INTRODUCTORY QUANTUM MECHANICS

M.Sc. PHYSICS

SEMESTER-I, PAPER-II

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M.Sc. PHYSICS: INTRODUCTORY QUANTUM MECHANICS

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lessonwriters of the Centre who have helped in these endeavors.

> Prof. K. Gangadhara Rao M.Tech., Ph.D., Vice-Chancellor I/c Acharya Nagarjuna University.

M.SC. PHYSICS SYLLABUS SEMESTER-I, PAPER-II 102PH24-INTRODUCTORY QUANTUM MECHANICS

Course Objectives:

- ✤ Introduction of Quantum Mechanics and the Schrodinger equation
- ✤ To acquire mathematical skills require to develop theory of quantum mechanics
- To develop understanding of postulates of quantum mechanics and to learn to apply them to solve some quantum mechanical systems
- To offer systematic methodology for the application of approximation methods to solve complicated quantum mechanical systems

UNIT-I (Schrodinger Wave Equation and One Dimensional Problem)

Why QM? Revision; Inadequacy of classical mechanics; Schrodinger equation; continuity equation; Ehrenfest theorem; admissible wave functions; Stationary states. One- dimensional problems, wells and barriers. Harmonic oscillator by Schrodinger equation.

Learning Outcomes:

• Students will learn the difference between classical mechanics and quantum mechanics.

UNIT-II (Linear Vector Spaces and Operators)

Linear Vector Spaces in Quantum Mechanics: Vectors and operators, change of basis, Dirac's bra and ket notations. Eigen value problem for operators. The continuous Hermitian, unitary, spectrum. Application to wave mechanics in one dimension. projection operators. Positive operators. Change of orthonormal basis, Orthogonalization procedure, uncertainty relation.

Learning Outcomes:

• Students will learn the mathematical formalism of eigen values, eigen states of wells and barriers and unitary operators, hermitian operators, which form the fundamental basis of quantum theory.

UNIT III (Orbital Angular Momentum)

Angular momentum: Commutation relations for angular momentum operator, Angular Momentum in spherical polar coordinates, Eigen value problem for L2 and L2, L + and L operators Eigen values and eigen functions of rigid rotator and Hydrogen atom

Learning Outcomes:

- Learn commutations relations for angular momentum operator and its applications in daily life.
- Application to rigid rotator, hydrogen-like atoms and angular momentum operators will teach the students how to obtain eigen values and eigen states for such systems elegantly.

UNIT IV (Time-Independent Perturbation Theory)

Time-independent perturbation theory; Non-degenerate and degenerate cases; applications to (a) normal helium atom (b) Stark effect in Hydrogen atom. Variation method. Application to ground state of Helium atom, WKB method.

Learning Outcomes:

- To understand the concepts of time-independent perturbation theory and their applications to physical situations.
- Studying the applications of Non-degenerate and degenerate cases in perturbation theory
- Learning the variation and WKB methods

UNIT V (Time Dependent Perturbation Theory)

Time Dependent Perturbation: General perturbations, variation of constants, transition into closely spaced levels -Fermi's Golden rule. Einstein transition probabilities, Interaction of an atom with the electromagnetic radiation. Sudden and adiabatic approximation.

Learning Outcomes:

- Students will learn how to use perturbation theory to obtain corrections to energy eigen-states and eigen-values when an external electric or magnetic field is applied to a system.
- Learning the significances of Fermi's Golden rule.
- To teach the students various approximation methods in quantum mechanics.

Course Outcomes:

- ✤ Understand historical aspects of development of quantum mechanics.
- Understand and explain the differences between classical and quantum mechanics.
- Understand the central concepts and principles in quantum mechanics, such as the Schrodinger equation, the wave function and its statistical interpretation, the uncertainty principle, stationary and non-stationary states, wells and barriers, harmonic oscillator, as well as the relation between quantum mechanics and linear algebra including understanding of linear vector spaces.

They will master the concepts of angular momentum and spin, as well as the rules for quantization and addition of these. Hence they will be able to solve the complex systems by approximation method.

Text and Reference Books:

- 1) Eugen Merzbacher, Quantum Mechanics, Wiley.
- 2) LI Schiff, Quantum Mechanics (Mc Graw-Hill).
- 3) B Crasemann and JD Powell, Quantum Mechanics (Addison Wesley).
- 4) A P Messiah, Quantum Mechanics.
- 5) J J Sakural, Modem Quantum Mechanics.
- 6) Mathews and Venkatesan Quantum Mechanics.
- 7) Quantum Mechanics" by R.D. Ratna Raju.
- Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics by S.P. Kuila, Books and Allied, Kolkata.

(**102PH24**)

M.Sc. DEGREE EXAMINATION, MODEL QUESTION PAPER M.Sc. PHYSICS-FIRST SEMESTER INTRODUCTORY QUANTUM MECHANICS

Time: Three hours

Maximum: 70 marks

Answer ALL Questions

All Questions Carry Equal Marks

- 1 a) Explain about the Schrodinger wave equation.
 - b) Explain about the One-dimensional problems.

OR

- c) Explain about the Stationary states.
- d) Briefly explain about the admissible wave functions.
- 2 a) Explain about the change of basis in linear vector spaces.
 - b) Write a note on vectors and operators

OR

- c) Explain about Dirac's bra and ket notations.
- d) Write about the Change of orthonormal basis.
- 3 a) Write about the Eigen values and Eigen functions of rigid rotator and hydrogen atom.
 - b) Explain about the Angular momentum in spherical polar coordinates.

OR

- c) Write about the communication relations for angular momentum operator.
- d) Explain about the Eigen value for L^2 and L_z .
- 4 a) Briefly explain about the Variation method
 - b) Explain about the Time-independent perturbation theory for Non degenerate system.

OR

- c) Briefly explain about the WKB method.
- d) Explain about the Application to ground state of Helium atom.
- 5 a) Explain about the Time dependent perturbation theory.
 - b) Write a note on Fermi's Golden rule.

OR

- a) Describe the Interaction of an atom with the electromagnetic radiation.
- b) Describe the Sudden and adiabatic approximation.

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LESSON-1

SCHRODINGER EQUATION

1.0 AIM AND OBJECTIVES:

The primary goal of this chapter is to understand the concept of Schrodinger Equation. The chapter began with understanding of Introduction of Quantum Mechanics and the Schrodinger equation and to acquire mathematical skills, require to develop theory of quantum mechanics. After completion of this lesson student should have the knowledge of fundamentals of Quantum Mechanics.

- Introduction of Quantum Mechanics and the Schrodinger equation.
- To acquire mathematical skills, require to develop theory of quantum mechanics

STRUCTURE:

- 1.1 Why QM
- **1.2 Inadequacy of Classical Mechanics**
- **1.3 Schrodinger Equation**
- 1.4 Continuity Equation or Equation of Continuity or Probability of Current Density
- 1.5 Ehrenfest's Theorem
- 1.6 Summary
- 1.7 Technical Terms
- 1.8 Self Assessment Questions
- 1.9 Suggested Readings

1.1 WHY QM:

In 1900, Plank introduced a revolutionary hypothesis known as Plank's Hypothesis, according to which every radiating atom in a solid emits energy only discretely in quanta, the energy of an individual quantum being equal to hv.

$\mathbf{E}_{\mathbf{n}} = \mathbf{n}\mathbf{h}\mathbf{v}$

where n is an integer and h is Plank's constant = 6.625×10^{-34} J.sec

By the aid of this hypothesis, Plank was able to explain law of distribution of energy in the spectrum of black body. This theory was given by Plank in historic paper titled "Theory of law of distribution of energy in a normal spectrum" presented before the Berlin

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Academy of Sciences on Dec 14, 1900. This day, in fact, may be considered as the birthday of Quantum Mechanics.

1.2

After the intension of de Broglie's hypothesis of matter waves (1924), it develops the new type Physics. It is called Quantum Mechanics.

The development of Quantum Mechanics is based on the scientists, namely Erwin Schrodinger, Werner Heisenberg, Max Born, Paul Dirac etc. Quantum mechanics classifies the all limitations of Bohr's Theory.

The inadequacy of Classical mechanics led to the development of Quantum Mechanics.

1.2 INADEQUACY OF CLASSICAL MECHANICS:

The development of classical mechanics is based on Newton's three laws. These laws included the concepts of absolute mass, absolute space and absolute time. The classical mechanics explains correctly the motion of celestial bodies like planets, stars and macroscopic as well as microscopic terrestrial bodies moving with non-relativistic speeds. The inadequacies of classical mechanics are

- 1) It does not hold in the region of atomics dimensions i.e., it cannot explain the non relativistic motion of atoms, photons etc.
- 2) It could not explain the stability of atoms.
- 3) It could not explain observed spectrum of black body radiations.
- 4) It could not explain the origin of discrete spectra of atoms since according to classical mechanics the energy changes are always continuous.

In spite of this classical mechanics could not explain a large number of observed phenomenon's like Photoelectric Effect, Compton Effect, Raman Effect etc. The inadequacy of Classical mechanics led to the development of Quantum Mechanics.

1.3 SCHRODINGER EQUATION:

Schrodinger's Time Independent and Time Dependent Wave Equations

We know that the total energy is the sum of kinetic and potential energies.

$$\mathbf{T} = \mathbf{K}.\mathbf{E}. + \mathbf{P}.\mathbf{E}.$$

Where K.E. = $\frac{p^2}{2m}$ here p is momentum and P.E. = V(r)

$$\therefore T = \frac{p^2}{2m} + V(r)$$

We know that

1.3

Hermitian Operator
$$H = \frac{p^2}{2m} + \hat{V}(r)$$

Where Ψ is wave function, H is Hermitian Operator and E is energy.

 $H\Psi = E\Psi$

By substituting Hamiltonian value $H = \frac{p^2}{2m} + \hat{V}(r)$, we get

$$\left(\frac{p^2}{2m} + \widehat{V}(r)\right)\Psi = E\Psi$$

 $\left(\frac{-\hbar^2 \nabla^2}{2m} + \widehat{V}(r)\right) \Psi = E \Psi$ or

$$\frac{-\hbar^2 \nabla^2 \Psi}{2m} + \widehat{V}(r)\Psi = E\Psi$$

Multiplying by negative sign throughout the equation and then dividing with

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

This equation is known as Schrodinger Time Independent Wave Equation.

For a free particle, potential energy is zero i.e., P.E. = 0 then the equation is reduced to

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

We know that $H\Psi = E\Psi$

We have Hamiltonian value $H = \frac{p^2}{2m} + \hat{V}(r)$ and Energy $E = i\hbar \frac{\partial}{\partial t}$

$$\Rightarrow \left(\frac{p^2}{2m} + \widehat{V}(r)\right) \Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \text{or}$$

on replacing momentum p, we have

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

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here Ψ is a function of (r, t) where r = (x,y,z) and t is time.

This equation is called **Time Dependent Schrodinger Wave Equation**.

1.4 CONTINUITY EQUATION OR EQUATION OF CONTINUITY OR PROBABILITY OF CURRENT DENSITY:

We have Schrodinger wave equation for a free particle.

$$\nabla^2 \Psi + \frac{2m}{\hbar^2} E \Psi = 0$$
 (for free particle V=0)

On rearrangement, we have

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

or

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

or

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = i\hbar\frac{\partial\Psi}{\partial t}\left[: E = i\hbar\frac{\partial}{\partial t}\right] \qquad \dots (1)$$

The complex conjugate of eq. (1) is

$$-\frac{\hbar^2}{2m}\nabla^2\Psi^* = -i\hbar\frac{d\Psi^*}{dt} \qquad \dots (2)$$

Pre-multiplying eq. (1) with Ψ^* and post multiplying eq. (2) with Ψ on both sides.

$$-\frac{\hbar^2}{2m}\Psi^*\nabla^2\Psi = i\hbar\Psi^*\frac{d\Psi}{dt} \qquad \dots (3)$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi^*\Psi = -i\hbar\frac{d\Psi^*}{dt}\Psi \qquad \dots (4)$$

from eq. (3) and eq. (4), we can write

$$-\frac{\hbar^2}{2m} [\Psi^* \nabla^2 \Psi - \nabla^2 \Psi^* \Psi] = i\hbar \left[\Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \right]$$

or
$$-\frac{\hbar^2}{2m} [\Psi^* \nabla^2 \Psi - \nabla^2 \Psi^* \Psi] = i\hbar \frac{\partial}{\partial t} (\Psi^* \Psi)$$

1.5

or

$$\frac{\partial}{\partial t}(\Psi^*\Psi) = -\frac{\hbar}{2\mathrm{m}i}[\Psi^*\nabla^2\Psi - \nabla^2\Psi^*\Psi]$$

$$\frac{\partial \mathbf{p}}{\partial \mathbf{t}} + \nabla \cdot \mathbf{s} = \mathbf{0}$$

Where $p = \Psi^* \Psi$ and $\nabla \cdot \mathbf{s} = -\frac{\hbar}{2mi} [\Psi^* \nabla^2 \Psi - \nabla^2 \Psi^* \Psi]$

This equation is known as **Equation of Continuity**. Here p is probability of density and s is probability of current.

If
$$\nabla \cdot s = 0$$
 then $\frac{\partial p}{\partial t} = 0$. Here p is constant i.e., probability is constant in time and then

such states are called Stationary States.

1.5 EHRENFEST'S THEOREM:

The theorem states that the average motion of a wave packet agrees with the motion of the corresponding classical particle.

In simple mechanics $F = -\nabla V$

$$F = \frac{d(p)}{dt}$$
 Where p is linear momentum

$$\frac{d\langle p\rangle}{dt} = \frac{d}{dt} \int (\Psi^* p \Psi) d\tau (\because \langle p \rangle = \int \Psi^* p \Psi d\tau)$$

$$= \frac{\mathrm{d}}{\mathrm{d}t} \int [\Psi^*(-\mathrm{i}\hbar\nabla)\Psi] \mathrm{d}\tau$$

$$= -i\hbar \int \left[\frac{d}{dt}\Psi^*\nabla\Psi + \Psi^*\frac{d}{dt}(\nabla\Psi)\right]d\tau$$
$$= \int \left[-i\hbar \frac{d\Psi^*}{dt}\nabla\Psi - i\hbar \Psi^*\nabla \frac{d\Psi}{dt}\right]d\tau$$
$$i\hbar \frac{d\Psi}{dt} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(r)\Psi$$

and it's complex conjugate is

$$-i\hbar \frac{d\Psi^*}{dt} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V(r) \Psi^*$$

$$\Rightarrow \frac{d\langle p \rangle}{dt} = \int \left\{ \left[-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V(r) \Psi^* \right] \nabla \Psi - \Psi^* \nabla \left[-\frac{\hbar^2}{2m} \nabla^2 \Psi + V(r) \Psi \right] \right\} d\tau$$
$$= -\frac{\hbar^2}{2m} \int \left[\nabla^2 \Psi^* \nabla \Psi - \Psi^* \nabla \left(\nabla^2 \Psi \right) \right] d\tau + \int \left[V(r) \Psi^* \nabla \Psi - \Psi^* \nabla V(r) \Psi \right] d\tau$$

Taking first term

$$\begin{split} -\frac{\hbar^2}{2m} \int \left[\nabla^2 \Psi^* \nabla \Psi - \Psi^* \nabla (\nabla^2 \Psi) \right] d\tau &= \int \frac{-\hbar^2}{2m} \left[\nabla^2 \Psi^* \nabla \Psi - \Psi^* \nabla (\nabla^2 \Psi) \right] d\tau \\ &= \frac{-\hbar^2}{2m} \int \left[\nabla^2 \Psi^* \nabla \Psi - \Psi^* \nabla (\nabla^2 \Psi) \right] d\tau \\ &\left[\int (v \nabla^2 u - u \nabla^2 v) d\tau = \iint (u \nabla v - v \nabla u) ds \right] \left[u = \Psi^*; v = \nabla \Psi \right] \\ &\Rightarrow \frac{-\hbar^2}{2m} \iint \left[\Psi^* \nabla^2 \Psi - (\nabla \Psi) \nabla \Psi^* \right] ds \end{split}$$

For the larger values of Ψ , this integral will be vanished because Ψ is finite.

$$\therefore \frac{d\langle p \rangle}{dt} = \int [V(r)\Psi^*\nabla\Psi - \Psi^*\nabla (V(r)\Psi)]d\tau$$

$$= \int [V(r)\Psi^*\nabla\Psi - \Psi^*\nabla V\Psi - \Psi^*V\nabla\Psi]d\tau$$

$$= \int (-\Psi^*\nabla V\Psi) d\tau$$

$$\Rightarrow \frac{d\langle p \rangle}{dt} = \langle -\nabla V \rangle$$

$$\therefore \mathbf{F} = -\nabla \mathbf{V}$$

Therefore, the quantum mechanical description of average motion of particle is identical with the classical description of the particle. It proves the Ehrenfest's theorem.

1.6 SUMMARY:

In this lesson student will learn how quantum mechanics has been developed and the inadequacy of classical mechanics. Subsequently in Quantum Mechanics Schrodinger Wave Equation was developed. Student has learned the continuity equation in quantum mechanics and he has learned the importance of Ehrenfest theorem.

Introductory Quantum Mechanics

1.7 TECHNICAL TERMS:

Quantum mechanics, Schrodinger equation, continuity equation, Ehrenfest theorem.

1.8 SELF-ASSESSMENT QUESTIONS:

- 1) What is the failure of Classical Mechanics?
- 2) Derive One Dimensional Schrodinger Wave Equation.
- 3) Derive Continuity Equation.
- 4) Explain Ehrenfest Theorem.

1.9 SUGGESTED READINGS:

- 1) Eugen Merzbacher, Quantum Mechanics, Wiley.
- 2) L I Schiff, Quantum Mechanics (Mc Graw-Hill).
- 3) B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley).
- 4) A P Messiah, Quantum Mechanics.

Prof. M. Rami Reddy

LESSON-2

ONE-DIMENSIONAL PROBLEMS

2.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept of One-dimensional problems. The chapter began with understanding of admissible wave function, Stationary States, One-Dimensional Problems, Wells and Barriers, Harmonic Oscillator by Schrodinger Equation. After completion of this lesson student should have the knowledge of fundamentals of onedimensional problem.

STRUCTURE:

2.0	Introduction

- 2.1 Admissible Wave Function
- 2.2 Stationary States
- 2.3 One-Dimensional Problems
- 2.4 Wells and Barriers
- 2.5 Harmonic Oscillator by Schrodinger Equation
- 2.6 Summary
- 2.7 Technical Terms
- 2.8 Self-Assessment Questions
- 2.9 Suggested Readings

2.0 INTRODUCTION:

One-dimensional problems in quantum mechanics provide an essential foundation for understanding the behavior of quantum systems. Although real-world systems typically exist in three-dimensional space, the one-dimensional approximation is often the first step in simplifying complex problems. These problems not only give insights into quantum mechanics but also help develop the mathematical and conceptual tools used for more complicated systems.

2.1 ADMISSIBLE WAVE FUNCTION:

In quantum mechanics, **admissible wave functions** (also known as **physical wave functions**) are wave functions that satisfy the conditions necessary for describing the state of

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a quantum system. These conditions ensure that the wave function is physically meaningful and mathematically consistent. The key properties of admissible wave functions include:

1) Normalization:

- The wave function $\psi(x,t)$ must be **normalizable**. This means that the total probability of finding a particle somewhere in space must be 1.
- Mathematically, this is expressed as:

$$\int_{-\infty}^{\infty} \psi(x,t)^2 \, dx = 1$$

For a single spatial dimension. For more than one spatial dimension, the integral is over the entire space.

2) Continuity and Smoothness:

- The wave function $\psi(x,t)$ should be continuous and smooth (differentiable) where possible, especially in regions where the potential is finite. Discontinuities or sharp corners in the wave function could imply infinite physical quantities like momentum or energy, which are non-physical.
- At points where the potential has discontinuities (like in the case of delta-function potentials), the wave function may be discontinuous, but its derivative should remain continuous.

3) Square-Integrability:

• The wave function must be square-integrable, $\psi(x, t)^2$ meaning should fall off sufficiently fast at infinity so that the integral over all space converges to a finite value. This condition ensures the normalizability condition is satisfied.

4) Boundary Conditions:

- The wave function should go to zero at infinity for systems confined to a finite region of space. For instance, in problems like the infinite potential well, ψ(x)=0 at the walls of the well.
- For systems where particles are free to move in infinite space, the wave function typically tends to zero as x → ±∞.

5) Hermiticity of Operators:

• In quantum mechanics, physical observables are represented by Hermitian operators. The wave function $\psi(x,t)$ must be such that the expectation value of

any physical observable (like position, momentum, energy, etc.) is well-defined. This ensures that the probability distributions derived from the wave function are physical and consistent.

6) Time Dependence:

• In time-dependent problems, the wave function may be written as a solution to the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\widehat{H}\psi(x,t)$$

Where \hat{H} is the Hamiltonian operator. The wave function should evolve according to this equation and maintain the probabilistic interpretation.

7) Physical Interpretation

- The modulus squared of the wave function ψ(x,t)², is interpreted as the probability density for finding a particle at position x (or in a region of space) at time t.
- The wave function must not yield negative probabilities, so it must be a complexvalued function with a well-defined probability interpretation.

8) Eigen functions of Operators

• In some cases, wave functions are also eigenfunctions of certain operators. For example, in systems like the quantum harmonic oscillator or the hydrogen atom, the wave function may be an eigenfunction of the Hamiltonian (energy operator) or the momentum operator.

9) Symmetry Properties

• The wave function may possess certain symmetries depending on the system, such as rotational symmetry in the case of central potentials. These symmetries help determine the form of the wave function and can simplify solving the Schrödinger equation.

10) Relativistic Considerations

• For systems requiring relativistic quantum mechanics (like the Dirac equation), the wave function must satisfy the relativistic equation of motion. In these cases, the wave function may be represented by spinors (for spin-1/2 particles) or other mathematical objects.

2.2 STATIONARY STATES:

A stationary state refers to a quantum state whose probability distribution does not change with time. These states are characterized by having a definite energy (associated with an energy eigenvalue). In mathematical terms, a stationary state $\psi(x,t)$ can be written as:

$$\psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

Here:

- $\psi(x)$ is the spatial part of the wavefunction (which describes the probability distribution of the particle's position).
- E is the energy eigenvalue associated with the state.
- \hbar is the reduced Planck's constant.
- $e^{-iEt/\hbar}$ is the time-dependent phase factor.

The key feature of a stationary state is that while the wavefunction undergoes a phase evolution over time (due to the factor $e^{-iE/\hbar}$), the **probability density** (i.e., $|\psi(x,t)|^2$) remains constant over time.

Time Evolution and the Schrödinger Equation

The time-dependent Schrödinger equation governs the behavior of quantum systems. For a particle in a potential V(x), it is written as:

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = \widehat{H}\psi(x,t)$$

where \hat{H} is the Hamiltonian operator, which represents the total energy of the system. The Hamiltonian is typically the sum of the kinetic energy (\hat{T}) and potential energy (\hat{V}) :

$$\widehat{H} = \widehat{T} + \widehat{V}$$

Now, if the wave function $\psi(x,t)$ is in a stationary state, it can be written as:

$$\psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

Substituting this into the Schrödinger equation, we get:

$$i\hbar \frac{\partial}{\partial t} \psi(x) e^{-iEt/\hbar} = \widehat{H} \psi(x) e^{-iEt/\hbar}$$

The time derivative of the wave function gives:

$$i\hbar - \frac{iE}{\hbar} \psi(x)e^{-iEt/\hbar} = \widehat{H} \psi(x)e^{-iEt/\hbar}$$

Simplifying:

$$E\psi(x)e^{-iEt/\hbar} = \widehat{H}\psi(x)e^{-iEt/\hbar}$$

Cancelling the time-dependent phase factor $e^{-iEt/\hbar}$, we get the **time-independent** Schrödinger equation:

$$\widehat{H}\psi(x) = E\psi(x)$$

This equation tells us that the spatial part of the wavefunction $\psi(x)$ is an eigenfunction of the Hamiltonian operator

 \hat{H} with eigenvalue E. The solutions $\psi(x)$ to this equation represent the stationary states, and the corresponding eigenvalues E represent the energy levels associated with these states.

2.3 ONE DIMENSIONAL PROBLEMS:

One-Dimensional Quantum Mechanics Problem: The Particle in a Box

A classic one-dimensional problem in quantum mechanics is the **Particle in a Box** (also known as the **Infinite Potential Well**). This problem serves as a foundational example to understand quantum behavior, such as quantized energy levels and wave functions, and is often used to introduce the basic principles of quantum mechanics.

Problem Setup:

Imagine a particle of mass m confined to a box with infinitely high walls. The particle is free to move within the box, but it cannot escape because the potential outside the box is infinitely large.

- The **box** is a one-dimensional region, say between x=0 and x=L, and outside this region, the potential is infinite.
- Inside the box (between x=0 and x=L), the potential is zero, i.e., V(x)=0.

Thus, the potential function V(x) is:

$$V(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & otherwise \end{cases}$$

This means that the particle is confined to move only within the interval $0 \le x \le L$.

Schrödinger Equation for the Problem:

To solve this problem, we apply the **time-independent Schrödinger equation** for a particle in a potential:

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

Since V(x)=0 inside the box, the equation simplifies to:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(\mathbf{x})}{dx^2} = \mathbf{E}\psi(\mathbf{x})$$

Rearranging:

$$\frac{d^2\psi(\mathbf{x})}{dx^2} = -k^2\,\psi(\mathbf{x})$$

Where $k = \sqrt{\frac{2mE}{\hbar^2}}$. This is a second-order differential equation that describes the wavefunction $\psi(\mathbf{x})$ inside the box.

General Solution of the Schrödinger Equation:

The general solution to the above differential equation is:

$\psi(x) = Asin(kx) + Bcos(kx)$

where A and B are constants to be determined by boundary conditions and k is related to the energy of the particle.

Applying Boundary Conditions:

Since the particle is confined to the box, the wavefunction must be zero at the boundaries x=0 and x=L (because the potential is infinite outside the box, the particle cannot exist outside):

 $\psi(0)=0$

Substituting into the general solution:

 $0 = Asin(0) + Bcos(0) \implies B = 0$

Therefore, the wavefunction simplifies to:

 $\psi(x) = Asin(kx)$

2) At x=L:

 $\psi(L)=0$

Substituting into the wavefunction:

Asin(kL)=0

Since $A \neq 0$, we must have:

sin(kL)=0

This implies that $kL=n\pi$, where n is a positive integer. Thus, the allowed values of k are:

$$k_n = \frac{n\pi}{L}, \ n = 1,2,3....$$

Quantized Energy Levels:

The energy of the particle is related to the wave number k by:

$$E_n = \frac{\hbar^2 k_n^2}{2m}$$

Substituting

 $k_n = \frac{n\pi}{L}$ gives the quantized energy levels:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \qquad n = 1, 2, 3, \dots \dots$$

Thus, the energy levels are discrete (quantized), and the particle can only occupy certain energy states, corresponding to the integer values of nnn.

Wave functions (Eigen Functions):

The wavefunctions corresponding to these energy levels are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \quad n = 1, 2, 3 \dots \dots$$

These wave functions describe the probability distribution of the particle's position within the box. The probability of finding the particle in a given region is proportional to $|\psi n(x)|2||psin(x)|^{2}|\psi n(x)|2|$.

Probability Density:

The probability density P(x) is the square of the wave function:

$$P(x) = |\psi_n(x)|^2 = \frac{2}{L}sin^2\frac{n\pi x}{L}$$

This gives the likelihood of finding the particle at position x within the box for a given energy level E_n .

2.4 WELLS AND BARRIERS:

Quantum Wells:

A **quantum well** refers to a region in which a particle is confined within a specific spatial region due to a potential that is lower inside the well than outside it. Essentially, it is a "well" that traps the particle. Quantum wells are often used to model systems where particles (such as electrons or atoms) are constrained to move in a particular region, leading to quantized energy levels.

Types of Quantum Wells:

• Infinite Quantum Well: In this case, the potential inside the well is zero, and the potential outside the well is infinite. A particle inside this well is completely confined and cannot escape. The energy levels are quantized, meaning that only certain discrete energies are allowed.

Potential Profile:

$$V(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & otherwise \end{cases}$$

The solutions to the Schrödinger equation inside the well are standing waves, and the energy eigenvalues are quantized as:

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

Where n is a positive integer.

• Finite Quantum Well: In a finite quantum well, the potential inside the well is still lower than outside, but the potential outside the well is not infinite. This means the particle has a non-zero probability of being found outside the well, though the probability decreases exponentially beyond the well's boundaries.

Potential Profile:

$$V(x) = \begin{cases} -V_{0,} & 0 \le x \le L\\ 0, & otherwise \end{cases}$$

Where V_{0} is the depth of the well and L is the width of the well.

For a finite well, the energy levels are still quantized, but there are also **bound states** and **leaky states**. The solutions to the Schrödinger equation lead to both discrete bound state energies (for which the particle is confined) and continuous energies (for which the particle is free to escape).

Bound States in Quantum Wells:

- Bound states occur when the particle's energy is less than the potential outside the well (i.e., E<0in the case of a negative potential).
- In these states, the wavefunction is localized inside the well, and the particle has discrete energy levels.

Tunnelling Through a Well (Finite Potential Well):

• In a finite quantum well, the particle may **tunnel** through the walls if its energy is higher than the potential at the boundaries of the well but still less than the potential outside. This is known as **quantum tunnelling**.

Quantum Barriers:

A **quantum barrier** is a region where the potential energy of the system is higher than the energy of the particle. Particles encountering a quantum barrier may reflect or tunnel through the barrier, depending on their energy.

Types of Quantum Barriers:

• **Infinite Barrier**: An infinite potential barrier is one where the potential is infinitely large, making it impossible for the particle to exist in the region beyond the barrier.

Potential Profile:

$$V(x) = \begin{cases} 0 & \text{for } x < 0 \text{ or } x > L \\ \infty, & \text{for } 0 \le x \le L \end{cases}$$

This is similar to the **infinite potential well** described earlier, but with the barrier preventing the particle from existing within the region where the potential is infinite. This scenario is typically used to model particle confinement.

• Finite Barrier: A finite potential barrier, unlike the infinite barrier, has a finite height, allowing a particle to potentially pass through it via quantum tunneling.

Potential Profile:

$$V(x) = \begin{cases} 0 & x < 0 \text{ or } x > L \\ -V_{0,} & 0 \le x \le L \end{cases}$$

Where $V_{0,}$ is the height of the barrier and L is the width of the barrier.

If a particle with energy E (where $E < V_{0,}$) approaches a finite barrier, it may be reflected, but there is a non-zero probability that it will **tunnel** through the barrier (this phenomenon is known as **quantum tunneling**).

Tunneling and Transmission Coefficient

The probability of a particle tunneling through a finite barrier depends on:

- The energy of the particle.
- The width and height of the barrier.

The **transmission coefficient** TTT describes the probability that a particle will tunnel through a barrier. For a rectangular potential barrier, the transmission coefficient is given by:

$$T = e^{-2\gamma L}$$

where:

- $\gamma = \sqrt{\frac{2m(V_0 E}{\hbar^2}}$ is the decay constant.
- L is the width of the barrier.
- V_{0} , is the height of the barrier.
- E is the energy of the particle.

For **high barriers** and **narrow widths**, the transmission probability decreases exponentially, meaning that tunneling becomes less probable.

Reflection and Transmission:

• If the particle's energy is less than the barrier height $E < V_{0,}$, it will experience partial reflection and partial transmission.

The particle's wavefunction on the other side of the barrier decays exponentially, but • there is still a small non-zero probability of finding the particle beyond the barrier. This is known as quantum tunneling.

2.5 HARMONIC OSCILLATOR:

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

In Simple harmonic motion the restoring force is proportional to displacement.

F = -kx,

Where k is positive constant-force constant.

The one dimensional Schrodinger time independent equation is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \Psi = 0 \qquad \dots \dots (1)$$

The potential energy of the Oscillator is $V = \frac{1}{2}kx^2$. Substitute in eq. (1)

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

$$\frac{\partial^2 \Psi}{\partial x^2} + \left(\frac{2mE}{\hbar^2} - \frac{kmx^2}{\hbar^2} \right) \Psi = 0 \qquad \dots \dots (2)$$

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For our convenience, let $\xi = \alpha x \implies x = \frac{\xi}{\alpha}$

$$\Rightarrow \frac{d\xi}{dx} = \alpha$$
$$\therefore \frac{d\Psi}{dx} = \frac{d\Psi}{d\xi} \cdot \frac{d\xi}{dx}$$
$$\frac{d\Psi}{dx} = \alpha \cdot \frac{d\Psi}{d\xi}$$
$$\frac{d^2\Psi}{dx^2} = \alpha \cdot \frac{d}{dx} \left(\frac{d\Psi}{d\xi}\right)$$
$$= \alpha \cdot \frac{d^2\Psi}{d\xi^2} \cdot \frac{d\Psi}{d\xi}$$

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$\frac{d^2\Psi}{dx^2} = \alpha^2 \frac{d^2\Psi}{d\xi^2} \Big[\because \frac{d\xi}{dx} = \alpha \Big]$

Substitute the above in equation (2)

$$\alpha^2 \frac{d^2 \Psi}{d\xi^2} + \left(\frac{2mE}{\hbar^2} - \frac{kmx^2}{\hbar^2}\right) \Psi = 0$$

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}\xi^2} + \left(\frac{2\mathrm{mE}}{\hbar^2\alpha^2} - \frac{\mathrm{mk}\xi^2}{\hbar^2\alpha^4}\right)\Psi = 0 \qquad \dots \dots (3)$$

then let $\lambda = \frac{2m}{\hbar^2 \alpha^2}$ and $\frac{km}{\hbar^2 \alpha^4} = 1 \implies \alpha^4 = \frac{km}{\hbar^2}$

$$\Rightarrow \alpha^2 = \left(\frac{mk}{\hbar^2}\right)^{\frac{1}{2}}$$

Substitute in equation (3)

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}\xi^2} + (\lambda - \xi^2)\Psi = 0 \qquad \dots \dots (4)$$

then let $\Psi = H_n(\xi)e^{-\frac{\xi}{2}}$

$$\Rightarrow \frac{d^2 \Psi}{d\xi^2} = H'_n(\xi) e^{-\frac{\xi^2}{2}} + H_n(\xi) e^{-\frac{\xi^2}{2}}(-\xi)$$

$$\Rightarrow \frac{d^2 \Psi}{d\xi^2} = H''_n(\xi) e^{-\frac{\xi^2}{2}} + H'_n(\xi) e^{-\frac{\xi^2}{2}}(-\xi) + H'_n(\xi) e^{-\frac{\xi^2}{2}}(-\xi) - H_n(\xi) e^{-\frac{\xi^2}{2}}$$

$$+ H_n(\xi)(-\xi) e^{-\frac{\xi^2}{2}}(-\xi)$$

$$\Rightarrow \frac{d^2 \Psi}{d\xi^2} = H''_n(\xi) e^{-\frac{\xi^2}{2}} - 2\xi H'_n(\xi) e^{-\frac{\xi^2}{2}}(-\xi) + H_n(\xi) e^{-\frac{\xi^2}{2}}(\xi^2 - 1)$$

Substitute the above in equation (4)

$$H_{n}^{"}(\xi)e^{-\frac{\xi^{2}}{2}} - 2\xi H_{n}^{\prime}(\xi)e^{-\frac{\xi^{2}}{2}}(-\xi) + H_{n}(\xi)e^{-\frac{\xi^{2}}{2}}(\xi^{2} - 1) + (\lambda - \xi^{2})H_{n}(\xi)e^{-\frac{\xi}{2}} = 0$$

$$\Rightarrow H_{n}^{"}(\xi)e^{-\frac{\xi^{2}}{2}} - 2\xi H_{n}^{\prime}(\xi)e^{-\frac{\xi^{2}}{2}}(-\xi) + (\lambda - 1)H_{n}(\xi)e^{-\frac{\xi}{2}} = 0$$

 $\Rightarrow H_n^{"}(\xi) - 2\xi H_n'(\xi) + (\lambda - 1)H_n(\xi) = 0$

This equation is identical to Hermites polynomial, then

$$\frac{\mathrm{d}^2 \mathrm{y}}{\mathrm{d}\mathrm{x}^2} - 2\mathrm{x}\frac{\mathrm{d}\mathrm{y}}{\mathrm{d}\mathrm{x}} + 2\mathrm{n}\mathrm{y} = 0$$

then $2n = \lambda - 1 \implies \lambda = 1 + 2n$

But we know that $\lambda = \frac{2m}{\hbar^2 \alpha^2} = 2n + 1 \Rightarrow \alpha^2 = \left(\frac{mk}{\hbar^2}\right)^{\frac{1}{2}}$

$$\Rightarrow \alpha^{2} = \left(\frac{m^{2}\omega^{2}}{\hbar^{2}}\right)^{\frac{1}{2}} [\because k = m\omega]$$

$$\alpha^{2} = \frac{m\omega}{\hbar}$$

$$\text{then } \lambda = \frac{2mE}{\hbar^{2}\alpha^{2}} = 2n + 1$$

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

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

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

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

where $n = 0, 1, 2, 3, \dots$ (Eigen Values)

This equation indicates that the energy levels of harmonic oscillator are equally spaced.

Significance of Zero-Point Energy:

For ground state, n = 0.

$$\mathbf{E_0} = \frac{1}{2}\hbar\boldsymbol{\omega}$$

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This equation is called **Zero-point energy**.

Even if all the vibrations of the atom are possible at 0° Kelvin, still some energy is associated the oscillator, that energy is called zero-point energy.

Eigen Functions of Harmonic Oscillator:

The Eigen function Ψ can be set equal to the product of polynomial $H_n(\xi)$ and factor $e^{-\frac{\xi^2}{2}}$ i.e.,

$$\Psi = N_n H_n(\xi) e^{-\frac{\xi^2}{2}} \qquad \dots \dots (5)$$
$$\int \Psi_n^* \Psi_n d\tau = N_m N_n \int H_m(\xi) H_n(\xi) e^{-\frac{\xi^2}{2}} \frac{d\xi}{\alpha}$$
$$= \frac{N_m N_n}{\alpha} \int H_m(\xi) H_n(\xi) e^{-\frac{\xi^2}{2}} d\xi$$

where $\int H_m(\xi)H_n(\xi)e^{-\frac{\xi^2}{2}}d\xi = 2^n n!\sqrt{\pi}$

$$\therefore \int \Psi_n^* \Psi_n d\tau = \frac{N_m N_n}{\alpha} 2^n n! \sqrt{\pi}$$
$$\int \Psi_n^* \Psi_n d\tau = \frac{N^2}{\alpha} 2^n n! \sqrt{\pi} = 1 \quad \text{for } m = n$$
$$\Rightarrow N_n = \left(\frac{\alpha}{2^n n! \sqrt{\pi}}\right)^{\frac{1}{2}}$$

substitute above equation in equation (5)

$$\Psi = \left(\frac{\alpha}{2^n n! \sqrt{\pi}}\right)^{\frac{1}{2}} \mathsf{H}_n(\xi) e^{-\frac{\xi^2}{2}}$$

Zero Point Energy and Eigen Values:

Let
$$a|k\rangle = |p\rangle$$
 and $\langle k|a^{\dagger} = \langle p|$

 $\langle k | a^{\dagger} a | k \rangle = \langle p | p \rangle$ p= Normal of the Ket

Then $a|k\rangle = 0$ and $\langle 0|a^{\dagger} = 0$

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$$\langle 0 | a^{\dagger} a | 0 \rangle = \left\langle 0 \left| \frac{H}{\hbar \omega} - \frac{1}{2} \right| 0 \right\rangle \ge 0 \therefore H | 0 \rangle = E_0 | 0 \rangle$$

$$= \left(\frac{E_0}{\hbar \omega} - \frac{1}{2} \right) \langle 0 | 0 \rangle$$

$$= 0$$

$$\Rightarrow \frac{E_0}{\hbar \omega} - \frac{1}{2} = 0 \therefore \left[E_0 = \frac{\hbar \omega}{2} \right]$$

This is called ground state zero point energy.

Hence wave function of the ground state is like this

Then we have $|a|0\rangle = 0$

But we know that $a = \sqrt{\frac{\mu\omega}{2\hbar}} \left[q + \frac{ip}{\mu\omega} \right]$ $\sqrt{\frac{\mu\omega}{2\hbar}} \left[q + \frac{ip}{\mu\omega} \right] | 0 \rangle = 0$ $\sqrt{\frac{\mu\omega}{2\hbar}} \left[q + \frac{ip}{\mu\omega} \right] | 0 \rangle = 0$ $\left[q + \frac{ip}{\mu\omega} \right] | 0 \rangle = 0$

$$q\Psi_{0} + \frac{\hbar}{\mu\omega} \frac{\partial\Psi_{0}}{\partial q} = 0$$

$$q\Psi_{0} = -\frac{\hbar}{\mu\omega} \frac{\partial\Psi_{0}}{\partial q}$$

$$q\partial q = -\frac{\hbar}{\mu\omega} \frac{\partial\Psi_{0}}{\Psi_{0}}$$

Apply integration on both sides

$$\frac{q^2}{2} = -\frac{\hbar}{\mu\omega}\log\Psi_0$$
$$\log\Psi_0 = -\frac{q^2\mu\omega}{2\hbar}$$

$$\Psi_0 = e^{-\frac{q^2\mu\omega}{2\hbar}} \times \text{Constant}$$

$$:: \Psi_0(q) = constant \operatorname{H}_n(q) e^{\left(-\frac{\mu\omega}{2\hbar}\right)q^2} \quad \text{We can write}$$

$$\therefore \Psi(q) = \left(\frac{\alpha}{2^n n! \sqrt{\pi}}\right)^{\frac{1}{2}} \mathrm{H}_n(q) e^{\left(-\frac{\mu\omega}{2\hbar}\right)q^2}$$

2.6 SUMMARY:

Student will know about the Quantum Mechanics and Schrodinger Wave equation. The student will solve the physics problems by using Schrodinger Wave Equation.

2.7 TECHNICAL TERMS:

Admissible wave functions, Stationary states, One-dimensional problems, wells and barriers, Quantum Mechanics, Harmonic Oscillator.

2.8 SELF-ASSESSMENT QUESTIONS:

- 1) Explain about the one dimensional problems.
- 2) Solve the problem of Harmonic Oscillator using Schrodinger Wave equation.
- 3) Briefly explain about the Admissible wave functions.

2.9 SUGGESTED READINGS:

- 1) L I Schiff, Quantum Mechanics (Mc Graw-Hill).
- 2) B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley).
- 3) A P Messiah, Quantum Mechanics.
- 4) Mathews and Venkatesan Quantum Mechanics.
- 5) Fundamentals of quantum Mechanics, Statistical Mechanics & Solid State Physics by S.P.Kuila, Books and Allied, Kolkata.

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LESSON-3

LINEAR VECTOR SPACES IN QUANTUM MECHANICS

3.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept ofLinear vector spaces in Quantum mechanics. The chapter began with understanding Vectors and operators, Change of Basis, Dirac Ket-Bra notations, Eigen value problem for operators. After completion of this lesson student should have the knowledge of fundamentals of Linear vector spaces in Quantum mechanics.

STRUCTURE:

3.1	Introduction
3.2	Vectors and Operators
3.3	Change of Basis
3.4	Dirac Ket-Branotations
3.5	Eigen Value Problem for Operators
3.6	Summary
3.7	Technical Terms
3.8	Self-Assessment Questions
3.9	Suggested Readings
3.1	INTRODUCTION:

Quantum Mechanics was developed by eminent scientists who had strong foundation in both physics and mathematics. Modern approach treats quantum mechanics as a new subject with its own set of postulates. The development of the theory is based on mathematical techniques using operators. Operator algebra follows the general laws of commutation, association and distribution with respect to addition. But multiplication is not necessarily commutative, as is with matrices. It is of interest to understand operators.

3.2 VECTORS AND OPERATORS:

An operator is a rule by which one wave function is changed to another.

 $\widehat{A}\Psi = \varphi$

Here \hat{A} = operator, Ψ = wave function, ϕ = New wave function

Ex:
$$\widehat{A} = \frac{\partial}{\partial x} \Psi = x^2$$

 $\frac{\partial}{\partial x} x^2 = 2x$

1) Linear Operator:

Any operator \hat{A} linear operator is for any two arbitrary wave function wave function $\Psi_a(x)$, $\Psi_b(x)$ we get

$$\widehat{A}[\Psi_{a}(x) + \Psi_{b}(x)] = \widehat{A}\Psi_{a}(x) + \widehat{A}\Psi_{b}(x)$$

 $\widehat{A}[\lambda \Psi_{a}(x)] = \lambda \widehat{A} \Psi_{a}(x)$

Where λ is a constant which may or may not be a complex number and $\Psi_a(x)$, $\Psi_b(x)$ are arbitrary wave functions. Here \hat{A} is said to be an anti linear operator then it satisfies the following relations.

$$\widehat{A}[\lambda \Psi_{a}(\mathbf{x})] = \lambda^{*} \widehat{A} \Psi_{a}(\mathbf{x})$$

2) Identity Operator:

An operator which leaves energy vector of a given space unchanged is known as identity operator.

$$\mathbf{\hat{I}}\Psi = \mathbf{\Psi}\mathbf{\hat{I}} = \mathbf{\Psi}$$

Where \hat{I} is identity operator.

3) Null or Zero operator:

When an operator is applied on one wave function. Then after operator the function becomes zero. Then such on operator is called null operator.

$$\hat{0}\Psi == \Psi \hat{0} = 0$$

Where $\hat{0}$ is null operator.

4) Unitary Operator:

When the inverse and ad-joint of an operator are identical. Then the operator is known as unitary operator. If \hat{U} is unitary operator then

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$$\widehat{U}^{\dagger} = = \widehat{U}^{-1}$$

$$U\widehat{U}^{\dagger} = \widehat{U}^{\dagger}$$
 U = I and $U\widehat{U}^{-1} = \widehat{U}^{-1}U = I$

Again for two state function Ψ and ϕ

$$\langle \boldsymbol{\Phi} | \boldsymbol{\Psi} \rangle = \left\langle \boldsymbol{\Phi} | \widehat{U}^{\dagger} \mathsf{U} | \boldsymbol{\Psi} \right\rangle = \left\langle \mathsf{U} \boldsymbol{\Phi} | \boldsymbol{U} \boldsymbol{\Psi} \right\rangle$$

5) Inverse Operator:

Consider two wave function $\Psi_1(x)$ and $\Psi_2(x)$. Let the operator \hat{A} real's than

$$\Psi_1(x) = \hat{A}\Psi_2(x)$$
 and $\hat{A}\Psi_2(x) = \Psi_1(x)(1)$

If there exist another operator \hat{B} which reverse the action of \hat{A}_1 such that

$$\widehat{B}\Psi(\mathbf{x}) = \Psi_2(\mathbf{x})(2)$$

From (1)and(2) the operator $\hat{B} = \hat{A}^{-1}$ is called inverse operator of \hat{A} . The operator \hat{A} satisfy the following condition then it is called inverse operator.

$$\hat{A}\hat{A}^{\dagger} = I$$

6) Adjoint Operator or Hermitian Operator:

Let \hat{A} is an arbitrary operator can define another linear operator \hat{A}^{\dagger} .

$$\int \Psi^* \widehat{A}^{\dagger} \phi \, d\tau = \int \left(\widehat{A} \Psi \right)^* \phi \, d\tau \left(\Psi \widehat{A}^{\dagger} \phi \right) = \widehat{A} \Psi \phi(1)$$

When equation Ψ_1 and ϕ are two arbitrary function if \hat{A} Hermitian we can write

$$\hat{A}\Psi\phi = \hat{A}\Psi\phi - \dots (2)$$

By comparing eq. (1) & (2), we get

 $\hat{A}^+ = \hat{A}$

i.e., \hat{A} is Hermitian operator.

7) Projection Operator:

Consider a 'N' decimal space formed by a set of 'N' mutually orthogonal unit vectors, If each other. " $\langle i \rangle$ " of an orthogonal we introduce a projection operator ' \hat{P}_i '.

The effect of ' \hat{P}_i ' on arbitrary vector $\langle \Psi \rangle$ space is to produce a new vector whose direction is along the basis vector " $|\langle i \rangle$ ".

Hilbert space defined by a complete set of

Eigen kets
$$|\Psi_i\rangle' s(i = 1, 2, 3, 4...)$$

 $|\Psi\rangle = \sum_{i=1}^{\infty} c_i |\Psi_i\rangle$ Where $c_i = \langle \Psi_i |\Psi\rangle$
 $|\Psi\rangle = \sum_{i=1}^{\infty} \langle \Psi_i |\Psi\rangle |\Psi_i\rangle = \sum_{i=1}^{\infty} |\Psi_i\rangle \langle \Psi_i |\Psi\rangle$ If $|\Psi\rangle = |\Psi_i\rangle$
 $|\Psi_i\rangle = \sum_{i=1}^{\infty} |\Psi_i\rangle \langle \Psi_i |\Psi_i\rangle = \sum_{i=1}^{\infty} P_i |\Psi_i\rangle$

Where $P_i = |\Psi_i\rangle\langle\Psi_i|P_i$ is called projection operator.

$$\sum_{i=1}^{\infty} P_i = 1$$

Properties of Projection Operator:

$$(i). \ \widehat{P}_{l}^{2} = \widehat{P}_{l}$$

$$\widehat{P}_{l}^{2} |\Psi\rangle = \widehat{P}_{l} (\widehat{P}_{l} |\Psi\rangle) = \widehat{P}_{l} |\Psi_{l}\rangle \langle\Psi_{i}|\Psi\rangle = |\Psi_{l}\rangle \langle\Psi_{i}|\Psi_{i}\rangle \langle\Psi_{i}|\Psi\rangle$$

$$= |\Psi_{l}\rangle \langle\Psi_{i}|\Psi\rangle = \widehat{P}_{l} |\Psi\rangle \because \langle\Psi_{i}|\Psi_{i}\rangle = 1$$

$$\widehat{P}_{l}^{2} = \widehat{P}_{l}$$

(*ii*). Projection operator \hat{P}_i is Hermitian

For any two arbitrary Kets $|m\rangle$ and $|n\rangle$, we have

$$\langle n|\hat{P}_i|m\rangle = \langle n|i\rangle\langle i|m\rangle = \langle m|i\rangle^*\langle i|n\rangle^* = \langle m|\hat{P}_i|n\rangle^* = \langle \hat{P}_in|m\rangle$$

8) Momentum Operator:

Momentum operator \hat{p} is represented as " $\frac{\hbar}{i}\nabla$ " in terms of components

$$\hat{P}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}; \hat{P}_y = \frac{\hbar}{i} \frac{\partial}{\partial y}; \hat{P}_z = \frac{\hbar}{i} \frac{\partial}{\partial z}$$

9) Product of Two Unitary Operators:

If \hat{A} and \hat{B} are two unitary operators.

Then,

$$(\hat{A}\hat{B}) (\hat{A}\hat{B})^{+} = \hat{A}\hat{B}\hat{B}^{+}\hat{A}^{+}$$

$$= \hat{A} I \hat{A}^{+} \qquad [::\hat{B}\hat{B}^{+} = I]$$

$$= \hat{A}\hat{A}^{+}$$

$$= I$$

$$(\hat{A}\hat{B})^{+}(\hat{A}\hat{B}) = \hat{B}^{+}\hat{A}^{+}\hat{A}\hat{B}$$

$$= \hat{B}^{+}I \hat{B} \quad [::\hat{A}\hat{A}^{+} = I]$$

$$= \hat{B}^{+}\hat{B}$$

$$= I$$

$$:. (\hat{A}\hat{B}) (\hat{A}\hat{B})^{+} = (\hat{A}\hat{B})^{+}(\hat{A}\hat{B}) = I$$

Thus \hat{A} and \hat{B} are two unitary operators, then their product is also a unitary operator.

10) Parity Operator:

It is defined as $\hat{\pi}\Psi(x) = \Psi(x)$. That is when the wave function $\Psi(x)$ is operated by parity operator it gets reflected n its co-ordinates.

(i)
$$\hat{\pi}[\Psi_1(x) + \Psi_2(x)] = \Psi_1(-x) + \Psi_2(-x) = \hat{\pi}\Psi_1(x) + \hat{\pi}\Psi_2(x)$$

(ii)
$$\hat{\pi}[\Psi(x)] = (\Psi(-x)) = (\hat{\pi}\Psi(x))$$
 Hence $\hat{\pi}$ is a linear operator.
(iii) The Eigen value of $\hat{\pi}$ operator is $\hat{\pi}\Psi = \lambda\Psi$

$$\hat{\pi}^{2}\Psi(x) = \hat{\pi}\hat{\pi}\Psi(x) = \hat{\pi}\lambda\Psi(x) = \lambda\hat{\pi}\Psi(x) = \lambda(\lambda\Psi(x)) = \lambda^{2}\Psi(x) \quad (1)$$
$$\hat{\pi}^{2}\Psi(x) = \hat{\pi}\hat{\pi}\Psi(x) = \hat{\pi}\Psi(-x) = \Psi(x) \quad (2)$$

From (1)&(2) $\lambda^2 = 1$ then $\lambda = \pm 1$

The Eigen function corresponding $\lambda = +1$ are called Even functions represents by Ψ_e

$$\Psi_e(x) = \Psi_e(-x)$$

The Eigen function corresponding $\lambda = -1$ are called Odd functions represents by Ψ_0

$$\Psi_o(x) = -\Psi_o(-x)$$

11) Addition and Subtraction Operator:

The Addition and Subtraction of operator gives new operators. The sum and difference of operator as defined by

$$(\hat{A} \pm \hat{B})f(x) = \hat{A} f(x) \pm \hat{B} f(x)$$

EX:- $\hat{A} = \log_{e}, \hat{B} = \frac{d}{dx}, f(x) = x^{2}$
$$(\log_{e} \pm \frac{d}{dx})x^{2} = \log_{e}x^{2} \pm \frac{d}{dx}x^{2}$$
$$= 2\log_{e}x \pm 2x$$
$$= 2(\log_{e}x \pm x)$$

12) Multiplication Operator:

Multiplication of two operators means operation by the two operators of after the order of operation being from right to left.

 $\hat{A}\hat{B}f(x)$ Means that the function f(x) is first operated by \hat{B} operator gives a new function g(x) and g(x) is operated by the operator $\hat{A}\hat{\otimes}\hat{B}$ finally gives the function h(x)

$$\hat{A}\hat{B}f(x) = \hat{A}\left(\hat{B}f(x)\right) = \hat{A}(g(x)) = h(x)$$

3.6

Linear Vector Spaces in Quant. Mech.

EX:-
$$\hat{A} = 4x^2\hat{B} = \frac{\partial}{\partial x}f(x) = ax^3$$

$$\hat{A}\hat{B}f(x) = 4x^2 \frac{\partial}{\partial x}(ax^3) = 4x^2(3ax^2) = 12 a x^4$$

3.3 CHANGE OF BASIS:

We must now consider the transformation from one representation from one representation to another in the general space. Along with the old unprimed basis we consider a new primed basis. The new basis vectors may be expressed in terms of the old ones.

3.7

$$\widehat{\Psi}'_{k} = \sum_{i} \widehat{\Psi}_{i} S_{ik}$$

$$S = \begin{pmatrix} S_{11} & S_{11} & \dots & S_{11} \\ S_{11} & S_{11} & \dots & S_{11} \\ \vdots & \vdots & \ddots & \cdots & \cdots \\ S_{11} & S_{11} & \dots & S_{11} \end{pmatrix}$$
(1)

Two such basis changes, S and R, performed in this order, is equivalent to a single one whose matrix is simply the product matrix RS. To obtain the new components of an arbitrary vector we write

$$\Psi_{a} = \sum_{i} a_{i} \widehat{\Psi}_{i} = \sum_{k} a'_{k} \widehat{\Psi}'_{k}$$
(2)

Substituting Eq. (1) we get $a_i = \sum_i a'_k S_{ik}$ (3)

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} = S \begin{pmatrix} a'_1 \\ a'_2 \\ \vdots \\ a'_n \end{pmatrix}$$

We must also determine the connection between the matrices A and A'representing the operator A in the old and new representations.

$$A\widehat{\Psi}'_{j} = \sum_{i} \widehat{\Psi}'_{i}A'_{ij} = \sum_{i} \sum_{k} \widehat{\Psi}_{k}S_{ki}A'_{ij} \quad (4)$$

But on the other hand

$$A\widehat{\Psi}'_{j} = A\sum_{l}\widehat{\Psi}_{l}S_{lj} = \sum_{l}\sum_{k}\widehat{\Psi}_{k}A_{kl}S_{li} \quad (5)$$

Comparing Eq. (4) and (5) we get SA' = AS

 $A' = S^{-1}AS$

We say that A' is obtained from A by a similarity transformation.

3.4 DIRAC'S BRA AND KET NOTATIONS:

Consider the product $\langle \lambda \Psi_a \Psi_b \rangle = \lambda^* \langle \Psi_a \Psi_b \rangle$

The scalar product is said to be dependent on the prefatory in antilinear fashion. This type of symmetry can be aviated. If we take two factors belonging to two different vectors spaces each space is linear in itself related to each other in an anti linear manner.

Thus we have a space of post factor vector and a space of three factor vectors. The connection between the dual spaces is given by

$$\langle \Psi_a | \Psi_b \rangle$$
 or $\langle a | b \rangle = \delta_{ab}$
 $\langle \Psi_a | \Psi_b \rangle = \int \Psi^*_a \Psi_b \, d\tau$

Then in this '< ' is called bra and '> ' is called ket. The operator α is said to be linear

if
$$\alpha |A\rangle = \alpha |A\rangle$$
 or $\langle B |\alpha |A\rangle = \int \Psi_B^* \alpha \Psi_A d\tau$

Properties of Bra and Ket Notation:

- 1) Operation on a Ket vector from the left with an operator \hat{A} produces another Ket vector $\hat{A}|\Psi\rangle = |\Psi'\rangle$ and the operation on a bra vector from the right with an operator \hat{A} produces another bra vector $\langle \Psi | \hat{A} = \langle \Psi' |$
- 2) The Kets may be multiplied by complex numbers and may be added to give other

Ketsi.e
$$a_1|Q\rangle + a_2|R\rangle = |S\rangle$$

The sum of two Bras is defined by the condition that its scalar product with any Ket vector $|Q\rangle$ is the sum of the scalar product of $\langle R|$ and $\langle S|$ with $|Q\rangle$. In notation

$$\{\langle \mathsf{R} | + \langle \mathsf{S} | \} | Q \rangle = \langle \mathsf{R} | Q \rangle + \langle \mathsf{S} | Q \rangle$$

- 3) The expectation value of an operator \hat{A} in the state Ψ can be written in this notation as $\langle \hat{A} \rangle = \int \Psi^* \hat{A} \Psi \, d\tau = \int \Psi^* \Psi' \, d\tau = \langle \Psi | \Psi' \rangle = \langle \Psi | \hat{A} | \Psi \rangle$
- The Eigen value problem for quantum mechanical state in these notations. If an operator Âoperates on a Ket|Ψ⟩ from left.

3.8

Linear Vector Spaces in Quant. Mech.

$$\hat{A}|\Psi\rangle = \lambda|\Psi\rangle$$

3.9

5) The set of Eigenkets $\{|\Psi_1\rangle, |\Psi_2\rangle, \dots, |\Psi_n\rangle, \dots, |\Psi_m\rangle$ will be an orthonormal set of eigenkets if $\langle \Psi_n | \Psi_m \rangle = \delta_{nm} n, m = 1, 2, 3, \dots$

A bra and a Ket vector will be called orthogonal if their scalar product is zero.

6) If we have a complete set of eigenkets $|\Psi_i\rangle$'s, (i = 1, 2, 3, ...), then in analogy with the complete set of eigen-functions, we can express any arbitrary Ket $|\Psi\rangle$ as

$$|\Psi\rangle = \sum_{i=1}^{\infty} c_i |\Psi_i\rangle$$
 Where $c_i = \langle \Psi_i | \Psi \rangle$

3.5 THE EIGEN VALUE PROBLEM FOR OPERATORS:

A ket $|A'\rangle$ is called an Eigen vector, or Eigen ket, of the operator A if

$$A|A'\rangle = A'|A'\rangle$$

An Eigen value enclosed in a ket $|A\rangle$, as in $|A'\rangle$, denotes the Eigen ket belonging to that Eigen value. Assume that 'K - 1' of the Eigen vectors are linearly independent but that the K^{th} Eigen vector depends linearly on these.

If
$$A\Psi_j = A'\Psi_j\Psi_k = \sum_{i=1}^{k-1} \lambda_i \Psi_i$$

 $A\Psi_j = A'_k\Psi_j = A'_k\sum\lambda_i\Psi_i = \sum\lambda_iA'_i\Psi_i$

Hence $A'_{k} = A'_{i}$

Let A be a Hermitian operator

$$A|A'\rangle = A'|A'\rangle ---(1)$$
 and $A|A''\rangle = A''|A''\rangle ---(2)$

Multiplication Eq(1) on left with a bra,

 $\langle \mathsf{A}'' | \mathsf{A} | \mathsf{A}' \rangle = \mathsf{A}' \langle \mathsf{A}'' | \mathsf{A}' \rangle --- (3)$

From the Eq(2), by the Hermitian property A,

$$\langle \mathsf{A}'' | A = \mathsf{A}''^* \langle \mathsf{A}'' |$$

Hence

Combing Eq(3) and (4)

If we let A'' = A', and recall that $\langle A' | A' \rangle > 0$, It follows that

$$A' = A'^* = Real$$

All Eigen values of a Hermitian operator are real. Eq(5) can be written as

$$(\mathsf{A}'-\mathsf{A}'')\big\langle\mathsf{A}''\big|\mathsf{A}'\big\rangle=0$$

Eigen values are orthogonal $\langle A'' | A' \rangle = 0$ we shall usually assume that

$$\langle \mathsf{A}'' | \mathsf{A}' \rangle = \delta_{\mathsf{A}'\mathsf{A}''}$$

3.6 SUMMARY:

In this chapter change of basis and different operators were discussed. Addition, subtraction and multiplication of operators is also discussed. Dirac notation is also explained. Eigen value problem for operators is also discussed.

3.7 TECHNICAL TERMS:

Vectors and Operators, Change of Basis, Dirac's Bra and Ketnotations, Eigen Value.

3.7 SELF-ASSESSMENT QUESTIONS:

- 1) How do you change the basis?
- 2) Explain about the Vectors and Operators?
- 3) Briefly explain about the Dirac's bra and Ket notations?
- 4) What is the Eigen value problem for operators?

3.9 SUGGESTED READINGS:

- 1) J J Sakural, Modem Quantum Mechanics.
- 2) Mathews and Venkatesan Quantum Mechanics.
- 3) Quantum Mechanics" by R.D. Ratna Raju.
- 4) Fundamentals of Quantum Mechanics, Statistical Mechanics & Solid State Physics by S.P. Kuila, Books and Allied, Kolkata.

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LESSON-4

LINEAR VECTOR SPACES AND OPERATORS

4.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept of Linear vector spaces in Quantum mechanics. The chapter began with understanding of the continuous spectrum, Application to Wave Mechanics in One Dimension, Hermitian operator, Unitary operator, Projection operatorAfter completion of this lesson student should have the knowledge of fundamentals of Linear vector spaces in Quantum mechanics. To develop understanding of postulates of quantum mechanics and to learn to apply them to solve some quantum mechanical systems To offer systematic methodology for the application of approximation methods to solve complicated quantum mechanical systems

STRUCTURE:

- 4.1 Introduction
- 4.2 The Continuous Spectrum
- 4.3 Application to Wave Mechanics in One Dimension
- 4.4 Hermitian Operator
- 4.5 Unitary Operator
- 4.6 Projection Operator
- 4.7 Summary
- 4.8 Technical Terms
- 4.9 Self-Assessment Questions
- 4.10 Suggested Readings

4.1 INTRODUCTION:

Quantum Mechanics was developed by eminent scientists who had strong foundation in both physics and mathematics. Modern approach treats quantum mechanics as a new subject with its own set of postulates. The development of the theory is based on mathematical techniques using operators. Operator algebra follows the general laws of commutation, association and distribution with respect to addition. But multiplication is not necessarily commutative, as is with matrices.

4.2 THE CONTINUOUS SPECTRUM:

The spectrum of Eigen values consists of discrete points and continuous portion. The Eigen vectors corresponding to discrete Eigen values can be normalized to unity. In the continuous portion of the spectrum, we assume that the Eigen vector is a continuous function of the Eigen value.

 $A|A'\rangle = A'|A'\rangle$ Where A' is real. $\langle A'|A''\rangle = \delta(A' - A'')$ In analogy with $\langle A'|A''\rangle = \delta_{A'A''}$ For the discrete Eigen values.

These normalizations all the formulas for the discrete and continuous cases are very similar, except that integrals in the latter replace sums in the former. An arbitrary vector can be written as

$$|\mathbf{a}\rangle = \sum_{k'} |k'\rangle \langle k'|a\rangle + \int |k''\rangle dk'' \langle k''|a\rangle$$

The discrete and the integral over the continuous Eigen values of the complete set of commuting observables symbolized by k.

The Eigen value problem of an operator A, assuming a purely continuous set of basis vectors. The equation

$$A|A'\rangle = A'|A'\rangle \text{Becomes} \qquad \int A|k'\rangle dk' \langle k'|A'\rangle = A'\int |k'\rangle dk' \langle k'|A'\rangle \qquad \text{or}$$
$$\int \langle k''|A|k'\rangle dk' \langle k'|A'\rangle = A' \langle k''|A'\rangle$$

4.3 APPLICATION TO WAVE MECHANICS INONE DIMENSION:

The wave mechanics of a point particle, for simplicity restricted to one dimension. The state of the system is determined by a ket $|a\rangle$. Since we can always measure the particle's position along the x-axis, there must be a Hermitian operator x corresponding to this observable. Hence, the Eigen values of x, denoted by x', form a continuum. The corresponding Eigen vectors are denoted by $|x'\rangle$

$$x|x'\rangle = x'|x'\rangle$$

With the assumed normalization

$$\langle \mathbf{x}'' | \mathbf{x}' \rangle = \delta(\mathbf{x}' - \mathbf{x}'')$$

The vector $|a\rangle$ can be expanded as

$$|a\rangle = \int |x'\rangle dx' \langle x'|a\rangle$$

If we write

$$\Psi_a(x') = \langle x' | a \rangle$$

The connection between state vectors $|a\rangle$ and the wave function $\Psi_a(x')$ is established x' is the continuously variable label of the components $\Psi_a(x')$ of state vector $\Psi_a = |a\rangle$ in an infinitely dimensional abstract space. The Eigen vectors of the position operator x, is called coordinate representation, and we might say that wave mechanics is quantum mechanics conducted in the coordinate representation. The scalar product of two states becomes

$$\langle b|a\rangle = \iint \langle b|\mathbf{x}''\rangle dx'' \langle \mathbf{x}''|\mathbf{x}'\rangle dx' \langle \mathbf{x}'|a\rangle$$
$$\langle b|a\rangle = \iint \langle b|\mathbf{x}''\rangle dx''\delta(\mathbf{x}'' - \mathbf{x}')dx' \langle \mathbf{x}'|a\rangle$$
$$\langle b|a\rangle = \int_{-\infty}^{+\infty} \Psi_b^*(x')\Psi_a(x')dx'$$

The Orthogonality of two states is expressed by the equation

$$\langle b|a\rangle = \int_{-\infty}^{+\infty} \Psi_b^*(x')\Psi_a(x')\,dx' = 0$$

4.4 HERMITIAN OPERATORS:

Hermitian operators are very important in the development of Quantum Mechanics. Therefore, it is necessary to understand the essential features of this class of operators.

If, for any two arbitrary eigenfunctions $\varphi_m(x)$ and $\varphi_n(x)$,

$$\int \phi_{\rm m}^* \hat{A} \phi_{\rm n} dx = \int (\hat{A}^{\dagger} \phi_{\rm m})^* \phi_{\rm n} dx \qquad (1)$$

then \hat{A}^{\dagger} is called the adjoint of the operator \hat{A} . If $\hat{A} = \hat{A}^{\dagger}$, then the operator \hat{A} is called the self-adjoint or Hermitian operator. Thus a Hermitian Operator is defined according to the following equation:

$$\int \phi_{\rm m}^* \hat{A} \phi_{\rm n} dx = \int (\hat{A} \phi_{\rm m})^* \phi_{\rm n} dx$$
⁽²⁾

Properties:

- i) The eigen functions of a Hermitian operator are real.
- ii) Any two eigen functions which belong to two different eigen values of a Hermitian operator are orthogonal.

Proof:

In the case of operator A, consider two eigen functions ϕ_m and ϕ_n with eigen values a_m and a_n respectively.

$$\hat{A} \phi_{\rm m} = a_{\rm m} \phi_{\rm m} \tag{3}$$

$$\stackrel{\wedge}{A} \varphi_{n} = a_{n} \varphi_{n} \tag{4}$$

Multiplying equation-4 with φ_m^* and equation-13 by φ_n^* from left and integrating,

$$\int \phi_{\rm m}^{*} \stackrel{\wedge}{A} \phi_{\rm n} dx = a_{\rm n} \int \phi_{\rm m}^{*} \phi_{\rm n} dx \qquad (5)$$

$$\int \phi_n^* \stackrel{\wedge}{A} \phi_m dx = a_m \int \phi_n^* \phi_m dx$$
 (6)

Taking the complex conjugation of equation-6, we have

$$\int (\hat{A} \phi_m)^* \phi_n dx = a_m^* \int \phi_m^* \phi_n dx$$
(7)

Using the Hermitian property of operator A (equation-12), LHS of equations-5 and 7 are equal; hence the RHS must also be equal. Therefore,

$$a_n \int \phi_m^* \phi_n dx = a_m^* \int \phi_m^* \phi_n dx \qquad (8)$$

If we consider the case $\mathbf{n} = \mathbf{m}$, the above equation becomes

$$a_{m}\int \phi_{m}^{*}\phi_{m}dx = a_{m}^{*}\int \phi_{m}^{*}\phi_{m}dx \qquad (9)$$

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From the above equations, it is obvious that $a_m = a_m^*$ and hence $a_m =$ real. This proves the first property that the eigen functions of a Hermitian Operator are real.

Using $a_m^* = a_m$ and rewriting equation-18, we have

$$(a_n - a_m) \int \phi_m^* \phi_n \, dx = 0 \tag{10}$$

For two different eigenvalues, i.e., for $(a_n - a_m) \neq 0$, we have

$$\int \phi_m^* \phi_n \, \mathrm{d}x = 0$$

This is the condition for orthogonality of φ_m and φ_n and this proves the second property.

Note:

- (i) In the case of matrix operators, a matrix (M) is said to be Hermitian, if it is equal to its transpose conjugate (M[†]): (M[†]) = M.
- (ii) M is said to be unitary, if $M^{\dagger} = M^{-1}$, where M⁻¹ is the inverse of M
- (iii) M is said to be orthogonal, if $M^{T} = M^{-1}$, where M^{T} is the transpose of M.

4.5 UNITARY OPERATOR:

When the inverse and ad-joint of an operator are identical. Then the operator is known as unitary operator. If \hat{U} is unitary operator then

$$\hat{U}^{\dagger} = = \hat{U}^{-1}$$

 $U\widehat{U}^{\dagger} = \widehat{U}^{\dagger}$ U = I and $U\widehat{U}^{-1} = \widehat{U}^{-1}U = I$

Again for two state function Ψ and ϕ

$$\langle \phi | \Psi \rangle = \langle \phi | \widehat{U}^{\dagger} \cup | \Psi \rangle = \langle \cup \phi | U \Psi \rangle$$

4.6 **PROJECTION OPERATOR:**

Consider a 'N' decimal space formed by a set of 'N' mutually orthogonal unit vectors, If each other. " $\langle i \rangle$ " of an orthogonal we introduce a projection operator ' \hat{P}_i '.

The effect of ' \hat{P}_i ' on arbitrary vector $\langle \Psi \rangle$ space is to produce a new vector whose direction is along the basis vector " $|\langle i \rangle$ ".

Hilbert space defined by a complete set of Eigen kets $|\Psi_i\rangle$'s (i = 1,2,3,4...)

$$|\Psi\rangle = \sum_{i=1}^{\infty} c_i |\Psi_i\rangle$$
 Where $c_i = \langle \Psi_i | \Psi \rangle$

 $|\Psi\rangle = \sum_{i=1}^{\infty} \langle \Psi_i | \Psi \rangle \, |\Psi_i\rangle = \sum_{i=1}^{\infty} |\Psi_i\rangle \langle \Psi_i | \Psi \rangle \quad \text{If} \quad |\Psi\rangle = \, |\Psi_i\rangle$

$$|\Psi_i\rangle = \sum_{i=1}^{\infty} |\Psi_i\rangle \langle \Psi_i |\Psi_i\rangle = \sum_{i=1}^{\infty} P_i |\Psi_i\rangle$$

Where $P_i = |\Psi_i\rangle\langle\Psi_i|P_i$ Is called projection operator.

$$\sum_{i=1}^{\infty} P_i = 1$$

Properties of Projection Operator:

(*i*). $\widehat{P}_{\iota}^{2} = \widehat{P}_{\iota}$

(*ii*). Projection operator \hat{P}_i is Hermitian

For any two arbitrary Kets $|m\rangle$ and $|n\rangle$, we have

$$\langle n|\hat{P}_i|m\rangle = \langle n|i\rangle\langle i|m\rangle = \langle m|i\rangle^*\langle i|n\rangle^* = \langle m|\hat{P}_i|n\rangle^* = \langle \hat{P}_in|m\rangle$$

4.7 SUMMARY:

In this chapter continuous spectrum, application in wave mechanics and some of the operators are discussed.

4.8 TECHNICAL TERMS:

Continuous spectrum, Wave mechanics, Hermitian, Unitary, Projection operators.

4.6

4.9 SELF-ASSESSMENT QUESTIONS

- 1) Describe about the continuous spectrum.
- 2) Write the application in Wave mechanics.
- 3) Briefly explain about the projection operators.

4.10 SUGGESTED READINGS:

- 1) Eugen Merzbacher, Quantum Mechanics, Wiley.
- 2) B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley).
- 3) J JSakural, Modem Quantum Mechanics.
- 4) Mathews and Venkatesan Quantum Mechanics.
- 5) Quantum Mechanics" by R.D. Ratna Raju.

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LESSON-5

LINEAR VECTOR SPACES AND OPERATORS

5.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept of Linear vector spaces in Quantum mechanics. The chapter began with understanding Positive operators, Change of orthonormal basis, Uncertainity Relation. After completion of this lesson student should have the knowledge of fundamentals of Linear vector spaces in Quantum mechanics. To develop understanding of postulates of quantum mechanics and to learn to apply them to solve some quantum mechanical systems. To offer systematic methodology for the application of approximation methods to solve complicated quantum mechanical systems

STRUCTURE:

- 5.1 Introduction
- 5.2 **Positive Operators**
- 5.3 Change of Orthonormal Basis
- **5.4** Orthogonalization Procedure
- 5.5 Uncertainity Relation.
- 5.6 Summary
- 5.7 Technical Terms
- 5.8 Self-Assessment Questions
- 5.9 Suggested Readings

5.1 INTRODUCTION:

Quantum Mechanics was developed by eminent scientists who had strong foundation in both physics and mathematics. Modern approach treats quantum mechanics as a new subject with its own set of postulates. The development of the theory is based on mathematical techniques using operators. Operator algebra follows the general laws of commutation, association and distribution with respect to addition. But multiplication is not necessarily commutative, as is with matrices. It is of interest to understand operators

5.2 **POSITIVE OPERATORS:**

A **positive operator** is a special type of self-adjoint operator that has the following property: for any vector $|\psi\rangle$ in the Hilbert space, the expectation value of the operator is non-negative:

 $\langle \psi | \hat{A} | \psi \rangle \geq 0$

Mathematically, we say that \hat{A} is positive if:

 $\hat{A} \ge 0$

This condition means that the operator \hat{A} has no negative eigen values, i.e., its spectrum (the set of its eigen values) is non-negative.

In other words, for a self-adjoint operator \hat{A} , the operator is positive if all of its eigen values λ satisfy:

λ≥0

Mathematical Definition of Positive Operators:

An operator \hat{A} is positive if it satisfies the following condition for all states $|\psi\rangle$ in the Hilbert space:

$$\langle \psi | \hat{A} | \psi \rangle \geq 0$$

If \hat{A} is positive, it can be shown that:

- The operator is self-adjoint.
- The operator's eigen values are non-negative (i.e., $\lambda \ge 0$).

One way to express this mathematically is that for a self-adjoint operator \hat{A} , it is positive if all of its eigen values are non-negative. In terms of the spectral decomposition of the operator:

$$\hat{A} = \lambda |\psi_{\lambda}\rangle \langle \psi_{\lambda}| d \lambda$$

Where λ represents the eigen values, the operator \hat{A} is positive if $\lambda \ge 0$ for all eigen values.

5.3 CHANGE OF ORTHONORMAL BASIS:

Suppose we have two different orthonormal bases in the Hilbert space:

- One basis $\{|\psi_i\rangle\}$ for the original representation.
- Another basis $\{|\phi_i\rangle\}$ for the new representation.

To perform a **change of orthonormal basis**, we express the new basis vectors $\{|\phi_i\rangle\}$ in terms of the original basis vectors $\{|\psi_i\rangle\}$. This is done by finding a unitary transformation matrix UUU that relates the two bases.

Unitary Transformation

The key idea is that a change of basis can be represented by a **unitary transformation**. A unitary operator U satisfies:

Where U[†] is the Hermitian conjugate (or adjoint) of U, and I is the identity operator.

Let $\{|\phi_i\rangle\}$ be the new basis vectors, and we want to express these in terms of the original basis $\{|\psi_i\rangle\}$. The relationship is:

$$|\phi_i\rangle = U_{ij}|\psi_i\rangle$$

Where U_{ij} are the components of the unitary transformation matrix U.

The inverse relationship, where we express the original basis vectors $\{|\psi_i\rangle\}$ in terms of the new basis $\{|\phi_i\rangle\}$, is given by:

$$|\psi_i\rangle = U \uparrow_{ij} |\phi_i\rangle$$

or equivalently, U⁺ is the matrix corresponding to the inverse of the unitary transformation.

5.4 ORTHOGONALIZATION PROCEDURE

In quantum mechanics, **orthogonalization** is an essential process for obtaining an orthonormal set of basis vectors from a set of linearly independent vectors. This procedure is crucial because many quantum mechanical calculations, such as those involving wave functions, operators, and measurements, are easier to perform in an orthonormal basis. The most common method for orthogonalizing a set of vectors is **Gram-Schmidt orthogonalization**.

Here's a detailed breakdown of the orthogonalization procedure in the context of quantum mechanics:

Orthonormal Basis:

Before diving into the procedure, let's clarify the concepts of **orthogonal** and **orthonormal** sets:

Orthogonal Vectors: A set of vectors |ψ_i > is orthogonal if the inner product of any two distinct vectors is zero:

$$\langle \psi_i | \psi_i \rangle = 0$$
 for $i \neq j$

 Orthonormal Vectors: A set of vectors |ψ_i > is orthonormal if it is orthogonal and every vector has unit length:

$$\langle \psi_i | \psi_i \rangle = 1$$

In quantum mechanics, states are typically represented as vectors in a Hilbert space, and the orthonormal basis plays an important role in expanding and manipulating quantum states.

Properties of the Orthonormalization Procedure:

- **Preservation of Linear Independence**: The Gram-Schmidt procedure takes a linearly independent set and transforms it into an orthonormal set. The vectors remain linearly independent because the process only involves subtraction of projections, which does not introduce any linear dependence.
- Normalization: Each vector is normalized after the orthogonalization step, ensuring that the final set is orthonormal, meaning that the vectors are both orthogonal and have unit length.
- Inner Product Preservation: The inner product between two vectors

 $|\psi_i\rangle$ and $|\psi_i\rangle$ in the resulting orthonormal set will be:

$$|\langle \psi_i | \psi_i \rangle = \delta_{ij}$$

Where δ_{ij} is the **Kronecker delta**.

5.5 UNCERTAINTY RELATION:

Suppose that $\hat{A}and\hat{B}$ are Hermitian operators $\hat{A}^{\dagger} = \hat{A}\&\hat{B}^{\dagger} = \hat{B}and \lambda$ is a real number. The mean value of the product of the operators and its adjoint is never negative. i.e.

$$\langle (\hat{A} + i\lambda\hat{B})(\hat{A} + i\lambda\hat{B})^{\dagger} \rangle \ge 0$$
$$\langle (\hat{A} + i\lambda\hat{B})(\hat{A} - i\lambda\hat{B}) \rangle \ge 0 \text{ or}$$
$$f(\lambda) = \langle \hat{A}^2 \rangle + \langle \hat{B}^2 \rangle \lambda^2 - i\lambda \langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle \ge 0$$

Since $f(\lambda)$ is real, $\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle$ is purely imaginary. To determine the minimum value of $f(\lambda)$, We must take that value of λ which makes $\frac{df}{d\lambda}$ equal to zero.

$$\frac{df}{d\lambda} = 2\langle \hat{B}^2 \rangle \lambda - i \langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle = 0$$

The minimum value of λ is given by

$$\lambda_{min} = \frac{\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle}{\langle \hat{B}^2 \rangle} \frac{i}{2}$$

$$\begin{split} \left[f(\lambda)\right]_{min} &= \langle \hat{A}^2 \rangle + \langle \hat{B}^2 \rangle \left\{\frac{\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle}{\langle \hat{B}^2 \rangle} \frac{i}{2}\right\}^2 - i\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle \left\{\frac{\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle}{\langle \hat{B}^2 \rangle} \frac{i}{2}\right\} \ge 0 \\ \left[f(\lambda)\right]_{min} &= \langle \hat{A}^2 \rangle + \frac{1}{4} \frac{\langle (\hat{A}\hat{B} - \hat{B}\hat{A}) \rangle^2}{\langle \hat{B}^2 \rangle} \ge 0 \quad \text{we get} \\ &\langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle \ge -\frac{1}{4} \left\{\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle\right\}^2 \qquad (1) \end{split}$$

Heisenberg uncertainty relations-Which is valid for two canonically conjugate observables $\hat{A}and\hat{B}$ such that $[\hat{A}, \hat{B}] = i\hbar$. We define uncertainties $\Delta Aand\Delta B$ to be the r.m.s.

$$\Delta \hat{A} = \left\{ \left\langle \left(\hat{A} - \left\langle \hat{A} \right\rangle \right)^2 \right\rangle \right\}^{\frac{1}{2}}$$
$$\left(\Delta \hat{A}\right)^2 = \left\langle \left(\hat{A} - \left\langle \hat{A} \right\rangle \right)^2 \right\rangle = \left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2$$
$$\Delta \hat{B} = \left\{ \left\langle \left(\hat{B} - \left\langle \hat{B} \right\rangle \right)^2 \right\rangle \right\}^{\frac{1}{2}}$$
$$\left(\Delta \hat{B}\right)^2 = \left\langle \left(\hat{B} - \left\langle \hat{B} \right\rangle \right)^2 \right\rangle = \left\langle \hat{B}^2 \right\rangle - \left\langle \hat{B} \right\rangle^2$$

 $\text{From Eq.}(1) \langle \Delta \hat{A}^2 \rangle \langle \Delta \hat{B}^2 \rangle \geq -\frac{1}{4} \left\{ \langle \Delta \hat{A} \Delta \hat{B} - \Delta \hat{B} \Delta \hat{A} \rangle \right\}^2$

$$\langle \Delta \hat{A}^2 \rangle \langle \Delta \hat{B}^2 \rangle \geq -\frac{1}{4} \{ \langle \left[\Delta \hat{A}, \Delta \hat{B} \right] \rangle \}^2$$

Reduced to

$$(\Delta \hat{A})(\Delta \hat{B}) \geq \frac{i}{2}(\langle [\hat{A}, \hat{B}] \rangle)$$

We know that $[\hat{A}, \hat{B}] = i\hbar$

$$(\Delta A)(\Delta B) \geq \frac{\hbar}{2}$$

This is the Heisenberg uncertainty relation.

5.6 SUMMARY:

In this chapter about the Positive operators, change of orthonormal basis, orthogonalization procedure and Uncertainty relation is discussed.

5.7 TECHNICAL TERMS:

Positive operators, Change of orthonormal basis, uncertainty relation.

5.8 SELF-ASSESSMENT QUESTIONS:

- 1) What is Positive operator? Explain in brief.
- 2) How do you change Orthonormal basis?
- 3) What is the Orthogonalization procedure?
- 4) What is uncertainty relation? Explain.

5.9 SUGGESTED READINGS:

- 1) Eugen Merzbacher, Quantum Mechanics, Wiley.
- 2) L I Schiff, Quantum Mechanics (Mc Graw-Hill).
- 3) B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley).
- 4) A P Messiah, Quantum Mechanics.
- 5) J J Sakural, Modem Quantum Mechanics.
- 6) Mathews and Venkatesan Quantum Mechanics.
- 7) Quantum Mechanics" by R.D. Ratna Raju.

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LESSON-6

ANGULAR MOMENTUM

6.0 AIM ABD OBJECTIVE:

The primary goal of this chapter is to understand the concept of Angular momentum. The chapter began with understanding of communication relations of angular momentum operator, angular momentum in spherical polar coordinates. After completing this chapter, the student will understand the complete idea about angular momentum.

STRUCTURE:

- 6.1 Introduction of Angular Momentum
- 6.2 Communication Relations for Angular Momentum Operator
- 6.3 Angular Momentum in Spherical Polar Coordinates
- 6.4 Summary
- 6.5 Technical Terms
- 6.6 Self Assessment Questions
- 6.7 Suggested Readings

6.1 INTRODUCTION OF ANGULAR MOMENTUM:

Angular momentum (which is described as an operator) plays a much importance role in quantum mechanics than in classical mechanics (where it is described as a dynamical variable). This is probably due to greater importance of periodic motions in quantum mechanics. A periodic motion can be understood as a motion in a closed orbit, which involves angular momentum. The existence of the intrinsic angular momentum (spin angular momentum) could also be another reason and another most importance reason is that the angular momentum is quantized which is not the case with the linear momentum.

Whenever a conservation law holds good for a physical quantum system, the Hamiltonian of the system is invariant under the corresponding group of transformations. The converse of this statement is not true as even if the system has a Hamiltonian, which is invariant under a group of transformations, there may not be a corresponding conservation law. Wigner showed that all symmetry transformations of quantum mechanical states can be chosen so as to correspond to either unitary orantiunitary operators. It is unitary transformations; it has other consequences which may be tested by the experiments.

The present chapter is devoted to symmetries with respect to rotations, which is reflected in the angular momentum vector operator (not an ordinary vector as in classical mechanics) has been defined by the commutation rules for its components, the orbital angular

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momentum and spin angular momentum of particle have been constructed, their eigen values and eigen functions have been obtained and the connection between rotations and angular momentum has been established.

This entire unit is divided in to five parts:

- i) Deals with the preliminaries of the angular momentum, commutator algebra etc.
- ii) The eigen value problem of orbital angular momentum is described in detail;
- iii) In this the spin angular momentum, the pauli spin matrices and their properties have been discussed;
- iv) In this lesson the emphasize is given to the eigen value problem of total angular momentum J.
- v) The last part of the unit consist of the addition of angular momenta associated with different physical systems and related numerical problems

6.2 COMMUNICATION RELATIONS FOR ANGULAR MOMENTUM OPERATOR:

1) Commutation Algebra of Angular Momentum Operator:

(i) With position co-ordinates:

$$\begin{split} [L_x, x] &= \left[y P_z - z P_y, x \right] \\ &= \left[y P_z, x \right] - \left[z P_y, x \right] \\ &= y [P_z, x] + [y, x] P_z - z [P_y, x] - [z, x] P_y \\ &= 0 \\ \\ [L_x, y] &= \left[y P_z - z P_y, y \right] \\ &= \left[y P_z, y \right] - \left[z P_y, y \right] \\ &= y [P_z, y] + [y, y] P_z - z [P_y, y] - [z, y] P_y \\ &= i \hbar z \end{split}$$

 $[L_x, z] = [yP_z - zP_y, z]$

$$= [yP_{z}, z] - [zP_{y}, z]$$

= y[P_{z}, z] + [y, z]P_{z} - z[P_{y}, z] - [z, z]P_{y}
= -ihy
[L_{x}, x] = 0; [L_{x}, y] = ihz; [L_{x}, z] = -ihy

Similarly,

$$[L_y, x] = -i\hbar z; [L_y, y] = 0; [L_y, z] = i\hbar x$$

 $[L_z, x] = i\hbar y; [L_z, y] = -i\hbar x; [L_z, z] = 0;$

ii) With position co-ordinates:

$$\begin{split} [L_x, P_x] &= \left[yP_z - zP_y, P_x\right] \\ &= \left[yP_z, P_x\right] - \left[zP_y, P_x\right] \\ &= y[P_z, P_x] + \left[y, P_x\right]P_z - z[P_y, P_x] - [z, P_x]P_y \\ &= 0 \\ \\ [L_x, P_y] &= \left[yP_z - zP_y, P_y\right] \\ &= \left[yP_z, P_y\right] - \left[zP_y, P_y\right] \\ &= y[P_z, P_y] + \left[y, P_y\right]P_z - z[P_y, P_y] - [z, P_y]P_y \\ &= i\hbar P_z \\ \\ [L_x, P_z] &= \left[yP_z - zP_y, P_z\right] \\ &= \left[yP_z, P_z\right] - \left[zP_y, P_z\right] \\ &= y[P_z, P_z] - \left[zP_y, P_z\right] - [z, P_z]P_y \end{split}$$

 $= -i\hbar P_y$

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$$[L_{x}, P_{x}] = 0; \ [L_{x}, P_{y}] = i\hbar P_{z}; \ [L_{x}, P_{z}] = -i\hbar P_{y}$$

Similarly,

$$\begin{bmatrix} L_y, P_x \end{bmatrix} = -i\hbar P_z; \begin{bmatrix} L_y, P_y \end{bmatrix} = 0; \begin{bmatrix} L_y, P_z \end{bmatrix} = i\hbar P_x$$
$$\begin{bmatrix} L_z, P_x \end{bmatrix} = i\hbar P_y; \begin{bmatrix} L_z, P_y \end{bmatrix} = -i\hbar P_x; \begin{bmatrix} L_z, P_z \end{bmatrix} = 0$$

2) Commutation Relations with Angular Momentum Co-ordinates:

$$\begin{split} [L_x, L_x] &= 0; \\ [L_x, L_y] &= \left[y P_z - z P_y, L_y \right] \\ &= \left[y P_z, L_y \right] - \left[z P_y, L_y \right] \\ &= y [P_z, L_y] + \left[y, L_y \right] P_z - z [P_y, L_y] - [z, L_y] P_y \\ &= y (-i\hbar) P_x + 0 - z (0) - i\hbar x P_y \\ &= (x P_y - y P_x) i\hbar \end{split}$$

$$\left[L_{x}, L_{y}\right] = i\hbar L_{z}$$

Similarly

$$\begin{bmatrix} L_{y}, L_{z} \end{bmatrix} = i\hbar L_{x}$$
$$\begin{bmatrix} L_{z}, L_{x} \end{bmatrix} = i\hbar L_{y}$$

3)
$$\vec{L} \times \vec{L} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ L_x & L_y & L_z \\ L_x & L_y & L_z \end{vmatrix}$$

$$= \vec{i} (L_y L_z - L_z L_y) + \vec{j} (L_z L_x - L_x L_z) + \vec{k} (L_x L_y - L_y L_x)$$

$$= \vec{i} [L_y, L_z] + \vec{j} [L_z, L_x] + \vec{k} [L_x, L_y]$$

$$= i\hbar L_x \vec{i} + i\hbar L_y \vec{j} + i\hbar L_z \vec{k}$$

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

$$= [L_{x}^{2}, L_{z}] + [L_{y}^{2}, L_{z}] + [L_{z}^{2}, L_{z}]$$

$$= [L_{x}L_{x}, L_{z}] + [L_{y}L_{y}, L_{z}]$$

$$= L_{x}[L_{x}, L_{z}] + [L_{x}, L_{z}]L_{x} + L_{y}[L_{y}, L_{z}] + [L_{y}, L_{z}]L_{y}$$

$$= L_{x}(-i\hbar L_{y}) + (-i\hbar L_{y})L_{x} + L_{y}(i\hbar L_{x}) + (i\hbar L_{x})L_{y}$$

$$= -i\hbar L_{x}L_{y} - i\hbar L_{x}L_{y} + i\hbar L_{x}L_{y} + i\hbar L_{x}L_{y}$$

$$[L^{2}, L_{z}] = 0$$

Similarly

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

6.3 ANGULAR MOMENTUM IN SPHERICAL POLAR COORDINATES:

Orbital angular momentum f aparticle is defined in Classical Mechanics as

$$\vec{L} = \vec{r} \times \vec{p}$$

where $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$ is the position co-ordinate or position vector of the particle from the origin.

The vector $\vec{p} = p_x \vec{i} + p_y \vec{j} + p_z \vec{k}$ is the momentum operator of the particle and

 $\vec{L} = L_x \vec{i} + L_y \vec{j} + L_z \vec{k}$ is the orbital angular momentum vector.

 $: \vec{L} = \vec{r} \times \vec{p}$ the direction of \vec{L} is perpendicular to both \vec{r} and \vec{p} .

$$\vec{L} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$
$$\vec{L} = L_x \vec{i} + L_y \vec{j} + L_z \vec{k} = (yp_z - zp_y) \vec{i} + (zp_x - xp_z) \vec{j} + (xp_y - yp_x) \vec{k}$$

Therefore

$$\begin{split} L_x &= \left(yp_z - zp_y\right) = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) L_y = (zp_x - xp_z) = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_z &= \left(xp_y - yp_x\right) = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{split}$$

The components of orbital angular momentum in spherical polar co-ordinates (r, θ, ϕ)

$$\begin{split} \mathrm{L}_{\mathrm{x}} &= -i\hbar \left(-\mathrm{sin} \varphi \frac{\partial}{\partial \theta} - \mathrm{cos} \varphi \, \mathrm{cot} \theta \frac{\partial}{\partial \varphi} \right) \\ \mathrm{L}_{\mathrm{y}} &= -i\hbar \left(-\mathrm{cos} \varphi \frac{\partial}{\partial \theta} - \mathrm{sin} \varphi \, \mathrm{cot} \theta \frac{\partial}{\partial \varphi} \right) \\ \mathrm{L}_{\mathrm{z}} &= -i\hbar \frac{\partial}{\partial \varphi} \end{split}$$

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

$$= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

6.4 SUMMARY OF THE LESSON:

The angular momentum definition and its three components are given in detail. The three components of angular momentum are also described in spherical polar coordinates. The commutation relations of angular momentum with the position operators, with the components of the linear momentum are worked out. The values of the commutator between angular momentumcomponents in pairs have also been obtained and it is also shown that the commutator $[L^2, L_i]=0$ for any value of i.

6.6

6.5 TECHNICAL TERMS:

Angular Momentum, Communication Relations for Angular Momentum Operator, Angular Momentum in Spherical Polar Coordinates.

6.6 SELF ASSESSMENTS:

- 1) Explain the communication relations for angular momentum
- 2) Explain the Angular momentum in spherical polar coordinates

6.7 SUGGESTED READINGS:

- 1) A Textbook of Quantum Mechanics-Mathews P M and Venkatesan K (Tata Mc Graw Hill Publication Co. Ltd., N. Delhi).
- 2) Quantum Mechanics-Merzbacher E (John Wiley & Sons, New York).
- 3) Introduction to Quantum Mechanics-Mathews P T (Mc Graw Hill Book Co., New York).
- 4) Quantum Mechanics by V. K. Thankappan (Wiley Eastern. Ltd, New Delhi, 1986.

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LESSON-7

EIGEN VALUE PROBLEM AND EIGEN VALUE FUNCTION

7.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept of Eigen value problem and Eigen value functions. The chapter began with understanding of Eigen value problem for $L_z and L^2$ operators Eigen value and eigen function of rigid rotator and Hydrogen atom. After completing this chapter, the student will understand the Eigen value problem and Eigen value functions.

STRUCTURE:

- 7.1 Introduction
- 7.2 Eigen Value Problem for L_z , L^2L_+ and L_- Operators
- 7.3 Eigen Value and Eigen Function of Rigid Rotator and Hydrogen Atom
- 7.5 Summary
- 7.6 Technical Terms
- 7.7 Self Assessment Questions
- 7.8 Suggested Readings

7.1 INTRODUCTION:

In linear algebra, **Eigen values** and **Eigen vectors** are fundamental concepts that arise from the study of linear transformations. These concepts are important in various fields, including physics, computer science, engineering, and economics, as they help understand the behavior of linear systems and matrices.

7.2 EIGEN VALUE PROBLEM FOR L_z , L^2L_+ and L_- OPERATORS:

Problem of L_z

Consider

 $Lz = xp_v - yp_x$

 Similarly

In spherical polar coordinates

$$x = r \sin\theta \cos\phi;$$

$$y = r \sin\theta \sin\phi;$$

$$z = r \cos\theta$$
$$r = \sqrt{x^2 + y^2 + z^2};$$

Tan $\Phi = y/x$;

$$Tan\theta = \sqrt{x^{2} + y^{2}} / z$$

$$\frac{\partial r}{\partial y} = \frac{y}{r};$$

$$\frac{\partial \theta}{\partial y} \cdot \sec^{2} \theta = \frac{2y}{2z\sqrt{x^{2} + y^{2}}}$$

$$Tan \Phi = y/x$$

$$\frac{\partial \theta}{\partial y} = \frac{y}{z \sec^{2} \theta \sqrt{x^{2} + y^{2}}}$$

$$(4)$$

$$\frac{\partial \phi}{\partial y} = \frac{1}{x \sec^{2} \phi}$$

Similarly

$$\frac{\partial\theta}{\partial x} = \frac{x}{z \sec^2 \theta \cdot \sqrt{x^2 + y^2}} \quad ; \quad \frac{\partial\phi}{\partial x} = \frac{-y}{x^2 \sec^2 \phi} \quad ; \quad \frac{\partial r}{\partial x} = \frac{x}{r} \; ; \; \dots \dots \; (5)$$

Substituting (4) in (2), we get

and

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y.
$$\frac{\partial}{\partial x} = \frac{xy}{r} \cdot \frac{\partial}{\partial r} + \frac{xy}{z \sec 2\theta \sqrt{x^2 + y^2}} \frac{\partial}{\partial \theta} - \frac{y^2}{x^2 \sec 2\phi} \cdot \frac{\partial}{\partial \phi}$$
 (7)

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Eigen value problem and Eigen value function

then eqn (1) becomes

$$L_{z} = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$
$$= -i\hbar \left(\frac{1}{\sec^{2} \phi} + \frac{y^{2}}{x^{2} \sec^{2} \phi} \right) \frac{\partial}{\partial \phi}$$
$$= -i\hbar \left(1 + \frac{y^{2}}{x^{2}} \right) \frac{1}{\sec^{2} \phi} \cdot \frac{\partial}{\partial \phi}$$
$$= -i\hbar \frac{\partial}{\partial \phi} \left(\because \sec^{2} \phi = 1 + \frac{y^{2}}{x^{2}} \right)$$
$$\therefore \quad L_{z} = -i\hbar \frac{\partial}{\partial \phi}$$

Eigen value and Eigen function of L_z

Let the operator L_z acts on the ϕ , gives the eigen value m.

$$L_{z} \Phi = m\Phi$$
$$-i\hbar \frac{\partial \Phi}{\partial \phi} = m\Phi \Longrightarrow \frac{d\Phi}{\Phi} = \frac{i}{\hbar} m$$
$$\Phi = \Phi o \exp\left(\frac{i}{\hbar} m\phi\right)$$

 Φ is the eigen function of $\,L_z$

In one complete rotation ϕ changes to $(\phi+2\theta)$ or n complete revolutions. It will be $(\phi+2\pi n)$. During this process, the wave function remains unchanged.

i.e.,
$$\Phi(\phi + 2\pi n) = \Phi_0 \exp(\frac{im}{\hbar}(\phi + 2\pi n))$$

From this $\frac{mn}{\hbar}$ is an integer, if n=1, $\frac{mn}{\hbar} = \frac{m}{\hbar}$ in one revolution; So on can take only inter

times \hbar values.

Problem of L²

$$L^2 = L^2_x + L^2_y + L^2_z$$

Consider

 $L_x = y p_z - z p_y$

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

$$\mathbf{L}_{\mathbf{x}}^{2} = -\hbar^{2} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right]$$

$$\mathbf{L}_{\mathbf{x}}^{2} = -\hbar^{2} \left[y^{2} \frac{\partial^{2}}{\partial z^{2}} + z^{2} \frac{\partial^{2}}{\partial y^{2}} - 2yz \frac{\partial^{2}}{\partial y \partial z} - y \frac{\partial}{\partial y} - z \frac{\partial}{\partial z} \right]$$

Similarly

$$L^{2}_{y} = -\hbar^{2} \left[z^{2} \frac{\partial^{2}}{\partial x^{2}} + x^{2} \frac{\partial^{2}}{\partial z^{2}} - 2zx \frac{\partial^{2}}{\partial z \partial x} - x \frac{\partial}{\partial x} - z \frac{\partial}{\partial z} \right]$$

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

Then

$$L^2 \qquad = \quad L_x^2 + L_y^2 + L_z^2$$

$$= \left[\left(y^2 + z^2 \right) \frac{\partial^2}{\partial z^2} + \left(x^2 + z^2 \right) \frac{\partial^2}{\partial y^2} + \left(x^2 + y^2 \right) \frac{\partial^2}{\partial z^2} - 2x \frac{\partial}{\partial x} - 2y \frac{\partial}{\partial y} - 2z \frac{\partial}{\partial z} - 2x y \frac{\partial^2}{\partial x \partial y} - 2y z \frac{\partial^2}{\partial x \partial y} - 2z x \frac{\partial^2}{\partial x \partial y} \right]$$

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=

$$= -\hbar^{2} \left[r^{2} \nabla^{2} - r \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) \right]$$
$$= \hbar^{2} \left[r^{2} \nabla^{2} - r^{2} \frac{\partial^{2}}{\partial r^{2}} - 2r \frac{\partial}{\partial r} \right]$$

but the value of Laplacian operator ∇^2 in terms of spherical polar coordinates is given by

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

or $r^{2} \nabla^{2} = \frac{r^{2}}{r^{2}} \frac{\partial}{\partial r} + \frac{2r}{r^{2}} \frac{\partial}{\partial r} + \frac{1}{r^{2} \sin^{2} \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^{2} \sin^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}}$
Hence, $L^{2} = -\hbar^{2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}} \right]$

Let $Y_l^m(\theta, \phi)$ is the eigen function for the operator L^2 then L^2 Y=c Y is the eigen value

equation. Then

$$\hbar^{2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^{2} \theta} \frac{\partial^{2} Y}{\partial \phi^{2}} \right] + c Y = 0$$

Let $Y_{m}^{1}(\theta, \phi) = \eta(\theta) \xi(\phi)$

is the solution of the above equation. By applying variable and separable method, the above equation can be divided in two separate equations

Multiplying with $\sin^2\theta$ on both sides, the above equation becomes ,

$$\sin\theta \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial Y}{\partial\theta}) + c\sin^2\theta Y + \frac{\partial Y^2}{\partial\phi^2} = 0$$

Separating the two variables

$$\sin\theta \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial Y}{\partial\theta}) + c\sin^2\theta Y = -\frac{\partial Y^2}{\partial\phi^2} = m^2 (say)$$
$$\frac{\partial Y^2}{\partial\phi^2} + m^2\theta = 0$$

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$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial Y}{\partial\theta}) + (c - \frac{m^2}{\sin^2\theta})Y = 0$$

then solution of the I of above two equations is

$$\xi(\theta) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$$

The second is associated Legendre polynomial if $C=\ell$ ($\ell+1$)

And hence its solution is

$$\eta(\theta) = \sqrt{\frac{(2l+1)(l-|m||)}{2(l+m)|}} P^{m_l}(\cos\theta)$$

Therefore eigen value equation for L^2 is

$$L^{2}Y_{m}^{l}(\theta,\phi) = \ell_{1}(\ell+1)\hbar^{2}Y_{m}^{l}(\theta,\phi)(\theta,\phi)$$

The eigen value of the operator L^2 is ℓ (ℓ +1) and the eigen function for L^2 is

$$Y_m^l(\theta,\phi) = \sqrt{\frac{(2l+1)(l-|m|)}{4\pi(l+m)}} P_l^m(\cos\theta) \exp(im\phi)$$

thus from the above equation the eigen value equations for the two operators are represented by

$$L_z y_l^m = \frac{\hbar}{i} \frac{\partial Y_l^m}{\partial \phi} = m\hbar y_l^m$$

$$L^2 y_l^m = \frac{\hbar}{i} \frac{\partial Y_l^m}{\partial \phi} = l(l+1)\hbar^2 y_l^m$$

The first few spherical harmonics are listed below:

$$Y_0^{\ 0} = \frac{1}{\sqrt{4\,\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$

$$Y_{1}^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin \theta = \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r}$$

$$Y_{2}^{0} = \mp \sqrt{\frac{5}{16\pi}} (3\cos^{2}\theta - 1) = \mp \sqrt{\frac{5}{16\pi}} \frac{2z^{2} - x^{2} - y^{2}}{r^{2}}$$

$$Y_{2}^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \cos \theta \sin \theta = \mp \sqrt{\frac{15}{8\pi}} \frac{(x \pm iy)z}{r^{2}}$$

$$Y_{2}^{\pm 2} = \mp \sqrt{\frac{15}{32\pi}} e^{\pm 2i\phi} \sin^{2}\theta = \mp \sqrt{\frac{15}{32\pi}} \frac{(x \pm iy)^{2}}{r^{2}}$$

Under a coordinate reflection, or inversion, through the origin, which is realized by the transformation $\varphi \varphi + \pi \varphi \pi$ - θ , the azimuthal wave function $e^{im\theta}$ is multiplied by(-1)^m, and $P_l^m(\cos \theta)$ by (-1)^{l+m}, hence, $Y_m^l(\theta, \phi)$ is multiplied by(-1)¹, when r is changed to -r.

The spherical harmonics are thus eigen functions of the parity operator Up which changes r in to –r.

Up
$$\psi$$
 (r) = ψ (-r)
Up $Y_l^m(\theta, \phi) = (-1)^l Y_l^m(\theta, \phi)$

i.e., Y_l^m has definite parity in consonance with the parity of angular momentum quantum number ℓ .

The spherical harmonics form an orthonormal set since

$$\int_0^{2\pi} \int_0^{\pi} \mathbf{Y}_m^1(\theta, \phi) * \mathbf{Y}_{m^1}^{\mathbf{I}^i}(\theta, \phi) \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = \delta_{\ell \ell^1} \delta_{mm^1}$$

We may now define two new operators:

$$L_{+} = L_{x} + iL_{y},$$
$$L_{-} = L_{x} - iL_{y}$$

Which can be written in terms of spherical polar coordinates as

$$\mathbf{L}_{+} = \hbar e^{i\theta} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \theta} \right)$$

$$\mathbf{L} = -\hbar e^{-i\theta} \left(\frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \theta} \right)$$

The eigen value equations for these two operators are

$$L_{+}Y_{l}^{m}(\theta,\phi) = \hbar \overline{\big)(\ell-m)(\ell+m+1)}Y_{l}^{m+1}(\theta,\phi)$$
$$L_{-}Y_{l}^{m}(\theta,\phi) = \hbar \overline{\big)(\ell-m)(\ell-m+1)}Y_{l}^{m-1}(\theta,\phi)$$

The operators L_+ and L_- are in fact raising and lowering operators for the magnetic quantum number.

L₊ AND L₋ OPERATORS:

 $(L_{+} and L_{-} operators Eigen problem with Orbital Angular Momentum):$

$$L_{+} = L_{x} + iL_{y}$$
 and $L_{-} = L_{x} - iL_{y}$

Finding Commutation relation between L_{z} and L_{+}

$$\begin{split} [\mathrm{L}_{\mathrm{z}},\mathrm{L}_{+}] &= \left[\mathrm{L}_{\mathrm{z}},\mathrm{L}_{\mathrm{x}} + i\mathrm{L}_{\mathrm{y}}\right] \\ &= \left[\mathrm{L}_{\mathrm{z}},\mathrm{L}_{\mathrm{x}}\right] + i\left[\mathrm{L}_{\mathrm{z}},\mathrm{L}_{\mathrm{y}}\right] \\ &= i\hbar\mathrm{L}_{\mathrm{y}} + i\left(-i\hbar\mathrm{L}_{\mathrm{x}}\right) \\ &= i\hbar[\mathrm{L}_{\mathrm{y}} + i(-i\hbar\mathrm{L}_{\mathrm{x}}) \\ &= i\hbar[\mathrm{L}_{\mathrm{y}} - i\mathrm{L}_{\mathrm{x}}] \\ &= \hbar[i\mathrm{L}_{\mathrm{y}} + \mathrm{L}_{\mathrm{x}}] \\ &= \hbar[\mathrm{L}_{\mathrm{x}} + i\mathrm{L}_{\mathrm{y}}] \\ &= \hbar\mathrm{L}_{+} \end{split}$$

Similarly

$$[L_z, L_-] = [L_z, L_x - iL_y]$$
$$= [L_z, L_x] - i[L_z, L_y]$$
$$= i\hbar L_y - i(-i\hbar L_x)$$

 $= i\hbar [L_y + iL_x]$ $= \hbar [iL_y - L_x]$ $= -\hbar [L_x - iL_y]$ $= -\hbar L_-$

7.9

7.3 EIGEN VALUES AND EIGEN FUNCTIONS OF RIGID ROTATOR:

Hydrogen Atom:

is

The problem of hydrogen atom, is a two-body problem (namely of the electron of mass 'm' and proton of mass 'M'). Since, we are not interested in translational motion of the atom as a whole, the centre of mass of the system is taken as the origin of the coordinate system. Since the system is centro-symmetric, it is most convenient to use spherical polar coordinates. The problem can be treated (as in the case of rigid rotator) as a single particle problem of reduced mass $\mu = \frac{mM}{m+M}$, with the radial coordinate 'r' which is equal to the distance between the electron and the nucleus. Potential energy of attraction between the electron and the nucleus

$$V = \frac{-Ze^2}{r}$$
(8)

(Here Z = 1 for H-atom. But for generality 'Z' is retained. The treatment, then, remains same for H-like ions He⁺, Li⁺⁺ etc. with appropriate μ)

Schrodinger's equation for H-atom is

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2} (\mathbf{E} + \frac{Ze^2}{r}) \psi = 0 \tag{9}$$

where
$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$
 (10)

It is well known that the operator for the square of the orbital angular momentum

$$\hat{L}^2 = -\hbar^2 \tag{11}$$

Using this in equation-10, we have $\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2}$$
(12)

 $\stackrel{\,{}_\circ}{L^2}$ has eigenfunctions $Y_{\ell,m}(\theta,\phi)$ and eigenvalues ℓ (ℓ +1) \hbar^2

where $\ell = 0, 1, 2, \dots$ and $\ell \ge |m|$.

$$\therefore \hat{L}^{2} Y_{l}^{m}(\theta,\phi) = \ell (\ell+1) \hbar^{2} Y_{l}^{m}(\theta,\phi); \ell = 0,1,2,...; \ell \ge |m|$$
(13)

From equations 9 and 12,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\hat{L}^2\psi + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0$$
(14)

Using separable variable technique with $\psi(\mathbf{r}, \theta, \phi) = N R (\mathbf{r}) Y (\theta, \phi)$ (15)

$$\frac{1}{R}\frac{d}{dr}(r^{2}\frac{dR}{dr}) + \frac{2\mu r^{2}}{\hbar^{2}}(E + \frac{Ze^{2}}{r}) = \frac{1}{\hbar^{2}Y}(\hat{L}^{2}Y)$$
(16)

The LHS is dependent only on 'r' whereas the RHS is dependent only on θ and ϕ . But they are equal to each other. Therefore they must be independent of r, θ and ϕ ; and each must be equal to a constant, say ' λ '.

$$\therefore \frac{1}{\hbar^2 Y} (\hat{L^2} Y) = \lambda \Longrightarrow \hat{L^2} Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi)$$

We know already (equation-13) that $\lambda = \ell$ (ℓ +1) with $\ell = 0, 1, 2, ...$

Therefore equation-16 becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[\left(E + \frac{Ze^2}{r} \right) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R = 0$$
(17)

The term $\frac{l(l+1)\hbar^2}{2\mu r^2}$ appears as an addition to the potential and can be considered as centrifugal potential since its negative gradient is equal to the centrifugal force experienced
by a particle moving in an orbit of radius 'r' with angular momentum $\sqrt{l(l+1)\hbar^2}$. Alternatively, it may be looked upon as the K.E associated with the rotary part of the motion $(\hat{L}^2/2 I)$ where $I = \mu r^2$ is the moment of inertia.

7.11

Equation-17 can also be written as

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left[\left(E + \frac{Ze^2}{r} \right) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R = 0$$
(18)

With the change of the variable as $\rho = \alpha r$, the above equation becomes

$$\frac{d^2 R}{d\rho^2} + \frac{2}{r} \frac{dR}{d\rho} + \left[\left(\frac{2\mu E}{\alpha^2 \hbar^2} + \frac{2\mu}{\hbar^2} \frac{Ze^2}{\rho \alpha} \right) - \frac{l(l+1)}{\rho^2} \right] \mathbf{R} = 0$$
(19)

For bound states (E<0)

Let us introduce a new parameter n and also write ' α ' in terms of other known constants as

$$\alpha = \frac{2}{\hbar} \sqrt{-2\mu E} \text{ and } n = \frac{2\mu Z e^2}{\hbar^2 \alpha}$$
(20)

With these parameters, equation-19 can be written as

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[\frac{-1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right] R = 0$$
(21)

(or)
$$\frac{d^2}{d\rho^2}(\rho R) + \left[\frac{-1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right](\rho R) = 0$$
 (22)

The asymptotic solution (for $\rho \rightarrow \infty$) can be obtained using equation – 21:

$$\frac{d^2 R}{d\rho^2} = \frac{R}{4} \Longrightarrow \mathbb{R}(\rho) \sim e^{-\rho/2}$$
(23)

The asymptotic solution (for $\rho \rightarrow 0$) can be obtained using equation 22:

$$\frac{d^2}{d\rho^2} (\rho R) - \frac{l(l+1)}{\rho^2} (\rho R) = 0 \Longrightarrow R(\rho) \sim \rho^{\ell}$$
(24)

The correctness can be checked by back substitution

7.12

Therefore, the actual solutions for all values of ρ (or) r may be of the form

$$\mathbf{R}(\rho) \sim \mathbf{f}(\rho)\rho^{\ell} e^{-\rho/2}$$
(25)

With this substitution in equation 21 or 22, we have

$$\rho \frac{d^2 f}{d\rho^2} + (2\ell + 2 - \rho) \frac{df}{d\rho} + (n - \ell - 1) f = 0$$
(26)

This equation is similar to the Associated Laguere Differential Equation

$$\rho L'' + (p+1 - \rho) L' + (q-p) L = 0$$
(27)

if $q = n + \ell$ and $p = 2\ell + 1$

(or)
$$(q-p) = (n - \ell - 1)$$
 and $(p+1 - \rho) = (2\ell + 2 - \rho)$ (28)

This differential equation has a polynomial solution when q - p = +ve integer.

$$\therefore \mathbf{n} - \ell - 1 = + \text{ve integer}$$
(29)

Since $\ell = 0, 1, 2, \dots$, from equation-1.5.39 we have $n = \ell + 1 = 1, 2, 3, \dots$ (30)

From equation-21

$$E_{n} = \frac{-\hbar^{2} \alpha^{2}}{8\mu} = \frac{-\hbar^{2}}{8\mu} \left[\frac{2\mu Z e^{2}}{\hbar^{2} n} \right]^{2}$$
$$\Rightarrow E_{n} = \frac{-2\pi^{2} \mu Z^{2} e^{4}}{n^{2} h^{2}}; n = 1, 2, 3....$$
(31)

These bound state energies are in accordance with those obtained from Bohr's theory. The wave functions are

$$\Psi_{\mathbf{n},\ell,\mathbf{m}}(\mathbf{r},\theta,\phi) = \mathbf{R}_{\mathbf{n},\ell}(\mathbf{r}) Y_l^m(\theta,\phi)$$

where R $_{n,\ell}$ (r) are radial function and Y $_{\ell,m}$ (θ, ϕ) are spherical harmonics involving angular functions.

Note: The normalised radial wave functions are as follows:

$$\mathbf{R}_{n,\ell}(\mathbf{r}) = -\sqrt{\left(\frac{2Z}{na_o}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2Zr}{na_o}\right)^l e^{-Zr/(na_o)} L_{n+l}^{2l+1}\left(\frac{2Zr}{na_o}\right)$$

where
$$\sum_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1} [(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!}$$
 and

 $a_o=\mu e^2/\,\hbar^2=Bohr's$ first orbit radius.

7.4 SUMMARY:

The summary of the problem of the orbital angular momentum can be written as follows:

7.13

Quantity	Operator form	Eigen function	Eigen value
Lz	$-i\hbarrac{\partial}{\partial\phi}$	$\xi(\theta) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$	mħ
L ²	$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$	$\eta(\theta) = \sqrt{\frac{(2l+1)(l- m)}{2(l+m) }} P^{m_{l}}(\cos\theta)$	$l(l+1)\hbar^2$

7.5 TECHNICAL TERMS:

Eigen value problem for L_z and L^2 operators, Eigen value and eigen function of rigid rotator and Hydrogen atom

7.6 SELF ASSESSMENTS:

- 1) Explain about the Eigen value problem for L_z and L^2 operators
- 2) Explain about the Eigen value and eigen function of rigid rotator and Hydrogen atom

7.7 SUGGESTED READINGS:

- 1) Advanced Quantum Mechanics-B.S. Rajput (Pragati Prakasan, Meerut 1990).
- 2) Quantum Mechanics-Merzbacher E (John Wiley & Sons, New York).
- 3) Introduction to Quantum Mechanics-Mathews P T (Mc Graw Hill Book Co., New York).
- 4) Quantum Mechanics by V.K. Thankappan (Wiley Eastern. Ltd., New Delhi, 1986.

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LESSON-8

TIME INDEPENDENT PERTURBATION THEORY (FOR NON - DEGENERATE AND DEGENERATE CASES)

8.0 AIM AND OBJETIVE:

The primary goal of this chapter is to understand the concept of Time Independent Perturbation Theory (for Non-degenerate system and degenerate system). The chapter began with understanding of degenerate system, Time Independent Perturbation Theory for Nondegenerate system, Time Independent Perturbation Theory for degenerate system. After completing this chapter, the student will understand the complete idea about Time Independent Perturbation Theory (for Non-degenerate system and degenerate system).

STRUCTURE:

- 8.1 Introduction
- 8.2 Time Independent Perturbation Theory
- 8.3 Time Independent Perturbation Theory for Non-Degenerate System
- 8.4 Time Independent Perturbation Theory for Degenerate System
- 8.5 Summary
- 8.6 Technical Terms
- 8.7 Self Assessment Questions
- 8.9 Suggested Readings

8.1 INTRODUCTION:

In quantum mechanics, perturbation theory is an approximation scheme for describing such a complicated quantum system in terms of a simpler one. The main idea here is to start with a simple system and gradually turn on an additional perturbing Hamiltonian representing a weak disturbance to the system. As such Hamiltonian can be split into several terms, some of which may play by far the most significant role than others and such terms can be treated exactly to obtain analytic solution to the eigen value problem, and the effect of the rest of the terms can be estimated in an approximate way.

The perturbation theory enables us to calculate these small changes. Similarly quantum mechanical systems can be treated with perturbation methods.

In the case of perturbation theory, these are two cases which can treated separately as (i) Time-dependent perturbation theory (ii) Time-independent perturbation theory. Further Time-independent perturbation theory is applied to degenerate and non-degenerate system separately.

8.2

The stationary perturbation theory concerns with finding the changes in energy levels and eigen functions of a system when a small disturbance is applied. In such cases, the Hamiltonian may be considered as split into two parts, one of them is a major part, which characterizes the system for which exact solution is obtained for the wave equation; while the second part is small and treated as perturbation.

8.2 TIME INDEPENDENT PERTURBATION THEORY:

Now, in this section we study the time-independent perturbation theory applied to a non-degenerate system. If one energy value or energy level is corresponding to only one wave function, then such a system is called as non-degenerate system.

We start with the Schrodinger wave equation, which basically describes a single particle, for obtaining the energy values and eigen functions for the 1^{st} order and 2^{nd} order perturbations.

We begin with an unperturbed Hamiltonian $H^{(0)}$ which is also assumed to have no time dependence. It has known eigen functions arising from the time independent Schrodinger equation which is written as.

$$H^{(o)}\psi_{n}^{\nu} = E_{n}^{(o)}\psi_{-n}^{-(o)} \quad \dots \dots \quad (1)$$

Where E_n^o is the energy of the nth level of the system and corresponding eigen function is $\psi_n^{(o)}$. This means eigen values and eigen /functions of the unperturbed problem is E_1^o , $E_2^{(1)}, E_3^{(0)}, \dots, E_n^{(0)}$ and $\psi_1^{(0)}, \psi_2^{(0)}, \psi_3^{(0)}, \dots, \psi_m^{(0)}$ respectively.

For the perturbed system, the eigen function ψ_n satisfies the equation.

$$H\Psi_n = E_n \Psi_n \qquad \dots \dots \dots (2)$$

Where E_n are the energy values of the modified Hamiltonian; representing the operator

$$\hat{H} = \left(\frac{-h^2}{2m}\nabla^2 + v\right) \qquad \dots \dots \dots (3)$$

Let us assume that it is possible to expand H interms of some parameter, giving the expression.

$$H = H^{0} + \lambda H^{(1)} + \lambda^{2} H^{(2)} + \dots \dots (4)$$

8.3

Where H^0 is the unperturbed Hamiltonian and is large compared with $H^{(1)}$ (i.e.) the energy associated with $H^{(0)}$ is large when compared with the energy associated with $H^{(1)}$.

Further it is also assumed that it is possible to expand eigen function ψ_n , and eigen value E_n of the total Hamiltonian of equation (4) in terms of λ as.

in which the quantities $E_n^{(1)}, E_n^{(2)} \dots$ and $\psi_n^{(1)}, \psi_n^{(2)} \dots$ is to be found.

Equations (4), (5) and (6) and now substituted in eq.(3), yielding.

$$[\mathbf{H}^{(0)} + \lambda \mathbf{H}^{(1)}] [\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots] = [\mathbf{E}_n^{(0)} + \lambda \mathbf{E}_n^{(1)} + \lambda^2 \mathbf{E}_n^{(2)} - \dots]$$
$$[\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots]$$

Which in turn gives

$$H^{(0)}\psi_{n}^{(0)} + \lambda(H^{0}\psi_{n}^{(1)} + H^{(0)}\psi_{n}^{(0)}) + \lambda^{2}(H^{(0)}\psi_{n}^{(2)} + H^{(1)}\psi_{n}^{(1)}) + \dots \dots (7)$$
$$= E_{n}^{(0)}\psi_{n}^{(0)} + \lambda(E_{n}^{(0)}\psi_{n}^{(1)} + E_{n}^{(1)}\psi_{n}^{(0)})\lambda^{2}(E_{n}^{(1)}\psi_{n}^{(1)} + E_{n}^{(1)}\psi_{n}^{(1)} + E_{n}^{(2)}\psi_{n}^{(0)}) + \dots \dots (7)$$

The above equation is satisfied for all powers of λ , only if the equal powers of λ on either side are equal. On comparing equal powers of $\lambda^0, \lambda^1, \lambda^2$. ----we get.

For
$$\lambda^0$$
, $H^0 \psi_n^{(0)} = E_n^{(0)} \psi_n 0$ (8)

For
$$\lambda^1$$
, $H^0 \psi_n^{(1)} + H^{(1)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$ (9)

For
$$\lambda^2$$
, $H^{(0)}\psi_m^{(2)} + H^{(1)}\psi_m^{(1)} = E_m^{(1)}\psi_m^{(1)} + E_m^{(2)}\psi_m^{(0)}$ (10)

Equations (8), (9), (10) corresponds to unperturbed, first order perturbation and second order perturbation equation respectively, we can also obtain higher order terms to get more and more accurate corrections to exact solution. Using the equation (9) and (10) we calculate the 1^{st} order and 2^{nd} order energy values and eigen functions respectively.

First Order correction to the energy value $E_n^{\ (1)}$

Taking the eq.(9) we now obtain the first order corrections to the energy value $E_n^{(1)}$.

(i.e)
$$H^0 \psi_n^{(1)} + H^{(1)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$$
(9).

Using the expansion theorem, the perturbed eigen function $\psi_n^{(1)}$ can be expanded interms of the unperturbed eigen function as

Substituting this equation (13) in eq(11), we determine the first order correction, we have.

From the unperturbed system for mth level, we know

so that (13) now rewritten as.

$$\sum_{m} \alpha_{m} E_{m}^{(0)} \psi_{m}^{(0)} + H^{1} \psi_{n}^{(0)} - \sum_{m} \alpha_{m} E_{n}^{(0)} \psi_{m}^{(0)} = E_{n}^{(1)} \psi_{n}^{(0)}$$
(OR)
$$\sum_{m} \alpha_{m} \left(E_{n}^{(0)} - E_{n}^{(0)} \right) \psi_{m}^{(0)} + H^{1} \psi_{n}^{(0)} = E_{n}^{(0)} \psi_{n}^{(0)} \qquad \dots \dots \dots (14)$$

On multiplying both sides with $\psi_n^{(0)^*}$ from left side and integrating over the space integral, we get

$$\int \sum_{m} \alpha_{m} \left(E_{m}^{(0)} - E_{n}^{(0)} \right) \psi_{n}^{(0)^{*}} \psi_{m}^{(0)} d\tau + \int \psi_{n}^{(0)^{*}} H^{1} \psi_{n}^{(0)} d\tau = E_{n}^{(0)} \int \psi_{n}^{(0)^{*}} \psi_{n}^{(0)} d\tau \quad \dots \dots \quad (15)$$

Making use of the orthonormal condition of the wave function

(i.e.)
$$\int \psi_n^{(0)^*} \psi_n^{(0)} d\tau = \delta_{ij}$$

where $\delta_{ij} = 0$ if $i \neq j$
= 1 if $i \neq j$ -----(16)

8.4

Time Independent Perturbation Theory

The equation (15) below:

$$\int \psi_n^{(0)} H^{(1)} \psi_n^{(0)} d\tau = E_n^{(1)}$$
OR
$$E_n^{(1)} = \int \psi_n^{(0)^*} H^1 \psi_n^{(0)} d\tau = H_{nn}^{(1)} \qquad -----(17)$$

$$= \left\langle \psi_n^{(0)} \mid H^1 \mid \psi_n^{(0)} \right\rangle = H_{nn}^{(1)} \qquad -----(17a)$$

8.5

which is first order perturbation of the energy value.

First order correction for wave function $\psi_n{}^{(1)}$

For obtaining the first order wave function $\psi_n^{(1)}$, we once again consider the eq.(11) and multiplying on both sides with $\psi_m^{(0)*}$ from left side and then integrate over the space integral, we get the situation as

$$\int \sum_{m} \alpha_{m} \left[E_{n}^{(0)} - E_{n}^{(0)} \right] \psi_{n}^{(0)^{*}} \psi_{m}^{(0)} d\tau + \int \psi_{m}^{(0)^{*}} H^{(1)} \psi_{n}^{(0)} d\tau$$
$$= \int E_{n}^{(1)} \psi_{m}^{(0)^{*}} \psi_{n}^{(0)} d\tau \qquad -----(18)$$

Using the condition as per eq. (18), we have

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

Now after the first order corrections to energy value and eigen function, we get.

$$E_{n} = E_{n}^{(0)} + \lambda E_{n}^{(1)}$$
$$= E_{n}^{(0)} + \lambda \int \psi_{n}^{(0)} H^{(1)} \psi_{n}^{(0)^{*}} d\tau = E_{n}^{(0)} + \lambda H_{nn}^{(1)} \quad \text{-----}(20)$$
$$\psi_{n} = \psi_{n}^{(0)} + \lambda \psi_{n}^{(1)}$$

$$=\psi_{n}^{(0)}-\lambda\sum_{m=0}^{\alpha}\left[\frac{\int\psi_{n}^{(0)}H^{(1)}\psi_{n}^{(0)}d\tau}{E_{n}^{(0)}-E_{n}^{(0)}}\right]\psi_{n}^{(0)}$$

 $(\Sigma^1 \text{ is written omitting } m=n)$

Second order correction for energy value $E_n^{(2)}$

We consider the eq. (2.1.10) for evaluation $a^2 En^{(2)}$. Again the function $\psi_n^{(2)}$ is expressed as a linear combination of known function $\psi_m^{(0)}$, as

$$\Psi_n^{(2)} = \sum_m \beta_m \Psi_m^{(0)}$$
 -----(22)

On substituting eqs. (22) and (11) in eq.(10), we get

on using eq.(13), we have

Now multiplying both sides of eq. (24) with $\psi_n^{(0)*}$ from left side, and integrating over the space integrals, we get.

8.6

8.7

Applying condition (18) to eq. (25) we get.

$$E_m^{(2)} = \sum_m \alpha_m \int \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau$$
$$= \sum_m \alpha_m \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \sum_m (\alpha_m H_{nn}^{(1)} - \dots - (26))$$

Substituting the value of α_m from eq. (19), we have

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

or $E_n^{(2)} = -\sum_m^1 \frac{H_{nn}^{(1)} H_n^{(1)}}{E_n^{(0)} - E_n^{(0)}}$ ------(27)

Second order correction to eigen function $\psi_n{}^{(2)}$

For obtaining $\underline{\psi_n}^{(2)}$, multiply eq.(24) with $\psi_n^{(0)*}$ on both sides from left; and integrating over the space integral, we get.

$$\sum_{m} \beta_{m} \int \left(E_{m}^{(0)} - E_{n}^{(0)} \right) \psi_{m}^{(0)^{*}} \psi_{m}^{(0)} d\tau$$

$$= \alpha_{m} \sum_{m} \int \psi_{m}^{(0)^{*}} \left(E_{n}^{(1)} - H_{n}^{1} \right) \int \psi_{m}^{(0)} d\tau + E_{n}^{(2)} \int \psi_{m}^{(0)^{*}} \psi_{n}^{(0)} d\tau. \quad -----(28)$$

on using condition (18) again here also, the above equation is reduced to .

$(\Sigma^1 \text{ is used to omit } m=n)$

In order to get the energy values and eigen functions, the values of $E_n^{(1)}$, $E_n^{(2)}$ and $\psi_n^{(1)}$, $\psi_n^{(2)}$ are substituted from the equation (17), (27) and (19a), (30) in the following equation.

$$E_{n}^{(0)} = E_{n}^{(0)} + \lambda E_{n}^{(1)} + \lambda^{2} E_{n}^{(2)}$$
$$\psi_{n} = \psi_{n}^{(0)} + \lambda \psi_{n}^{(1)} \lambda^{2} \psi_{n}^{(2)}$$

Using the above theoretical considerations, the corresponding 1^{st} order and 2^{nd} corrections to the perturbed system can be calculated.

Proceeding in the above manner, we can evaluate higher order corrections for the perturbed systems to more and more accuracy.

8.3 TIME INDEPENDENT PERTURBATION ON THEORY FOR NON-DEGENERATE SYSTEM:

In this we take up the following examples and evaluate the perturbed energy and eigen function.

- (i) The perturbed Harmonic oscillator.
- (ii) The Normal Helium atom.

i) The Perturbed Harmonic Oscillator

Let us consider the wave equation for the perturbed Harmonic oscillator in one dimensions as.

This equation reduces to Harmonic oscillator wave equation if the constants a and b are zero. Assuming a and b are small, we treat these terms as perturbation.

(i.e.)
$$H^{(1)} = ax^3 + bx^4$$
(32)

Let us calculate the first order correction to the energy $En^{(1)}$ given by eq.(17)

8.9

(i.e.).
$$E_n^{(1)} = \int_{\alpha} \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau$$

$$\int_{-\alpha}^{\alpha} \psi_n^{(0)^*} ax_3 \psi_m^0 d\tau + \int_{-\alpha}^{\alpha} \psi_n^0 bx^4 \psi_n^{(0)} d\tau ----(33)$$

Since the first integral on the right side is an odd function as x^3 is odd and $\psi_n^{(0)*}\psi_n^{(0)}$ is even function, over a symmetrical limits whose value is zero. As such the value of the first integral is zero (i.e.) first order perturbation due to ax^3 is zero.

Hence
$$E_n^{(1)} = b \int_{-\alpha}^{\alpha} \psi_n^{(0)^*} x^4 \psi_n^{(0)} d\lambda$$
(34)

From the knowledge of the linear Harmonic oscillator, whose wave function is given by .

$$\psi_n^{(0)^*}(x) = N_n H_n(\xi) \exp\left[-\xi^2/2\right] \dots (35)$$

Where $\xi = \alpha x \& \alpha = \left(\frac{mk}{x^2}\right)^{\frac{1}{4}} andh^2 = m\omega^2$

Substituting (5) in eq. (4) we get.

$$E_{n}^{(1)} = b \int_{-\alpha}^{\alpha} N_{n}^{2} H_{n}^{2}(\xi) e^{-\xi^{2}} \left(\frac{\xi^{4}}{\alpha^{4}} \right) \left(\frac{d\xi}{\alpha} \right)$$
$$= b \frac{N_{n}^{2}}{\alpha^{5}} \int_{\alpha}^{p} H_{n}^{2}(\xi) e^{-\xi^{2}} \xi^{4} d\xi \dots (36)$$

For evaluating this integral, consider the following recurrence relations from Hermite polynomials.

$$\xi H_n(\xi) = \frac{1}{2} H_n + 1(\xi) + n H_n - 1(\xi) \dots (37)$$

or $\xi^2 H_n(\xi) = \frac{1}{2} \xi H_n(+1(\xi) + n \xi H_n - 1(\xi) \dots (38))$

Replaying n=n+1 and n=n-1 in eq.(2.1.38), we have

Now Substituting eqs. (39) and (40) in eq. (38), we get.

Squaring and substituting in eq. (2.1.36), we have

$$E_n^{(1)} = b \cdot \frac{N_n^2}{\alpha^5} \int_{\alpha^5}^{\alpha-\xi^2} \left[\frac{1}{4} H_{n+2}(\xi) + (n+\frac{1}{2}) + n(n-1)H_{n-2}(\xi) \right]^2 d\xi \qquad \dots \dots (42)$$

From Hermite polynomials, we know that

$$\int_{-\alpha}^{\alpha} e^{-\xi^{2}} H_{n}(\xi) H_{m}(\xi) d\xi = 0 \text{ if } m \neq m$$
$$= 2^{\wedge} n! \sqrt{\pi} \quad \text{if } m = n.....(42)$$

Using those result in eq.(2.1.42), it becomes

$$E_n^{(1)} = b \cdot \frac{N_n^2}{\alpha^5} \sqrt{\pi} \left\{ \frac{1}{16} \left(n+2 \right)! 2^{n+2} + \left(n+\frac{1}{2} \right)^2 n! 2^n (n-1)^2 2^{n-2} (n-2)! \right) \right.$$
$$= \left[\frac{\alpha}{\prod^{\frac{1}{2}} 2^n n!} \right] \frac{1}{\alpha^5} \sqrt{\pi} \left\{ \frac{1}{16} (n+2)^{\frac{n+2}{2}} + \left(n+\frac{1}{2} \right) (n!) 2^n + n^2 (n-1)^2 2^{n-2} (n-2)! \right\}$$

Where we used the normalized function of Harmonic oscillator.

N_n value as
$$N_n = \left[\frac{\alpha}{\pi^{\frac{1}{2}}2^n n!}\right]$$

On simplification, we get

$$E_n^{(1)} = b \cdot \frac{3}{4\alpha^4} (2n^2 + 2n + 1)$$

Now the total energy to first order becomes.

$$E_n = E_n^{(0)} + E_n^{(1)} = (n + \frac{1}{2})\hbar\omega_c + \frac{3b}{4}\frac{\lambda^2\hbar^2}{mK}(2n^2 + 2n + 1)$$

ii) The Normal Helium Atom:

Helium atom consists of a nucleus of charge Ze at the origin and two electrons with radius vectors r_1 and r_2 as shown in Fig. (1)



Neglecting the motion of the nucleus, the Hamiltonian of the system is written as.

In which ∇_1 and ∇_2 represent the coordinates of electrons 1 and 2 respectively.

Now, the wave equation for the two electrons is written as

$$\nabla_1^2 \psi + \nabla_2^2 \psi + \frac{2m}{\hbar^2} \left[E + \frac{ze^2}{r_1} + \frac{ze^2}{r_2} - \frac{e^2}{r_{12}} \right] \psi = 0 \quad \dots \dots (44)$$

The term $\frac{e^2}{r_{12}}$ is considered as the perturbed term, since omitting this term, the above

equation can be exactly solved. Hence, the perturbed Hamiltonian is written as.

$$H^{(1)} = \frac{e^2}{r_{12}}$$
(45)

Separately writing the unperturbed wave equation into two equation by substituting.

 $\psi^{0}(x_{1}y_{1}z_{1}, x_{2}y_{2}z_{2}) = v_{1}^{0}(x_{1}y_{1}z_{1})u_{2}^{0}(x_{2}y_{2}z_{2})$(46)

In polar coordinates r_1 , θ_1 , ϕ_1 , and r_2 , θ_2 , ϕ_2 to the normal state, the wave function is:

$$\psi_{100,100}^{(0)} = \psi_{100}^{0}(r_{1}\theta_{1}\phi_{1})\psi_{100}^{(0)}(r_{2}\theta_{2}\phi_{2})\dots(47)$$
$$= u_{1}^{0}(r_{1}\theta_{1}\phi_{1})u_{2}^{(0)}(r_{2}\theta_{2}\phi_{2})$$

and the corresponding energy value is:

$$E_{100,100}^{(0)} = E_1^{(0)} + E_2^{(0)} = -2Z^2 E_{++} \quad \dots (48)$$

Where E_H is the energy corresponding to one electron = $\frac{me^4}{2\hbar^2} = 13.6eu$

The first order perturbed energy function $E^{(1)}$ is the average value of the perturbation function $H^{(1)}$ over the unperturbed state of the system. Hence, First order correction to the ground state energy is

$$E^{(1)} = \int \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau = \int \frac{e^2}{r_{12}} \left[\psi_{100,100}^{(0)} \right]^2 d\tau \dots (49)$$
$$= \int \int u_1^{(0)^*} u_2^{(0)^*} \frac{e^2}{r_{12}} u_1^{(0)} u_2^{(0)} d\tau_1 d\tau_2$$

We know that

in which
$$\rho_1 = \frac{2Zr_1}{a_0}$$
 and radius $r_0 = \frac{\hbar^2}{4\pi^2 me^2}$

and space integral $d\tau$ is

$$d\tau = d\tau_1 d\tau_2 = r_1^2 dr_1 Sin\theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 Sin\theta_2 d\theta_2 d\phi_2$$

on substituting (49) in energy equation (50), we get

$$E^{(1)} = \frac{Z^6 e^2}{\pi^2 a_0^6} \int \int \frac{1}{r_{12}} \exp\left[-\frac{2Z}{a_0}(r_1 + r_2)\right] d\tau_1 d\tau_2 \dots \dots (52)$$

Evaluation of the integral in eq.(50) may be done by expanding $\frac{1}{r_{12}}$ in terms of legendre

polynomials and hence the value of the integral leads to a value of $\frac{5ZE_H}{4}$ for the first order

correction to the ground state.

The energy corrected to first order is then given by:

$$E = -2Z^{2}E_{H} + \frac{5}{4}Z.E_{H} = -\left[2Z^{2} - \frac{5}{4}Z\right]E_{H}$$

It may be noted that $E^{(1)}$ is about 31% of $E^{(0)}$, since

$$\frac{E^{(1)}}{E_0} = \frac{5ZE_{H/4}}{2Z^2E_H} = \frac{5}{8Z}$$

The correction is subtractive which is understandable since the effect of the electron-electron contraction is to reduce the electron nucleus attraction. Then the result holds good for two electron atoms like Li^+ , B_{e}^{++} , B^{3+} etc., with Z= 3,4,5

8.4 TIME INDEPENDENT PERTURBATION THEORY FOR DEGENERATE SYSTEM:

An energy level is called α -fold degenerate when these exist α linearly independent wave functions such as $\psi_{k1}, \psi_{k2}, \dots, \psi_{k\alpha}$ satisfying the wave equation.

Clearly, we can explain this if we have α eigen function $\psi_{k1}^{(0)}, \psi_{k2}^{(0)}\psi_{k3}^{(0)}, \dots, \psi_{k\alpha}^{(0)}$ corresponding

to the eigen state $E_k^{(0)}$. Such that there is no relation of the form.

$$C_{1}\psi_{k1}^{(0)} + C_{2}\psi_{k2}^{(0)} - 1 - \dots - C_{\alpha}\psi_{k\alpha}^{(0)} = 0 \dots (53)$$

connecting them, then we say that the α eigen functions are linearly independent and this eigen state $E_k^{(0)}$ is α fold degenerate.

We have shown earlier that eigen functions belonging to different eigen values are orthogonal, however eigen functions belonging to the same eigen value need not be orthogonal.

Let, in the perturbed state, the Schrodinger wave equation be given by

$$H\psi = E\psi$$
(54)

Where H is the perturbed Hamiltonian, E the perturbed energy and ψ the perturbed wave function.

Now, the perturbed Hamiltonian can be expressed in terms of unperturbed Hamiltonian $H^{(0)}$ as.

Let us assume $\psi_{k1}^{(0)}, \psi_{k2}^{(0)}, \dots, \psi_{k\alpha}^{(0)}$ are not orthogonal. We have,

$$H^{0}\psi_{k1}^{(0)} = E_{k}^{(0)}\psi_{k1}^{(0)}, H^{0}\psi_{k2}^{(0)} = E_{k}^{(0)}\psi_{k2}^{(0)}....H^{0}\psi_{k\alpha}^{(0)} = E_{k}^{(0)}\psi_{k\alpha}^{(0)}$$

Consider the linear combination X_k^0

$$C_{1}\psi \begin{pmatrix} 0 \\ k1 \end{pmatrix} + C_{2}\psi \begin{pmatrix} 0 \\ k2 \end{pmatrix} \dots C_{\alpha}\psi \begin{pmatrix} 0 \\ k\alpha \end{pmatrix} = X \begin{pmatrix} 0 \\ k \end{pmatrix} \dots (56)$$

so that we have

$$H^{0}X_{k}^{(0)} = C_{1}E_{k}^{(0)}\psi_{k1}^{(0)} + C^{2}E_{k}^{(0)}\psi_{k2}^{(0)} + \dots + C_{\alpha}E_{k2}^{(0)}\psi_{k\alpha}^{(0)} \dots$$

$$= E_{k}^{0}X_{k}^{0}$$
(57)

which proves that the linear combination X_k^0 is also an eigen function corresponding to the same degenerate energy value.

We can choose the constants in eq.(56) in an infinite number of ways, we can construct infinite number of such linear combinations, all of them being eigen function of the same eigen value. There is nothing unique about any set of eigen functions for a degenerate level.

For instance, we can select the following α linear combination:

$$X_{k1}^{(0)} = C_{11}\psi_{k1}^{(0)} + C_{12}\psi_{k2}^{(0)} + \dots + C_{1\alpha}\psi_{k\alpha}^{(0)}$$

$$X_{k2}^{(0)} = C_{21}\psi_{k1}^{(0)} + C_{22}\psi_{k2}^{(0)} + \dots + C_{2\alpha}\psi_{k\alpha}^{(0)}$$

$$X_{k\alpha}^{(0)} = C_{\alpha1}\psi_{k1}^{(0)} + C_{\alpha2}\psi_{k2}^{(0)} + \dots + C_{\alpha\alpha}\psi_{k\alpha}^{(0)}$$

which may be represented as :

$$x_{kl}^{(0)} = \sum_{l=1}^{\alpha} C_{ll} \psi_{kl}^{(0)}$$
 (l=1,2,3,.....a)59.

These combinations are entirely equivalent to the original set $\psi_{k1}^{(0)}, \psi_{k2}^{(0)}, \dots, \psi_{k\alpha}^{(0)}$. The transformation expressed by eq. (59) is known as linear transformation with constant coefficients. With this background about degenerate states, we now discuss the perturbation for such states.

The wave equation for unperturbed system is:

There are severed eigen states for this unperturbed system, each of them corresponding to several degenerate eigen function as

Energy value eigen functions.

$$E_{0}^{(0)} \psi_{01}^{(0)}, \psi_{02}^{(0)}, \psi_{03}^{(0)}, \dots, \psi_{0\alpha}^{(0)}$$

$$E_{1}^{(0)} \psi_{01}^{(0)}, \psi_{12}^{(0)}, \dots, \psi_{0\alpha}^{(0)}$$

$$E_{k}^{(0)} \psi_{k1}^{(0)}, \psi_{k2}^{(0)}, \dots, \psi_{0\alpha}^{(0)}$$

We can assume the linear combination of eq.(59), provided the function ψ_{kl} is:

$$\psi_{kl} = \psi_{kl} + \lambda \psi_{kl}^{(1)} + \lambda^2 \psi_{kl}^{(2)}$$
(61)

and
$$E_{kl} = E_k^{(0)} + \lambda E_{kl}^{(1)} + \lambda^2 E_{kl}^{(2)}$$
(62)

Now substitute the values of H, ψ_{kl} , E_{kl} from equation (55), (61) and (62) the perturbed equation given by

8.16

We have

$$\left(H^{0} + \lambda H^{(1)} + \lambda^{2} H^{(2)} + \dots \right) \left(X_{kl}^{(0)} + \lambda \psi_{kl}^{(1)} + \lambda^{2} \psi_{kl}^{(2)} + \dots \right)$$
$$- \left(E_{k}^{0} + \lambda E_{kl}^{(1)} + \lambda^{2} E_{kl}^{(2)} + \dots \right) \left(X_{kl}^{(0)} + \lambda \psi_{kl}^{(1)} + \lambda^{2} \psi_{kl}^{(2)} + \dots \right) = 0$$

Rewriting the above.

We now take up the first order perturbation equation, which can be obtained by equating coefficient of λ equal to zero.

(i.e.)
$$H^{0}\psi_{kl}^{(1)} + H^{1}\psi_{kl}^{(0)} - E_{k}^{(0)}\psi_{kl}^{(0)} - E_{kl}^{(1)}X_{kl}^{(0)} = 0$$
(65)

Let us expand $\psi_{kl}^{(1)}$ as.

On substituting equation (66) and (59) in equation (65)

We get

$$\sum C_{klk^{1}l^{1}} H^{(0)} \psi_{k^{1}l^{1}}^{(0)} + \sum_{l=1}^{\alpha} C_{kl} H^{(1)} \psi_{kl^{1}}^{(0)} - \sum_{k^{1}l^{1}} C_{klk^{1}l^{1}} E_{k}^{(0)} \psi_{k^{1}l^{1}}^{(0)} - \sum_{l=1}^{\alpha} C_{ll^{1}} E_{kl}^{(1)} \psi_{kl^{1}}^{(0)} = 0$$

Since $H^{(0)}\psi_{k^{l}l^{l}}^{(0)} = E_{k^{l}}^{(0)}\psi_{k^{l}l^{l}}^{(0)}$ we have after recommendation.

Multiplying both sides with $\psi_{kj}^{(0)^*}$ from left, and integrating over configuration space

8.17 Time Independent Perturbation Theory

when $k^1 \neq k$, $\int \psi_{kj}^{(0)} \psi_{kll}^{(0)} d\tau = 0$ and when $k = k^1$, $E_{k}^{(0)} - E_{k}^{(0)} = 0$ L.H.S. reduces to zero.

So that eq....(69)

We use the notation

and since $\psi_{kl}^{(0)}, \psi_{k2}^{(0)}, \dots, \psi_{k\alpha}^{(0)}$ are non-orthogonal.

we introduce the symbol $\Delta_{jl^1} = \int \psi_{kj}^{(0)} \psi_{kl^1}^{(0)} d\tau$ (71)

Using the above symbols, eq. (69) becomes

$$\sum_{l=1}^{\alpha} C_{ll} (E_{kl}^{1} \Delta_{jl} - H_{jl}^{(1)}) = 0$$

or
$$\sum_{l=1}^{\alpha} C_{ll} C_{ll} (H_{jl}^{(1)} - E_{kl}^{(1)} \Delta_{jl}) = 0$$
(72)

As there are α eigen functions $\psi_{k1}^{(1)}, \psi_{k2}^{(0)}, \dots, \psi_{k\alpha}^{(0)}$ we can similarly get α equations like eq.(72) for j=0,1,2,3.... α Eq.(72) represents a system of α homogeneous linear simultaneous equation in α unknown quantities

In the expanded from, these α equations are.

$$(H_{11}^{1} - E_{kl}^{(1)}\Delta_{11})C_{11} + (H_{12}^{(1)} - E_{kl}^{(1)}\Delta_{12})C_{12} + \dots + (H_{1\alpha}^{(1)} - E_{kl}^{(1)}\Delta_{1\alpha})C_{1\alpha} = 0$$

$$(H_{21}^{1} - E_{kl}^{(1)}\Delta_{21})C_{21} + (H_{22}^{(1)} - E_{kl}^{(1)}\Delta_{22})C_{22} + \dots + (H_{2\alpha}^{(1)} - E_{1l}^{(1)}\Delta_{2\alpha})C_{2\alpha} = 0 \quad \dots \dots (73)$$

$$(H_{\alpha 1}^{1} - E_{kl}^{(1)}\Delta_{\alpha 1})C_{\alpha 1} + (H_{\alpha 2}^{(1)} - E_{kl}^{(1)}\Delta_{\alpha 2})C_{\alpha 2} + \dots + (H_{\alpha \alpha}^{(1)} - E_{kl}^{(1)}\Delta_{\alpha \alpha})C_{\alpha \alpha} = 0$$

To understand how this set of equations is solved, a knowledge of determinations and their use in solving such equations is necessary, if such a set of homogeneous linear equations is to have non-zero solutions is that the determinant of the coefficients of the unknown quantities vanish i.e.

$$H_{11}^{(1)} - E_{kl}^{(1)} \Delta_{11} H_{12}^{(1)} - E_{kl}^{(1)} \Delta_{12} \dots H_{\alpha}^{(1)} - E_{kl}^{(1)} \Delta_{1\alpha}$$

$$H_{21}^{(1)} - E_{kl}^{(1)} \Delta_{12} H_{22}^{(1)} - E_{kl}^{(1)} \Delta_{22} \dots H_{2\alpha}^{(1)} - E_{kl}^{(1)} \Delta_{2\alpha}$$

$$= 0 \quad (74)$$

$$H_{\alpha 1}^{(1)} - E_{kl}^{(1)} \Delta_{\alpha 1} H_{\alpha 2}^{(1)} - E_{kl}^{(1)} \Delta_{2\alpha} \dots H_{\alpha \alpha}^{(1)} - E_{kl}^{(1)} \Delta_{\alpha \alpha}$$

Using the condition $\Delta_{jl}^{l}=0$ if $j\neq l^{1}$

= 1 if $j = \Delta_{jl}$.

We have

$$(H_{11}^{1} - E_{kl}^{(1)}) H_{12}^{(1)} \dots H_{1\alpha}^{(1)}$$

$$H_{21}^{(1)} (H_{22}^{(1)} - E_{kl}^{(1)}) \dots H_{2\alpha}^{(1)}$$

$$= 0 \dots (75)$$

$$H_{\alpha 1}^{(1)} H_{2\alpha}^{(1)} \dots H_{\alpha \alpha}^{(1)} - E_{kl}^{(1)}$$

equation (74) and (75) are known as secular equation.

If the secular equation is in diagonal form that is all the elements except on the principal diagonal are zero, then the initially assumed eigen functions $\psi_{k1}^{(0)}, \psi_{k2}^{(0)}, \dots, \psi_{k\alpha}^{(0)}$ are themselves the correct zeroth order wave functions.

The secular equation in which all the elements on the principal diagonal is in the form.

0 0 0----- $H_{\alpha\alpha}^{(1)} - E_{kl}^{(1)}$

then its expansion is

$$(H_{11}^{(1)} - E_{kl}^{(1)})(H_{22}^{(1)} - E_{kl}^{(1)}) - - - - - (H_{\alpha\alpha}^{(1)} - E_{kl}^{(1)}) = 0$$

The roots of the equation are:

$$E_{kl}^{(1)} = H_{11}^{(1)}, H_{22}^{(1)}, - - - - - H_{\alpha\alpha}^{(1)}$$

In such a case, all the coefficients $C_{l1}, C_{l2}, \ldots, C_{l\alpha}$ turn out to the zero.

Equation (25) may be written in another useful from by making use of the substitution.

$$H_{ij} = H_{ij}^{(0)} + \lambda H_{ij}^{(1)}$$
 or $H_{ij}^{(1)} = \frac{H_{ij} - H_{ij}^{(0)}}{\lambda}$

and $E_{kl} - E_{k}^{(0)} + \lambda E_{kl}^{(1)}$ or $E_{kl}^{(1)} = \frac{E_{kl} - E_{k}^{0}}{\lambda}$

After taking $\alpha t 1/\lambda$ and using.

$$H_{jl}^{(0)} = 0$$
 if $j \neq l$
= $E_k^{(0)}$ if $j = l$.

With the above eq. (75) becomes

Observing the equations (24) and (25), we note that if a perturbation has non-vanishing matrix elements H_{ij} among a set of degenerate states, then it will change the wave function in the zeroth order. If the set of wave functions is non-degenerate on the other hand. The perturbation effect the wave functions only in the first and second orders.

8.5 SUMMARY:

Perturbation theory is an extremely important tool for describing real quantum systems, as it turns out to be very difficult to find exact solutions to the Schrodinger equation for Hamiltonians of even moderate complexity, most of the Hamiltonians to which we know exact solutions, such as the hydrogen atom, the quantum harmonic oscillator and the particle in a box, are too idealized to adequately describe most systems. Using perturbation theory, we can use the known solutions of these simple Hamiltonians to generate solutions for a wide range of more complicated systems.

8.6 TECHNICAL TERMS:

Time Independent Perturbation Theory, Time Independent Perturbation Theory for Non Degenerate System, Time Independent Perturbation Theory for Degenerate System.

8.7 SELF-ASSESSMENT QUESTIONS:

- 1) Explain about the Time independent perturbation theory.
- 2) Explain about the Degenerate system of Time independent perturbation theory.
- 3) Explain about the Non-Degenerate system of Time independent perturbation theory

8.8 SUGGESTED READINGS:

- 1) Quantum Mechanics G. Aruldhas. (Prentice-Hall of India)
- 2) Quantum Mechanics-Theory and applications A.K.Ghatak and S.Lokanathan (Macmillan)
- 3) Quantum Mechanics Gupta, Kumar & Sharma.
- 4) Quantum Mechanics E.Merzbacher.
- 5) Principles of Quantum Mechanics R.Shankar (Plenum Press)

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LESSON-9

APPLICATIONS TO NORMAL HELIUM ATOM AND STARK EFFECT

9.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept of Application to normal helium atom and Stark effect. The chapter began with understanding of Application to normal helium atom and Stark effect. After completing this chapter, the student will understand the complete idea about Application to normal helium atom and Stark effect

STRUCTURE:

- 9.2 Application to Normal Helium Atom
- 9.3 Application to Stark Effect
- 9.4 Summary
- 9.5 Technical Terms
- 9.6 Self Assessment Questions
- 9.7 Suggested Readings

9.1 INTRODUCTION:

The **Stark effect** refers to the splitting and shifting of atomic energy levels when an atom is placed in an external electric field. In the case of a **normal helium atom (He)**, which consists of two protons, two neutrons, and two electrons, the Stark effect offers valuable insights into its electronic structure and behavior under external influences. Helium is particularly interesting because, unlike hydrogen (with only one electron), it has two electrons, leading to more complex interactions and a richer variety of phenomena when subjected to an external electric field.

9.2 APPLICATION TO NORMAL HELIUM ATOM:

The Normal Helium atom:

Helium atom consists of a nucleus of charge Ze at the origin and two electrons with radius vectors r_1 and r_2 as shown in Fig. (1)



9.2

Fig. 9.1

Neglecting the motion of the nucleus, the Hamiltonian of the system is written as.

in which ∇_1 and ∇_2 represent the coordinates of electrons 1 and 2 respectively.

Now, the wave equation for the two electrons is written as

The term $\frac{e^2}{r_{12}}$ is considered as the perturbed term, since omitting this term, the above

equation can be exactly solved. Hence, the perturbed Hamiltonian is written as.

$$H^{(1)} = \frac{e^2}{r_{12}}$$
 ------ (3)

Separately writing the unperturbed wave equation into two equation by substituting.

$$\psi^{0}(x_{1}y_{1}z_{1}, x_{2}y_{2}z_{2}) = \psi^{0}_{1}(x_{1}y_{1}z_{1})u^{0}_{2}(x_{2}y_{2}z_{2}) \quad ----- (4)$$

In polar coordinates r_1 , θ_1 , ϕ_1 , and r_2 , θ_2 , ϕ_2 to the normal state, the wave function is:

$$\psi_{100,100}^{(0)} = \psi_{100}^{0} (r_1 \theta_1 \phi_1) \psi_{100}^{(0)} (r_2 \theta_2 \phi_2) \qquad -----(5)$$

$$= u_1^0 (r_1 \theta_1 \phi_1) u_2^{(0)} (r_2 \theta_2 \phi_2)$$

and the corresponding energy value is:

$$E_{100,100}^{(0)} = E_1^{(0)} + E_2^{(0)} = -2Z^2 E_{++}$$
 (6)

Where E_H is the energy corresponding to one electron = $\frac{me^4}{2\hbar^2} = 13.6eu$

The first order perturbed energy function $E^{(1)}$ is the average value of the perturbation function $H^{(1)}$ over the unperturbed state of the system. Hence, First order correction to the ground state energy is

We know that

in which $\rho_1 = \frac{2Zr_1}{a_0}$ and radius $r_0 = \frac{\hbar^2}{4\pi^2 m e^2}$

so that
$$\psi_{100,100}^{(0)} = \frac{Z^3}{\pi a_0^3} e^{-\frac{a_1}{2} - \frac{p_2}{2}} p$$
 ------(9)

and space integral $d\tau$ is

$$d\tau = d\tau_1 d\tau_2 = r_1^2 dr_1 Sin\theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 Sin\theta_2 d\theta_2 d\phi_2$$

on substituting (2.1.51) in energy equation (10), we get

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Evaluation of the integral in eq.(2.1.52.) may be done by expanding $\frac{1}{r_{12}}$ in terms of legendre polynomials and hence the value of the integral leads to a value of $\frac{5ZE_H}{4}$ for the first order correction to the ground state.

The energy corrected to first order is then given by :

$$E = -2Z^{2}E_{H} + \frac{5}{4}Z.E_{H} = -\left[2Z^{2} - \frac{5}{4}Z\right]E_{H}$$

It may be noted that $E^{(1)}$ is about 31% of $E^{(0)}$, since

$$\frac{E^{(1)}}{E_0} = \frac{5ZE_{H/4}}{2Z^2E_H} = \frac{5}{8Z}$$

The correction is subtractive which is understandable since the effect of the electron-electron contraction is to reduce the electron nucleus attraction. Then the result holds good for two electron atoms like Li⁺, B_e^{++} , B^{3+} etc.,with Z= 3,4,5

9.3 APPLICATION TO STARK EFFECT IN HYDROGEN ATOM:

Stark effect of Hydrogen atom:

When an atom is placed in a uniform electric field, the energy levels are shifted. The shifting of energy levels produce a splitting of spectral line, called stark effect which was first observed in 1913 by stark in hydrogen atom.

Let us consider the first order change in energy levels of a hydrogen atom due to an external electric field of strength, E, along the positive Z-axis which is polar axis whose coordinates are $Z=rCos\theta$.

For the hydrogen atom, the unperturbed Hamiltonian is given as

$$H^{(0)} = \frac{-\lambda^2}{2\mu} \nabla^2 - \frac{e^2}{r}$$
 (12)

Where μ is the reduced mass.

9.5 Applications to Normal Helium Atom..

Now considering the perturbation H⁽¹⁾ is taken as

$$H^{(1)} = +eEz = +eErCos\theta \qquad -----(13)$$

in which e is electric charge and the external electric field E.

In case of hydrogen atom, potential energy and wave function are spherically symmetric. Now, the parity of the spherical harmonics depends on the azimuthal quantum number $\frac{1}{l}$ as (-1)¹, which gives odd parity, if $\frac{1}{l}$ is odd and even parity when 1 is even. Further, even if parities were different, matrix elements connecting states with different m values also vanish, making the interaction impotent to split m-degeneracy.

For the ground state of the hydrogen atom(n=1,l=0,m=0), the wave function is spherically symmetric and has the same form for all orientation, there is no degeneracy.

The ground state wave function for hydrogen atom is

$$\psi_{100} = R_{10}(r) Y_{00}(\theta, \phi)$$

$$=R_{10}(r)\frac{1}{\sqrt{4\pi}}$$
 ------(14)

The perturbation $H^{(1)}$ has the odd parity according the eq. (15)

$$H_{100,100}^{(1)} = \int \psi_{100} H^{(1)} \psi_{100} d\tau = 0$$

In order to understand the above, we have

$$\mathbf{H}^{(1)} = +\mathbf{e}\mathbf{E}\mathbf{r}\mathbf{C}\mathbf{o}\mathbf{s}\mathbf{\theta}$$

The first order perturbation energy in the ground state of Hydrogen atom is.

$$H_{100,100}^{(1)} = +eE \int \int \psi_{100}(+r\cos\theta)\psi_{100}r^2 \sin\theta d\theta dr d\phi$$

where $\psi_{100} = R_{10} Y_{00} (\theta, \phi)$

and
$$Y_{00}(\theta,\phi) = N_{00} P_0^0(\cos\theta) \Phi_0(\phi) = \frac{1}{\sqrt{4\pi}}$$

$$\therefore \phi_0(\phi) = \frac{1}{\sqrt{2\pi}} p_0^0(\cos\theta) = .1$$

$$N_{00} = \frac{1}{\sqrt{2}}$$

R₁₀(r) =
$$\left[\frac{2^2}{a_0}\right]^{\frac{1}{2}} \cdot \exp(\frac{-r}{a_0})$$

so that $\psi_{100} = \left[\frac{2^2}{a_0}\right]^{\frac{1}{2}} ... \exp(\frac{-r}{a_0}) ... \frac{1}{\sqrt{4\pi}}$

Now
$$\lambda H_{100,100}^{(1)} = +eE \int_{0}^{\alpha} \int_{0}^{2\pi\pi} \int_{0}^{\pi} rCos\theta \frac{1}{\pi a_0^3} e^{\frac{-2r}{a_0}} r^2 Sin\theta dr d\theta d\theta = 0$$
 ------(16)

Thus we observe that there is no first order stark effect to the ground state of the hydrogen atom.

The first excited state (n=R) of hydrogen atom is four-fold degenerate since it has the (l,m) values (0,0), (1,0),(1,1) and (1,-1). Let the electric field E is applied along the positive Z-axis which interacts with the electric dipole moment giving the perturbing Hamiltonian, $H^{(1)}=eEZ=erECos\theta$.

With the help of the quantum number (n l m), the four-fold degenerates states are specified as

$$\psi(nlm): \psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}$$

As the degeneracy is four-fold. We have to evaluate sixteen matrix elements of $H^{(1)}$ in the perturbation theory for degenerate states.

Clearly, we write the above four wave function as.

$$\psi_{200} = R_{20}(r)Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}R_{20}(r)$$
 ------(17)

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$$\psi_{210} = R_{21}(r)Y_{10}(\theta,\phi) = \frac{3}{\sqrt{4\pi}}R_{21}(r)Cos\theta$$
 ------(18)

$$\psi_{211} = R_{21}Y_{11} = \sqrt{\frac{3}{8\pi}}R_{21}(r)Sin\theta e^{i\phi}$$
 ------(19)

$$\psi_{2,1,-1} = R_{21}Y_{1,-1} = \sqrt{\frac{3}{8\Pi}} Sin\theta e^{-i\phi} R_{21}(r)$$
 ------ (20)

In these ψ_{200} has even parity and $\psi_{210}, \psi_{211},$ and $\psi_{2.1.\text{--}1}$ have odd parity.

Writing down the secular equation with the sixteen matrix elements, we have.

$$H_{200,200}^{(1)} - E H_{200,211}^{(1)} H_{200,211}^{(1)} H_{200,21,-1}^{(1)}$$

$$H_{211,200}^{(1)} H_{211,211}^{(1)} - E H_{211,210}^{(1)} H_{211,21,-1}^{(1)}$$

$$H_{210,200}^{(1)} H_{210,211}^{(1)} H_{210,211}^{(1)} - E H_{210,21,-1}^{(1)}$$

$$H_{21,-1,200} H_{21,-1,211}^{(1)} H_{21,-1,210}^{(1)} H_{21,-1,21,-1}^{(1)} - E^{(1)}$$

Since ψ_{200} and ψ_{200} have even parity. He element of the secular determinant.

Similar to the equation (22)

In a similar way,

$$H_{211,211}^{(1)}, H_{210,210}^{(1)}, H_{21,-1,21,-1}^{(1)}$$
 are Zero

That means the four diagonal elements of matrix are Zero since they correspond to same parity.

Now the off-diagonal elements between states of different in values (i.e.)

$$H_{21,210}^{(1)}; H_{21,21,-1}^{(1)}; H_{210,21,-1}^{(1)}; H_{210,21,-1}^{(1)}; H_{21,-1,211}^{(1)}; H_{21,-1,210}^{(1)}; H_{200,21,1}^{(1)}; H_{200,21,-1}^{(1)}; and H_{21,-1,200}^{(1)}; H_{200,21,-1}^{(1)}; H_{200,2$$

are also Zero since.

Hence, out of the sixteen matrix elements, the only two matrix elements remains non-Zero are $H_{200,210}^{(1)}$ and $H_{210,200}^{1}$ These two are again symmetrical, it is enough if we valuate one element out of the two.

Let us consider.

For which

$$\psi_{200} = \frac{1}{\sqrt{4\pi}} R_{20} / r)$$

The evaluation of $R_{20}^{(r)}$ is taken up from the radial part of the hydrogen atom wave function.

$$R_{nl}(r) - \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n \left\{ (n+l)! \right\}^3} \right]^{\frac{1}{2}} \cdot \exp(\frac{-Zr}{na_0}) \cdot \left(\frac{2Zrl}{na_0} \right) \cdot \left(\frac{2l+1}{n+l} \left(\frac{2Zr}{na_0} \right) \right)$$

Which in turn gives

$$R_{20}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \cdot \left(2\frac{-r}{(2-\frac{r}{a_0})}\exp(\frac{-r}{2a_0}\right)$$

so that

In a similar way

$$\psi_{210} = \sqrt{\frac{3}{4\pi}} Cos \theta R_{21}(r)$$

$$=\sqrt{\frac{3}{4\pi}}\cos\theta(\frac{1}{Ra_0})^{\frac{3}{2}}\cdot\frac{r}{a_0\sqrt{3}}\cdot\exp(\frac{-r}{2a_0})$$
 ------(26)

Where a_0 is the radius of the first Bohr orbit

Substituting the values of (36) and 37in eq.(35) gives.

Now

$$\int_{0}^{\pi} \cos^{2}\theta \sin \theta d\theta = -\int_{0}^{\pi} \cos^{2}\theta d(\cos \theta) = -\frac{\cos^{3}\theta}{3} = -\left[\frac{-1}{3} - \frac{1}{3}\right] = \frac{2}{3}$$

$$\int_{0}^{2\pi} d\phi = 2\pi$$

$$\int_{0}^{a} \left(\frac{1}{2a_{0}}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_{0}}\right)^{\frac{3}{2}} \cdot \frac{r}{a_{0}\sqrt{3}} e^{\frac{-r}{2a_{0}}} e^{x^{3}} dr.$$

$$= \left(\frac{1}{2a_{0}}\right)^{3} \cdot \frac{1}{a_{0}\sqrt{3}} \left[\int_{0}^{\alpha} (2 - x) e^{x} \cdot a_{0}^{4} x^{4} a_{0} dx.$$
using $x = \frac{r}{a_{0}}$

$$= \frac{a_{0}}{8\sqrt{3}} \int_{0}^{\alpha} (2 - x) e^{x} \cdot a_{0}^{4} x^{4} a_{0} dx.$$

$$= \frac{a_{0}}{8\sqrt{3}} \left[2\int_{0}^{\alpha} x^{4} e^{\frac{-x}{dx}} - \int_{0}^{\alpha} x^{5} e^{\frac{-x}{dx}}\right]$$

$$= \frac{a_{0}}{8\sqrt{3}} \left[48 - 120\right] = \frac{-a_{0}}{8\sqrt{3}} 42 = -3\sqrt{3}a_{0}$$

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$$\therefore H_{200,210}^{(1)} = \frac{eF}{\sqrt{4\pi}} \sqrt{\frac{3}{4\pi}} \cdot \frac{2}{3} \cdot 2\pi \cdot (-3\sqrt{3a_0})$$

 $= -3a_0eF$, Now, the secular equation becomes

(nlm)	200	210	211	21,-1	
200	- E	-3a ₀ eE	-0	0	
210	-3a ₀ eE	-E ⁽¹⁾	0	0	=0
211	0	0	-E ⁽¹⁾	0	
21,1	0	0	0	-E ⁽¹⁾	

It can be observed that the states ψ_{200}, ψ_{210} are affected by the electric field and the sates ψ_{211} , ψ_{21-1} remain unchanged.

The eigen states corresponding to the eigen value $3eEa_0$ is $(\psi_{200}-\psi_{210})/\sqrt{2}$ and the eigen state for $-3eEa_0$ is $(\psi_{200}+\psi_{210})/\sqrt{2}$. The energy along with the eigen states of the n=2 state of hydrogen atom in an electric field E along the Z-direction is illustrated in Fig.2.1.



Fig. 9.2

Figure 9.2 Energies and wave functions of the first excited state of hydrogen atom in an electric field E.

This means that the hydrogen atom in the first excited state behaves as though it has a permanent dipole moment of magnitude $3a_0eE$ with three different orientations-one state parallel to the external electric field, one state anti-parallel to the field and two states with

Zero component along the field. The state's ψ_{211} and ψ_{21-1} do not posses dipole moments and therefore do not have a first order interaction with the field. Since the ground state of all atoms and nuclei are very likely to be non-degenerate, it is expected that an atom or nucleus in the ground state do not possess a permanent electric dipole moment. This means, atoms and nuclei in the ground state can possess electric charge, electric quadrupole moment, magnetic dipole moment etc., but not magnetic pole, electric dipole moment, magnetic quadrupole moment etc.,

9.4 SUMMARY:

The **Stark effect** in a normal helium atom, which has two electrons, leads to the shifting and splitting of energy levels when exposed to an external electric field.

The **Stark effect** in hydrogen refers to the shifting and splitting of the atom's energy levels when an external electric field is applied. Since hydrogen is the simplest atom, consisting of one proton and one electron, the Stark effect in hydrogen is easier to analyze compared to multi-electron atoms. Here are the key points of the Stark effect in hydrogen:

9.5 TECHNICAL TERMS:

Normal helium atom, Stark effect in hydrogen atom.

9.6 SELF ASSESSMENT QUESTIONS:

- 1) Explain about the application to a normal helium atom.
- 2) Briefly explain about the Stark effect in hydrogen atom.

9.7 SUGGESTED READINGS:

- 1) Quantum Mechanics- G. Aruldhas. (Prentice-Hall of India)
- 2) Quantum Mechanics-Theory and applications- A.K.Ghatak and S.Lokanathan (Macmillan)
- 3) Quantum Mechanics- Gupta, Kumar & Sharma.
- 4) Principles of Quantum Mechanics- R.Shankar (Plenum press)
- 5) Molecular Quantum Mechanics- P.W.Atkins.

LESSON-10

THE VARIATION METHOD AND WKB METHOD

10.0 AIM AND OBJECTIVE:

The primary goal of this chapter is to understand the concept of the variation method and WKB method. The chapter began with understanding of variation methods, Application to ground state of Helium atom, WKB method. After completing this chapter, the student will understand the complete idea about the variation method and WKB method.

STRUCTURE:

10.1	Introd	uction

- **10.2** Variation Method
- **10.3** Application to Ground State of Helium Atom
- 10.4 The WKB Method
- 10.5 Summary
- **10.6** Technical Terms
- **10.7** Self Assessments Questions
- 10.8 Suggested Readings

10.1 INTRODUCTION:

Under some circumstances, perturbation theory is an invalid approach to take. This happens when the system we wish to describe cannot be described by a small perturbation imposed on simple system .in quantum electrodynamics, for instance, the interaction of quarks with the gluon field cannot be treated perturbatively at low energy because the interaction energy becomes too large. When faced with such systems, one usually turns into other approximation schemes, such as the variation methods and W.K.B approximation.

In the variation method, one has to make some guess of the wave function, they apply the variation principle to improve the guess of the wave function and obtain the upper bound for the ground state energy. Here we do not try to find a correction to already known

unperturbed eigen value and eigen function, but determine the total eigen values and eigen functions as close to the experimental values as possible through a variation calculation.

10.2 THE VARIATION METHOD:

(a) The variation principle and theory:

The Variation Principle:

The essential idea of the method is to evaluate the expectation value $\langle H \rangle$ of the Hamiltonian operator H of the system with respect to a trial wave function. In order to explain the principle involved to evaluate the energy of the ground state, let us consider the wave equation as

$$H\psi = E\psi \tag{1}$$

Where the Hamiltonian operator $H = -\frac{\hbar^2}{2m}\nabla^2 + V$ (r) and E is the energy value.

Multiplying eq.(2) with and integrating over all variables

$$\int \psi^* H \psi d\tau = \int \psi^* E \psi d\tau = E \int \psi^* \psi d\tau$$

if φ is normalized wave function

$$E = \int \psi^* H \psi d\tau \dots (3)$$

The equations give the expectation value of the energy of the system in the state represented by the wave function ψ .

The approximate wave function ψ can be obtained by variation principle. In this approach, we guess a wave function and calculate the energy value .The energy of the system is correct, if the trial wave function is correct. In accordance with principle of variation, if the true
Introductory Quantum Mechanics	10.3	The Variation Method and WKB
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energy is E_0 and the correct wave function ψ_0 , then any other acceptable wave function ψi , indicates which trial wave functions is close to the true wave function to give the best energy value. For a proof of the theorem, express the trial wave function ψ as a linear combination of the true (but unknown) wave functions

$$\phi_1, \phi_2, \phi_3, \dots$$
 of H₀

$$\psi = \alpha_1 \phi_1 + \alpha_2 \phi_2 + \alpha_3 \phi_3 + \dots + \alpha_n \phi_n \qquad \dots + (4)$$

Where $\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_n$ are the arbitrary parameters that can be varied to minimum in the energy .for our convenience, let us take

Substitute this in equation (2), we get

$$E = \frac{\int (\alpha_1 \phi_1^* + \alpha_2 \phi_2^*) H(\alpha_1 \phi_1 + \alpha_2 \phi_2) d\tau}{\int (\alpha_1 \phi_1^* + \alpha_2 \phi_2^*) (\alpha_1 \phi_1 + \alpha_2 \phi_2) d\tau}$$

(i.e)
$$E[\alpha_1^2 \int \phi_1^* \phi_1 d\tau + 2\alpha_2 \alpha_2 \int \phi_1^* \phi_2 d\tau + \alpha_2^2 \int \phi_2^* \phi_2 d\tau]$$
$$= \alpha_1^2 \int \phi_1^* H \phi_2 d\tau + 2\alpha_2 \alpha_2 \int \phi_2^* H \phi_2 d\tau + \alpha_2^2 \int \phi_2^* H \phi_2 d\tau.....(6)$$

As we require the minimum value of E, it is necessary to minimize the energy E with respect to the parameter α_1 and α_2

Differentiating with respect to α_1 , we get.

$$E[2\alpha_{1}\int\phi_{1}^{*}\phi_{1}\,d\tau + 2\alpha_{2}\int\phi_{1}^{*}\phi_{2}\,d\tau] + \frac{\partial E}{\partial\alpha_{1}}[\alpha_{1}^{2}\int\phi_{1}^{*}\phi_{1}\,d\tau + 2\alpha_{1}\alpha_{2}\int\phi_{1}^{*}\phi_{2}\,d\tau + \alpha_{2}^{2}\int\phi_{1}^{*}\phi_{2}\,d\tau] = 2\alpha_{1}\int\phi_{1}^{*}H\phi_{1}\,d\tau + 2\alpha_{2}\int\phi_{1}^{*}H\phi_{2}\,d\tau].....(7)$$

In a similar way, differentiating with respect to α_2 , we get

$$E[2\alpha_{1}\int\phi_{1}^{*}\phi_{2}d\tau + 2\alpha_{2}\int\phi_{2}^{*}\phi_{2}d\tau] + \frac{\partial E}{\partial\alpha_{2}}[\alpha_{1}^{2}\int\phi_{1}^{*}\phi_{1}d\tau + 2\alpha_{1}\alpha_{2}\int\phi_{1}^{*}\phi_{2}d\tau + \alpha_{2}^{2}\int\phi_{2}^{*}\phi_{2}d\tau] = 2\alpha_{1}\int\phi_{1}^{*}H\phi_{2}d\tau + 2\alpha_{2}\int\phi_{2}^{*}H\phi_{2}d\tau]......(8)$$

in order to minimize E with respect to α_1 , and α_2 , the

$$\left(\frac{\partial E}{\partial \alpha_1}\right)_{\alpha_2} = \left(\frac{\partial E}{\partial \alpha_2}\right)_{\alpha_2} = 0....(9)$$

and using the symbols

$$\Delta_{ij} = \int \phi_i^* \phi_j d\tau$$

Applying the equation (2.3.9) and (2.3.10) to (2.3.7) we get

$$(H_{11} - E\Delta_{11})\alpha_1 + (H_{12} - E\Delta_{12})\alpha_2 = 0.....(11)$$

Similarly, from the equation (2.3.8), we get after minor rearrangements for $H_{12}=H_{21}$ and $\Delta_{12}=\Delta_{12}$ for convenience and symmetry.

$$(H_{21} - E\Delta_{21})\alpha_1 + (H_{22} - E\Delta_{22})\alpha_2 = 0....(12)$$

Equation (11) and (12) together are called secular equations.

In our case, we consider only the first two terms of the variation function ψ , we can generalize to other term also.

Equation 11 and 12 can be solved for ad provided the determinant for trivial solution is

in a more general way, for n independent functions the secular equation in the form of determinant is

10.5

10.3 APPLICATION TO GROUND STATE OF HELIUM ATOM:

Application to the ground (normal) state of the Helium atom

As an example, we take up to obtain the energy of Helium atom in the ground state.

Helium atoms consist of electrons of charge '-e', and nucleus '+Ze'.

The total potential is

$$V = V_1 + V_2 + V_3$$
(14)

Where the potential energies are given as:



Fig 10.1: Helium Atom

Neglecting the nuclear motion, the Hamiltonian is represented as

In atomic units, representing the Bohr radius $a_0 = \frac{h^2}{4\pi^2 m e^2}$

$$H = -\frac{1}{2} \frac{e^2}{a_0} \left[\nabla_1^2 + \nabla_2^2 \right] - \frac{Ze^2}{a_0 R_1} - \frac{Ze^2}{a_0 R_2} + \frac{Ze^2}{a_0 R_{12}} \dots \dots \dots (17)$$

The Hamiltonian becomes:

Here e^2/a_0 is the atomic unit of energy.

In Atomic units H takes the form

For the case of Helium, suppose one of the electrons is labeled 1, in the ground states, and the other labeled 2 is in the exited state 2. The ground state electron experiences the full attractive force of charge '+2e'.

The wave function is represented as

Even though the electron 2 does not experience attractive force from nuclear, in choosing the

$$\Psi_{1}^{(0)} = \frac{1}{\sqrt{\pi}} Z^{\frac{3}{2}} e^{-ZR_{2}} (a.u.)....(19)$$
$$\Psi_{2}^{(0)} = \frac{1}{\sqrt{\pi}} Z^{\frac{3}{2}} e^{-ZR_{2}} (a.u.)...(20)$$

trial wave function for electron 2 is taken as

These considerations show that good trial wave function must be of the form.

Where Z^1 is between 1 and 2.

Since $\Psi_1^{(0)}$, $\Psi_2^{(0)}$ are normalized wave functions for hydrogen like atoms, Φ must be a normalized wave function.

10.7

The expression for H given in eq.(20) is now modified by adding and subtracting $(Z'/R_1+Z'/R_2)$ becomes

Since Φ is assumed a normalized function, the variational energy E_{Φ} is given as Let

$$E_{\phi} = \int \phi^* H \phi d\tau....(23)$$

We have,
$$H\phi = H_0^1 \phi - \left(Z - Z^1 \right) \left[\frac{1}{R_1} + \frac{1}{R_2} \right] \phi + \frac{1}{R_{12}} \phi....(24)$$

Which is similar to two individual hydrogen-like atom wave function; whose energy is

Now eq 25 becomes

$$E_0^1\phi = -(Z^1)^2 a.u$$

$H\phi = -(Z^{1})^{2}\phi - (Z - Z^{1})\left(\frac{1}{R_{1}} + \frac{1}{R_{2}}\right)\phi + \frac{1}{R_{12}}\phi.....(26)$

Now the variational energy E_{Φ} of eq (23) becomes.

Since Φ is normalized.

$$\int \phi \phi * d\tau = 1 \qquad \dots \dots (28)$$

And we write other integrals as.

$$I_{1} = \int \frac{\left[-\left(Z^{1}\right)^{3} e^{-Z^{1}(R_{1}+R_{2})}\right]^{*}}{\pi} \left(\frac{1}{R_{1}} + \frac{1}{R_{2}}\right) \frac{\left(Z^{1}\right)^{3}}{\pi} e^{-Z^{1}(R_{1}+R_{2})} d\tau_{1} d\tau_{2}$$
$$= -\frac{\left(Z^{1}\right)^{6}}{\pi^{2}} \left[\int \frac{e^{-2Z^{1}(R_{1}+R_{2})}}{R_{1}} d\tau_{1} d\tau_{2} + \int \frac{e^{-2Z^{1}(R_{1}+R_{2})}}{R_{2}} d\tau_{1} d\tau_{2} + \right] \dots (29)$$

The first of the integral in the integral I, is

$$\begin{split} I &= \int \frac{e^{-2Z^{l}(R_{1})}}{R_{1}} d\tau_{1} \int e^{-2Z^{l}(R_{2})} d\tau_{2} \\ &= \int \frac{e^{-2Z^{l}(R_{1})}}{R_{1}} R_{1}^{2} dR_{1} d\theta_{1} \sin\theta_{1} d\theta_{1} \int e^{-2Z^{l}(R_{2})} R_{1}^{2} dR_{2} \sin\theta_{2} d\theta_{2} d\theta_{2} \end{split}$$

Using the knowledge of gamma functions and other simple integrals.

$$\mathbf{I} = 16\pi^2 \int \frac{e^{-2Z^1 R_1}}{R_1^2} R_1^2 dR_{11} \int e^{-2Z^1 R_2} R_1^2 dR_2 \dots \dots (30)$$

Similarly, the second integral in I, becomes.

$$E_{\phi} = -(Z^{1})^{2} - (Z - Z^{1})^{2} - (Z -$$

Inserting these values of integral in eq29

$$I_1 = \frac{(Z^1)^6}{\pi^2} \frac{2\pi^2}{(Z^1)^5} = 2Z^1.....(32)$$

Inserting these values of integral in eq29

Now the remaining integral in eq.27 is

$$I_{2} = \int \phi^{*} \frac{1}{R_{12}} \phi d\tau$$
$$= \frac{(Z^{1})^{6}}{\pi^{2}} \int \frac{e^{-2Z^{1}R_{1}}e^{-2Z^{1}R_{2}}}{R_{12}} d\tau_{1} d\tau_{2} \dots (33)$$

$$I_2 = \frac{(Z^1)^6}{\pi^2} \frac{5}{8} \frac{\pi}{(Z^1)^5} = \frac{5}{8} Z^1 \dots (34)$$

The above integral can be evaluated using the knowledge of Legendre polynomial and electrodynamics which yields the value.

Using the results of eq.32 and eq.27 We get

to minimise E_{Φ} with respect to variational parameter Z^1 , we set $dE/dZ^1=0$.

This gives

$$\frac{dE}{dZ^{1}} = 2Z^{1} - 2Z + \frac{5}{8} = 0$$

Where $Z^{1} = Z - 5/16$(.37)

Thus Z^1 is taken as the effective nuclear charge of helium. The factor 5/16 is called the screening factor.

Substituting the Z^1 in the energy equation (36)

$$E\phi = (Z^{1})^{2} - 2Z^{1} (Z^{1} + \frac{5}{16}) + \frac{5}{8} Z^{1} \quad .a.$$

= - (Z¹)²a.u....(37.1)
= 2 (Z¹)² E_{1s}(H) [:: E₁orE_{1s}(H) = -1/2]

which is ground state energy of hydrogen atom in the 1s orbital

$$=2(Z-5/16)^{2}E1s (B)$$

$$=2(\frac{27}{16})^{2}E_{1s}H \qquad (\therefore Z = 2 \text{ for Helium atom })$$

$$=2(\frac{27}{16})^{2} (-13.60 \text{ eV}) \qquad (\therefore E_{1}=-13.60 \text{ eV})$$

$$=-77.45 \text{ eV}$$

Which is the approximate ground state energy of helium atom. Further, the energy of the ground state He^+ ion is $4\text{E}_{1\text{s}}(\text{H}) = -54.40 \text{ eV}$.

Hence the ionization potential of helium is (-54.40) - (-77.45) = 23 eV.

The experimental value is 24.58 eV.

By introducing more parameters in the trial function, the accuracy may be improved further.

10.4 THE WKB METHOD:

- (a) Validity of the Method
- (b) Principle of the Method
- (c) Connection formula for penetration of a barrier.

Introduction:

Wentzel-Kramers-Brillouin (WKB) approximation is a final type of time independent approximate calculations. It applies to only situations in which the potential energy is slowly varying function of position. Problems of one dimension and also of three dimensions reducible in one dimension (radial) are solved by this method.

A slowly changing potential means the variation of potential energy V(r) slightly over several wavelengths (De Broglie waves) of the particles.

The De Broglie wavelength associated with a particle moving with energy E in a region of potential V is

$$\lambda = \frac{h}{p} = \frac{\hbar}{\left[2m(E-V)\right]^{\frac{1}{2}}} \dots (38)$$

Since $\frac{1}{2}$ mv² = E - V
 $m^2 v^2 = 2 m (E-V)$
 $p = mv = \sqrt{\left[2m(E-V)\right]}$

The propagation constant

$$k = \frac{2\pi}{\lambda} = (2m/\hbar) [E-V(x)]^{1/2}$$

Mathematically slowly varying potential can be expressed by the conditions

$$\left|\frac{1}{\hbar^2}\frac{dk}{d\lambda}\right| << 1$$

Substituting value of k from (39), we get

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

Principle of the Method:

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

Let $\psi(\mathbf{x})$ be the wave function satisfying Schrodinger's equation.

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{2m}{\hbar^2} \left[E - V(x) \right] \varphi = 0_{\dots(41)}$$

Let the solution of eqn. (2.3.41) be of the form

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

$$\frac{\partial \varphi}{\partial x} = C e^{i\phi(x)/\hbar} \cdot \frac{\partial \phi}{\partial x}$$

now substituting $\frac{\partial \phi}{\partial x} = \phi'$ and $\frac{\partial \phi'}{\partial x} = \phi''$ equation (43) takes the form

Substituting values of ϕ and $\frac{\partial^2 \varphi}{\partial x^2}$ from (42) and (44) in (41), we get

As $\psi = Ce^{i\phi(x)/\hbar} \neq 0$, therefore above equation gives

$$i\hbar\phi''-\phi'^2+2m(E-V)=0$$
(45)

To get an approximate solution of (4.8), we apply W.K.B. method and hence expand

10.13

 $\phi(\mathbf{x})$ in powers of \hbar i.e.,

$$\phi(x) = \phi_0(x) + \hbar \phi_1(x) + \frac{\hbar^2}{2} \phi_2'(x) + \dots$$
 (46)

where the subscripts ϕ 's are independent of \hbar . Let us assume that on account of the smallness of \hbar , the first two terms in equation (46) give a sufficiently good approximation to ϕ .

Differentiating equation (43), we get

$$\phi'(x) = \phi_0'(x) + \hbar \phi_1'(x) + \frac{\hbar^2}{2} \phi'_2(x) + \dots$$

$$\phi''(x) = \phi_0'' + \hbar \phi''_1'(x) + \frac{\hbar^2}{2} \phi'_2(x) + \dots$$
(47)

Substituting values of ϕ' and ϕ'' from (47) in equation (45), we get

$$i\hbar \left[\phi_{0}^{'}+\hbar\phi_{1}^{''}(x)+\frac{\hbar^{2}}{2}\phi_{2}^{'}(x)+-\right]-\left[\phi_{0}^{'}(x)+\hbar\phi_{1}^{'}(x)+\frac{\hbar^{2}}{2}\phi_{2}^{'}(x)+-\right]^{2}+2m(E-V)=0....(48)$$

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

$$\left[2m(E-V) - \phi_{0}^{'2}\right] + \hbar \left[i\phi_{0}^{''} - 2\phi_{0}^{'}\phi_{2}^{'}\right] + \hbar^{2}\left[i\phi_{1}\right] + \hbar^{2}\left[i\phi_{1}^{''} - \phi_{0}^{'2} - \phi_{0}^{'}\phi_{2}^{''}\right] = 0 \dots (49)$$

in order to that equation (49) may hold identically in \hbar , the coefficients of each power of \hbar mustvanish separately. This requirement leads to the following leads series of equations.

$$2m(E - V) - \phi_{0}^{'2} = 0 \quad (a)$$

$$i\phi_{0}^{'} - 2\phi_{0}^{'} \phi_{2}^{'} = 0 \quad (b)$$

$$i\phi_{1}^{''} - \phi_{1}^{'2} - \phi_{0}^{'} \phi_{2}^{''2} = 0 \quad (c)$$
(50)

and so on..

These equations may be solved successively. That is the first equation, ϕ_0 in terms of (E-V), the second equation defines ϕ_1 , the third defines ϕ_2 in terms of ϕ_1 and ϕ_0 etc..

From equation (50), we obtain,

$$\phi'_0 = \pm \sqrt{2m(E-V)}$$
(51)

integration of above eq. gives,

where x_0 is an arbitrary fixed value of x.

From equation(50) we obtain

$$\phi_1 = \frac{i\phi_0^{"}}{2\phi_0^{'}}$$

Integration of above equation yields

Where C_1 is a constant integration. This result is inconvenient if ϕ'_0 is negative. Therefore keeping in mind the log of negative of function differs only by an imaginary constant from the logarithm of absolute value of the function. We replace eqn.53 by

$$\phi_1 = \frac{i}{2} \log \left| \phi_0^{'} \right| + C_2$$
(54)

Where C_2 is an arbitrary constant.

Similarly

From equation 22 we see that ϕ_2 is represented as logarithm of $|\phi_0|$, therefore it is not, in general, small compared with ϕ_2 . Consequently ϕ_2 and ϕ_2 both must be retained. On the

other hand from eqn.(56) we see that ϕ_2 will be small whenever dv/dx is small and(E-V) is not too close to zero. Further it can be seen easily that the smallness of the higher approximations (ϕ_2 , ϕ_2etc) requires the smallness of all derivatives of V. Thus the W.K.B. approximation will be suitable in cases where V is a sufficiently smooth and slowly varying function of position.

Thus the approximate W.K.B. solution of eqn. (45) may be expressed in the form

Assuming constant C₂ is absorbed in $\phi_0(x)$

Substituting value of $\phi(x)$ from (6) in equation (42) and rearranging the result, we finally obtain the approximate solution ϕ_{app} of equation (44) in the form

Where C remains arbitrary. The two solutions contained in (57) and differing in sign of the exponent are linearly independent, and hence the approximate general solution, according to W.K.B. approximation is

$$\psi_{app} = C[2m(E-V)]^{-\frac{1}{4}} \left[\left(A \exp\left(\frac{i}{\hbar}\right) \int_{x_0}^x \left(\sqrt{2m(E-V)}\right) dx \right) + \left(B \exp\left(\frac{-i}{\hbar}\right) \int_{x_0}^x \left(\sqrt{2m(E-V)}\right) dx \right) \right] \dots (58)$$

Where A and B are arbitrary constants. The positive exponential corresponds to a wave moving in the positive direction and the negative exponential corresponds to a wave moving in the negative direction. For the special case when V(x) is a constant, these reduce respectively to the plane waves.

$$e^{\frac{ipx}{\hbar}}$$
 and $e^{\frac{-ipx}{\hbar}}$

The alternative from of equation (58) may be expressed as

$$\psi_{app} = C[2m(E-V)]^{-\frac{1}{4}} \cos \int_{x_0}^x (\sqrt{2m(E-V)}) dx + \phi$$

Where C and $\Box \Box \Box$ are arbitrary constants.

The approximate solutions (57) and (58) of the Schrodinger equation are usually called W.K.B. ψ -functions.

Connection Formulas for penetration of a barrier

W.K.B. method is applicable to the problems only where the potential function does not change too rapidly, because in the regions approximation considered do not apply. In the problems where the potential function vary slowly in some regions, so that W.K.B. method is inapplicable; we find the solution in the regions of inapplicability of W.K.B. method by some other methods and carry it to the regions where W.K.B. method is applicable. In order to connect these two solutions: we need for the connection formulas.

To treat the problem of barrier penetration where W.K.B approximation is valid, we must find how to connect solutions in the region where V>E with those where



Fig. 10.2

Consider the potential barrier shown in Fig. 10.2 suppose the energy of particle is such that E = V at point x = a..

Classically, the particle should slow down to zero velocity at this point and then turn back. Quantum mechanically we know that the wave penetrates some distance further into the barrier. Obviously we cannot use the W.K.B. approximation in the region near x=a because when E=V, the condition for its applicability breaks down.

Thus if we start with a given solution at some distance to the right of x = a (in I region) say,

$$\varphi \sim \frac{1}{\sqrt{p_1}} \exp \int_a^x \frac{P_1 dx}{\hbar}$$
 (59)

The Variation Method and WKB...

Where $P_1 = \sqrt{2m(V-E)}$

From W.K.B. approximation method, we know that a sufficient distance to left of x = a (in region II), the approximate solution will be

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 φ where $P_2 = \sqrt{2m(E-V)}$ and A and B are unknown constants. The values of A and B cannot be found By W.K.B. method alone, because they are determined by the nature of the solution in the region of inapplicability of W.K.B. method. To obtain the values of A and B we need an exact solution near x = a; but it is too complex problem to be solved. If the W.K.B. method is applicable at small enough region x = a; then the potential function can be represented approximately by a straight line with in region, with slope equal to that of potential curve at the classical turning point x = a. as E = V, we can write,

V-
$$E = C (x-a),$$

Where C is a constant equal to $\left(\frac{\partial V}{\partial x}\right)_{x=a}$. Thus in the region x = a, the Schrodinger equation

reduces approximately to

This difficult equation can be solved by Bessel's function The solution of the equation (61) is carried far enough from x = a, so that W.K.B. approximation becomes applicable. In this way, we may determine the constants A and B. Here we shall simply results without going through the complex procedure.

Case (A) Barrier to the Right:

Let V>E, to the right of x = a and P₁ =
$$\sqrt{2m(V-E)}$$
; P₂ = $\sqrt{2m(E-V)}$

Let us consider that far to the right of x= a, the W.K.B. approximate solution, which is exponential, Viz.,

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for to the left to x=a, the connection formula states this solution approaches,

Thus the connection formula may be expressed as

Similarly, if the approximate solution is an increasing exponential to the right of x=a, the following connection hold.

Case (B) Barrier to the Left:

For the solution which decays exponentially to the left of x=a, we obtain the connection formula.

If the solution increases exponentially to the left, we obtain the following connection formula.

$$\frac{1}{\sqrt{p_1}}\sin\left(-i\int_a^x \frac{P_2 dx}{\hbar} - \frac{\pi}{4}\right) = \frac{1}{\sqrt{p_2}}\exp\left(i\int_a^x \frac{P_2 dx}{\hbar}\right)$$

10.5 SUMMARY:

In this lesson, we develop another approximate method, which gives a direct solution of Schrodinger equation. This method, which is usually referred to as W.K.B. method is applicable to potentials which are such that the Schrodinger equation is separable to one dimensional equation,

Introductory Quantum Mechanics	10.19	The Variation Method and WKB
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further, the potential should be slowly varying we obtain the W.K.B. solution of the one dimensional schrodinger equation. Those solutions are used to describe the quantization condition which determiner the energy values corresponding to bound state problem.

10.6 SELF ASSESSMENT QUESTIONS:

- 1) Explain about the Variation method.
- 2) Explain about the Application to ground state of Helium atom.
- 3) Briefly explain about the WKB method.

10.7 TECHNICAL TERMS:

The Variation method, Application to ground state of Helium atom, WKB method.

10.8 SUGGESTED READINGS:

- 1) Quantum Mechanics-G. Aruldhas. (Prentice-Hall of India)
- 2) Quantum Mechanics-Theory and Applications-A.K.Ghatak and S.Lokanathan (Macmillan)
- 3) Quantum Mechanics-Gupta, Kumar & Sharma.
- 4) Quantum Mechanics-E.Merzbacher.

Prof. G. Naga Raju

LESSON-11

PERTURBATION THEORY

11.0 AIM AND OBJECTIVE:

Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation v (.t.) applied to a time independent Hamiltonian H^0 . The eigen functions and eigen state of this perturbed Hamiltonian is also time-dependent.

We are interested in the following quantities:

- (i) Time-dependent expected value of some observable, with a specified initial state.
- (ii) The time-dependent amplitudes of those quantum states that are energy eigen kets in the unperturbed systems.

The first quantity is important because it gives rise to the classical result of a measurement performed on a macroscopic number of copies of the perturbed system. The second quantity looks at the time-dependent probability of occupation for each eigen state, which is particularly useful in <u>laser physics</u>, where one is interested in the populations of different atomic states in a gas where a time-dependent electric field is applied.

STRUCTURE:

- 11.1 Time dependent perturbation: General perturbations
- **11.2** Variation of constants
- 11.3 Summary
- **11.4** Technical terms
- 11.5 Self-assessment questions
- 11.6 Suggested readings

11.1 TIME DEPENDENT PERTURBATION: GENERAL PERTURBATIONS:

The theory of time-dependent perturbation theory was developed by Dirac and is often called as Theory of variation of constant. Let us consider an unperturbed system with wave equation including the time.

11.2 VARIATION OF CONSTANTS:

Consider the time-dependent Schrodinger wave equation of an unperturbed system.

If the unperturbed system is conservative, then the Hamiltonian $H^{(0)}$ depends only on the space variable r but not on time t. Now, for such a case, the total wave function $\psi_n^0(r,t)$ including time is

Where $E_n^{(0)}$ is the energy of the stationary states and $\psi_n^{(0)}(r)$ are eigen functions of the time-independent wave equation.

The general solution of eq. (1) is a linear combination of solutions representing different stationary states.

(i.e.)
$$\psi^{(0)}(r,t) = \sum_{n} a_n \psi_n^{(0)}(r,t)$$
(4.)

If $\psi_n^{(0)}(r)$ is normalized like the functions $\psi_n^{(0)}(r,t)$ forming an orthonormal set, then for each n value, $|a_n|^2$ represents the probability of the system in that particular stationary state. The sum of the squares of the mixing Coefficients a_n is represented as.

$$\sum |a_n|^2 = 1$$
(5)

since $\int \psi^* \psi d\tau = \sum_n a_n^* a_n = \sum_n |a_n|^2 = 1$

Further $|a_n|^2 = 1$, $a_n = 1$, when the unperturbed system is in the stationary state $\psi_n^{(0)}(r,t)$, then all the coefficients $a_k(k \neq n)$ in eq. (4) are zero.

Now, consider the wave equation of a perturbed system.

$$H(r,t)\psi(r,t) = -\frac{*}{i}\frac{\partial}{\partial t}[\psi(r,t)]\dots(6)$$

As the Hamiltonian depends on space variables r as well as on time t, the energy cannot be conserved and there can be no stationary states. For solving eq.(6) by perturbation theory, let us

take the Hamiltonian $H^{(r,t)}$ as sum of two terms, the time-independent Hamiltonian $H^{0}(r)$ of the unperturbed system and a small perturbation $H^{1}(r,t)$ which depends on space variables r and time t.

Now, the perturbed wave equation is.

Whose general solution is of the form.

$$\psi(x_1, x_2, \dots, t) = \sum a_n(t)\psi_n^{(0)}(x_1, x_2, \dots, t) \dots \dots (8)$$

The Coefficients $a_n(t)$ being functions of time t.

Substituting eq. (8) in eq. (6) gives

$$\sum a_n(t)H^0\psi_n^{(0)} + \sum a_n(+)H^{(1)}\psi_n^{(0)}$$

Again $H^0 \psi_n^{(0)} = -\frac{\hbar}{2\pi i} \frac{\partial \psi_n^{(0)}}{\partial t}$

Hence, we get from (8)

multiply eq.(10) by $\psi_m^{(0)^*}$ and integrating over the configuration space. We have

with m=0,1,2,3,....

Thus we obtained a set of first-order differential equations involving the functions $a_m(t)$. At the time t=0 a measurement of energy will lead to a particular value corresponding to one of the stationary states of an unperturbed system because it is only for stationary states that the energy has a definite value. Let this be denoted as $E_l^{(0)}$.

This means at time t=0, the wave equation is represented by $\psi_l^{(0)}$ but not by eq. (4)

Hence, at time t=0,

$$a_{l}(0)=1, n=l=m.$$

 $a_{n}(0)=0, n\neq l.$ }(2.4.12..)

or
$$a_n(0) = \delta_{mn}$$

Therefore, we can find solution of eq.(11) numerically but physically it cannot be done, as there are infinite equations.

If $H^{(1)}(\mathbf{r}, \mathbf{t})$ is small, the rate of change of the Coefficients $\frac{da}{dt}$ is small in the time interval t=0 to t in which it acts and the relation (12) is valid throughout this interval. We now solve the equation (11) by neglecting all terms except with n=l, retaining $a_l^1(t)$ on the right hand side, we have.

Where $H_{ll}^{(1)} = \int \psi_l^{(0)^*} H^{(1)} \psi_l^{(0)} d\tau$

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Rewriting equation 13 as

$$\frac{da_{l}(t)}{a_{l}(t)} = -\frac{2\pi i}{\hbar} \cdot H_{ll}^{(1)} dt$$

Integrating

$$\int_{0}^{t} \frac{da_{l}(t)}{dt} = -\frac{2\pi i}{\hbar} \int_{0}^{t} H_{ll}^{(0)} dt$$

(i.e.) $\log[a_{l}(t)] = -\frac{2\pi i}{\hbar} H_{ll}^{(1)} t$
or $a_{n}(t) = \exp\left[-\frac{2\pi i}{\hbar} H_{ll}^{(1)} t\right]$ (14).

From eq.(14), we can understand how the Coefficient a_l changes during the time when the perturbation is acting, during the time, the wave function is

$$a_{n}(t)\psi_{l}^{(0)} = \exp\left[-\frac{2\pi i}{\hbar}H_{ll}^{(1)}t\right]\psi_{l}^{(0)} \quad \text{(from eq. 8)}$$
$$=\psi_{l}^{(0)}\exp\left[-\frac{2\pi i}{\hbar}\left(E_{l}^{(0)}+H_{ll}^{(1)}\right)+\right] \quad \text{(using eq. 2)} \quad \dots\dots\dots(15)$$

Now, our aim is to consider the remaining set of equation in (11) and find the behaviour of the Coefficients $a_m(t)$ with $m \neq l$.

Using the initial value of $a_1(0)=1$, on the R.H.S. of eq.2.4. 11. and neglecting all other a_n 's we obtain.

$$\frac{da_m(t)}{dt} = -\frac{2\pi i}{h} \int \psi_m^{(0)^*} H^{(1)} \psi_l^{(0)} d\tau$$
$$= -\frac{2\pi i}{h} \int \psi_m^{(0)^*} \exp\left[+\frac{2\pi i}{h} E_m^{(0)} t\right] H^{(1)} \psi_l^{(0)} \exp\left[-\frac{2\pi i}{h} E_l^{(0)} t\right] d\tau$$

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With $H_{ml}^{(1)} = \int \psi_m^{(0)^*} H^{(1)} \psi_l^{(0)} d\tau$

Let the field act during the time interval t=0 to t in which perturbation $H^{(1)}$ remains constant and it is zero before and after the field applied.

Now, we integrate eq.(16) during the interval t from 0 to t.

We have

$$a_m(t) = -\frac{2\pi i}{h} \int_0^t H_{ml}^{(0)} e^{-\frac{2\pi i}{h}} \left(E_l^{(0)} = E_m^{(0)} \right) + dt \quad \text{for } m \neq 1.$$

$$= -\frac{2\pi i}{h} H_{ml}^{(1)} \left[\frac{e^{\frac{-2\pi i}{h}} \left(E_l^{(0)} - E_m^{(0)} t \right) t}{-\frac{2\pi i \left(E_l^{(0)} - E_m^{(0)} \right)}{h}} \right]$$

$$= H_{ml}^{(1)} \left[\frac{e^{\frac{-2\pi i \left(E_{l}^{(0)} - E_{m}^{(0)r} \right)}{h}}}{E_{l}^{(0)} - E_{m}^{(0)}} \right]$$

$$= -\frac{H^{(1)}_{ml}}{\hbar} \frac{e^{i\omega_{ml}t} - 1}{\omega_{ml}} \quad \text{where } \omega_{ml} = \frac{E_m^{(0)} - E_l^{(0)}}{\hbar}$$

Which is the first order perturbation theory.

Now, we calculate the probability of the particle in the mth state in the following procedure:

Probability =
$$a_m^*(t)a_m(t) = (a_m(t))^2$$
(18)

$$=\frac{1}{\omega^2 ml} \left(e^{i\omega_m lt} - 1\right) \left(e^{-i\omega_m lt} - 1\right) X \frac{1}{\hbar^2} |H_{ml}^{(1)}|^2$$

Let us plot y against $x=\omega_{ml}$ as shown in Fig. 11.1. It can be observed that the most important contributions to the transition probability come from those final states with energy E_m which are very close to and centered around the initial state of energy E_l . The full width of the

curve at half maximum $\frac{\Delta E}{2\pi} \sim \frac{\pi}{\tau}$ (20)





Fig. 11.1

If we interpret ΔE as the uncertain by in energy and $\Delta t(\tau)$ is the certainty in time 't', the equation(20) then implies that

$\Delta E \; \Delta t \sim 2 \hbar$

This can be explained more clearly as below: for maximum value of Y we get.

$$\frac{Sin^2\left(\omega_{ml} \frac{t}{2}\right)}{\omega^2 ml} = \frac{1}{\omega^2 ml} \left[\left(\frac{\omega_{ml}t}{2}\right) - \left(\frac{\omega_{ml}t}{2}\right)^3 \frac{1}{3!} + \left(\frac{\omega_{ml}t}{2}\right)^5 \frac{1}{5!} - + \dots - - \right]^2$$

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$$= \frac{1}{(\omega_{ml})^2} \left(\frac{\omega_{ml}t}{2}\right)^2 \quad \text{neglecting higher powers of t.}$$
$$= \frac{t^2}{4}$$

The highest peak value is $\frac{t^2}{4}$, which can be easily observed from the Fig. (1).

The peak values we get, when Y is zero.

(ie.)
$$\frac{\sin^2\left(\omega_{ml} t/2\right)}{\omega^2 ml} = 0$$

(ie.)
$$\omega_{ml} = \pm \frac{2\pi n}{t}$$
 where n=0, 1,2,3

This means the height of the peak values is proportional to t^2 and its width decreases inversely as t. Since the area under the curve is proportional to t, the probability of time during the system in one or another state is proportional to t, which implies the probability per unit time.

11.3 SUMMARY:

This lesson explores Time-Dependent Perturbation Theory in quantum mechanics, which deals with systems subjected to external forces or perturbations that vary with time. The key concepts discussed include. Perturbations are small changes in the system that modify its Hamiltonian, and when these changes vary with time, they are described by time-dependent perturbations. The total Hamiltonian of a system under perturbation. The goal is to find how the system evolves in time under the influence of this perturbation, typically using perturbation theory to approximate the effects of V(t)V(t)V(t) on the system's state. The variation of constants method is used to solve the time-dependent Schrödinger equation with a perturbation. The time-dependent wavefunction can be written as a sum of unperturbed states with time-dependent coefficients. Using this method, the time evolution of the coefficients $cn(t)c_n(t)cn(t)$ can be determined by solving the time-dependent differential equations derived from the Schrödinger equation. This approach provides an approximation.

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In essence, this lesson addresses how to approach quantum systems subject to timedependent external influences, using perturbation theory and solving for the system's evolution through the variation of constants.

11.4 TECHNICAL TERMS:

Time dependent perturbation theory, variation of constants.

11.5 SELF-ASSESSMENT QUESTIONS:

- 1) Outline the theory of time-dependent perturbation theory.
- 2) Give a brief note on the variation of constants.

11.6 SUGGESTED READINGS:

- 1) Quantum Mechanics-R.D.Ratna Raju.
- 2) Principles of Quantum Mechanics-R.Shankar (Plenum Press).
- 3) Molecular Quantum Mechanics-P.W.Atkins.

Dr. S. Balamurali Krishna

LESSON-12

EINSTEIN TRANSITION PROBABILITY

12.0 AIM AND OBJECTIVES:

The aim of this lesson is to introduce the concept of transition to the continuum and the Einstein transition probabilities in quantum mechanics. Students will understand how a quantum system interacts with an electromagnetic field, leading to transitions between discrete states and the continuous spectrum. Additionally, they will learn how to calculate transition rates and probabilities using Einstein's theory. By the end of this lesson, students should be able to: Understand the concept of **transition to the continuum**, which occurs when a quantum system, initially in a discrete energy state, interacts with an external field and transitions to a continuous energy spectrum. Apply **Einstein transition probabilities** to calculate the likelihood of these transitions occurring between discrete and continuum states. Derive and understand the **selection rules** governing these transitions, including the conditions for allowed and forbidden transitions. Gain familiarity with the practical applications of these concepts in atomic, molecular, and solid-state physics, particularly in processes such as absorption, emission, and ionization.

STRUCTURE:

- **12.1** Transition to the Continuum
- **12.2** Einstein Transition Probabilities
- 12.3 Summary
- 12.4 Technical Terms
- 12.5 Self-Assessment Questions
- 12.6 Suggested Readings

12.1 TRANSITION TO THE CONTINUUM:

We have so far considered transition between states and m and l. We shall now consider transitions from a discrete state m to a continuum of states around E_l , where the densities of state are $\rho(m)$. When the final states are densely packed forming a continuum, we can replace the summation by an integral. In order to obtain the explicit expression for transition

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probability, let us assume that the system is enclosed in a cubical box. The stationary states of the system are discrete, but separated in energy by an interval, which is inversely proportional to the volume of the box.

If we consider a box of infinite size, the levels within the energy interval increases and merge into a continuum.

Now the transition probability for mth state is given as.

$$T = |a_m(t)|^2 = |H_{ml}^{(1)}|^2 \frac{4.Sin^2(\omega_{ml}t/2)}{\hbar^2 \omega_{ml}^2}$$

In this, the probability is largest for the states whose unperturbed energy $E_m^{(0)}$ is close to $E_l^{(0)}$. As the levels are closer, they form a cluster around $E_m^{(0)} - E_l^{(0)}$ and all the levels in the cluster nearly represent the same physical properties. Summing all levels in the cluster and we get the total transition.

Probability (i.e.) $\sum |a_m(t)|^2$

(i.e.)
$$\sum |a_m(t)|^2 = \int |a_m(t)| \rho(m) dE$$

Where $\rho(m)$ is the density of final states and $\rho(m)dE$ is the number of such states in the range dE.

Instead of considering transition to a particular state, we may consider transition to group of states of nearly equal energies. The probability of transition per unit time is now obtained, by considering the central peak of $\frac{4Sin^2(\omega_{ml}t/2)}{\omega_{ml}^2}$ as the domain of integration in the interval

 $(-\infty,\infty)$.

$$\therefore P(t) = \frac{1}{\hbar^2} |H_{ml}^{(1)}|^2 \rho(m) \int_{-\infty}^{\infty} \frac{4.Sin^2 (\omega_{ml} t/2)}{\omega_{ml}^2} dE$$

 $:: E = \hbar \omega, dE = \hbar d\omega$

$$\mathbf{p}(\mathbf{t}) = \frac{1}{\hbar} |H_{ml}^{(1)}|^2 \rho_m \int_{-\infty}^{-\infty} \frac{4Sin^2(\omega_{ml}t/2)}{\omega_{ml}^2} d\omega$$

12.3

on integration, we get.

$$P(t) = \frac{1}{\hbar} |H_{ml}^{(1)}|^2 \rho(m).2\pi n$$

Transition per unit time is

$$\mathrm{T} = \frac{2\pi}{\hbar} |H_{ml}^{(1)}|^2 \rho(m)$$

Which has wide application in quantum mechanics.

This is known as Fermi's Golden Rule. It may be concluded that the transition probability per unit time⁽ⁱ⁾

is proportional to $|H_{ml}^{(1)}|^2$.

Is proportional to $\rho(m)$ density states.

Is non-zero only between continuum states of the equal energy.

12.2 EINSTEIN TRANSITION PROBABILITIES:

Spontaneous emission, absorption and induced emission of radiation were satisfactorily given by Direct. In this we discuss the Einstein Coefficients of emission and absorption of radiation.

The transition taking place from a non-degenerate stationary state of energy E_k to another degenerate stationary state $E_l(E_k>E_l)$ causing an emission or absorption of radiation of frequency, is given, according to Bohr's frequency rules, as

The probability that a system in the lower energy state absorb a quantum of radiation energy and goes to the higher state in unit time is.

$$B_{l->k}\rho(\theta_{kl})$$

 $B_{n \rightarrow m}$ is known as Einstein's Coefficient of absorption. Let N_1 atoms are present in a state at any instant of time then number of transition per second is

 $N_l B_l \rightarrow k p(\theta_{kl})$

The probability of emission consists of two parts (i.e.) one part independent of the radiation density and the other proportional to the density.

Since the transition from the upper state to lower state energy causes an emission of radiation of energy is.

$$A_{k \rightarrow l} + B_{k \rightarrow l} p(\theta_{lk})$$

in which $A_{k->l}$ is the Einstein Coefficient of spontaneous emission $B_{K->l}$ is the Einstein Coefficient of induced emission.

Now, let the number of atoms in this state is denoted by N_k then the number of reverse transition is.

$$N_k \left[A_{k->l} + B_{k \to l} p(\mathcal{G}_{kl}) \right]$$

The emission and absorption must be equal at the thermal equilibrium.

$$N_{l}B_{l->kp}(g_{kl}) = N_{k} \left[A_{k->l} + B_{k->l} p(g_{kl}) \right]$$

or
$$\frac{N_{l}}{N_{k}} = \frac{A_{k->l} + B_{k->l} \rho(g_{kl})}{B_{l->k} \rho(g_{kl})} \quad (1)$$

From quantum statistical mechanics.

$$\frac{N_l}{N_k} = -(E_l - E_k) | KT = e^{h \mathcal{G} k l | KT}$$
(2)

Equating (1) and (2), we get

$$e^{h \mathscr{G}kl|KT} = \frac{\left[A_{k->l} + B_{k->l} p(\mathscr{G}_{kl})\right]}{B_{l->k} p(\mathscr{G}_{Kl})}$$

or
$$B_{l->k} p(\mathfrak{G}_{Kl}) e^{\hbar^2} Kl / KT - B_{K->l} p(\mathfrak{G}_{kl}) = A_{K->l}$$

or
$$\rho(g_{kl}) = \frac{A_{k->l}}{B_{l->k}e^{\hbar g_{kl}|Kt} - B_{K->l}}$$

The radiation energy, according to Planck's law, is

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$$\rho(\nu) = \frac{8 \prod h \mathcal{G}^3}{C^3} \cdot \frac{1}{[ex(-h\mathcal{G}/Kt)-1]}$$

Hence Einstein Coefficients are related by

$$B_{n\text{-}>m}\!\!=\!\!B_{m\text{-}>n}$$

and $A_{l\to k=} \frac{8\pi h \mathcal{G}_{kl}^3}{C^3} \dots B_{l\to k}$

12.3 SUMMARY:

This lesson focuses on two key topics in quantum mechanics: the transition to the continuum and Einstein transition probabilities.

1) Transition to the Continuum:

- In quantum systems, when an electron absorbs enough energy (for example, from a photon), it can transition from a discrete bound state to a continuum of unbound states, known as ionization.
- This phenomenon is important in understanding processes like photoionization, where an atom or molecule absorbs a photon and an electron is ejected, entering the continuous spectrum.

2) Einstein Transition Probabilities:

- Einstein transition probabilities describe the likelihood of quantum transitions between energy states induced by electromagnetic radiation (absorption or emission).
- These probabilities are derived from the interaction between the system and the electromagnetic field and depend on factors like the dipole matrix elements and the frequency of the radiation.
- The lesson covers Einstein's relations for the transition rates in both absorption and spontaneous emission, and explains how these are related to the lifetime of excited states and the intensity of radiation.

In addition, the lesson addresses selection rules, which determine the allowed and forbidden transitions based on symmetries and conservation laws. These rules help to predict the outcome of radiation interactions with quantum systems.

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In summary, the lesson provides students with the theoretical framework for understanding how transitions occur between bound and unbound states in quantum systems, along with practical methods for calculating transition rates using Einstein's formalism.

12.4 TECHNICAL TERMS:

Transition to the Continuum, Fermi golden rule.

12.5 SELF-ASSESSMENT QUESTIONS:

- 1) Discuss Einstein transition probabilities.
- 2) State and probe Fermi-Goden rule for the rate of transitions induced by a constant
- 3) Perturbation.
- 4) Calculate the transition probability per unit time and per unit of radiation.

12.6 SUGGESTED READINGS:

- 1) Quantum Mechanics-R.D.Ratna Raju.
- 2) Principles of Quantum Mechanics-R.Shankar (Plenum Press).
- 3) Molecular Quantum Mechanics-P.W.Atkins.

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LESSON-13

APPROXIMATION EXPRESSIONS

13.0 AIM AND OBJECTIVE:

The aim of this lesson is to explore the behavior of a charged particle in an electromagnetic field under different approximations, specifically the adiabatic approximation and the sudden approximation. Students will learn how these approximations influence the particle's dynamics and gain insight into how the system responds to time-varying electromagnetic fields.By the end of this lesson, students should be able to:

- 1) Understand the dynamics of a **charged particle in an electromagnetic field**, including the forces exerted on the particle by both electric and magnetic fields.
- 2) Apply the adiabatic approximation to systems where the external parameters (such as the magnetic field) change slowly over time, and explain the resulting effects on the particle's motion.
- 3) Use the **sudden approximation** to describe systems where the external parameters change abruptly, and understand the implications for the particle's energy and state.
- 4) Compare and contrast the adiabatic and sudden approximations in terms of their assumptions and applications to quantum and classical systems.

STRUCTURE:

- 13.1 A Charged Particle in an Electromagnetic Field
- 13.2 Adiabatic Approximation
- 13.3 Sudden Approximation
- 13.4 Summary
- 13.5 Technical Terms
- 13.6 Self-Assessment Questions
- 13.7 Suggested Readings

13.1 A CHARGED PARTICLE IN AN ELECTROMAGNETIC FIELD:

In order to apply the time-dependent perturbation theory to the charged particle, the effect of electric and magnetic fields on the particle must be investigated.

The electromagnetic force on a particle of charge e, and mass m moving with velocity v in an electromagnetic field characterised by electric field E and magnetic field B (or scalar potential ϕ and vector potential A) is

$$F = cE + e\frac{vxB}{c}$$

c being speed of electromagnetic waves.

 $<\phi_n |\phi_n>+<\phi_n |\phi_n>=0$

 $<\phi_n | \phi_n >= i\alpha(t), \alpha \rightarrow real.$

For new eigen function $\phi'_n = \phi_n e^{tr(.)}$.

We have $<\phi_n |\phi_n>=I(\alpha+\gamma).$

Choosing γ suitably, we can make this vanish. Hence

$$\partial_n = \sum_{l}^{'} \frac{a_l}{\hbar_{\omega_{nn}}} \left\langle \phi_n \left| \frac{\partial H}{\partial t} \right| \phi_l \right\rangle \exp \left[i \int_{0}^{t} \omega_{nl}(l') dt' \right]$$

Let the System be initially at state m and the time variation is small: thus

$$\partial_n \approx \frac{1}{\hbar_{\omega_{nn}}} \left\langle \phi_n \left| \frac{\partial \omega}{\partial t} \right| \phi_m \right\rangle e^{i\omega_{mn}t}; n \neq m$$

$$\partial_n(t) \approx \frac{1}{\hbar_{\omega_{nn}}} \left\langle \phi_n \mid \frac{\partial \omega}{\partial t} \mid \phi_m \right\rangle e^{i\omega_{mn}t} - l.$$

With the above approximation this equation shows that the probability amplitude for a state other than the initial states oscillates in time and show no steady increase over long periods of time even though H changes by a finite amount.

13.2 ADIABATIC APPROXIMATION:

In the adiabatic case, we expect on physical grounds that solutions of the Schrodinger equation can be approximated by means of stationary eigenfunctions of the instantaneous Hamiltonian, so that a particular eigenfunction at one time goes over continuously into corresponding eigenfunction at a later time.

If the equation

$$H(t)\phi_n(t) = E_n(t)\phi_n(t)$$

can be solved at any time we assume that a system that is discrete non-degenerate state $\psi_m^{(0)}$ with energy $E_m^{(0)}$ at t=(0) is likely to be in the state $\phi_n^{(t)}$ with energy $E_n^{(t)}$ at time t, provided that H(t) varies very slowly with time.

The wave function $\boldsymbol{\psi}$ obeys the time-dependent schrodinger equation.

$$i\hbar \frac{\partial \psi}{\partial t} = H(t)\psi$$

$$\psi = \sum_{l} a_{l}(t)\phi_{l}(t) \exp\left[\frac{1}{i\hbar}\int_{0}^{t} E_{l}(t')dt'\right]$$
Then $\sum_{l} l\hbar \left[a_{l}\phi_{l} + a_{1}\phi_{l}\right] \left[\exp\frac{1}{l\hbar}\int_{0}^{t} E_{l}(t')dt'\right] = 0$

Multiplying by ϕ_{ψ} we has

$$\sum_{l} \left[\partial_{l} < \phi_{n} \mid \phi_{l} > +a_{l} < \phi_{n} \mid \phi_{l} > \right] \exp \left[\frac{1}{l\hbar} \int_{0}^{t} E_{l}(t') - E_{n}(t') dt' \right] = 0$$

or $\partial_{n} = -\sum a_{t} < \phi_{n} \mid \phi_{l} > \exp \left[\frac{1}{l\hbar} \int_{0}^{t} E_{l}(t') - E_{n}^{(1')} dt' \right]$

To evaluate $\langle \phi_n | \phi_l \rangle$, we have

$$\frac{\partial H}{\partial t}\phi_{l} + H\phi_{l} = E_{l\phi l} + E_{l\phi l}$$
or
$$\left\langle\phi_{n} \mid \frac{\partial H}{\partial t} \mid \phi_{l}\right\rangle + E_{n}\left\langle\phi_{n} \mid \phi_{l}\right\rangle = E_{l}\left\langle\phi_{n} \mid \phi_{l}\right\rangle = E_{l}\left\langle\phi_{n} \mid \phi_{l}\right\rangle$$
or
$$\left\langle\phi_{n} \mid \phi_{l}\right\rangle = \frac{\left\langle\phi_{n} \mid \frac{\partial H}{\partial t} \mid \phi_{l}\right\rangle}{E_{l} - E_{n}}$$

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To find $\langle \phi_n | \phi_n \rangle$, on differentiating $\langle \phi_n | \phi_n \rangle = 1$ w.r.t. time.

13.3 SUDDEN APPROXIMATION:

The sudden approximation consists of the change in Hamiltonian discontinuous on different times.

Suppose that $H=H_0$ for t < 0

and $H=H_1$ for t > 0

Then

$$H_0 u_n = E_n^0 \mathcal{G}_n \quad \text{for } t < 0$$

$$H_0 u_n = E_n \mathcal{G}_n \quad \text{for } t > 0$$

$$\psi = \sum_{e} a_n u_n e^{-iE_n} \frac{1}{\hbar}$$

and

and

$$\psi = \sum_{e} a_t u_t e^{-iE_n} \frac{1}{\hbar}$$

Equating the two solutions at t(0)=0.

$$b_t = \sum_e a_n < u_e \mid u_n >$$

The sudden approximation consists in using above equation when the change in the Hamiltonian occupies a very short finite interval of time t_0 . Suppose that

$$\begin{array}{ll} H = H_0 & \mbox{ for } t < 0, \\ H = H_1 & \mbox{ for } t > 0 \\ H = H_1 & \mbox{ for } 0 < t < t_0. \end{array}$$

The intermediate Hamiltonian H₁ which is taken constant in time, has a complete set of energy eigen functions:

$$H_l W_k = E_k W_k$$

The exact solution can be expanded in terms of the u's with constant coefficients.

$$\psi = \sum_{k} C_k W_k \exp\left(-iE_k t/\hbar\right), \text{ for } 0 < t < t_0$$
Application of the continuity condition at t=0 gives

$$C_k = \sum_n a_n < W_k \mid W_n > = \sum_n a_{n < k \mid n > n}$$

and at t=t₀ gives

$$b_{t} = \sum_{k} C_{k} \langle \mu | k \rangle \exp\{-i(E_{k} - E_{\mu})t_{\alpha} / \hbar\}$$
$$= \sum_{n} a_{n} \langle \mu | k \rangle \exp\{-i(E_{k} - E_{t})t_{0/\hbar}\} < k | n >$$

When $t_0=0$, the exponential is equal to unity and b_e is given by (1).

The sudden approximation will be best only when t_2 is small. So on expansion exponential term in above equation.

$$a_{\beta} \approx \sum a_{n} \sum_{n} \left\langle \mu \mid k \right\rangle \left[1 - \frac{it_{0}}{\hbar} \left(E_{k} - E_{t} \right) \right] \left\langle k \mid n \right\rangle$$

or
$$a_{i} \approx \sum a_{n} \left\langle \mu \mid \left[\frac{it_{0}}{\hbar} \left(H_{i} - H_{i} \right) \right] \mid n \right\rangle$$

Thus error in sudden approximation is proportional to t_0 for small t_0 . If H_1 depends upon time, then $\int_0^{f_0} H_1 dt$ can be taken in place of $H_1 t_0$.

$$b_t = \partial_{km} \frac{u_0}{\hbar} \langle k \mid H_i - H_0 \mid m \rangle$$

This can be used even when (h-H₀) is not small as compared to H₀ taking t₀ small.

13.4 SUMMARY:

This lesson examines the motion of a charged particle in an electromagnetic field, considering two important approximations: the adiabatic approximation and the sudden approximation.Charged Particle in an Electromagnetic Field: The motion of a charged particle under the influence of both electric and magnetic fields is governed by the Lorentz force law. This force combines the effects of the electric field E and the magnetic field B, influencing the particle's trajectory.

The adiabatic approximation is used when the external fields (such as the magnetic field) change slowly with time compared to the particle's response time. In this approximation, the system remains in an instantaneous eigenstate of the Hamiltonian as it evolves. The particle's energy changes smoothly as the system's parameters evolve. For example, in a magnetic field that changes slowly, the charged particle's quantum states (such as Landau levels) will adapt adiabatically to the changing field, preserving their quantum numbers. This approximation is particularly useful in processes where the time scale of the external perturbation is much longer than the time scale of the particle's dynamics. The sudden approximation applies when the external parameters (such as the magnetic field) change abruptly, much faster than the particle can adjust. In this case, the system's wavefunction does not follow the instantaneous eigenstate of the new Hamiltonian. Instead, it is assumed that the system retains its initial quantum state immediately after the change, with the energy adjusting according to the new conditions. This approximation is often used in processes like sudden changes in potential, where the particle's state "jumps" to a new configuration due to the rapid change in the environment. The adiabatic approximation assumes slow changes and smooth evolution of the system, leading to a gradual transition between states. The sudden approximation, on the other hand, assumes rapid changes and immediate response, where the system does not have time to adapt. These two approximations provide useful tools for solving different types of problems involving time-dependent fields, depending on how fast the external parameters change in comparison to the system's dynamics.

In summary, the lesson discusses how a charged particle behaves in electromagnetic fields under different temporal conditions, emphasizing the roles of the adiabatic and sudden approximations. These approximations allow for simplified models that make it possible to predict the behavior of the system under various external influences, with practical applications in both classical and quantum systems.

13.5 TECHNICAL TERMS:

Adiabatic Approximation, Sudden Approximation.

13.6 SELF-ASSESSMENT QUESTIONS:

- 1) Write notes on Adiabatic approximation.
- 2) Sudden approximation.

13.7 SUGGESTED READINGS:

- 1) Quantum Mechanics Gupta, Kumar & Sharma.
- 2) Advanced Quantum Mechanics Rajput.
- 3) Quantum Mechanics R.D.Ratna Raju.
- 4) Principles of Quantum Mechanics R.Shankar (Plenum Press).
- 5) Molecular Quantum Mechanics P.W.Atkins.

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