section for low energy limit is

$$\sigma_{total} = \left[\frac{4\pi}{k^2} \Sigma\,(2l+1) \sin^2 \delta_l \right]_{l=0} = \frac{4\pi}{k^2} \sin^2 \delta_0$$

$$= \frac{4\pi}{k^2} \sin^2 ka, \qquad ka << 0$$

$$\cong \frac{4\pi}{k^2} (ka)^2 \cong 4\pi a^2 \qquad \text{...(17)}$$

Classically the scattering cross-section is πa^2 only. quantum mechanically the cross-section is just 4 times of classical expression for the same radius., Thus for *low energy particles the cross-section is 4 times the geometrical cross-section of the rigid sphere.*

(2) High Energy Limit : For high energy limit $ka >> 1$ for fixed l

Substituting the asymptotic forms of j_l and n_l, we get

$$\sin^2 \delta_l = \sin^2 ka, \; l << ka \qquad \text{...(18)}$$

This indicates that the phase shift oscillates rapidly between 0 and π; but this is contrary to observations. For infinite potential and so for large k, the phase shift is simply ka if $l << ka$. Thus assuming

---

* When $\xi \to \infty$

$$J_{1/2}(\xi) = \sqrt{\frac{2}{\pi\xi}} \sin \xi$$

and

$$J_{-1/2}(\xi) = \sqrt{\frac{2}{\pi\xi}} \cos \xi$$

that only those waves contribute to partial waves for which $l = 0$ to ka, then the total scattering cross-section is given by

$$\sigma_{total} = \frac{4\pi}{k^2} \sum_{l=0}^{ka} (2l+1) \sin^2 ka \approx 4\pi a^2 \sin^2 ka$$

We note that σ_{total} oscillates rapidly between 0 and $4\pi a^2$. In high energy limit the average cross-section is obtained by taking the average value of $\sin^2 ka$ over all directions, which is $\sin^2 ka = \frac{1}{2}$. Hence we get

$$\sigma_{total} = 2\pi a^2$$

Thus we note that *in high energy limit the scattering cross-section* is twice the *geometrical cross-section*. The reason for this anomalous result is the *shadow scattering*. For finite value of ka, the diffraction around the sphere in the forward direction actually takes place and the total measured cross-section is nearly $2\pi a^2$.

11·18. SCATTERING FROM A SQUARE WELL POTENTIAL

Let the potential function for an attractive square well be represented as

$$V(r) = \begin{cases} -V_0 \text{ for } r<a \\ 0 \text{ for } r>a \end{cases} \qquad \text{...(1)}$$

The radial part of the wave function satisfied by *s*-state ($l = 0$) is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) + \frac{2m}{\hbar^2}[E - V(r)]R = 0 \qquad \text{...(2)}$$

Substituting

$$R(r) = ru(r). \qquad \text{...(3)}$$

we get

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}[E - V(r)]u(r) = 0.$$

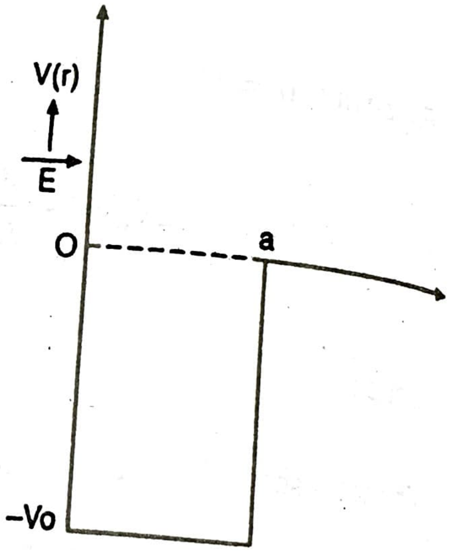


Fig 11.12.

Using potential function characterised by (1), equation (4) comes

$$\frac{d^2u(r)}{dr^2} + \frac{2m}{\hbar^2}[E + V_0]u(r) = 0 \text{ for } r<a \qquad \text{...(5)}$$

$$\frac{d^2u(r)}{dr^2} + \frac{2m}{\hbar^2}Eu(r) = 0 \text{ for } r>a \qquad \text{...(6)}$$

ubstituting $\sqrt{\left(\frac{2mE}{\hbar^2}\right)} = k$ and $\sqrt{\left(\frac{2m(E+V_0)}{\hbar^2}\right)} = k'$

n (5) and (6) take the form

$$\frac{d^2u}{dr^2} + k'^2 u = 0 \text{ for } r<a \qquad \text{...(8)}$$

$$\frac{d^2u}{dr^2} + k^2 u = 0 \text{ for } r>a \qquad \text{...(9)}$$

olutions of (8) and (9) may be expressed as

$$u = A \sin k'r \text{ for } r<a$$

The orientation ϕ_2 in $d\Omega_2$ is irrelevant so we can integrate over it. Moreover, we can now also integrate over $d\Omega$, since no further constraint is involved. This gives

$$dN = \frac{4\pi . 2\pi}{(2\pi\hbar)^6} p_1 dp_1\, p_2 dp_2 \varepsilon_3\, dE\, V^2 \tag{137}$$

Since $p_i dp_i = \varepsilon_i d\varepsilon_i$, we have finally (inserting the factors c which we had dropped)

$$\rho = \frac{dN}{dE} = \frac{8\pi^2 V^2}{(2\pi\hbar)^6 c^6} \varepsilon_1 \varepsilon_2 \varepsilon_3\, d\varepsilon_1\, d\varepsilon_2 \tag{138}$$

The transition probability is, therefore,

$$\Gamma = \frac{2\pi}{\hbar} |M|^2 \rho \sim d\varepsilon_1\, d\varepsilon_2 = dt_1\, dt_2 \tag{139}$$

where t_1 and t_2 are kinetic energies of any two pions. The energy distribution of the π^- is obtained by integrating over the energy of the other. But Eq. (139) tells us that there must be an equal number of π^- emitted per unit energy for the entire energy range allowed by energy momentum constraint.

It can be shown that if the pions are emitted in the $l = 0$ state (low energy) and the interaction of the pions in the final state can be neglected, (which means that they can be represented by plane waves) then the matrix element will have the simple dependence $M \sim 1/(\varepsilon_1 \varepsilon_2 \varepsilon_3)^{1/2}$ as assumed. This means that any deviation from the prediction Eq. (139), which can be called the "phase space spectrum", may be attributed to some interaction of the pions in the final state. In the extreme case where two of the pions really are the products of the *decay* of a particle which emerged from the original reaction, there would be a very strong deviation from the phase space spectrum. As an example, we may have

$$\pi^+ + d \to \omega + p + p$$
$$\qquad\qquad \hookrightarrow (\pi^+ + \pi^- + \pi^\circ)$$

In a bubble chamber, only the 3 pions are seen but from their energy spectrum one can infer the existence and properties of ω. A very short-lived particle such as the ω is sometimes referred to as a resonance.

25.8 References and suggested reading

1. H. Enge, *Introduction to Nuclear Physics*, Addison-Wesley Publishing Co., Reading, Massachusetts (1966),
2. E. Fermi, *Quantum Theory of Radiation*, Reviews of Modern Physics, **4**, 87 (1932).
3. L.S. Hughes, *Elementary Particles*, Penguin, London (1972).
4. A.K. Ghatak and L.S. Kothari, *An introduction to Lattice Dynamics*, Addison-Wesley Publishing Co., Reading Massachusetts (1972).
5. M. Born, *Physics in my Generation*, Springer Verlag, New york (1962).
6. L.I. Schiff, *Quantum Mechanics*, McGraw-Hill Book Co., New York (1955).
7. W.E. Lamb, *Lectures on Mossbauer Effect*, Tata Institute of Fundamental Research, Bombay (1960).

Chapter 26

The semi-classical theory of radiation and the Einstein coefficients

> *If we have an atom that is in an excited state and so is going to emit a photon, we cannot say* **when** *it will emit the photon. It has a certain amplitude to emit the photon at any time, and we can predict only a probability for emission; we cannot predict the future exactly. This has given rise to all kinds of nonsense and questions on the meaning of freedom of will, and of the idea that the world is uncertain..*
>
> — R.P. FEYNMAN in *Feynman Lectures on Physics*, Vol. III, p. 1422.

26.1 Introduction

In the previous chapter we developed time dependent perturbation theory which we will now use to study the interaction of an atom with electromagnetic field. The theory presented in this chapter is a curious mixture of classical and quantum pictures. Matter, i.e. atoms, are assumed to exist in discrete (quasi-stationary) states. But the electromagnetic radiation with which it interacts, is described classically. This semi-classical theory of atom–field interaction will be discussed in Sec. 26.3 which will enable us to calculate probabilities of absorption and induced emission. It may be mentioned that the semi-classical theory is insufficient to describe the spontaneous emission of radiation because the electromagnetic field is described classically; the fully quantum theory of radiation, which we will discuss in the next chapter, describes the spontaneous emission automatically.

An ingenious idea of Einstein enabled him to obtain a relation which would determine the rate at which spontaneous emissions take place. The idea was based on consideration of matter in equilibrium with radiation assuming that the resultant radiation must obey Planck's law. Einstein introduced coefficients, which are now known as Einstein coefficients, which described induced emission, absorption and spontaneous emission. In Sec. 26.2 we will give the original argument of Einstein (Ref.1) which gave rise to the relation between different coefficients. In Sec. 26.3 we will discuss the atom–field interaction using the semi-classical theory and will derive expressions for stimulated emission rate and stimulated absorption rate. In Sec. 26.4 we will use the Einstein relations to calculate the spontaneous emission rate and hence the lifetime of atomic states. In Sec. 26.5, we will discuss the selection rules governing the transitions.

26.2 The Einstein coefficients

Figure 26.1 represents two of the energy levels of an atomic system corresponding

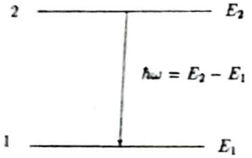


Figure 26.1 The two states of an atomic system. The transition frequency is $\omega_{21} = (E_2 - E_1)/\hbar$.

to energies E_1 and E_2. Let N_1 and N_2 represent the number of atoms (per unit volume) in levels 1 and 2 respectively. An atom in the lower energy level can absorb radiation and get excited to the level E_2. This excitation process can occur only in the presence of radiation. Such a process is known as *stimulated absorption* or simply as absorption. The rate of absorption would depend on the energy density, $u(\omega)$, associated with the radiation field corresponding to the frequency

Stimulated absorption

$$\omega = \frac{E_2 - E_1}{\hbar} \tag{1}$$

The energy density $u(\omega)$ is defined such that $u(\omega)\,d\omega$ represents the radiation energy per unit volume within the frequency interval ω and $\omega + d\omega$. The rate of absorption would be proportional to N_1 and also to $u(\omega)$. Thus, the number of absorptions per unit time per unit volume can be written as

$$N_1 B_{12} u(\omega) \tag{2}$$

where B_{12} is the coefficient of proportionality and is a characteristic of the energy levels.

On the other hand, when the atom is in an excited state, it can make a transition to a lower energy state through the emission of electromagnetic radiation; however, in contrast to the absorption process, the emission process can occur in two different ways:

Spontaneous emission

(i) The first is referred to as *spontaneous emission* in which an atom in the excited state emits radiation even in the absence of any incident radiation. It is thus not stimulated by any incident signal but occurs spontaneously. Further, the rate of spontaneous emissions is proportional to the number of atoms in the excited state; thus if we represent the coefficient of proportionality by A_{21} then

$$N_2 A_{21} \tag{3}$$

would represent the number of spontaneous emissions per unit volume per unit time to the lower energy level.

Stimulated emission

(ii) The second is referred to as *stimulated emission* in which an incident signal of appropriate frequency triggers an atom in an excited state to emit

radiation. The rate of transition to the lower energy level is directly proportional to the energy density of the radiation at the frequency ω. Thus the number of stimulated emissions per unit time per unit volume would be given by

$$N_2 B_{21} u(\omega) \tag{4}$$

The quantities A_{21}, B_{12} and B_{21} are known as Einstein coefficients and are determined by the atomic system.

At thermal equilibrium, the number of upward transitions must be equal to the number of downward transitions. Thus, we may write

$$N_1 B_{12} u(\omega) = N_2 A_{21} + N_2 B_{21} u(\omega)$$

or

$$u(\omega) = \frac{A_{21}}{\frac{N_1}{N_2} B_{12} - B_{21}} \tag{5}$$

From Boltzmann's law, we have the following expression for the ratio of the populations of two levels at temperature T:

$$\frac{N_1}{N_2} = \exp\left[\frac{E_2 - E_1}{k_B T}\right] = \exp\left[\frac{\hbar\omega}{k_B T}\right] \tag{6}$$

where k_B represents the Boltzmann constant. Thus, we may write

$$u(\omega) = \frac{A_{21}}{B_{12}\exp(\hbar\omega/k_B T) - B_{21}} \tag{7}$$

Now, according to Planck's law the energy density of radiation (at thermal equilibrium) is given by (see, e.g. Ref 2 and 3):

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{\exp(\hbar\omega/k_B T) - 1} \tag{8}$$

Comparing Eqs (7) and (8) we obtain[1]

$$B_{12} = B_{21} = B \text{ (say)} \tag{9}$$

and

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2 c^3} \tag{10}$$

Thus, the probabilities of stimulated absorption and stimulated emission are the same and the ratio of the A and B coefficients is given by Eq. (10). It is of interest to mention that at thermal equilibrium corresponding to ordinary temperatures ($T \sim 1000$°K) the spontaneous emission rate for optical sources far exceeds the stimulated emission rate (see Problem 26.1).

26.3 The atom–field interaction

In order to calculate the Einstein coefficients we consider an atom in the presence of an oscillating electric field given by[2]

$$\mathcal{E}(t) = \hat{\mathbf{e}}\mathcal{E}_0 \cos\omega t \tag{11}$$

---

[1] If the levels 1 and 2 are g_1- and g_2-fold degenerate, then $N_1/N_2 = (g_1/g_2)\exp(\hbar\omega/k_B T)$, $B_{12} = B_{21}(g_2/g_1)$ and $A_{21}/B_{21} = \hbar\omega^3/\pi^2 c^3$.

[2] The electric field associated with an electromagnetic wave will be of the form $\hat{\mathbf{e}}\cos(\omega t - \mathbf{k}.\mathbf{r})$; however, for radiation in the visible region, the wavelength associated ($\sim 5 \times 10^{-5}$ cm) is much larger

which is switched on at $t = 0$; $\hat{\mathbf{e}}$ represents the unit vector along the direction of the electric field and the oscillation frequency ω is assumed to be close to the resonant frequency $\omega_{21}\, [= (E_2 - E_1)/\hbar]$ corresponding to the transition from state 2 to state 1 (see Fig. 26.1). Now, the interaction energy of the electron with the electric field is given by

Interaction energy

$$H'(\mathbf{r},t) = q\mathcal{E}.\mathbf{r} = q\mathcal{E}_0\,(\hat{\mathbf{e}}.\mathbf{r})\cos\omega t \tag{12}$$

where $q\,(>0)$ represents the magnitude of the electronic charge[3]. Let H_0 represent the Hamiltonian corresponding to the atomic system and let ψ_n denote the eigenfunctions of H_0 belonging to the energy $E_n\,(= \hbar\omega_n)$:

Position rep for a particle moving in some pot $V(r)$
$i\hbar\frac{\partial\psi}{\partial t}(r,t) = H\psi(r,t)$

$$H_0\psi_n = E_n\psi_n = \hbar\omega_n\psi_n \tag{13}$$

Our objective is to solve the equation

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = H\Psi = \left[H_0 + H'(\mathbf{r},t)\right]\Psi(\mathbf{r},t) \tag{14}$$

Following the approach developed in Sec. 25.2, we write

$$\Psi(\mathbf{r},t) = \sum_n C_n(t)\, e^{-i\omega_n t}\,\psi_n(\mathbf{r}) \tag{15}$$

$\sum_n C_n(t)\, e^{-i\omega_n t}\, \psi_n(r)$

and obtain [see Eq. (9) of the previous chapter]

$$i\hbar\frac{dC_s}{dt} = \sum_n C_n(t)\, H'_{sn}(t)\, e^{i\omega_{sn}t} \tag{16}$$

where

$$\begin{aligned} H'_{sn}(t) &= \int \psi_s^*(\mathbf{r})\, H'(\mathbf{r},t)\, \psi_n(\mathbf{r})\, d\tau = \langle s|H'|n\rangle \\ &= \frac{1}{2} q\mathcal{E}_0 \hat{\mathbf{e}}.\langle s|\mathbf{r}|n\rangle \left[e^{i\omega t} + e^{-i\omega t}\right] \end{aligned} \tag{17}$$

Substituting for $H'(\mathbf{r},t)$ from Eq. (12), we get

$$i\hbar\frac{dC_s}{dt} = \frac{1}{2}\mathcal{E}_0 \sum_n D_{sn} C_n(t) \left[e^{i(\omega_{sn}+\omega)t} + e^{i(\omega_{sn}-\omega)t}\right] \tag{18}$$

where

Dipole matrix element

and

$$D_{sn} = \hat{\mathbf{e}}.\mathbf{P}_{sn} \tag{19}$$

$$\mathbf{P}_{sn} = q\int \psi_s^*(\mathbf{r})\, \mathbf{r}\, \psi_n(\mathbf{r})\, d\tau = q\langle s|\mathbf{r}|n\rangle \tag{20}$$

is known as the dipole matrix element. We assume that at $t = 0$ the atom is in the state ψ_k, i.e.

$$\left.\begin{aligned} C_k(t=0) &= 1 \\ C_n(t=0) &= 0 \text{ for } n \neq k \end{aligned}\right\} \tag{21}$$

---

than atomic dimensions ($\sim 10^{-8}$cm) and we can use the value of $\mathcal{E}$ at $\mathbf{r} = 0$. This is immediately obvious from Eq. (17) where the atomic wave functions are almost zero for $r \gtrsim 10^{-8}$cm and since $k \simeq 10^5\text{cm}^{-1}$, the quantity $\mathbf{k}.\mathbf{r} \ll 1$ in the domain of integration.

[3] We are considering here a single electron atom with $\mathbf{r}$ representing the position vector of the electron with respect to the nucleus. Thus the electric dipole moment of the atom is given by $\mathbf{p} = -q\mathbf{r}$ because the direction of the dipole moment is from the negative charge to the positive charge. The interaction energy of a dipole placed in an electric field is $-\mathbf{p}.\mathcal{E}$ which is precisely Eq. (12). It may be mentioned that the interaction term described by Eq. (12) is consistent with the Schrödinger equation for the electron in the dipole approximation (see Sec. 26.4).

$e^{i\theta} - 1 = e^{i\theta/2}.e^{i\theta/2} - e^{i\theta/2}.e^{-i\theta/2}$
$= \frac{e^{i\theta/2}\left[e^{i\theta/2} - e^{-i\theta/2}\right]}{2i} = \sin\theta/2$

$\frac{e^{ix} - e^{-ix}}{2i} = \sin x$

$\frac{\sin x\,(e^{-iy} + e^{iy})}{2}$

Equation (18) represents an infinite set of coupled equations and as a first approximation we replace $C_n(t)$ by $C_n(0)$ on the right-hand side of Eq. (18) giving

$$i\hbar\frac{dC_s}{dt} \simeq \frac{1}{2}\mathcal{E}_0 D_{sk}\left[e^{i(\omega_{sk}+\omega)t} + e^{i(\omega_{sk}-\omega)t}\right]$$

Integrating, we obtain

$\cos x = \frac{e^{ix} + e^{-ix}}{2}$

$$C_s(t) - C_s(0) = -\frac{i\mathcal{E}_0}{2\hbar}D_{sk}\left[\frac{e^{i(\omega_{sk}+\omega)t} - 1}{i(\omega_{sk}+\omega)} + \frac{e^{i(\omega_{sk}-\omega)t} - 1}{i(\omega_{sk}-\omega)}\right]$$

or, for $s \neq k$

$$\begin{aligned} C_s(t) = -\frac{i\mathcal{E}_0}{2\hbar}D_{sk}\Bigg[& e^{i(\omega_{sk}+\omega)t/2}\frac{\sin(\omega_{sk}+\omega)t/2}{(\omega_{sk}+\omega)/2} \\ & + e^{i(\omega_{sk}-\omega)t/2}\frac{\sin(\omega_{sk}-\omega)t/2}{(\omega_{sk}-\omega)/2}\Bigg] \end{aligned} \tag{22}$$

It can be easily seen that for large values of t, the function

$$\frac{\sin(\omega_{sk}-\omega)t/2}{(\omega_{sk}-\omega)/2} \tag{23}$$

is very sharply peaked around $\omega \simeq \omega_{sk}$ and negligible everywhere else (see Fig. 26.2). Thus for states for which ω_{sk} is significantly different from ω, $C_s(t)$ would be negligible, and transitions between such states will not be stimulated by the incident field. This implies that in the summation appearing on the right-hand side of Eq. (18) we need only consider those states which correspond closely to the resonance frequency.

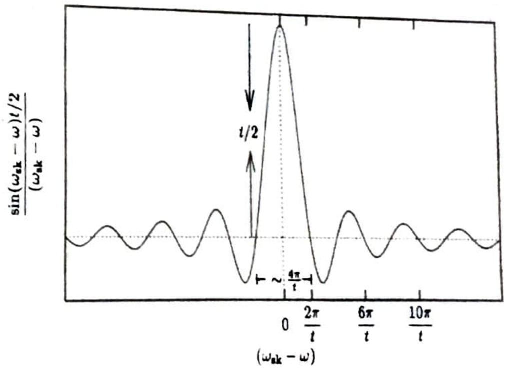


Figure 26.2: For large values of t, the function given by Eq. (23) is a very sharply peaked function of ω about $\omega = \omega_{sk}$.

In an emission process, $E_k > E_s$ and hence $\omega_{sk}\left(= \frac{E_s - E_k}{\hbar}\right)$ is negative; thus it is the first term on the right-hand side of Eq. (22) which contributes. On the other hand, in an absorption process, $E_k < E_s$ and hence ω_{sk} is positive and consequently it will be the second term on the right-hand side of Eq. (22) which contributes.

Let us consider the emission of radiation and assume that at $t = 0$ the atom is in state 2 (see Fig. 26.1). We also assume ω to be close to $\omega_{21}\,(= [E_2 - E_1]/\hbar)$. The probability for the transition to state 1 is given by

* Now, the radiation energy (per unit volume) associated with a near monochromatic field at frequency ω is given by $u_\omega = \frac{1}{2}\varepsilon_0 \mathcal{E}_0^2$ - ㉖

We assume that there is a continuous spectrum of freq.⁴ and that there is no correlation between the polarisation vectors of diff. components (· · -). Thus if u(ω)dω represents the radiation energy per unit vol. in the freq. interval ω and ω+dω, then we may replace in eqn ㉔ $\mathcal{E}_0^2 = \frac{2}{\varepsilon_0} u(\omega) d\omega$ - ㉗ and integrate ⊛

Probability for stimulated emission

$$|C_1(t)|^2 = \frac{|D_{12}|^2 \mathcal{E}_0^2}{4\hbar^2} \left[\frac{\sin\left(\frac{-\omega_{21}+\omega}{2}\right)t}{\frac{-\omega_{21}+\omega}{2}} \right]^2 \tag{24}$$

Equation (24) represents the probability for stimulated emission of radiation. In deriving this equation, we have assumed that $|C_1(t)|^2 \ll 1$; thus the result will be valid when either

$$\left(\frac{D_{12}\mathcal{E}_0 t}{\hbar}\right)^2 \ll 1 \text{ or } \left(\frac{D_{12}\mathcal{E}_0}{\hbar}\right)^2 / (\omega - \omega_{21})^2 \ll 1 \tag{25}$$

A more accurate result for a two state system will be discussed in Problem 26.8.

Now, the intensity of an electromagnetic wave is related to $\mathcal{E}$ through the relation (e.g. Ref. 4, Sec. 19.5).

$$I = \frac{1}{2}\varepsilon_0 c \mathcal{E}_0^2 \tag{26}$$

where ε_0 is the dielectric permittivity of free space and c is the speed of light in free space. Thus

$$|C_1(t)|^2 = \frac{1}{2}\frac{|D_{12}|^2}{\hbar^2}\frac{1}{\varepsilon_0 c}\left[\frac{\sin\left(\frac{\omega-\omega_{21}}{2}t\right)}{\frac{\omega-\omega_{21}}{2}}\right]^2 I \tag{27}$$

We apply this formula to the case where there is a continuous spectrum of frequency[4] and there is no correlation between the polarization vectors of different components (as in the case of black body radiation). If $u(\omega)\,d\omega$ represents the radiation energy per unit volume in the frequency interval ω and ω + dω then I should be replaced[5] by $cu(\omega)\,d\omega$ and the expression integrated over all frequencies to obtain the following expression for the transition probability

$$\Gamma_{21} = \frac{1}{2\varepsilon_0\hbar^2}\overline{|D_{12}|^2}\int u(\omega)\left[\frac{\sin(\omega-\omega_{21})t/2}{(\omega-\omega_{21})/2}\right]^2 d\omega \tag{28}$$

where the bar denotes the averaging over different orientations:

$$\overline{|D_{12}|^2} = \overline{q^2|\langle 1|\mathbf{r}|2\rangle\cdot\hat{\mathbf{e}}|^2} = q^2|\langle 1|\mathbf{r}|2\rangle|^2\,\overline{\cos^2\theta}$$
$$= \frac{q^2}{3}|\langle 1|\mathbf{r}|2\rangle|^2 = \frac{1}{3}|\mathbf{P}_{12}|^2$$

because

$$\overline{\cos^2\theta} = \frac{1}{4\pi}\int_0^\pi\int_0^{2\pi}\cos^2\theta\sin\theta\,d\theta\,d\phi = \frac{1}{3} \tag{29}$$

Assuming that $u(\omega)$ varies much slowly in comparison to the quantity

$$\left[\frac{\sin(\omega-\omega_{21})t/2}{(\omega-\omega_{21})/2}\right]^2 \tag{30}$$

we replace $u(\omega)$ by its value at $\omega = \omega_{21}$ and take it out of the integral (in Eq. 28) to obtain

$$\Gamma_{21} \simeq \frac{1}{6\varepsilon_0\hbar^2}|\mathbf{P}_{12}|^2 u(\omega_{21})\,G \tag{31}$$

where

$$G \simeq \int_{-\infty}^{+\infty}\left[\frac{\sin(\omega_{21}-\omega)t/2}{(\omega_{21}-\omega)/2}\right]^2 d\omega = 2t\int_{-\infty}^{+\infty}\frac{\sin^2\xi}{\xi^2}\,d\xi$$
$$= 2\pi t$$

Thus

Transition probability

$$\Gamma_{21} \simeq \frac{\pi}{3\varepsilon_0}\frac{|\mathbf{P}_{12}|^2}{\hbar^2}u(\omega_{21})\,t = \beta t \text{ (say)} \tag{32}$$

The above expression shows that the probability of transition is proportional to time with $\beta\left(= \frac{\pi}{3\varepsilon_0\hbar^2}|\mathbf{P}_{12}|^2 u(\omega_{21})\right)$ representing the proportionality constant. This immediately implies the radioactive decay law, because if there are $N_2(t)$ atoms (per unit volume) in state 2 at time t and if $-dN_2$ represents the number of transitions (per unit volume) in time dt then according to Eq. (32)

$$-\frac{dN_2}{N_2} = \beta dt \tag{33}$$

the negative sign implying that N_2 will decrease with times. Equation (33) immediately leads to

$$N_2(t) = N_2(0)\,e^{-\beta t} \tag{34}$$

which is the radioactive decay law with $1/\beta$ representing the mean lifetime of the state.

It may be noted that Eq. (32) predicts an indefinite increase in the transition probability with time; however, the first-order perturbation theory itself breaks down when Γ_{21} is not appreciably less than unity. Thus, Eq. (32) is valid for times for which

$$\beta t \ll 1 \tag{35}$$

If the lifetime of the state is $\sim 10^{-9}$sec, then $\beta \sim 10^9\text{sec}^{-1}$ and we must have

$$t \ll 10^{-9}\,\text{sec} \tag{36}$$

However, the large time behaviour[6] is given by Eq. (34).

It should also be noted that in our analysis we have assumed the quantity given by Eq. (30) to be very sharply peaked around $\omega \approx \omega_{21}$, for this to happen t should be large enough so that[7]

$$\frac{1}{t\omega_{21}} \ll 1$$

or

$$t \gg \frac{1}{\omega_{21}} \tag{37}$$

Now in the optical region

$$\omega_{21} \sim 10^{15}\,\text{sec}^{-1}$$

---

[4] One could also have an interaction of a near monochromatic wave (as in a laser) with an atom having a broad frequency spectrum. This is discussed in Problem 26.10.

[5] The energy density associated with a monochromatic field is I/c.

[6] Equation (32) may, therefore, be interpreted as: If the state has not made a transition upto time t then the probability that it will make a transition in dt will be $\beta\,dt$ from which Eq. (34) follows.

[7] This follows from the fact that the maximum of (30) occurs at $\omega = \omega_{21}$ and the first zero at $\omega = \omega_{21} \pm \frac{\pi}{t}$.

then we must have

$$t \gg 10^{-15}\,\text{sec}$$

for atomic state (ω_{21})

Thus t in Eq. (32) should satisfy Eq. (37).

Returning to Eq. (32), we get the following expression for the transition probability per unit time (which we denote by w_{21}):

$$w_{21} \simeq \frac{\pi}{3\varepsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21}) \tag{38}$$

If there are N_2 atoms per unit volume in state 2 then the number of stimulated emissions per unit time per unit volume would be given by

$$W_{21} = N_2 w_{21} = N_2 \frac{\pi}{3\varepsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21}) \tag{39}$$

$N_2 B_{21} u(\omega)$

Comparing the above equation with Eq. (4), we obtain

Einstein's B coefficient

$$B_{21} = \frac{\pi}{3\varepsilon_0}\frac{P^2}{\hbar^2} = \frac{4\pi^2}{3\hbar^2}\left(\frac{q^2}{4\pi\varepsilon_0}\right)\left|\int \psi_1^* \mathbf{r} \psi_2 d\mathbf{r}\right|^2$$

$$= \frac{4\pi^2 \alpha c}{3\hbar} |\langle 1|\mathbf{r}|2\rangle|^2 \tag{40}$$

$P_{12} = \frac{q^2}{3} |\langle 1|r|2\rangle|^2$

$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2 c^3}$

where

$$\alpha = \frac{q^2}{4\pi\varepsilon_0 \hbar c} \simeq \frac{1}{137} \tag{41}$$

represents the fine-structure constant.

The corresponding expression for stimulated absorption is obtained by starting with the first term on the right-hand side of Eq. (22) and proceeding in a similar manner. The final expression is identical to Eq. (40) except for an interchange of indices 1 and 2 and since

$$\left|\int \psi_2^* \mathbf{r} \psi_1 d\mathbf{r}\right|^2 = \left|\int \psi_1^* \mathbf{r} \psi_2 d\mathbf{r}\right|^2 \tag{42}$$

we get

$$B_{12} = B_{21}$$

consistent with Eq. (9).

26.4 Spontaneous emission rate

Einstein's A coefficient

Using Eqs (9), (10) and (40), we get the following expression for the A coefficient

$$A = \frac{4}{3}\alpha\frac{\omega^3}{c^2}\left|\int \psi_2^* \mathbf{r} \psi_2 d\tau\right|^2 \tag{43}$$

For the $2P \to 1S$ transition in the hydrogen atom, i.e. for the transition from any one of the $(n = 2, l = 1, m = +1, 0, -1)$ states to the $(n = 1, l = 0, m = 0)$ state, we get (see Problem 26.3)

$\frac{\hbar\omega^2}{\pi^2 c^2} B_{21}$

$$\left|\int \psi_{1S}^* \mathbf{r} \psi_{2P} d\tau\right|^2 = 2^5 \left(\frac{2}{3}\right)^{10} a_0^2 \tag{44}$$

independent of the initial value of m; here $a_0 \left(= \frac{\hbar^2}{me^2} \simeq 0.5 \times 10^{-10} m\right)$ is the Bohr radius. Further, for $2P \to 1S$ transition

$$\hbar\omega = \left(-\frac{1}{4} + 1\right) E_H = \frac{3}{8}\frac{e^2}{a_0}$$

---

or

$$\omega = \frac{3c}{8a_0}\alpha \tag{45}$$

On substitution in Eq. (43), we get

$$A = \left(\frac{4}{9}\alpha\right)^4 \frac{c}{a_0} \simeq 6 \times 10^8\,\text{sec}^{-1}$$

The coefficient A gives the probability per unit time for spontaneous emission from state 2 to state 1. Thus if there are N_2 atoms per unit volume in state 2 and if $-dN_2$ represents the number of atoms undergoing spontaneous transitions in time dt then

$$dN_2 = -AN_2 dt \tag{46}$$

giving once again the radioactive decay law

$$N_2(t) = N_2(0)e^{-At}$$

Mean lifetime

Thus the mean lifetime of the state is given by

$$\tau = \frac{1}{A} \simeq 1.6 \times 10^{-9}\,\text{sec} \tag{47}$$

In Eq. (46), dt should be small enough so that $Adt \ll 1$. Equation (47) tells us that the mean lifetime of the hydrogen atom in the upper level corresponding to the $2P \to 1S$ transition is about 1.6×10^{-9} sec. Transitions having such small lifetimes are referred to as strongly allowed transitions[8]. One can similarly calculate lifetimes for other atomic states.

The spontaneous emission rate will give rise to finite widths of the spectral lines which can be estimated from the uncertainty principle

$$\Delta E \sim \frac{\hbar}{\tau} \tag{48}$$

In practice, the observed widths are much larger because of other factors such as Doppler broadening, collision broadening, etc.

We should also mention here that the A coefficient for the $2S \to 1S$ transition is zero. Such transitions are said to be forbidden transitions.

26.5 The selection rules

Whenever the quantity

$$\hat{\mathbf{e}} \cdot \int \psi_f^* \mathbf{r} \psi_i d\tau$$

(also written as $\hat{\mathbf{e}} \cdot \langle f|\mathbf{r}|i\rangle$) vanishes, the transition probability is zero [see Eq. (24)] and the corresponding transition is said to be forbidden (in the dipole approximation)[9]; the subscripts i and f refer to initial and final states respectively.

---

[8] In contrast, levels used in the laser transition are such that the upper level has a very long lifetime ($\sim 10^{-3}$ to 10^{-5} sec). They are referred to as metastable states. The strength of an atomic transition is usually expressed in terms of the f-value defined by the equation

$$f = \frac{2}{3}\frac{m\omega_{21}}{\hbar}|D_{21}|^2 \cdot$$

For strongly allowed transitions $f \sim 1$ and for transitions from metastable states $f \sim 10^{-3} - 10^{-6}$.

[9] See Problem 27.1 for higher order transitions.

If we assume that the electron moves in a central field, then the angular part of the wave function will be of the form $Y_{lm}(\theta,\phi)$; thus, the initial and final states will be given by

$$\left.\begin{aligned}\psi_i &= R_{n_i l_i} Y_{l_i m_i}(\theta,\phi)\\ \psi_f &= R_{n_f l_f} Y_{l_f m_f}(\theta,\phi)\end{aligned}\right\} \tag{49}$$

$R_{n_i l_i} Y_{l_i m_i}(\theta,\phi)$

$R_{n_f l_f} Y_{l_f m_f}$

Now, it can be shown that (see Problem 26.2)

$$\int \psi_f^* z \psi_i d\tau = G\left[\delta_{l_f,l_i+1}\left(\frac{(l_i+m_i+1)(l_i-m_i+1)}{(2l_i+1)(2l_i+3)}\right)^{1/2} + \delta_{l_f,l_i-1}\left(\frac{(l_i+m_i)(l_i-m_i)}{(2l_i+1)(2l_i+3)}\right)^{1/2}\right]\delta_{m_f,m_i} \tag{50}$$

δ_{l_f, l_i+1} $\delta_{m_f m_i}$

δ_{l_f, l_i+1}

and

$$\int \psi_f^* (x \pm iy) \psi_i d\tau = G\left[\delta_{l_f,l_i+1}\left(\frac{(l_i+m_i+1)(l_i+m_i+2)}{(2l_i+1)(2l_i+3)}\right)^{1/2} \pm \delta_{l_f,l_i-1}\left(\frac{(l_i-m_i)(l_i-m_i-1)}{(2l_i+1)(2l_i-1)}\right)^{1/2}\right]\delta_{m_f,m_i\pm 1} \tag{51}$$

$\delta_{l_f\, l_i+1}$

where

$$G = \int_0^\infty r^3 R_{n_f l_f}(r) R_{n_i l_i}(r)\, dr \tag{52}$$

where R_{nl} represents the radial part of the wave functions. Equations (50) and (51) tell us that for a transition to occur, we must have

Selection rules

$$\left.\begin{aligned}\Delta l &= l_f - l_i = \pm 1\\ \Delta m &= m_f - m_i = 0\end{aligned}\right\} \tag{53}$$

and

$$\left.\begin{aligned}\Delta l &= l_f - l_i = \pm 1\\ \Delta m &= m_f - m_i = \pm 1\end{aligned}\right\} \tag{54}$$

which are known as the *selection rules*. Since spin angular momenta are not involved, we have

$$\Delta j = \pm 1 \tag{55}$$

as well.

For the $\Delta m = 0$ transition, the dipole moment vector

$$\mathbf{P} = q\int \psi_f^* \mathbf{r} \psi_i d\tau \tag{56}$$

$\int \psi_f^* r \psi_i d\tau$

is along the z–direction [because $P_x = P_y = 0$—see Eq. (51)].

Now, if we consider an oscillatory dipole in the z–direction

$$\mathbf{p} = p_0 e^{-i\omega t}\hat{\mathbf{z}}$$

$p_0 e^{j\omega t}\hat{z}$

then at large distaces from such a dipole, the electric and magnetic fields are of the form (see, e.g. Ref. 5).

$$\mathcal{E} = -\left(\frac{k^2 p_0}{4\pi\varepsilon_0}\right)\sin\theta\,\frac{e^{i(kr-\omega t)}}{r}\,\hat{\boldsymbol{\theta}} \tag{57}$$

$$\mathcal{H} = -\left(\frac{\omega k p_0}{4\pi}\right)\sin\theta\,\frac{e^{i(kr-\omega t)}}{r}\,\hat{\boldsymbol{\phi}} \tag{58}$$

where θ represents the polar angle that $\mathbf{r}$ makes with the z–axis. Further, the Poynting vector (associated with the emitted radiation field) is given by

$$\mathbf{S} = \frac{\omega k^3 p_0^2}{16\pi^2\varepsilon_0}\sin^2\theta\,\frac{\cos^2(kr-\omega t)}{r^2}\,\hat{\mathbf{r}} \tag{59}$$

Thus the electric field associated with the emitted radiation will be linearly polarized with its electric vector oscillating in the plane defined by $\hat{\mathbf{z}}$ and the direction of the emitted radiation $\mathbf{k}$ (see Fig. 26.3). Further, the intensity of the radiation will vary as $\sin^2\theta \left(= |\hat{\mathbf{e}}\cdot\hat{\mathbf{z}}|^2\right)$. For $\theta = \pi/2$ (i.e. for the emitted radiation propagating along any direction which is perpendicular to the z–axis), the electric field vector will be oscillating in the z–direction.

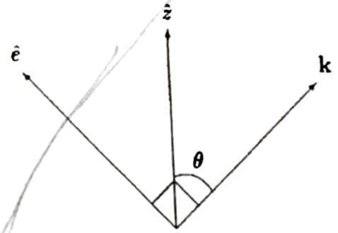


Figure 26.3: The vector $\mathbf{k}$ represents the direction of propagation of the emitted radiation. The plane of the paper is defined by the vectors $\mathbf{k}$ and $\hat{\mathbf{z}}$. For the $\Delta m = 0$ transition, the polarization vector of the emitted radiation $\hat{\mathbf{e}}$ will lie in the $\mathbf{k}-\hat{\mathbf{z}}$ plane with the intensity of radiation maximum for $\theta = \pi/2$ and zero for $\theta = 0$.

For the

$$m_f = m_i + 1$$

transition

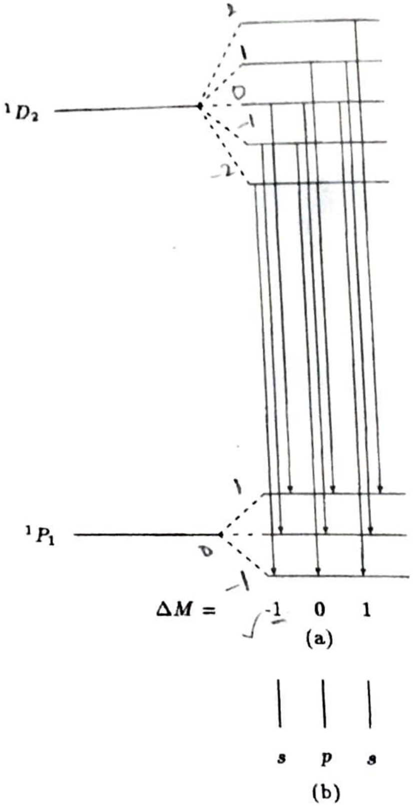
$$P_z = 0 \quad \text{and} \quad P_x - iP_y = 0$$

[see Eqs (50) and (51)]. Thus

$$P_y = -iP_x \tag{60}$$

The above equation implies that the emitted radiation will be superposition of radiation from two dipoles oscillating (with a phase difference of $\pi/2$) in the x– and y– directions. Using formulae similar to Eqs (57) and (58) one can easily if $\mathbf{k}$ is along $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$, the emitted radiation is plane polarized along the $\hat{\mathbf{y}}$– and $\hat{\mathbf{x}}$–directions respectively and if $\mathbf{k}$ is along $\hat{\mathbf{z}}$, the radiation is left circularly polarized. For $\mathbf{k}$ in any other direction, the polarization is elliptical.

As an example, we consider the ${}^1D_2 \to {}^1P_1$ transition (as in the case of the Cd 6438.17 Å line). Since we have neglected spin, we consider only singlet states. If we place the atom in a magnetic field in the z–direction, the levels will split up as shown in Fig. 26.4 (this is the Zeeman effect). Using the selection rules, we have



$^1D_2 \to {}^1P_1$

Figure 26.4: (a) The Zeeman pattern for the $^1D_2 \to {}^1P_1$ transition. (b) If viewed ⊥ to **B**, three lines are seen; if light polarized ∥ to **B** is allowed to reach the film then only the p components are seen and if light polarized ⊥ to **B** is allowed to reach the film then only the s components are seen.

Zeeman effect

Viewed ⊥ to **B** [i.e. **k** along $\hat{\mathbf{x}}$ (say)]
- $m_f = m_i$ (i.e. $\Delta m = 0$) transitions plane polarized ∥ to **B** ($p-$components)
- $m_f = m_i \pm 1$ (i.e. $\Delta m = \pm 1$) transitions plane polarized ⊥ to **B** ($s-$components)

Viewed ∥ to **B** [i.e. **k** along $\hat{\mathbf{z}}$ (say)]
- $m_f = m_i$ (i.e. $\Delta m = 0$) transitions not seen ($p-$components)
- $m_f = m_i \pm 1$ (i.e. $\Delta m = \pm 1$) transitions circularly polarized ($s-$components)

This is known as the normal Zeeman effect and the lines are known as the Lorentz triplet.

In the presence of spin-orbit interaction of the form $\xi(r)\,\mathbf{L}\cdot\mathbf{s}$, the atomic states are characterized by the quantum numbers l, s, j and m_j (see Problem 20.2). The corresponding selection rules are

$$\left.\begin{array}{l}\Delta j = 0, \pm 1 \\ \Delta l = \pm 1 \\ \Delta m_j = 0, \pm 1\end{array}\right\} \qquad (61)$$

l+s = j

However,

$$(m_j)_i = 0 \to (m_j)_f = 0 \quad \text{transition forbidden if } \Delta j = 0$$

It may be noted that the transition $\Delta j = 0$ is allowed but $j_i = j_f = 0$ transition is not allowed. The Zeeman pattern for the $^2P_{3/2,1/2} \to {}^2S_{1/2}$ transition (as in the case of D lines of Sodium) is shown in Fig. 26.5 (see also Problem 26.7).

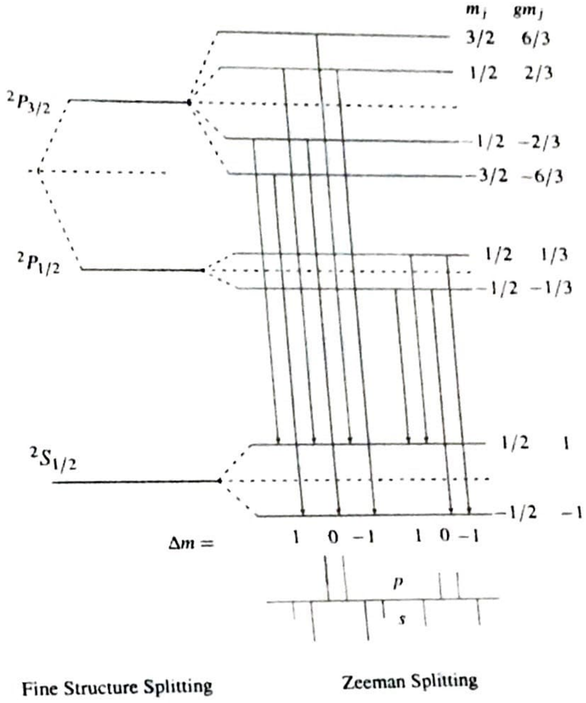


Figure 26.5: The Zeeman pattern for the $^2P_{3/2.1/2} \to {}^2S_{1/2}$ doublet in sodium. Notice that the Zeeman splitting is different for different levels [the splitting is proportional to gm_j, see Eq. (66) of Chapter 20]. The lower part of the figure shows that in the transition there are two p components and four s components.

26.6 Problems

Problem 26.1 Show that for optical frequencies, at thermal equilibrium (corresponding to $T \sim 1000°K$), the number of spontaneous emissions far exceeds the number of stimulated emissions.

Chapter 27

The quantum theory of radiation and its interaction with matter

> *Quantum mechanics is very impressive. But an inner voice tells me that it is not yet the real thing. The theory produces a good deal but hardly brings us closer to the secret of the Old One. I am at all events convinced that* **He** *does not play dice.*
>
> — ALBERT EINSTEIN in a letter to Max Born 4 December 1926.
>
> *Neils Bohr's response is somewhat less well known*[1]*: But still, it cannot be for us to tell God, how he is to run the world.*

27.1 Introduction

In the previous chapter we developed the semi-classical theory of interaction of radiation with matter in which matter, i.e. atoms, were assumed to exist in discrete (quasi-stationary states) but the electromagnetic field with which it interacts was described classically. In this chapter we will develop the fully quantum theory of radiation and discuss its interaction with matter.

We will first consider the Hamiltonian of an atomic system in a radiation field (Sec. 27.2). We will next show that the electromagnetic field in a closed cavity can be considered as an infinite set of oscillators, each corresponding to a particular value of the wave vector and particular direction of polarization. By imposing the commutation relations between the canonical variables, it will be shown that the energy of each oscillator can increase or decrease by integral multiples of certain quantum of energy; this quantum of energy is known as the *photon*. In Sec. 27.4 we will use the quantum mechanical description of the radiation field to study its interaction with an atom and thereby obtain explicit expressions for the Einstein *A* and *B* coefficients which will be shown to be identical to the results obtained in the previous chapter. It may be mentioned that the theory developed in Sec. 27.4

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[1] The authors found this quotation in Jim Baggott's book on *The Meaning of Quantum Theory*, Oxford University Press, Oxford (1992).

automatically leads to spontaneous emissions which in the semi-classical theory had to be introduced in an ad hoc manner through the Einstein coefficients (see Sec. 26.4). In Sec. 27.5 we will discuss the properties of the eigenstates of the Hamiltonian of the radiation field and will show that the state which corresponds to a given number of photons for a particular mode does *not* correspond to the classical plane wave. Indeed, in Sec. 27.6, we will show that the eigenstates of the annihilation operator (which are known as the *coherent states*) resemble the classical plane wave for large intensities. In fact when a laser is operated much beyond the threshold, it generates a coherent state excitation of a cavity mode. Finally, in Sec. 27.7, we will show that it is difficult to give a quantum mechanical description of the phase of the electromagnetic wave.

27.2 The Hamiltonian

The Hamiltonian of an atomic system in a radiation field can be written as

$$\begin{aligned} H &= H_0 + H' \\ &= H_a + H_r + H' \end{aligned} \tag{1}$$

$H_a + H_r$

where H_a represents the Hamiltonian of the atom, H_r the Hamiltonian corresponding to the pure radiation field, which is given by

Radiation field Hamiltonian

$$H_r = \frac{1}{2}\int (\varepsilon_0 \mathcal{E}\cdot\mathcal{E} + \mu_0 \mathcal{H}\cdot\mathcal{H})\, d\tau \tag{2}$$

and H' represents the interaction between the atom and the radiation field. In Eq. (2) ε_0 and μ_0 represent the dielectric permittivity and magnetic permeability of free space, $\mathcal{E}$ and $\mathcal{H}$ represent the electric and magnetic fields associated with the radiation field. For example, for a non-relativistic electron (of charge $-q$) in a radiation field, we have

$$H = \frac{1}{2m}(\mathbf{p} + q\mathbf{A})^2 + V + H_r \tag{3}$$

since the recipe is to replace the electron momentum operator $\mathbf{p}$ by $\mathbf{p} + q\mathbf{A}$ (see Sec. 20.2), where $\mathbf{A}$ is the vector potential and V is the potential energy of the electron. We can rewrite Eq. (3) as

$$H = H_0 + H' \tag{4}$$

where

$$\left.\begin{aligned} H_0 &= H_a + H_r \\ H_a &= \frac{p^2}{2m} + V(r) \\ H' &= \frac{q}{2m}(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}) + \frac{q^2}{2m}A^2 \end{aligned}\right\} \tag{5}$$

and H_r is given by Eq. (2). In Sec. 27.4 we will treat H' as a perturbation and study the transitions between eigenstates of H_0. The term $\frac{q^2}{2m}A^2$ appearing in the expression for H' usually represents a very small perturbation and hence will be neglected. Thus the interaction term is given by

$$H' = +\frac{q}{m}(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}) \tag{6}$$

Now

$$\begin{aligned} \mathbf{p}\cdot\mathbf{A}\Psi &= -i\hbar\nabla\cdot(\mathbf{A}\Psi) \\ &= -i\hbar[(\nabla\cdot\mathbf{A})\Psi + \mathbf{A}\cdot\nabla\Psi] \\ &= \mathbf{A}\cdot\mathbf{p}\Psi \end{aligned}$$

where we have chosen the Coulomb gauge in which $\nabla\cdot\mathbf{A} = 0$ (see Sec. 20.3). Thus

$$H' = \frac{q}{m}\mathbf{A}\cdot\mathbf{p} = \frac{q}{m}\mathbf{p}\cdot\mathbf{A} \tag{7}$$

There are now two ways of proceeding further. The first is to treat the electromagnetic field classically; this has indeed been done in the previous chapter. The second and more powerful method is to quantize the radiation field and calculate rates of transition between states of matter and quanta; this will be done in Sections 27.3 and 27.4. However, before we do so, we will first show (in Sec. 27.2.1) that the interaction term given by Eq. (12) of the previous chapter is consistent with Eq. (7) under certain approximation which is known as the dipole approximation.

27.2.1 The interaction term in the semi-classical theory of radiation

For a plane electromagnetic wave, the vector potential can be written in the form

$$\mathbf{A} = \hat{\mathbf{e}}A_0\cos(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{8}$$

where $\hat{\mathbf{e}}$ represents the unit vector along $\mathbf{A}$ (denoting the polarization of the wave), and

$$\mathbf{k} = \frac{\omega}{c}\hat{\mathbf{k}} \tag{9}$$

where $\hat{\mathbf{k}}$ represents the unit vector along the direction of propagation. The condition $\nabla\cdot\mathbf{A} = 0$ gives

$$\hat{\mathbf{e}}\cdot\mathbf{k} = 0 \tag{10}$$

implying that $\hat{\mathbf{e}}$ is at right angles to the direction of propagation, i.e. the wave is transverse. The electric field is given by

$$\mathcal{E} = -\frac{\partial\mathbf{A}}{\partial t} = -\hat{\mathbf{e}}\mathcal{E}_0\sin(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{11}$$

where

$$\mathcal{E}_0 = \omega A_0 \tag{12}$$

Now

$$\begin{aligned} H' &= \frac{q}{m}\mathbf{A}\cdot\mathbf{p} \\ &= \frac{q\mathcal{E}_0}{2m\omega}\hat{\mathbf{e}}\left[e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right]\cdot\mathbf{p} \end{aligned}$$

The matrix element of transition is given by (cf. Eq. 17 of the previous chapter):

$$\begin{aligned} H'_{sn} = \langle s \mid H' \mid n\rangle = \frac{q\mathcal{E}_0}{2m\omega}\hat{\mathbf{e}}\cdot\Big[&\langle s|e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{p}|n\rangle e^{-i\omega t} \\ &+ \langle s|e^{-i\mathbf{k}\cdot\mathbf{r}}\mathbf{p}|n\rangle e^{-i\omega t}\Big] \end{aligned} \tag{13}$$

where the kets $| n >$ and $| s >$ are eigenstates of the atomic Hamiltonian H_a and represent the initial and final states. Now

$$e^{\pm i\mathbf{k}\cdot\mathbf{r}} = 1 \pm i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2!}(\mathbf{k}\cdot\mathbf{r})^2 + \dots$$

Since atomic dimensions are $\sim 10^{-8}$ cm and for optical wavelength

$$k\left(=\frac{2\pi}{\lambda}\right) \sim 10^5\ \text{cm}^{-1}$$

we obtain (in the region of integration) $kr \ll 1$. Thus, negligible error will be involved if the exponential is replaced by unity[2] and the transition is said to be an electric dipole transition – a very important case. In this approximation

$$\langle s | e^{\pm i\mathbf{k}\cdot\mathbf{r}}\mathbf{p} | n\rangle \simeq \langle s | \mathbf{p} | n\rangle \tag{14}$$

Now the kets $| n >$ and $| s >$ are eigenkets[3] of the atomic Hamiltonian H_a

$$H_a | n\rangle = E_n | n\rangle = \hbar\omega_n | n\rangle \tag{15}$$

$$H_a | s\rangle = E_s | s\rangle = \hbar\omega_s | s\rangle \tag{16}$$

Further

$$H_a = \frac{p^2}{2m} + V(\mathbf{r})$$

Thus

$$[x, H_a] = \left[x, \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\mathbf{r})\right]$$

$$= \frac{1}{2m}\left([x, p_x]\,p_x + p_x[x, p_x]\right)$$

$$= \frac{i\hbar}{m}p_x \tag{17}$$

or,

$$\mathbf{p} = \frac{m}{i\hbar}[\mathbf{r}, H_a] \tag{18}$$

Hence

$$\langle s | \mathbf{p} | n\rangle = \frac{m}{i\hbar}\langle s | \mathbf{r}H_a - H_a\mathbf{r} | n\rangle$$

$$= \frac{m}{i\hbar}(E_n - E_s)\,\langle s | \mathbf{r} | n\rangle$$

$$= \frac{m\omega_{ns}}{i}\langle s | \mathbf{r} | n\rangle \tag{19}$$

where we have used Eq. (15) and conjugate of Eq. (16) and

$$\hbar\omega_{ns} = E_n - E_s$$

On substitution in Eq. (13), we get

$$\langle s | H' | n\rangle = \frac{q\mathcal{E}_0\omega_{ns}}{2\omega}\,\hat{\mathbf{e}}\cdot\langle s | \mathbf{r} | n\rangle\left[e^{i\omega t} - e^{-i\omega t}\right] \tag{20}$$

$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = 0$

$\nabla\cdot A = 0$

The above equation is of a form similar (although not identical) to that of Eq. (17) of the previous chapter. However, for $\omega \approx |\omega_{ns}|$ after one carries out the integration which leads to Eq. (22) of the previous chapter, one obtains identical expressions for probabilities of absorption and of emission [see Eq. (24) of the previous chapter].

27.3 Quantization of the radiation field

We now develop the second method mentioned in Sec. 27.1. In this method, the electromagnetic field is described in terms of numbers of photons in various states.

We consider first a pure radiation field. In Coulomb gauge, such a field can be derived from the vector potential **A** only, with $\Phi = 0$ and

$$\nabla\cdot\mathbf{A} = 0 \tag{21}$$

In this gauge, the magnetic and electric fields are given by (see Sec. 20.2)

$$\mathcal{B} = \mu_0\mathcal{H} = \nabla\times\mathbf{A} \tag{22}$$

and

$$\mathcal{E} = -\frac{\partial\mathbf{A}}{\partial t} \tag{23}$$

where we have assumed $\Phi = 0$ since we are considering free space. Substituting for $\mathcal{H}$ and $\mathcal{E}$ in the Maxwell equation

$$\nabla\times\mathcal{H} = \frac{\partial\mathbf{D}}{\partial t} = \varepsilon_0\frac{\partial\mathcal{E}}{\partial t} \tag{24}$$

we get

$$\nabla\times(\nabla\times\mathbf{A}) = -\varepsilon_0\mu_0\frac{\partial^2\mathbf{A}}{\partial t^2} \tag{25}$$

If we now use the identity[4]

$$\nabla\times(\nabla\times\mathbf{A}) \equiv \nabla(\nabla\cdot\mathbf{A}) - \nabla^2\mathbf{A} = -\nabla^2\mathbf{A} \tag{26}$$

(because $\nabla\cdot\mathbf{A} = 0$), we finally obtain

$$\nabla^2\mathbf{A} = \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} \tag{27}$$

A(r,t)

where

$$c = (\varepsilon_0\mu_0)^{-1/2} \tag{28}$$

represents the speed of light in free space. Equation (27) represents the three-dimensional wave equation. In order to solve the wave equation, we use the method of separation of variables:

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r})\,q(t) \tag{29}$$

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[2] However, if the replacement of $e^{\pm i\mathbf{k}\cdot\mathbf{r}}$ by unity leads to a vanishing matrix element, one must use higher order terms like $(\pm i\mathbf{k}\cdot\mathbf{r})$ etc., these are said to correspond to higher order transitions (see Problems 27.1).

[3] We may warn the reader of some confusion of notation. The initial and final states of the atomic Hamiltonian are also sometimes denoted by $| i >$ and $| f >$ and sometimes by $| a >$ and $| b >$

[4] It may be worthwhile to point out that the operator ∇^2 is *defined* by the following equation

$$\nabla^2\mathbf{A} \equiv \nabla(\nabla\cdot\mathbf{A}) - \nabla\times(\nabla\times\mathbf{A})$$

However,

$$(\nabla^2\mathbf{A})_x = \nabla\cdot(\nabla A_x)$$

i.e. a Cartesian component of $\nabla^2\mathbf{A}$ is div grad of the Cartesian component but

$$(\nabla^2\mathbf{A})_r \neq \nabla\cdot(\nabla A_r)$$

Thus

$$q(t)\nabla^2\mathbf{A}(\mathbf{r}) = \mathbf{A}(\mathbf{r})\frac{1}{c^2}\frac{d^2q}{dt^2} \tag{30}$$

We next consider a Cartesian component (say the x–component) of $\mathbf{A}(\mathbf{r})$ which we denote by $A_x(\mathbf{r})$; thus

$$\frac{c^2}{A_x(\mathbf{r})}\nabla^2 A_x(\mathbf{r}) = \frac{1}{q(t)}\frac{d^2q}{dt^2} = -\omega^2 \text{ (say)} \tag{31}$$

Thus

$$q(t) \sim e^{-i\omega t} \tag{32}$$

and

$$\nabla^2 A_x(\mathbf{r}) + k^2 A_x(\mathbf{r}) = 0 \tag{33}$$

where $k^2 = \omega^2/c^2$. The solutions of Eq. (33) are plane waves; and similarly if we consider the y– and z–components we obtain

$$\mathbf{A}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\,\hat{\mathbf{e}} \tag{34}$$

where $\mathbf{k}\cdot\mathbf{k} = k^2$, $\hat{\mathbf{e}}$ is the unit vector along $\mathbf{A}$. The condition $\nabla\cdot\mathbf{A} = 0$ gives us $\mathbf{k}\cdot\hat{\mathbf{e}} = 0$, implying the transverse character of the wave [see Eq. (10)].

The allowed values of $\mathbf{k}$ (and hence of ω) are determined from the boundary conditions. If we assume the radiation to be confined in a cubical cavity of volume $V\ (= L^3)$ and use the periodic boundary condition then

$$\mathbf{A}(x=0,y,z) = \mathbf{A}(x=L,y,z) \qquad \text{etc.} \tag{35}$$

giving

$$e^{ik_xL} = 1 = e^{ik_yL} = e^{ik_zL} \tag{36}$$

Thus

$$\left.\begin{aligned} k_x &= \frac{2\pi\nu_x}{L} \\ k_y &= \frac{2\pi\nu_y}{L} \\ k_z &= \frac{2\pi\nu_z}{L} \end{aligned}\right\} \nu_x,\nu_y,\nu_z = 0,\pm1,\pm2,\dots \tag{37}$$

The complete solution of Eq. (27) is therefore given by

$$\mathbf{A}(\mathbf{r},t) = \sum_\lambda \left[q_\lambda(t)\,\mathbf{A}_\lambda(\mathbf{r}) + q_\lambda^*(t)\,\mathbf{A}_\lambda^*(\mathbf{r})\right] \tag{38}$$

where

$$\mathbf{A}_\lambda(\mathbf{r}) = e^{i\mathbf{k}_\lambda\cdot\mathbf{r}}\,\hat{\mathbf{e}}_\lambda \tag{39}$$

$$q_\lambda(t) = |q_\lambda|\,e^{-i\omega_\lambda t} \tag{40}$$

and the subscript λ signifies the various modes of the field [see Eq. (37)] including the two states of polarization. Thus, a particular value of λ corresponds to a particular set of values of ν_x,ν_y,ν_z and a particular direction of $\hat{\mathbf{e}}$. In Eq. (38) the second term on the RHS is complex conjugate of the first term making $\mathbf{A}$ necessarily real. Because of the allowed values of $\mathbf{k}_\lambda$ [see Eq. (37)], we readily obtain

$$\iiint_V \mathbf{A}_\lambda\cdot\mathbf{A}_\mu^*\,d\tau = \iiint_V \mathbf{A}_\lambda\cdot\mathbf{A}_{-\mu}\,d\tau = V\,\delta_{\lambda,\mu} \tag{41}$$

where the integration is over the entire volume of the cavity. Using Eq. (38), we obtain the following expressions for the electric and magnetic fields:

$$\mathcal{E} = -\frac{\partial\mathbf{A}}{\partial t} = \sum_\lambda \mathcal{E}_\lambda \tag{42}$$

$$\mathcal{H} = \frac{1}{\mu_0}\nabla\times\mathbf{A} = \sum_\lambda \mathcal{H}_\lambda \tag{43}$$

where

$$\mathcal{E}_\lambda = i\omega_\lambda\left[q_\lambda(t)\,\mathbf{A}_\lambda(\mathbf{r}) - q_\lambda^*(t)\,\mathbf{A}_\lambda^*(\mathbf{r})\right] \tag{44}$$

and

$$\mathcal{H}_\lambda = \frac{i}{\mu_0}\mathbf{k}_\lambda\times\left[q_\lambda\mathbf{A}_\lambda - q_\lambda^*\mathbf{A}_\lambda^*\right] \tag{45}$$

The total energy of the radiation field is given by

$$H_r = \frac{1}{2}\int\left(\varepsilon_0\mathcal{E}\cdot\mathcal{E} + \mu_0\mathcal{H}\cdot\mathcal{H}\right)d\tau \tag{46}$$

Now

$$\begin{aligned}
\frac{1}{2}\varepsilon_0\int_V \mathcal{E}\cdot\mathcal{E}\,d\tau &= -\frac{1}{2}\varepsilon_0\sum_\lambda\sum_\mu \omega_\lambda\omega_\mu\Big[q_\lambda q_\mu\int \mathbf{A}_\lambda\cdot\mathbf{A}_\mu\,d\tau \\
&\quad - q_\lambda q_\mu^*\int \mathbf{A}_\lambda\cdot\mathbf{A}_\mu^*\,d\tau - q_\lambda^* q_\mu\int \mathbf{A}_\lambda^*\cdot\mathbf{A}_\mu\,d\tau \\
&\quad + q_\lambda^* q_\mu^*\int \mathbf{A}_\lambda^*\cdot\mathbf{A}_\mu^*\,d\tau\Big] \\
&= -\frac{1}{2}\varepsilon_0 V\sum_\lambda\sum_\mu \omega_\lambda\omega_\mu\big[q_\lambda q_\mu\delta_{\lambda,-\mu} \\
&\quad - q_\lambda q_\mu^*\delta_{\lambda,\mu} - q_\lambda^* q_\mu\delta_{\lambda,\mu} + q_\lambda^* q_\mu^*\delta_{\lambda,-\mu}\big] \\
&= -\frac{1}{2}\varepsilon_0 V\sum_\lambda \omega_\lambda^2\left[q_\lambda q_{-\lambda} + q_\lambda^* q_{-\lambda}^* - 2q_\lambda q_\lambda^*\right]
\end{aligned} \tag{47}$$

Similarly one can evaluate $\int \mathcal{H}\cdot\mathcal{H}\,d\tau$. The final result is

$$\frac{1}{2}\mu_0\int \mathcal{H}\cdot\mathcal{H}\,d\tau = \frac{1}{2}\varepsilon_0 V\sum_\lambda \omega_\lambda^2\left[q_\lambda q_{-\lambda} + q_\lambda^* q_{-\lambda}^* + 2q_\lambda q_\lambda^*\right] \tag{48}$$

where use has to be made of the vector identity

$$(\mathbf{a}\times\mathbf{b})\cdot(\mathbf{c}\times\mathbf{d}) = (\mathbf{a}\cdot\mathbf{c})(\mathbf{b}\cdot\mathbf{d}) - (\mathbf{b}\cdot\mathbf{c})(\mathbf{a}\cdot\mathbf{d}) \tag{49}$$

and the relation

$$k_\lambda^2 = \frac{\omega_\lambda^2}{c^2} = \varepsilon_0\mu_0\omega_\lambda^2 \tag{50}$$

Thus

$$H_r = 2\varepsilon_0 V\sum_\lambda \omega_\lambda^2 q_\lambda(t)\,q_\lambda^*(t) \tag{51}$$

We next introduce the dimensionless variables Q_λ and P_λ defined through the equations

$$Q_\lambda(t) = (\varepsilon_0 V)^{1/2}\left(q_\lambda(t) + q_\lambda^*(t)\right) \tag{52}$$

and

$$P_\lambda(t) = \frac{1}{i}\left(\varepsilon_0 V \omega_\lambda^2\right)^{1/2}\left(q_\lambda(t) - q_\lambda^*(t)\right) \tag{53}$$

Thus

$$q_\lambda(t) = \left(4\varepsilon_0 V \omega_\lambda^2\right)^{-1/2}\left(\omega_\lambda Q_\lambda(t) + iP_\lambda(t)\right) \tag{54}$$

$$q_\lambda^*(t) = \left(4\varepsilon_0 V \omega_\lambda^2\right)^{-1/2}\left(\omega_\lambda Q_\lambda(t) - iP_\lambda(t)\right) \tag{55}$$

and

$$H_r = \sum_\lambda H_\lambda \tag{56}$$

where[5]

$$H_\lambda = \frac{1}{2}\left(P_\lambda^2 + \omega_\lambda^2 Q_\lambda^2\right) \tag{57}$$

The Hamiltonian given by Eq. (57) is identical to that of the linear harmonic oscillator (see Sec. 12.2) which suggests that the electromagnetic field can be regarded as an infinite set of harmonic oscillators, one corresponding to each value of $\mathbf{k}_\lambda$ and to a particular direction of polarization.

Quantization of electromagnetic field

In order to quantize the electromagnetic field we use the same approach as in Sec. 12.2. We consider Q_λ and P_λ to be real operators satisfying the commutation relations

$$[Q_\lambda(t), P_\lambda(t)] \equiv Q_\lambda(t)\,P_\lambda(t) - P_\lambda(t)\,Q_\lambda(t) = i\hbar \tag{58}$$

$$[Q_\lambda(t), P_{\lambda'}(t)] = 0;\ \lambda \neq \lambda' \tag{59}$$

$$[Q_\lambda(t), Q_\mu(t)] = 0 = [P_\lambda(t), P_\mu(t)] \tag{60}$$

where all the operators are in the Heisenberg representation (see Sec. 12.9). We next introduce the dimensionless variables

$$a_\lambda(t) = \frac{1}{\sqrt{2\hbar\omega_\lambda}}\left[\omega_\lambda Q_\lambda(t) + iP_\lambda(t)\right] \tag{61}$$

$$\bar{a}_\lambda(t) = \frac{1}{\sqrt{2\hbar\omega_\lambda}}\left[\omega_\lambda Q_\lambda(t) - iP_\lambda(t)\right] \tag{62}$$

Since $[\omega_\lambda Q_\lambda(t) + iP_\lambda(t)]$ is proportional to $q_\lambda(t)$ [see Eq. (54)] which has a time dependence of the form $e^{-i\omega_\lambda t}$, we may write (see also Sec. 12.8)

$$a_\lambda(t) = a_\lambda e^{-i\omega_\lambda t} \tag{63}$$

Similarly,

$$\bar{a}_\lambda(t) = \bar{a}_\lambda e^{+i\omega_\lambda t} \tag{64}$$

where

$$a_\lambda \equiv a_\lambda(0) \quad \text{and} \quad \bar{a}_\lambda \equiv \bar{a}_\lambda(0) \tag{65}$$

---

[5] Notice that

$$\frac{\partial H_\lambda}{\partial Q_\lambda} = \omega_\lambda^2 Q_\lambda = \omega_\lambda^2\left(\varepsilon_0 V\right)^{1/2}\left(q_\lambda + q_\lambda^*\right) = i\left(\varepsilon_0 V \omega_\lambda^2\right)^{1/2}\left(\dot{q}_\lambda - \dot{q}_\lambda^*\right) = -\dot{P}_\lambda$$

Similarly

$$\frac{\partial H_\lambda}{\partial P_\lambda} = +\dot{Q}_\lambda$$

which are nothing but Hamilton's equations of motion [see, Ref. 1]. Thus Q_λ and P_λ are the canonical coordinates.

Solving Eqs (61) and (62) for $Q_\lambda(t)$ and $P_\lambda(t)$ we obtain

$$Q_\lambda(t) = \sqrt{\frac{\hbar}{2\omega_\lambda}}\left[\bar{a}_\lambda(t) + a_\lambda(t)\right] \tag{66}$$

$$P_\lambda(t) = i\sqrt{\frac{\hbar\omega_\lambda}{2}}\left[\bar{a}_\lambda(t) - a_\lambda(t)\right] \tag{67}$$

Substituting the above expressions for $Q_\lambda(t)$ and $P_\lambda(t)$ in Eq. (57), we obtain

$$\begin{aligned} H_r = \sum_\lambda H_\lambda &= \sum_\lambda \frac{1}{2}\hbar\omega_\lambda\left(\bar{a}_\lambda(t)\,a_\lambda(t) + a_\lambda(t)\,\bar{a}_\lambda(t)\right) \\ &= \sum_\lambda \frac{1}{2}\hbar\omega_\lambda\left(\bar{a}_\lambda a_\lambda + a_\lambda\bar{a}_\lambda\right) \end{aligned} \tag{68}$$

If we now carry out an analysis similar to that followed in Sec. 12.2, we obtain

$$\left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda\,;\ n_\lambda = 0, 1, 2, \ldots \tag{69}$$

as the eigenvalues of H_λ and

$$\sum_\lambda\left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda \tag{70}$$

as the eigenvalues of the total Hamiltonian $H_r (= \sum H_\lambda)$. Thus, quantum mechanically, we can visualize the radiation field as consisting of an infinite number of simple harmonic oscillators; the energy of each oscillator can increase or decrease by integral multiples of $\hbar\omega_\lambda$. If we consider $\hbar\omega_\lambda$ as the energy of a photon, each oscillator can have energy corresponding to n_λ photons.

The eigenkets of the total Hamiltonian would be

$$|n_1\rangle\,|n_2\rangle\,|n_3\rangle\ldots = |n_1, n_2, n_3, \ldots n_\lambda, \ldots\rangle \tag{71}$$

where n_λ represents the number of photons in the mode characterized by λ. Thus

$$H_r\,|n_1, n_2, \ldots n_\lambda, \ldots\rangle = \left(\sum_\lambda\left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda\right)|n_1, n_2, \ldots n_\lambda, \ldots\rangle \tag{72}$$

Further [see Eqs (24) and (25) of Chapter 12]:

$$a_\lambda\,|n_1, n_2, \ldots n_\lambda, \ldots\rangle = \sqrt{n_\lambda}\,|n_1, n_2, \ldots n_\lambda - 1, \ldots\rangle \tag{73}$$

$$\bar{a}_\lambda\,|n_1, n_2, \ldots n_\lambda, \ldots\rangle = \sqrt{n_\lambda + 1}\,|n_1, n_2, \ldots n_\lambda + 1, \ldots\rangle \tag{74}$$

and

$$\langle n_1', n_2', \ldots n_\lambda', \ldots\,|\,n_1, n_2, \ldots n_\lambda, \ldots\rangle = \delta_{n_1, n_1'}\,\delta_{n_2, n_2'}, \ldots, \delta_{n_\lambda, n_\lambda'} \cdots \tag{75}$$

Finally, the state of the radiation field need not be an eigenstate of H_r, it could be a superposition of the eigenstates like that given by the following equation

$$|\Psi\rangle = \sum_{n_1, \ldots} C_{n_1, n_2, \ldots n_\lambda \ldots}\,|n_1, n_2, \ldots n_\lambda, \ldots\rangle \tag{76}$$

Physically $\left|C_{n_1, n_2, \cdots n_\lambda \ldots}\right|^2$ would represent the probability of finding n_1 photons in the first mode, n_2 in the second mode, etc.

27.4 Spontaneous and stimulated emissions

We next express the vector potential **A** (and hence the interaction term H') in terms of the operators a_λ and $\bar{a}_\lambda$. Now using Eqs (54) and (61), we get

$$q_\lambda(t) = \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} a_\lambda(t) \tag{77}$$

which is now to be considered as an operator. Using Eq. (38) we get

$$\begin{aligned}\mathbf{A} &= \sum_\lambda \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} \left[a_\lambda(t)\mathbf{A}_\lambda(\mathbf{r}) + \bar{a}_\lambda(t)\mathbf{A}^*_\lambda(\mathbf{r})\right] \\ &= \sum_\lambda \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} \left[a_\lambda(t)\, e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda(t)\, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right]\hat{\mathbf{e}}_\lambda\end{aligned} \tag{78}$$

where all the operators are in the Heisenberg representation (see Sec. 12.9). In the Schrödinger representation, we will have

$$\mathbf{A} = \sum_\lambda \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} \left[a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right]\hat{\mathbf{e}}_\lambda \tag{79}$$

which will be independent of time. The interaction energy is

$$H' = \frac{q}{m}\mathbf{A}\cdot\mathbf{p} \tag{80}$$

or

Interaction energy

$$H' = \frac{q}{m}\sum_\lambda \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} \left[a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right]\hat{\mathbf{e}}_\lambda\cdot\mathbf{p} \tag{81}$$

Now, the eigenvalue equations for H_a and H_r are

$$H_a \mid \Psi\rangle = E_i \mid \Psi_i\rangle \tag{82}$$

and

$$H_r \mid n_1, n_2, \ldots\rangle = \left[\sum_\lambda \left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda\right] \mid n_1, n_2, \ldots n_\lambda, \ldots\rangle \tag{83}$$

where $\mid \psi_i\rangle$ and E_i represent respectively the eigenkets and energy eigenvalues of the isolated atom and $\mid n_1, n_2, \ldots\rangle$ represent the eigenket of the pure radiation field with $\sum_\lambda (n_\lambda + \frac{1}{2})\hbar\omega_\lambda$ representing the corresponding eigenvalue (see Eq. 72).

Thus the eigenvalue equation for H_0 will be

$$H_0 \mid u_n\rangle = W_n \mid u_n\rangle \tag{84}$$

where

$$W_n = E_n + \sum \left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda \tag{85}$$

and

$$\mid u_n\rangle = \mid i\rangle \mid n_1, n_2, \ldots n_\lambda, \ldots\rangle = \mid i; n_1, n_2, \ldots n_\lambda, \ldots\rangle \tag{86}$$

represents the ket corresponding to the atom being in state $\mid i\rangle$ and the radiation being in the state $\mid n_1, n_2, \ldots n_\lambda, \ldots\rangle$.

Now the Schrödinger equation for the system consisting of the atom and the radiation field is

$$i\hbar\frac{\partial \mid \Psi\rangle}{\partial t} = (H_0 + H') \mid \Psi\rangle \tag{87}$$

The solution of the above equation can be written as a linear combination of the eigenkets of H_0 (cf. Eq. 15 of the previous chapter):

$$\mid \Psi\rangle = \sum_n C_n(t)\, e^{-iW_n t/\hbar} \mid u_n\rangle \tag{88}$$

Substituting in Eq. (87), we obtain

$$\begin{aligned} i\hbar\sum_n \left[\frac{dC_n}{dt} - i\frac{W_n}{\hbar}C_n\right] e^{-iW_n t/\hbar} \mid u_n\rangle \\ = \sum_n C_n(t)\, W_n e^{-iW_n t/\hbar} \mid u_n\rangle + H'\sum_n C_n(t)\, e^{-iW_n t/\hbar} \mid u_n\rangle \end{aligned}$$

where we have used Eq. (84). Premultiplying by $\langle u_s \mid$ we get (cf. Eq. 16 of Chapter 26)

$$i\hbar\frac{dC_s}{dt} = \sum_n \langle u_s \mid H' \mid u_n\rangle\, e^{i(W_m - W_n)t/\hbar} C_n(t) \tag{89}$$

Now using Eq. (81)

$$\begin{aligned}\langle u_s \mid H' \mid u_n\rangle = \frac{q}{m}\sum_\lambda \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} \hat{\mathbf{e}}_\lambda \cdot \\ \langle u_s \mid \left(a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right)\mathbf{p} \mid u_n\rangle\end{aligned} \tag{90}$$

Because of the appearance of a_λ and $\bar{a}_\lambda$ in the expression for H', the various terms in $\langle u_s|H'|u_n\rangle$ will be non-zero only if the number of photons in $\mid u_s\rangle$ differs by unity from the number of photons in $\mid u_n\rangle$. If we write out completely the right-hand side of Eq. (89) it will lead to a coupled set of an infinite number of equations which would be impossible to solve. We employ the perturbation theory and consider the absorption of one photon (of energy $\hbar\omega_i$) from the i^{th} mode. Further, if we assume the frequency ω_i to be very close to the resonant frequency corresponding to the transition from the atomic state $\mid a\rangle$ to $\mid b\rangle$, then Eq. (89) reduces to the following two coupled equations (see also Solution 27.3):

$$i\hbar\frac{dC_1}{dt} = H'_{12}\, e^{i(W_1 - W_2)t/\hbar} C_2(t) \tag{91}$$

$$i\hbar\frac{dC_2}{dt} = H'_{21}\, e^{-i(W_1 - W_2)t/\hbar} C_1(t) \tag{92}$$

where

$$\mid 1\rangle = \mid a; n_1, n_2, \ldots n_\lambda, \ldots, n_i, \ldots\rangle \tag{93}$$

and

$$\mid 2\rangle = \mid b; n_1, n_2, \ldots n_\lambda, \ldots, n_i - 1, \ldots\rangle \tag{94}$$

represent the initial and final states of the system. Obviously, because of relations like Eq. (115), $H'_{11} = 0 = H'_{22}$. Further,

$$\left.\begin{aligned} W_1 &= E_a + \sum_{\substack{\lambda \\ \lambda \neq i}} \left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda + \left(n_i + \frac{1}{2}\right)\hbar\omega_i \\ W_2 &= E_b + \sum_{\substack{\lambda \\ \lambda \neq i}} \left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda + \left(n_i - 1 + \frac{1}{2}\right)\hbar\omega_i \end{aligned}\right\} \tag{95}$$

Thus,

$$W_1 - W_2 = (E_a - E_b) + \hbar\omega_i \tag{96}$$

Now

$$\begin{aligned} H'^{*}_{21} = H'_{12} &= \frac{q}{m}\sum_\lambda \left(\frac{\hbar}{2\varepsilon_0 V\omega_\lambda}\right)^{1/2} \hat{\mathbf{e}}_\lambda \cdot \langle a; n_1, n_2, \ldots n_i, \ldots | \\ &\qquad \left(a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right)\mathbf{p} \mid b; n_1, n_2, \ldots n_i - 1, \ldots\rangle \\ &= \frac{q}{m}\left(\frac{\hbar}{2\varepsilon_0 V\omega_i}\right)^{1/2} \sqrt{n_i}\,\hat{\mathbf{e}}_\lambda \cdot \langle a \mid e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\mathbf{p} \mid b\rangle \\ &\simeq \frac{q}{m}\left(\frac{\hbar}{2\varepsilon_0 V\omega_i}\right)^{1/2} \sqrt{n_i}\,\hat{\mathbf{e}}_\lambda \cdot \langle a \mid \mathbf{p} \mid b\rangle \end{aligned} \tag{97}$$

where in the last step we have used the dipole approximation in which we have replaced $e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}$ by unity (see Eq. 14). If we now use Eq. (19) we get

$$\begin{aligned} \langle a \mid \mathbf{p} \mid b\rangle &= \frac{m}{i\hbar}(E_b - E_a)\langle a \mid \mathbf{r} \mid b\rangle \\ &= -im\omega_{ba}\langle a \mid \mathbf{r} \mid b\rangle \end{aligned}$$

Thus

$$H'^{*}_{21} = H'_{12} = -i\left(\frac{\hbar}{2\varepsilon_0 V\omega_i}\right)^{1/2} \omega_{ba}\sqrt{n_i}\,D_{ab} \tag{98}$$

where

$$D_{ab} = q\hat{\mathbf{e}}_\lambda \cdot \langle a \mid \mathbf{r} \mid b\rangle = \frac{iq}{m\omega_{ba}}\hat{\mathbf{e}}_\lambda \cdot \langle a \mid \mathbf{p} \mid b\rangle \tag{99}$$

[see Eq. (20) of Chapter 26]. We next try to solve Eqs (91) and (92) by using a method similar to that employed in Problem 26.8. We assume that at $t = 0$ the system is in the state represented by $\mid 1\rangle$, i.e.

$$C_1(0) = 1 \quad , \quad C_2(0) = 0 \tag{100}$$

On working out the solution one obtains

$$|C_2(t)|^2 \simeq \left(\frac{\Omega_0}{2}\right)^2 \left[\frac{\sin\Omega' t/2}{\Omega'/2}\right]^2 \tag{101}$$

where

$$\Omega_0 = \left[\frac{2n_i |D_{ab}|^2}{\hbar\varepsilon_0 V}\frac{\omega_{ab}^2}{\omega_i}\right]^{1/2} \tag{102}$$

and

$$\Omega' = \left[(\omega_{ba} - \omega_i)^2 + \Omega_0^2\right]^{1/2} \tag{103}$$

For $\Omega_0 t/\hbar \ll 1$, we obtain

$$|C_2(t)|^2 \simeq \frac{n\omega |D_{ab}|^2}{2\hbar\varepsilon_0 V}\left[\frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2}\right]^2 \tag{104}$$

where we have dropped the subscript i and have taken into account the fact that $|C_2(t)|^2$ is negligible except when $\omega \approx \omega_{ba}$ and have thus replaced ω_{ba} by ω. Equation (104) is the same as Eq. (24) of the previous chapter provided we replace[6] $\mathcal{E}_0^2$ by $2n\hbar\omega/V\varepsilon_0$. Using Eq. (104) and proceeding as in Sec. 26.4, we would get an expression for the Einstein B coefficient identical to Eq. (40) of Chapter 26.

In a similar manner, if we consider the emission process, we would obtain

$$|C_2(t)|^2 \simeq \frac{\omega(n+1)}{2\hbar\varepsilon_0 V}|D_{ab}|^2\left[\frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2}\right]^2 \tag{105}$$

where the initial and final states $\mid 1\rangle$ and $\mid 2\rangle$ are now given by[7]

$$\left.\begin{aligned} \mid \text{initial}\rangle &= \mid 1\rangle = \mid b; n_1, n_2, \ldots n_i, \ldots\rangle \\ \mid \text{final}\rangle &= \mid 2\rangle = \mid a; n_1, n_2, \ldots n_i + 1, \ldots\rangle \end{aligned}\right\} \tag{106}$$

Notice the presence of the term[8] $(n+1)$ in Eq. (105). This implies that even if the number of photons were zero originally, the emission probability is finite. The term proportional to n in Eq. (105) gives the probability for induced or stimulated emission since the rate at which it occurs is proportional to the intensity of the applied radiation. On the other hand, the second term which is independent of n gives the spontaneous emission rate into the mode (see also Problem 27.3). It may be noted that the spontaneous emission probability into a particular mode is exactly the same as the stimulated emission probability caused by a single photon into the same mode.

We next calculate the probability per unit time for spontaneous emission of radiation. If we consider the emission to be in the solid angle $d\Omega$ then the number of modes for which the photon frequency lies between ω and $\omega + d\omega$ is (see Appendix M)

$$N(\omega)\,d\omega d\Omega = \frac{V\omega^2\,d\omega}{8\pi^3 c^3}\,d\Omega \tag{107}$$

---

[6] This is justified because the energy density associated with an electromagnetic field is $\frac{1}{2}\varepsilon_0\mathcal{E}_0^2$ and the energy density is also equal to $n\hbar\omega/V$.

[7] We would have

$$i\hbar\frac{dC_2}{dt} \simeq H'_{21}e^{-i(W_1 - W_2)t/\hbar}C_1(t) \simeq H'_{21}e^{-i(\omega_{ba} - \omega_i)t}$$

and integration of which would lead to Eq. (105). However, it may be mentioned that the equation for $C_1(t)$ would be a sum over states as discussed in Solution 27.3.

[8] The appearance of the term $(n+1)$ is because of the relation $|\langle n+1|\bar{a}|n\rangle|^2 = |\sqrt{n+1}\langle n+1 \mid n+1\rangle|^2 = (n+1)$.

Thus, the total probability of emission in the solid angle $d\Omega$ would be given by

$$\begin{aligned}\Gamma &= \frac{|D_{ab}|^2}{2\hbar\varepsilon_0 V}\int\left[\frac{\sin\left(\omega_{ba}-\omega\right)t/2}{\left(\omega_{ba}-\omega\right)/2}\right]^2 \omega\frac{V}{8\pi^3c^3}\omega^2\,d\omega\,d\Omega \\ &\simeq \frac{|D_{ab}|^2}{2\hbar\varepsilon_0 8\pi^3c^3}\,d\Omega\,\omega_{ba}^3\int\left[\frac{\sin\left(\omega_{ba}-\omega\right)t/2}{\left(\omega_{ba}-\omega\right)/2}\right]^2 d\omega \end{aligned}\tag{108}$$

where use has been made of the fact that the quantity inside the square brackets is a sharply peaked function around $\omega = \omega_{ba}$. Carrying out the integration, using the fact that

$$\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}\,dx = \pi$$

we obtain

$$\Gamma \cong \frac{1}{2\pi}\left[\frac{q^2}{4\pi\varepsilon_0\hbar c}\right]\frac{\omega^3}{c^2}\left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\cdot\hat{\mathbf{e}}\right|^2 d\Omega\, t$$

Thus the transition rate is given

Transition rate

$$w_{sp} = \frac{1}{2\pi}\left[\frac{q^2}{4\pi\varepsilon_0\hbar c}\right]\frac{\omega}{m^2c^2}\left|\langle a\,|\,\mathbf{p}\,|\,b\rangle\cdot\hat{\mathbf{e}}\right|^2 d\Omega \tag{109}$$

$$= \frac{1}{2\pi}\left[\frac{q^2}{4\pi\varepsilon_0\hbar c}\right]\frac{\omega^3}{c^2}\left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\cdot\hat{\mathbf{e}}\right|^2 d\Omega \tag{110}$$

In order to calculate the total probability per unit time for the spontaneous emission to occur (the inverse of which will give the spontaneous lifetime of the state), we must sum over the two independent states of polarization and integrate over the solid angle. Assuming the direction of **k** to be along the z–axis, we may choose $\hat{\mathbf{e}}$ to be along the x– or y– axes. Thus, if we sum

$$\left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\cdot\hat{\mathbf{e}}\right|^2$$

over the two independent states of polarization, we obtain

$$\begin{aligned}&\left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\cdot\hat{\mathbf{x}}\right|^2 + \left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\cdot\hat{y}\right|^2 \\ &= P_x^2 + P_y^2 = P^2\sin^2\theta\end{aligned}$$

where $\mathbf{P} \equiv \langle a|\mathbf{r}|b\rangle$ and θ is the angle that **P** makes with the z–axis. Thus in order to obtain the Einstein A coefficient (which represents the total probability per unit time for the spontaneous emission to occur), in Eq. (110), we replace $|\langle a|\mathbf{r}|b\rangle\cdot\widehat{\mathbf{e}}|^2$ by $|\langle a|\mathbf{r}|b\rangle|^2\sin^2\theta$ and integrate over the solid angle $d\Omega$ to obtain

Einstein's A coefficient

$$\begin{aligned}A &= \frac{1}{2\pi}\left[\frac{q^2}{4\pi\varepsilon_0\hbar c}\right]\frac{\omega^3}{c^2}\left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\right|^2\iint\sin^2\theta\sin\theta\,d\theta\,d\phi \\ &= \frac{4}{3}\left[\frac{q^2}{4\pi\varepsilon_0\hbar c}\right]\frac{\omega^3}{c^2}\left|\langle a\,|\,\mathbf{r}\,|\,b\rangle\right|^2\end{aligned}\tag{111}$$

which is identical to Eq. (43) of the previous chapter.

27.5 Properties of the eigenstates of the Hamiltonian of the radiation field

If we substitute for $q_\lambda(t)$ from Eq. (77) in Eq. (44) we would obtain

$$\mathcal{E} = \sum_\lambda \mathcal{E}_\lambda \tag{112}$$

where

$$\mathcal{E}_\lambda = i\left(\frac{\hbar\omega_\lambda}{2\varepsilon_0 V}\right)^{1/2}\left[a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right]\hat{\mathbf{e}}_\lambda \tag{113}$$

and all operators are in the Schrödinger representation. We consider the state of the radiation field for which there are n_λ photons in the λ^{th} state. The expectation value of $\mathcal{E}_\lambda$ in this state would be given by

Expectation value of $\mathcal{E}_\lambda$

$$\begin{aligned}&\langle n_1,n_2,\ldots,n_\lambda,\ldots\,|\,\mathcal{E}_\lambda\,|\,n_1,n_2,\ldots,n_\lambda,\ldots\rangle \\ &= \langle n_1\,|\,n_1\rangle\langle n_2\,|\,n_2\rangle\ldots\langle n_\lambda\,|\,\mathcal{E}_\lambda\,|\,n_\lambda\rangle \\ &= 0\end{aligned}\tag{114}$$

because

$$\langle n_\lambda\,|\,a_\lambda\,|\,n_\lambda\rangle = 0 = \langle n_\lambda\,|\,\bar{a}_\lambda\,|\,n_\lambda\rangle \tag{115}$$

Similarly

$$\begin{aligned}&\langle n_1,n_2,\ldots,n_\lambda,\ldots\,|\,\mathcal{E}_\lambda^2\,|\,n_1,n_2,\ldots,n_\lambda,\ldots\rangle \\ &= \langle n_1\,|\,n_1\rangle\langle n_2\,|\,n_2\rangle\ldots\langle n_\lambda\,|\,\mathcal{E}_\lambda^2\,|\,n_\lambda\rangle\ldots \\ &= -\left(\frac{\hbar\omega_\lambda}{2\varepsilon_0 V}\right)\langle n_\lambda\,|\left(a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right)\left(a_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right)\,|\,n_\lambda\rangle \\ &= \left(\frac{\hbar\omega_\lambda}{\varepsilon_0 V}\right)\left(n_\lambda + \frac{1}{2}\right)\end{aligned}\tag{116}$$

where use has been made of relations like (see Sec. 12.2):

$$\langle n_\lambda\,|\,a_\lambda\bar{a}_\lambda\,|\,n_\lambda\rangle = \sqrt{n_\lambda+1}\,\langle n_\lambda\,|\,a_\lambda\,|\,n_\lambda+1\rangle = n_\lambda+1 \tag{117}$$

$$\langle n_\lambda\,|\,\bar{a}_\lambda a_\lambda\,|\,n_\lambda\rangle = \sqrt{n_\lambda}\,\langle n_\lambda\,|\,\bar{a}_\lambda\,|\,n_\lambda-1\rangle = n_\lambda \tag{118}$$

$$\langle n_\lambda\,|\,a_\lambda a_\lambda\,|\,n_\lambda\rangle = 0 \tag{119}$$

$$\langle n_\lambda\,|\,\bar{a}_\lambda\bar{a}_\lambda\,|\,n_\lambda\rangle = 0 \tag{120}$$

The uncertainty in $\mathcal{E}_\lambda, \Delta\mathcal{E}_\lambda$, can be defined through the relation

$$\begin{aligned}(\Delta\mathcal{E}_\lambda)^2 &= \langle\mathcal{E}_\lambda^2\rangle - \langle\mathcal{E}_\lambda\rangle^2 \\ &= \left(\frac{\hbar\omega_\lambda}{\varepsilon_0 V}\right)\left(n_\lambda + \frac{1}{2}\right)\end{aligned}\tag{121}$$

Equation (114) tells us that the expectation value of the electric field in the state $|\,n\rangle$ $(=|\,n_1,n_2,\ldots n_\lambda\ldots\rangle)$ is zero. Since the average of sine waves with random phases is zero, we may loosely say that the state $|\,n\rangle$ does not specify the phase[9]. Some authors tend to explain this by resorting to the uncertainty principle

$$\Delta E\,\Delta t \underset{\sim}{>} \hbar \tag{122}$$

where ΔE is the uncertainty in the energy of the radiation field and Δt is related to the uncertainty in the phase angle through the relation

$$\Delta\phi = \omega\Delta t \tag{123}$$

Since $E = (n+1/2)\hbar\omega$, $\Delta E = \hbar\omega\Delta n$ and we obtain

$$\Delta n\,\Delta\phi \underset{\sim}{>} 1 \tag{124}$$

---

[9] We say it loosely because it is not possible to define a phase operator which is real (see Sec. 27.7).

If the number of photons is exactly known, then $\Delta n = 0$ and consequently there is no knowledge of the phase. However, such arguments are not rigorously correct because it is not possible to give a precise definition of $\Delta\phi$ (see Sec. 27.7). Nevertheless, we can say that the states described by $| n\rangle$ do not correspond to the classical electromagnetic wave with a certain phase.

Returning to Eq. (116), we notice that the states $| n\rangle$ have a definite amplitude $(2\hbar\omega_\lambda/\varepsilon V)^{1/2}(n_\lambda + 1/2)^{1/2}$ for the mode λ which is directly related to the number of photons.

27.6 The coherent states

We next consider the radiation field to be in one of the coherent states which are, the eigenkets of the operator a_λ (see Sec. 12.5). We will show that when the radiation field is in a coherent state, the field has properties very similar to that of a classical electromagnetic wave with a certain phase and amplitude. However, before we do so, we would like to discuss some of the properties of the coherent state.

The coherent states satisfy the equation

$$a_\lambda \,| \alpha_\lambda\rangle = \alpha_\lambda \,| \alpha_\lambda\rangle \tag{125}$$

where α_λ, which represents the eigenvalues of a_λ, can be an arbitrary complex number. In Sec. 12.5 we had shown that

$$| \alpha_\lambda\rangle = \exp\left[-\frac{1}{2}|\alpha_\lambda|^2\right] \sum_{n_\lambda = 0,1,2,\ldots} \frac{\alpha_\lambda^{n_\lambda}}{\sqrt{n_\lambda!}}\,| n_\lambda\rangle$$

For convenience, we drop the subscript λ and write the above equation as

$$| \alpha\rangle = \exp[-N/2] \sum_n \frac{\alpha^n}{\sqrt{n!}}\,| n\rangle \tag{126}$$

where $N\left(= |\alpha|^2\right)$ represents the expectation value of the number operator N_{op} (see Sec. 12.7). Since $| H\rangle$ are eigenkets of H, if the field is in the coherent state at $t = 0$, then at a later time t, the state will be given by (see Sec. 12.6)

$$| \Psi(t)\rangle = e^{-N/2} \sum_n \frac{\alpha^n}{\sqrt{n!}} \exp\left[-i\left(n + \frac{1}{2}\right)\omega t\right] | n\rangle \tag{127}$$

It is easy to see that

$$|\Psi(0)\rangle = |\alpha\rangle$$

Further[10]

$$\begin{aligned}\langle\Psi(t)|\overline{a}|\Psi(t)\rangle &= e^{-N} \sum_m \sum_n \frac{\alpha^{*m}\alpha^n}{\sqrt{m!n!}} e^{i(m-n)\omega t} \sqrt{n+1}\,\langle m \,|\, n+1\rangle \\ &= e^{i\omega t} e^{-N} \sum \frac{\alpha^* |\alpha|^{2n}}{n!} = \alpha^* e^{i\omega t}\end{aligned} \tag{128}$$

---

[10] In the Heisenberg representation, the expectation value of $\overline{a}$ would have been

$$\langle\Psi(0)|\overline{a}(t)|\Psi(0)\rangle = \langle\alpha|\overline{a}e^{i\omega t}|\alpha\rangle = \alpha^* e^{i\omega t}$$

which is the same as expressed by Eq. (128).

Similarly, or taking the complex conjugate of the above equation

$$\langle\Psi(t)|a|\Psi(t)\rangle = \alpha e^{-i\omega t} \tag{129}$$

We now consider the radiation field to be in the coherent state and calculate the expectation value of $\mathcal{E}$ and $\mathcal{E}^2$:

$$\begin{aligned}\langle\Psi(t)|\mathcal{E}|\Psi(t)\rangle &= i\left(\frac{\hbar\omega}{2\varepsilon_0 V}\right)^{1/2} \Big[\langle\Psi(t)|a|\Psi(t)\rangle\, e^{i\mathbf{k}\cdot\mathbf{r}} \\ &\qquad - \langle\Psi(t)|\overline{a}|\Psi(t)\rangle\, e^{-i\mathbf{k}\cdot\mathbf{r}}\Big]\,\hat{\mathbf{e}} \\ &= i\left(\frac{\hbar\omega}{2\varepsilon_0 V}\right)^{1/2} \left[\alpha e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - \alpha^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right]\hat{\mathbf{e}} \\ &= -2\left(\frac{\hbar\omega}{2\varepsilon_0 V}\right)^{1/2} |\alpha| \sin(\mathbf{k}\cdot\mathbf{r} - \omega t + \phi)\,\hat{\mathbf{e}}\end{aligned} \tag{130}$$

where

$$\alpha = |\alpha|\, e^{i\phi} \tag{131}$$

Thus the coherent state can be interpreted to represent a harmonic wave with phase ϕ. In a similar manner, we can calculate the expectation value $\mathcal{E}^2$. The result is

$$\langle\Psi(t)|\mathcal{E}\cdot\mathcal{E}|\Psi(t)\rangle = \left(\frac{\hbar\omega}{2\varepsilon_0 V}\right)\left[4|\alpha|^2 \sin^2(\mathbf{k}\cdot\mathbf{r} - \omega t + \phi) + 1\right] \tag{132}$$

Finally, the uncertainty in $\mathcal{E}$ would be given by (cf. Eq. 121):

$$\begin{aligned}(\Delta\mathcal{E})^2 &= \langle\Psi(t)|\mathcal{E}^2|\Psi(t)\rangle - \langle\Psi(t)|\mathcal{E}|\Psi(t)\rangle^2 \\ &= \left(\frac{\hbar\omega}{2\varepsilon_0 V}\right)\end{aligned} \tag{133}$$

Notice that the uncertainty $\Delta\mathcal{E}$ is independent of the amplitude $|\alpha|$; thus, greater the intensity of the beam greater will be the proximity of the radiation field (corresponding to the coherent state) to the classical plane wave. Indeed when a laser is operated much beyond the threshold, it generates a coherent state excitation of a cavity mode.

27.7 The phase operator

In classical mechanics the displacement and momentum of a linear harmonic oscillator are given by

$$x = Ae^{i\phi} + Ae^{-i\phi}\ , \quad \phi = \omega t \tag{134}$$

and

$$p = m\dot{x} = im\omega A\left[e^{i\phi} - e^{-i\phi}\right] \tag{135}$$

where A has been assumed to be real. In quantum mechanics, we have [see Eqs 30 and 31 of chapter 12]:

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2} [\overline{a} + a] \tag{136}$$

$$p = im\omega\left(\frac{\hbar}{2m\omega}\right)^{1/2} [\overline{a} - a] \tag{137}$$

UNIT IV : Atomic and molecular Structure

Approximations in atomic structure – Central field approximation – Thomas Fermi Statistical model – Hartree - Fock Equation – The method of self consistent field – Residual electrostatic and spin orbit interaction – Alkali atoms – Doublet separation – Coupling schemes – Hydrogen molecule – Covalent bond.

CONTENTS

1. **Central Field Approximation:**

   i. The starting point for the calculation of energy of many electron atoms except the light ones is the central field approximation.
   ii. In this procedure each electron is assumed to move in a spherically symmetric potential V(r) produced by the nucleus and all the remaining electrons.
   iii. The Hamiltonian in this central field approximation evidently commutes with the angular momentum operator L_i of each electron.
   iv. So the state of each indidual electron can be characterized by the quantum numbers n, *l*, m_l with spin orientation m_s (+1/2 or -1/2)
   v. The energy is independent of ml and ms at this stage because no interactions involving the orientations of the L_i and S_i (such as the spin –orbit interactions) have been taken into account.
   vi. Thus for given n and *l* there are 2(2*l*+1) available wave functions or orbital's, all having the same energy.
   vii. Each of them can accommodate no more than one electron in view of the Pauli Exclusion Principle.
   viii. This set of states or orbital's (for given n, *l*) is said to constitute a shell of the atom, and if all these orbitals are occupied, the shell is said to be closed.
   ix. In the ground state of an atom, the electrons should arrange themselves in the lowest available levels.
   x. For instance, in an atom with 11 electrons (neutral sodium) the first three shells in the above scheme would be completely filled and the last remaining electron would go into a 3s state. This is summarized in the notation

$$(1s)^2\ (2s)^2\ (2p)^6\ 3s$$

This specifies what is called the electronic configuration of the atom.

n	1	2		3			4			
l	0	0	1	0	1	2	0	1	2	3
Spectroscopic Notation	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
Max no of electrons	2	2	6	2	6	10	2	6	10	14

2. **What is Central Field Approximation method for evaluation potential energy function of many electron atoms?**

i. The starting point for the calculation of energy of many electron atoms except the light ones is the central field approximation.

ii. In this procedure each electron is assumed to move in a spherically symmetric potential V(r) produced by the nucleus and all the remaining electrons.

Consider a helium atom which consists of a nucleus of charge +Ze and two electrons circulating about the nucleus. The Hamiltonian of ground state helium atom is

H = K.E + P.E

i.e $H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - Z\,e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}$ -------------1

K.E = $-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)$---------------------2

$P.E\,(V) = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$ -------------3

Where

$Z\,e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ is the interaction energy due to **columbic attractive term.**

$\frac{e^2}{r_{12}}$ is the interaction energy due to **electrons mutual repulsive term.**

If we extend the equation for N electron atom

$$\left[\sum_{i=1}^{n}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}\right) + \sum_{i>}\frac{e^2}{r_{ij}}\right]\Psi = E\Psi \quad \text{--------------------4}$$

- This equation cannot be solved by the method of separation of variables due to the presence of interaction terms.
- Moreover this equation as such can also not be solved by perturbation method.
- In such cases, we consider a modified field (central field) in which all the electrons experience centrally symmetric field by superimposing the radial components of coulomb interaction term $\left(\sum_{i=1}^{n} - \frac{Ze^2}{r_i}\right)$ between the electrons and the nucleus. (coulomb field – attractive field)

- The remaining interaction term $\sum_{i>} \frac{e^2}{r_{ij}}$ is the mutual repulsion term and may be treated as small perturbation term and the problem can be handled by the perturbation theory or variation techniques.

Let the mutual repulsion term $\sum_{i>} \frac{e^2}{r_{ij}}$ be divided into two parts

1. **$\sum_i S(r_i)$ ------------ 5 (directed away from the nucleus central part) and**
2. **remainder $\sum_i R_i = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i S(r_i)$ ----------------6**

- The first part weakens the coulomb potential when superimposed on the latter.
- Therefore the central potential is $\sum_i \left[-\frac{Ze^2}{r_i} + S(r_i) \right]$.
- It is often called **the Screened coulomb Potential**.

The total Hamiltonian is now expressed as **H = H₀ + H’ --------------7**

where H_0 is the Hamiltonian with central potential. i.e.,

$$H_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i) \right] \text{ ---------------8}$$

Where $V(r_i) = -\frac{Ze^2}{r_i} + S(r_i)$ ---------------9

$$H' = \sum_i R_i = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i S(r_i) \text{ -------------------10}$$

$$= \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i \left[\frac{Ze^2}{r_i} + V(r_i) \right] \text{ -----------------11}$$

When in zeroth order approximation the interaction term H’ is negligibly small and left with only the central field, hence this approximation method is called Central Field Approximation.

Two methods are commonly used for obtaining the central potential v(r). They are

1. Thormas - Fermi method :- this method is simple but less accurate
2. Self consistent method of Hartee :- more cumbersome

3. Find an expression for the electron density in Fermi – Thomas model and show that the radius of the sphere enclosing a fixed fraction of all electrons is proportional to Z$^{-1/3}$.

- This model assumes that the central potential function V(r) is spherically symmetric and is produced by the nucleus and the other entire electron except the one whose motion is under consideration.
- Here the potential V(r) is assumed to be slowly varying, slow enough to have number of electrons in an electron wavelength.
- This model assumes that the electrons are treated as a gas obeying Fermi –Dirac statistics.
- Many electrons are localized within a volume over which the potential is almost a constant.
- As electrons are treated as a gas of fermions, one can apply the concept of cells in phase space to the states of individual electrons.

The volume of phase space occupied by electrons which have momentum less than p and are in the volume dV **is** $\boldsymbol{\frac{4}{3}\pi p^3 dV}$ **------------1**

The number of cells (states) corresponding to this volume is $\boldsymbol{\frac{2}{h^3}\left(\frac{4}{3}\pi p^3 dV\right)}$ ------------2

The factor 2 is included to account for the two possible spin states.

Assuming that all these states are occupied, the number of electrons per unit volume n(r) is given by $\boldsymbol{n(r) = \frac{8\pi p^3}{3h^3} = \frac{p^3}{3\pi^2\hbar^3}}$ ---------------3

For the electrons not to escape from the nucleus, the maximum allowed kinetic energy at any distance r from the nucleus is –V(r)

That is $\boldsymbol{\frac{p^2}{2m} = -V(r)}$ --------------4

From eqns 3 and 4

$$\boldsymbol{n(r) = \frac{[-2mV(r)]^{\frac{3}{2}}}{3\pi^2\hbar^3}} \text{ -----------------}\mathbf{5}$$

This equation is the integral form of the Thomas Fermi one;

It is possible to transform it into a differential form by using the Poisson equation, which links the electrostatic potential $\mathbf{V(r)}$ to the density of charge $\boldsymbol{\rho(r) = -e\, n(r)}$ as $\boldsymbol{\nabla^2 V(r) = -\, e\, \rho(r)}$ *****

∗Here, the Poisson equation is written in the rationalized M.K.S. unit system (SI units) as $\boldsymbol{\nabla^2 V(r) = -\, e\, \rho(r)},$ rather than in the un rationalized Gaussian unit system where

$$\boldsymbol{\nabla^2 V(r) = -4\pi e \rho(r)} ------6$$

Since the nucleus is at the origin, the potential is spherically symmetric and therefore,

$$\boldsymbol{\nabla^2 V = \frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dV}{dr}\right]} \qquad \text{-------------------7}$$

With this value of $\nabla^2 V$, eqn 7 reduces to

$$\boldsymbol{\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dV}{dr}\right] = -4\pi e^2 \mathrm{n}(r)} \text{ -------------------8}$$

Substituting the value of n(r) from eqn 5 in eqn 8

$$\boldsymbol{\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dV}{dr}\right] = -4\pi e^2 \frac{[-2mV\,(r)]^{\frac{3}{2}}}{3\pi^2\hbar^3}} \text{ ------------9}$$

When r →0 the leading term in the potential is due to the nucleus, so that $V(r) \to \frac{-Ze^2}{r}$.

Therefore it is convenient to introduce a function χ(r) defined by

$$\boldsymbol{V(r) = \frac{-Ze^2}{r}\chi(\mathrm{r}) \quad \text{and } \mathrm{r} = \mathrm{bx}} \text{ ------------10}$$

Substituting the value of V(r) and r in eqn 9

$$\boldsymbol{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\left(\frac{-Ze^2}{r}\chi(\mathrm{r})\right)\right) = -4\pi e^2\frac{\left[-2m\frac{-Ze^2}{r}\chi(\mathrm{r})\right]^{\frac{3}{2}}}{3\pi^2\hbar^3} ----11}$$

$$\boldsymbol{-\frac{1}{r^2}\frac{r^2}{r}Ze^2\frac{d^2\chi(\mathrm{r})}{dr^2} = -\frac{4e^2\,(2m)^{\frac{3}{2}}}{3\pi\hbar^3}\frac{(Ze^2)(Ze^2)^{1/2}\left(\chi(\mathrm{r})^{3/2}\right)}{r\,r^{1/2}} ----12}$$

$$\boldsymbol{\frac{d^2\chi}{dr^2} = \frac{4e^3(2m)^{3/2}\; Z^{1/2}\,\chi^{3/2}}{3\pi\hbar^3 r^{1/2}} --- 13}$$

Now sub $\boldsymbol{\mathrm{r} = \mathrm{bx}}$

$$\boldsymbol{\frac{d^2\chi}{b^2dx^2} = \frac{4e^3(2m)^{3/2}\; Z^{1/2}\,\chi^{3/2}}{3\pi\hbar^3(bx)^{1/2}} ----- 14}$$

$$\frac{d^2\chi}{b^{3/2}dx^2} = \frac{4e^3(2m)^{3/2}\ Z^{1/2}\,\chi^{3/2}}{3\pi\hbar^3(x)^{1/2}} - - - - - - - - 15$$

$$\text{Where}\ \ b = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3}\frac{\hbar^2}{me^2}\frac{1}{Z^{1/3}} - - - - 16$$

$$\text{Sub}\ \frac{\hbar^2}{me^2} = a_0 \quad \therefore \quad b = \frac{0.885\ a_0}{Z^{1/3}} - - - 17$$

With these substitutions

$$\frac{d^2\chi}{dx^2} = \frac{0.885\ a_0\ \chi^{3/2}}{Z^{1/3}\ (x)^{1/2}} - - - - 18$$

Therefore the result is

$$(x)^{1/2}\frac{d^2\chi}{dx^2} = \ \chi^{3/2}$$

The boundary conditions are

$$\begin{pmatrix} \chi = 1 \text{ at } x = 0 \\ \chi = 0 \text{ at } x = \infty \end{pmatrix}$$

Thus we have the following important results

i. The radius of an atom is inversely proportional to the cube root of atomic number.
ii. This model is applicable to atoms with large atomic number Z where the number of electrons in a small volume is comparatively greater so that the statistical calculations are valid.
iii. Electronic charge density n(r) gives smooth charge variation over atomic dimensions and does not involve the shell structure.
iv. The form of potential energy function in this model is useful in the self- consistent field calculations.

4. **Show how the Hartree approximation can be used to solve for the wave functions and energies of multi-electron atoms.**

The Hartree Approximation

- The method for finding best possible one-electron wave functions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock.
- The Hartree method is used to approximate the wave function and the energy of a quantum multi-electron system in a stationary state.
- The Hartree approximation assumes that the multi-electron wave function can be expanded as a product of single-electron wave functions (i.e., orbitals).
- $|\boldsymbol{\Psi}(\mathbf{r_1}, \mathbf{r_2}, \dots . \mathbf{r_n})\rangle \approx \boldsymbol{\Psi_1}(\boldsymbol{r_1})\boldsymbol{\Psi_2}(\boldsymbol{r_2}) \dots . \boldsymbol{\Psi_n}(\boldsymbol{r_n})$
- This method ignores the effect of spin on the wave function.
- The multi-electron Schrödinger equation is formulated and solved to determine the wave functions and energies belonging to ground and excited states of the multi electron atom.
- Also the charge densities at position r due to the remaining electrons except (i) is calculated.
- The central field can be calculated from the nuclear potential and the wave functions of the remaining electrons, by assuming that the charge density associated with an electron is (– e) times the position probability density.

According to Hartee for a Z- electron system the wave function **Ψ** is assumed to be

$$|\boldsymbol{\Psi}(\mathbf{r_1}, \mathbf{r_2}, \dots . \mathbf{r_n})\rangle \approx \boldsymbol{\Psi_1}(\boldsymbol{r_1})\boldsymbol{\Psi_2}(\boldsymbol{r_2}) \dots . \boldsymbol{\Psi_n}(\boldsymbol{r_n}) \text{ -------------}\mathbf{1}$$

i. The Hamiltonian for a multi electron atom includes **nucleus-electron attraction terms** with a general charge Z; e.g.

$$\boldsymbol{V_{nucleus-electron}(r_i)} = -\frac{\boldsymbol{Z}}{\boldsymbol{|r_i - R|}} = -\sum_{\boldsymbol{R}} \frac{\boldsymbol{Ze^2}}{\boldsymbol{4\pi\epsilon_0}} \frac{\boldsymbol{1}}{\boldsymbol{|r_i - R|}} \text{ ---------------}\mathbf{2}$$

where V (r_i)is the potential in which the electron moves; this includes both the nuclear-electron interaction and the mean field arising from the **N**-1 other electrons and $|\boldsymbol{r_i} - R|$ is the distance between the electron and the nucleus,

ii. The Hamiltonian must also have terms for electron-electron repulsion.

$$\boldsymbol{V_{electron-electron}(r_{ij}) = -\frac{Z}{|r_i - r_j|}} \text{ ---------------}\mathbf{3}$$

Where $|r_i - r_j|$ is the distance between electron i and electron j.

So the proper multi- electron Hamiltonian can be

$$\mathbf{H}\ \boldsymbol{(r_1, r_2, \ldots .r_n) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{n-e}\ (r_i) + \sum_{i\neq j} V_{e-e}\ (r_{ij})} \text{ -------------}\mathbf{4}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms. We smear the other electrons out into a smooth negative charge density $\boldsymbol{\rho}\ (\boldsymbol{r})$ leading to a potential of the form (i.e) the total charge density creates an extra mean potential

$$\boldsymbol{\nabla^2 V(r) = -\frac{\rho(r)}{\varepsilon_0}}$$

In order to find the wave equation for **ith** electron, we first find potential energy of **ith** electron in the field of remaining (Z-1) electrons as follows

The term $e\boldsymbol{\Psi}_j^*\boldsymbol{\Psi}_j = e|\boldsymbol{\Psi}_j(\mathbf{r}_j)|^2$ represents the charge distribution (charge density) $\rho(r)$ of jth electron.

The potential due to jth electron at the vicinity of ith electron is

$$\boldsymbol{\rho(r) = \int \frac{e\,|\Psi_j(r_j)|^2}{|r_i - r_j|}\, d\tau_j ----5}$$

According to Poisson equation the electrostatic potential $-\mathbf{V(r)}$ and the charge density – **e ρ(r)** is related by the equation

$$-\frac{1}{e}\nabla^2 V(r) = -e\frac{\rho(\mathbf{r})}{\varepsilon_0}$$

Therefore the potential due to all other electrons in the vicinity of i$^{\text{th}}$ electron is

$$V_{\text{electron-electron}}(\mathbf{r}) = \frac{e^2}{4\pi\,\epsilon_0}\sum_{i\neq j}\int\frac{\left|\Psi_j(\mathbf{r_j})\right|^2}{|\mathbf{r_i}-\mathbf{r_j}|}\,d\tau ---6$$

Finally the potential energy of the i$^{\text{th}}$ electron in the field of all other electrons is

$$V_{\text{electron-electron}}(\mathbf{r}) = \frac{e^2}{4\pi\,\epsilon_0}\sum_{i\neq j}\int\frac{\left|\Psi_j(\mathbf{r_j})\right|^2}{|\mathbf{r_i}-\mathbf{r_j}|}\,d\tau ----7$$

Finally we have the system of Hartree equations as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r_i}-R|} + \frac{e^2}{4\pi\epsilon_0}\sum\nolimits_{i\neq j}\int\frac{|\Psi_j(r_j)|^2}{|r_i-r_j|}\,d\tau\right]\Psi_i(\mathbf{r_i}) = E_i\phi_i\ (\mathbf{r_i}) ----------8$$

The third term is the charge density associated with the j th electron.

$e|\Psi_i(r_i)|^2$ will be known only when we solve eqn 11.

- Therefore one has to go in for an iterative procedure assuming an approximate form for the **Ψ_i‘s.**
- The insertion of the refined wave function back into the equation leads to a better one.
- The process is continued until the wave functions are self consistent to a high degree of accuracy.
- The potential thus obtained is called the self consistent potential.

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5. Derive HARTEE – FOCK EQUATION

- In the Hartee method, the many electron wave functions are simply a product of one - electron wave functions.
- This is not acceptable when the particles are indistinguishable.
- The Hartee Fock method incorporates the effect of exchange symmetry into the formalism.
- In this theory, Fock used an antisymmetrized trial wave function for the variational calculations.
- The wave function including the spin is assumed to take the form of a slater determinant of one – electron wave functions.

$$\Psi\left(x_{1,}x_2 \ldots\ldots x_z\right) = \frac{1}{\sqrt{z!}}\begin{vmatrix} U_1(X_1) & U_1(X_2) & \cdots & U_1(X_z) \\ U_2(X_1) & U_2(X_2) & \ldots & U_2(X_z) \\ \vdots & \vdots & \ddots & \vdots \\ U_z(X_1) & U_z(X_2) & \cdots & U_z(X_z) \end{vmatrix} \quad -----\ -1$$

Where $X_1, X_{2,}$ …… represent the co-ordinates both spin and space.

The Hamiltonian of a system having Z interacting electrons is given as

$$H = \sum_{i=1}^{z}\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i)\right] + \frac{1}{2}\sum_{i,j\neq i}^{n}\frac{e^2}{r_{ij}} \text{--------------------}2$$

Rewriting the Hamiltonian of the interacting system

The Schrodinger equation to be solved is

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i) + F(r)\right]\emptyset(r) = E\,\emptyset(r) \text{ ------------------------}3$$

And the operator F has to be selected so as to minimize the total energy. Use of a single determinant with these functions as the ground state wave function is known as Hartee – Fock equation.

The choice of F in accordance with the variational principle is given by

$$\langle n|F|m\rangle = \sum_i[\langle in|v|im\rangle - \langle ni|v|im\rangle] \text{ ---------------}4$$

It may be noted here that the Hamiltonian is not affected by this choice of F, however the one-electron functions u_i change, Next let us proceed to get the explicit form of the Hartee – Fock equation. Writing eqn 4 in the integral form, we have

$$\int u_n^*\ (x)F(r)u_m\ (x)dx = \sum_i \iint u_i^*(x_1)u_n^*(x_2)v\big(r_{1,}r_2\big)u_i(x_1)u_m(x_2)dx_1dx_2 - \sum_i \iint u_n^*(x_1)u_i^*(x_2)v\big(r_{1,}r_2\big)u_i(x_1)u_m(x_2)dx_1dx_2 \quad \text{-----------5}$$

$$\int u_n^*\ (x)F(r)u_m\ (x)dx = \sum_i \int u_n^*\ (x_2)[\int |u_i(x_1)|^2\, dx_1]v(r_1,r_2)u_m\ (x_2)\, dx_2 - \sum_i \int u_n^*\ (x_2)[\int u_i^*(x_1)\, u_m(x_1)\, v(r_1r_2)dx_1]\, u_i\ (x_2)dx_2 \quad \text{------------6}$$

We have interchanged x_1 and x_2 in the second integral which is possible as the value of the definite integral does not depend on the variable of integration. Under the same rule, replacing the variable x_2 by x and r_2 by r we get

$$\int u_n^*\ (x)F(r)u_m\ (x)dx = \sum_i \int u_n^*\ (x)[\int |u_i(x_1)|^2\, v\big(r_{1,}r\big)u_m\ (x)dx_1]\, dx - \sum_i \int u_n^*\ (x)[\int u_i^*(x_1)\, u_m(x_1)\, v(r_1,r)u_i\ (x)dx_1]\, dx \quad \text{----7}$$

$$\int u_n^*\ (x)F(r)u_m\ (x)dx = \sum_i \int u_n^*\ (x)[\int |u_i(x_1)|^2\, v(r_1,r)u_m\ (x)]dx_1 - \int u_n^*\ (x)[\int u_i^*(x_1)\, u_m(x_1)\, v(r_1,r)u_i\ (x)dx_1\ ]dx \quad \text{---8}$$

From the comparison of the two sides it follows that,

$$F(r)u_m\ (x)dx = \sum_i \int |u_i(x_1)|^2\, v(r_1,r)u_m\ (x)dx_1 - \sum_i \int u_i^*(x_1)\, u_m(x_1)\, v(r_1,r)u_i\ (x)dx_1 \quad \text{----------9}$$

As u(x) is the product of orbital part $\emptyset(r)$ and a spin function $\Psi(r)$, the integral implies a sum over the two values of the spin variable. Carrying out the sum over the spin variable, we have

$$F(r)\emptyset_m\ (r)dx = \sum_i \int |\emptyset_i(r_1)|^2\, v(r_1,r)\emptyset_m\ (r)dr_1 - \sum_{\substack{i\\ spin\ i=spin\ m}} \int \emptyset_i^*(r_1)\, \Psi_m(r_1)\, v(r_1,r)\emptyset_i\ (r)dr_1 \quad \text{------10}$$

Then eqn 10 reduces to

$$F(r)\emptyset_m\ (r)dx = 2\left[\sum_{i=1}^{Z/2} \int |\emptyset_i(r_1)|^2\, v(r_1,r)\emptyset_m\ (r)dr_1 - \sum_{i=1}^{Z/2} \int \emptyset_i^*(r_1)\, \Psi_m(r_1)\, v(r_1,r)\emptyset_i\ (r)dr_1\right] \quad \text{---------------11}$$

The Hartee – Fock equation (Eqn 3) now becomes

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i)\emptyset_m\ (r) + 2\sum_{i=1}^{Z/2}\int |\emptyset_i(r_1)|^2\, v(r_1,r)\emptyset_m\ (r)dr_1 - \sum_{i=1}^{Z/2}\int \emptyset_i^*(r_1)\, \Psi_m(r_1)\, v(r_1,r)\emptyset_i\ (r)dr_1\right] = \epsilon_m\ \ \emptyset_m(r)$$

6. Residual Electrostatic Interaction:

i. According to Hartree's self consistent field for calculating potentials, and to solve Schrödinger equation, consider that if the system has N electrons and the Nth electron experiences the electrostatic interaction from other electrons as a single entity which helps us in considering it a central field

ii. The electrostatic potential energy $\boldsymbol{H_{el}} = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_i \left[\frac{\mathbf{Ze^2}}{\mathbf{r_i}}\right]$

iii. In reality the electrostatic interactions couple each electron to all others (as well as to the nucleus).

iv. This implies that an energy Eigen function will not consist of a single configuration, but be a linear combination of wave functions belonging to different configurations.

v. However the averaged out potential energy functions $V_i(r_i)$ employed in the central field approximation are expected to be the difference between $\boldsymbol{H_{el}}$ **and** $\mathbf{V_i(r_i)}$

vi. $\boldsymbol{H_{el}} - \mathbf{V_i(r_i)} = \mathbf{H_{res}}$ the so called Residual Electrostatic Interaction

vii. The residual electrostatic interaction energy is very small compared to electrostatic potential energy.

viii. The electronic configuration corresponding to E_{res} will also be small for any given configuration E.

ix. Thus for a given LS there is a multiplet of (2L +1) x (2S+1) states with energy E_{cL}.

7. ALKALI ATOM :-

(Li, Na, K, Rb, Cs, Fr)

i. The ground state configuration of an alkali atom consists of a series of full shells followed by a single S electron and so is ${}^2S_{1/2}$.
ii. Careful examination of the spectra of alkali metals shows that each member of some of the series are closed doublets.
iii. For example, sodium yellow line, corresponding to 3p→ 3 s transition, is a close doublet with separation of 6A^0.
iv. Further investigations show that only the S-terms are singlet, while all the other terms P, D, F etc. are doublets.
v. Such doublet structure in energy is observed for all the atoms possessing a single valence electron i.e., in the outer most shell.
vi. Spin is essentially a quantum phenomenon.
vii. The spin of the electron is found to be $\frac{1}{2}\hbar$ and $S^2 = (s+1)\hbar^2$ where s $=\frac{1}{2}$, the quantum number for spin.

8. Explanation of doublet structure of alkali atom:

The Hamiltonian for the lone electron of an alkali atom relative to the atomic core is given by,

$$H_0 = \frac{P^2}{2m} + V(r)$$

Where, P^2 = momentum of the lone electron

V(r) = Potential.

r = Distance of the lone electron from the centre of the atomic core, i.e., nucleus.

Now considering the spin orbit interaction the total Hamiltonian is given by,

$$H = \frac{P^2}{2m} + V(r) + H^{s-o}$$

Where H^{s-o} is the spin orbit interaction term

An electron with orbital angular momentum l and spin *s* will behave a total angular momentum
j= l +*s*

Which gives the quantum numbers for j as *j*= l +*s* ------ *j*= l – *s*.

Since for a single electron $S = \frac{1}{2}\hbar$ or $= -\frac{1}{2}\hbar$.

Therefore $j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$

$$for\ l = 0\ , j = \frac{1}{2} \text{ only.}$$

The coupling of spin with orbital angular momentum gives rise to the fine structure splitting of spectral lines and it gives to the doublet structure of alkali spectra.

This interaction is called **spin orbit interaction.**

The existence of electron spin and the doublet structure comes as a natural consequence of relativistic theory.

Now the spin orbit term can be considered as perturbation term. The contribution of the spin orbit term can be calculated by considering its expectation value.

Consider the first order correction,

$$\Delta E = \langle \Psi | H^{s-o} | \Psi \rangle$$

Where Ψ is the effective wave function of the one particle system.

In an atom the total angular momentum j is always conserved even if individual l and s may not be conserved. Hence we can work in a representation or system where H^{s-o} is diagonal. Also we choose $n, l_{j,}\ m_j\rangle$ representation, (where individual l and s combined to form the conserved quantity j)

Thus

$$\Delta E = \left\langle \Psi_{n\,l_{j,}m_j} \middle| H^{s-o} \middle| \Psi_{n\,l_{j,}m_j} \right\rangle$$

$$\Delta E = \langle \Psi_{n\,l} | \xi(r) | \Psi_{n\,l} \rangle \left\langle \Psi_{l\,s_{j,}m_j} \middle| l.s \middle| \Psi_{l\,s_{j,}m_j} \right\rangle$$

$$\Delta E = U_{nl}\,\langle l.s \rangle$$

$$where\ U_{nl} = \langle \Psi_{n\,l} | \xi(r) | \Psi_{n\,l} \rangle = \frac{me^4}{2\hbar^2}\,\frac{e^2}{\hbar c}\,\frac{Z^4}{n^3 l\,(l+\frac{1}{2})} = R_y\,\alpha\,\frac{Z^4}{n^3 l\,(l+\frac{1}{2})}$$

Where $R_y = \frac{me^4}{2\hbar^2}$, *the Rydberg constant and* $\alpha = \frac{e^2}{\hbar c}$ *the fine structure constant.*

To calculate the angular term $l.s$

$$\langle l.s \rangle = \frac{1}{2}[j^2 - l^2 - s^2]$$

$$\left\langle \Psi_{l\,s_{j,}m_j} \middle| l.s \middle| \Psi_{l\,s_{j,}m_j} \right\rangle = \langle l.s \rangle = \frac{1}{2}[j^2 - l^2 - s^2]$$

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

Since $s = \frac{1}{2}$; $\langle l.s \rangle = \left[\frac{1}{2}\, j(j+1) - \, l(l+1) - \, \frac{3}{4}\right]$

$then\ for\ a\ given\ l, j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$

For $j = l + \frac{1}{2}$; $\langle l.s \rangle = \left[\frac{1}{2}\left(l + \frac{1}{2}\right)\left(l + \frac{3}{2}\right) - \, l(l+1) - \, \frac{3}{4}\right] = \frac{1}{2}\left[l^2 + \frac{3l}{2} + \frac{1}{2}l + \frac{3}{4} - l^2 - l - \frac{3}{4}\right]$

$$\langle l.s \rangle = \frac{l}{2}$$

Similarly for $j = l - \frac{1}{2}$ *we have*

$$\langle l.s \rangle = -\frac{1}{2}\,(l+1)$$

Thus the energy levels are given as

$E = \mathrm{E}_0 + \mathrm{E}' = \mathrm{E}_0 + U_{nl}\frac{l}{2}$

$$E_1\left(for\ j = l + \frac{1}{2}\right) = \mathrm{E}_0 + U_{nl}\frac{l}{2}$$

$$E_2\left(for\ j = l - \frac{1}{2}\right) = \mathrm{E}_0 - \, U_{nl}\frac{l+1}{2}$$

Therefore the separation is given by $\Delta E = E_1 - E_2 = U_{nl}\left(l + \frac{1}{2}\right)$

Thus the splitting of energy levels i.e., separation between the two levels for each value of *l is* $U_{nl}\left(l + \frac{1}{2}\right)$. This is the so called fine structure of spectral lines for spin orbit interaction of energy levels.

9. COUPLING SCHEMES

Total angular momentum :

The addition of angular momentum for a many electron system is much more involved than that of one electron system. When more than one electron contributes orbital and spin angular momentum to the total angular momentum J of an atom then J is the vector sum of these individual momentums.

There are two types of couplings

1. L-S coupling or Russel – Saunders coupling
2. j-j coupling

L-S coupling or Russel – Saunders coupling

i. This is also called as normal coupling as this occurs most frequently.
ii. Orbital angular momentum L_i of all the electrons are coupled together into a single resultant L.

iii. Similarly the spin angular momentum S_i is also coupled together into another single resultant S.

iv. The momentum L and S then interact via the spin-orbit effect to form the total angular momentum J.

v. **This scheme is called LS coupling**

Thus L = L1+L2+L3+----

S= S1+S2+S3+----

Then **J = L+S**

vi. These are simply the integers or half integers.

vii. **ħ** is included while writing the magnitude of angular momentum vectors

viii. when two orbital angular momentum l_1 and l_2 combine, then allowed values of L are

$$L = (l_1 + l_2) + (l_1 + l_2 - 1) \ldots . |l_1 - l_2|$$

Similarly for a given values of L and S the allowed values of J are

$$J = (L + S) + (L + S - 1) \ldots . |L - S|$$

For L>S, there are 2S+1values of J, and for L<S, there are 2L+1 values of J.

The value 2S+1 is called the multiplicity of the state.

For a two electron system $\left(S_1 = S_2 = {}^1\!/_2\right)$

If the spins are ant parallel then S = 0, or parallel then S=1

When S= 0 we have J=2S+1=1 state. Such states are referred as singlet states.

When S=1, we have J =2S+1 = 3 states. Such states are referred as triplet states.

Often singlet and triplet states are grouped separately.

Usually the state of a L-S coupling is represented as $n^{2s+1}L_J$

For example if S=1/2, L=1,S=3/2,1/2 then the corresponding state of LS coupling will be ${}^2p_{3/2}$, ${}^2p_{1/2}$

(where *l* stands for s,p,d,f . for *l* =1, p state). It may be read as doublet p three halves, doublet p halves.

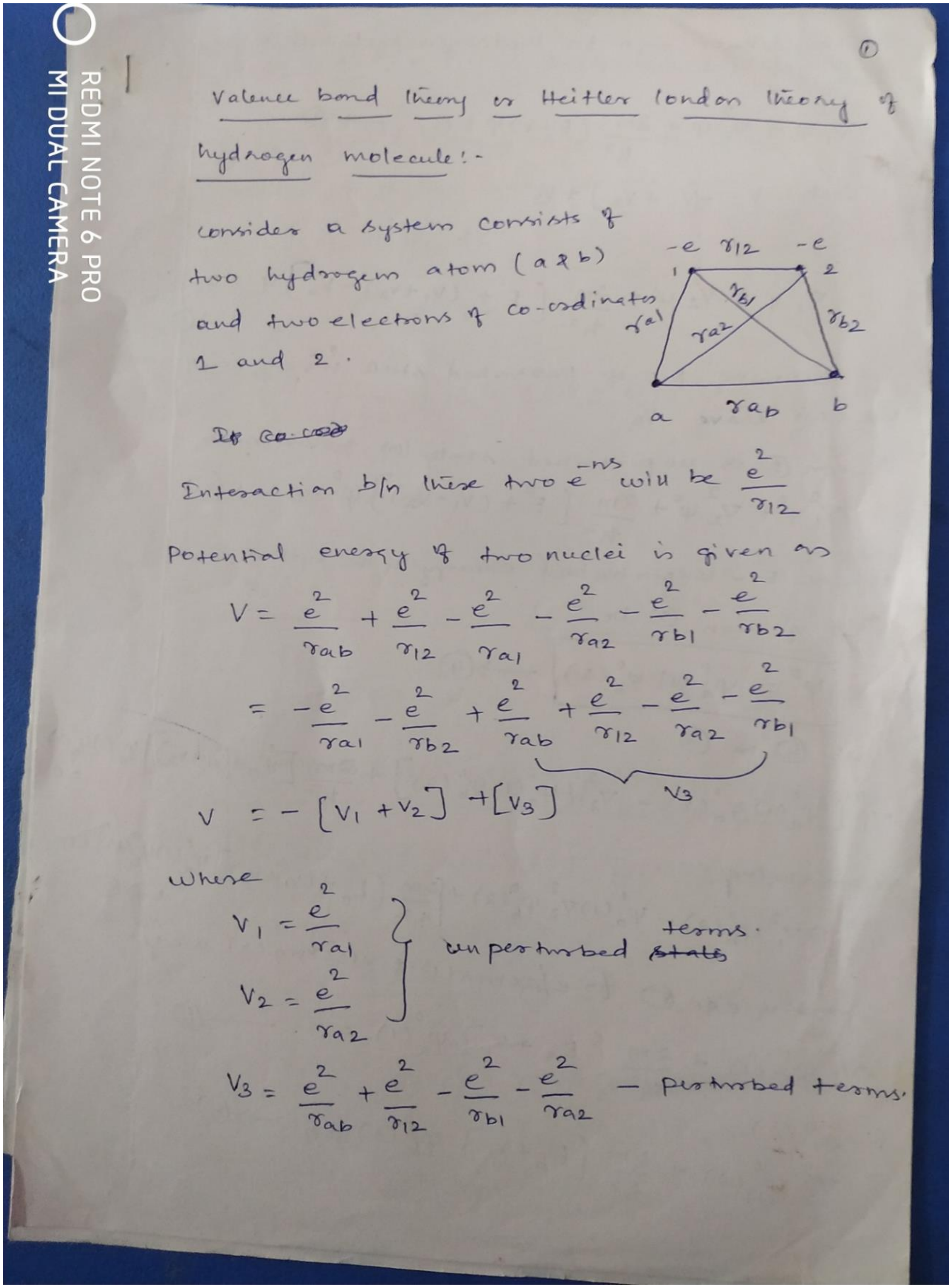
j-j coupling:

l and s vectors for each separate electron combine to form a separate J and all the J vectors are then vectorially added to form J

Thus for each active electron $J_1 = l_1 + s_1, J_2 = l_2 + s_2\ etc., and\ J = J_1 + J_2 + J_3 + \cdots = \sum J_i$.

This coupling scheme is known as J-J coupling which is distinctly different from L-S coupling scheme.

10. Hydrogen atom – Covalent Bond: Heitler London Theory



①

Valence bond theory or Heitler london theory of hydrogen molecule:-

consider a system consists of two hydrogen atom (a & b) and two electrons of co-ordinates 1 and 2.

~~If co-ord~~

Interaction b/n these two e^{-ns} will be $\frac{e^2}{r_{12}}$

Potential energy of two nuclei is given as

$$V = \frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}$$

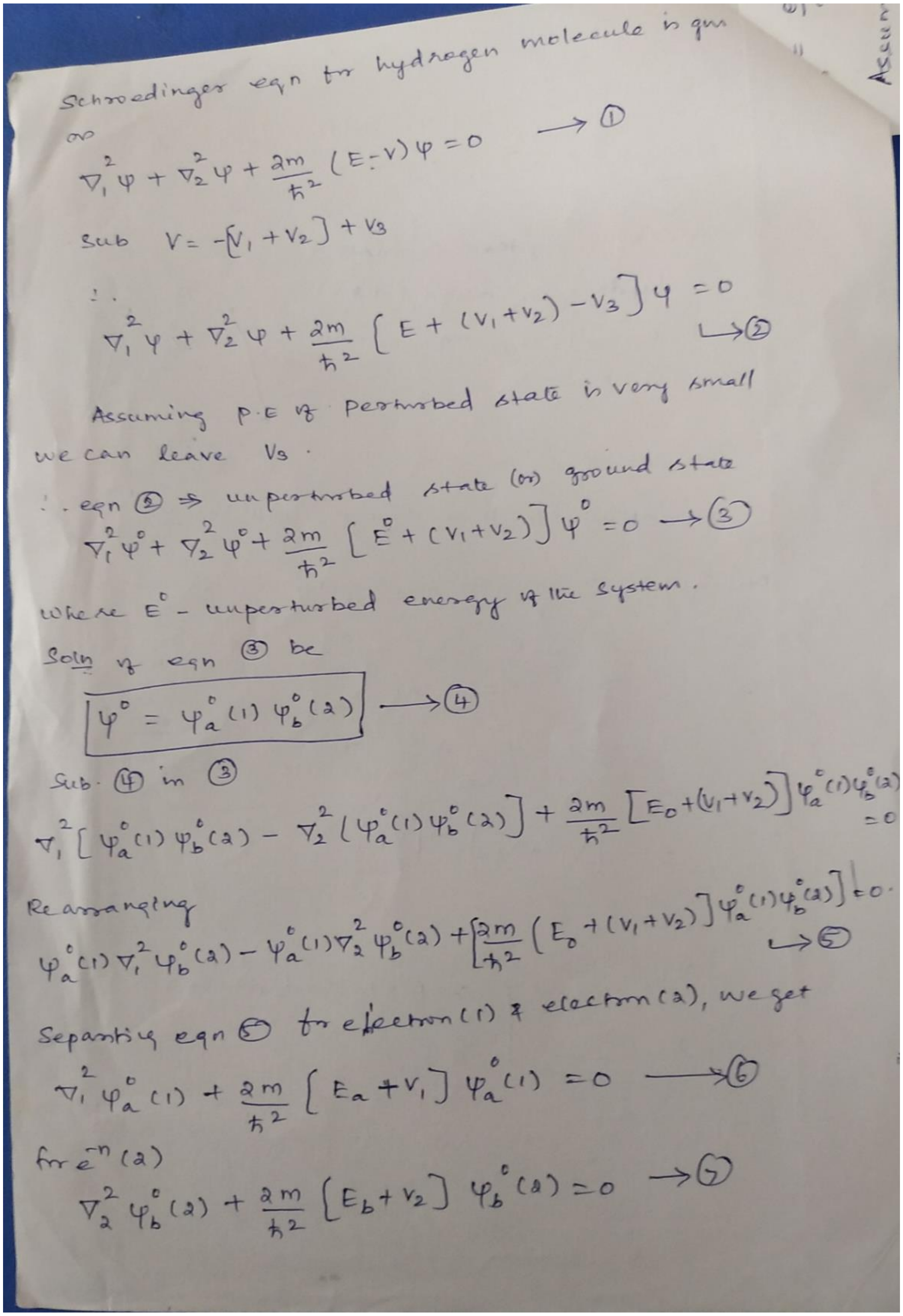
$$= -\frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}} + \underbrace{\frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}}}_{V_3}$$

$$V = -[V_1 + V_2] + [V_3]$$

where

$$\left.\begin{aligned} V_1 &= \frac{e^2}{r_{a1}} \\ V_2 &= \frac{e^2}{r_{a2}} \end{aligned}\right\}$$ unperturbed ~~stats~~ terms.

$$V_3 = \frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}}$$ – perturbed terms.



Schroedinger eqn for hydrogen molecule is given as

$$\nabla_1^2 \psi + \nabla_2^2 \psi + \frac{2m}{\hbar^2}(E-V)\psi = 0 \longrightarrow ①$$

Sub $V = -[V_1 + V_2] + V_3$

∴

$$\nabla_1^2 \psi + \nabla_2^2 \psi + \frac{2m}{\hbar^2}\left[E + (V_1+V_2) - V_3\right]\psi = 0 \hookrightarrow ②$$

Assuming P.E of perturbed state is very small we can leave V_3.

∴ eqn ② ⇒ unperturbed state (or) ground state

$$\nabla_1^2 \psi^0 + \nabla_2^2 \psi^0 + \frac{2m}{\hbar^2}\left[E^0 + (V_1+V_2)\right]\psi^0 = 0 \longrightarrow ③$$

where E^0 - unperturbed energy of the system.

Soln of eqn ③ be

$$\boxed{\psi^0 = \psi_a^0(1)\,\psi_b^0(2)} \longrightarrow ④$$

Sub. ④ in ③

$$\nabla_1^2\left[\psi_a^0(1)\psi_b^0(2) - \nabla_2^2(\psi_a^0(1)\psi_b^0(2)\right] + \frac{2m}{\hbar^2}\left[E_0 + (V_1+V_2)\right]\psi_a^0(1)\psi_b^0(2) = 0$$

Rearranging

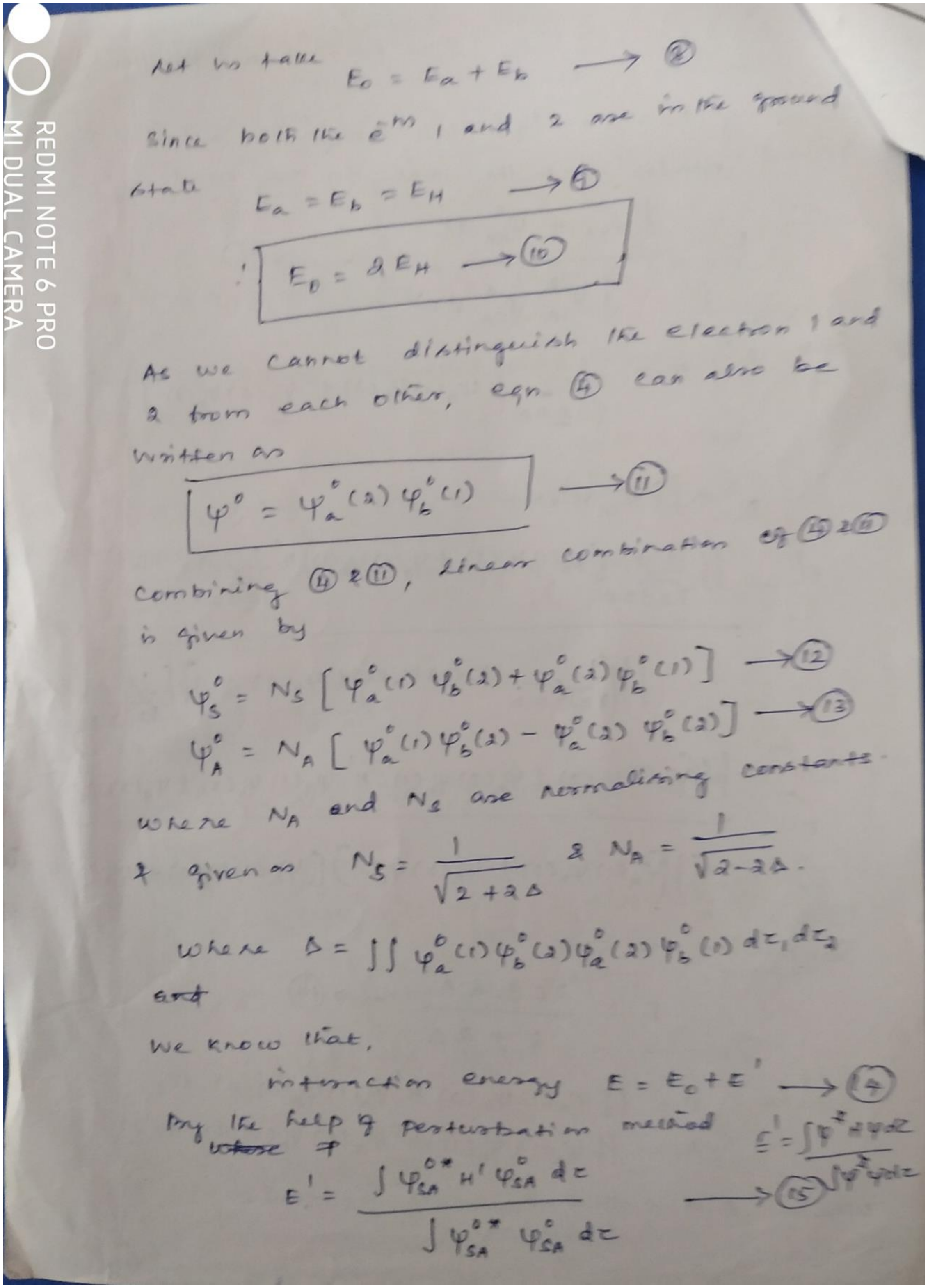
$$\psi_a^0(1)\nabla_1^2\psi_b^0(2) - \psi_a^0(1)\nabla_2^2\psi_b^0(2) + \left[\frac{2m}{\hbar^2}\left(E_0 + (V_1+V_2)\right]\psi_a^0(1)\psi_b^0(2)\right] = 0. \hookrightarrow ⑤$$

Separating eqn ⑤ for electron (1) & electron (2), we get

$$\nabla_1^2 \psi_a^0(1) + \frac{2m}{\hbar^2}\left[E_a + V_1\right]\psi_a^0(1) = 0 \longrightarrow ⑥$$

for e^{-n} (2)

$$\nabla_2^2 \psi_b^0(2) + \frac{2m}{\hbar^2}\left[E_b + V_2\right]\psi_b^0(2) = 0 \longrightarrow ⑦$$



Let us take $E_0 = E_a + E_b \longrightarrow$ ⑧

Since both the $\bar{e}^{ns}$ 1 and 2 are in the ground state

$E_a = E_b = E_H \longrightarrow$ ⑨

$$\boxed{E_0 = 2E_H} \longrightarrow ⑩$$

As we cannot distinguish the electron 1 and 2 from each other, eqn ④ can also be written as

$$\boxed{\psi^0 = \psi_a^0(2)\,\psi_b^0(1)} \longrightarrow ⑪$$

Combining ④ & ⑪, linear combination of ④ & ⑪ is given by

$$\psi_S^0 = N_S\left[\psi_a^0(1)\,\psi_b^0(2) + \psi_a^0(2)\,\psi_b^0(1)\right] \longrightarrow ⑫$$

$$\psi_A^0 = N_A\left[\psi_a^0(1)\,\psi_b^0(2) - \psi_a^0(2)\,\psi_b^0(2)\right] \longrightarrow ⑬$$

where N_A and N_S are normalising constants. & given as $N_S = \frac{1}{\sqrt{2+2\Delta}}$ & $N_A = \frac{1}{\sqrt{2-2\Delta}}$.

where $\Delta = \iint \psi_a^0(1)\,\psi_b^0(2)\,\psi_a^0(2)\,\psi_b^0(1)\,d\tau_1\,d\tau_2$

~~and~~

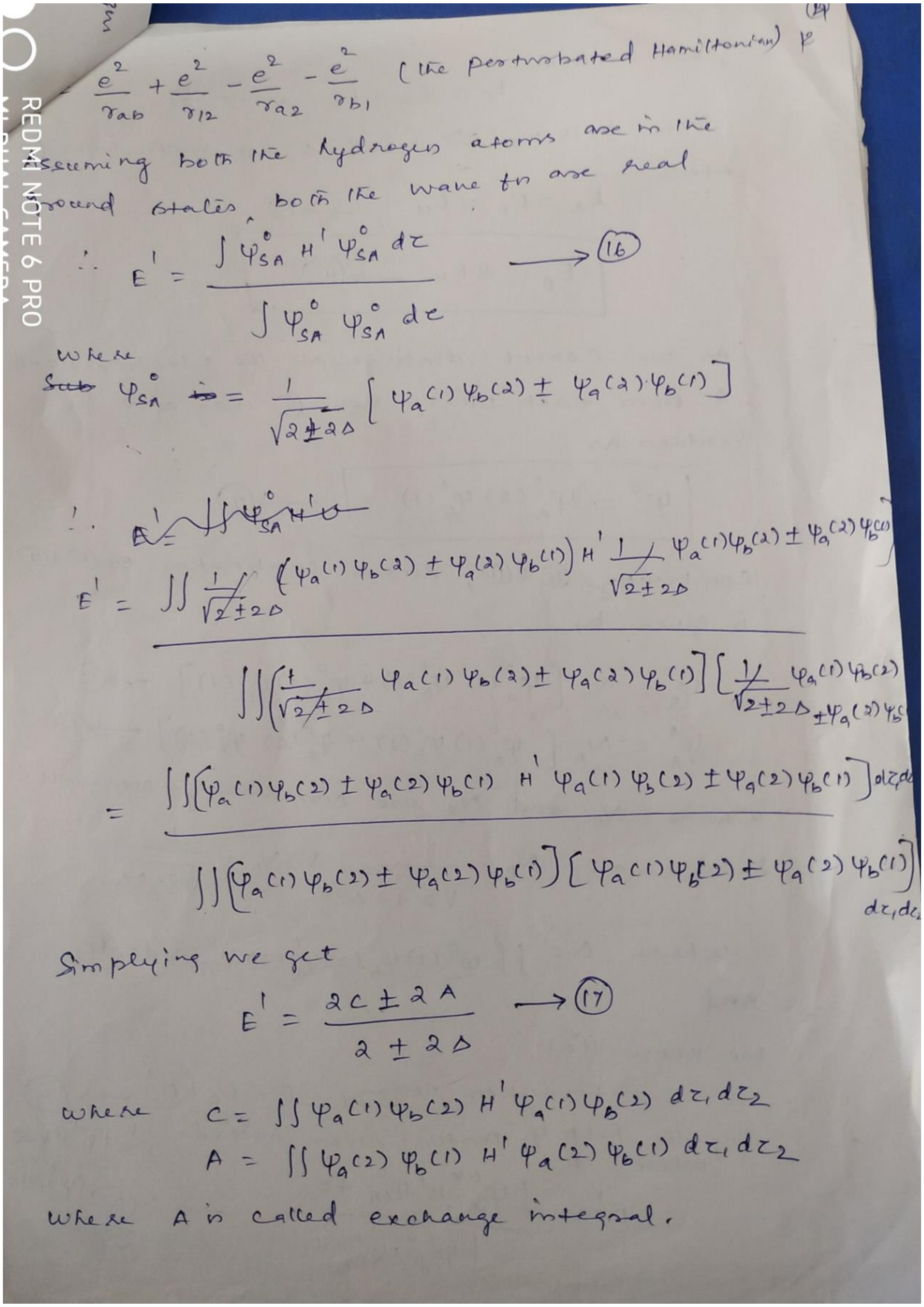
We know that,

interaction energy $E = E_0 + E' \longrightarrow$ ⑭

By the help of perturbation method
~~whose~~

$$E' = \frac{\int \psi_{SA}^{0*} H' \psi_{SA}^0\, d\tau}{\int \psi_{SA}^{0*} \psi_{SA}^0\, d\tau} \longrightarrow ⑮$$

$E' = \frac{\int\psi^* H\psi d\tau}{\int\psi^*\psi d\tau}$



$$\frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}}$$ (the perturbated Hamiltonian) $\hat{H}'$

Assuming both the hydrogen atoms are in the ground states, both the wave fn are real

$$\therefore E' = \frac{\int \psi^0_{SA} H' \psi^0_{SA}\, d\tau}{\int \psi^0_{SA} \psi^0_{SA}\, d\tau} \longrightarrow ⑯$$

where

~~Sub~~ ψ^0_{SA} ~~is~~ $= \frac{1}{\sqrt{2 \pm 2\Delta}} \left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\cdot\psi_b(1) \right]$

$\therefore$ ~~$E' = \iint \psi^0_{SA} H' \psi$~~

$$E' = \frac{\iint \cancel{\frac{1}{\sqrt{2\pm 2\Delta}}} \left(\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right) H' \cancel{\frac{1}{\sqrt{2\pm 2\Delta}}} \psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)}{\iint \left(\cancel{\frac{1}{\sqrt{2\pm 2\Delta}}} \psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right] \left[\cancel{\frac{1}{\sqrt{2\pm 2\Delta}}} \psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b\right.}$$

$$= \frac{\iint \left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\;\; H'\; \psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right] d\tau_1 d\tau_2}{\iint \left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right]\left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right] d\tau_1 d\tau_2}$$

Simplying we get

$$E' = \frac{2C \pm 2A}{2 \pm 2\Delta} \longrightarrow ⑰$$

where $C = \iint \psi_a(1)\psi_b(2)\, H'\, \psi_a(1)\psi_b(2)\, d\tau_1 d\tau_2$

$A = \iint \psi_a(2)\psi_b(1)\, H'\, \psi_a(2)\psi_b(1)\, d\tau_1 d\tau_2$

where A is called exchange integral.

UNIT V : Relativistic Wave equation The Klein – Gordon Equation – Charge and current densities in four vector – KG equation in electromagnetic field – The Dirac relativistic equation: The Dirac matrices – Free particle solutions – Meaning of negative energy states– Electromagnetic potential: magnetic moment of the electron – Existence of electron spin – Spin orbit energy

CONTENTS

12

Relativistic Quantum Mechanics

12·0 INTRODUCTION.

So far we have considered non-relativistic quantum mechanics and it is not applicable to the phenomena involving particles moving with relativistic velocities. Therefore it is desirable to include the requirements imposed on our theory by the relativistic theory, at least required by special theory of relativity which deals with inertial systems. Since the use of general theory is not essential due to negligible gravitational field in atomic systems. The idea of relativity may be introduced to two ways :

(1) taking into account the concepts only
(2) formulation of quantum theory in lorentz invariant form.

Here we shall include only the concepts of special theory of relativity.

12·1 KLEIN GORDAN EQUATION.

The *Schroedinger equation in operator from* is

$$\hat{H}\,\psi = i\hbar\,\frac{\partial\psi}{\partial t} \qquad ...(1)$$

The *non-relativistic Hamiltonian for a free particle* is

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\,\frac{\hbar^2\nabla^2}{2m} \qquad ...(2)$$

$$\left(\text{since } \hat{p} = \frac{\hbar}{i}\,\nabla = -\,i\hbar\nabla\right)$$

Substituting this in (1), we obtain

$$-\,\frac{\hbar^2}{2m}\,\nabla^2\,\psi\,(\mathbf{r},t) = i\hbar\,\frac{\partial\psi}{\partial t}\,(\mathbf{r},t)\,. \qquad ..(3)$$

Let us now discuss the general situation in cartesian co-ordinates. This means that the transformations (under which the requirements of special theory of relativity are invariant) to be considered are the linear transformation

$x^{\mu} = a^{\mu}_{\alpha}\, x^{\alpha}$

$$\bar{x}^{\mu} = a^{\mu}_{\nu}\,.\,x^{\nu} \qquad ...(4)$$

These transformations leaves the metric tensor $g_{\mu\nu}$ invariant, where

$$g_{\mu\nu} = \begin{cases} 1 & \text{for } \mu = \nu \\ 0 & \text{for } \mu \neq \nu \end{cases}$$

$\bar{x}^{\mu} = a^{\mu}_{\alpha}\, x^{\alpha}$

i.e. $\qquad g_{11} = g_{22} = g_{33} = g_{44} = 1$ and $g_{\mu\nu} = 0$ for $\mu \neq \nu$

As special theory of relativity treats spatial and temporal (time) variables on equal footings in Minkowski four-dimensional space, a co-ordinate representation must necessarily be cast into Schroedinger picture. In tensor notations equation (3) may be written as

$$-\frac{\hbar^2}{2m} g^{\mu\nu} \frac{\partial}{\partial x^\mu} \frac{\partial}{\partial x^\nu} \psi(x^\alpha) = -\hbar c g^{44} \frac{\partial}{\partial x^4} \psi(x^\alpha)$$

where

$$x^4 = ict \qquad \text{...(5)}$$

This equation while invariant under linear transformations of space co-ordinates alone, is not invariant under more general transformations known as Lorentz transformations in special relativity. Under these transformations this equation can become of second-order in new time co-ordinates $\bar{x}^4$ and mixed space time second order partial derivatives will appear. Such a result is not surprising since the Hamiltonian used here was non-relativistic. But if we consider the relativistic Hamiltonian more serious difficulties arise. The relativistic *Hamiltonian for a free particle* is

$$\hat{H} = E = \pm\sqrt{(\hat{p}^2c^2 + m^2c^4)} = \pm(\hat{p}^2c^2 + m^2c^4)^{1/2} \qquad \text{...(6)}$$

The Schroedinger's equation would then become

$$\pm(\hat{p}^2c^2 + m^2c^4)^{1/2}\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{...(7)}$$

There are **two difficulties** in the interpretation of above equation.

The first *difficulty* is to interpret the positive and negative signs. In classical theory this was no problem; since in classical theory the energy changes continuously with a gap of $2mc^2$ between the minimum positive and the maximum negative value, a particle whose energy at one instant is known to be positive will always have a positive energy. Under such conditions the negative energies could be ignored. But in quantum mechanics the energy of the particle can change discontinuously and either we must show that the negative energies are spurious or we must take them into account.

The second *difficulty* is even more serious. If we write the equation (7) as

$$(-\hbar^2c^2\nabla^2 + m^2c^4)^{1/2}\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{...(8a)}$$

i.e.

$$\left[-\hbar^2c^2 g^{\mu\nu}\frac{\partial}{\partial x^\mu}\frac{\partial}{\partial x^\nu} + m^2c^4\right]^{1/2}\psi(x^\alpha) = -\hbar c\frac{\partial\psi(x^\alpha)}{\partial x^4} \qquad \text{...(8b)}$$

where $\mu, \nu = 1, 2, 3$

We are unable to interpret the square root of an operator. However if we get rid of square root of an operator by expanding it in terms of power series, the expansion will cause the space and time derivatives in unsymmetrical form and thereby would make impossible the formulation of a covariant theory. Moreover the left hand side will contain a large number of terms involving various powers of operator ∇, making it difficult to be solved.

Obviously the equation (8) still lacks the necessary invariance under Lorentz transformations. Hence some further modification is required. This was done by *Klein-Gordon*. He operated the entire equation $\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$ by $\hat{H}$ and obtained

$$\hat{H}^2\psi = \hat{H}\left(i\hbar\frac{\partial\psi}{\partial t}\right)$$

$$= i\hbar\frac{\partial(\hat{H}\psi)}{\partial t}$$

(since the operations of $\hat{H}$ and $\frac{\partial}{\partial t}$ are interchangeable)

$$= i\hbar \frac{\partial}{\partial t}\left(i\hbar \frac{\partial \psi}{\partial t}\right) \qquad \text{using (1)}$$

i.e.
$$\hat{H}^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial t^2} \qquad \text{...(9)}$$

This equation is called the *Klein-Gordan equation* or *relativistic Schroedinger equation.*

For a free particle
$$\hat{H}^2 = \hat{p}^2 c^2 + m^2 c^4$$
$$= \left(\frac{\hbar}{i}\nabla\right)^2 c^2 + m^2 c^4$$

i.e.
$$\hat{H}^2 = -\hbar^2 c^2 \nabla^2 + m^2 c^4 \qquad \text{...(10)}$$

Therefore *Klein-Gordan equation for a free particle* takes the form
$$(-\hbar^2 c^2 \nabla^2 + m^2 c^4)\,\psi = -\hbar^2 \frac{\partial^2 \psi}{\partial t^2}$$

This equation may be written as
$$\left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2 c^2}{\hbar^2}\right]\psi = 0 \qquad \text{...(11a)}$$

or
$$\left[\Box^2 - \frac{m^2 c^2}{\hbar^2}\right]\psi = 0 \qquad \text{...(11b)}$$

where
$$\Box^2 = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \frac{\partial}{\partial x^\mu}\frac{\partial}{\partial x^\nu}.$$

is called the *D' Alembertian operator.*

In co-ordinate representation equation (11) takes the form
$$\left(g^{\mu\nu}\frac{\partial}{\partial x^\nu}\frac{\partial}{\partial x_\nu} - k^2\right)\psi(x^\alpha) = 0 \qquad \text{...(12)}$$

where $k = \frac{mc}{\hbar}$. In this form the invariance of Klein-Gordan equation is obvious.

(a) Charge and Current Densities : The Klein-Gordan equation for a free particle is
$$\left(\Box^2 - \frac{m^2 c^2}{\hbar^2}\right)\psi = 0$$

or
$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2 c^2}{\hbar^2}\right)\psi = 0$$

or
$$\nabla^2 \psi - \frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} - \frac{m^2 c^2}{\hbar^2}\psi = 0. \qquad \text{...(13)}$$

Taking complex conjugate of above equation, we get
$$\nabla^2 \psi^* - \frac{1}{c^2}\frac{\partial^2 \psi^*}{\partial t^2} - \frac{m^2 c^2}{\hbar^2}\psi^* = 0. \qquad \text{...(14)}$$

Multiplying equations (13) and (14) by ψ^* and ψ respectively, we obtain

$$\psi^* \nabla^2 \psi - \frac{1}{c^2} \psi^* \frac{\partial^2 \psi}{\partial t^2} - \frac{m^2 c^2}{\hbar^2} \psi^* \psi = 0 \qquad \text{...(15)}$$

and

$$\psi \nabla^2 \psi^* - \frac{1}{c^2} \psi \frac{\partial^2 \psi^*}{\partial t^2} - \frac{m^2 c^2}{\hbar^2} \psi^* \psi = 0. \qquad \text{...(16)}$$

Substracting (16) from (15), we get

$$\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* - \frac{1}{c^2} \left(\psi^* \frac{\partial^2 \psi}{\partial t^2} - \psi \frac{\partial^2 \psi^*}{\partial t^2} \right) = 0$$

or

$$\nabla \cdot [\psi^* \nabla \psi - \psi \nabla \psi^*] - \frac{1}{c^2} \frac{\partial}{\partial t} \left[\psi^* \frac{\partial \psi}{\partial t} - \frac{\partial \psi^*}{\partial t} \psi \right] = 0.$$

Multiplying throughout by $\frac{\hbar}{2im}$, we get

$$\nabla \cdot \left[\frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*) \right] \div \frac{\partial}{\partial t} \left[\frac{\hbar}{2imc^2} \left(\psi \frac{\partial \psi^*}{\partial t} - \psi^* \frac{\partial \psi}{\psi t} \right) \right] = 0 \qquad \text{...(17)}$$

Substituting

$$\left.\begin{aligned} P(\mathbf{r}, t) &= \frac{\hbar}{2imc^2} \left(\psi \frac{\partial \psi^*}{\partial t} - \psi^* \frac{\partial \psi}{\partial t} \right) && \text{...}(a) \\ \text{and} \quad S(\mathbf{r}, t) &= \frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*) && \text{...}(b) \end{aligned}\right\} \text{...(18)}$$

equation (17) takes the form

$$\nabla \cdot S(\mathbf{r}, t) + \frac{\partial P}{\partial t} (\mathbf{r}, t) = 0, \qquad \text{...(19)}$$

which is *well known equation of continuity*. The current density expressions **S** (**r**, *t*) has the same form as in non-relativistic case, but the inspection of expression *P* (**r**, *t*) indicates that it can not be interpreted as *position probability density* in analogy with non-relativistic case in which $P(\mathbf{r}, t) = \psi^* \psi$ due to following reason, :

The expression *P* (**r**, *t*) may be expressed as

$$P(\mathbf{r}, t) = \frac{\hbar}{2imc^2} \left(\psi \frac{\partial \psi^*}{\partial t} - \psi^* \frac{\partial \psi}{\partial t} \right)$$

$$= \frac{1}{2mc^2} \left[\left(-i\hbar \frac{\partial \psi^*}{\partial t} \right) \psi + \psi^* \left(i\hbar \frac{\partial \psi}{\partial t} \right) \right] \qquad \text{...(20)}$$

Now using Schroedinger equation in operator form and keeping in mind that the Hamiltonian operator associated with dynamic observable energy *E* is Hermitian, we have

$$H \psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{i.e.} \quad i\hbar \frac{\partial \psi^*}{\partial t} = E \psi^*.$$

and

$$H^* \psi^* = -i\hbar \frac{\partial \psi^*}{\partial t} \quad \text{i.e.} \quad -i\hbar \frac{\partial \psi^*}{\partial t} = E \psi^*.$$

So equation (20) may be expressed as

$$P(\mathbf{r}, t) = \frac{1}{2mc^2} [(E\psi^*) \psi + \psi^* (E\psi)]$$

$$= \frac{1}{2mc^2}\,[2E\psi^*\,\psi] \qquad ...(21)$$

i.e.
$$P(\mathbf{r}, t) = \frac{E}{mc^2}\,[\psi^*\,\psi].$$

From expression $E = \pm\sqrt{(p^2c^2 + m^2c^4)}$, we note that the energy of a particle can be either positive or negative. Thus it follows that the expression for $P(\mathbf{r}, t)$ is not definitely positive and hence it can not be regarded as conventional *position probability density*. Thus it is necessary to reinterpret ψ if Klein-Gordan equation is to be used. This was done by Pauli and Wesskopf in 1934 (after about 7 years the Klein-Gordan equation was proposed); according to them P multplied by e *i.e.* $(e\,P)$ cn be interpreted as *charge density* which may be positive and negative since charge can have either sign ; then $e\mathbf{S}$ will be corresponding *current density*.

Remarks. 1. Klein-Gordan equation with new interpretation of charge and current densities would inherently represent many particle theory, since it would have to encompass particles on both signs of charge,

2. The wavefunction ψ in Klein-Gordan equation has only one component (scalar). If the wavefunction has more than one component as Pauli wavefunction, then more degress of freedom than those required to describe translatory motion are available. The additional degrees of freedom describe *spin motion*. Thus in the absence of other components, the Klein-Gordan equation will describe *particles of zero spin* like π-mesons.

3. The *probability density expression in Klein-Gordan equation reduces to correct non-relativistic expression as may be seen as follows.*

Substituting
$$\psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-iEt/\hbar}. \qquad ...(22)$$

If E' is non-relativistic energy, then total energy E may be expressed as $E = E' + mc^2$; mc^2 being rest energy.

$$\therefore \quad \psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-i(E' + mc^2)\,t/\hbar}$$
$$= \psi(\mathbf{r})\, e^{-iE't/\hbar} \cdot e^{-imc^2 t/\hbar}$$
$$= \psi'(\mathbf{r}, t)\, e^{-imc^2 t/\hbar} \qquad ...(23)$$

where *non-relativistic wavefunction*
$$\psi'(\mathbf{r}, t) = \phi(\mathbf{r})\, e^{-iE't/\hbar} \qquad ...(24)$$

Differentiating (23) with respect to t, we get
$$\frac{\partial\psi}{\partial t} = \left(\frac{\partial\psi'}{\partial t} - \frac{imc^2}{\hbar}\,\psi'\right) e^{-imc^2 t/\hbar} \qquad ...(25)$$

Taking complex conjugates of (23) and (25), we get
$$\psi^*(\mathbf{r}, t) = \psi'^*(\mathbf{r}, t)\, e^{icm^2 t/\hbar}$$

and
$$\frac{\partial\psi^*}{\partial t} = \left(\frac{\partial\psi'^*}{\partial t} + \frac{imc^2}{\hbar}\,\psi'^*\right) e^{imc^2 t/\hbar}. \qquad ...(27)$$

Substituting these values in (18a), we get
$$P(\mathbf{r}, t) = \frac{\hbar}{2imc^2}\Bigg[\{\psi'(\mathbf{r}, t)\, e^{-imc^2 t/\hbar}\}\left\{\left(\frac{\partial\psi'^*}{\partial t} + \frac{imc^2}{\hbar}\,\psi'^*\right) e^{imc^2 t/\hbar}\right\}$$
$$- \{\psi'^*(\mathbf{r}, t)\, e^{imc^2 t/\hbar}\}\left\{\left(\frac{\partial\psi'}{\partial t} - \frac{imc^2}{\hbar}\,\psi'\right) e^{-imc^2 t/\hbar}\right\}\Bigg]$$

$$= \frac{\hbar}{2\,i\,mc^2}\left[\psi'(\mathbf{r},t)\left(\frac{\partial\psi'}{\partial t}+\frac{imc^2}{\hbar}\psi'^*\right)-\psi'^*(\mathbf{r},t)\left(\frac{\partial\psi'}{\partial t}-\frac{imc^2}{\hbar}\psi'\right)\right]$$

$$= \frac{1}{2mc^2}\left[\psi'(\mathbf{r},t)\left(\frac{\hbar}{i}\frac{\partial\psi'^*}{\partial t}\right)-\psi'^*\left(i\hbar\frac{\partial\psi'}{\partial t}\right)\right]+\psi'^*\psi'$$

$$= \frac{1}{2mc^2}\left[\psi'(\mathbf{r},t)\left(-i\hbar\frac{\partial\psi'^*}{\partial t}\right)+\psi'^*\left(i\hbar\frac{\partial\psi'}{\partial t}\right)\right]+\psi'^*\psi'$$

$$= \frac{E'}{mc^2}\psi'^*\psi'+\psi'^*\psi' \qquad \text{(Since } E'^* = E'\text{, eigen-value of } H \text{ being real)}$$

$$= \psi'^*\psi'. \qquad \text{...(28)}$$

(Since non-relativistic energy $E' << mc^2$)

which is correct non-relativistic expression for *probability density.*

12·2. KLEIN-GORDAN EQUATION IN ELECTROMAGNETIC FIELD.

An electromagnetic field can be uniquely represented by a vector potential **A** and a scalar potential ϕ. These potentials form a four vector A_μ whose components are A_1, A_2, A_3 and $A_4 = i\phi$ and transform like momentum-energy four vector p_μ having components $p_1, p_2, p_3, p_4 = \frac{iE}{c}$. Therefore the potentials **A** and ϕ should be included in Klein Gordan equation with momentum and energy.

If e is the charge on the particle, then in analogy with non-relativistic expression **p** and E are replaced by $\mathbf{p} - \frac{e\mathbf{A}}{c}$ and $E - e\phi$ respectively *i.e.*

$$\left.\begin{aligned}\mathbf{p} &\to \mathbf{p} - \frac{e\mathbf{A}}{c}\\ E &\to E - e\phi\end{aligned}\right\} \qquad \text{...(29)}$$

So the relativistic expression between momentum and energy of a particle of charge e in electromagnetic field becomes.

$$(E - e\phi)^2 = c^2\left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right)^2 + m^2c^4$$

i.e.

$$(E - e\phi)^2 = (c\mathbf{p} - e\mathbf{A})^2 + m^2c^4. \qquad \text{...(30)}$$

Replacing operators E and p by $i\hbar\frac{\partial}{\partial t}$ and $-i\hbar\nabla$ respectively

we get *Klein Gordan equation as*

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2\psi = [(-i\hbar c\nabla - e\mathbf{A})^2 + m^2c^4]\,\psi. \qquad \text{...(31)}$$

Now

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2\psi = \left[-\hbar^2\frac{\partial^2}{\partial t^2} - ie\hbar\frac{\partial\phi}{\partial t} - ie\hbar\phi\frac{\partial}{\partial t} + e^2\phi^2\right]\psi$$

$$= -\hbar^2\frac{\partial^2\psi}{\partial t^2} - ie\hbar\psi\frac{\partial\phi}{\partial t} - 2\,ie\hbar\,\phi\frac{\partial\psi}{\partial t} + e^2\phi^2\psi$$

and
$$(-i\hbar c\nabla - e\mathbf{A})^2\psi = i^2\hbar^2c^2\nabla^2\psi + iec\hbar\nabla\cdot(\mathbf{A}\psi) + iec\hbar\mathbf{A}\cdot\nabla\psi + e^2\mathbf{A}^2\psi$$
$$= [-\hbar^2c^2\nabla^2 + ie\hbar c\ \nabla\cdot\mathbf{A} + 2ie\hbar c\ \mathbf{A}\cdot\nabla + e^2A^2]\ \psi.$$

Substituting these values in (31), the Klein-Gordan equation for a particle of charge e in electromagnetic field takes the form.

$$\left[-\hbar^2\frac{\partial^2}{\partial t^2} - ie\hbar\frac{\partial\phi}{\partial t} - 2ie\hbar\phi\frac{\partial}{\partial t} + e^2\phi^2\right]\psi$$
$$= [-\hbar^2c^2\nabla^2 + ie\hbar c\ \nabla\cdot\mathbf{A} + 2ie\hbar c\mathbf{A}\cdot\nabla + e^2\mathbf{A}^2 + m^2c^4]\ \psi \qquad \text{...(32)}$$

To find connection between equation (32) and similar non-relativistic equation, let us make the following substitution taking mc^2 as the rest energy,

$$\psi(\mathbf{r}, t) = \psi'(\mathbf{r}, t)\ e^{-imc^2t/\hbar}$$
$$\frac{\partial\psi}{\partial t} = \left(\frac{\partial\psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right)e^{-imc^2t/\hbar}$$
$$\frac{\partial^2\psi}{\partial t^2} = \left(\frac{\partial^2\psi'}{\partial t^2} - \frac{2imc^2}{\hbar}\frac{\partial\psi'}{\partial t} - \frac{m^2c^4}{\hbar^2}\psi'\right)e^{-imc^2t/\hbar}$$

Substituting these values in (32), we get

$$\left[-\hbar^2\frac{\partial^2\psi'}{\partial t^2} + 2imc^2\hbar\frac{\partial\psi'}{\partial t} + m^2c^4\psi' - ie\hbar\frac{\partial\phi}{\partial t}\psi' - 2ie\hbar\phi\frac{\partial\psi'}{\partial t} - 2mc^2\ e\phi\psi' + e^2\phi^2\psi'\right].\ e^{-imc^2t/\hbar}$$
$$\equiv [-\hbar^2c^2\nabla^2 + ie\hbar c\ \nabla\cdot\mathbf{A} + 2ie\hbar c\ \mathbf{A}\cdot\nabla + e^2A^2 + m^2c^4]\ \psi'\ e^{-imc^2t/\hbar}$$

Concelling out the common factor $e^{-imc^2t/\hbar}$, $m^2c^4\psi'$ on both sides and dividing throughout by $2mc^2$, we get

$$-\frac{\hbar^2}{2mc^2}\frac{\partial^2\psi'}{\partial t^2} + i\hbar\frac{\partial\psi'}{\partial t} - \frac{ie\hbar}{2mc^2}\frac{\partial\phi}{\partial t}\psi' - \frac{ic\hbar\phi}{mc^2}\frac{\partial\psi'}{\partial t} - e\phi\psi' + \frac{e^2\phi^2}{2mc^2}\psi'$$
$$= \left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{ie\hbar}{2mc}\nabla\cdot\mathbf{A} + \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla + \frac{e^2A^2}{2mc^2}\right]\psi'.$$

Keepding mind that rest energy $mc^2 >>$ non-relativistic energy E and $mc^2 >> e\phi$, we may neglect the terms of order $1/mc^2$ as compared to E' and $e\phi$ and rearranging.

$$i\hbar\frac{\partial\psi'}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{ie\hbar}{2mc}\nabla\cdot\mathbf{A} + \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla + \frac{e^2A^2}{2mc^2} + e\phi\right]\psi'.$$

This is simply *non-relativistic Schroedinger equation for a particle of charge* e in electromagnetic field. Thus Klein-Gordan equation in electromagnetic field reduces to correct non-relativistic limit with appropriate approximations.

12·3. SOLUTION OF KLEIN GORDAN EQUATION FOR A PARTICLE WITH COULOMB POTENTIAL V_0.

observed fine structure of the hydrogen atom. Therefore the Klein-Gordan particle cannot be an electron. The spin is absent in this solution. It is valid for spin zero particle orbiting about a nucleus.

12.4. DIRAC'S RELATIVISTIC EQUATION :

In 1962, Dirac formulated an equation to avoid the difficulties arising in Klein Gordan equation on the basis of requirements of Lorentz invariance which demand that an equation which is linear in H and hence in E must also be linear in $\mathbf{p}$. This is because both E and $\mathbf{p}$ enter linearly in four momentum p^{μ} given by $\left(\mathbf{p}, i\frac{E}{c}\right)$.

Dirac approached the problem of finding a relativistic wave equation from

$$\hat{H}\,\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} \qquad \text{...(1)}$$

Linearization of Hamiltonian H : Dirac took a bolder approach by assuming that the Hamiltonian H is linear in energy and momentum. The simplest linearized Hamiltonian for a free particle is

$$H = c\,\vec{\alpha}\cdot\mathbf{p} + \beta\,mc^2 \qquad \text{...(2)}$$

Here β and the components of $\vec{\alpha}$ are yet undetermined except that we postulate them to be independent of $\mathbf{p}$. This implies that they commute with $\mathbf{r}$. We can also require that they must be independent of $\mathbf{r}$ and t, since otherwise the energy of a particle in empty space would depend on the position of the particle and the instant of observation. Thus they also commute with $\mathbf{p}$.

Substituting H from (2) in (1), we get the wave equation

$$(c\,\vec{\alpha}\cdot\mathbf{p} + \beta\,mc^2)\,\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} \qquad \text{...(3)}$$

Substituting operator for $\mathbf{p}$ viz $\mathbf{p} \to -i\hbar\nabla$, we obtain

$$[c\,\vec{\alpha}\cdot(-i\hbar\nabla) + \beta mc^2]\,\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}$$

or

$$\left(i\hbar\frac{\partial}{\partial t} + i\hbar c\,\vec{\alpha}\cdot\nabla - \beta mc^2\right)\psi(\mathbf{r},t) = 0. \qquad \text{...(4)}$$

As already indicated if this equation is to describe a free particle, there can be no term in the Hamiltonian that depend upon the space and time coordinates. Consequently $\vec{\alpha}$ and β are independent of $\mathbf{r}$, t, $\mathbf{p}$ and E and hence commute with all of them. This does not necessarily mean that $\vec{\alpha}$ and β are numbers, since they need not commute with each other.

For simplicity writing again E for $i\hbar\,(\partial/\partial t)$ and $\mathbf{p}$ for $-i\hbar\nabla$, equation (1.1) may be expressed as

$$(E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2)\,\psi(\mathbf{r},t) = 0 \qquad \text{...(5)}$$

or

Operating above equation by $(E + c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)$, from left we get

$$(E + c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)\,(E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2)\,\psi = 0$$

or

$$[E^2 - (c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)^2]\,\psi = 0$$

or

$$\{E^2 - c^2(\vec{\alpha}\cdot\mathbf{p})^2 - \beta^2 m^2c^4 - mc^3(\vec{\alpha}\cdot\mathbf{p})\,\beta - mc^3\,\beta\,\vec{\alpha}\cdot\mathbf{p}\}\,\psi = 0 \qquad \text{...(6)}$$

But

$$\vec{\alpha} = \mathbf{i}\,\alpha_x + \mathbf{j}\,\alpha_y + \mathbf{k}\,\alpha_z,\quad \mathbf{p} = \mathbf{i}\,p_x + \mathbf{j}\,p_y + \mathbf{k}p_z.$$

∴

$$\vec{\alpha}\cdot\mathbf{p} = \alpha_x p_x + \alpha_y p_y + \alpha_z p_z.$$

Therefore equation (6) becomes

$$\Big[E^2 - c^2(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z)^2 - \beta^2 m^2 c^4 - mc^3(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z)\,\beta$$

$$- mc^3 \beta (\alpha_x p_x + \alpha_y p_y + \alpha_z p_z)\Big] \psi = 0 \qquad ...(7)$$

or
$$\Big[E^2 - c^2 \{\alpha_x^2 p_x^2 + \alpha_y^2 p_y^2 + \alpha_z^2 p_z^2 + (\alpha_x \alpha_y + \alpha_y \alpha_x) p_x p_y + (\alpha_y \alpha_z + \alpha_z \alpha_y) p_y p_z + (\alpha_z \alpha_x + \alpha_x \alpha_z) p_z p_x\} - \beta^2 m^2 c^4 - mc^3 \{(\alpha_x \beta + \beta \alpha_x) p_x + (\alpha_y \beta + \beta \alpha_y) p_y + (\alpha_z \beta + \beta \alpha_z) p_z\Big] \psi = 0. \qquad ...(8)$$

where the substitutions $i\hbar\ (\partial/\partial t)$ for E and $+\ i\hbar\ \nabla$ for **p** are implied. Klein-Gordan equation is

$$\Big[E^2 - c^2\ (p_x^2 + p_y^2 + p_z^2) - m^2 c^4\Big]\ \psi = 0. \qquad ...(9)$$

Comparing equations (8) and (9), we obtain

$$\left.\begin{aligned} &\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1 \\ \text{and} \quad &\alpha_x \alpha_y + \alpha_y \alpha_x = 0;\ (\alpha_y \alpha_z + \alpha_z \alpha_y) = 0;\ (\alpha_z \alpha_x + \alpha_x \alpha_z) = 0 \\ &\alpha_x \beta + \beta \alpha_x = 0\ ;\ (\alpha_y \beta + \beta \alpha_y) = 0;\ (\alpha_z \beta + \beta \alpha_z) = 0 \end{aligned}\right\} \qquad ...(10)$$

That is the four quantities α_x, α_y, α_z and β have the following properties :

(i) their squares are unity and ;

(ii) They anticommute with one another in pairs.

Since $\vec{\alpha}$ and β anticommute rather than commute with each other, they connot be numbers. Moreover the quantities of this type can be expressed in terms of matrices and it is convenient to find a matrix representation of them.

Matrices for $\vec{\alpha}$ and β :

The squares of all the four matrices are unity; so that their eigen-values are + 1 and − 1. Let us 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

$$\beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad ...(10a)$$

which is an abbreviation of

$$\beta = \left[\begin{array}{cc:cc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \hdashline 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{array}\right] \qquad ...(10b$$

All the four matrices α_x, α_y, α_z and β are such that their squares are unity and they anticommute wi one another in pairs. We already have three well known 2 × 2 matrices σ_z, σ_y and *σ_z called Pauli sp matrices;* which satisfy the above properties, given by

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},\ \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix},\ \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad ...(1$$

Since a 2 × 2 matrix has four elements, there are four and only four, independent 2 × 2 matric three of these are σ_x, σ_y, σ_z. The only other matrix linearly independent of these three is

$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad ...(1$$

which is a unit matrix and therefore commutes rather than anticommutes with every σ. Hence 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 representatioin in which β is diagonal $N \times N$ matrix *i.e.*

$$\beta = \begin{bmatrix} b_1 & & O \\ & b_i & \\ O & & b_N \end{bmatrix} \qquad \ldots(13)$$

As $\beta^2 = 1$, $b_i^2 = 1$ and $b_i = \pm 1$ $(i = 1, 2, \ldots N)$

Also since $\beta^2 = \alpha_k^2 = 1$ $(k = x, y, z)$; det α_k or det $\beta \neq 0$.

This implies that matrices α_k $(k = x, y, z)$ and β has an inverse

Since β anticommutes with each component of $\vec{\alpha}$, we have

$$\alpha_k \beta + \beta \alpha_k = 0 \quad (k = x, y, z)$$

This relation may be expressed as

$$\beta \alpha_k = - \alpha_k \beta$$

or

$$\alpha_k^{-1} \beta \alpha_k = - \alpha_k^{-1} \alpha_k \beta$$

As $\alpha_k^{-1} \alpha_k = 1$; we have

$$\alpha_k^{-1} \beta \alpha_k = - \beta \qquad \ldots(14)$$

Taking trace of both sides, we get

$$\text{Trace } (\alpha_k^{-1} \beta \alpha_k) = - \text{ Trace } \beta$$

or

$$\text{Trace } (\alpha_k \alpha_k^{-1} \beta) = - \text{ Trace } \beta \text{ [Since Trace (ABC) = Trace (CAB)]}$$

or

$$\text{Trace } (\beta) = - \text{ Trace } (\beta) \qquad (\text{Since } \alpha_k \alpha_k^{-1} = I)$$

This gives $\quad 2 \text{ (Trace } \beta) = \text{or Trace } (\beta) = 0$

Similarly $\quad \text{Trace } (\alpha_k) = 0$

Thus

$$\text{Trace } (\beta) = \text{ Trace } (\alpha_k) = 0 \qquad \ldots(15)$$

This equation *shows that the trace of each of the matrices* α_k *and* β *must be zero :*

In matrix (13) let r of the b_i s are + 1 and the rest s of b_i's are – 1 *i.e.*

$$b_1 = b_2 = \;\; = b_r = 1$$

and

$$b_{r+1} = b_{r+2} = \ldots = b_N = -1 \qquad \ldots(16)$$

so that

$$r + s = N$$

But the condition that Trace $(\beta) = 0$ requires that

$$\sum_{i=l}^{N} b_i = r - s = 0 \text{ i.e. } r = s$$

In view of this equation (16) shows

$$N = 2r \qquad \ldots(17)$$

Thus Dirac matrices $\vec{\alpha}$ and β must be even dimensional. Therefore we can not use 3 × 3 matrices. The next simplest choice is 4 × 4 matrices.

---

*The necessary and sufficient condition for a matrix A to possess inverse in that det $A \neq 0$.

As eigen values of all the four matrices are + 1 and − 1. Let us arbitrarily choose β as the matrix which is to be diagonal and we arrange its rows and columns so that all the + 1 eigen values are grouped together and all the − 1 eigen values are grouped together in a matrix as

$$\beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \qquad \text{...(18a)}$$

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad \text{...(18b)}$$

As β anticommutes with each component of $\vec{\alpha}$ we have

$$\alpha_k \beta + \beta \alpha_k = 0.$$

the jl element of which is $(\alpha_k)_{jl}\ (\beta_j + \beta_l) = 0$.

Here β_j and β_l are the two eigen values of β, which are arranged in accordance with equation (18). If $\beta_j = \beta_l$ then $(\beta_j + \beta_l) \neq 0$ and so $(\alpha_k)_{jl} = 0$; whereas if β_j and β_l have opposite signs, then $\beta_j + \beta_l = 0$; so $(\alpha_k)_{jl}$ need not be zero. Therefore the matrix for α_k may be expressed as

$$\alpha_k = \begin{bmatrix} 0 & \alpha_{x1} \\ \alpha_{x2} & 0 \end{bmatrix} \qquad \text{...(19)}$$

where α_{x1} has n rows and m columns and α_{x2} has m rows and n columns. Since the square of (19) is a unit matrix, we note that

$$\alpha_{x1}\,\alpha_{x2} = 1 \qquad \text{...(20a)}$$

$$\alpha_{x2}\,\alpha_{x1} = 1 \qquad \text{...(20b)}$$

The unit matrix appearing on R.H.S. of (20) has n rows and m columns while the unit matrix on R.H.S. of (20b) has m rows and n columns.

But no two matrices exist that satisfy (20a) and (20b) simultaneoulsy if $m \neq n$. Therefore we must have $m = n = 2$ for 4×4 matrices. It is apparent that α_y and α_z can be put in a form similar to (19).

Using Pauli spin matrices σ_x, σ_y and σ_z and choosing

$$\alpha_{x1} = \alpha_{x2} = \sigma_x \text{ ; then}$$

$$\alpha_x = \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} = \left[\begin{array}{cc|cc} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ \hline 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{array}\right] \qquad \text{...(21a)}$$

Similarly

$$\alpha_y = \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} = \left[\begin{array}{cc|cc} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ \hline 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{array}\right] \qquad \text{...(21b)}$$

$$\alpha_z = \begin{bmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{bmatrix} = \left[\begin{array}{cc|cc} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ \hline 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{array}\right] \qquad \text{...(21c)}$$

We already have

$$\beta = \left[\begin{array}{cc|cc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \hline 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{array}\right] \qquad ...(21d)$$

These 4 × 4 matrices are evidently Hermitian and in abbreviate form may be expressed as

$$\beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}; \vec{\alpha} = \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix} \qquad ...(22)$$

where each element is a matrix with two rows and two columns.

The four components of ψ's : If the Dirac operators are to involve 4 by 4 matrices, then the Dirac operands must have the four components, that is Dirac ψ function, must have the form

$$\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \qquad ...(23)$$

where each of four components is an ordinary function of x, y, z and t. Then ψ^* or $\overline{\psi}$'s corresponding to above equation are denoted by the row symbol

$$\overline{\psi} = [\overline{\psi}_1, \overline{\psi}_2, \overline{\psi}_3, \overline{\psi}_4] \qquad ...(24)$$

and the corresponding Dirac $\overline{\psi}\,\psi$ is the following orbinary function.

$$\overline{\psi}\,\psi = \overline{\psi}_1\psi_1 + \overline{\psi}_2\psi_2 + \overline{\psi}_3\psi_3 + \overline{\psi}_4\psi_4 \qquad ...(25)$$

Two Dirac ψ's ψ_I and ψ_{II} are said to be orthogonal to each other if

$$\int \overline{\psi}_I\,\psi_{II}\,d\tau = 0. \qquad ...(26)$$

this is, if

$$\int (\overline{\psi}_{1I}\psi_{1II} + \overline{\psi}_{2I}\psi_{2II} + \overline{\psi}_{3I}\psi_{3II} + \overline{\psi}_{4I}\psi_{4II})\,d\tau = 0. \qquad ...(27)$$

The time dependence of a Dirac pertaining to a system whose Hamiltonian is H is determined through the equation

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

where

$$\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial t}\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} \partial\psi_1/\partial t \\ \partial\psi_2/\partial t \\ \partial\psi_3/\partial t \\ \partial\psi_4/\partial t \end{bmatrix}$$

The Dirac Equation :

The equation $H\psi = E\psi$ with H given by (2) that is, equation

$$(c\vec{\alpha}\cdot\mathbf{p} + \beta mc^2)\,\psi = E\psi \qquad ...(29a)$$

or

$$(c\alpha_x p_x + c\alpha_y p_y + c\alpha_z p_z + \beta mc^2)\,\psi = E\psi \qquad ...(29b)$$

with $p_x = -i\hbar\,\partial/\partial x$ and so on, is called the *Dirac equation for free particle.*

To write it an more explicit form we replace α's and β by specific matrices and replace ψ by four-component column symbol.

$$\begin{bmatrix} mc^2 & 0 & cp_z & c(p_x - ip_y) \\ 0 & mc^2 & c(p_x + ip_y) & -cp_z \\ cp_z & c(p_x - ip_y) & -mc^2 & 0 \\ c(p_x + ip_y) & -cp_z & 0 & -mc^2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

so that this equation reduces to the four simultaneous equations

$$\left.\begin{aligned} (mc^2)\,\psi_1 + cp_z\,\psi_3 + c\,(p_x - ip_y)\,\psi_4 &= E\,\psi_1 \\ (mc^2)\,\psi_2 + cp_z\,\psi_4 + c\,(p_x + ip_y)\,\psi_3 &= E\,\psi_2 \\ (-mc^2)\,\psi_3 + cp_z\,\psi_1 + c\,(p_x + ip_y)\,\psi_2 &= E\,\psi_3 \\ (-mc^2)\,\psi_4 + cp_z\,\psi_2 + c\,(p_x + ip_y)\,\psi_1 &= E\,\psi_4 \end{aligned}\right\}$$

These equations may be expressed as

$$\left.\begin{aligned} (E - mc^2)\,\psi_1 - cp_z\,\psi_3 - c\,(p_x - ip_y)\,\psi_4 &= 0 \\ (E - mc^2)\,\psi_2 - c\,(p_x + ip_y)\,\psi_3 + cp_z\,\psi_4 &= 0 \\ (E + mc^2)\,\psi_3 - cp_z\,\psi_1 - c\,(p_x - ip_y)\,\psi_2 &= 0 \\ (E + mc^2)\,\psi_4 - c\,(p_x + ip_y)\,\psi_1 + cp_z\,\psi_2 &= 0 \end{aligned}\right\} \qquad \text{...(30)}$$

Finally we replace p_x by $-i\hbar\dfrac{\partial}{\partial x}$ etc. and get

$$\left.\begin{aligned} (E - mc^2)\,\psi_1 + i\hbar c\,\frac{\partial \psi_3}{\partial z} + i\hbar c\left(\frac{\partial}{\partial x} - i\,\frac{\partial}{\partial y}\right)\psi_4 &= 0 \\ (E - mc^2)\,\psi_2 + i\hbar c\left(\frac{\partial}{\partial x} + i\,\frac{\partial}{\partial y}\right)\psi_3 - i\hbar c\,\frac{\partial \psi_4}{\partial z} &= 0 \\ (E + mc^2)\,\psi_3 + i\hbar c\,\frac{\partial \psi_1}{\partial z} + i\hbar c\left(\frac{\partial}{\partial x} - i\,\frac{\partial}{\partial y}\right)\psi_2 &= 0 \\ (E + mc^2)\,\psi_4 + i\hbar c\left(\frac{\partial}{\partial x} + i\,\frac{\partial}{\partial y}\right)\psi_1 - i\hbar c\,\frac{\partial \psi_2}{\partial z} &= 0 \end{aligned}\right\} \qquad \text{...(31)}$$

Ex. 1. *If $\vec{\alpha}$ represents three Dirac matrices $\alpha_x, \alpha_y, \alpha_z$ and* **B** *and* **C** *are usual three dimensional vectors, then show that*

$$(\vec{\alpha} \cdot \mathbf{B})\,(\vec{\alpha} \cdot \mathbf{C}) = \mathbf{B} \cdot \mathbf{C} + i\,\vec{\sigma}' \cdot \mathbf{B} \times \mathbf{C}$$

where $\vec{\sigma}' = \begin{bmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{bmatrix}$ *is a 4 × 4 matrix.*

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$\vec{\sigma}$ *being 2 × 2 Pauli spin matrices.*

Solution.

$$(\vec{\alpha} \cdot B)\,(\vec{\alpha} \cdot C) = (\alpha_x B_x + \alpha_y B_y + \alpha_z B_z)\,(\alpha_x C_x + \alpha_y C_y + \alpha_z C_z)$$

$$= \alpha_x^2 B_x C_x + \alpha_y^2 B_y C_y + \alpha_z^2 B_z C_z + \alpha_x \alpha_y\,(B_x C_y - B_y C_x) + \alpha_y \alpha_z\,(B_y C_z - B_z C_y)$$

$$+ \alpha_z \alpha_x\,(B_z C_x - B_x C$$

[Since $\alpha_x \alpha_y = -\alpha_y \alpha_x$

$$= B_x C_x + B_y C_y + B_z C_z + \alpha_x \alpha_y\,(B_x C_y - B_y C_x) + \alpha_y \alpha_z\,(B_y C_z - B_z C_y) + \alpha_z \alpha_x\,(B_z C_x - B_x C$$

(Since $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = 1$

12·5. DIRAC FREE PARTICLE SOLUTIONS OR PLANE WAVE SOLUTIONS.

The wave function ψ has 4 components and the Dirac equation is exactly a set of 4 first order linear partial differential equations. The plane wave solution of these component wave-functions will have the form

$$\psi_j\ (\mathbf{r}, t) = u_j\, e^{i\,(\mathbf{k}\cdot\mathbf{r} - \omega t)}, \qquad \text{...(1)}$$

where $j = 1, 2, 3, 4$.

u_j are numbers, $\psi_j\,(\mathbf{r}, t)$ are eigen functions of the energy and momentum operators with eigen values $E = \hbar\ \omega$ and $\mathbf{p} = \hbar\ k$ respectively. After substitution, we get

Similarly if we choose the negative square root

$$E_- = -(c^2p^2 + m^2c^4)^{1/2},$$

we obtain two new solutions from first two of (2)

$$\left.\begin{aligned} u_1 &= \frac{cp_z}{E_- - mc^2},\ u_2 = \frac{c\,(p_x - ip_y)}{E_- - mc^2},\ u_3 = 1,\ u_4 = 0 \\ u_1 &= \frac{c\,(p_x - ip_y)}{E_- - mc^2},\ u_2 = \frac{-cp_z}{E_- - mc^2},\ u_3 = 0,\ u_4 = 1 \end{aligned}\right\} \qquad -(5)$$

Each of these solutions can be normalised by multiplying it by N in the sense

$$\psi^*\psi = 1,$$

i.e.

$$u_1^*u_1 + u_2^*u_2 + u_3^*u_3 + u_4^*u_4 = 1$$

or

$$N^2\left[1 + 0 + \frac{c^2p_z^2}{(E_+ + mc^2)^2} + \frac{c^2(p_x^2 + p_y^2)}{(E_+ + mc^2)^2}\right] = 1$$

or

$$N^2 = \frac{1}{1 + \dfrac{c^2(p_x^2 + p_y^2 + p_z^2)}{(E_+ + mc^2)^2}} = \frac{1}{1 + \dfrac{c^2\mathbf{p}^2}{(E_+ + mc^2)^2}}$$

∴

$$N = \left[1 + \frac{c^2\mathbf{p}^2}{(E_+ + mc^2)^2}\right]^{-1/2} \qquad -(6)$$

12·6. PROBABILITY DENSITY AND CURRENT DENSITY.

Let us check whether the Dirac equation leads to the correct probability density.

The Dirac equation for a free particle is

$$[E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta mc^2]\,\psi = 0,$$

where E and $\mathbf{p}$ are operators given by

$$E \to i\hbar\frac{\partial}{\partial t},$$

$$\mathbf{p} \to -i\hbar\nabla.$$

So

$$i\hbar\frac{\partial\psi}{\partial t} + i\hbar c\,\vec{\alpha}\cdot\nabla\psi - \beta mc^2\psi = 0. \qquad -(1)$$

A Hermitian conjugate equation give (Hermitian conjugate is denoted by dagger †)

$$-i\hbar\frac{\partial\psi^\dagger}{\partial i} - i\hbar c\,\nabla\psi^\dagger\cdot\vec{\alpha} - \psi^\dagger\beta mc^2 = 0 \qquad -(2$$

Recall $\vec{\alpha}$ and β are Hermitian. Multiply (1) on the left by $\psi^\dagger$ and (2) on the right side by ψ.

$$i\hbar\psi^\dagger\frac{\partial\psi}{\partial t} + i\hbar c\,\psi^\dagger\vec{\alpha}\cdot\nabla\psi - mc^2\psi^\dagger\beta\psi = 0$$

$$-i\hbar\frac{\partial\psi^\dagger}{\partial t}\psi - i\hbar c\,\nabla\psi^\dagger\cdot\vec{\alpha}\psi - mc^2\psi^\dagger\beta\psi = 0$$

On subtracting,

$$i\hbar\frac{\partial}{\partial t}(\psi^\dagger\psi) + i\hbar c\,\nabla\cdot(\psi^\dagger\vec{\alpha}\psi) = 0.$$

We can thus identify the probability density and current density:

$$\left.\begin{aligned} P\,(\mathbf{r}, t) &= \psi^{\dagger}\,\psi \\ S\,(\mathbf{r}, t) &= c\,\psi^{\dagger}\,\alpha\,\psi \end{aligned}\right| \qquad \text{...(4)}$$

The probability density is familiar. The current density expression looks more plausible if we note $c\,\vec{\alpha}$ is the velocity of the particle in the usual sense

$$i\hbar\,\frac{\partial x}{\partial t} = [x\,,\,H] = [x,\,c\,\vec{\alpha}\cdot\mathbf{p} + \beta\,mc^2] = i\hbar\,c\,\vec{\alpha}$$

$$\frac{dx}{dt} = c\,\vec{\alpha} \qquad \text{...(5)}$$

This implise however, that the eigen values of the velocity operator (in the usual sense) are $c\vec{\alpha}$ This result is often attributed to Zitterbewegung and interpreted by uncertainly principle. A very precise measurement of instantaneous velocity (which is distinct from momentum in the relativity theory) requires the accurate measurement of the position of the particle at two slightly different times. Such accurate position measurements imply that the momentum of the particle is completely unknown, so that very large momenta of the particle become possible and large velocities result. In a rigorous sense (5) is not quite correct, because the position operator and the velocity operator have to be defined properly. This requires the Foldy-Wouthuysen transformation.

12.7. ELECTROMAGNETIC POTENTIALS : MAGNETIC MOMENT OF THE ELECTRON.

In order to introduce electromagnetic potentials, we make the usual changes. If A and ϕ are electromagnetic vector and scalar potentials, then

$$\mathbf{p} \to \mathbf{p} - \frac{e\,\mathbf{A}}{c} \text{ or } c\mathbf{p} \to c\,\mathbf{p} - e\,\mathbf{A}$$

$$E \to E - e\,\phi$$

where e represents charge on the particle.

So that the Dirac equation

$$(E - c\,\vec{\alpha}\cdot\mathbf{p} - \beta\,mc^2)\,\psi = 0$$

takes the form

$$[E - e\,\phi - \vec{\alpha}\cdot(c\mathbf{p} - e\,\mathbf{A}) - \beta\,mc^2]\,\psi = 0 \qquad \text{...(1)}$$

Here E and $\mathbf{p}$ stand for corresponding operators, viz

$$E \to i\hbar\,\frac{\partial}{\partial t},\ \mathbf{p} = -\,i\hbar\,\nabla.$$

Multiplying equation (1) by

$$[E - e\,\phi + \vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A}) + \beta\,mc^2]$$

on the left, we obtain

$$[E - e\,\phi + \vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A}) + \beta\,mc^2]\,[E - e\,\phi - \vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A}) - \beta\,mc^2]\,\psi = 0$$

$$\text{or } \Big[(E - e\,\phi)^2 - \{\vec{\alpha}\cdot(c\,\vec{\mathbf{p}} - e\,\mathbf{A})\}^2 - m^2c^4 - (E - e\,\phi)\,\vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A}) + \vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A})\,(E - e\,\phi)\Big]\,\psi = 0 \qquad \text{...(2)}$$

(since $\beta^2 = 1$)

We know the identity

$$(\vec{\alpha}\cdot\mathbf{B})\,(\vec{\alpha}\cdot\mathbf{C}) = \mathbf{B}\cdot\mathbf{C} + i\,\vec{\sigma}\cdot(\mathbf{B}\times\mathbf{C}) \qquad \text{...(3)}$$

where B and C commute with $\vec{\alpha}$ but not necessarily with each other.

Now replace **B** and **C** both by $(c\,\mathbf{p} - e\,\mathbf{A})$ then

$$[\vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A})]^2 = (c\,\mathbf{p} - e\,\mathbf{A})^2 + i\,\vec{\sigma}\cdot(c\,\mathbf{p} - e\,\mathbf{A}) \times (c\,\mathbf{p} - e\,\mathbf{A}) \quad ...(4)$$

But

$$(c\,\mathbf{p} - e\,\mathbf{A}) \times (c\,\mathbf{p} - e\,\mathbf{A}) = -\,ce\,(\mathbf{A} \times \mathbf{p} + \mathbf{p} \times \mathbf{A}) \quad ...(5)$$

We have

$$[(\mathbf{A} \times \mathbf{p}) + (\mathbf{p} \times \mathbf{A})]\,\psi = \mathbf{A} \times \mathbf{p}\,\psi + \mathbf{p} \times \mathbf{A}\,\psi$$

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

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

[Since curl $(\psi\,\mathbf{A}) = \psi$ curl $\mathbf{A}$ + grad $\psi \times \mathbf{A}$]

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

$$= \mathbf{A} \times \frac{\hbar}{i}\,\nabla\psi + \frac{\hbar}{i}\,(\psi\,\nabla \times \mathbf{A} - \mathbf{A} \times \nabla\psi) = \left(\frac{\hbar}{i}\,\nabla \times \mathbf{A}\right)\psi$$

∴

$$\mathbf{A} \times \mathbf{p} + \mathbf{p} \times \mathbf{A} = \frac{\hbar}{i}\,\nabla \times \mathbf{A} = -\,i\hbar\,\nabla \times \mathbf{A} \quad ...(6)$$

Using this result, equation (5) takes the form

$$(c\,\mathbf{p} - e\,\mathbf{A}) \times (c\,\mathbf{p} - e\,\mathbf{A}) = -\,ce\,(-\,i\hbar\,\nabla \times \mathbf{A}) = iec\hbar\,\nabla \times \mathbf{A}$$

But $\nabla \times \mathbf{A} = \mathbf{B}$ (Magnetic field)

∴

$$(c\,\mathbf{p} - e\,\mathbf{A}) \times (c\,\mathbf{p} - e\,\mathbf{A}) = iec\hbar\,\mathbf{B} \quad ...(7$$

Hence equation (4) gives

$$[\vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A})]^2 = (c\,\mathbf{p} - e\,\mathbf{A})^2 + i\,\vec{\sigma}\cdot iec\hbar\,\mathbf{B}$$

$$= (c\,\mathbf{p} - e\,\mathbf{A})^2 - e\hbar c\,\vec{\sigma}\cdot\mathbf{B} \quad ...($$

The last two operators in equation (2) can be simplified as follows

$$-\,(E - e\,\phi)\,\vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A}) + \vec{\alpha}\cdot(c\,\mathbf{p} - e\,\mathbf{A})\,(E - e\,\phi)$$

$$= e\,\vec{\alpha}\cdot(E\,\mathbf{A} - \mathbf{A}\,E) + ce\,\vec{\alpha}\cdot(\phi\,\mathbf{p} - p\,\phi)$$

$$= e\,\vec{\alpha}\cdot i\hbar\,\frac{\partial\mathbf{A}}{\partial t} + ce\,\vec{\alpha}\cdot i\hbar\,\nabla\phi$$

$\Big[$ Since $\mathrm{E} = \mathrm{i}\hbar\,\dfrac{\partial}{\partial \mathrm{t}}$ and $\mathbf{p} = \dfrac{\hbar}{\mathrm{t}}\,\nabla$ and then $\mathrm{E}\,\mathbf{A} - \mathbf{A}\,\mathrm{E} = \mathrm{i}\hbar\,\dfrac{\partial\,\mathbf{A}}{\partial \mathrm{t}}$; $\phi\,\mathbf{p} - \mathbf{p}\,\phi = \mathrm{i}\hbar\,\nabla$

$$= -\,ie\hbar c\,\vec{\alpha}\cdot\left(-\,\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} - \nabla\phi\right)$$

$$= -\,ie\hbar c\,\vec{\alpha}\cdot\mathbf{E}$$

$\Big[$ Since electric field, $\mathbf{E} = -\,\dfrac{1}{c}\,\dfrac{\partial\mathbf{A}}{\partial t} - \nabla$

Now substituting the values from (8) and (9) in equation (2), we get

$$\left[(E - e\,\phi)^2 - [(c\,\mathbf{p} - e\,\mathbf{A})^2 - e\hbar c\,\vec{\sigma}\cdot\mathbf{B}] - m^2c^4 - ie\hbar c\,\vec{\alpha}\cdot\mathbf{E}\right]\psi = 0$$

or

$$\left[(E - e\,\phi)^2 - (c\,\mathbf{p} - e\,\mathbf{A})^2 - m^2c^4 + e\hbar c\,\vec{\sigma}\cdot\mathbf{B} - ie\hbar c\,\vec{\alpha}\cdot\mathbf{E}\right]\psi = 0$$

The first three terms in the above equation are precisely the same as in relativistic wave equatio electromagnetic field. The physical significance of the last two terms may be understood by ta non-relativistic limit of the entire equation.

In the non-relativistic limit

$$E \rightarrow E' + mc^2 \text{ and } E' << mc^2 ;\ e\phi << mc^2$$

$$\therefore \quad (E - e\phi)^2 = (E' + mc^2 - e\phi)^2$$

$(1+x)^n$

$$= m^2c^4\left[1 + \frac{E' - e\phi}{mc^2}\right]^2$$

$$= m^2c^4\left[1 + \frac{2\,(E' - e\phi)}{mc^2}\right] = m^2c^4 + 2\,(E' - e\phi)\,mc^2$$

$$\therefore \quad (E - e\phi)^2 - m^2c^4 = 2mc^2\,(E' - e\phi) \qquad \text{...(11)}$$

Substituting this in (10), we obtain

$$(2mc^2\,(E' - e\phi) - (c\,\mathbf{p} - e\,\mathbf{A})^2 + e\hbar c\,\vec{\sigma}'\cdot\mathbf{B} - ie\hbar\,\vec{\alpha}\cdot\mathbf{E}]\,\psi = 0$$

or
$$E'\psi = \left[\frac{1}{2m}\left(p - \frac{e\,\mathbf{A}}{c}\right) + e\phi - \frac{e\hbar}{2mc}\,\vec{\sigma}'\cdot\mathbf{B} + \frac{ie\hbar}{2mc}\,\vec{\alpha}\cdot\mathbf{E}\right]\psi \qquad \text{...(12)}$$

Now Schroedinger equation for a free particle is

$$E\psi = \frac{\mathbf{p}^2}{2m}\,\psi$$

In electromagnetic field it takes the form

$$(E - e\phi)\,\psi = \left[\frac{1}{2m}\left(p - \frac{e\mathbf{A}}{c}\right)^2\right]\psi$$

or
$$E\,\psi = \left[e\phi + \frac{1}{2m}\left(p - \frac{e\mathbf{A}}{c}\right)^2\right]\psi \qquad \text{...(13)}$$

Comparing (12) and (13) we note that

$$E' = E \rightarrow i\hbar\,(\partial/\partial t)$$

and equation (12) involves two additional terms containing **B** and **E**. The term containing **B** may be interpreted to represent *magnetic energy* and that containing **E** to represent the *electrical energy*.

We know magnetic energy $= -\vec{\mu}\cdot\mathbf{B}$ where $\vec{\mu}$ is the magnetic moment. Hence on comparing the third term (containing **B**) in (12) with magnetic energy expression, we get

Magnetic dipole moment,
$$\vec{\mu} = \frac{e\hbar}{2mc}\,\vec{\sigma}' \qquad \text{...(14)}$$

In a similar manner the electric dipole moment $= -\dfrac{ie\hbar\,\vec{\alpha}}{2mc}$; but in most of the practical cases the term containing **E** in (12) is of order $\left(\dfrac{v}{c}\right)^2$ times the $e\,\phi$ term and so it may be neglected in the non-relativistic limit.

12·8. EXISTENCE OF ELECTRON SPIN

The Dirac's Hamiltonian in a stationary central field represented by potential V (r) is

$$H = c\,\vec{\alpha}\cdot\vec{p} + \beta\,mc^2 + V(r) \qquad \text{...(1)}$$

For a paticle under the influence of a central force the torque is zero, therefore the angular momentum of the particle is conserved.

Classically the orbital angular momentum **L** = **r** × **p** is a constant of motion in a central field. W shall now see whether this is so in Dirac's theory or not. In Quantum Mechanics any operator th commutes with Hamiltonian H is a constant of motion. Let us examine this for x-component of momentum viz.

$$i\hbar \frac{dL_x}{dt} = [L_x, H] = [L_x, c\,\vec{\alpha}\cdot \mathbf{p} + \beta mc^2 + V(r)]$$

$$= \left[L_x, c\,\{\alpha_x p_x + \alpha_y p_y + \alpha_z p_z\} + \beta mc^2 + V(r)\right]$$

$$= [L_x, c\,\alpha_x p_x] + [L_x, c\,\alpha_y p_y] + (L_x, c\,\alpha_z p_z) + [L_x, \beta mc^2] + [L_x, V(r)] \qquad ...(2)$$

But L_x commutes with energy quantity in H except for p_y, p_z *i.e.*

$$[L_x, c\,\alpha_x p_x] = [L_x, \beta mc^2] = [L_x, V(r)] = 0.$$

Therefore, we get

$$i\hbar \frac{dL_x}{dt} = [L_x, c\,\alpha_y p_y] + [L_x, c\,\alpha_z p_z] \qquad ...(3)$$

But

$$[L_x, c\,\alpha_y p_y] = c\,\alpha_y [L_x, p_y]$$

$$= c\,\alpha_y\, [y p_z - z p_y, p_y]$$

$$= c\,\alpha_y \left\{[y p_z, p_y] - [z p_y, p_y]\right\}$$

$$= c\,\alpha_y \left\{[y, p_y]\, p_z - y[p_z, p_y] - 0\right\}$$

$$= c\,\alpha_y \left\{i\hbar\, p_z - 0\right\} = c\,\alpha_y\, i\hbar\, p_z \qquad ...(4)$$

Similarly

$$[L_x, c\,\alpha_z p_z] = c\,\alpha_z . (-\,i\hbar\, p_y) \qquad ...(5)$$

Therefore equation (5) yeilds.

$$\therefore \quad i\hbar \frac{dL_x}{dt} = c\,\alpha_y\,(i\hbar\, p_z) + c\,\alpha_z\,(-\,i\hbar\, p_y)$$

$$= -\,i\hbar c\,(\alpha_z p_y - \alpha_y p_z)$$

$$\neq 0 \qquad ...(6)$$

i.e. $\frac{dL_x}{dt} \neq 0$ or $L_x \neq$ constant.

Hence in *Dirac's theory the x-component of orbital angular momentum of an electron moving in a central electrostatic field is not a constant of motion.* In other words orbital angulr momenutum **L** does not commute with H. However we expect on physical grounds that it is posiible to define a *total angular momentum that is a constant in a central field of force.* This means that we must find another operator such that the commutator of its x-component with H is equal and opposite of the right hand side of (5); so that the sum of this operator and **L** is then a constant of motion and can be interpreted as the total angular momentum.

It is not difficult to see that the desired operator is multiple of $\vec{\sigma}''$ defined by

$$\vec{\sigma}'' = \begin{bmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{bmatrix}$$

Let us take, x-component of $\vec{\sigma}''$

$$i\hbar \frac{d\sigma_x'}{dt} = [\sigma_x', H]$$

where

$$\vec{\sigma}_x'' = \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix}$$

i.e. $$i\hbar \frac{d\sigma_x'}{dt} = [\sigma_x', (c\,\vec{\alpha}\cdot \mathbf{p} + \beta mc^2 + V(r))]$$

$$= [\sigma_x', c\,(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z) + \beta mc^2 + V(r)] \qquad ...(7)$$

But σ_x' commutes with every quantity in above equation except α_y and α_z,

i.e.

$$\sigma_x' \beta - \beta \sigma_x' = \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} - \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix}$$

$$= \begin{bmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{bmatrix} - \begin{bmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{bmatrix} = 0$$

$$\sigma_x' \alpha_x - \alpha_x \sigma_x' = \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix} \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} - \begin{bmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{bmatrix} \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix}$$

$$= \begin{bmatrix} 0 & \sigma_x^2 \\ \sigma_x^2 & 0 \end{bmatrix} - \begin{bmatrix} 0 & \sigma_x^2 \\ \sigma_x^2 & 0 \end{bmatrix} = 0$$

Hence equation (7) gives

$$i\hbar \frac{d\sigma_x'}{dt} = [\sigma_x', c\,\alpha_y\, p_y + c\,\alpha_z\, p_z].$$

$$= [\sigma_x', c\,\alpha_y p_z] + [\sigma_x', c\,\alpha_z p_z]. \qquad ...(8)$$

Also

$$[\sigma_x', \alpha_y] = \sigma_x' \alpha_y - \alpha_y \sigma_x' = \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix} \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} - \begin{bmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{bmatrix} \begin{bmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{bmatrix}$$

$$= \begin{bmatrix} 0 & \sigma_x \sigma_y \\ \sigma_x \sigma_y & 0 \end{bmatrix} - \begin{bmatrix} 0 & -\sigma_x \sigma_y \\ -\sigma_x \sigma_y & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & i\sigma_z \\ i\sigma_z & 0 \end{bmatrix} - \begin{bmatrix} 0 & -i\sigma_z \\ -i\sigma_z & 0 \end{bmatrix}$$

$$= 2\,i\,\alpha_z.$$

Similarly $\quad [\sigma_x', \sigma_z] = -\,2\,i\,\alpha_y.$

Hence equation (8) gives

$$i\hbar \frac{d\,\sigma_x'}{dt} = c\,2\,i\,\alpha_z\, p_y + c\,(-\,2\,i\,\alpha_y)\, p_z$$

$$= 2\,i\,c\,(\alpha_z p_y - \alpha_y p_z). \qquad ...(9)$$

Multiplying both sides by $\frac{1}{2}\hbar$

$$i\hbar \frac{d}{dt}(\tfrac{1}{2}\hbar\,\sigma_x') = i\hbar\, c\,(\alpha_z p_y - \alpha_y p_z). \qquad ...(10)$$

Adding (6) and (10) we note that

$$i\hbar \frac{dL_x}{dt} + i\hbar \frac{d}{dt}(\tfrac{1}{2}\hbar\,\sigma_x') = 0$$

or

$$\frac{d}{dt}(L_x + \tfrac{1}{2}\hbar\,\sigma_x') = 0 \qquad ...(11)$$

or

$$L_x + \tfrac{1}{2}\hbar\,\sigma_x' = \text{constant}$$

Hence the quantity $\mathbf{J} = (\mathbf{L} + \frac{1}{2}\hbar\,\vec{\sigma}')$ commutes with H and therefore can be taken as the *total angular momentum.* ...(12)

We refer to the operator

$$\mathbf{S} = \tfrac{1}{2}\hbar\,\vec{\sigma}'$$

as the spin angular momentum of the electron.

Hence Dirac's theory automatically endows the electron with properties that account for the phenomenon previously ascribed to a hypothetically spinning motion of the electron.

12.9. SPIN-ORBIT ENERGY.

The spin orbit coupling energy follows as a result to Dirac equation in a central field. The term is however of order v^2/c^2 and in order to obtain a consistent approximation we proceed by two-component reduction of Dirac equation in the central field $V(r)$.

The Dirac equation for the central field is

$$[c\,\vec{\alpha}\cdot\mathbf{p} + \beta mc^2 + V(r)]\,\psi = E\psi.$$

Writing $\psi = \begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}$ which represent the first and the last two components of ψ respectively.

i.e. $$\left\{c\begin{bmatrix}0 & \vec{\sigma}\\ \vec{\sigma} & 0\end{bmatrix}\cdot\mathbf{p}+\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}mc^2+V(r)\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\right\}\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}=E\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}$$

i.e. $$\begin{bmatrix}c & \vec{\sigma}\cdot\mathbf{p} & \psi_2\\ c & \vec{\sigma}\cdot\mathbf{p} & \psi_1\end{bmatrix}+\begin{bmatrix}mc^2\psi_1\\ -mc^2\psi_2\end{bmatrix}+\begin{bmatrix}V\psi_1\\ V\psi_2\end{bmatrix}=\begin{bmatrix}E\psi_1\\ E\psi_2\end{bmatrix}$$

This equation is equivalent to following two equations

$$c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_2+mc^2\psi_1+V\psi_1=E\psi_1$$

and $$c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1-mc^2\psi_2+V\psi_2=E\psi_2$$

or $$\left.\begin{aligned}(E-V-mc^2)\,\psi_1-c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_2&=0\\ (E-V+mc^2)\,\psi_2-c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1&=0\end{aligned}\right]\quad\text{...(1)}$$

Assuming that ψ_1 and ψ_2 together constitute a non-relativistic energy eigen-function, which means that

$$E = E' + mc^2$$

is regarded as a number rather than an operator; the non-relativistic energy E' and V are assumed to be smaller in comparison with mc^2.

The wave equations (1) then become

$$\left.\begin{aligned}\{E'-V(r)\}\,\psi_1-c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_2&=0 &&\text{...(a)}\\ \{E'+2mc^2-V(r)\}\,\psi_2-c\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1&=0 &&\text{...(b)}\end{aligned}\right]\quad\text{...(3)}$$

From (3b), we have

$$\psi_2=\frac{c\,\vec{\sigma}\cdot\mathbf{p}}{E'+2mc^2-V(r)}\,\psi_1 \quad\text{...(4)}$$

Substituting this value of ψ_2 in (3a), we get

$$\begin{aligned}[E'-V(r)]\,\psi_1&=c^2(\vec{\sigma}\cdot\mathbf{p})\,[E'+2mc^2-V(r)]^{-1}\,\vec{\sigma}\cdot\mathbf{p}\,\psi_1\\ &=\frac{\vec{\sigma}\cdot\mathbf{p}}{2m}\left[1+\frac{E'-V(r)}{2mc^2}\right]^{-1}\vec{\sigma}\cdot\mathbf{p}\,\psi_1\\ &=\frac{\vec{\sigma}\cdot\mathbf{p}}{2m}\left[1-\frac{E'-V}{2mc^2}\right]\vec{\sigma}\cdot\mathbf{p}\,\psi_1\end{aligned}$$

$$= \frac{1}{2m}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p})\psi_1 - (\vec{\sigma}\cdot\mathbf{p})\frac{(E'-V)}{4m^2c^2}\vec{\sigma}\cdot\mathbf{p}\,\psi_1 \qquad \text{...(5)}$$

Using the identity

$$(\vec{\sigma}\cdot\mathbf{B})(\vec{\sigma}\cdot\mathbf{C}) = \mathbf{B}\cdot\mathbf{C} + i\vec{\sigma}\cdot\mathbf{B}\times\mathbf{C}$$

we have

$$(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) = \mathbf{p}\cdot\mathbf{p} + i\vec{\sigma}\cdot\mathbf{p}\times\mathbf{p} = \mathbf{p}^2$$

Also if u is any function

$$[\mathbf{p}, V]u = (\mathbf{p}V - V\mathbf{p})u = \mathbf{p}Vu - V\mathbf{p}u \qquad \text{...(6)}$$

$$= \frac{\hbar}{i}\nabla(Vu) - V\frac{\hbar}{i}\nabla u$$

$$= \frac{\hbar}{i}[V\nabla u + u\nabla V] - V\frac{\hbar}{i}\nabla u$$

$$= \frac{\hbar}{i}u\nabla V = \left(\frac{\hbar}{i}\nabla V\right)u$$

i.e.

$$(\mathbf{p}V - V\mathbf{p})u = (-i\hbar\nabla V)u$$

or

$$(\mathbf{p}V - V\mathbf{p}) = -i\hbar\nabla V$$

$\therefore$

$$\mathbf{p}V = V\mathbf{p} - i\hbar\nabla V \qquad \text{...(7)}$$

$\therefore$

$$(\vec{\sigma}\cdot\mathbf{p})V = V(\vec{\sigma}\cdot\mathbf{p}) - \vec{\sigma}\cdot i\hbar\nabla V \qquad \text{...(8)}$$

$\therefore$

$$(\vec{\sigma}\cdot\mathbf{p})\frac{(E'-V)}{4m^2c^2}\vec{\sigma}\cdot\mathbf{p} = \frac{E'}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \frac{1}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})V(\vec{\sigma}\cdot\mathbf{p})$$

$$= \frac{E'}{4m^2c^2}(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \frac{1}{4m^2c^2}\{V(\vec{\sigma}\cdot\mathbf{p})(\vec{\sigma}\cdot\mathbf{p}) - \vec{\sigma}\cdot(i\hbar\nabla V)(\vec{\sigma}\cdot\mathbf{p})\}$$

$$= \frac{E'}{4m^2c^2}p^2 - \frac{1}{4m^2c^2}Vp^2 + \frac{i\hbar}{4m^2c^2}(\vec{\sigma}\cdot\nabla V)(\vec{\sigma}\cdot\mathbf{p})$$

$$= \left(\frac{E'-V}{4m^2c^2}\right)p^2 + \frac{i\hbar}{4m^2c^2}\{\nabla V\cdot\mathbf{p} + i\vec{\sigma}\cdot\nabla V\times\mathbf{p}\}$$

Using (6) and (9), equation (5) gives

$$(E'-V)\psi_1 = \frac{1}{2m}p^2\psi_1 - \left\{\left(\frac{E'-V}{4m^2c^2}\right)p^2 + \frac{i\hbar}{4m^2c^2}(\nabla V\cdot\mathbf{p} + i\vec{\sigma}\cdot\nabla V\times\mathbf{p})\right\}\psi_1.$$

$\therefore$

$$E'\psi_1 = \left\{\left(1 - \frac{E'-V}{2mc^2}\right)\frac{p^2}{2m} + V\right\}\psi_1 - \frac{\hbar^2}{4m^2c^2}\nabla V\cdot\nabla\psi_1 + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\nabla V\times\mathbf{p}\,\psi_1 \qquad \text{...(10)}$$

Now if V is spherically symmetric, we have

$$\nabla V = \frac{1}{r}\frac{dV}{dr}\mathbf{r}$$

and

$$(\nabla V)\cdot\nabla = \frac{dV}{dr}\frac{\partial}{\partial r}.$$

$\therefore$

$$\nabla V\times\mathbf{p} = \left(\frac{1}{r}\frac{dV}{dr}\mathbf{r}\right)\times\mathbf{p} = \frac{1}{r}\frac{dV}{dr}(\mathbf{r}\times\mathbf{p})$$

and noting that $E' - V = \frac{p^2}{2m}$, equation (10) gives

$$E'\psi_1 = \left\{\left(1-\frac{(p^2/2m)}{2mc^2}\right)\frac{p^2}{2m}+V\right\}\psi_1 - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial\psi_1}{\partial r} + \frac{\hbar^2}{4m^2c^2}\vec{\sigma}\cdot\frac{1}{r}\frac{dV}{dr}\mathbf{r}\times\mathbf{p}\,\psi_1$$

Now using $\frac{1}{2}\hbar\,\vec{\sigma} = \mathbf{S}$ and $\mathbf{r}\times\mathbf{p} = \mathbf{L}$, we have

$$E'\psi_1 = \left(\frac{p^2}{2m}+V-\frac{p^4}{8m^3c^2}-\frac{\hbar^2}{4m^2c^2}\frac{dV}{\partial r}\frac{\partial}{\partial r}+\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S.L}\right)\psi_1 \qquad ...(11)$$

The first and second terms on right hand side of above equation give the non-relativistic Schroedinger equation. The third term is the classical relativistic mass correction term which can be obtained by the expression

$$\begin{aligned} E' &= E - mc^2 = (p^2c^2+m^2c^4)^{1/2} - mc^2 \\ &= mc^2\left(1+\frac{p^2c^2}{m^2c^4}\right)^{1/2} - mc^2 = mc^2\left(1+\frac{p^2}{m^2c^2}\right)^{1/2} - mc^2 \\ &\approx mc^2\left(1+\frac{p^2}{2m^2c^2}-\frac{p^4}{8m^4c^4}+\ldots\ldots\right) - mc^2 \\ &\approx \frac{p^2}{2m}-\frac{p^4}{8m^3c^2}. \end{aligned} \qquad ...(12)$$

The fourth term is a similar relativistic correction to the potential energy, which does not have a classical analogue and the last term is the **spin orbit coupling energy** which appears as an automatic consequence of the Dirac equation.

Thus the spin-orbit coupling energy is

$$U_{s-0} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\,\mathbf{S}\bullet\mathbf{L}, \qquad ...(13)$$

where **S** is spin angular momentum and **L** is orbital angular momentum.

12·10. ZITTERBEWEGUNG

Let us consider the motion of an electron according to Dirac equation in Heisenberg representation