**Uttar Pradesh Rajarshi Tandon
Open University**

Bachelor of Science

DCEPHS-108

Quantum Mechanics And Spectroscopy

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BLOCK

1

WAVE MECHANICS

UNIT-1

Basic Concept

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UNIT-3

Operator Algebra

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ISBN :

Printed and Published by Vinay Kumar, Registrar, Uttar Pradesh Rajarshi Tandon Open University, 2023.

Printed By : Chandrakala Universal Pvt. Ltd. 42/7 Jawahar Lal Neharu Road, Prayagraj.

UNIT 1 BASIC CONCPET

Structure

1.1 INTRODUCTION

On the one hand the **quantum theory** of light cannot be considered satisfactory since it defines the energy of a light particle (photon) by the equation E=hf containing the frequency f. Now a purely particle theory contains nothing that enables us to define a frequency; for this reason alone, therefore, we are compelled, in the case of light, to introduce the idea of a particle and that of frequency simultaneously. On the other hand, determination of the stable motion of electrons in the atom introduces integers, and up to this point the only phenomena involving integers in physics were those of **interference and of normal modes of vibration**. This fact suggested to me the idea that electrons too could not be considered simply as particles, but that frequency (**wave properties**) must be assigned to them also. (**Louis de Broglie**, Nobel Prize Speech, Quantum Physics, 1929)

The development during the present century is characterized by two theoretical systems essentially independent of each other: the **theory of relativity** and the **quantum theory**. The two systems do not directly contradict each other; but they seem little adapted to fusion into one unified theory. ... Experiments on interference made with particle rays have given brilliant proof that the **wave character of the phenomena of motion** as assumed by the theory do, really, correspond to the facts. ... de Broglie conceived an electron revolving about the atomic nucleus as being connected with a hypothetical wave train, and made intelligible to some extent the discrete character of Bohr's 'permitted' paths by the **stationary (standing) character of the corresponding waves**. (**Albert Einstein**, On Quantum Mechanics, 1940)

A careful analysis of the process of observation in atomic physics has shown that the subatomic particles have no meaning as isolated entities, but can only be understood as interconnections between the preparation of an experiment and the subsequent measurement. Quantum theory thus reveals a basic oneness of the universe. It shows that we cannot decompose the world into independently existing smallest units. As we penetrate into matter, nature does not show us any isolated ‘basic building blocks’, but rather appears as a complicated web of relations between the various parts of the whole. (**Fritjof Capra**, The Tao of Physics, On Quantum Theory)

From 1900 to 1930 there was a revolution in the foundations of our understanding of light and matter interactions. In 1900 Planck showed that light energy must be emitted and absorbed in discrete 'quanta' to explain blackbody radiation. Then in 1905 Einstein showed that the energy of light is determined by its frequency, where E=hf. Finally, in the late 1920s, de Broglie and Schrodinger introduced the concept of Standing Waves to explain these discrete frequency and energy states of light and matter (standing waves only exist at discrete frequencies and thus energy states).

So, it is clear that Waves are central to Quantum Physics and our understanding of the structure and discrete energy states of Matter (which explains why Quantum Theory is also called Quantum Wave Mechanics). As we shall explain, the problems and absurdities of quantum theory have been caused by the continuing assumption of the discrete 'particle' concept for both light and matter, and thus the resulting paradox of the 'Particle / Wave' duality.

As we are dealing with a scientific theory, it is necessary to begin by stating the central Principles of the **'Metaphysics of Space and Motion and the Wave Structure of Matter'**, which describe how Matter exists in Space as a Spherical Standing Wave and interacts with other Matter in the Space around it. From this foundation we can then deduce the solutions to many problems currently found in Quantum Theory caused by this ancient concept that matter exists as 'particles'.

For example, the obvious solution to the paradox of the particle / wave duality of matter is to realise that the Wave-Center of the Spherical Standing Wave causes the observed 'particle' effects of Matter (see wave diagram below). Likewise, the discrete 'particle' properties of Light (quanta / photons) are caused by Standing Wave interactions which only occur at discrete frequencies and thus energy states.

What we observe as material bodies and forces are nothing but shapes and variations in the structure of space. Particles are just schaumkommen (appearances). The world is given to me only once, not one existing and one perceived. Subject and object are only one. The barrier between them cannot be said to have broken down as a result of recent experience in the physical sciences, for this barrier does not exist. (Erwin Schrodinger, on Quantum Theory)

Because Schrodinger believed in real waves, he was never happy with Max Born's statistical / probability interpretation of the waves that became commonly accepted (and was actively promoted by Heisenberg and Bohr) in Quantum Theory / Mechanics.

Secondly, David Bohm provides a clear account of how this incorrect 'particle' conception of matter not only causes harm to the Sciences, but also to the way we think and live, and thus to our very society and its future evolution.

The notion that all these fragments is separately existent is evidently an illusion, and this illusion cannot do other than lead to endless conflict and confusion. Indeed, the attempt to live according to the notion that the fragments are really separate is, in essence, what has led to the growing series of extremely urgent crises that is confronting us today. Thus, as is now well known, this way of life has brought about pollution, destruction of the balance of nature, over-population, world-wide economic and political disorder and the creation of an overall environment that is neither physically nor mentally healthy for most of the people who live in it. Individually there has developed a widespread feeling of helplessness and despair, in the face of what seems to be an overwhelming mass of disparate social forces, going beyond the control and even the comprehension caught up in it.

In this unit we will discuss some basic fundamentals and need of quantum mechanics.

1.2 OBJECTIVES

- After studying this unit, student should able to,
- Concept of Quantum Mechanics
- Explain the concept of stationary states
- Know about wave function
- Explain the concept of probability current density
- Know about equation of continuity

1.3 NEED OF QUANTUM THEORY AND QUANTUM MECHANICS

(Quantum theory is needed because many phenomena at the microscopic level cannot be explained using classical theory, eg: Photoelectric effect, interaction among elementary particles.)

Quantum mechanics and classical mechanics are two cornerstones of physics we know today. Classical mechanics describes the behavior of macroscopic bodies, which have relatively small velocities compared to the speed of light. Quantum mechanics describes the behavior of microscopic bodies such as subatomic particles, atoms, and other small bodies. These two are the most important fields in physics. It is vital to have a proper understanding in these fields in order to excel in any part of physics. In this article, we are going to discuss what quantum mechanics and classical mechanics are, where they are applied, their special characteristics, the similarities between quantum mechanics and classical mechanics, their variations, and finally the difference between quantum mechanics and classical mechanics.

What is Classical Mechanics?

Classical mechanics is the study of macroscopic bodies. The movements and statics of macroscopic bodies are discussed under classical mechanics. Classical mechanics has three different branches. They are, namely, Newtonian mechanics, Lagrangian mechanics, and Hamiltonian mechanics. These three branches are based on the mathematical methods and quantities used to study the motion. For an example, Newtonian mechanics uses vectors such as displacement, velocity, and acceleration to study the motion of the object, whereas Lagrangian mechanics uses energy equations and rate of energy change to study. The proper method is selected depending on the problem to be solved. Classical mechanics is applied in places such as planetary motion, projectiles, and most of the events in daily lives. In classical mechanics, energy is treated as a continuous quantity. A system can take any amount of energy in classical mechanics.

What is Quantum Mechanics?

Quantum mechanics is the study of microscopic bodies. The term “quantum” comes from the fact that energy of a microscopic system is quantized. The photon theory is one of the cornerstones of quantum mechanics. It states that the energy of light is in the form of wave packets. Heisenberg, Max Plank, Albert Einstein are some of the prominent scientists involved in developing the quantum mechanics. Quantum mechanics falls into two categories. The first one is quantum mechanics of non-relativistic bodies. This field studies the quantum mechanics of particles with relatively small speeds compared to the speed of light. The other form is relativistic quantum mechanics, which studies particles moving with speeds compatible with the speed of light. Heisenberg’s uncertainty Principal is also a very important theory behind quantum mechanics. It states that the linear momentum of a particle and the position of that particle in the same direction cannot be measured simultaneously with 100% accuracy.

Difference between Classical and Quantum Mechanics

1. Classical Mechanics deals with macroscopic particles whereas Quantum Mechanics deals with microscopic particles.
2. Classical Mechanics is based on Newtons laws of motion. Quantum Mechanics takes into account Heisenberg’s uncertainty principle and de Broglie concept of dual nature of matter.
3. Classical Mechanics is based on Maxwells electromagnetic wave theory. According to it any amount of energy may be emitted or absorbed continuously. Quantum Mechanics is based on Planck’s quantum theory according to which only discrete values of energy are emitted or absorbed.

4. In Classical Mechanics, the state of a system is defined by specifying all the forces acting on the particles. It also counts, particles positions and velocities (moment). The future state then can be predicted with certainty. Quantum Mechanics gives probabilities of finding the particles at various locations in space.

1.4 FUNDAMENTAL EQUATION OF WAVE MECHANICS

The Schrödinger equation is the fundamental equation of physics for describing quantum mechanical behavior. It is also often called the Schrödinger wave equation, and is a partial differential equation that describes how the wavefunction of a physical system evolves over time.

Quantum mechanics is a branch of physics that studies the behaviors of matter and light on an atomic and subatomic level. It tries to explain and classify the properties of molecules and atoms as well as their constituents, which include electrons, protons, neutrons, and other more esoteric particles including quarks and gluons. These properties include the interactions of the particles with one another and with electromagnetic radiation (i.e., light, X-rays, and gamma rays).

Quantum mechanics is based on the Schrodinger equation, which is a fundamental equation. In classical mechanics, the Schrodinger equation plays the function of Newton's laws and energy conservation, predicting the potential behaviour of a complex system. It is a wave equation in terms of the wavefunction that predicts the likelihood of events or outcomes analytically and precisely. The precise outcome is not predetermined, but the Schrodinger equation can predict the distribution of outcomes provided a large number of events.

Kinetic energy + Potential energy = E

The kinetic and potential energies are combined into the Hamiltonian, which acts on the wavefunction to cause it to evolve in time and space. The Schrodinger equation gives the system's quantized energies as well as the wavefunction's structure, which can be used to calculate other properties. It is written as –

$$H\psi = E\psi$$

Where, H =Hamiltonian Operator, $\psi =$ Wave function and E=Energy.

THEORY OF SCHRODINGER EQUATION

The theory of Schrodinger equation was formulated by Erwin Schrodinger in the year 1926. His formulation is based on de-Broglie’s concept of matter-wave. The theory aims at setting up a differential equation (wave equation) for a wavefunction that can describe the detailed behavior of matter wave.

The main assumptions made in the theory are :

(i) Creation and destruction of material particles do not take place.

(ii) All material particles move with small velocities so that they can be treated non-relativistically.

Inspire of the above assumptions, the theory has proved to be immensely successful when applied to atoms and molecules. The theory provides a quantitative formulation of some of the basic principles of quantum mechanics, shows how a wave theory of matter works out in practice, tells how physical quantities, for systems for which the laws of classical mechanics are not applicable, can be actually computer within the framework of the theory.

The Schrodinger equation for a free non-relativistic particle may be arrived at by making straightforward uses of the new concepts that have been obtained in the domain of microscopic particle.

TIME-DEPENDENT SCHRODINGER EQUATION FOR A FREE PARTICLE: EQUATION OF MOTION FOR MATTER WAVE

The wavelength λ of the de-Broglie wave associated with a free particle of mass m moving along the x-axis with momentum p_x is given by

$$\lambda = \frac{h}{p_x} \qquad \text{……… (1)}$$

The wave-vector k is related to the wavelength λ as

$$k = \frac{2\pi}{\lambda} \qquad \text{……… (2)}$$

From the above two equation, we get

$$p_x = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k \qquad \text{……… (3)}$$

The kinetic energy E of the particle is related to the angular frequency of the wave associated with it as

$$E = \hbar\omega \qquad \text{……… (4)}$$

Further, we have

$$E = \frac{px^2}{2m} \qquad \text{……… (5)}$$

so that Eqs. (3), (4) yields

$$\omega = \frac{E}{\hbar} = \frac{p_x^2}{\hbar 2m} = \frac{\hbar^2 k^2}{\hbar 2m} = \frac{\hbar k^2}{2m}$$

……… (6)

The wave function ψ(x, t) which describes the free particle localilzed in the region of the x-axis is given by

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k)\, e^{i(kx-\omega t)}\, dk$$

……… (7)

Using ω given by Eq. (6), the above becomes

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m}t\right]} dk$$

……… (8)

Differentiating Eq. (8) with respect to time t, we get

$$\frac{\partial \psi(x,t)}{\partial t} = \frac{-i\hbar}{2m} \int k^2 A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m}t\right]} dk$$

……… (9)

Further, differentiation of Eq. (9) with respect to x gives

$$\frac{\partial \psi(x,t)}{\partial x} = i \int_{-\alpha}^{+\alpha} k\, A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m}t\right]} dk$$

The above on differentiation with respect to *x* gives

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = -\int_{-\alpha}^{+\alpha} k^2 A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m}t\right]} dk$$

……… (10)

Multiplying Eq. (9) by $i\hbar$ we obtain

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{\hbar^2}{2m} \int_{-\alpha}^{+\alpha} k^2 A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk$$ ……… (11)

In view of Eqs. (10) and (11) we obtain

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial t^2}$$ ……… (12)

Equation (12) is the one-dimensional time-dependent Schrodinger equation for a particle of mass m localized in the region of the x-axis and described by the wave function ψ(r, t).

OPERATORS CORESPONDING TO ENERGY AND LINEAR MOMENTUM

It is possible to write the one-dimensional Schrodinger equation for a free particle given by Eq. (12) as

$$\left(i\hbar \frac{\partial}{\partial t}\right) \psi(x,t) = \frac{1}{2m}\left(-i\hbar \frac{\partial}{\partial x}\right)\left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x,t)$$ ……… (13)

The energy E of the free particle is related to the momentum component p_x as

$$E = \frac{1}{2m} p_x^2 = \frac{1}{2m}(p_x)(p_x)$$ ……… (14)

Comparison of Eqs (13) and (14) allows us the associate differential operators with the energy E and the momentum component p_x, which operate on the wave function ψ(x, t), as

$$(E)_{op} = \hat{E} \rightarrow i\hbar \frac{\partial}{\partial t}$$ ……… (15)

as

$$(p_x)_{op} = \hat{p}_x \rightarrow -i\hbar \frac{\partial}{\partial x}$$ ……… (16)

Extending the above for the three-dimensional case the operators associated with the momentum components p_x, p_y, p_z are given as

$$\left.\begin{aligned}\hat{p}_x &\to -i\hbar\frac{\partial}{\partial x}\\ \hat{p}_y &\to -i\hbar\frac{\partial}{\partial y}\\ \hat{p}_z &\to -i\hbar\frac{\partial}{\partial z}\end{aligned}\right\} \qquad \ldots\ldots\ldots (17)$$

In view of the above, the operator corresponding to the linear momentum vector $\vec{p}$ is

$$\hat{\vec{p}} = \hat{i}\hat{p}_x + \hat{j}\hat{p}_y + \hat{k}\hat{p}_z$$

i.e. $$\hat{\vec{p}} \to -i\hbar\vec{\nabla} \qquad \ldots\ldots\ldots (18)$$

$$\left(\vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right).$$

TIME-DEPENDENT SCHRODINGER EQUATION FOR A PARTICLE MOVING IN A FORCE FIELD

Let us now consider the particle to be moving in space under the influence of a force field and not freely. Under such a case, the particle possesses potential energy besides kinetic energy. Let us consider the potential energy of the particle to be a function of position $\vec{r}$ and time t.

Denoting the potential energy as V($\vec{r}$, t), we may write the total energy of the particle

$$E = \frac{p^2}{2m} + V(\vec{r}, t) \qquad \ldots\ldots\ldots (19)$$

According to Schrodinger, the operators for $\vec{r}$ and t are respectively

$$\hat{\vec{r}} = \vec{r} \qquad \ldots\ldots\ldots (20)$$

and $$\hat{t} = t \qquad \ldots\ldots\ldots (21)$$

Replacing E, p, r and t by their respective operators given by Eqs. (15), (18), (19) and (20) in Eq. (19) we obtain

$$i\hbar\frac{\partial}{\partial t} \rightarrow -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}, t)$$ ……… (22)

Allowing the operator Eq. (22) to operate on the wave function $\psi(\vec{r}, t)$ describing the state of the particle, we get$V(\vec{r}, t)$.

$$i\hbar\frac{\partial\psi(\vec{r}, t)}{\partial t} = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}, t)\right]\psi(\vec{r}, t)$$ ……… (23)

Equation (23) is the time- dependent Schrodinger equation for a particle of mass m moving in space in a force field describe by the potential energy function$V(\vec{r}, t)$.

The operator $\left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}, t)\right]$ is the operator corresponding to the total energy of the particle or the Hamiltonian of the particle. It is usual to denote this operator as $\widehat{H}$ so that the Schrodinger Eq. (23) can be written in its usual form as

$$i\hbar\frac{\partial\psi(\vec{r}, t)}{\partial t} = \hat{H}\,\psi(\vec{r}, t)$$ ……… (24)

TIME-INDEPENDENT SCHRODINGER EQUATION

Consider a particle of mass m moving freely in space. Let $\psi(\vec{r}, t)$ or $\psi(x, y, z, t)$ be the wave function for the de-Broglie wave associated with the particle at the location $\vec{r}$ or (x, y, z) at the instant of time t.

In analogy with classical mechanics, the differential equation for the wave function can be written as

$$\frac{\partial^2\psi(x,y,z,t)}{\partial x^2} + \frac{\partial^2\psi(x,y,z,t)}{\partial y^2} + \frac{\partial^2\psi(x,y,z,t)}{\partial z^2} = \frac{1}{u^2}\frac{\partial^2\psi(x,y,z,t)}{\partial t^2}$$

Where u in the wave velocity of the de-Broglie wave. The above equation can also be written as

$$\nabla^2\psi(x, y, z, t) = \frac{1}{u^2}\frac{\partial^2\psi(x,y,z,t)}{\partial t^2}$$

or $$\nabla^2\psi(\vec{r}, t) = \frac{1}{u^2}\frac{\partial^2\psi(\vec{r}, t)}{\partial t^2}$$ ……… (25)

The solution of Eq. (25) in its most general form is given by

$$\psi(\vec{r}, t) = \psi(\vec{r})\, e^{-i\omega t} \qquad \text{……… (26)}$$

where $$\omega = 2\pi\nu \qquad \text{……… (27)}$$

v being the frequency of the wave and $\psi(\vec{r})$ is the time-independent function and represents the amplitude of the wave at the location $\vec{r}$.

We get from Eq. (26) an differentiation with respect to time t

$$\frac{\partial\psi(\vec{r},t)}{\partial t} = -i\omega\, \psi(\vec{r})\, e^{-i\omega t}$$

Differentiating the above equation with respect to time t we get

$$\frac{\partial^2\psi(\vec{r},t)}{\partial t^2} = -\omega^2\, \psi(\vec{r})\, e^{-i\omega t} \qquad \text{……… (28)}$$

Using Eq. (28) in Eq. (25) we get

$$\nabla^2\psi(\vec{r},t) = -\frac{\omega^2}{u^2}\, \psi(\vec{r},t) \qquad \text{……… (29)}$$

We have

$$\omega = 2\pi\nu = 2\pi\, \frac{u}{\lambda} \qquad \text{……… (30)}$$

where λ is the wavelength of the de-Broglie wave. Equation (30) gives

$$\frac{\omega}{u} = \frac{2\pi}{\lambda} \qquad \text{……… (31)}$$

Use of Eq. (31) in Eq. (29) gives

$$\nabla^2\psi(\vec{r},t) = -\frac{4\pi^2}{\lambda^2}\, \psi(\vec{r},t)$$

or $$\nabla^2\psi(\vec{r},t) + \frac{4\pi^2}{\lambda^2}\, \psi(\vec{r},t) = 0$$

or
$$\nabla^2[\psi(\vec{r})\, e^{-i\omega t}] + \frac{4\pi^2}{\lambda^2}\,\psi(\vec{r})\, e^{-i\omega t} = 0$$

or
$$\nabla^2\psi(\vec{r}) + \frac{4\pi^2}{\lambda^2}\,\psi(\vec{r}) = 0 \qquad \text{……… (32)}$$

It v the velocity of the particle, we have

$$\lambda = \frac{h}{mv}$$

Substituting the above in Eq. (32) we obtain

$$\nabla^2\psi(\vec{r}) + \frac{4\pi^2 m^2 v^2}{h^2}\,\psi(\vec{r}) = 0$$

or
$$\nabla^2\psi(r) + \frac{m^2 v^2}{\hbar^2}\,\psi(\vec{r}) = 0 \qquad \text{……… (33)}$$

It E be the total energy of the particle and V be its potential energy then we have the kinetic energy of the particle

$$\frac{1}{2}\, mv^2 = E - V$$

so that

$$m^2 v^2 = 2m\,(E - V) \qquad \text{……… (34)}$$

Substituting Eq. (34) in Eq. (35) we obtain

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}\,(E - V)\,\psi(\vec{r}) = 0 \qquad \text{……… (35)}$$

Equation (35) is the time-independent Schrodinger equation for a particle of mass m, total energy E moving in a force field described by the potential energy function V.

For a freely moving particle in space, V = 0, so that Eq. (34) reduces to

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}E\,\psi(\vec{r}) = 0 \qquad \text{……… (36)}$$

For one-dimensional motion localized in the region along the x-axis, Eq. (35) gives

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\,\psi(x) = 0 \qquad \text{……… (37)}$$

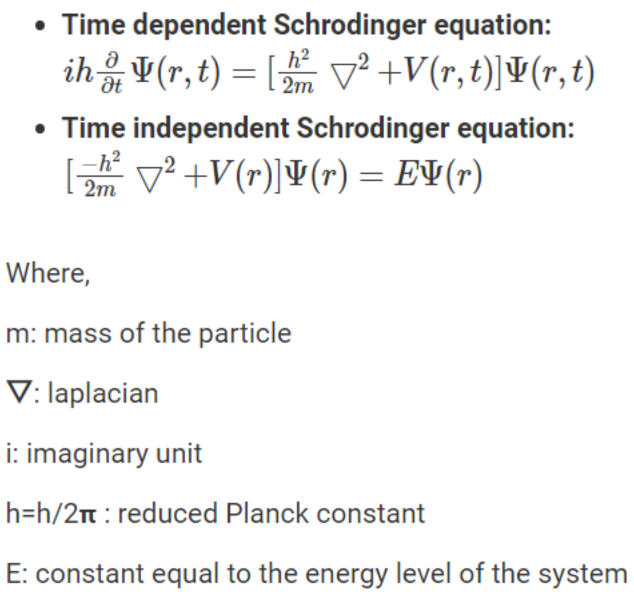
1.5 WAVE FUNCTION

In quantum physics, a wave function is a mathematical description of a quantum state of a particle as a function of momentum, time, position, and spin. The symbol used for a wave function is a Greek letter called psi, **Ψ**.

By using a wave function, the probability of finding an electron within the matter-wave can be explained. This can be obtained by including an imaginary number that is squared to get a real number solution resulting in the position of an electron. The concept of wave function was introduced in the year 1925 with the help of the Schrodinger equation.

Schrodinger equation is defined as the linear partial differential equation describing the wave function, **Ψ**. The equation is named after Erwin Schrodinger. Using the postulates of quantum mechanics, Schrodinger could work on the wave function.

Following is the equation of the Schrodinger equation:



- **Time dependent Schrodinger equation:**
  $ih\frac{\partial}{\partial t}\Psi(r,t) = [\frac{h^2}{2m}\nabla^2 + V(r,t)]\Psi(r,t)$
- **Time independent Schrodinger equation:**
  $[\frac{-h^2}{2m}\nabla^2 + V(r)]\Psi(r) = E\Psi(r)$

Where,

m: mass of the particle

∇: laplacian

i: imaginary unit

h=h/2**π** : reduced Planck constant

E: constant equal to the energy level of the system

Properties of Wave Function

- All measurable information about the particle is available.
- **Ψ** should be continuous and single-valued.
- Using the Schrodinger equation, energy calculations become easy.
- Probability distribution in three dimensions is established using the wave function.
- The probability of finding a particle if it exists is 1.

Postulates of Quantum Mechanics

- With the help of the time-dependent Schrodinger equation, the time evolution of the wave function is given.
- For a particle in a conservative field of force system, using wave function, it becomes easy to understand the system.
- The linear set of independent functions is formed from the set of eigenfunctions of operator Q.
- Operator Q associated with a physically measurable property q is Hermitian.
- By performing the expectation value integral with respect to the wave function associated with the system, the expectation value of the property q can be determined.
- For every physical observable q, there is an operator Q operating on a wave function associated with a definite value of that observable such that it yields a wave function of that many times.

PHYSICAL INTERPRETATION OF WAVE FUNCTION

Schrodinger wave function $\psi(x, t)$ or $\psi(\vec{r}, t)$ is the amplitude of the de-Broglie wave for a particle. A rough interpretation of the wave function is that the particle is most likely to be found in those regions of space in which $\psi(x, t)$ (in one dimension) or $\psi(\vec{r}, t)$ (in three dimensions) is large.

The wave function $\psi(x, t)$ or $\psi(\vec{r}, t)$ being a complex valued function of position and time cannot as such have any physical existence. However, the wave function must, in some way, be related to the presence of the particle at the position x or $\vec{r}$ at the instant of time t. Furthermore, the behavior of the particle should become completely known if the wave function is known at all possible positions at all possible of time.

(a) **Max Born and Jordan's probabilistic Interpretation.** Max Born and Jordan in 1926 gave a probabilistic interpretation of the wave function which is characteristic of and fundamental to the Schrodinger theory. This interpretation of the wave function is found to be both convenient and physically transparent enabling us to make precise computations regarding the behavior of the particle. According to Max Born and Jordan, the wave function describes the probability distribution of the particle in space and time as follows. If we try to locate the particle through a measurement of its position at a given instant of time *t*, the probability of finding the particle in a small region of volume $d^3(\vec{r})$ containing the position r in space is given by

$$P(\vec{r}, t)\, d^3(\vec{r}) = \psi^*(\vec{r}, t)\, \psi(\vec{r}, t)\, d^3(\vec{r})$$

$$= |\psi(\vec{r}, t)|^2\, d^3(\vec{r}) \qquad \text{……… (38)}$$

where $\psi^*(\vec{r}, t)$ is the complex conjugate of $\psi(\vec{r}, t)$.

The probability density is thus proportional to the square modulus of the wave function (b) The Schrodinger wave function is a complex valued function of position and time which satisfies the linear Schrodinger equation [Eq. (12) in one dimension.

Every definite wave function describes a definite state of motion of the particle.

It is important to note that if $\psi(\vec{r}, t)$ is a possible wave function then $\psi'(\vec{r}, t) = e^{i\theta}(\vec{r}, t)$ is also a possible wave function if θ is an arbitrary real constant. The probability distribution define by ψ and ψ' are exactly identical $\left[\because |\psi'(\vec{r}, t)|\ d^3(\vec{r}) = \left|e^{i\theta}\psi(\vec{r}, t)\right|\ d^3(\vec{r}) = |\psi(\vec{r}, t)|\ d^3(\vec{r})\right]$. This means that two wave function ψ and ψ' describe the same state of motion of the particle.

From the above we find:

To every wave function there corresponds a unique state of motion of the particle. However, a given state of motion of the particle does not correspond to a unique wave function. The wave function corresponding to a given state is known only to within a constant complex factor (phase factor) of modulus unity.

ACCEPTABLE WAVE FUNCTIONS FOR A PHYSICAL SYSTEM

The dynamical state of a physical system say, a particle moving in space, is defined by the wave function $\psi(\vec{r}, t)$ which is a complex valued function of position $\vec{r}$ in space and time *t*.

The quantity $\psi^*(r, t)\, \psi(\vec{r}, t) d^3\, (\vec{r})$, i.e., the quantity $|\psi(\vec{r}, t)|^2 d^3(\vec{r})$ gives the probability of finding the particle within a volume element $d^3(\vec{r})$ about the position $\vec{r}$. In other words, $|\psi(\vec{r}, t)|^2$ is the probability density, i.e., the probability density, i.e., the probality of finding the particle within a unit volume about the position $\vec{r}$ at the time *t*. This probabilistic interpretation of the wave function necessitates some conditions that must be satisfied by it for its physical acceptability. These conditions are:

(i) Wave function must be finite at all positions at all instants of time. This requirement stems from the fact that $|\psi(\vec{r}, t)|^2 d^3(\vec{r})$ must lie between 0 and 1.

(ii) Wave function must be single valued at any position at all instants of time. This requirement of single validness arises from the fact that at any given position, the wave function must be unique so that the probability density at the position be uniquely defined at all instants of time.

(iii) Wave function $\psi(\vec{r}, t)$ must be a continuous function of position $\vec{r}$ and time t. Further, the gradient of the wave function $\vec{\nabla}\psi(\vec{r}, t)$ should be continuous at all points in space. These requirements follow from the fact that the probability current density $\vec{J}(\vec{r}, t)$, which is intimately related to the probabilistic interpretation, is define through $\psi(\vec{r}, t)$ and $\vec{\nabla}\psi(\vec{r}, t)$. The Schrodinger equation satisfied by the wave function contains the term $\vec{\nabla}\psi$ which can exist provided $\vec{\nabla}\psi$ is a continuous function at all points in space.

(iv) The wave function must be quadratically integrable, i.e., we must have

$$\int_{-\infty}^{+\infty} \psi^*(\bar{r}, t)\, \psi(\bar{r}, t) d^3(\bar{r}) = \text{a finite quantity}$$

If the above condition is satisfied then we may define a normalized wave function that corresponds to a total probability to unity.

1.6 STATIONARY STATES

The time-dependent states of a quantum system are the solutions of the general time-dependent Schrodinger equation

$$i\hbar \frac{\partial \psi(\bar{r}, t)}{\partial t} = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\bar{r}, t) \right] \psi(\bar{r}, t)$$

$$= \hat{H}\psi(\vec{r}, t) \qquad \text{……… (39)}$$

the operator $\hat{H}$ being the Hamiltonian for the system. The solution of the above equation when $\hat{H}$ is explicitly dependent on time is generally a difficult task and is treated most commonly by approximate methods. For the moment, it will suffice to consider conservative system, that is, system for which $\hat{H}$ does not depend explicitly on time. If such is the case, the above equation becomes.

$$i\hbar \frac{\partial \psi(\bar{r}, t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\bar{r}) \right] \psi(\bar{r}, t)] \qquad \text{……… (40)}$$

Since the operator $\left(i\hbar\frac{\partial}{\partial t}\right)$ on the left is independent of coordinates while the operator $\left[\frac{-\hbar^2}{m}\nabla \ \ + v(\vec{r})\right]$ on the right is independent of time, it is reasonable to use, as a trial solution of eq. (40), one in the separated form:

$$\psi(\vec{r}, t) = \psi(\vec{r})T\ (t) \qquad \text{………} (41)$$

Substituting Eq. (41) in Eq. (40) we get

$$\psi(\vec{r})i\hbar\frac{dT(t)}{dt} = \left[\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})\right]T(t)$$

Dividing throughout by $\psi(\vec{r})$T (t), we get

$$\frac{1}{T(t)}i\hbar\frac{dT(t)}{dt} = \frac{1}{\psi(\vec{r})}\left[\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})\right] \qquad \text{……} (42)$$

The left-hand side of the above equation is a function of only time while the right-hand side is a function of only coordinates. Hence for the above equation to hold, each side must be equal to some constant. Taking this constant as equal to E we obtain.

$$\text{(a)}\ \frac{i\hbar}{T(t)}\frac{dT(t)}{dt} = E \qquad \text{or}\ i\hbar\frac{dT(t)}{dt} = ET(t) \qquad \text{……} (43)$$

$$\text{(b)}\ \frac{1}{\psi(\vec{r})}\left[\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r})\right] = E \quad \text{or}\ \left[\frac{-\hbar^2}{2m}\nabla^2\ V(\vec{r})\right]\psi(\vec{r}) = E\psi(r)$$

$$\text{………} (44)$$

Solution of eq. (43) is given by

$$T(t) = e^{\frac{-i}{\hbar}Et} \qquad \text{………} (45)$$

Using Eq. (45) in Eq. (41) we may write the solution of the Schrodinger Eq. 40 as

$$\psi(\vec{r}, t) = \psi(\vec{r})\,e^{\frac{-i}{\hbar}Et} \qquad \text{………} (46)$$

Equation (44) can be written as

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \qquad \text{……… (47)}$$

where $$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}) = \frac{\hat{p}^2}{2m} + V(\vec{r}) \qquad \text{……… (48)}$$

i.e., $\hat{H}$ = operator corresponding to kinetic energy + operator corresponding to potential energy

or $\hat{H}$ = operator corresponding to the total energy of the system.

Equation (47) is the energy eigenvalue equation and the constant is thus identified as the energy eigenvalue. In general, Eq. (47) has a complete set of solutions $\psi_n(\vec{r})$ such that

$$\hat{H}\psi_n(\vec{r}) = E_n\psi_n(\vec{r}) \qquad \text{……… (49)}$$

E_n represent the possible results of energy measurement performed on the system. Including the time-dependent part, we have the wave function of the system

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{\frac{-i}{\hbar}E_n t} \qquad \text{……… (50)}$$

Equation (50) gives the time-dependent states of the system.

The probability density, i.e., the probability of finding the particle, with energy eigenvalue En within unit volume about the position $\vec{r}$ at the instant t is given by

$$P_n(\vec{r}, t) = |\psi_n(\vec{r}, t)|^2$$

$$= \psi_n^*(\vec{r})e^{\frac{i}{\hbar}E_n t}\, \psi_n^*(\vec{r})e^{\frac{-i}{\hbar}E_n t}$$

$$= |\psi_n(\vec{r})|^2 \qquad \text{……… (51)}$$

We find that $P_n(\vec{r}, t)$ = constant in time. ……… (52)

The states describe by wave function such as $\psi_n(\vec{r}, t)$ given by eq. (50) for which the probability density is constant in time are called stationary or steady states of the system.

Let us now consider an observable A for the system whose operator $\hat{A}$ does not depend on time explicitly. By definition, the expectation value of A in the stationary state describe by the wave function $\psi_n(\vec{r}, t)$ is given by

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}, t)\, \hat{A}\psi_n(\vec{r}, t) d^3(\vec{r})$$

$$= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}, t)\, e^{\frac{iEn}{\hbar}t} \hat{A}\psi_n(\vec{r})\, e^{\frac{-iEn}{\hbar}t} d^3(\vec{r})$$

$$= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r})\, \hat{A}\psi_n(r)\, d^3(\vec{r}) = \text{constant in time} \qquad \text{……… (53)}$$

We find that the expectation value of an observable, which is not an explicit function of time, in any stationary state is constant in time.

We know that the equation of continuity for probability is given by

$$\frac{\partial P(\vec{r}, t)}{\partial t} + \vec{\nabla}.\vec{J}(\vec{r}, t) = 0 \qquad \text{……… (54)}$$

For stationary states, probability density $P(\vec{r}, t)$ is independent of time so that $\frac{\partial P(\vec{r},t)}{\partial t} = o.$

Clearly, for stationary states, the current density $\vec{J}(\vec{r}, t)$, according to Eq. (54), satisfies

$$\vec{\nabla} \cdot \vec{J}(\vec{r}, t) = 0$$

or

$$\text{div } \vec{J}(\vec{r}, t) = 0 \qquad \text{……… (55)}$$

Bound States

Under many physical situations, we come across states of a quantum system called the bound states. These are essentially stationary states which are described by wave functions which vanish at infinity. Clearly, for bound states, the probability also vanishes at infinity.

Superposition States

As we have seen, the particular solution of Eq. (40) are of the form

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{\frac{-iE_n}{\hbar}t} \qquad \text{……… (56)}$$

The general solution of Eq. (40) are of the form

$$\psi_n(\vec{r}, t) = \sum_n a_n\, \psi_n(\vec{r}, t) = \sum a_n \psi_n(\vec{r}) e^{\frac{-iE_n}{\hbar}t} \qquad \text{……… (57)}$$

Where a_n are constants and, in particular, do not depend on time. The state of the system described by the wave function $\psi(\vec{r}, t)$ [eq. (57)] is called a superposition state.

The probability density corresponding to the superposition state is given by

$$P(\vec{r}, t) = |\psi(\vec{r}, t)|^2 = \left|\sum_n a_n \psi_n(\vec{r}) e^{\frac{-iE_n}{\hbar}t}\right|^2 \qquad \text{……… (58)}$$

$$= \sum_m \sum_n a_m^* a_n \psi_m^*(\vec{r}) \psi_n(\vec{r}) e^{\frac{i(E_m - E_n)}{\hbar}t}$$

Clearly, $P(\vec{r}, t)$ is not independent of time in a super position state. Further, the expectation value of an observable A in a super position state is given by

$$\langle A \rangle = \int \psi^*(\vec{r}, t)\, \hat{A} \psi(\vec{r}, t) d^3\vec{r}$$

$$= \sum_m \sum_n a_m^* a_n\, e^{\frac{i(E_m - E_n)t}{\hbar}} \int \psi_m^*(\vec{r}) \hat{A} \psi_n(\vec{r}) d^3(\vec{r}) \qquad \text{……… (59)}$$

As we have seen earlier ψ_n's are the energy eigen functions, i.e., the eigen functions of the Hamiltonian operator $\widehat{H}$.

If $\hat{A}$ commuters with $\hat{H}$, then ψ_n's are also the eigen function of $\hat{A}$. In such a case we may write

$$\langle A\rangle = \sum_m \sum_n a_m^* a_n \, e^{\frac{i(E_m - E_n)t}{\hbar}} A_n \int \psi_m^*(\vec{r})\psi_n(\vec{r})d^3(\vec{r})$$

$$= \sum_m \sum_n a_m^* a_n \, e^{\frac{i(E_m - E_n)t}{\hbar}} A_n \, \delta_{mn}$$

where $\delta_{mn} = \int \psi_m^*(\vec{r})\psi_n(\vec{r})d^3(\vec{r}) = 1, \quad \text{if } m = n$

$= 0, \quad \text{if } m \neq n$

Hence, we obtain

$$\langle A\rangle = \sum |a_m|^2 \, A_m \qquad \text{……… (60)}$$

Clearly <A> is constant in time in a super position state provided $\hat{A}$ commutes with $\hat{H}$. If A does not commute with $\hat{H}$, $(\hat{A})$ is time-dependent in general as indicated by Eq. (134).

1.7 PROBABILITY CURRENT DENSITY

The wave function $\psi(\vec{r},t)$ which describes the state of motion of a particle of mass m moving under a force field described by the potential energy function $V(\vec{r},t)$ [assumed real] satisfies the time dependent Schrodinger equation

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \left[\frac{-\hbar^2}{m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t) \qquad \text{………… (61)}$$

Taking complex conjugate of Eq. (61) we get

$$-i\hbar\frac{\partial\psi^*(\vec{r},t)}{\partial t} = \left[\frac{-\hbar^2}{m}\nabla^2 + V(\vec{r},t)\right]\psi^*(\vec{r},t) \qquad \text{………….. (62)}$$

Multiplying Eq. (61) by $\psi^*(\vec{r},t)$ from the left and Eq. (62) by $\psi(\vec{r},t)$ from the left and subtracting we obtain

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

or $\quad i\hbar\frac{\partial\psi}{\partial t}[\psi^*\psi] = \frac{-\hbar^2}{m}[\psi^*\nabla \quad - \psi\nabla \ \psi \ ]$

or $\quad \frac{\partial\psi}{\partial t}[\psi^*\psi] = \frac{i\hbar}{m}[\psi^*\nabla \quad - \psi\nabla \ \psi \ ] \qquad$ …….. (63)

Writing the Laplacian operator ∇ in term of derivatives we get according to Eq. (63),

$$\frac{\partial\psi}{\partial t}[\psi^*\psi] = \frac{i\hbar}{2m}\left[\psi^*\frac{\partial\ \psi}{\partial x} + \psi^*\frac{\partial\ \psi}{\partial y} + \psi^*\frac{\partial\ \psi}{\partial z} - \psi\ \frac{\partial\ \psi^*}{\partial x} - \psi\ \frac{\partial\ \psi^*}{\partial y} - \psi\ \frac{\partial\ \psi^*}{\partial z}\right]$$

or $$\frac{\partial\psi}{\partial t}[\psi^*\psi] = -\frac{i\hbar}{m}\frac{\partial}{\partial x}\left[\psi\ \frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right] - \frac{i\hbar}{m}\frac{\partial}{\partial y}\left[\psi\ \frac{\partial\psi^*}{\partial y} - \psi^*\frac{\partial\psi}{\partial y}\right] - \frac{i\hbar}{m}\frac{\partial}{\partial z}\left[\psi\ \frac{\partial\psi^*}{\partial z} - \psi^*\frac{\partial\psi}{\partial z}\right] \quad \text{………. (64)}$$

Let us define

$$J_x = \frac{i\hbar}{m}\left[\psi\ \frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right] \quad \text{………. (65)}$$

$$J_y = \frac{i\hbar}{m}\left[\psi\ \frac{\partial\psi^*}{\partial y} - \psi^*\frac{\partial\psi}{\partial y}\right] \quad \text{…………. (66)}$$

$$J_z = \frac{i\hbar}{m}\left[\psi\ \frac{\partial\psi^*}{\partial z} - \psi^*\frac{\partial\psi}{\partial z}\right] \quad \text{…………. (67)}$$

Then using Eqs. (65), (66) and (67) in Eq. (64) we obtain

$$\frac{\partial}{\partial t}[\psi^*\psi] = \left[\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right] = 0 \quad \text{……………. (68)}$$

Equation (68) can alternatively be expressed as

$$\frac{\partial}{\partial t}[\rho(\vec{r},t)] + \vec{\nabla}.\vec{J}(\vec{r},t) = 0 \quad \text{……………. (69)}$$

where $$\vec{J}(\vec{r},t) = \frac{i\hbar}{m}\left[\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right] \quad \text{……..……. (70)}$$

$$\rho(\vec{r},t) = \psi^*\psi \quad \text{………….. (71)}$$

We have the well-known equation of continuity in fluid dynamics

$$\frac{\partial\rho}{\partial t} + \vec{\nabla}.\vec{J} = 0 \quad \text{………….. (72)}$$

Where,

ρ = number of fluid particles per unit volume or particle density

$\vec{J}$= the number of fluid particles that cross unit area in unit time in a direction perpendicular to the area, and is called the current density.

Comparing Eq. (69) with Eq. (72) we may interpret $\rho(\vec{r},t) = \psi^*\psi$ as the position probability density so that ψ ψ $d^3(\vec{r})$ is the probability of finding the particle in the volume element $d^3(\vec{r})$about the point $(\vec{r})$ at the instant t.

and

$$\vec{J}(\vec{r},t) = probability\ current\ density.$$

The above result is referred to as the conservation of probability. The result holds as long as the particle under consideration is stable and does not undergo any kind of decay or does not annihilate or disappear due to some reason.

1.8 EQUATION OF CONTINUITY

We generate one equation by multiplying the Schrödinger equation with, where * means conjugate complex. We generate another equation by multiplying the (Schrödinger equation)* with $-\Psi(x,t)$ and add both equations. The result is

$$i\hbar(\Psi^*\partial_t\Psi + \Psi\partial_t\Psi^*) = -\frac{\hbar^2}{2m}\left[\Psi^*\partial_x^2\Psi - \Psi\partial_x^2\Psi^*\right]$$

$$i\hbar\partial_t(\Psi\Psi^*) = -\frac{\hbar^2}{2m}\partial_x\left[\Psi^*\partial_x\Psi - \Psi\partial_x\Psi^*\right].$$

This can be written in the form of a continuity equation:

$$\boxed{\begin{array}{rcl} & & \frac{\partial}{\partial t}\rho(x,t) + \frac{\partial}{\partial x}j(x,t) = 0 \\ \rho(x,t) & \equiv & \Psi(x,t)\Psi^*(x,t) \\ j(x,t) & \equiv & -\frac{i\hbar}{2m}\left[\Psi(x,t)^*\frac{\partial}{\partial x}\Psi(x,t) - \Psi(x,t)\frac{\partial}{\partial x}\Psi^*(x,t)\right]. \end{array}}$$

1.9 SUMMARY

Quantum mechanics is the branch of physics that deals with the behavior of matter and light on a subatomic and atomic level. It attempts to explain the properties of atoms and molecules and their fundamental particles like protons, neutrons, electrons, gluons, and quarks. The properties of particles include their interactions with each other and with electromagnetic radiation. So below mentioned are those two pointers one should know necessarily before tackling quantum mechanics.

Schrodinger wave equation is a mathematical expression describing the energy and position of the electron in space and time, taking into account the matter wave nature of the electron inside an atom.

It is based on three considerations. They are;

a. Classical plane wave equation,

b. Broglie’s Hypothesis of matter-wave, and

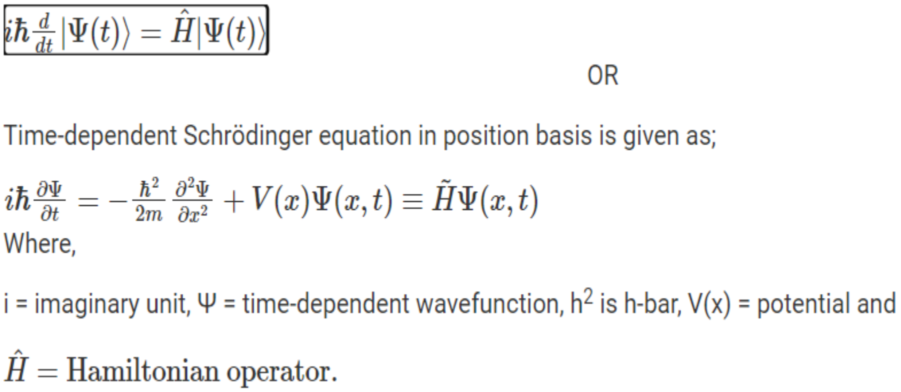
c. Conservation of Energy.

Schrodinger equation gives us a detailed account of the form of the wave functions or probability waves that control the motion of some smaller particles. The equation also describes how these waves are influenced by external factors. Moreover, the equation makes use of the energy conservation concept that offers details about the behaviour of an electron that is attached to the nucleus.

Besides, by calculating the Schrödinger equation we obtain Ψ and Ψ2, which helps us determine the quantum numbers as well as the orientations and the shape of orbitals where electrons are found in a molecule or an atom.

There are two equations, which are time-dependent Schrödinger equation and a time-independent Schrödinger equation.

Time-dependent Schrödinger equation is represented as;



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

OR

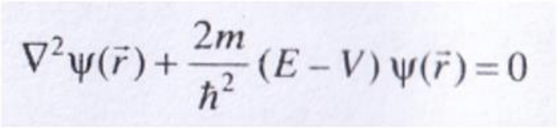
Time-dependent Schrödinger equation in position basis is given as;

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi(x,t) \equiv \tilde{H}\Psi(x,t)$$

Where,

i = imaginary unit, Ψ = time-dependent wavefunction, h^2 is h-bar, V(x) = potential and

$\hat{H}$ = Hamiltonian operator.



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

………………M

Equation (M) is the time-independent Schrodinger equation for a particle of mass m, total energy E moving in a force field described by the potential energy function V.

1.10 TERMINAL QUESTIONS

1. Explain the concept of Quantum Mechanics.
2. Difference between Classical Mechanics and Quantum Mechanic.
3. Describe the concept of Stationary States.
4. Discuss about Probability current density.
5. Explain equation of continuity.

1.11 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 1.3
2. Section 1.3
3. Section 1.6
4. Section 1.7
5. Section 1.8

1.12 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

UNIT 2 CONDITION OF WAVE FUNCTION

Structure

2.1 INTRODUCTION

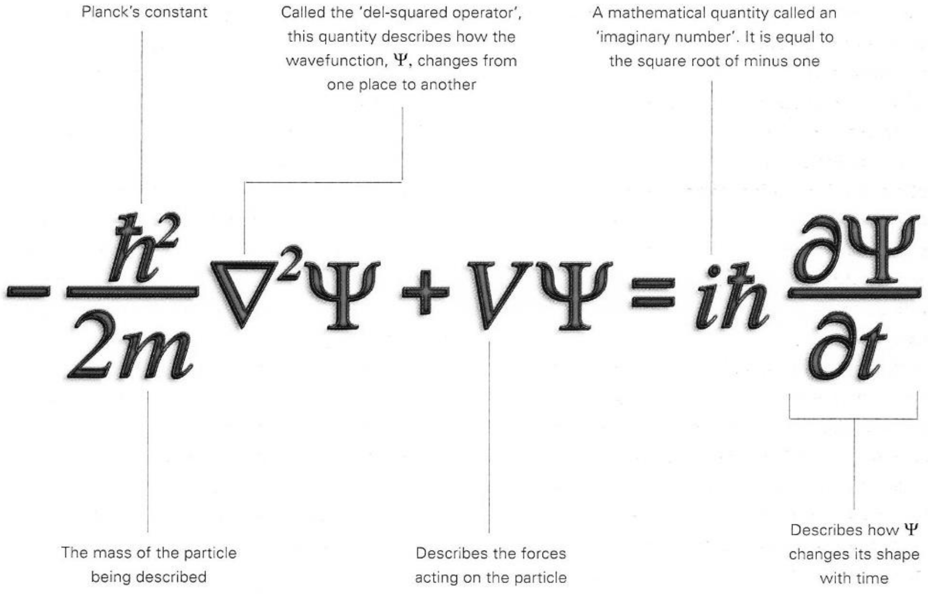
In quantum physics, a wave function is a mathematical description of a quantum state of a particle as a function of momentum, time, position, and spin. The symbol used for a wave function is a Greek letter called psi, **Ψ**.

By using a wave function, the probability of finding an electron within the matter-wave can be explained. This can be obtained by including an imaginary number that is squared to get a real number solution resulting in the position of an electron. The concept of wave function was introduced in the year 1925 with the help of the Schrodinger equation.

Significance of wave function

The wave function ψ itself has no physical significance but the square of its absolute magnitude $|\psi 2|$ has significance when evaluated at a particular point and at a particular time $|\psi 2|$ gives the probability of finding the particle there at that time. The wave function $\psi(x,t)$ is a quantity such that the product $P(x,t)=\psi*(x,t)\psi(x,t)$ is the probability per unit length of finding the particle at the position x at time t. $P(x,t)$ is the probability density and $\psi^*(x,t)$ is complex conjugate of ψ(x,t). Hence the probability of finding the particle is large wherever ψ is large and vice-versa.

We have learned about Schrödinger's wave equation in previous unit.



2.2 OBJECTIVES

- Know about the normalizable wave function.
- Discuss about condition for normalized wave function.
- Define Dirac Delta Function.
- Explain Ehrenfest Theorem.
- Understand Expectation value of a Physical Quantity.

2.3 PHYSICAL INTERPRETATION OF WAVE FUNCTION

- We know that the moving particle has a wave nature. The mathematical function which describes motion is the wave function ψ(x, y, z, t). The wave function actually contains all the information which the uncertainty principle allows us to know about the associated particle. But the wave uncertainty ψ itself has no physical interpretation, as it may be positive, negative or complex.
- The basic connection between the properties of the particle and its associated wave function is expressed in terms of the probability density. The square of absolute magnitude of wave function |ψ|2 (called probability density) evaluated at a particular place at a particular instant of time is

proportional to the probability of finding the particle there at that time. As the wave functions are usually complex with real and imaginary parts, the probability |ψ|2 is taken as the product ψψ*, where ψ* is a complex conjugate of ψ. This interpretation was given by Max Born in 1926. According to Born's postulate.

"If at an instant t, a measurement is made to located a particle having the wave function ψ(x, t), then the probability P(x, t) of finding the particle in a range x and x + dx will be equal to ψ(x, t)ψ*(x, t) dx".

- In general, the probability of finding the particle in volume element dV is

$$P(r, t)\ dV = |\psi(r, t)|2\ dV$$

The function ψ(r, t) is called probability amplitude.

- Since |ψ|2 or ψψ* represents the probability density, the integral of |ψ|2 over all space representing the total probability must be finite because the particle is present somewhere. Because of the way of definition of ψ, |ψ|2 cannot be negative or complex. Since the particle under consideration will always be found somewhere, total probability always equal to unity i.e.

$$\int |\psi|\ \ dV = 1 \qquad or \qquad \int \psi\psi^*\ \mathrm{dV} = 1$$

- The integral in the above equation is carried out over the entire space. The above condition on ψ is called the normalization condition. The wave function that satisfies the above condition is called normalized wave function.

- If the wave function is not normalized, in order to normalize the wave, function it is multiplied by some arbitrary constant and then the above integral is evaluated over the entire space. The normalization procedure is as follows:

If ψ is not normalized, multiply it by some constant A. Then evaluate the integral and equate it to unity calculate the constant A called normalization constant i.e.

$$\int A\psi(\mathrm{A}\psi)^*\ \mathrm{dV} = 1$$

or $AA^* \int \psi\psi^*\ dV = 1$

As A is real constant, we get

$$|A|^2 \int \psi\psi\ \ dV = 1$$

This gives normalization constant as

$$|A|\ \ = \frac{1}{\int \psi\psi^*\ dV}$$

The normalization constant can be taken as positive square root of the above result.

2.3.1 NORMALIZABLE AND UNNORMALIZABLE WAVE FUNCTION NORMALIZED WAVE FUNCTION

If the motion of the particle takes place in a space of finite extent, then the total probability P of finding the particle in the space is unity, i.e.,

P = 1

or $\int P\,(\vec{r},t)d^3(\vec{r}) = 1$

or $\int \psi^*(\vec{r},t)\ \psi\,(\vec{r},t)d^3(\vec{r}) = 1$

or $\int |\psi\,(\vec{r},t)|^2\ d^2(\vec{r}) = 1$ …………… (1)

The wave functions which satisfy Eq. (1) are called normalized wave functions. Equation (1) is usually referred to as the normalization integral.

Normalization of wave function can be understood from the following:

The Schrodinger equation given by is linear and homogeneous in the wave function $\psi(\vec{r},t)$ and its derivatives. Hence, if the solution of Equation is multiplied by a constant the resulting function is also a solution. Let $\psi(\vec{r},t)$be a solution of the Schrodinger equation. We know from the discussions in the earlier section that $|\psi'(\vec{r},t)^2|$ is a positive real number and hence its integral over the entire space is also a real positive number. We may hence write

$\int |\psi\,(\vec{r},t)|^2\ d^3(\vec{r}) = N^2$ ……….. (2)

The number N2 is called the norm of the wave function $\psi'(\vec{r},t)$.

Let us define

$\psi(\vec{r},t) = \frac{1}{N}\psi'(\vec{r},t)$ ……. (3)

Since $\psi(\vec{r},t)$ is different from $\psi'(\vec{r},t)$ only by the multiplicative constant $\frac{1}{N}$, it is also a possible function which satisfies the Schrodinger equation.

We get

$$\int |\psi\,(\vec{r},t)|\ \ d^3(\vec{r}) = \int \frac{1}{N}\,|\psi'(\vec{r},t)|\ \ d^3(\vec{r})$$

In view of Eq. (2), the above gives

$\int |\psi\,(\vec{r},t)|\ \ d^3(\vec{r}) = 1$ ………(4)

The wave function $\psi(\vec{r},t)$ satisfies Eq. (1) and is hence a normalized wave function. Comparing Eq. (4) we find that the norm of the wave function $\psi(\vec{r},t)$ is unity.

We can thus define a normalized wave function as one which has unit norm.

In Eq. (3), through which normalized wave function is defined, N must be finite. In other words, normalizable wave functions must have finite norms. For N and hence N2 to be finite we get according to Eq. (2).

$$|\psi'(\vec{r},t)^2| \rightarrow 0 \quad as \quad r \rightarrow \pm\infty$$

or

$$\psi'(\vec{r},t)^2 \rightarrow 0 \quad as \quad r \rightarrow \pm\infty \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Equation (5) is the boundary condition that must be satisfied by normalizable wave functions.

2.4 CONDITION FOR NORMALIZED WAVE FUNCTION

1. In Classical Physics (CP), we use momentum and position to describe an object. In Quantum Physics (QP), we use “wave function”. Wave function does the job of what momentum and position do in CP.
2. CP is “deterministic”. It means that an object is “definitely there at x”. QP is not. QP is “probabilistic”. In QP, at a given point, we only have a “probability of finding the object at that point”. At a given point in time, different points in space have different probabilities of existence of the particle. It means that unlike CP an object is NOT at one point, its existence (probability) is spread out.
3. To get the probability of finding a particle at a given point in space, you have to calculate the modulus of square of the value of wave function at a given point.
4. Now, logic suggests that at a given point in time, if I calculate the probability of finding an electron at every point in space, and add up all those probabilities, it should be equal to 1. In the mathematical form we write it as

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

OR

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

OR

$$\int_{-\infty}^{+\infty} \psi^* \psi dx = 1$$

This is the summation of probability at all possible points of its existence, from minus infinity to plus infinity. Such sum should be equal to 1.

A valid wave function should satisfy this property. We call this "normalization condition".

To "normalize" a wave function, calculate the sum of probabilities of finding the electron at all points in space (at a given time). It is the above integral. Let us say that this turns out to be x. But the actual answer should be 1. So, it means that you have to divide the actual wave function by x to make it 1. This process of adjusting the integral to 1 is called normalizing a vector.

ORTHONORMAL WAVE FUNCTIONS

- Normalized wave function- A wave function is said to be normalized if it satisfy following condition

$$\boxed{\int_{-\infty}^{+\infty} \psi^* \psi dx = 1}$$

- Orthogonal wave function- Two wave functions are said to be orthogonal if it satisfy following condition

$$\boxed{\int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = 0}$$

- Orthonormal Functions- which satisfy the following condition

$$\boxed{\int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = \delta_{mn}}$$

where δ_{mn} =1 for m=n and δ_{mn} =0 for m n.

REQUIREMENTS OF WAVE FUNCTION

- To be an acceptable solution of Schrodinger's time-independent equation, the wave function $\psi(x)$ and its first order derivative $\frac{d\psi}{dx}$ should satisfy certain requirements. These requirements are:

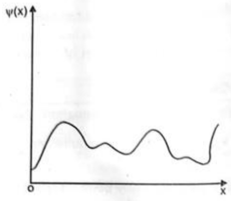
  1. $\psi(x)$ must be continuous everywhere i.e., at each and every point on space.
  2. $\psi(x)$ must be finite everywhere.
  3. $\psi(x)$ musts be single valued everywhere.
  4. Similarly, the first order derivative must be continuous, finite and single valued everywhere.

- In order to ensure that the wave function must be mathematically 'well behaved' above requirements are imposed on the wave function. (Fig. 1) illustrates the meaning of the properties of wave functions. If ψ(x) and $\frac{d\psi}{dx}$ are not finite and single valued, then the wave function $\psi(x,t) = \psi(x)e^{-iE/\hbar}$ and its derivative $\frac{d\psi(x,t)}{dx} = e^{-iE/\hbar}\frac{d\psi(x)}{dx}$ will not be continuous and single valued. The general formula of calculation of expectation values of x and p contain either $\psi(x,t)\ or\ \frac{d\psi(x,t)}{dx}$. Therefore, in any of these cases we might not obtain finite and definite values of the measurable quantity. This is completely unacceptable because the measurable quantities like <x> and <p> do not behave in unreasonable way.

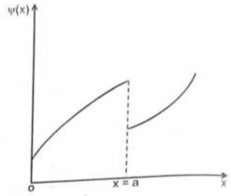
- In order that $\frac{d\psi}{dx}$ be finite, the wave function must be continuous. If the wave function ψ(x) is discontinuous, the first order derivative $\frac{d\psi}{dx}$ will be infinite at the discontinuity and the second order derivative will also be infinite. We have Schrodinger's time-independent equation

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

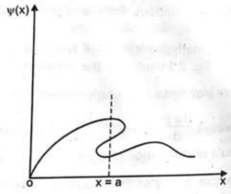
- For finite values of E, V and ψ(x), the second order derivative $\frac{d^2\psi}{dx^2}$ must be finite. This requires that dψ/dx must be finite and hence the wave function should be continuous.
- Thus, it is necessary that the wave function must be mathematically 'well behaved' and satisfies the above requirements. In Fig. 1 the wave functions in (a), (b), (c) and (d) are not acceptable. The wave function in (e) is well behaved and hence acceptable.



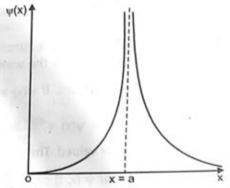
(a) Not well behaved



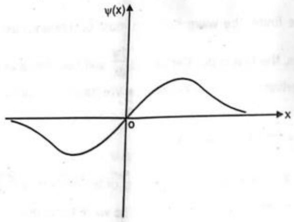
(b) Discontinuous at x = a



(c) Not single valued



(d) Not finite at x = a



(e) Well behaved

2.5 EXPECTATION VALUES OF A PHYSICAL QUANTITY

Let us consider a particle in a definite state described by the normalized wave function $\psi(\vec{r},t)$. Let us make a large number of observations (measurement) of the position vector $\vec{r}$ of the particle. We know that each observation causes the wave function to undergo some change. Let us suppose that we have at our disposal some technique to bring the wave function to the original form before any observation is made. Even if we ensure that before any measurement the wave function is restored to its original form, we do not get the same result each time. The average of the value obtained in these measurements is called the measured value or the expectation value and is denoted as $(\vec{r})$. Since $\psi^*(\vec{r},t)\ \psi(\vec{r},t)$ represents the probability with which the value $\vec{r}$ occurs in the measurement we get

$$\langle\vec{r}\rangle = \int \vec{r}\psi^*\psi\ d^3(\vec{r}) = \int \psi^*\vec{r}\psi\ d^3(\vec{r}) \qquad \text{.......}\ (6)$$

If the wave function $\psi(\vec{r},t)$ is not normalized the expectation value of $\vec{r}$ is given by

$$\langle\vec{r}\rangle = \frac{\int \psi^*\vec{r}\ \psi\ d^3(\vec{r})}{\int \psi^*\psi\ d^3(\vec{r})} \qquad \text{..........}\ (7)$$

Generalizing, the expectation value of any quantity f($\vec{r}$), which is a function of $\vec{r}$, in the state described by the normalized wave function $\psi(\vec{r},t)$may be written as

$$\langle f(\vec{r})\rangle = \int P(\vec{r},t)\ f(\vec{r}) d^3(\vec{r})$$

or $$\langle f(\vec{r})\rangle = \int \psi^*(\vec{r},t)\ f(\vec{r})\ \psi(\vec{r},t) d^3(\vec{r}) \qquad \text{......}\ (8)$$

Expectation Value of Total Energy E of a Particle

Consider a particle of mass m moving in space under the action of a force field describe by the potential energy function $V(\vec{r},t)$. Let $\psi(\vec{r},t)$be the normalized wave function that describes the state of the particle. The time evolution of the wave function is given by the Schrodinger equation

$$i\hbar \frac{\partial\psi(\vec{r},t)}{\partial t} = \left[\frac{-h}{2m}\nabla \ + V(\vec{r},t)\right]\psi(\vec{r},t)$$

Multiplying the above by $\psi^*(\vec{r},t)$ from the left and integrating over the entire space we get

$$\int \psi^*(\vec{r},t)\ i\hbar \frac{\partial\psi(\vec{r},t)}{\partial t} d^3(\vec{r}) = \int \psi^*(\vec{r},t)\left[\frac{-\hbar}{2m}\nabla \ + V(\vec{r},t)\right]\psi(\vec{r},t) d^3(\vec{r})$$

or $$\int \psi^*(\vec{r},t)\left[i\hbar\frac{\partial}{\partial t}\right]\ \psi(\vec{r},t) d^3(\vec{r}) = \int \psi^*(\vec{r},t)\left[\frac{-\hbar^2}{m}\nabla\ \right]\ \psi(\vec{r},t) d^3(\vec{r})$$

$$+\int \psi^*\ (\vec{r},t)\ V(\vec{r},t)\ \psi(\vec{r},t) d^3(\vec{r})$$

Using the definition of expectation value given above we obtain

$$\langle i\hbar\frac{\partial}{\partial t}\rangle = \langle\frac{-\hbar^2}{m}\nabla^2\rangle + \langle\, V(\vec{r},t)\rangle \qquad \text{………} \quad (9)$$

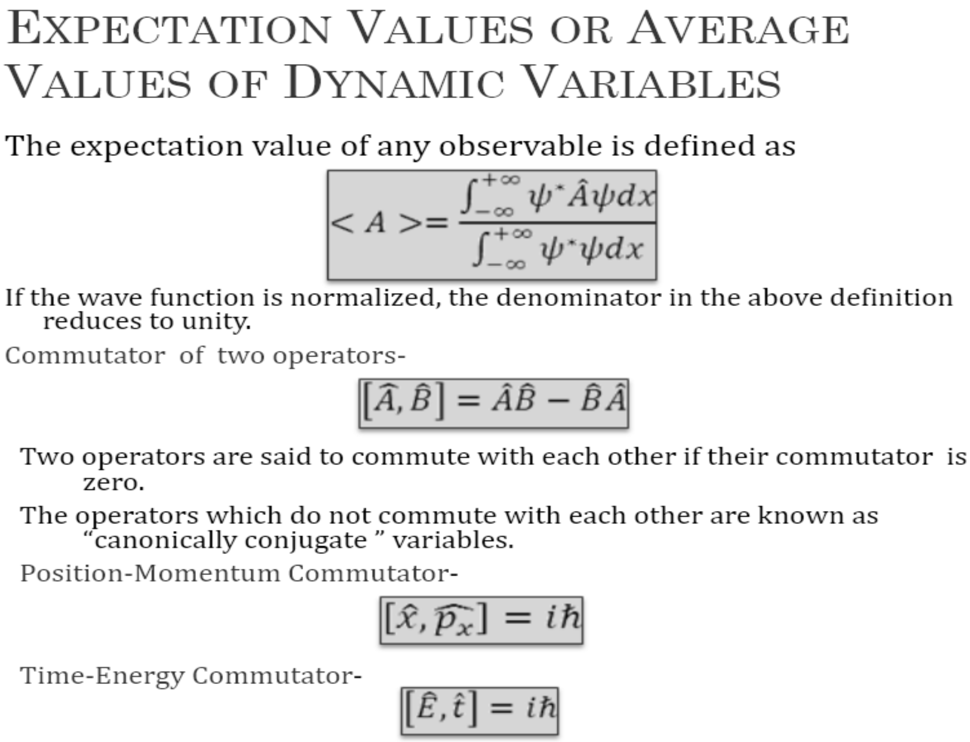
In view of Eq. (15) and Eq. (18) from Unit 1(Basic Concept) of block I, Eq. (9) gives

$$\langle E\rangle = \langle\frac{p^2}{m}\rangle + \langle V\rangle. \qquad \text{……..…} \ (10)$$

Classically, the total energy is

$$E = Kinetic\ energy + Potential\ energy\ \frac{p^2}{m} + V \qquad \text{…... } (11)$$

Equation (10) tells that the expectation value of the total energy is the sum of the expectation values of the kinetic energy and the potential energy.



Expectation Values or Average Values of Dynamic Variables

The expectation value of any observable is defined as

$$\boxed{< A >= \frac{\int_{-\infty}^{+\infty} \psi^* \hat{A}\psi dx}{\int_{-\infty}^{+\infty} \psi^* \psi dx}}$$

If the wave function is normalized, the denominator in the above definition reduces to unity.

Commutator of two operators-

$$\boxed{[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}}$$

Two operators are said to commute with each other if their commutator is zero.

The operators which do not commute with each other are known as "canonically conjugate " variables.

Position-Momentum Commutator-

$$\boxed{[\hat{x},\widehat{p_x}] = i\hbar}$$

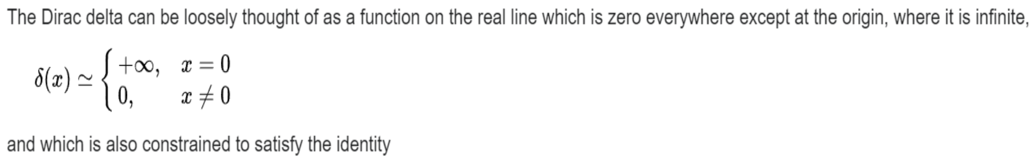
Time-Energy Commutator-

$$\boxed{[\hat{E},\hat{t}] = i\hbar}$$

2.6 DIRAC-DELTA FUNCTION

The Dirac delta function is the name given to a mathematical structure that is intended to represent an idealized point object, such as a point mass or point charge. It has broad applications within quantum mechanics and the rest of quantum physics, as it is usually used within the quantum wave function. The delta function is represented with the Greek lowercase symbol delta, written as a function: δ(x).

This representation is achieved by defining the Dirac delta function so that it has a value of 0 everywhere except at the input value of 0. At that point, it represents a spike that is infinitely high. The integral taken over the entire line is equal to 1.



The Dirac delta can be loosely thought of as a function on the real line which is zero everywhere except at the origin, where it is infinite,

$$\delta(x) \simeq \begin{cases} +\infty, & x = 0 \\ 0, & x \neq 0 \end{cases}$$

and which is also constrained to satisfy the identity

$$\int_{-\infty}^{\infty} \delta(x)\,\mathrm{d}x = 1.$$

Properties of Dirac Delta Function

$$\int_{-\infty}^{\infty} \delta(x)\mathrm{d}x = 1,$$

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\mathrm{d}k = \delta(x)$$

$$\delta(x-a) = \delta(a-x),$$

$$(x-a)\delta(x-a) = 0,$$

$$\delta(ax) = |a|^{-1}\delta(x) \quad (a \neq 0),$$

$$f(x)\delta(x-a) = f(a)\delta(x-a),$$

$$\int_{-\infty}^{\infty} \delta(x-y)\delta(y-a)\mathrm{d}y = \delta(x-a)$$

2.7 KRONECKER DELTA FUNCTION

The Kronecker delta (named after Leopold Kronecker) is a function of two variables, usually just non-negative integers. The function is 1 if the variables are equal, and 0 otherwise:

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j, \\ 1 & \text{if } i = j. \end{cases}$$

or with use of Iverson brackets:

$$\delta_{ij} = [i = j]$$

where the Kronecker delta δij is a piecewise function of variables i and j. For example, δ1 2 = 0, whereas δ3 3 = 1.

The Kronecker delta appears naturally in many areas of mathematics, physics and engineering, as a means of compactly expressing its definition above.

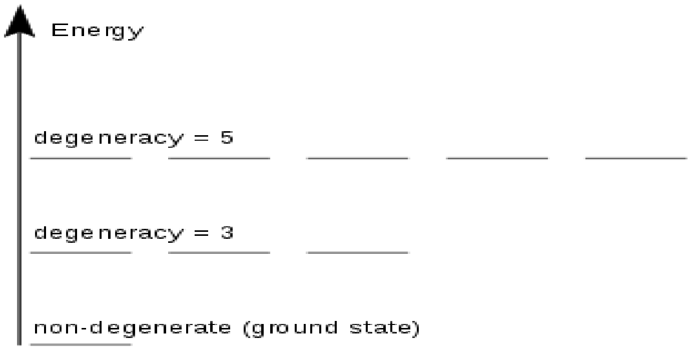
2.8 NON-DEGENERATE STATES AND DEGENERATE STATE

Degeneracy of an energy state means number of different ways (given by number of different wavefunctions) an energy state occurs.

Non-degenerate state is a state differing in both energy and the quantum state of the system. Like, a degenerate state is those having a state defined by combination of different quantum but all these states have same energy level, which is not the case in non-degenerate state.

The dimension of the eigenspace corresponding to that eigenvalue is known as its degree of degeneracy, which can be finite or infinite. An eigenvalue is said to be non-degenerate if its eigenspace is one-dimensional

An eigenvalue is degenerate if there is more than one linearly independent eigenstate belonging to the same eigenvalue.



2.9 EHRENFEST THEOREM

- We know that a particle's momentum is equal to its mass times group velocity of a wave packet of a particular type that is associated with it. But this type of treatment is not adequate to the general case, in which the shape and size of wave packet changes as the packet moves.

  Then the questions arise how the <x> and <px> behave as wave packet moves, that is, what is $\frac{d<x>}{dt}$? this difficulty was solved by Ehrenfest.

- According to him Newton's laws of motion in classical physics of the form like

$$m\frac{dx}{dt} = p \qquad and \qquad \frac{dp}{dt} = \frac{dV}{dx}$$

  Are still valid in quantum mechanics provided that we use the expectation values of the dynamical variables. This is Ehrenfest's theorem.

- In other words, the theorem states that the average motion of wave packet agrees with the motion of the corresponding classical motion of particle.

Ehrenfest's theorems are

1. First theorem:

$$m\frac{d<x>}{dt} = <p_x>$$

For all components,

$$m\frac{d<\vec{r}>}{dt} = <\vec{p}>$$

2. Second theorem: For conservative force field,

$$\frac{d<p_x>}{dt} = \langle -\frac{dV}{dx}\rangle$$

For all components,

$$\frac{d<\vec{p}>}{dt} = < -\nabla V >$$

Thus, there exists a relation among expectation values which is exactly parallel to Newton's second law expressed in terms of potential energy.

2.10 SUMMARY

Normalization of ψ(*x*,*t*):

$|\Psi(x,t)|^2$: is the probability density for finding the particle at point x, at time t.

Because the particle must be found somewhere between $x=-\infty$ and $x=+\infty$ the wave function must obey the normalization condition

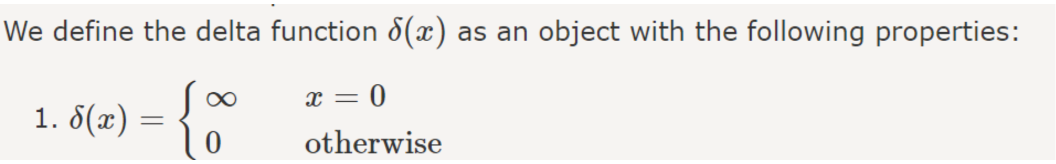
$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \, dx = 1.$$

Without this, the statistical interpretation would be meaningless. Thus, there is a multiplication factor. However, the wave function is a solution of the Schrodinger eq:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi.$$

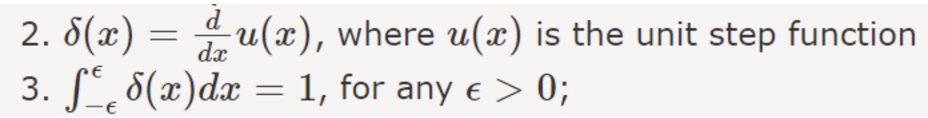
Therefore, one can't impose an arbitrary condition on ψ without checking that the two are consistent. Interestingly, if ψ(x, t) is a solution, Aψ(x, t) is also a solution where A is any (complex) constant. Therefore, one must pick a undetermined multiplicative factor in such a way that the Schrodinger Equation is satisfied. This process is called normalizing the wave function.

For some solutions to the Schrodinger equation, the integral is infinite; in that case no multiplicative factor is going to make it 1. The same goes for the trivial solution ψ= 0. Such non-normalizable solutions cannot represent particles, and must be rejected. Physically realizable states correspond to the "square-integrable" solutions to Schrodinger's equation.

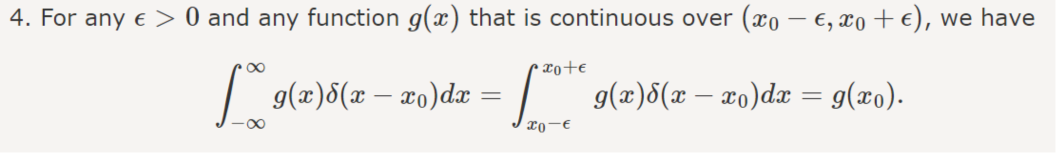


We define the delta function $\delta(x)$ as an object with the following properties:

1. $\delta(x) = \begin{cases} \infty & x = 0 \\ 0 & \text{otherwise} \end{cases}$

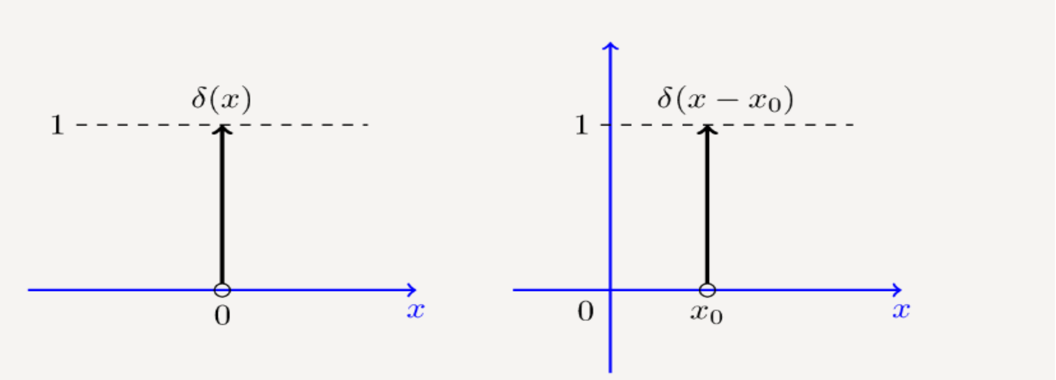


2. $\delta(x) = \frac{d}{dx}u(x)$, where $u(x)$ is the unit step function
3. $\int_{-\epsilon}^{\epsilon} \delta(x)dx = 1$, for any $\epsilon > 0$;

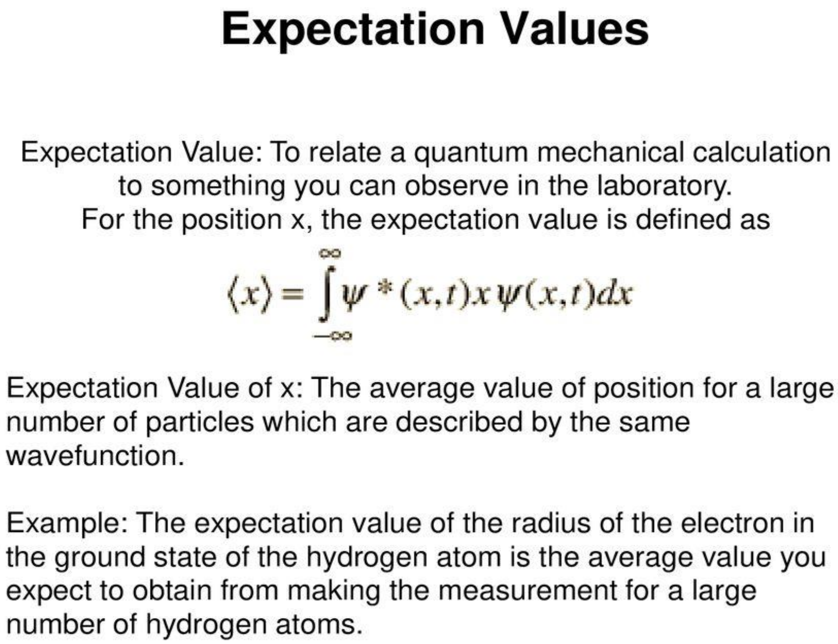


4. For any $\epsilon > 0$ and any function $g(x)$ that is continuous over $(x_0 - \epsilon, x_0 + \epsilon)$, we have

$$\int_{-\infty}^{\infty} g(x)\delta(x - x_0)dx = \int_{x_0-\epsilon}^{x_0+\epsilon} g(x)\delta(x - x_0)dx = g(x_0).$$



It shows how we represent the delta function. The delta function, δ(x), is shown by an arrow at x=0. The height of the arrow is equal to 1. If we want to represent 2δ(x), the height would be equal to 2. In the figure, we also show the function δ(x−x0), which is the shifted version of δ(x).



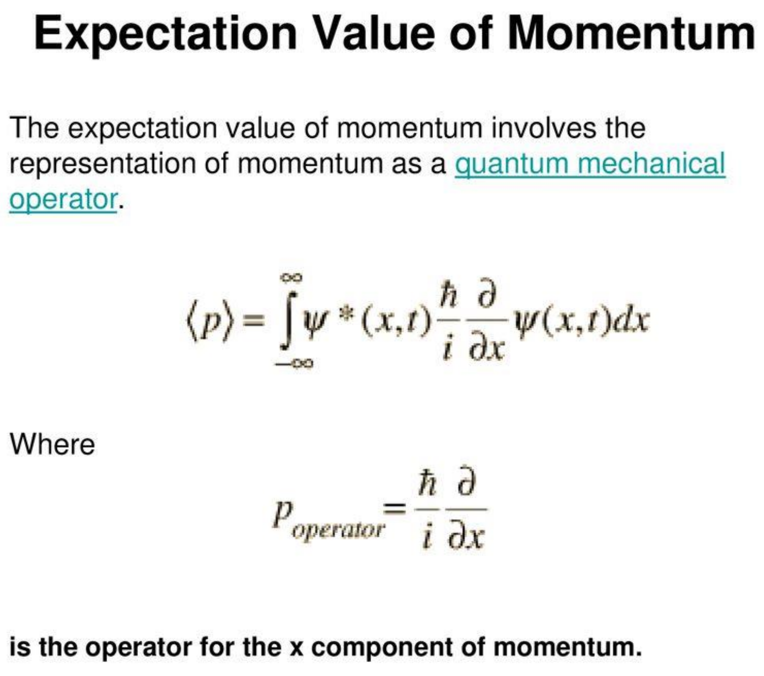
Expectation Values

Expectation Value: To relate a quantum mechanical calculation to something you can observe in the laboratory.
For the position x, the expectation value is defined as

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, x\, \psi(x,t)dx$$

Expectation Value of x: The average value of position for a large number of particles which are described by the same wavefunction.

Example: The expectation value of the radius of the electron in the ground state of the hydrogen atom is the average value you expect to obtain from making the measurement for a large number of hydrogen atoms.



Expectation Value of Momentum

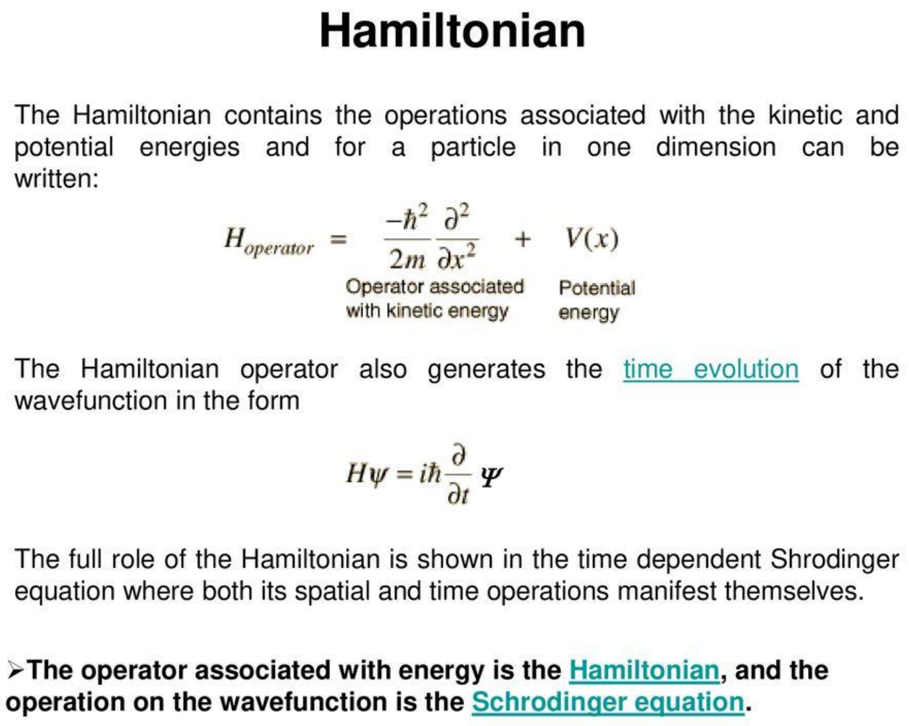
The expectation value of momentum involves the representation of momentum as a quantum mechanical operator.

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x,t)\,dx$$

Where

$$p_{operator} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

is the operator for the x component of momentum.



Hamiltonian

The Hamiltonian contains the operations associated with the kinetic and potential energies and for a particle in one dimension can be written:

$$H_{operator} = \underbrace{\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_{\text{Operator associated with kinetic energy}} + \underbrace{V(x)}_{\text{Potential energy}}$$

The Hamiltonian operator also generates the time evolution of the wavefunction in the form

$$H\psi = i\hbar \frac{\partial}{\partial t} \Psi$$

The full role of the Hamiltonian is shown in the time dependent Shrodinger equation where both its spatial and time operations manifest themselves.

➢**The operator associated with energy is the Hamiltonian, and the operation on the wavefunction is the Schrodinger equation.**

2.11 TERMINAL QUESTIONS

1. Define Expectation value

2. Explain Ehrenfest Theorem.
3. Give the Physical interpretation of the wave function.
4. Write down the condition for normalized wave function.
5. Explain Dirac Delta Function.
6. Define Kronecker Delta Function.

2.12 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 2.5
2. Section 2.9
3. Section 2.3
4. Section 2.4
5. Section 2.6
6. Section 2.7

2.13 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

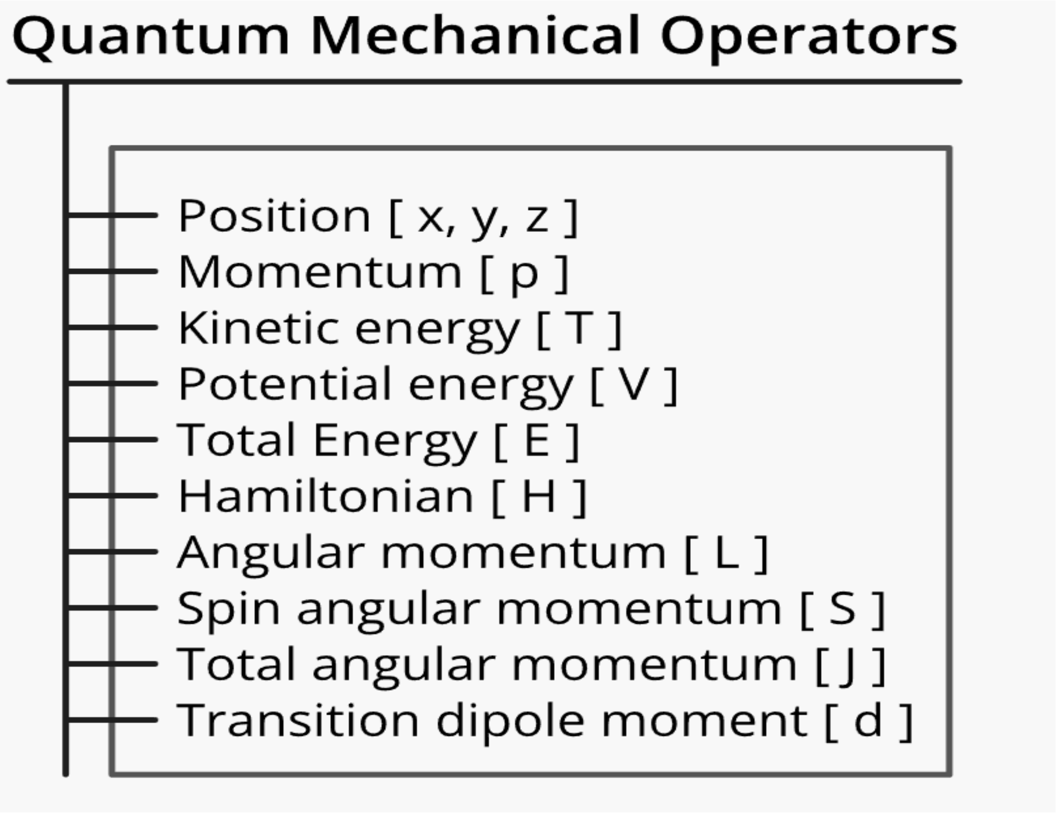
UNIT-3 OPERATOR ALGEBRA

Structure

3.1 INTRODUCTION

An operator can be imaginary as well as a complex quantity. It is a mathematical rule that acts upon a function and produces another function. As the operators of mathematical algebra, quantum mechanical operators also function under certain rules like addition, multiplication, etc. An operator has no meaning if it is written alone. Linear operators, SQR – Square operators, and Hermitian operators are some types of operators.

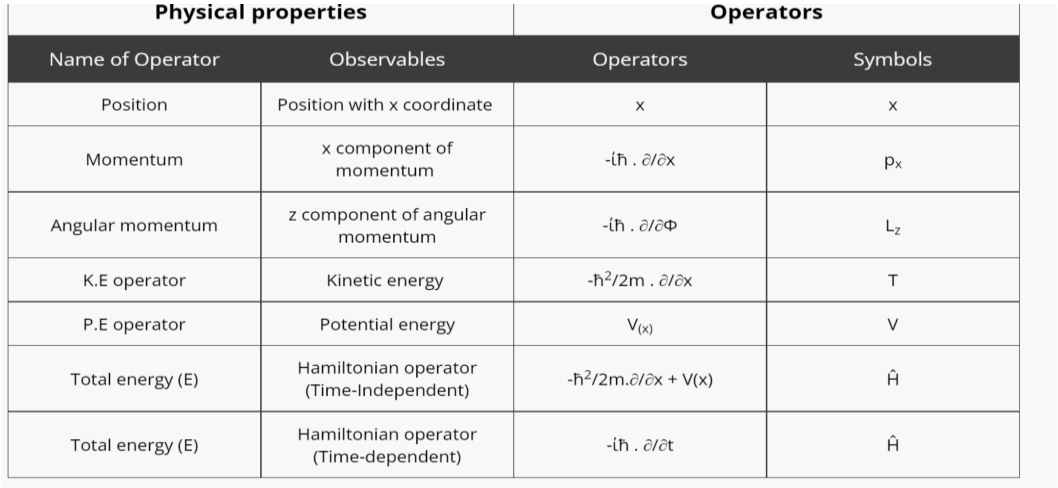
Classical observables have an associated quantum mechanical operator. In other words, for every measurable parameter in physical systems, there exists a quantum mechanical (QM) operator.



Quantum Mechanical Operators

- Position [x, y, z]
- Momentum [p]
- Kinetic energy [T]
- Potential energy [V]
- Total Energy [E]
- Hamiltonian [H]
- Angular momentum [L]
- Spin angular momentum [S]
- Total angular momentum [J]
- Transition dipole moment [d]

Quantum Operators:



Physical properties		Operators	
Name of Operator	Observables	Operators	Symbols
Position	Position with x coordinate	x	x
Momentum	x component of momentum	$-i\hbar \,.\, \partial/\partial x$	p_x
Angular momentum	z component of angular momentum	$-i\hbar \,.\, \partial/\partial \Phi$	L_z
K.E operator	Kinetic energy	$-\hbar^2/2m \,.\, \partial/\partial x$	T
P.E operator	Potential energy	$V_{(x)}$	V
Total energy (E)	Hamiltonian operator (Time-Independent)	$-\hbar^2/2m.\partial/\partial x + V(x)$	$\hat{H}$
Total energy (E)	Hamiltonian operator (Time-dependent)	$-i\hbar \,.\, \partial/\partial t$	$\hat{H}$

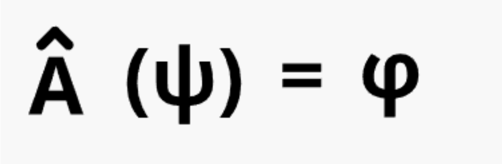
3.2 OBJECTIVES

After studying this Unit, student should able to:

- Know about Operators in QM.
- Define Null operator and Inverse Operator.
- Explain the concepts of Linear and Hermitian Operators.
- Discuss the Concept of Orbital angular Momentum.
- Know about Ladder Operators

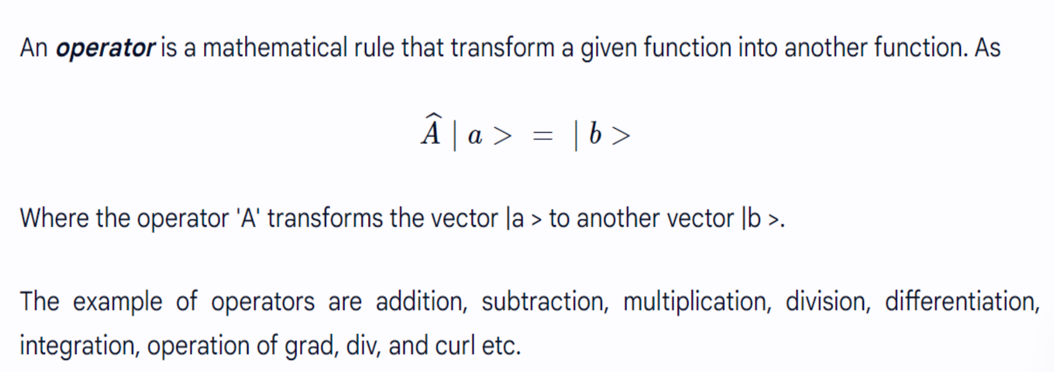
3.3 CONCEPT OF OPERATOR

An operator is a symbol that tells you to do something to whatever follows that operator. They are commonly used to perform specified mathematical operations on certain functions. Operators may be used in mathematics, physics, or chemistry but their primary purpose is always to perform operations on variables. The quantum mechanical operators are used in quantum mechanics to operate on complex and theoretical formulations. The Hamiltonian operator is an example of operators used in complex quantum mechanical equations i.e. Schrodinger's wave energy equation.



$$\hat{A}\ (\psi) = \varphi$$

Â is a function here, acting on a function (ψ). Now if Â is an operator, it will map one state vector (ψ) into another one (Φ).



An ***operator*** is a mathematical rule that transform a given function into another function. As

$$\hat{A} \mid a > \; = \; \mid b >$$

Where the operator 'A' transforms the vector |a > to another vector |b >.

The example of operators are addition, subtraction, multiplication, division, differentiation, integration, operation of grad, div, and curl etc.

Consider a function of n independent variable, $q_1, q_2, \ldots\ldots, q_n$, such as

$$\psi = \psi\ (q_1, \ldots, q_n) \qquad \ldots\ldots\ldots\ldots..\ (1)$$

Using this function, it is possible to generate any number of other functions by a simple mathematical procedure, namely, the application of a mathematical operator. Such an operator may take any one of many forms, for example

Addition operator $q_i + \psi = \phi_i$

Multiplication operator $q_i\,\psi = T_i$

Differential operator $\frac{\partial}{\partial d_i}\psi = A_i$

Integral operator $\int_A^B \psi dq_i = \Omega_i$ etc.

An operator thus defines a relationship between two functions. If the function ϕ is obtained from a function ψ then the relationship between ψ and ϕ can be expressed as

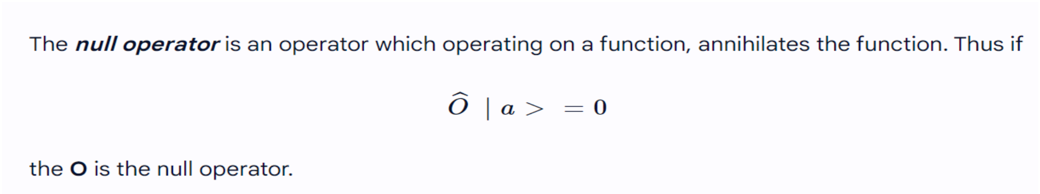
$$\hat{A}\,\psi = \phi \qquad \ldots\ldots\ldots\ (2)$$

We then say that $\hat{A}$ is the operator representing the generation of ϕ from ψ. It is important to note that the left-hand side of Eq. (2) does not necessarily mean that the function ψ is multiplied by the operator $\hat{A}$, instead, it may represent addition, differentiation, integration. Alternatively, we can say, in view of Eq. (2) that an operator maps a given function. As indicated in Eq. (2), it is usual to write an operator with the symbol of cap (^)overhead.

The set of functions $\{\psi_1\}$ for which $\hat{A}$ $\{\psi_1\}$ has a meaning is called the **domain** of $\hat{A}$.

The set of function $\{\phi_1\}$ which can be expressed as $\phi_i = \hat{A}\psi_i$, is called the **range** of $\hat{A}$.

3.4 NULL OPERATOR



The ***null operator*** is an operator which operating on a function, annihilates the function. Thus if

$$\hat{O} \mid a > \ = 0$$

the **O** is the null operator.

3.5 INVERSE OPERATOR

Consider an operator $\hat{A}$ defined in a certain domain of definition.

The inverse of $\hat{A}$ is written as $\hat{A}^{-1}$ and is defined such that

$$\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = 1$$

It is easy to see that any operator commutes with its inverse

$$[\hat{A}, \hat{A}^{-1}] = \hat{A}\,\hat{A}^{-1} - \hat{A}^{-1}\hat{A} = 1 - 1 = 0$$

3.6 OPERATOR IN QUANTUM MECHANICS

- The mathematical operations like differentiation, integration, multiplication, division, addition, subtraction etc. can be represented by certain symbols known as operators. In other words, an operator $\hat{O}$ is a mathematical operation which may be applied to function f(x), which changes the function f(x) to another function g(x). This can be represented as

  $$\hat{O}\, f(x) = g(x)$$

  For example, $\frac{d}{dx}(4x \ \ + 2x) = 8x + 2$

- In operator language $\hat{O} = \frac{d}{dx}$ operates on the function $f(x) = 4x^2 + 2x$ and changes the function f(x) to function g(x) + 2.

  Now, The wave function is given as

$\psi(x,t) = Ae^{\frac{i}{\hbar}(px-Et)}$ ……………………….(3)

Differentiating equation (3) with respect to x, we get

$$\frac{\partial\psi}{\partial x} = \frac{ip}{\hbar}\, Ae^{\frac{i}{\hbar}(px-Et)}$$

or $\frac{\partial\psi}{\partial x} = \frac{ip}{\hbar}\,\psi$

∴ $p\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x}$

or $p\psi = -i\hbar\frac{\partial\psi}{\partial x}$ ……………. (4)

Differentiating ψ(x, t) with respect to t, we get

$$\frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar}\, Ae^{\frac{i}{\hbar}(px-Et)}$$

or $\frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar}\,\psi$

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

or $E\psi = i\hbar\frac{\partial\psi}{\partial x}$ ……………… (5)

- Equation (4) indicates that there is an association between the dynamical quantity p and the differential operator $-i\hbar\frac{\partial}{\partial x}$. That is the effect of multiplying ψ(x, t) by p is same as the operating the differential operator $-i\hbar\frac{\partial}{\partial x}$ on ψ(x, t). This differential operator is called momentum operator. It can be written as

  $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ ……………. (6)

  As it is related to variable x, therefore, we have

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

  Corresponding components of momentum operators for y and z variables are

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

  and $\hat{p}z = -i\hbar\frac{\partial}{\partial z}$

  In three dimensions, the momentum operator is

- From equation (5), a similar association can be found between dynamical variable E and the differential operator $\frac{\partial}{\partial t}$. Thus,

  $E = i\hbar\frac{\partial}{\partial t}$ …………… (7)

  We have Schrodinger’s time independent equation

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

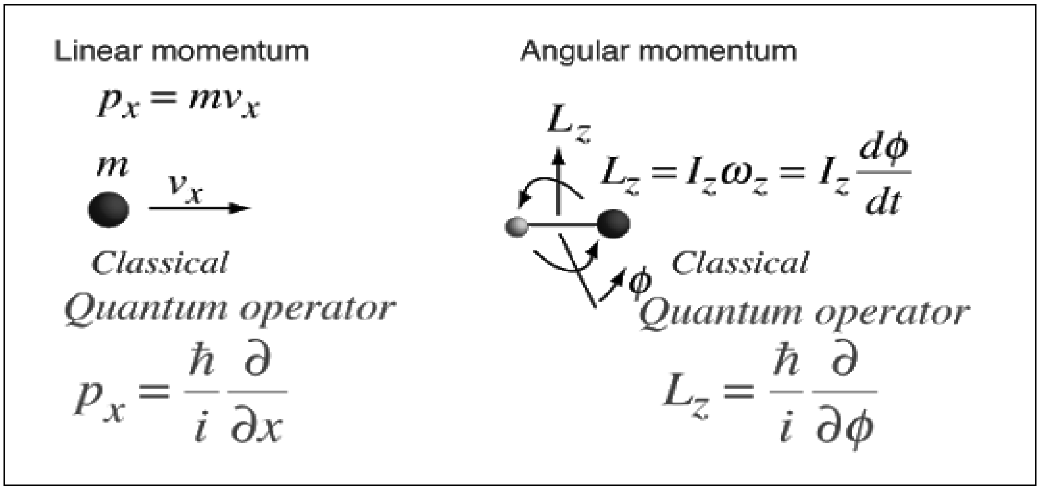
or $$-\frac{\hbar^2}{m}\nabla\ \psi + V\psi = E\psi$$

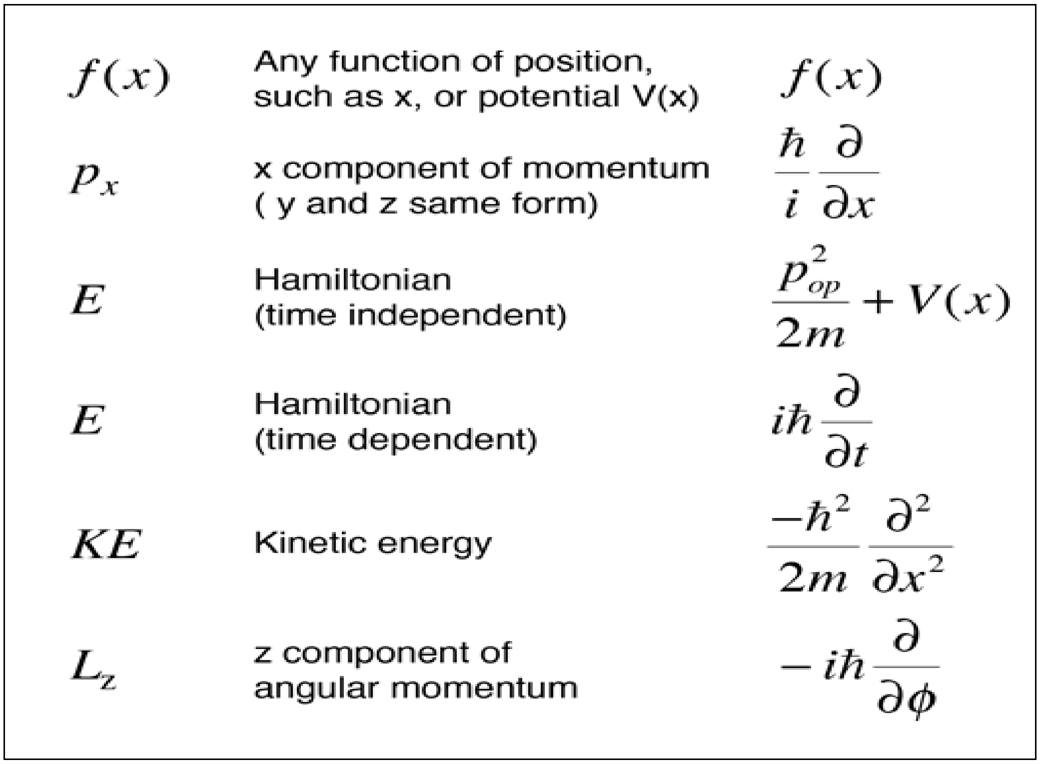
or $$\left[-\frac{\hbar^2}{m}\nabla\ \psi + V\right]\psi = E\psi \qquad \text{……….. (8)}$$

or

$$\boxed{H\psi = E\psi}$$

where $H = -\frac{\hbar^2}{m}\nabla\ + V$ is the differential operator and called as Hamiltonian operator.





$f(x)$	Any function of position, such as x, or potential V(x)	$f(x)$
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$
E	Hamiltonian (time dependent)	$i\hbar\frac{\partial}{\partial t}$
KE	Kinetic energy	$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar\frac{\partial}{\partial \phi}$

3.7 PHYSICAL OPERATORS

(1) LINEAR OPERATOR

A particular class of operators is of primary interest in the mathematical formulation of quantum theory. These are the so-called linear operators.

Consider an operator $\hat{A}$ define in a certain domain of definition. Let ψ_1 and ψ_2 be any two arbitrary functions defined in the domain of definition of $\hat{A}$.

If on operating on the sum of the functions ψ_1 and ψ_2 the operator $\hat{A}$ yields the same result as the sum of the operations on the two functions separately, then $\hat{A}$ is said to be linear operator. Thus, for the operator $\hat{A}$ to be linear we must have

$$\hat{A}(\psi_1 + \psi\ \ ) = \hat{A}\psi_1 + \hat{A}\psi \qquad \ldots\ldots\ldots\ldots (9)$$

For linearity of $\hat{A}$ we must also have

$$\hat{A}(c\psi_1) = c\hat{A}\psi_1$$

$$\hat{A}(c\psi\ \ ) = c\hat{A}\psi \qquad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

where c is a number.

The properties of linear operator expressed by the Eqs. (9) and (10) will be useful in later developments of quantum mechanics.

(2) HERMITIAN OPERATOR

Definition

The operators which play important role in quantum mechanics can be further specialized. They are not linear, they are Hermitian.

Before we define Hermitian operator, we need to define the complex conjugate of a linear operator $\hat{A}$. Let us suppose

$$\hat{A}\,\psi = \ \phi \qquad \ldots\ldots\ldots (11)$$

The operator denoted by $\hat{A}^*$ is called the complex conjugate of the operator $\hat{A}$ if, by the action $\hat{A}$ on the function ψ^* (complex conjugate of the function ψ), we get the function ϕ^* complex conjugate of the function ϕ), i.e., we get

$$\hat{A}^*\psi^* = \phi^* \qquad \ldots\ldots\ldots\ldots (12)$$

In the domain of definition V in which the operator $\hat{A}$ is define, let u and v be two functions subject to identical boundary conditions.

The operator $\hat{A}$ is said to be Hermitian operator if it satisfies the condition

$$\int_V\ u^*\hat{A}v d\tau = \int_V \left(\hat{A}u\right)^*\ vdt = \int_V\ \hat{A}^*u^*\ vd\tau \qquad \ldots.. (13)$$

Alternatively, the Hermitian character of the linear operator $\hat{A}$ is made through the definition of transpose of the operator $\hat{A}$. The transpose of the operator $\hat{A}$ is denoted by $\hat{A}$ and is defined according to the relation

$$\int_V v(\hat{A}u)d\tau = \int_V u(\hat{A}v)d\tau \qquad \text{…………….} (14)$$

The transposed operator $\hat{A}^*$ for the operator $\hat{A}^*$ is, according to Eq. (14), given by

$$\int v(\hat{A}^*u)d\tau = \int u(\hat{A}^*v)d\tau \qquad \text{……………….} (15)$$

It is usual to denote $\hat{A}^*$ and $\hat{A}^+$ (read as A-dagger) and is said to be the **Conjugate** to the operator $\hat{A}$. Now the operator $\hat{A}$ is called **Hermitian** or **self-adjoint** if.

$$\boldsymbol{\hat{A}} = \boldsymbol{\hat{A}^+} \qquad \text{…………….} (16)$$

3.8 COMMUTATOR AND NON-COMMUTATOR OPERATORS

(A) Commutator of Two Operators

Let $\hat{A}$ and $\hat{B}$ be two operators defined in the same domain of definition. A useful operator called the commutator of $\hat{A}$ and $\hat{B}$ which is usually written as $[\hat{A}, \hat{B}]$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \qquad \text{……..} (17)$$

From the definition given by Eq. (17) it follows that

$$[\hat{B}, \hat{A}] = \hat{B}\hat{A} - \hat{A}\hat{B} \qquad \text{…………….} (18)$$

Equations (17) and (18) give

$$[\hat{A}, \hat{B}] = [\hat{B}, \hat{A}] \qquad \text{………} (19)$$

The operator $\hat{A}$ and $\hat{B}$ are said to commute with each other or the operators $\hat{A}$ and $\hat{B}$ are said to be commutative, if

$$\hat{A}, \hat{B} = \hat{B}\hat{A} \qquad \text{………………} (20)$$

or

$$\hat{A}, \hat{B} - \hat{B}\hat{A} = 0 \qquad \text{…………} (21)$$

And hence the commutator

$$[\hat{A}, \hat{B}] = 0 \qquad \text{……………} (22)$$

If the operators $\hat{A}$ and $\hat{B}$ are such that Eq. (20) or Eq. (21) or Eq. (22) does not hold, then they said to be non-commutative.

(B) Anti-commutator of Two Operators

If $\hat{A}$ and $\hat{B}$ are two operators defined in the same domain of definition then an operator called the anti-commutator of the operators usually written as $[\hat{A}, \hat{B}]_+$ or $\{\hat{A}, \hat{B}\}$ is defined as

$$[\hat{A},\hat{B}]_+ \equiv \{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} \qquad \text{……….. (23)}$$

The operators are said to anticommute, if

$$[\hat{A},\hat{B}] = 0$$

or

$$\hat{A}\hat{B} + \hat{B}\hat{A} = 0$$

3.9 EIGEN FUNCTION, EIGEN VALUES

- Let ψ be the well-behaved function of the state of the system and an operator $\hat{A}$ operates on this function such that it satisfies the equation

$$\hat{A}\,\psi(x) = a\,\psi(x) \qquad \text{…………. (24)}$$

where a is number then we say that a is an eigen value of the operator $\hat{A}$ and the operand ψ(x) is called the eigen function of $\hat{A}$. Eigen is the German word meaning characteristic or proper.

- An operator is a rule which changes a function into another function. For example, when operator $\frac{d}{dx^2}$ operates on a function i.e.

$$f(x) = x^n$$

$$\frac{df}{dx} = n\,x^{n-1}$$

- Another example is, $\frac{d^2}{dx^2}e^{4x} = 16\,e^{4x}$

- We say that $\frac{d^2}{dx^2}$ is the operator operating on function e^{4x} giving result $16e^{4x}$. The operand e^{4x} is called eigen function of operator $\frac{d^2}{dx^2}$ and 16 is the eigen value.

The total energy operator E of equation is usually written as

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

and is called Hamiltonian operator. If the Hamiltonian operator $H = -\frac{\hbar^2}{m}\nabla \ + V$ operates on a wave function ψ_n, we get

$$\left[-\frac{\hbar}{2m}\nabla \ + V\right]\psi_n = E_n\psi_n$$

or

$$H\,\psi_n = E_n\psi_n$$

The wave function ψ_n is called eigen function and E_n is called energy eigen value of the Hamiltonian operator H for a state of the system.

Eigen Functions and Eigen Values of a Linear Operator

Consider a linear operator $\hat{A}$ defined in a certain domain of definition. If ψ is any function define in the domain of the definition of $\hat{A}$, then in general, we have

$$\hat{A}\psi = \phi \qquad \text{……} (25)$$

However, for every linear operator $\hat{A}$, there exists a set of functions ψ_1, ψ_2, …., ψ_n, such that

$$\hat{A}\,\psi_1 = a_1\psi_1$$

$$\begin{aligned} \hat{A}\,\psi &= a\,\psi \\ \vdots \quad & \quad \vdots \\ \hat{A}\,\psi_n &= a_n\psi_n \end{aligned} \qquad \text{…………} (26)$$

where d_1, d_2, ….., d_n are constants with respect to the variables of which ψ_1' S (i = 1, …., n) are functions. The set of functions ψ_1, ψ_2, ….., ψ_n are called eigenfunctions of the operator $\hat{A}$ and the constant a_1, a_2, ….., a_n are called the eigenvalues belonging to the eigenfunctions ψ_1, ψ_2, …., ψ_n, respectively.

Eigenvalue Equation

The equation

$$\hat{A}\psi_i = a_i\psi_i \qquad (i = 1, 2, \ldots\ldots, n) \qquad \text{………..} (27)$$

is called the eigenvalue equation for the operator $\hat{A}$.

COMMUTATION RELATIONS OF TOTAL ANGULAR MOMENTUM WITH COMPONENTS

The total angular momentum is defined by the relation

$$J^2 = J_x^2 + J_y^2 + J_z^2 \qquad \text{……….} (28)$$

We can derive the commutation relation of J^2 with components J_x, J_y, J_z. Let us take

$$[J^2, J_x] = [J_x^2 + J_y^2 + J_z^2, J_x] = [J_x^2, J_x] + [J_y^2, J_x] + [J_z^2, J_x] \qquad \text{…} (29)$$

We know that [ab, c] = a[b, c] + [a, c] b,

So

$$\begin{aligned} [J_x^2, J_x] &= [J_x J_x, J_x] \\ &= J_x [J_x, J_x] + [J_x, J_x] J_x = 0 \end{aligned}$$

$$
\begin{aligned}
[J^2, J_x] &= [J_y^2, J_x] + [J_z^2, J_x] \\
&= [J_y J_y, J_x] + [J_z J_z, J_x] \\
&= J_y [J_y, J_x] + [J_y, J_x] J_y + J_z [J_z, J_x] + [J_z, J_x] J_z \\
&= J_y (-i\hbar J_z) + (-i\hbar J_z) J_y + J_z (i\hbar J_y) + (i\hbar J_y) J_z \\
&= 0,
\end{aligned}
$$

………. (30)

$\therefore\ [J^2, J_x] = 0$

Similarly,

$[J^2, J_y] = 0,$ …………… (31)

$[J^2, J_z] = 0,$ ………….. (32)

3.10 LADDER OPERATES (J^+ AND J^-)

Ladder Operators J_+ and J_- Now let us define the new operators.

$$
\left.
\begin{aligned}
J_+ &= J_x + i J_y \\
J_- &= J_x - i J_y.
\end{aligned}
\right\}
$$

………. (33)

Commutation relation of J_z with J_+ an J_-.

$$
\begin{aligned}
[J_z, J_+] &= [J_z, J_x, + iJ_y] \\
&= [J_z, J_x] + i\,[J_z, J_y] = [J_z, J_x] - i\,[J_y, J_z] \\
&= i\hbar J_y -- i\,(i\hbar J_x),
\end{aligned}
$$

$$\{\text{since } [J_z, J_x] = i\hbar J_y \text{ and } [J_y, J_z] = i\hbar J_x\}$$

$$
\begin{aligned}
&= i\hbar J_y + \hbar J_x \\
&= \hbar (J_x + i J_y) \\
&= \hbar J_+
\end{aligned}
$$

………. (34)

And similarly,

$$\begin{aligned}[J_z, J_-] &= [J_z, J_x - iJ_y] \\ &= [J_z, J_x] - i[J_z, J_y] \\ &= i\hbar J_y - i(-i\hbar J_x) \\ &= i\hbar J_y - \hbar J_x \\ &= -\hbar(J_x - iJ_y)\end{aligned}$$

$= -\hbar J_-$ ……. (35)

or we can write (34) and (35) in compact form as

$$[J_z, J_\pm] = \hbar J_\pm. \quad \text{……… (36)}$$

3.11 COMMUTATOR RULES AMONGST J^+, J^-, J_z AND J^2

Commutation Relation of J_+ and J_- Mutually.

$$\begin{aligned}[J_+, J_-] &= [J_x + iJ_y, J_x - iJ_y] \\ &= [J_x, J_x] - [J_x, J_y] + i[J_y, J_x] + [J_y, J_y] \\ &= 0 - i[J_x, J_y] - i[J_x, J_y] + 0 \\ &= -2i[J_x, J_y] = -2i(i\hbar J_z) \\ &= 2\hbar J_z\end{aligned}$$

……. (37)

Commutation Relations of J^2 with J_+ and J_-. Let us take $[J^2, J_+]$ first,

$$\begin{aligned}[J^2, J_+] &= [J^2, J_x + iJ_y] \\ &= [J^2, J_x] + i[J^2, J_y]\end{aligned}$$

Using (30) and (31), we get

$[J^2, J_+] = 0 + 0 = 0$ ……………. (38)

Similarly
$$\begin{aligned}[J^2, J_-] &= [J^2, J_x - iJ_y] \\ &= [J^2, J_x] - i[J^2, J_y] = 0\end{aligned}$$
…. (39)

Combining (38) and (39), we have

$$[J^2, J_\pm] = 0$$

………. (40)

3.12 ANGULAR MOMENTUM OPERATOR IN POSITION REPRESENTATION

Classically the angular momentum L of a particle relative to some arbitrary origin is defined as

L = r × p ………. (41)

where $r = \hat{\imath}x + \hat{\jmath}y + \hat{k}z$ is position vector and p the linear momentum of the particle ($\hat{\imath}, \hat{\jmath}$ and $\hat{k}$) are unit vectors along X, Y, Z axes respectively. In quantum mechanics, the associated with linear momentum p is $\frac{\hbar}{i}\nabla\left(i = \sqrt{\ } - 1\right)$

Thus the angular momentum operator is

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times \left(\frac{\hbar}{i}\nabla\right) = \frac{\hbar}{i}\,\mathbf{r} \times \nabla$$

………. (42)

If L_x, L_y and L_z are components of angular momentum operator L, then equation (42) gives

$$(\hat{i}\,L_x k + \hat{j}\,L_y + \hat{k}L_z) = \frac{\hbar}{i}\,(\hat{i}x + \hat{j}y + \hat{k}z) \times \left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$$

$$= \frac{\hbar}{i}\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

Comparing coefficients of $\hat{\imath}$, $\hat{\jmath}$ and $\hat{k}$ and on either sides, the components of angular momentum operator can be explicitly written as

$$\left.\begin{aligned} L_x &= \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_y &= \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_z &= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right\}$$

………. (43)

and

Using these definitions, it is easy to show that Lx, Ly and Lz satisfy the following commutation rules

and
$$\left.\begin{aligned}[L_x, L_y] &= i\hbar L_z\\ [L_y, L_z] &= i\hbar L_x\\ [L_z, L_x] &= i\hbar L_y\end{aligned}\right\} \qquad \text{……….(44)}$$

These relations can be written in the compact form as

$$L \times L = i\hbar L. \qquad \text{…..…….. (45)}$$

THE ROTATION OPERATOR AND ANGULAR MOMENTUM

If we consider the rotation of a co-ordinate system through an angle θ about an axis specified by unit vector $\hat{n}$, then the transformation of a wave function ψ(r) under rotation is described by unitary transformation

$$\psi'(\mathbf{r}) = R(\hat{n}, \theta)\,\psi(\mathbf{r}) \qquad \text{………. (46)}$$

where R($\hat{n}$, θ) is the rotation operator and is unitary operator. This equation means that the rotated wave function ψ'(r) at any point r is equal to the value operated by rotation operator on unrotated wave function.

Let us first consider the rotation of angle ϕ_o about z-axis. The effect of this rotation is that it leaves the coordinates (r, θ) unchanged, while the coordinate ϕ is changed to $\phi - \phi_o$. Hence equation (1) implies

$$R(\hat{z}, \phi_0)\,\psi(r, \theta, \phi) = \psi'(r, \theta, \phi') = \psi(r, \theta, \phi - \phi_0) \qquad \text{………. (47)}$$

Now assuming the wave function as the well-behaved function, we may expand ψ by Taylor's series about (r, θ, ϕ), so that

$$\psi(r, \theta, \phi - \phi_0) = \sum_{k=0}^{\infty} \frac{\left(-\phi_0 \frac{\partial}{\partial \phi}\right)^k}{k!}\, \psi(r, \theta, \phi) \qquad \text{………. (48)}$$

But
$$\sum_{k=0}^{\infty} \frac{\left(-\phi_0 \frac{\partial}{\partial \phi}\right)^k}{k!} = \exp\left(-\phi_0 \frac{\partial}{\partial \phi}\right) \qquad \text{………. (49)}$$

Therefore equation (48) may be expressed as

$$\psi(r, \theta, \phi - \phi_0) = \exp\left(-\phi_0 \frac{\partial}{\partial \phi}\right)\psi(r, \theta, \phi) \qquad \text{………. (50)}$$

Now expressing components of angular momentum L in spherical polar coordinates, we get

$$\left.\begin{aligned} L_x &= \frac{\hbar}{i}\left(\sin\phi\frac{\partial}{\partial\theta}+\cos\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ L_y &= \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta}-\cos\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ L_z &= \frac{\hbar}{i}\frac{\partial}{\partial\phi} \end{aligned}\right\} \qquad \text{……….}\ (51)$$

Using third of equation (51), we may write equation (50) as

$$\phi\,(r,\theta,\phi-\phi_0) = \exp\,(-i\,\phi_0\,L_z/\hbar)\,\psi\,(r,\theta,\phi). \qquad \text{……….}\ (52)$$

Now comparing (46) and (52), we get

$$R\,(\hat{z},\phi_0)\,\psi\,(r,\theta,\phi) = \exp\,(-i\,\phi_0\,L_z/\hbar)\,\psi\,(r,\theta,\phi) \qquad \text{…….}\ (53)$$

Since above equations holds for any arbitrary wave function ψ(r, θ, ϕ), therefore equation (53) yields

$$R\,(\hat{z},\phi_0) = \exp\,(-i\,\phi_0\,L_z/\hbar\,) \qquad \text{……….}\ (54)$$

This equation shows that the rotation about z-axis are generated by an operator which depends on z-component of angular momentum.

In general equation (53) may be expressed as

$$R\,(\hat{n},\theta) = \exp\,(-i\,\phi\,\boldsymbol{L}\cdot\hat{n}) \qquad \text{……….}\ (55)$$

Now if there exists any operator Q(r, θ, ϕ) which satisfies the condition

$$[Q, R\,(\hat{n},\theta)] = 0 \qquad \text{……….}\ (56)$$

Then the operator Q is said to be rotationally invariant. Equation (56) is satisfied if operator Q satisfies the following commutation relations with components of angular momentum operator L.

$$[Q, L_x] = 0, [Q, L_y] = 0 \text{ and } [Q, L_z] = 0 \qquad \text{……….}\ (57)$$

As the components L are Hermitian, θ is real, therefore R($\hat{n}$, θ) is unitary.

Also, we require R = 1 for θ = 0. [This is also obvious from (55)]

Also, we must have R ($\hat{n}$. (2πk)) = 1., where k is an integer. Since physically the rotation of 2πk means no rotation at all.

Infinitesimal Rotation:

If the angle of rotation θ is very small, the rotations are said to be infinitesimal rotations. If $\delta\theta$ is very small rotation; then equation (55) may be approximated as

$$R(\hat{n}, \delta\theta) \approx 1 - \frac{i}{\hbar}\delta\theta(L \cdot \hat{n}) \quad \text{……… (58)}$$

$$\left[\text{Since } e^{\alpha} = 1 + \alpha + \frac{\alpha^2}{2!} + \frac{\alpha^3}{3!} + \dots \approx 1 + \alpha \text{ if } \alpha \text{ is very small} \right]$$

It is obvious that any finite rotation can be considered as the product of a large number of infinitesimal rotations. These infinitesimal rotations commute with each other, while rotations, in general, do not commute.

Another important property of infinitesimal rotations is the transformation of operators under them. This is achieved by substituting (58) in (56).

Thus, if we define $R = Q + \delta Q$ then we get

$$\delta Q \approx -\frac{i}{\hbar}\delta\theta[(L \cdot \hat{n}), Q] \quad \text{……… (59)}$$

Commutability of Angular Momentum Operators:

Equation (55) may be used to define the transportation operator for an arbitrary rotation about an arbitrary axis. In many cases it is convenient to express the arbitrary rotation as a sequence of rotations about, say, X, Y and Z axes. For example, if the desired rotation θ can be carried out by a rotation θ_y about Y-axis followed by a rotation θ_x about X-axis, we have

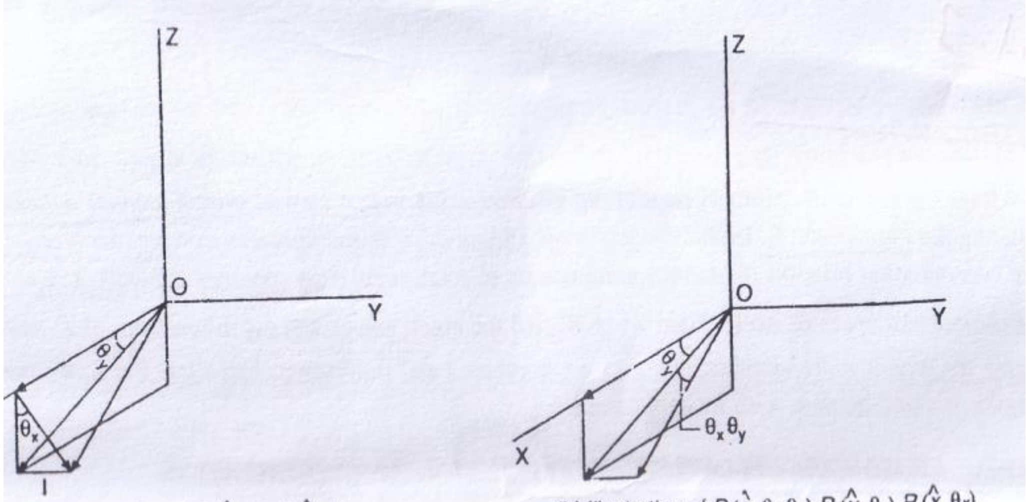
$$\begin{aligned} R(\hat{n}, \theta)\psi &= R(\hat{x}, \theta_x) R(\hat{y}, \theta_y)\psi \\ &= \exp(-i\theta_x L_x/\hbar)\exp(-i\theta_y L_y/\hbar)\psi \end{aligned}$$

Now finite rotations, in general, do not commute. Because if above rotations are made in opposite order (i.e. first θ_y about Y-axis and then θ_x about X-axis), then it would be essential to perform a further rotation of $\theta_x\,\theta_y$ about Z-axis to reach the same final position. This is represented geometrically in fig. (1).

The statement holds only for small angles (upto order θ^2 in exponential). Analytically this result may be expressed as

$$R(\hat{x}, \theta_x) R(\hat{y}, \theta_y) = R(\hat{z}, \theta_x\theta_y) R(\hat{y}, \theta_y) R(\hat{x}, \theta_x)$$

$$\text{or} \quad \exp(-i\,\theta_x L_x/\hbar)\exp(-i\,\theta_y L_y/\hbar) = \exp(-i\,\theta_x\theta_y L_z/\hbar)\exp(-\theta_y L_y/\hbar)\exp(-i\,\theta_x L_x/\hbar)$$



.1. (a) Illustration of $R(\hat{x}, \theta_x)\, R(\hat{y}, \theta_y)$ acting on vector along X-axis.

(b) Illustration of $R(\hat{z}, \theta_x\theta_y)\, R(\hat{y}, \theta_y)\, R(\hat{x}, \theta_x)$ on a vector along X-axis and yielding same result as in (a) to second order in angles. [It is obvious that $r(\hat{x}, \theta_x)$ has no effect in fig. (b)].

Expanding exponentials to second order in θ's, we get

$$\left[1-\frac{i\,\theta_x L_x}{\hbar}-\frac{\theta_x^2 L_x^2}{2\hbar^2}\right]\left[1-\frac{i\theta_y L_y}{\hbar}-\frac{\theta_y^2 L_y^2}{2\hbar^2}\right]$$

$$=\left[1-\frac{i\,\theta_x\,\theta_y\,L_z}{\hbar}-\frac{\theta_x^2\,\theta_y^2\,L_z^2}{2\,\hbar^2}\right]\left[1-\frac{i\,\theta_y L_y}{\hbar}-\frac{\theta_y^2 L_y^2}{2\hbar^2}\right]\left[1-\frac{i\,\theta_x\,L_x}{\hbar}-\frac{\theta_x^2\,L_x^2}{2\,\hbar^2}\right].$$

Retaining only second order terms in angles, we get

$$1-\frac{i\,\theta_y L_y}{\hbar}-\frac{\theta_y^2\,L_y^2}{2\,\hbar^2}-\frac{i\,\theta_x L_x}{\hbar}-\frac{\theta_x\,\theta_y\,L_x L_y}{\hbar^2}-\frac{\theta_x^2\,L_x^2}{2\,\hbar^2}$$

$$=1-\frac{i\,\theta_y L_y}{\hbar}-\frac{i\,\theta_x L_x}{\hbar}-\frac{\theta_y^2 L_y^2}{2\,\hbar^2}-\frac{\theta_x^2 L_x^2}{2\,\hbar^2}-\frac{i\,\theta_x\,\theta_y\,L_z}{\hbar}-\frac{\theta_x\theta_y\,L_y L_x}{\hbar^2}$$

or

$$-\frac{\theta_x\theta_y\,L_x L_y}{\hbar^2}=-\frac{i\,\theta_x\theta_y\,L_z}{\hbar}-\frac{\theta_x\theta_y\,L_y L_x}{\hbar^2}$$

Cancelling the common factors, this gives

$$L_x L_y - L_y L_x = i\hbar L_z, \quad i.e.\ [L_x, L_y] = i\hbar L_z$$

This is a familiar commutation relation of angular momentum operator.

The other commutation relation can be obtained by considering infinitesimal rotations about the other two pairs of coordinate axes, i.e.

$$[L_y, L_z] = L_y L_z - L_z L_y = i\hbar L_x$$

and $$[L_z, L_x] = L_z L_x - L_x L_z = i\hbar L_y$$

The relation in compact form is expressible as

$L \times L = i\hbar L$

SPIN ANGULAR MOMENTUM

The electron also possesses spin motion and hence contributes to the total angular momentum. It is denoted by S. It follows the same commutation relations as those of orbital angular momentum.

$$[S_x, S_y] = i\hbar S_z \,;\, [S_y, S_z] = i\hbar S_x \,;\, [S_z, S_x] = i\hbar S_y.$$
$$[S^2, S_x] = [S^2, S_y] = [S^2, S_z] = 0.$$

THE TOTAL ANGULAR MOMENTUM OPERATORS

The total angular momentum which may include the spin contribution is conveniently denoted by $J = (J_x, J_y, J_z)$ and is define as the generalized angular momentum operator J as any Hermitian operator whose components, satisfy the commutation rules.

$$[J_x, J_y] = i\hbar J_z, \quad [J_y, J_z] = i\hbar J_x, \quad [J_z, J_x] = i\hbar J_y. \qquad \text{……….} (60)$$

The above three equations can equivalently be written as

$$\mathbf{J} \times \mathbf{J} = i\hbar \mathbf{J} \qquad \text{……….} (61)$$

In order to avoid cumbersome factors of ħ, it is sometimes convenient to use quantum mechanical definition of angular momentum as

$$\mathbf{J} = \hbar^{-1} (\mathbf{r} \times \mathbf{p}) \qquad \text{……….} (62)$$

In other words we are choosing a system of units in which $\hbar = 1$.

If we use definition of angular momentum given by (62) the commutation rules satisfied by the components J_x, J_y, J_y takes the form

$$[J_x, J_y] = i J_z \,; \quad [J_y, J_z] = i J_x \,; \quad [J_z, J_x] = i J_y \qquad \text{…….} (63)$$

or equivalently

$$J \times J = i J \qquad \text{…………} (64)$$

It will be seen that these rules are satisfied by quantities which are more general than the angular momentum of a single particle and therefore the results obtained will be applicable to system of greater complexity.

Note: If sometimes the factors of ħ are omitted; then it means that quantum mechanical definition (62) of angular momentum has been used instead of classical definition.

$$J = r \times p.$$

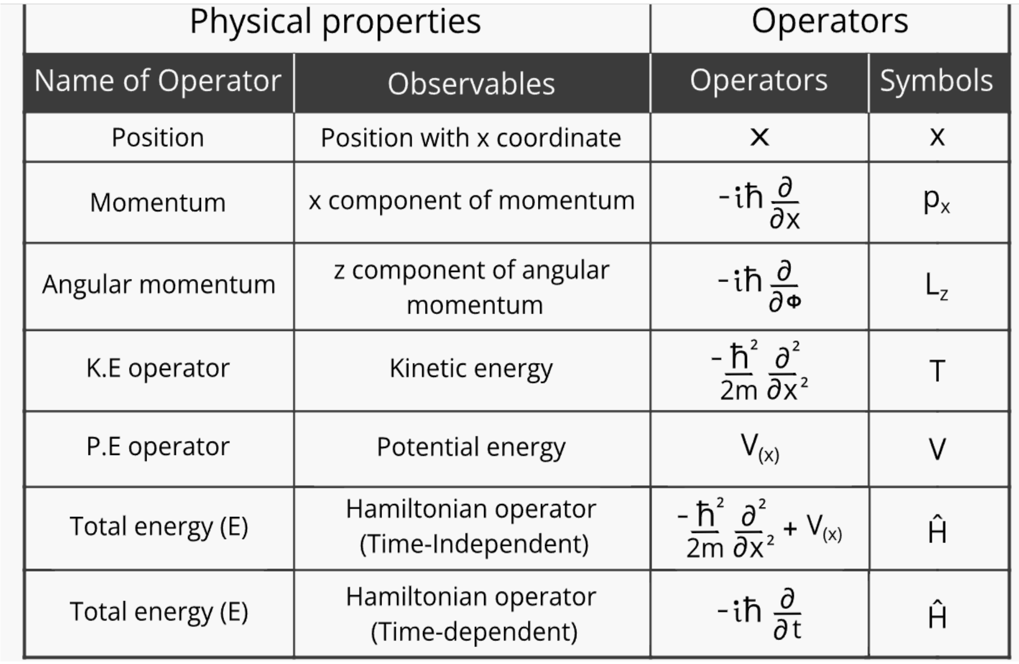
3.13 SUMMARY

The mathematical formulation of quantum mechanics (QM) is built upon the concept of an operator.

Physical pure states in quantum mechanics are represented as unit-norm vectors (probabilities are normalized to one) in a special complex Hilbert space. Time evolution in this vector space is given by the application of the evolution operator.

Any observable, i.e., any quantity which can be measured in a physical experiment, should be associated with a self-adjoint linear operator. The operators must yield real eigenvalues, since they are values which may come up as the result of the experiment. Mathematically this means the operators must be Hermitian. The probability of each eigenvalue is related to the projection of the physical state on the subspace related to that eigenvalue. See below for mathematical details about Hermitian operators.

In the wave mechanics formulation of QM, the wavefunction varies with space and time, or equivalently momentum and, so observables are differential operators.



Physical properties		Operators	
Name of Operator	Observables	Operators	Symbols
Position	Position with x coordinate	x	x
Momentum	x component of momentum	$-i\hbar \frac{\partial}{\partial x}$	p_x
Angular momentum	z component of angular momentum	$-i\hbar \frac{\partial}{\partial \Phi}$	L_z
K.E operator	Kinetic energy	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$	T
P.E operator	Potential energy	$V_{(x)}$	V
Total energy (E)	Hamiltonian operator (Time-Independent)	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_{(x)}$	$\hat{H}$
Total energy (E)	Hamiltonian operator (Time-dependent)	$-i\hbar \frac{\partial}{\partial t}$	$\hat{H}$

3.14 TERMINAL QUESTIONS

1. Explain the concept of Operator in Quantum Mechanics
2. Define Null Operator.
3. Discuss Linear Operator and Hermitian Operator.
4. Explain Ladder Operator.
5. Define Commutator and Non-Commutator Operators.

3.15 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 3.3
2. Section 3.4
3. Section3.7

4 Section 3.10

5. Section 3.8

3.16 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

Uttar Pradesh Rajarshi Tandon
Open University

Bachelor of Science

DCEPHS-108

Quantum Mechanics And Spectroscopy

BLOCK

2

APPLICATIONS OF SCHROEDINGER'S EQUATION

UNIT-4

One and Three Dimensional Problems

UNIT-5

Spherically Symmetric Systems

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ISBN :

Printed and Published by Vinay Kumar, Registrar, Uttar Pradesh Rajarshi Tandon Open University, 2023.

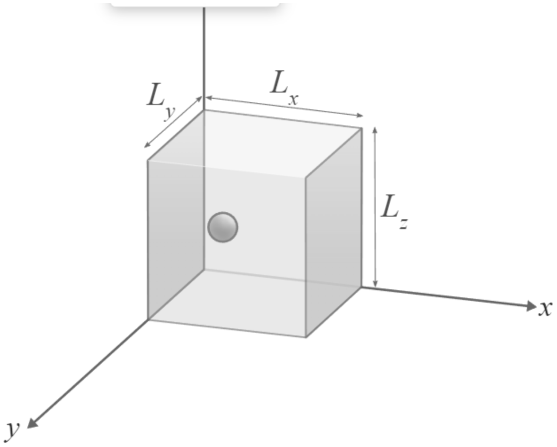
Printed By : Chandrakala Universal Pvt. 42/7 Jawahar Lal Neharu Road, Prayagraj.

UNIT-4 ONE AND THREE DIMENSIONAL PROBLEM

Structure

4.1 INTRODUCTION

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimension as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths Lx, Ly, and Lz. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box:



The potential for the particle inside the box:

$$V(\vec{r}) = 0$$

$$0 \le x \le L_x$$
$$0 \le y \le L_y$$
$$0 \le z \le L_z$$
$$L_x < x < 0$$
$$L_y < y < 0$$
$$L_z < z < 0$$

$\vec{r}$ is the vector with all three components along the three axes of the 3-D box: $\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$.

In this unit we will discuss Free particle and particle in a box also we will discuss about one dimensional linear harmonic Oscillator.

4.2 OBJECTIVES

After studying this unit, student should able to:

- Know about Free particle.
- Explain particle in a Box problem.
- Discuss Potential Step.
- Define Zero Point Energy.
- Concept of Rectangular Potential Barrier.

4.3 THE FREE PARTICLE

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

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\,\psi = 0 \qquad \text{……………….. (1)}$$

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

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

$$\nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0 \qquad \text{……………….. (2)}$$

or, in cartesian coordinates.

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

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

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

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

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

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

The equation may be written as

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

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

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

and

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

Equation (8) may be written as

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

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

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=k_y, \qquad \text{……………..} (10)$$

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

Equation (11) may be written as

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

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

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

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

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

For convenience let us substitute

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

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

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

The general solution of above equation can be written as

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

where N_x and x_0 are arbitrary constants.

Similarly we may obtain the differential equation in y and z by substituting

$k_y = -\frac{2m}{\hbar^2}E_y$ and $k_z = -\frac{2m}{\hbar^2}E_z$ in equation (10) and (12) respectively, viz.,

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

…………….. (17)

and

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

…………….. (18)

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

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

…………….. (19)

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

…………….. (20)

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

$$E_x + E_y + E_z = E.$$

…………….. (21)

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

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

$\Psi = X\,Y\,Z$

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

…………….. (22)

and

$$E = E_x + E_y + E_z.$$

…………….. (23)

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

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

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

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

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

…………….. (24)

4.4 PARTICLE IN A BOX

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

If m is the mass of the particle and E its total energy, the Schroedinger wave equation, for the case under consideration may be written as

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

or

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

…………….. (25)

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

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

…………….. (26)

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

Substituting value of ψ from equation (26) in (25) and dividing by X(x) Y(y) Z(z), we get

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

…………….. (27)

Above equation may be written as

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} - \frac{1}{2}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E. \qquad \ldots\ldots\ldots\ldots\ldots..\ (28)$$

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

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = k_x \qquad \ldots\ldots\ldots\ldots\ldots..\ (29)$$

and $$-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E = k_x \qquad \ldots\ldots\ldots\ldots\ldots..\ (30)$$

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

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = k_y \qquad \ldots\ldots\ldots\ldots\ldots..\ (31)$$

and $$-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E - k_x = k_y \qquad \ldots\ldots\ldots\ldots\ldots..\ (32)$$

Eqn. (32) may be written as

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

so that we have $$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = k_z \qquad \ldots\ldots\ldots\ldots\ldots..\ (33)$$

and $$k_x + k_y + k_z = \frac{2m}{\hbar^2}E. \qquad \ldots\ldots\ldots\ldots\ldots..\ (34)$$

For convenience let us substitute

and
$$\left.\begin{aligned} k_x &= -\frac{2m}{\hbar^2}E_x, \\ k_y &= -\frac{2m}{\hbar^2}E_y, \\ k_z &= -\frac{2m}{\hbar^2}E_z. \end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots\ldots..\ (35)$$

Then the differential equation in x, y and z from (29), (31) and (32) may be written as

$$\frac{\partial^2 X}{\partial x^2}+\frac{2m}{\hbar^2}E_x X = 0, \qquad \ldots\ldots\ldots\ldots\ldots..\ (36)$$

$$\frac{\partial^2 Y}{\partial y^2}+\frac{2m}{\hbar^2}E_y Y = 0, \qquad \ldots\ldots\ldots\ldots\ldots..\ (37)$$

and
$$\frac{\partial^2 Z}{\partial z^2}+\frac{2m}{\hbar^2}E_z Z = 0. \qquad \ldots\ldots\ldots\ldots\ldots..\ (38)$$

The general solution of equation (36) will be sine function of arbitrary amplitude, frequency and phase, i.e.,

$$X(x) = A\sin(Bx+C). \qquad \ldots\ldots\ldots\ldots\ldots..\ (39)$$

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

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

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

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

Using these boundary conditions, eqn. (39) give

$\sin C = 0$

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

which yields $C = 0$

and $\sin Bl_x = 0$

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

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

Substitution values of B and C in eqn. (39), we get

$$X(x) = A \sin \frac{n_x \pi x}{l_x}$$ …………….. (40)

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

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

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

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

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

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

or $$A = \sqrt{\left(\frac{2}{l_x} \right)}.$$ …………….. (41)

Substitution this value of A in eqn. (40), the normalized function X(x) is given by

$$X(x) = \sqrt{\left(\frac{2}{l_x} \right)} \sin \frac{n_x \pi x}{l_x}.$$ …………….. (42)

Finding its second derivative, we have

$$\frac{\partial^2 X}{\partial x^2} = -\left(\frac{n_x \pi}{l_x}\right)^2 X(x) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (43)$$

Substitution values from (42) and (43) in (36), we get

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

or $$E_x = \frac{1}{2m}\left(\frac{n_x \pi \hbar}{l_x}\right)^2 = \frac{n_x^2 h^2}{8\,m\,l_x^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (44)$$

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

Similarly, we may solve equations (37) and (38) and obtain

$$Y(y) = \sqrt{\left(\frac{2}{l_y}\right)} \sin \frac{n_y \pi y}{l_y} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (45)$$

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

$$Z(z) = \sqrt{\left(\frac{2}{l_z}\right)} \sin \frac{n_z \pi z}{l_z} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (46)$$

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

$$E_y = \frac{n_y^2 h^2}{8\,m l_y^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (47)$$

$$E_z = \frac{n_z^2 h^2}{8\,m l_z^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (48)$$

Using (34) and (35), we have

$$E = E_x + E_y + E_z.$$

Equations (44), (47) and (48) give the allowed values of energy along X, Y and Z axes respectively.

The allowed values of total energy are given by

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right] \qquad \text{……………..} (49)$$

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

The complete wave function $\psi_{nx,\ ny,\ nz}$has the form, for various values of the quantum numbers n_x, n_y, n_z,

$$\psi_{n_x, n_y, n_z}(x, y, z) = X(x)\, Y(y)\, Z(z)$$
$$= 2\sqrt{\left(\frac{2}{l_x l_y l_z}\right)} \sin\frac{n_x \pi x}{l_x} \sin\frac{n_y \pi y}{l_y} \sin\frac{n_z \pi z}{l_z} \qquad \text{……………..} (50)$$

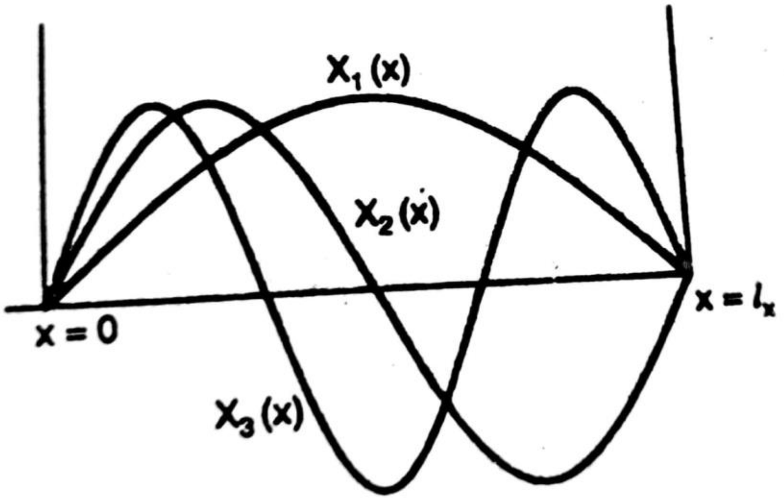


Fig.2 represents the first three normalized wave functions X(x) for a particle in a box.

4.5 POTENTIAL STEP

In the case of a potential step the potential function undergoes only one discontinuous change as shown in fig 3 and hence the potential function of a potential step may be represented as

$$V(x) = \begin{cases} 0 \text{ for } x < 0 \\ V_0 \text{ for } x > 0 \end{cases} \qquad \text{……………..} (51)$$

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

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

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

The Schrodinger equation for the first region is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0, \qquad \text{……………..} \ (52)$$

since for 1 region $V(x) = 0$.

The Schroedinger wave equation for II region is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V_0)\, \psi = 0. \qquad \text{……………..} \ (53)$$

The general solutions of equations (51) and (52) may be written

as $\psi_1 = Ae^{ip_1x/\hbar} + Be^{-ip_1x/\hbar}$ …………….. (53)

and $\psi_2 = Ce^{ip_2x/\hbar} + De^{-ip_2x/\hbar}$ …………….. (54)

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

$$\left\{ \begin{aligned} p_1 &= \sqrt{(2mE)} \\ p_2 &= \sqrt{[2m\,(E - V_0)]} \end{aligned} \right\} \qquad \text{……………..} \ (55)$$

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

In equation (53) the term represents the wave travelling along +ve X-axis in first region, i.e., the incident wave and the second term represents the wave travelling along +ve X-axis in first region, i.e., the incident wave and the second term represents the wave travelling along –ve X-axis in the 1st region, i.e., the reflected wave. In equation (54), the first term represents the wave travelling along +ve X-axis in 2nd region i.e., transmitted wave while the second term represents the wave travelling along –ve X-axis in second region : but there is no reflection of electrons in 2nd region and hence there will be no wave travelling along –ve X-axis Consequently D = 0 so that the solution of equation (51), i.e., equation (54) may be written as

$$\psi_2 = Ce^{ip_2x/\hbar} \quad \ldots\ldots\ldots\ldots\ldots (56)$$

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

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

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

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

Applying boundary condition (A) to equations (53) and (56), we get

$A + B = C$ ……………. (57)

Differentiating equation (53) and (56), we get

$$\frac{\partial\psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[Ae^{ip_1x/\hbar} - Be^{-ip_1x/\hbar}\right], \quad \ldots\ldots\ldots\ldots\ldots (58)$$

$$\frac{\partial\psi_2}{\partial x} = \frac{ip_2}{\hbar}Ce^{ip_2x/\hbar} \quad \ldots\ldots\ldots\ldots\ldots (59)$$

Applying boundary conditions (B) to (58) and (59), we get

$$p_2C = p_1[A - B]. \quad \ldots\ldots\ldots\ldots\ldots (60)$$

Solving (57) and (60), we get

$$C = \frac{2p_1A}{p_1 + p_2} \quad \ldots\ldots\ldots\ldots\ldots (61)$$

$$B = \frac{p_1 - p_2}{p_1 + p_2}A, \quad \ldots\ldots\ldots\ldots\ldots (62)$$

where B and C represent the amplitudes of reflected and transmitted beams respectively in terms of the amplitude of incident wave.

The reflectance of reflectivity or reflection coefficient and the transmittance or transmissivity or transmission coefficient at the potential discontinuity may be defined as follows.

The reflectance, i.e., the fraction of electrons reflected is equal to the ratio of reflected current to be incident current i.e.

$$Reflactance, R = \frac{magnitude\ of\ reflected\ current}{magnitude\ of\ incident\ current} \qquad \ldots\ldots\ldots\ (63)$$

The transmittance, i.e., the fraction of electrons transmitted, is equal to be ratio of transmitted current to the incident current, i.e.,

$$Transmittance, T = \frac{magnitude\ of\ transmitted\ current}{magnitude\ of\ incident\ current} \qquad \ldots\ldots\ (64)$$

There may be two cases:

Case I. $\boldsymbol{E > V_0\ i.e., p_2 = \sqrt{[\{2m(E - v_0)\}]}}$ **is real.**

In this case the expressions for the current density in the 1st and 2nd regions may be derived as follows:

In 1st region, we have

$$\psi_1 = Ae^{ip_1x/\hbar} + Be^{-ip_1x/\hbar} \qquad \ldots\ldots\ldots\ (65)$$

Its complex conjugate ψ_1^* is given by

$$\psi_1^* = A^* e^{-ip_1x/\hbar} + B^* e^{ip_1x/\hbar} \qquad \ldots\ldots\ldots\ (66)$$

so that we have

$$\frac{\partial\psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[Ae^{ip_1x/\hbar} - Be^{-ip_1x/\hbar}\right] \qquad \ldots\ldots\ldots\ (67)$$

and $$\frac{\partial\psi_1^*}{\partial x} = -\frac{ip_1}{\hbar}\left[A^* e^{-ip_1x/\hbar} - B^* e^{ip_1x/\hbar}\right] \qquad \ldots\ldots\ldots\ (68)$$

The probability current is defined as

$$\mathbf{J} = \frac{\hbar}{2im}\,[\psi^*\nabla\psi - \psi\nabla\psi^*].$$

The expression in the case for 1st region becomes

$$(J_x)_1 = \frac{\hbar}{2im}\left[\psi_1^* \frac{\partial \psi_1}{\partial x} - \psi_1 \frac{\partial \psi_1^*}{\partial x}\right].$$

…………….. (69)

Since in the electron are moving only along X-axis.

Using equations (65), (66), (67) and (68), we have

$$(J_x)_1 = \frac{\hbar}{2im}[\{(A^* e^{-ip_1x/\hbar} + B^* e^{ip_1x/\hbar}) \times \left(\frac{ip_1}{\hbar}\right)(Ae^{-ip_1x/\hbar} - B e^{ip_1x/\hbar})\}$$
$$- \{(Ae^{ip_1x/\hbar} + Be^{-ip_1x/\hbar}) \times \left(\frac{-ip_1}{\hbar}\right)(A^* e^{-ip_1x/\hbar} - B^* e^{ip_1x/\hbar})\}].$$
$$= \frac{p_1(AA^* - B^*B)}{m} = \frac{p_1}{m}[|A|^2 - |B|^2],$$

…………….. (69)

From above expression it is clear that the current in the 1st region is made up of the difference between two terms, of which the first is proportional to $p_1|A|^2$ and represent the wave travelling from left to right, i.e., the incident wave, while the second is proportional to $p_1|B|^2$ and represents the wave travelling from right to left, i.e., the reflected wave.

∴ The probability current of the incident beam $= |A|^2 \frac{p_1}{m}$ .....(70)

and the probability current of the reflected beam $= |B|^2 \frac{p_1}{m}$ .... (71)

In 2nd region, we have

$$\left\{\begin{aligned} \psi_2 &= Ce^{ip_2x/\hbar} \\ \psi_2^* &= C^* e^{-ip_2x/\hbar} \\ \frac{\partial \psi_2}{\partial x} &= \frac{ip_2}{\hbar} Ce^{ip_2x/\hbar} \\ \frac{\partial \psi_2^*}{\partial x} &= -\frac{ip_2}{\hbar} C^* e^{-ip_2x/\hbar} \end{aligned}\right\}$$

……. (72)

The probability current in this case is

$$(J_x)_{II} = \frac{\hbar}{2im}\left[\psi_2^* \frac{\partial \psi_2}{\partial x} - \psi_2 \frac{\partial \psi_2^*}{\partial x}\right].$$

Using (72), we get

$$(J_x)_{II} = \frac{\hbar}{2im}\left[\left\{C^{*}e^{-ip_2x/\hbar}\left(\frac{ip_2}{\hbar}\right)Ce^{ip_2x/\hbar}\right\}\left[-\left\{Ce^{ip_2x/\hbar}\left(-\frac{ip_2}{\hbar}\right)C^{*}e^{-ip_2x/\hbar}\right\}\right]\right]$$

$$= \frac{p_2}{2m}[CC^{*} + CC^{*}]$$

$$= \frac{p_2}{m}(CC^{*}) = \frac{|C|^2 p_2}{m}$$

……. (73)

In second region, there is only transmitted wave; therefore equation (73) represents the transmitted current.

Now we can obtain the expressions for reflectance and transmittance in this case, i.e., when E > V_0 or p_2 is real.

∴ $$The\ reflectance\ R = \frac{magnitude\ of\ reflected\ current}{magnitude\ of\ incident\ current}$$ {from (63)}

$$= \frac{|B|^2 p_1/m}{|A|^2 p_1/m}$$

∴ $$R = \frac{(p_1 - p_1)^2}{(p_1 + p_2)^2}.$$ ……. (74)

{from (62)}

$$The\ Transmittance\ T = \frac{magnitude\ of\ transmitted\ current}{magnitude\ of\ incident\ current}$$ {from (64)}

$$= \frac{|C|^2 p_2/m}{|A|^2 p_1/m}$$

$$= \left(\frac{2p_1}{p_1 + p_2}\right)^2 \cdot \frac{p_2}{p_1}$$

or $$T = \frac{4p_1p_2}{(p_1 + p_2)^2}.$$ ……. (75)

According to definitions the sum of reflectance and transmittance must be equal to unity. It may be verified from equation (74) and (75), i.e.,

$$R+T=\frac{(p_1-p_2)^2}{(p_2+p_2)^2}+\frac{4p_1p_2}{(p_1+p_2)^2}$$
$$=\frac{(p_1-p_2)^2+4p_1p_2}{(p_1+p_2)^2}=\frac{(p_1+p_2)^2}{(p_1+p_2)^2}=1.$$

……. (76)

From equation (74) it is clear that reflectance approaches zero as p_2 approaches p_1 and unity as p_2 approaches zero.

But $$p_2=\sqrt{[2m\,(E-V_0)]} \text{ and } p_1=\sqrt{(2mE)}.$$

Clearly p_2 will approach p_1 if V_0 is and hence the reflectance will be zero only if V_0 is equal to zero. Therefore, there must be some reflection even if $E>>V_0$. The reflectance will be large only if V0 becomes comparable in size with E. It should be noted that the property of reflection from a sudden change in potential aries from nature of matter and does not exist in classical theory if $E > V_0$. Thus we may say that it is purely a quantum mechanical effect.

Case II if $\boldsymbol{E > V_0\ i.e., p_2 = \sqrt{[\{2m(E-v_0)\}]} = \sqrt{\{2m(V_0-E)\}}}$ **is imaginary.**

We have $$p_2=i\sqrt{[2m\,\{(V_0-E)\}]}.$$

Its complex conjugate

$$p_2^*=-i\sqrt{[2m\,(V_0-E)]}=-p_2.$$

……. (77)

As p_2 imaginary, the probability current associated with wave function ψ_2 may be calculated as follows:

We have

$$\psi_2=Ce^{ip_2x/\hbar}$$
$$\psi_2^*=C^*e^{-ip_2x/\hbar}$$

so that $$\frac{\partial\psi_2}{\partial x}=\frac{ip_2}{\hbar}\,Ce^{ip_2x/\hbar},$$

$$\frac{\partial\psi_2^*}{\partial x}=-\frac{ip_2^*}{\hbar}C^*e^{-ip_2^*x/\hbar}.$$

The probability current, in this case, is given by

$$J_x = \frac{\hbar}{2im}\left[\psi_2^* \frac{\partial \psi_2}{\partial x} - \psi_2 \frac{\partial \psi_2^*}{\partial x}\right]$$

$$= \frac{\hbar}{2im}\left[C^* e^{-ip_2^* x/\hbar}\left(\frac{ip_2}{\hbar}\right) Ce^{+ip_2x/\hbar} - Ce^{ip_2x/\hbar}\left(-\frac{ip_2^*}{\hbar}\right) C^* e^{-ip_2^* x/\hbar}\right].$$

Substituting $p_2^* = - p_2$, we get

$$J_x = \frac{\hbar}{2im}\left[C^* e^{ip_2x/\hbar}\left(\frac{ip_2}{\hbar}\right) Ce^{+ip_2x/\hbar} - CC^*\left(\frac{ip_2}{\hbar}\right) e^{ip_2x/\hbar}\, e^{ip_2x/\hbar}\right] = 0$$

i.e., the transmitted current is zero.

$$Thus\ the\ transmittance = \frac{magnitude\ of\ transmitted\ current}{magnitude\ of\ reflected\ current}$$

$\therefore$ $T = 0$ …………. (78)

The reflectance = 1 (from definition i.e., since R + T = 1).

The reflectance may also be deduced as follows:

$$The\ reflectance\ R = \frac{magnitude\ of\ reflected\ current}{magnitude\ of\ incident\ current}$$

$$= \frac{(BB^*)\dfrac{p_1}{m}}{(AA^*)\dfrac{p_1}{m}} \text{ from (20)}$$

$$= \frac{\left(\dfrac{p_1 - p_2}{p_1 + p_2}\right) A \left(\dfrac{p_1 - p_2}{p_1 + p_2}\right)^* A^*}{AA^*} = \frac{(p_1 - p_2)(p_1 - p_2)^*}{(p_1 + p_2)(p_1 + p_2)^*}$$

[using (62) and its complex congugate]

$$= \frac{(p_1 - p_2)(p_1 - p_2^*)}{(p_1 + p_2)(p_1 + p_2^*)} = \frac{(p_1 - p_2)(p_1 + p_2)}{(p_1 + p_2)(p_1 - p_2)} \qquad (\text{since } p_2^* = -p_2).$$

$\therefore$ $R = 1$ …………. (79)

From (78) and (79) it is clear that in this the entire wave is reflected, i.e., all of the electrons are reflected and none of them is transmitted.

4.6 RECTANGULAR POTENTIAL BARRIER

Let us consider the one-dimensional problem where the potential function is defined as in fig. 3.6

$$\begin{Bmatrix} V(x) = 0 & \text{for } x < 0 \\ = V_0 & \text{for } 0 < x < a \\ = 0 & \text{for } x > a \end{Bmatrix} \qquad \ldots\ldots (80)$$

Here we have a potential barrier between x = 0 and x = a.

If a particle having energy less than V_0, i.e., $E < V_0$, approaches this barrier from the left, i.e., from 1st region, classically the particle will always be reflected and hence will not penetrate the barrier. However, wave mechanics predicts that the particle has some probability of penetrating to region 3rd, the probability of penetration being greater if $(V_0 - E)$ and a are smaller. Moreover, if $E > V_0$ classical mechanics predicts that the particle will always be transmitted; while according to wave mechanics, the particle has a finite probability of transmission and hence it is not certain that the particle will penetrate the barrier.

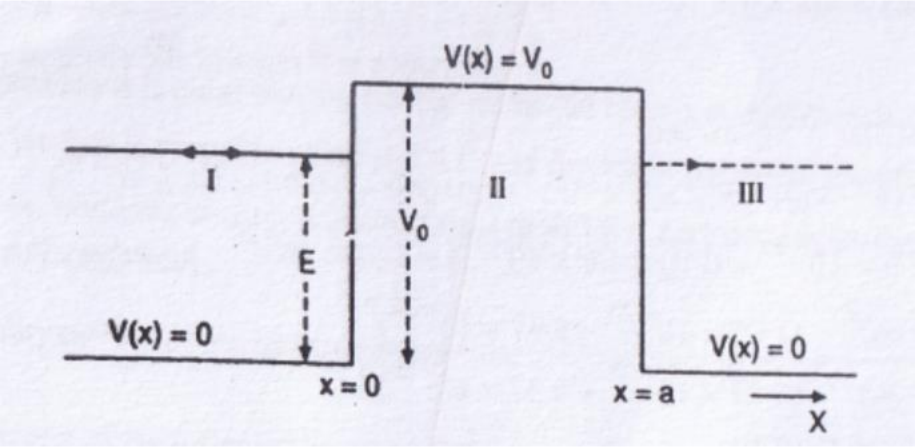


Figure: 3

To solve the problem, let us write there Schrödinger equations, one for each region.

The Schrödinger equation for I region is

$$\frac{\partial^2 \psi_1}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_1 = 0 \qquad \ldots\ldots (81)$$

(Since V = 0)

The Schrödinger equation for II region is

$$\frac{\partial^2 \psi_2}{\partial x^2} + \frac{2m}{\hbar^2} (E - V_0)\, \psi_2 = 0. \qquad \ldots\ldots (82)$$

The Schrödinger equation for III region is

$$\frac{\partial^2\psi_3}{\partial x^2}+\frac{2m}{\hbar^2}E\psi_3=0 \qquad \text{……. (83)}$$

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

The general solutions of equation (82), (83) and (84) may be written as

$$\psi_1=A_1e^{ip_1x/\hbar}+B_1e^{-ip_1x/\hbar} \qquad \text{……. (85)}$$

$$\psi_2=A_2e^{ip_2x/\hbar}+B_2e^{-ip_2x/\hbar} \qquad \text{……. (86)}$$

$$\psi_3=A_3e^{ip_1x/\hbar}+B_3e^{-ip_1x/\hbar} \qquad \text{……. (87)}$$

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

$$\left\{\begin{array}{l} p_1=\sqrt{(2mE)} \\ p_2=\sqrt{[2m(E-V_0)]} \end{array}\right\} \qquad \text{……. (88)}$$

A_1, B_1, A_2, B_2, A_3 and B_3 are constants to be determined by boundary conditions.

In equation (85) the first term represents the wave travelling along (+) ve X-axis in the I region, i.e., the incident wave and second term represents the wave travelling along negative X-axis i.e., wave reflected at x = 0.

In equation (86), the first term represents the wave travelling along (+)ve X-axis in II region i.e., the wave transmitted at x = 0 and second term represents the wave travelling (-)ve X-axis in II region, i.e., the wave reflected at x = a.

In equation (87) the first term represents the wave travelling along (+)ve X-axis in III region, i.e., the wave transmitted at x = a and the second term represents the wave travelling along (-)ve X-axis in III region ; but no wave travels back from infinity in III region. Consequently $B_3 = 0$, so that the solution of equation (83), i.e. equation (87) can be written as

$$\psi_3=A_3e^{ip_1x/\hbar} \qquad \text{……. (89)}$$

For evaluation the constants A_1, B_1, A_2, B_2, A_3 and B_3 we shall apply the conditions at the two boundaries x = 0 and x = a.

One condition is that ψ must be continuous at the boundaries, i.e.,

$$\left\{\begin{array}{ll} \psi_1=\psi_2 \text{ at } x=0 & \text{...}(A) \\ \psi_2=\psi_3 \text{ at } x=a & \text{...}(B) \end{array}\right\} \qquad \text{……. (90)}$$

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

$$\left\{ \begin{array}{ll} \dfrac{\partial\psi_1}{\partial x} = \dfrac{\partial\psi_2}{\partial x} \text{ at } x = 0 & \text{....}(A) \\ \dfrac{\partial\psi_2}{\partial x} = \dfrac{\partial\psi_3}{\partial x} \text{ at } x = a & \text{....}(B) \end{array} \right\} \qquad \text{.......} (91)$$

Applying boundary condition (90) to equations (85) and (86), we have

$$A_1 + B_1 = A_2 + B_2 \qquad \text{.......} (92)$$

Applying boundary condition (90B) to equations (86) and (89), we get

$$A_2 e^{ip_2 a/\hbar} + B_2 e^{-ip_2 a/\hbar} = A_3 e^{ip_1 a/\hbar} \qquad \text{.......} (93)$$

Differentiating equations (85), (86) and (89) we get

$$\frac{\partial\psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[A_1 e^{ip_1 x/\hbar} - B_1 e^{-ip_1 x/\hbar}\right]. \qquad \text{.......} (94)$$

$$\frac{\partial\psi_2}{\partial x} = \frac{ip_2}{\hbar}\left[A_2 e^{ip_2 x/\hbar} - B_2 e^{-ip_2 x/\hbar}\right]. \qquad \text{.......} (95)$$

$$\frac{\partial\psi_3}{\partial x} = \frac{ip_1}{\hbar} A_3 e^{ip_1 x/\hbar} \qquad \text{.......} (96)$$

Applying boundary conditions (91A) and (91B) to these equations, we get

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

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

or $$A_1 - B_1 = \frac{p_2}{p_1}(A_2 - B_2), \qquad \text{.......} (97)$$

$$A_2 e^{ip_2 a/\hbar} - B_2 e^{-ip_2 a/\hbar} = \frac{p_1}{p_2} A_3 e^{ip_1 a/\hbar} \qquad \text{.......} (98)$$

Solving (92) and (97) for A_1 and B_2, we get

$$A_1 = \frac{A_2}{2}\left(1 + \frac{p_2}{p_1}\right) + \frac{B_2}{2}\left(1 - \frac{p_2}{p_1}\right), \qquad \text{.......} (100)$$

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

……. (101)

Solving (93) and (98) for A_2 and B_2, we get

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

……. (102)

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

……. (103)

Substituting values of A_2 and B_2 from these equations in (102) and (103), we get

$$A_1 = \frac{A_3}{4}e^{ip_1a/\hbar}\left[\left(1 + \frac{p_2}{p_1}\right)\left(1 + \frac{p_1}{p_2}\right)e^{-ip_2a/\hbar} + \left(1 - \frac{p_2}{p_1}\right)\left(1 - \frac{p_1}{p_2}\right)e^{ip_2a/\hbar}\right]$$

……. (104)

$$B_1 = \frac{A_3}{4}e^{ip_1a/\hbar}\left[\left(1 - \frac{p_2}{p_1}\right)\left(1 + \frac{p_1}{p_2}\right)e^{-ip_2a/\hbar} + \left(1 + \frac{p_2}{p_1}\right)\left(1 - \frac{p_1}{p_2}\right)e^{ip_2a/\hbar}\right]$$

……. (105)

Equation (104) may be written as

$$\begin{aligned}
\frac{A_2}{A_1} &= \frac{4e^{-ip_1a/\hbar}}{\left\{\left(1 + \frac{p_2}{p_1}\right)\left(1 + \frac{p_1}{p_2}\right)e^{-ip_2a/\hbar} + \left(1 - \frac{p_2}{p_1}\right)\left(1 - \frac{p_1}{p_2}\right)e^{ip_2a/\hbar}\right\}} \\
&= \frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1 + p_2)^2e^{-ip_2a/\hbar} - (p_1 - p_2)^2e^{ip_2a/\hbar}} \\
&= \frac{4p_1p_2\,e^{-ip_1a/\hbar}}{(p_1^2 + p_2^2)(e^{-ip_2a/\hbar} - e^{ip_2a/\hbar}) + 2p_1p_2(e^{-ip_2a/\hbar} + e^{ip_2a/\hbar})} \\
&= \frac{2p_1p_2\,e^{-ip_1a/\hbar}}{(p_1^2 + p_2^2)\frac{(e^{-ip_2a/\hbar} - e^{ip_2a/\hbar})}{2} + 2p_1p_2\frac{(e^{-ip_2a/\hbar} + e^{ip_2a/\hbar})}{2}}
\end{aligned}$$

Here $p_2 = \sqrt{[2m(E - V_0)]}$ is imaginary since E < V_0, therefore p_2 is real, so that we have

$$\frac{A_3}{A_1} = \frac{2p_1p_2e^{-ip_1a/\hbar}}{-(p_1^2 + p_2^2)\sinh(ip_2a/\hbar) + 2p_1p_2\cosh(ip_2a/\hbar)}$$

$$= \frac{2p_1\,p_2\,e^{-ip_1a/\hbar}}{\cosh(ip_2a/\hbar)\,[-(p_1^2 + p_2^2)\tanh(ip_1a/\hbar) + 2p_1p_2]}$$

$$= \frac{2p_1p_2\,\mathrm{sech}\,(ip_2a/\hbar)\,e^{-ip_1a/\hbar}}{-(p_1^2 + p_2^2)\tanh(ip_2a/\hbar) + 2p_1p_2}$$

$$= \frac{-2\,p_1\,p_2\,\mathrm{sech}\,(ip_{2a}/\hbar)\;e^{-ip_1a/\hbar}}{(p_1^2 + p_2^2)\tanh\;(ip_2a/\hbar) - 2p_1p_2} \qquad \ldots\ldots (106)$$

The complex conjugate of above equation is written as

$$\frac{A_3^*}{A_1^*} = \frac{-2p_1p_2^*\,\mathrm{sech}\,(-ip_2^*a/\hbar)\,e^{ip_1a/\hbar}}{(p_1^2 + p_2^{*2})\tanh(-ip_2^*a/\hbar) - 2p_1p_2^*} \qquad \ldots\ldots (107)$$

But we have

[since $p_2 = \sqrt{\{2m\,(E - V_0)\}} = i\sqrt{\{2m\,(V_0 - E)\}}$ as $V_0 > E$].

∴ $p_2^* = -i\sqrt{[2m\,(V_0 - E)]} = -p_2$

and so $p_2^{*2} = p_2^2$.

Then equation (107) becomes

$$\frac{A_3^*}{A_1^*} = \frac{2p_1p_2\,\mathrm{sech}\,(ip_2a/\hbar)\,e^{ip_1a/\hbar}}{(p_1^2 + p_2^2)\tanh(ip_2a/\hbar) + 2p_1p_2} \qquad \ldots\ldots (108)$$

The transmittance or the transmission coefficient is given by

$$T = \frac{\text{magnitude of transmitted current}}{\text{magnitude of incident current}}$$

$$= \frac{(A_3A_3^*)\,p_1/m}{(A_1A_1^*)\,p_1/m} = \frac{A_3A_3^*}{A_1A_1^*}$$

$$= \frac{\{-2p_1p_2 \operatorname{sech}(ip_2a/\hbar)\, e^{-ip_1a/\hbar}\}\{2p_1p_2 \operatorname{sech}(ip_2a/\hbar)\, e^{ip_1a/\hbar}\}}{\{(p_1^2+p_2^2)\tanh(ip_2a/\hbar) - 2p_1p_2\}\{(p_1^2+p_2^2)\tanh(ip_2a/\hbar) + 2p_1p_2\}}$$

[Using (25) and (27)]

or $$T = \frac{-4p_1^2p_2^2 \operatorname{sech}^2(ip_2a/\hbar)}{(p_1^2+p_2^2)^2\tanh^2(ip_2a/\hbar) - 4p_1^2p_2^2}. \qquad \ldots\ldots (109)$$

Here p2 is imaginary, i.e., ip2 is real and so p_2^2 is real. Therefore, T is real.

The reflectance of the barrier or the reflection coefficient is given by

$$R = \frac{\text{magnitude of reflected current}}{\text{magnitude of incident current}} = \frac{B_1B_1^*}{A_1A_1^*}. \qquad \ldots\ldots (110)$$

Using equation (104) and (105), their conjugates and remembering the fact that $p_2^* = -p_2$, equation (110) after simplification yields

$$R = \frac{(p_1^2-p_2^2)^2\tanh^2(ip_2a/\hbar)}{(p_1^2+p_2^2)^2\tanh^2(ip_2a/\hbar) - 4p_1^2p_2^2}. \qquad \ldots\ldots (111)$$

The reflection coefficient R may be obtained by the fact

R + T = 1

i.e., R = 1 – T. ….. (112)

The property of the barrier penetration is entirely due to the wave nature of matter and is very similar to the total internal reflection of light waves. If two plates of glass are placed close to each other with a layer of air as a medium between them, the light will be transmitted from one plate to another, even though the angle of incidence is greater than the critical angle. However, the intensity of transmitted wave will decrease exponentially with thickness of the layer of air. In this case the intensity of electron waves decreases exponentially with the thickness of the barrier. The wave function has the form more or less as shown in fig. 4.

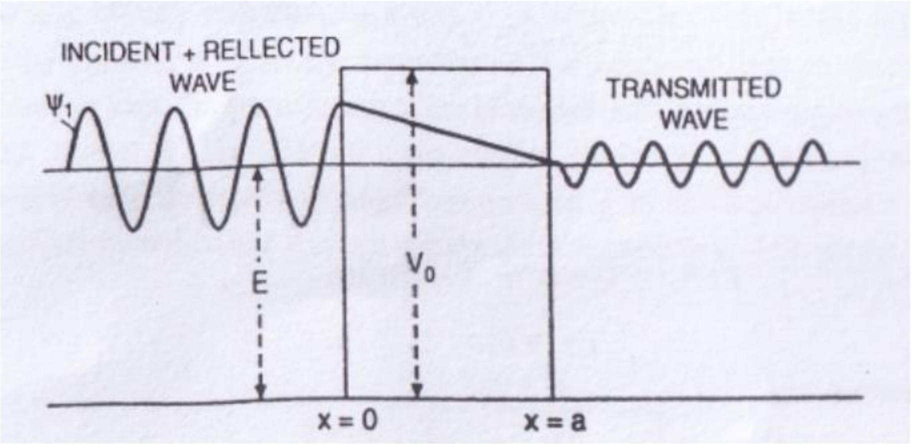


Figure: 4

Now let us consider a special case when the barrier is thick, i.e.,

$$ip_2a >> \hbar$$

In this case tanh (ip2)/a/ħ) = 1

and
$$\sec\left(\frac{(ip_2)\,a}{\hbar}\right) = 2e^{ip_2a/\hbar}.$$

It is to be noted that p_2 is imaginary and so ip_2 and p_2^2 are real and negative. Then equation (102) and (111) yield.

$$T = \frac{-16p_1^2p_2^2\,e^{2ip_2a/\hbar}}{(p_1^2+p_2^2)^2 - 4p_1^2p_2^2}$$

or
$$T = \frac{-16p_1^2p_2^2\,e^{2ip_2a/\hbar}}{(p_1^2-p_2^2)^2} \qquad \text{....... (113)}$$

and
$$R = \frac{(p_1^2-p_2^2)^2}{(p_1^2+p_2^2)-4p_1^2p_2^2} = \frac{(p_1^2-p_2^2)^2}{(p_1^2-p_2^2)^2} = 1. \qquad \text{....... (114)}$$

Substituting values of p_1 and p_2 from equation (88) equation (113) gives

$$T = \frac{-16\,(2mE)\,2m(E-V_0)\,e^{[2i\sqrt{2m\,(E-V_0)}\}\,a/\hbar]}}{\{2mE-2m\,(E-V_0)\}^2}$$
$$= \frac{16E\,(V_0-E)}{V_0^2}\,e^{[-2\sqrt{(2m\,(V_0-E)\}}\,a/\hbar]}$$

This is the expression for transmission coefficient for a very large barrier. The phenomenon of the particle's (electrons, say) penetrating the potential barrier is called the *"tunnel effect" and is especially important in thermionic and field emission.*

4.7 ONE DIMENSIONAL LINEAR HARMONIC OSCILLATOR

The wave equation for an oscillator

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

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

i.e. $F = -kx$ ……….. (115)

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

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

Where m is the mass of the particle.

∴ From (115) we have equation of oscillator as

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

or $$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0. \qquad \text{……. (116)}$$

This equation represents a periodic motion of angular frequency

$$\omega = \sqrt{\left(\frac{k}{m}\right)} \text{ or frequency } \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\left(\frac{k}{m}\right)} \qquad \text{……. (117)}$$

The potential energy of oscillator is

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

$$= \frac{1}{2}kx^2 \qquad \text{……. (118)}$$

The one-dimensional Schrödinger time independent equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\,\psi = 0. \qquad \text{……. (119)}$$

Substituting $V = \frac{1}{2}kx^2$ in (119), the wave equation for an harmonic oscillator becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}\left(E - \tfrac{1}{2}kx^2\right)\psi = 0, \qquad \text{……. (120)}$$

where k is given by eqn. (119),

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

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

or $$\frac{1}{\sqrt{\left(\frac{mk}{h}\right)}}\frac{\partial^2 \psi}{\partial x^2} + \left[2\sqrt{\left(\frac{m}{\hbar^2 k}\right)}E - \sqrt{\left(\frac{mk}{\hbar^2}\right)}x^2\right]\psi = 0. \qquad \text{…. (121)}$$

For convenience let us substitute

and $$\left.\begin{aligned} &\sqrt{\left(\frac{mk}{\hbar^2}\right)} = \alpha^2 && \text{...(A)} \\ &2E\sqrt{\left(\frac{m}{\hbar^2 k}\right)} = \lambda && \text{...(B)} \end{aligned}\right\} \qquad \text{……. (122)}$$

in eqn. (121) ; then we have

$$\frac{1}{\alpha^2}\frac{\partial^2 \psi}{\partial x^2} + (\lambda - \alpha^2 x^2)\,\psi = 0. \qquad \text{……. (123)}$$

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

$$q = \alpha x \qquad \text{……. (124)}$$

where α is a constant given by eqn. (122).

Now $$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial q} . \frac{\partial q}{\partial x} = \alpha \frac{\partial \psi}{\partial q}$$

from (124)

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

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

substituting these values in eqn. (123), we get

$$\frac{\partial^2 \psi}{\partial q^2} + (\lambda - q^2)\,\psi = 0. \qquad \text{……. (125)}$$

Asymptotic Solution.

To solve eqn. (125) let us first make an attempt to obtain an asymptotic solution for the case when $q^2 >> \lambda$, in this case, eqn. (125) becomes

$$\frac{\partial^2 \psi}{\partial q^2} - q^2 \psi = 0. \qquad \text{……. (126)}$$

The solution of above equation in

$$\psi = e^{\pm q^2/2}, \qquad \text{……. (127)}$$

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

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

$$= (q^2 \pm 1)\, e^{\pm q^2/2}. \qquad \text{……. (128)}$$

As q is very large $q^2 \pm 1 = q^2$ and so eqn. (128) becomes

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

which is same as eqn. (126).

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

Clearly out of the two possible solutions represented by (127).

$$\psi = e^{q^2/2} \text{ and } \psi = e^{-q^2/2},$$

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

Recursion formula.

From above consideration it is clear that the solution of eqn. (125) will contain the term $\psi = e^{-q^2/2}$ as a factor; the possible solution may be written as

$$\psi = e^{-q^2/2} \phi(q), \qquad \text{……. (129)}$$

where $\phi(q)$ is a function of q and hance of z.

Differentiating equations (129) twice with respect to q, we get

$$\frac{\partial^2 \psi}{\partial q^2} = e^{-q^2/2} \left\{ \frac{\partial^2 \phi}{\partial q^2} - 2q \frac{\partial \phi}{\partial q} + (q^2 - 1)\phi \right\} \qquad \text{……. (130)}$$

where ϕ is written for $\phi(q)$.

Substituting values of ψ and $\frac{\partial^2 \psi}{\partial q^2}$ from (129) and (130) in eqn. (125) we get

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

or

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

$$\therefore \quad \frac{\partial^2 \phi}{\partial q^2} - 2q\frac{\partial \phi}{\partial q} + (\lambda - 1)\,\phi = 0 \qquad \text{……. (131)}$$

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

Now let us assume that the function ϕ(q) may be expressed in the form power series in q, i.e.

$$\phi(q) = q^s \sum_{r=0}^{\infty} a_r q^r = \sum_r a_r q^{s+r}. \qquad \text{…… (131A)}$$

Differentiating, we get

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

and

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

Substituting these values in (131), we get

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

or

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

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

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

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

$s = 0$ or $s = 1$ …………… (132)

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

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

This gives either $a1 = 0$ or $s = 0$ or $s = -1$.

As $s \neq -1$, we have either $a_1 = 0$ or $s = 0$ or both. …… (133)

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

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

or $$a_{r+2} = \frac{2s+2r+1-\lambda}{(s+r+2)(s+r+1)}\,a_r \qquad \text{……. (134)}$$

where r is an integer or zero. This expression is called recursion formula. From this we can calculate the coefficients of q^2, q^4, q^6, etc. if that of q0 is known. Similarly, we calculate the coefficients of q^3, q^5, q^7 etc. if the coefficient of q^1 is known. Thus, if we choose $a_1 = 0$, then all odd coefficients a_r will be zero.

Examining the series.

If no restriction is placed on λ which is related to the energy E of the oscillator by eqn. (122) the series for ϕ(q) consists of infinite number of terms and does not correspond to a satisfactory wave function, for large values of r which may be seen as follows:

Examining eqn. (134) for large values of n, we get

$$\lim_{n\to\infty} \frac{a_{n+2}}{a_n} = \frac{2}{n}. \qquad \text{……. (135)}$$

Now consider the series

$$e^{q^2} = 1 + q^2 + \frac{q^4}{2\,!} + \ldots + \frac{q^n}{(\frac{1}{2}n)\,!} + \frac{q^{n+2}}{(\frac{1}{2}n+1)\,!} + \ldots$$

$$= 1 + b_2 q^2 + b_4 q^4 + \ldots + b_n q^n + b_{n+2}\, q^{n+2} + \ldots$$

then the recursion formula for the exponential series for e^{q2} is give by

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

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

$$\lim_{n\to\infty} \frac{b_{n+2}}{b_n} = \frac{2}{n} \qquad \text{……. (136)}$$

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

$$\psi = e^{-q^2/2}\,\phi(q) = e^{-q^2/2}\,.\,e^{q^2} = e^{q^2/2}. \qquad \text{……. (137)}$$

According to this equation if $q \to \infty, \psi \to \infty,$ thus making the ware function physically unacceptable. Thus, the series governed by the recursion formula (133) does not lead to a satisfactory wave function unless some restriction is introduced which make the series break off after a finite number of terms.

Eigen values of harmonic oscillator.

From above discuss we have seen that in order to obtain a satisfactory wave function, the series (126A) must break off after a finite number of terms. The series will break off after rth term if we get the numerator in the recursion formula (134) equal to zero, i.e.,

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

i.e. $$\lambda = 2s + 2r + 1 \qquad \text{……. (138)}$$

For s = 0, we have

$$\lambda = 2r + 1$$

For s = 1, we have

$$\lambda = 2r + 3$$

Thus equation (138) may be written more generally as

$$\lambda = 2n + 1 \; ; \; n = 0, 1, 2, ... \qquad \text{……. (139)}$$

Substituting this value of λ in equation (122B) we get

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

or $$2E\sqrt{\left(\frac{m}{\hbar^2 (m\omega^2)}\right)} = 2n + 1 \qquad [\text{since } k = m\omega^2 \text{ from (117)}$$

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

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

or $$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad (n = 0, 1, 2, 3, ...) \qquad \text{……. (140)}$$

The allowed integral values of n lead to certain discrete values of energy, represented by equation (140) known as eigen value of the harmonic oscillator.

Moreover equation (140) indicates that the energy levels of harmonic oscillator are equally spaced.

4.8 ZERO POINT ENERGY AND PARITY OSCILLATOR

Significance of zero-point energy.

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

$$E_0 = \frac{1}{2}\hbar\omega. \qquad \text{……. (141)}$$

This is called zero-point energy

A comparison with the result $E = n\hbar\omega_0$ obtained by old quantum they show that the only difference is that all the equally spaced energy levels are shifted upward by an amount equal to half the separation of energy levels, i.e. $\frac{1}{2}\hbar\omega_0$ equal to zero point energy. Thus, it is clear that even in the lowest state, the harmonic oscillator has finite energy while according to classical mechanics the harmonic oscillator possesses zero energy at state. The existence of zero-point energy is in agreement with experiment and is important feature of quantum mechanics.

The energy levels of the harmonic oscillator according to wave mechanics are represented in fig. 5.

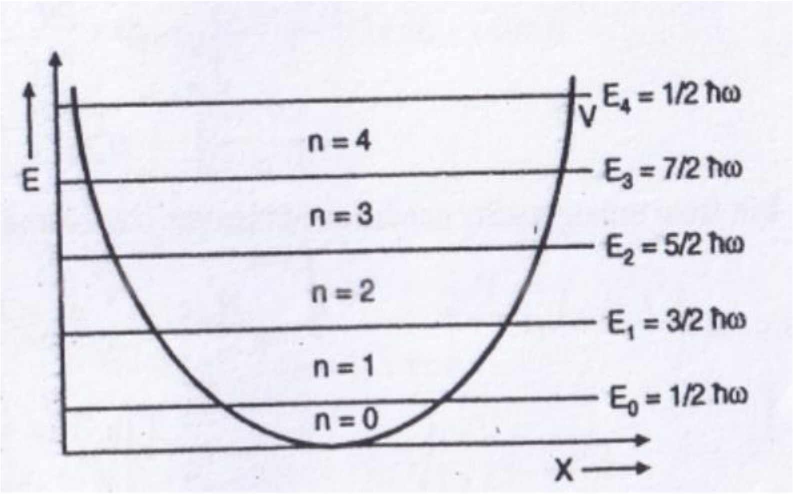


Figure: 5

Eigen functions of harmonic oscillator. We have seen that in order to have a satisfactory solution of wave equation (120), ϕ must break off after a finite number of terms, i.e. ϕ should be restricted in such a manner so as to make it a polynomial rather than a power series. The best suitable polyhomial is Hermite polynomial denoted by H_n (q). Then the eigen function ψ can be set equal to the product of polynomial H_n (q) and the factor $e^{-q^{2/2}}$, i.e.

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

where N_n in normalizing factor and the Hermite polynomial H_n (q) of degree n is defined by

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

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

$n = 0$, $H_o(q) = 1$ (Hermite polynomial of order zero)

$n = 1$, $H_1(q) = 2q$ (Hermite polynomial of order one)

$n = 2$, $H_2(q) = 4q^2 - 1$ (Hermite polynomial of order two)

$n = 3$, $H_3(q) = 8q^3 - 12q$ (Hermite polynomial of order three)

$n = 4$, $H_4(q) = 16q^4 - 48q^2 + 12$ (Hermite polynomial of order four)

and so on.

The orthogonality condition of Hermite polynomials is

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

where δ_{mn} Kronecker delta symbol defined as

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

The normalizing condition is

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

As q = αx, we have $dq = \alpha dx$

or

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

i.e.

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

But from orthogonality condition of Hermite polynomials

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

∴ $$\frac{N_n^2}{\alpha} . 2^n (n\,!)\, \sqrt{\pi} = 1,$$

or $$N_n = \left[\frac{\alpha}{2^n\, N\,!\, \sqrt{\pi}} \right]^{1/2}$$

Thus normalized wave functions of harmonic oscillator are

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

where α is given by equation (121).

The wave function corresponding to the lowest state of energy is

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

A few of these wave functions are shown in figures 6 (a), (b), (c).

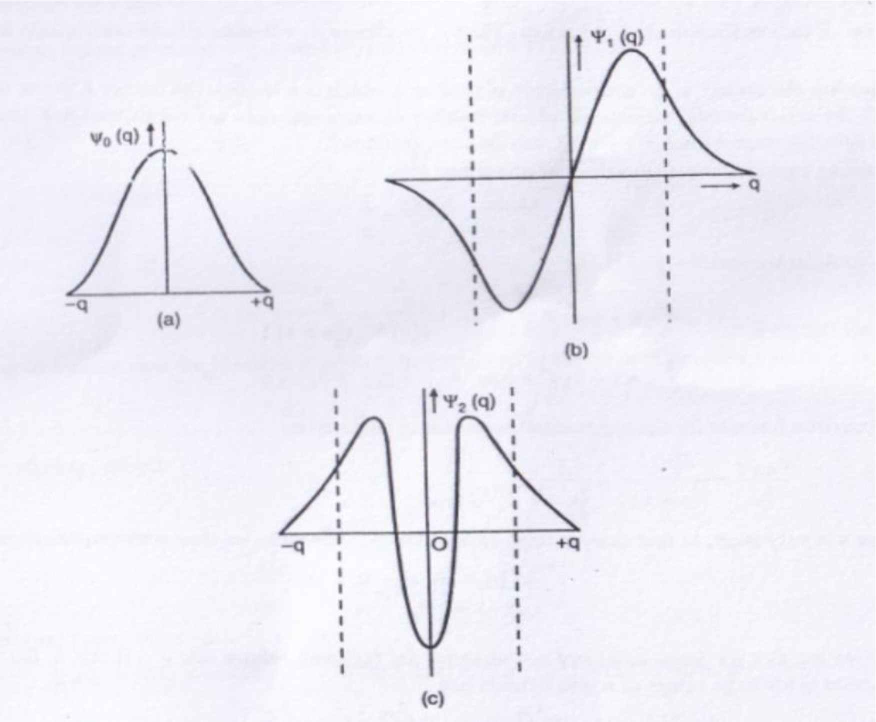


Figure : 6

The probability distribution function $\psi^*_n \psi_n$ for n = 0, 1, 6 are shown in fig. 2.18. The classical limits of x for corresponding energy are shown by A and B in each case. The departures of wave mechanical results from classical mechanical results are as under :

1. The probability distribution function $\psi^*_n \psi_n$ has finite value beyond the classical limits A and B.
2. For the lowest energy state $E_0 = \frac{1}{2\hbar}\omega$, the probability is maximum at centre while according to classical theory the maximum time is spent near the ends.
3. The probability distribution function does not very smoothly but shows (n + 1) maxima for energy state.

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

The wave mechanical predictions of the harmonic oscillator have been verified experimentally, thus establishing the superiority of wave mechanics over classical mechanics.

Parity : It may be observed that harmonic oscillator wave functions are even functions of x if n is even odd functions of x if n is odd. This property is due to the fact that the Hamiltonian of the oscillator is invariant under parity. If P is parity operator, then for every eigen state one has degenerate eigen state $P\psi(x)$. As the Hermite polynomials have definite parity, the functions $\psi(x)$ and $P(\psi)$ must be linearly dependent.

i.e. $P\psi(x) = \psi(-x) = C\psi(x).$

If the transformation x → - x through parity operator is made again. We gee

$P^2 \psi(x) = \psi(x).$

Also $P^2 \psi(x) = P C \psi(x) = C^2 \psi(x)$

i.e., C2 = 1 or C = ± 1

and so $\psi(-x) = \pm \psi(x)$

i.e., every eigen function for a bound state in a symmetric field $[u(x) = u(-x)]$ is either an even or odd function of x. This fact is expressed by the statement that for the oscillator wave function $\psi(x) = -\psi(x)$ the parity of ψ is odd. From parity considerations it can be deduced immediately that for states of definite parity the expectation value of any odd operator is always zero without reference to the explicit of ψ.

Recurrence relations: From the recurrence relations of Hermite polynomials, the recurrence relations of harmonic oscillator wave functions may be deduced.

From recurrence relation of Hermite polynomials, we have

$$2x\,H_n(x) = 2n\,H_{n-1}(x) + H_{n+1}(x).$$

This can be written equivalently as

$$H_{n+1}(q) - 2qH_n(q) + 2n\,H_{n-1}(q) = 0 \text{ (with } q = \alpha x).$$

Multiplying above equation by

$$\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right), \text{ we get}$$

$$\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_{n+1}(ax) - 2q\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_n(\alpha x)$$

$$+ 2n\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_{n-1}(\alpha x) = 0$$

or

$$\sqrt{[2(n+1)]}\left[\frac{\alpha}{2^{n+1}\,(n+1)\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_{n+1}(\alpha x)$$
$$- 2\alpha x\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_n(\alpha x)$$
$$+ \sqrt{(2n)}\left[\frac{\alpha}{2^{n-1}\,(n-1)\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_{n-1}(\alpha x) = 0$$

or

$$\sqrt{[(2n+1)}\;\psi_{n+1}(x) - 2\alpha x\psi_n(x) + \sqrt{(2n)}\;\psi_{n-1}(x) = 0$$

or

$$x\psi_n(x) = \frac{1}{\alpha}\left[\sqrt{\left(\frac{n+1}{2}\right)}\psi_{n+1}(x) + \sqrt{\left(\frac{n}{2}\right)}\psi_{n-1}(x)\right]. \qquad \text{…..(142)}$$

We have

$$\psi_n(x) = \frac{1}{\alpha}\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_n(\alpha x)$$

$$\frac{d\psi_n(x)}{dx} = \left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2}\left[-(\alpha^2x))\exp\left(-\frac{\alpha^2x^2}{2}\right)H_n(\alpha x)\;\left[+\exp\left(-\frac{\alpha^2x^2}{2}\right)\frac{dH_\alpha(\alpha x)}{dx}\right]\right.$$

$$= -\alpha^2x\left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2x^2}{2}\right) H_n(\alpha x) + \left[\frac{\alpha}{2^n\,n\,!\,\sqrt{\pi}}\right]^{1/2} \alpha\exp\left(-\frac{\alpha^2x^2}{2}\right)\frac{d\,H_n(\alpha x)}{d(\alpha x)}.$$

Using other recurrence relation for Hermite polynomials as

$$\frac{dH_n(x)}{dx} = 2n\, H_{n-1}(x),$$

we get

$$\frac{d\,\psi_n(x)}{dx} = -\alpha^2 x\psi(x) + \left[\frac{\alpha}{2^n\, n!\,\sqrt{\pi}}\right]^{1/2} \alpha \exp\left(-\frac{\alpha^2 x^2}{2}\right)[2n\, H_{n-1}(\alpha x)]$$

Now using eqn. (142), we get

$$\frac{d\psi_n(x)}{dx} = -\alpha^2 \frac{1}{\alpha}\left\{\sqrt{\left(\frac{n+1}{2}\right)}\psi_{n+1} + \sqrt{\left(\frac{n}{2}\right)}\psi_{n-1}(x)\right\}$$
$$+ 2\alpha n \cdot \frac{1}{\sqrt{(2n)}}\left[\frac{\alpha}{2^{n-1}\,(n-1)!\,\sqrt{\pi}}\right]^{1/2} \exp\left(-\frac{\alpha^2 x^2}{2}\right) H_{n-1}(\alpha x)$$

or

$$\frac{d\psi_n(x)}{dx} = -\alpha\left[\sqrt{\left(\frac{n+1}{2}\right)}\psi_{n+1}(x) + \sqrt{\left(\frac{n}{2}\right)}\psi_{n-1}(x)\right] + 2\alpha\sqrt{\left(\frac{n}{2}\right)}\psi_{n-1}(x)$$

or $$\frac{d\psi_n(x)}{dx} = \alpha\left[\sqrt{\left(\frac{n}{2}\right)}\psi_{n-1}(x) - \sqrt{\left(\frac{n+1}{2}\right)}\psi_{n+1}(x)\right]. \quad \text{……. (143)}$$

Equations (142) and (143) represent two important recurrence relations of the harmonic oscillator wave functions.

4.9 SUMMARY

In this unit we studied about particle in a Box problem, Potential Step, recursion formula, tunnel effect, Zero-point Energy.

4.10 TERMINAL QUESTIONS

1. What do you mean by Tunneling through a Barrier.
2. Discuss one dimensional linear harmonic oscillator.
3. Write down Schrödinger wave equation for a particle in a box.
4. Solve the Schrödinger wave equation in three dimensions for a free particle.
5. Discuss the motion of an electron across a potential step of finite height. calculate the reflection and transmission coefficients.

4.11 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 4.6
2. Section 4.7
3. Section 4.4
4. Section 4.3
5. Section 4.5

4.12 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

UNIT-5 SPHERICALLY SYMMETRIC SYSTEMS

Structure

5.1 INTRODUCTION

In the presence of spherical symmetry, the Schrödinger equation has solutions that can be separated into a product of a radial part and an angular part. In this unit, all possible solutions of the equation for the angular part will be determined once and for all.

We start by discussing symmetry transformations in general. In quantum mechanics, all symmetry transformations may be realized by unitary or antiunitary operators.

5.2 OBJECTIVES

After studying this unit, student should able to:

- Know about Schrodinger equation for Spherically Symmetric Potential.
- Discuss about Three-Dimensional Harmonic Oscillator.

- Explain The Rigid Rotator with free axis.
- Know about The Hydrogen Atom.

5.3 SCHRODINGER EQUATION FOR SPHERICALLY SYMMETRIC POTENTIAL

The potential energy of a particle moving under a central spherically field of force depends only upon is distance from the centre of force, i.e., the potential energy in such cases has the form V(r), r being the distance between the particle and the centre of force (i.e. origin). The Schroedinger equation for such a system would be given by

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

………………………..1

In such cases it is appropriate to write the Schredinger's equation in spherical polar co-ordinates (r, θ, ϕ) since the potential energy V(r) is independent of the angular variables θ and ϕ.

Let P be the point in space such that its cartesian co-ordinates of the point P are specified by (r, θ, ϕ), where r = OP is the radius of the sphere on which point P lies, θ is the colatitude, i.e., the angle between OP and z-axis and ϕ is the longitudinal or azimuthal angle, i.e., the angle included between XZ plane and the plane OPZ, from fig.1 the transformations between cartesian co-ordinates (x, y, z) and spherical co-ordinates (r, θ, ϕ) are given by

$$\left.\begin{aligned} x &= r \sin\theta \cos\phi, \\ y &= r \sin\theta \sin\phi, \\ z &= r \cos\theta. \end{aligned}\right\}$$

…………………..2

From (2), we have

$$x^2 + y^2 + z^2 = r^2$$

i.e.

$$r = \sqrt{(x^2 + y^2 + z^2)},$$

and

$$\left.\begin{aligned} \tan\phi &= \frac{y}{x} \\ \tan\theta &= \frac{\sqrt{(x^2 + y^2)}}{z} \end{aligned}\right]$$

……………………..3

Using (2) and (3), we have

$$\left.\begin{aligned}&\frac{\partial r}{\partial x} = \sin\theta\cos\phi\,,\ \frac{\partial r}{\partial y} = \sin\theta\sin\phi\,,\ \frac{\partial r}{\partial z} = \cos\theta,\\ &\frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r},\ \frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r},\ \frac{\partial\theta}{\partial z} = -\frac{\sin\theta}{r}\end{aligned}\right] \qquad \text{.……4}$$

$$\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta}, \frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta}, \frac{\partial\phi}{\partial z} = 0.$$

Then $$\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial r}\cdot\frac{\partial r}{\partial x} + \frac{\partial r}{\partial\theta}\cdot\frac{\partial\theta}{\partial x} + \frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x}$$

$$= \sin\theta\cos\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial\psi}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}.$$

∴ $$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

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

$$\begin{aligned}= &\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\\ &\times\left(\sin\theta\cos\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial\psi}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}\right)\end{aligned} \qquad \text{……5}$$

Similarly,

$$\frac{\partial\psi}{\partial y} = \left(\sin\theta\sin\phi\frac{\partial\psi}{\partial r} + \frac{\cos\vartheta\sin\phi}{r}\frac{\partial\psi}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}\right)$$

so that $$\frac{\partial}{\partial y} = \left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$\begin{aligned}\text{and } \frac{\partial^2\psi}{\partial y^2} = \frac{\partial}{\partial y}\left(\frac{\partial\psi}{\partial y}\right) = &\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right).\\ &\times\left(\sin\theta\sin\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial\psi}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial\psi}{\partial\psi}\right)\end{aligned}$$

…………..6

Also $\frac{\partial\psi}{\partial z} = \left(\cos\theta \frac{\partial\psi}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta}\right)$

so that $\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}$

and

$$\frac{\partial^2\psi}{\partial z^2} = \frac{\partial}{\partial z}\left(\frac{\partial\psi}{\partial z}\right) = \left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\left(\cos\theta\frac{\partial\psi}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta}\right)$$

……..7

Adding and simplifying (5), (6) and (7) we get

$$\begin{aligned}\nabla^2\psi &= \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}.\end{aligned}$$

Substituting this in equation (1), the Schrödinger wave equation for spherically symmetric potential in spherical polar co-ordinates is given by

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

……..8

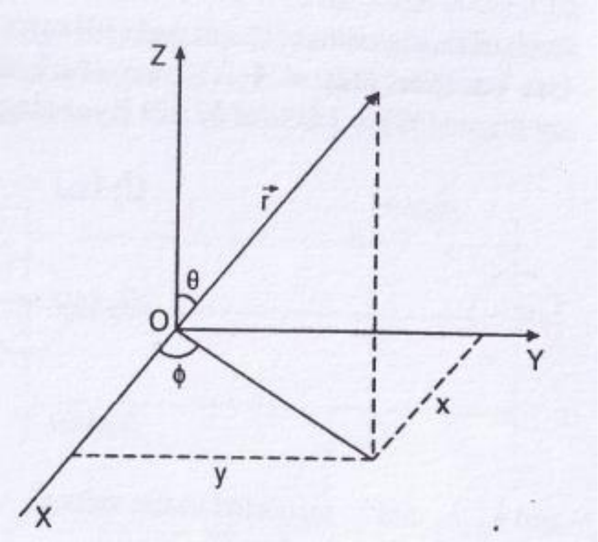


Figure 1

5.4 THREE DIMENSIONAL HARMONIC OSCILLATOR : (SPHERICALLY SYMMETRIC CASE)

Here we shall consider a particular case of the three-dimensional harmonic oscillator already discussed in previous unit 4, where the frequencies along X, Y, Z-axis are equal.

i.e., $\nu_x = \nu_y = \nu_z = \nu$ (say).

The system consists of a point bound to origin by a force proportional to the displacement r from the fixed point,

i.e. $F = - kr,$

where k is force constant given by

$k = 4\pi^2 \nu^2 m$ ……… (9)

so that the potential energy function of the oscillator will be

$$V = - \int_0^r F\,dr = \int_0^r kr\,dr = \frac{1}{2} kr^2$$

assuming V(r) = 0, where r = 0 i.e. at the origin

But $r^2 = x^2 + y^2 + z^2.$

$\therefore$ $V(r) = \frac{1}{2} kr^2 = \frac{1}{2} kr^2 = \frac{1}{2} k\,(x^2 + y^2 + z^2).$

The Schroediner were equation in this case will be

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2}\,[E - \frac{1}{2} k\,(x^2 + y^2 + z^2)]\,\psi = 0$$

or

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

or

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

…………..(10)

Substituting

$$\left.\begin{aligned} \sqrt{\left(\frac{mk}{\hbar^2}\right)} &= \alpha^2 \\ 2E\sqrt{\left(\frac{m}{\hbar^2 k}\right)} &= \lambda \end{aligned}\right\}$$

and

equation (10) becomes

$$\frac{1}{\alpha^2}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+[\lambda-\alpha^2(x^2+y^2+z^2)]\,\psi=0$$

……(11)

For convenience substituting

and
$$\left.\begin{aligned} q_x &= \alpha x \\ q_y &= \alpha y \\ q_z &= \alpha z \end{aligned}\right\}$$

………………………..(12)

in equation (11), we get

$$\frac{\partial^2\psi}{\partial q_x^2}+\frac{\partial^2\psi}{\partial q_y^2}+\frac{\partial^2\psi}{dq_z^2}+[\lambda-(q_x^2+q_y^2+q_z^2)]\,\psi=0$$

……….....(13)

The equation can be solved exactly in the same manner as in the case of free particle, i.e., by the method of separation of variables. Then the substitution of

$$\psi = Q_x(q_x)\,Q_x(q_y)\,Q_z(q_z).$$

where Q_x is function of q_x, Q_y is function of q_y and Q_z is function of q_z only, results in separate equations for Q_x, Q_y and Q_z i.e.

$$\frac{\partial^2 Q_x}{\partial q_x^2}+(\lambda_x-q_x^2)\,Q_x=0$$

…………………………(14)

$$\frac{\partial^2 Q_y}{\partial q_y^2}+(\lambda_y-q_y^2)\,Q_y=0$$

…...……………(15)

$$\frac{\partial^2 Q_z}{\partial q_z^2} + (\lambda_z - q_z^2)\, Q_z = 0, \qquad \text{...………………(16)}$$

where the constant λ_x, λ_y and λ_z are related by

$$\lambda_z + \lambda_y + \lambda_z = \lambda \qquad \text{………...……. (17)}$$

Each of the euqtions (14), (15) and (16) represents the wave equation for the dimensional harmonic oscillator (see equation (125) of unit 4 for which the eigen values and normalized wave functions are given by equations (140) and (140A) of unit 4. By analogy, we have

$$Q_2(q_x) = \frac{1}{[2^{n_x} n_x!\sqrt{\pi}]^{1/2}} e^{-q_x^2/2} H_{n_x}(q_x)$$

$$Q_y(q_y) = \frac{1}{[2^{n_y} n_y!\sqrt{\pi}]^{1/2}} e^{-q_y^2/2} H_{n_y}(q_y)$$

$$Q_z(q_z) = \frac{1}{[2^{n_z} n_z!\sqrt{\pi}]^{1/2}} e^{-q_z^2/2} H_{n_z}(q_z)$$

and λ_x, λ_y and λ_z restricted to the values

$$\left.\begin{aligned} \lambda_x &= 2n_x + 1 \\ \lambda_y &= 2n_y + 1 \\ \lambda_z &= 2n_z + 1 \end{aligned}\right\}$$

Here n_x, n_y and n_z are *non-naegative integers.*

Thus the *complete normalised wave function is given by* $\psi = Q_x Q_y Q_z$

$$= \frac{1}{[2^{(n_x+n_y+n_z)} n_x!\, n_y!\, n_z!\, \pi^{3/2}]^{1/2}} e^{-\frac{1}{2}(q_x^2+q_y^2+q_z^2)} \times H_{n_x}(q_x) H_{n_y}(q_y) H_{n_z}(q_z)$$

The given values are given by

$$E_n = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega = \left(n + \frac{3}{2}\right)\hbar\omega,$$

Where $n = n_z + n_y + n_z$ may the called total quantum number. As the energy of this system depends only on the total quantum number, a l the energy levels except the lowest one are degenerate with the quantum weight $p =$

$\frac{}{2}(n+1)(n+2)$. Fig.2 represents a few energy levels together with their quantum weights and quantum numbers.

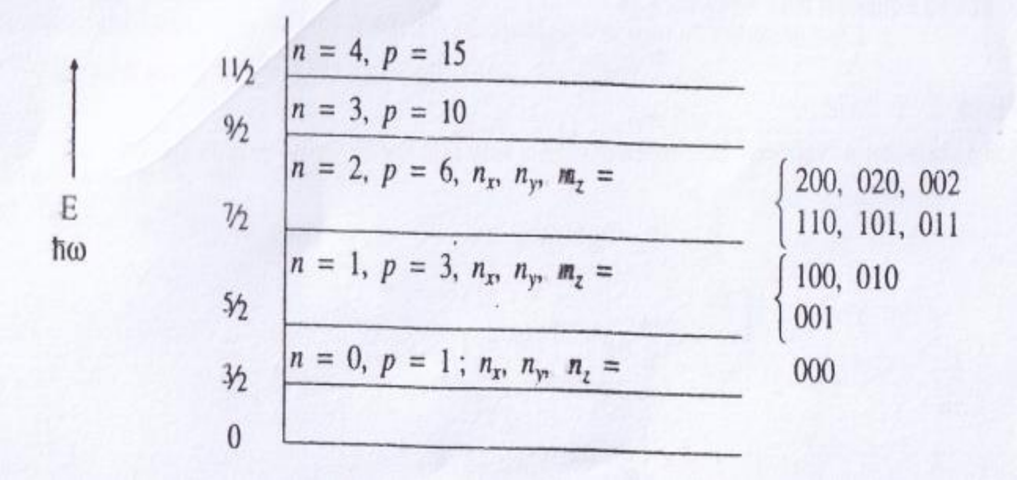


Figure:2

5.5 THE RIGID ROTATOR WITH FREE AXIS

The system, consisting of two spherical particles attached together, separated by finite fixed distance and capable of rotating about an axis passing through the centre of mass and normal to the plane containing the two particles, constitutes, a rigid rotation. If these two particles are constrained, to remain in one plane, then the direction of the axis of rotations in fixed and so the system is called the rigid rotator with axis. If the plane of these two particles can move, then the axis of rotation is free to take any position in space and so the system is called the rigid rotator with free axis. In a diatomic molecule the atoms vibrate with respect to each other and so the distance between atoms will not be always constant; while the distance apart of the equilibrium position is constant. Thus, the system of diatomic molecules is not really rigid; however, it may be treated, at least as a first approximation, as a rigid rotator with free axis.

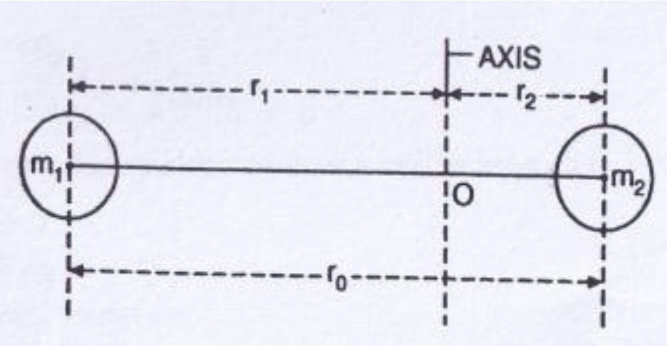


Figure:3

Energy for the rotator.

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

$$T = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$ ……………………….18

where $\dot{x}, \dot{y}, \dot{z}$ are the components of the velocity of a particle along X, Y and Z axes respectively.

the transformations between cartesian co-ordinates (x, y, z) and spherical co-ordinates (r, θ, ϕ) are given by

$$\left.\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}\right]$$

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

$$T = \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2\theta \, \dot{\phi}^2)$$ …………………….19

If the distance r of the particle from the origin is fixed, its derivative r will be zero, then from equation (19) the kinetic energy would be

$$T = \frac{1}{2} m r^2 (\dot{\theta}^2 + \sin^2\theta \, \dot{\phi}^2)$$ ………………………………20

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

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

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

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

Hence the total kinetic energy of the rotator will be

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

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

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

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 \right) (\dot{\theta}^2 + \sin^2\theta \, \dot{\phi}^2)$$ ………………………..21

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

The equation (21) may be written as

$$E = T = \frac{1}{2} I \left(\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2\right)$$ ………………………………22

The moment of inertia of the rotator may be expressed in a more convenient form as follows :

According to definition of centre of mass $r_{cm} = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2}$, we have

$$0 = \frac{-m_1 r_1 + m_2 r_2}{m_1 + m_2}$$ …………………………….23

i.e. $m_1 r_1 = m_2 r_2$

But $r_0 = r_1 + r_2$

i.e. $r_2 = r_0 - r_1$

Substituting this in eqn. (23) we get

$$m_1 r_1 = m_2 (r_0 - r_1)$$

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

Similarly

$$r_2 = \frac{m_1}{m_1 + m_2} r_0$$

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

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

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$\therefore$ $I = \mu r_0^2$ ……………………..24

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

is called the reduced mass of the system.

Form equation (20) and (22) it is evident that the rotator behaves like a single particle of mass μ given by eqn. (24) placed at a fixed distance, equal to unity (since r = 1) from the origin, which in this case in the centre of mass of the system.

Wave equation for the rotator: The Schroedinger wave equation in three dimensions in spherical co-ordinates is given by

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

For a rigid rotator we have seen that potential energy is zero r = 1 and the mass m may be replaced by the moment of inertia l. Therefore the Schroedinger wave equation for a rigid rotator becomes

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2I}{\hbar^2}E\psi = 0. \qquad \ldots\ldots\ldots\ldots 25$$

This equation consists of two variable θ and ϕ which represent the processional motion of the rotator’s free axis and the rotation of the system respectively.

Solution of wave equation : Eigen function for the rotator :

Equation (25) may be solved by the method of separation of variable, i.e., the wave function ψ(θ, ϕ) may be represented by

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

where Θ (θ) is function θ of alone and ϕ(θ) is the function of ϕ alone.

Substituting in equation (25) and dividing by Θ ϕ we get

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

Multiplying this equation by $\sin^2\theta$ we get

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

or

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

In this equation L.H.S. is a function of θ alone, while R.H.S. is a function of ϕ alone. Therefore if this equation is to be satisfied, both sides must be equal to the same constant, m^2 (say) i.e.

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\cdot\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2IE}{\hbar^2}\sin^2\theta = m^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots..26$$

and

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = m^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots27$$

Equation (27) may be rewritten as

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

the solution of above equation may be written as

$$\Phi = Ae^{im\phi}$$

where $m = 0, \pm 1, \pm\, 2, \pm 3\ etc.$

A is any arbitrary constant which may be chosen is such a way that the function is normalized i.e.

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

or

$$\int_0^{2\pi} Ae^{im\phi}\,Ae^{-im\phi}\,d\phi = 1,$$

i.e.

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

or

$$A^2\,2\pi = 1$$

i.e.

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

Thus the normalized function is

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

Multiplying equation (26) by $\frac{\theta}{sin^2\theta}$, we get

$$\frac{1}{\sin\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\frac{2IE}{\hbar^2}-\frac{m^2}{\sin^2\theta}\right)\Theta = 0$$ …………………28

Let us now define a new variable x such that

x = cos θ ………………………..*28(A)*

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

Then $\frac{\partial\Theta}{\partial\theta} = \frac{\partial\Theta}{\partial x}\cdot\frac{\partial x}{\partial\theta} = -\sin\theta\frac{\partial\Theta}{\partial x}$ ……………….29

And hence in general, we have

$$\frac{\partial}{\partial\theta} = -\sin\theta\frac{\partial}{\partial x}$$ …………………………….30

∴ $\sin\theta\frac{\partial\Theta}{\partial\theta} = -\sin^2\theta\cdot\frac{\partial\Theta}{\partial x}$

$$= -(1-x^2)\frac{\partial\Theta}{\partial x}$$ …………………..31

Using equations (29), (30) and (31) equation (28) can be written in terms of variable x as

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

……………….32

where $\beta = \frac{2IE}{\hbar^2}$ ……………………..33

Equation (33) is known as Legendre's equation. It has physical significance only for values of x between the limits of – 1 and + 1 since x is equal to cos θ [equation (28A)].

In order to solve eqn. (33) let us substitute, for convenience.

$$\Theta(\theta) = (1-x^2)^{m/2}X(x),$$ ………………….34

where X (x) is the function of x only.

Equation (34) yields

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

∴

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

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

………………35

where $$X' = \frac{dX}{dx} \text{ and } X'' = \frac{d^2X}{dx^2}.$$

Using equation (34) and (35), equation (32) becomes.

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

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

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

…………….36

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

$$\left. \begin{array}{ll} \text{where} & \alpha = m + 1 \\ \text{and} & \lambda = \beta - m\,(m+1) \end{array} \right\}$$

………………..36A

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

$$X = a_0 + a_1x + a_2x^2 + a_3x^3 + \ldots\ldots$$

so that $$X' = a_1 + 2a_2x + 3a_3x^2 + \ldots.$$

and $$X'' = 2a_2 + 6a_3x + 12a_4x^2 + ...$$

Substituting these values in equation (36) and simplifying, we get

$$(2a_2 + \lambda a_0) + \{6a_3 + (\lambda - 2\alpha)\, a_4\}\, x + \{12a_4 + (\lambda - 4\alpha - 2)\, a_2\}\, x^2 + \{20a_5 + (\lambda - 4\alpha - 6)\, a_3\}\, x^3 + ...$$

$$+\ [(n+1)(n+2)\, a_{n+2} + \{\lambda - 2n\alpha - n(n-1)\}\, a_n]\, x^n + ...\ = 0.$$

In order that the series may be zero for all possible values of x, the coefficients of individual powers of x must vanish separately, i.e., in general

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

where n = 0, 1, 2, 3, ……

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

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

$$\frac{a_{n+2}}{a_n} = \frac{(n+m)(n+m+1) - \beta}{(n+1)(n+2)} \qquad \text{…………………………37}$$

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

In order to obtain a satisfactory wave function ψ it is necessary that X(x) should be a polynomial breaking off after a finite number of terms, as in the case of harmonic oscillator. The series will break after nth term if the nominator of equation (37) is zero

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

or $$\beta = (n+m)(n+m+1) \qquad \text{…………………….38}$$

It has already been pointed out that m zero or an integer and n is also zero or integer. Therefore, the sum (n + m) may be replaced by I, is also zero or an integer.

Then equation (38) gives

$$\beta = l(l+1), \qquad \text{…………………39}$$

$$l = m + n = 0, 1, 2, 3, \ldots$$

Substituting this value of β in equation (27), we get

$$\frac{\partial}{\partial x}\left\{(1-x^2)\frac{\partial\Theta}{\partial x}\right\} + \left\{l(l+1) - \frac{m^2}{1-x^2}\right\}\Theta = 0.$$ ………………40

The solution of above of above equation contains the factor called the associated Legendre function$P_1^m(x)$ which may be defined as

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

where $P_1(x)$ is Legendre polynomial of degree l.

The solution of equation (40) is written as

$$\Theta = BP_l^m(x) = BP_l^m(\cos\theta)$$

[since x = cos θ]

where B is a constant which may be normalizing factor.

According to orthogonal properties of associated Legendre's Polynomials,

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

According to normalizing condition.

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

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

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

i.e. $$B = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)}$$

Substituting value of B in (36A), the normalized wave function Ɵ is given by

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

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

$$\Psi = \Theta(\theta)\,\Phi(\phi) = \sqrt{\left(\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right)} P_l^m(\cos\theta)\,.\,\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

or

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

Eigen values or energy levels of the rigid rotator. Form equations (33) and (39), we have

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

or

$$E = E_l = \frac{l(l+1)\hbar^2}{2I}$$

$l = 0, 1, 2, 3, \ldots\ldots$

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

5.6 RIGID ROTATOR IN A FIXED PLANE

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

$$\frac{\partial^2\psi}{\partial\phi^2} + \frac{2IE}{\hbar^2}\psi = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots.41$$

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

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

so that we have

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

i.e. $$\frac{\partial^2\Phi}{\partial\phi^2} + m^2\Phi = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 42$$

where $$\frac{2IE}{\hbar^2} = m^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 43$$

Eigen function : The solution of equation (42) can be written as

$$\Phi_m = Ae^{im\phi}$$

where A is arbitrary constant and m = 0, ± 1, ± 2, ……..

According to normalization condition,

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

or $$\int_0^{2\pi} Ae^{+im\phi} Ae^{-im\phi} \, d\phi = 1$$

or $$A^2 . 2\pi = 1$$

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

∴ The eigen functions are given by

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

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

Eigen values : From equation (43), we have

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

This equation represents the rotational energy eigen values of the rigid rotator.

5.7 THE HYDROGEN ATOM

Hydrogen atom may be regarded as a system fir two interacting point charges, the positively charged nucleus consisting of a proton and negatively charged electron, revolving around the nucleus.

For a system of two or more particles the equation of motion can be more conveniently written in the form

$H\psi = E\psi$ ……… (44)

where H is the Hamiltonian operator, ψ is the eigen function and E is thue energy of the whole system.

If (x_1, y_1, z_1) (x_2, y_2, z_2) are the cartesian co-ordinates of the nucleus and the electron and m1 and m2 their masses respectively. The Hamiltonian of the system is given by

$$H = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)+V$$

where V is the potential energy.

So the Schroedinger wave equation for the whole system is written as

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)\psi_T-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)\psi_T+V = E_T\psi_T$$

………………………………..45

Where ψ_T and E_T are the total eigen function and the total energy respectively.

Equation (45) may be written as

$$\frac{1}{m_1}\left(\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{\partial^2\psi_T}{\partial z_1^2}\right)+\frac{1}{m_2}\left(\frac{\partial^2\psi_T}{\partial x_2^2}+\frac{\partial^2\psi_T}{\partial y_2^2}+\frac{\partial^2\psi_T}{\partial z_2^2}\right)+\frac{2}{\hbar^2}(E_T-V)\,\psi_T = 0$$

…………………………………………46

In general the potential energy V of the system may be written as

$$\begin{aligned} V &= \frac{(Ze)\,(-e)}{|\mathbf{r}|} \\ &= \frac{(Ze)\,(-e)}{|\mathbf{r_2}-\mathbf{r_1}|} \\ &= -\frac{Ze^2}{\sqrt{\{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\}}} \end{aligned}$$

Equation (46) can be separated into two equations one of which represents translational motion of the whole system i.e., the centre or mass and the relative motion of the two particles. In order to separate the two equation let us introduce the new variables $\overline{x}, \overline{y}, \overline{z}$, the cartesian co-ordinates of the centre of mass of the system and (r, θ, ϕ) the polar co-ordinates of the electron relative to the nucleus. These new co-ordinates are related to the cartesian co-ordinates of the particles by the equations.

$$\left.\begin{aligned} \bar{x} &= \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \\ \bar{y} &= \frac{m_1y_1 + m_2y_2}{m_1 + m_2} \\ \bar{z} &= \frac{m_1z_1 + m_2z_2}{m_1 + m_2} \end{aligned}\right\}$$

$$\left.\begin{aligned} x_2 - x_1 &= r\sin\theta\cos\phi \\ y_2 - y_1 &= r\sin\theta\sin\phi \\ z_2 - z_1 &= r\cos\theta \end{aligned}\right\}$$

Introducing these new variable in equation (46), we get

$$\frac{1}{m_1 + m_2}\left(\frac{\partial^2\psi_T}{\partial\bar{x}^2} + \frac{\partial^2\psi_T}{\partial\bar{y}^2} + \frac{\partial^2\psi_T}{\partial\bar{z}^2}\right) + \frac{1}{\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\frac{\partial\psi_T}{\partial r}\right) + \frac{1}{r^2\sin\theta}\left(\sin\theta\cdot\frac{\partial\psi_T}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi_T}{\partial r}\right\}$$

$$+ \frac{2}{\hbar^2}\{E_T - V(r)\}\,\psi_T = 0$$

…………………………………….47

when $\mu = \frac{m_1m_2}{m_1+m_2} = reduced\ mass\ of\ the\ system.$

Let us now apply the principle of separation of variables to separate the two equations. For the purpose let us assume

$$\psi_T(\bar{x}, \bar{y}, \bar{z}, r, \theta, \phi) = f(x, y, z)\,\psi(r, \theta, \phi).$$

Substituting this value of ψ_T in equation (47) and dividing by $f\psi$, we get

$$\frac{1}{f(m_1 + m_2)}\left(\frac{\partial^2 f}{\partial\bar{x}^2} + \frac{\partial^2 f}{\partial\bar{y}^2} + \frac{\partial^2 f}{\partial\bar{z}^2}\right) + \frac{1}{\mu\psi}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}$$

$$+ \frac{2}{\hbar^2}\{E_T - V(r)\} = 0$$

$$\text{or}\quad \frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}\right)+\frac{2}{\hbar^2}E_T$$

$$=-\frac{1}{\mu\psi}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{2}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2}\right\}+\frac{2}{\hbar^2}V(r)$$

In above equation L.H.S. in a function of $(\bar{x},\bar{y},\bar{z})$. Therefore if above equation is to be satisfied both sides must be equal to a constant $2E/\hbar^2$, (say) i.e.

$$\frac{1}{f(m_1+m_2)}\left(\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}\right)+\frac{2}{\hbar^2}E_T=\frac{2}{\hbar^2}E$$

or

$$\frac{\partial^2 f}{\partial \bar{x}^2}+\frac{\partial^2 f}{\partial \bar{y}^2}+\frac{\partial^2 f}{\partial \bar{z}^2}+\frac{2}{\hbar^2}(m_1+m_2)(E_T-E)f=0$$

…………48

and

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

or

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

…………………………..49

Equation (48) represents the equation of motion of a free particle of mass m_1 + m_2 and

Energy (E_r – E) : thus the translational motion of the centre of mass is the same as that of a free particle of mass m_1 + m_2 and energy (E_r – E). Thus result corresponds to the classical result that the centre of mass moves in a straight line with constant speed. Equation (49) is identical with Schroedinger's wave equation for a single particle of mass μ and total energy E (exclusive of the translational energy) moving under the influence of a potential function $V(r) = -e^2/r$ since for hydrogen atom Z = 1. The energy E of the relative motion is determined as the eigen value of this equivalent problem.

In order to solve equation (49), let us express eigen function ψ(r, θ, ϕ) as the product of three functions, viz. R(r) Θ (θ) ϕ (ϕ), each of which is function of the one indicated variable, thus

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

Substituting this in equation (13) and dividing by R Θ ϕ, we get

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

Multiplying this equation by $r^2 \sin^2\theta$ and rearranging, we get

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

In this equation L.H.S. is function of r and θ is independent of ϕ, while R. H. S. is function of ϕ alone. Therefore if this equation is to be satisfied each side must be equal to same constant m^2 (say), i.e.

$$\frac{\sin^2\theta}{R}\frac{\partial}{\theta r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+r^2\sin^2\theta\cdot\frac{2\mu}{\hbar^2}\{E-V(r)\} = m^2 \qquad \text{……………………………50}$$

and

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

or

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi = 0 \qquad \text{……………..51}$$

Dividing equation (50) by $\sin^2\theta$ and rearranging, we get

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\cdot\frac{2\mu}{\hbar^2}\{E-V(r)\} = \frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

The L.H.S. of this equation is a function of the variable r only while R.H.S. is a function of the variable θ only. Therefore if above equation is to be satisfied each side must be equal to the same constant, β (say) i.e.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2\mu}{\hbar^2}\{E-V(r)\} = \beta$$

or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{\beta R}{r^2}+\frac{2\mu}{\hbar^2}\{E-V(r)\}R = 0$$

……………………..52

and $$\frac{m^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) = \beta$$

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\cdot\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0.$$ ………….53

The solution of Θ equation. As discussed in last article the solution of eqn. (53) can be written as

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

where the constant m = 0, ± 2, ± 3, …. and is called the magnetic quantum number.

The solution of Θ equation. Let us substitute a new variable x such that

x = cos θ

in equation (53), then we have

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

Therefore, we must have

$\beta = l\,(i+1)$

where i = 0, 1, 2, 3, ….. and is called the azimuthal quantum number.

Also solution of equation (53) may be written as

$$\Theta_{ml}(\theta) = \sqrt{\left\{\frac{(2l+l)}{2}\frac{(l-|m|)\,!}{(l+|m|)\,!}\right\}}P_l^{|m|}(\cos\theta).$$

where P^{lml} is called the associated Legendre function.

Solution of radial equation

Substituting value of β in equation (52), we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\frac{\partial R}{\partial r}\right\} - \frac{l\,(l+1)}{r^2}R + \frac{2\mu}{\hbar^2}\{E - V(r)\}R = 0$$

or
$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[\frac{-l\,(l+1)}{r^2}+\frac{2\mu}{\hbar^2}\{E-V\,(r)\}\right]R=0$$

…………………….54

This equation with $V\,(r)=-\frac{Ze^2}{r}$ is called the radial equation for hydrogen-like atoms and for Z = 1 it is radial equation for hydrogen atom.

Substituting $V\,(r)=-\frac{Ze^2}{r}$ in equation (54), we get

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

…………55

According to classical mechanics E < 0, i.e., negative energies correspond to elliptical orbits representing bound states in atomic system: while E < 0, i.e., positive energies correspond to hyperbolic orbits representing unbound states.

In this case let us consider that the electron in bound is the hydrogen atom, i.e. E < 0. Then let us substitute

and
$$\left.\begin{aligned}\alpha^2&=-\frac{2\mu E}{\hbar^2}\\ \lambda&=\frac{\mu Ze^2}{\hbar^2\alpha}\end{aligned}\right\}$$
……………………56

in equation (55), so that we have

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[-\frac{l\,(l+1)}{r^2}-\alpha^2+\frac{2\lambda\alpha}{r}\right]R=0.$$

…………….57

Let us now introduce a new independent variable ρ such that

$$\rho=2\alpha r,\ \Rightarrow\ \frac{\partial\rho}{\partial r}=2\alpha$$

so that we have
$$\frac{\partial R}{\partial r}=\frac{\partial R}{\partial\rho}\cdot\frac{\partial\rho}{\partial r}=2\alpha\frac{\partial R}{\partial\rho}$$

$$\frac{\partial^2 R}{\partial r^2} = \frac{\partial}{\partial r}\left\{\frac{\partial R}{\partial r}\right\} = \frac{\partial}{\partial \rho}\left\{2\alpha \frac{\partial R}{\partial \rho}\right\}\cdot\frac{\partial \rho}{\partial r} = 4\alpha^2 \frac{\partial^2 R}{\partial \rho^2}$$

Substituting these values of $\frac{\partial R}{\partial r}$ *and* $\frac{\partial^2 R}{\partial r^2}$ in equation (57) and dividing by $4\alpha^2$, we get

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left\{-\frac{l\,(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right\} R = 0. \qquad \text{……….58}$$

Asymptotic behaviour : If $\rho \to \infty$, equation (58) approaches the form

$$\frac{\partial^2 R\,(\rho)}{\partial \rho^2} - \frac{1}{4} R\,(\rho) = 0.$$

The solution of above equation is

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

As ρ may vary from 0 to ∞, former of these solutions will increase as ρ increases and so it will lead to an unacceptable wave function. On the other hand second solution decreases to zero as ρ (and hence r) increases to infinity. Consequently second solution is satisfactory.

Recursion Formula : Keeping in mindthe asymptotic solution, the exact solution of equation (58), must be of the form

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

where F(ρ) is another function of variable ρ.

Substituting this in equation (34), we get

$$F'' + \left\{\frac{2}{\rho} - 1\right\} F' + \left\{-\frac{l\,((l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{\rho}\right\} F = 0 \qquad \text{……………..59}$$

where $F' = \frac{dF}{d\rho}$ and $F'' = \frac{d^2F}{d\rho^2}$.

Let us now find a solution for F in the form

$$F(\rho) = \rho^{s}\ G(\rho),$$ …………………………60

where G(ρ) is a power series in ρ, beginning with a non-vanishing constant, i.e.,

$$G(\rho) = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots = \sum_{k=0}^{\infty} a_k\rho^k,\ a_0 \neq 0.$$

…….61

Differentiating equation (60), w.r. to ρ, we get

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

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

Substituting these values of F, F*’* and F*”* in equation (59), we get

$$\rho^{s+2}\ G'' + 2s\rho^{s+1}\ G' + s(s-1)\ \rho^{s} G + 2\rho^{s+1}\ G' + 2s\rho^{s} G - \rho^{s+2} G^2 + s\rho^{s+1}\ G \\ + (\lambda - 1)\rho^{s+1}\ G - l(l+1)\ \rho^{s} G = 0.$$

Dividing above equation by $\rho^s$and arranging the terms, we get

$$\rho^2 G'' + \rho\,[2(s+1) - \rho]\,G' + [\rho\ (\lambda - s - 1) + s(s+1) - l\ (l+1)]\,G = 0.$$

If ρ is set equal to zero in above equation, we get

$$\{s\,(s+1) - l\ (l+1)\}\ a_0 = 0$$ [using (61)]

$$s\,(s+1) - l\ (l+1) = 0$$

which yields $s = l \quad \text{or} \quad -(l+1).$

The boundary condition that R(ρ) be finite at $\rho = 0$ requires that s = *l* so that

$$\rho\, G'' + [2\ (l+1) - \rho]\ G' + (\lambda - l - 1)\ G = 0.$$ ………62

Differentiating equation (61) w.r. to ρ, we get

$$G = \sum_{k} a_k\,.\,k\,\rho^{k-1}$$

…………………63

and $$G'' = \sum_{k} a_k\,.\,k\ (k-1)\ \rho^{k-2}$$ …………………64

Substituting value of G, G' and G" from (61), (63) and (64) in equation (62), we get

$$\sum_k a_k\, k\,(k-1)\,\rho^{k-1} + \{2\,(l+1) - \rho\} \sum_k a_k\, k\,.\,\rho^{k-1} + (\lambda - l - 1) \sum_{k=0}^{\infty} a_k\, \rho^k = 0$$

If this equation is to be satisfied the coefficients of various powers of ρ must vanish separately.

$$a_{k+1}\, k\,(k+1) - a_k\, k + 2(l+1)\, a_{k+1}\,(k+1) + (\lambda - l - 1)\, a_k = 0$$

or $$a_{k+1}\,\{2l+2)\,(k+1) + k\,(k+1)\} + (\lambda - l - 1 - k)\, a_k = 0$$

or $$a_{k+1} = \frac{k + l + l - \lambda}{(k+1)\,(2l + k + 2)}\, a_k. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 65$$

This expression is called recursion formula. Here k is an integer or zero.

For any value of λ and *l* the series for F(ρ) consists of infinite number of terms and does not correspond to a satisfactory wave function; because value of the series as shown below, increases with increasing ρ and consequently with increasing r with the result that the function R(ρ), i.e., e- $\rho/2$ ρ^s G(ρ) increases without limit as ρ increases.

To prove this consider the series.

$$\rho^s e^\rho = e^s \left[1 + \rho + \frac{\rho^2}{2\,!} + \frac{\rho^3}{3\,!} + \ldots + \frac{\rho^k}{k\,!} + \frac{\rho^{k+1}}{(k+1)\,!} + \ldots \right]$$

so that $$\frac{a_{k+1}}{a_k} = \frac{k\,!}{(k+1)\,!} = \frac{1}{k+1}$$

If k is large k + 1, then

$$\lim_{k \to \infty} \frac{a_{k+1}}{a_k} \to \frac{1}{k}$$

Also from (65), we have

$$\lim_{k \to \infty} \frac{a_{k+1}}{a_k} \to \frac{1}{k}.$$

Thus the series for F(ρ) i.e. ρ^s G(ρ), for large values of ρ behaves like ρ^s e^ρ. If this is the case, the function R(ρ) for the large of ρ will behave like $e^{-\rho/2}\rho^s e^\rho = \rho^s e^{\rho/2}$: which approaches infinity as ρ approaches infinity : thus making the wave function physically unacceptable. Thus the series governed by the recursion formula (65) does not lead a satisfactory wave function unless some restriction some restriction is introduced which make the series break off finite number of terms.

Energy Eigen values for the hydrogen atom :

From the above discussion we have seen that in order to obtain a satisfactory wave function the series will break off after a finite number of terms. The series will break off after ρ^k if we see the nominator in the recursion formula (65) equal to zero, i.e.

$$k + l + 1 - \lambda = 0$$

or $$\lambda = k + l + 1 = n \text{ (say).} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.66$$

Here k is called the radial quantum number can have the values 1, 2, 3, ……, while n is called total quantum number and can have the values 1, 2, 3,….

$$\lambda^2 = \frac{\mu^2 Z^2 e^4}{\hbar^4 \alpha^2} = \frac{\mu^2 Z^2 e^4}{\hbar^4 \left(-\frac{2E\mu}{\hbar^2}\right)}$$

or $$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 \lambda^2}$$

so that $$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad \text{[using (66)]}$$

The equation gives the energy eigen values for hydrogen atom with Z = 1 and is agreement with the old quantum theory and experiment.

Radial wave function : Substituting λ = n in equation (62) we get

$$\rho G'' + \{2(l + 1) - \rho\} G' + (n - l - 1) G = 0. \qquad \ldots\ldots\ldots..67$$

Substituting $\left.\begin{array}{l} 2l + 1 = p \\ n + l = n' \end{array}\right\}$ and

$\left.\begin{array}{l} 2l + 1 = p \\ n + l = n' \end{array}\right\}$

in equation (67), we have

$$\rho G'' + \{p + 1 - \rho\} G' + (n' - p) G = 0.$$

The solution of this equation will be the associated Laguerre polynomial or more correctly the associated Laguerre polynomial multiplied by a constant factor i.e.

$$G(\rho) = CL_n^p\ (\rho)$$

$$= CL_{n+l}^{2l+1}\ (\rho)$$

where C is constant and may be made equal to the normalization factor

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

Thus the total wave function R(r) is given by

$$R_{nl}(r) = e^{-\rho/2}\ \rho^l\ G(\rho) = Ce^{-\rho/2}\ \rho^l\ L_{n+l}^{2n+l}\ (\rho). \qquad \text{…………..68}$$

The normalization condition, for the physically significant interval of zero to infinity is

$$\int_0^\infty R(r)\ R^*\ (r)\ r^2\ dr = 1. \qquad \text{……………….69}$$

Here the factor r^2 is necessary to convent the length the length dr into an element of volume.

We have

$$\rho = 2\alpha r = 2\,.\frac{\mu Ze^2}{\hbar^2\lambda}\ r = \frac{2\mu Ze^2}{\hbar^2 n}\ r$$

$$= \frac{2r}{n}\ \frac{\mu Ze^2}{\hbar^2}$$

$$= \frac{2Zr}{n}\cdot\frac{1}{a_0}, \qquad \text{……………………..70}$$

where $\frac{}{a_0} = \frac{\mu e^2}{\hbar^2}$, a_0 being Bohr's radius.

From (70)

$$r = \frac{na_0}{2Z}\ \rho$$

so that

$$dr = \frac{na_0}{2Z}\ d\rho$$

Substituting values of R(r), R*(r), r and dr in equation (69), we get

$$C^2 \int_0^\infty e^{-\rho} \rho^{2l} \left[L_{n+1}^{2l+1}(\rho)\right]^2 \left(\frac{na_0}{2Z}\rho\right)^2 \left(\frac{na_0}{2Z}\right) d\rho = 1$$

i.e.
$$C^2 \left(\frac{na_0}{2Z}\right)^2 \int_0^\infty e^{-\rho} \rho^{2l} \left[L_{n+l}^{2l+1}(\rho)\right] \rho^2 \, d\rho = 1$$

i.e.
$$C^2 \left(\frac{na_0}{2Z}\right)^3 \left[\frac{2n\,\{(n+l)\,!\}^3}{(n-l-1)\,!}\right] = 1$$

or
$$C = \sqrt{\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)\,!}{2n\,\{(n+l)\,!\}^3}\right]}$$

Substituting this value of C in (68), the radial wave function may be represented by

$$R_{nl}(r) = \sqrt{\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)\,!}{2n\,\{(n+l)\,!\}^3}\right]}\, e^{-Zr/na_0} \left(\frac{2Zr}{na_0}\right) L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

……………………71

The first radial functions, found from equn. (71), are

$$\left.\begin{aligned}
R_{10}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0} \\
R_{20}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/a_0} \\
R_{21}(r) &= \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0\sqrt{3}}\, e^{-Zr/a_0}
\end{aligned}\right\}$$

Complete wave function : The complete wave function or the normalized eigen functions for hydrogen like atoms are

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, \Theta_{ml}(\theta)\, \Phi_m(\phi)$$

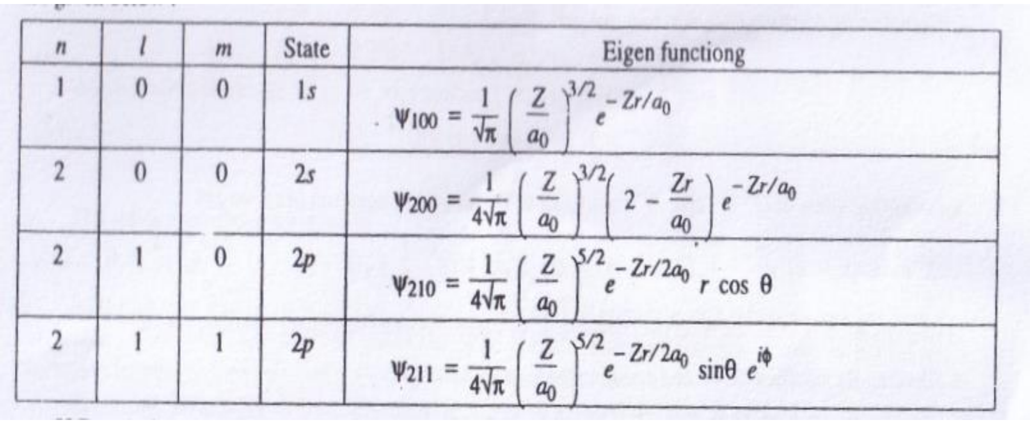
with
$$\Theta_{ml}(\theta) = \sqrt{\left(\frac{(2l+l)\,(l-|m|)\,!}{2\,(l+|m|)\,!}\right)}\, P_l^{|m|}(\cos\theta)$$

and

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

$$R_{nl}(r) = \sqrt{\left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} e^{-Zr/na_0} \left(\frac{2Zr}{na_0} \right) L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) \right.}$$

The real forms of the complete eigen function ψ_{nlm}. Exclusive of spin, for various values of n, *l* and m are given below :



n	l	m	State	Eigen functiong
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
2	0	0	2s	$\psi_{200} = \frac{1}{4\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/a_0}$
2	1	0	2p	$\psi_{210} = \frac{1}{4\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{5/2} e^{-Zr/2a_0} r \cos\theta$
2	1	1	2p	$\psi_{211} = \frac{1}{4\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{5/2} e^{-Zr/2a_0} \sin\theta\, e^{i\phi}$

If Z = 1, these wave function represent specifically the eigen function of hydrogen atom.

5.8 DEGENERACY

The energy eigen values given by equation (48) of section 3.5 depend only on n and hence are degenerate with respect to booty *l* and m. For each value of n, *l* can take value from o to n – 1 and for each or these *l* values, m can take values from – *l* to + *l*. Then the degeneracy of the energy level E_n is

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

The degeneracy with respect to m is the characteristic of the central force i.e. the force field depending only on the radial distance r, while the degeneracy with respect to *l*is characteristic of the Coulomb field. In the presence of some external field (such as a magnetic field) (2*l* + 1), fold m degeneracy disappears and the level is spited up into n^2 different energy levels.

The existence of the degenerate energy level means that the linear combinations of the corresponding eigen function are the solution of the wave equation with the same energy. For m degeneracy nth linear combination of the function $Y_{im}(\theta, \phi) = \Theta_{im}(\theta)\, \phi_m(\theta)$ can be found that correspond to new choice of the polar axis. In general the degeneracy will occur whenever the wave equation is solved in different co-ordinate systems; because in the absence of the degeneracy the wave functions obtained in different co-ordinate system would differ only by a multiplying constant, which is usually not possible. However, there occurs an exception in a general central field for *l* = 0 where the wave function is spherically symmetric and has the same form for all orientations of the polar axis : consequently these will be no degeneracy. A similar exception occurs for hydrogen atom when n = 1, where the solution obtained by spherical and parabolic separation of the wave equation are identical.

5.9 THE NORMAL STATE OF THE HYDROGEN ATOM

In the case of normal state of hydrogen atom (Z = 1, n = 1, *l* = 0, m = 0) the wave function takes the form

$$\psi_{100} = \frac{1}{\sqrt{(\pi a_0^3)}} e^{-r/a_0}$$

Then the probability distribution function of the electron relative to the nucleus is given by

$$\psi^*\psi = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

The probability that the electron will lie in the volume element

$$d\tau = r^2 \, dr \, \sin\theta \, d\theta \, d\phi$$

is given by

$$\psi^*\psi = \frac{1}{\pi a_0^3} e^{-2r/a_0} r^2 \, dr \, \sin\theta \, d\theta \, d\phi$$

The probability that the electron will lie between distance r and r + dr from the nucleus irrespective of its angular distribution is given by

$$\begin{aligned} P(r)\, dr &= \frac{1}{\pi a_0^3} e^{-2r/a_0} r^2 \, dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{\pi a_0^3} e^{-2r/a_0} r^2 \, dr \, [2] \times [2\pi] \\ &= \frac{4}{a_0^3} e^{-2r/a_0} r^2 \, dr. \end{aligned}$$

The radial distribution function P(r) dr is shown in fig. 3.4 together with ψ_{100} with $|\psi_{100}|^2$. The dotted curve represents the probability distribution function for a Bohr orbit

The most probable distance of the electron from the nucleus, i.e. the value of r at which P(r) is maximum may be obtained as follows :

For the most probable distance r, P(r) should be maximum,

i.e.,
$$\frac{d}{dr} P(r) = 0$$

or
$$\frac{d}{dr}\left(\frac{4}{a_0^3} r^2 e^{-2r/a_0} \right) = 0$$

which gives

$$r = a_0 = \text{Bohr's radius.}$$

Thus the most probable distance of the electron from the nucleus in the normal state of hydrogen atom is equal to the Bohr’s radius.

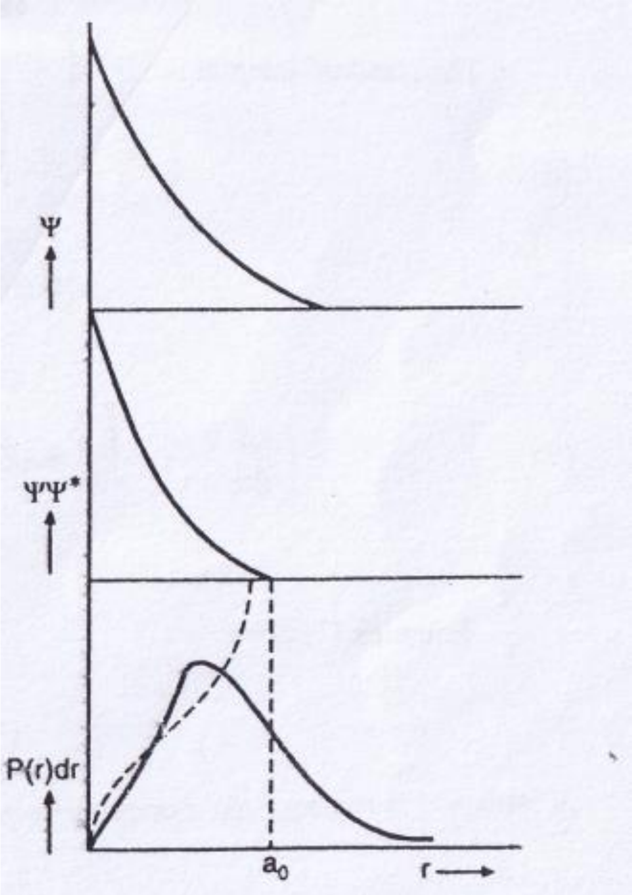


Figure:4

5.10 SUMMARY

In quantum mechanics description of a particle in spherical coordinates, a **spherically symmetric potential**, is a potential that depends only on the distance between the particle and a defined center point. In particular, if the particle in question is an electron and the potential is derived from Coulomb's law, then the problem can be used to describe a hydrogen-like (one-electron) atom (or ion).

In the general case, the dynamics of a particle in a spherically symmetric potential are governed by a Hamiltonian of the following form:

$$\hat{H} = \frac{\hat{p}^2}{2m_0} + V(r)$$

Where m_0 is the mass of the particle, $\hat{p}$ is the momentum operator, and the potential $V(r)$ depends only on r, the modulus of the radius vector **r**. The quantum mechanical wavefunctions and energies (eigenvalues) are found by solving the Schrödinger equation with this Hamiltonian. Due to the spherical symmetry of the system, it is natural to use spherical coordinates r, θ and ϕ. When this is done, the time-independent Schrödinger equation for the system is separable, allowing the angular problems to be dealt with easily, and leaving an ordinary differential equation in r to determine the energies for the particular potential $V(r)$ under discussion.

5.11 TERMINAL QUESTIONS

1. Obtain Schrödinger's equation for spherically symmetric potential in spherical co-ordinates.
2. Obtain Schrödinger's equation for spherically symmetric case of three-dimensional harmonic oscillator. Solve it obtain eigen functions and eigen values.
3. Obtain and solve the Schrödinger's equation for a rigid rotator with free size.
4. Solve Schrödinger's equation for the hydrogen atom and discuss the radial wave-function.
5. Obtain and solve the radial equation for the hydrogen atom. Calculate the most probable distance of the electron from the nucleus.5.

5.12 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 5.3
2. Section 5.4

3. Section 5.5
4. Section 5.7
5. Section 5.7

5.13 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

Uttar Pradesh Rajarshi Tandon
Open University

Bachelor of Science

DCEPHS-108

Quantum Mechanics And Spectroscopy

BLOCK

3

IDENTICAL PARTICLES AND PERTURBATION

UNIT-6

Identical Particles

UNIT-7

Approximation Methods

UNIT-8

Atomic Spectra

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ISBN :

Printed and Published by Vinay Kumar, Registrar, Uttar Pradesh Rajarshi Tandon Open University, 2023.

Printed By : Chandrakala Universal Pvt. 42/7 Jawahar Lal Neharu Road, Prayagraj.

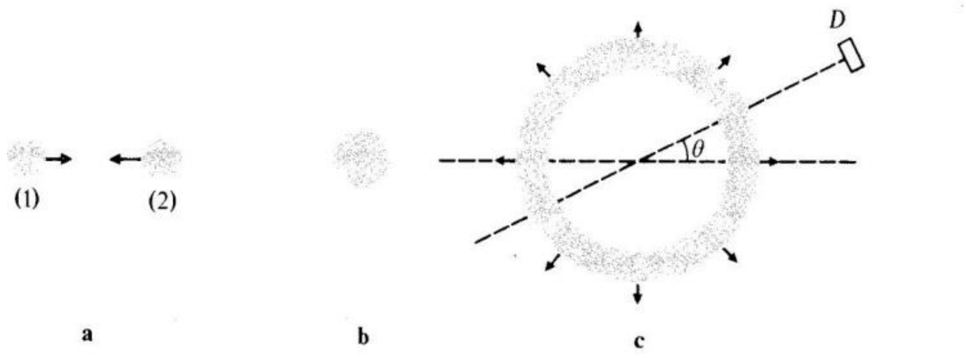
UNIT-6 IDENTICALS PARTICLES

Structure

6.1 INTRODUCTION

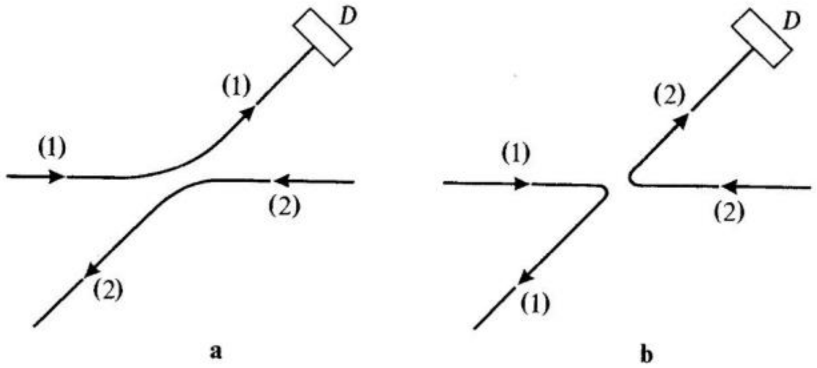
There are many systems in nature that are made of several particles of the same species. These particles all have the same mass, charge, and spin. For instance, the electrons in an atom are identical particles. Identical particles cannot be distinguished by measuring their properties. This is also true for classical particles. In classical mechanics we can always follow the trajectory of each individual particle, i.e., their time evolution in space. The trajectories identify each particle in classical mechanics, making identical particles distinguishable. In quantum mechanics the concept of trajectory does not exist and identical particles are indistinguishable

Two particles are said to be identical if all their intrinsic properties (mass, spin, charge, etc.) are exactly the same: no experiment can distinguish one from the other. Thus, all electrons in the universe are identical, as are all the protons and all the hydrogen atoms. Note that this definition is independent of the experimental conditions. Even if, in a given experiment, the charges of the particles are not measured, an electron and a positron can never be treated as identical particles. An important consequence can be deduced from this definition: when a physical system contains two identical particles, there is no change in its properties or its evolution if the roles of these two particles are exchanged. In classical mechanics, the presence of identical particles in a system poses no particular problems. Each particle moves along a well-defined trajectory, which enables us to distinguish it from the others and follow it throughout the evolution of the system. It is immediately apparent that the situation is radically different in quantum mechanics, since the particles no longer have definite trajectories, but rather are treated in a probabilistic manner. For example, in figure 2 two identical particles approach one another. When the two particles are still far away from each other, they are distinguishable due to their spatial separation: we can label them “1” and “2”. But when they interact with each other (when they collide), we lose track of which is which, so, looking at figure 3, we are not sure which particle hits the detector (labeled “D”). Nothing in the theory of quantum mechanics enables us to determine which particle hits the detector. The Symmetrization Postulate We add a new postulate to the theory of quantum mechanics to deal with this. Statement of the Postulate When a system includes several identical particles, only certain wavefunctions can describe its physical states. Physical wavefunctions are, depending of the nature of the indentical particles, either completely symmetric or completely antisymmetric with respect to permutation of these particles. Those particles for which the physical wavefunctions are symmetric are called bosons, and those for which they are antisymmetric, fermions. The symmetrization postulate thus limits the possible wavefunctions for a system of identical particles. From the point of view of this postulate, particles existing in nature are divided into two categories. All currently known particles obey the following empirical rule: particles of half-integral spin (electrons, positrons, protons, neutrons, muons, etc) are fermions, and particles of integral spin (photons, mesons, etc) are bosons. Once this rule has been verified for all the particles which are called “elementary”, it holds for all other particles as well, inasmuch as they are composed of these elementary particles. Consequently, nuclei whose mass number (the total number of nucleons) is even 2 are bosons, and those whose mass number is odd are fermions. Thus, the nucleus of the 3He isotope of helium is a fermion, and that of the 4He isotope, a boson. Predictions based on this principle, which are often spectacular, have always been confirmed experimentally.



Collision between two identical particles in the center of msss frame : Schematic representation of the probability density of the two particles.

Before the collision(fig. a), the two wave packets are clearly and can be labeled. During the collision (fig. b) the two packets overlap. After the collision (fig.c), the probability density is non-zero in a region shaped like a spherical shell whose radius increases over time. Because the two particles are identical, it is impossible, when a particle is detected at D, to know with which wave packet, (1) or (2), it was associated before the collision.



Schematic representation of two types of "paths" which the system could have followed in going from the initial state to the state found in the measurement. Because the two particles are identical, we cannont determine the path that was actually followed. Understand the concept of Assignment problem

6.2 OBJECTIVES

After studying this unit, student should able to:

- Know about Distinguishable and Indistinguishable Particles.
- Explain the concept of Spin.
- Discuss Pauli Spin Matrices.
- Define Exchange Operator
- Explain the Concept of Pauli Exclusion Principle

6.3 DISTINGUISHABLE AND INDISTINGUISHABLE PARTICLES

Distinguishable Particles:

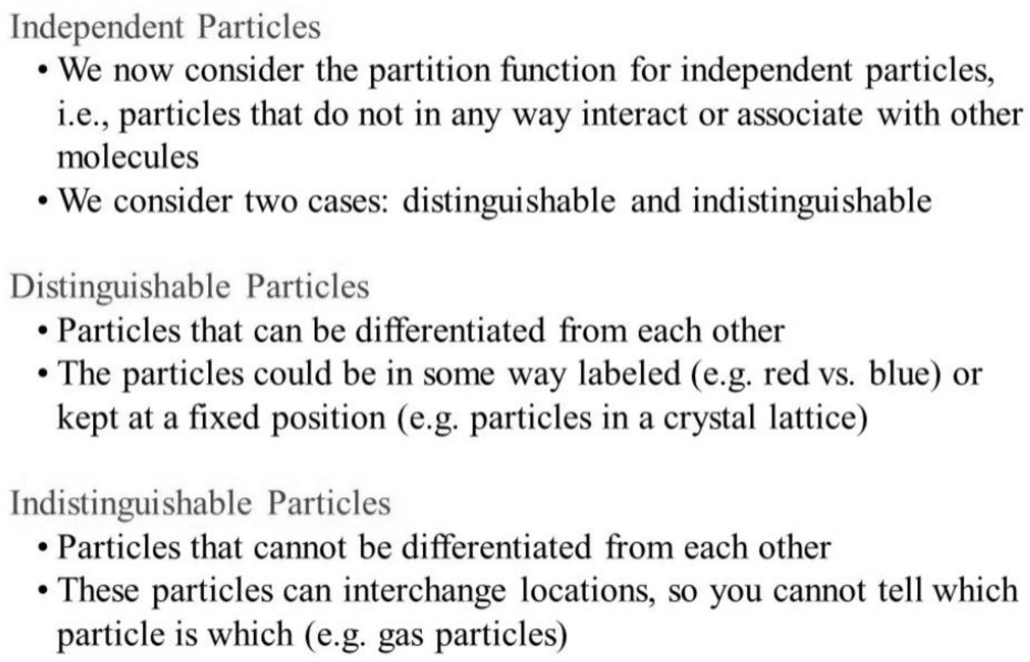
It is also known as classical particles. They follow classical statistics.

MB Statistics. Large distance and energy Barrier

Indistinguishable Particles:

It is also known as Quantum particles. They follow Quantum Statistics.

Small distance and Barrier.



Independent Particles

- We now consider the partition function for independent particles, i.e., particles that do not in any way interact or associate with other molecules
- We consider two cases: distinguishable and indistinguishable

Distinguishable Particles

- Particles that can be differentiated from each other
- The particles could be in some way labeled (e.g. red vs. blue) or kept at a fixed position (e.g. particles in a crystal lattice)

Indistinguishable Particles

- Particles that cannot be differentiated from each other
- These particles can interchange locations, so you cannot tell which particle is which (e.g. gas particles)

6.4 SYMMETRIC AND ANTI-SYMMETRIC WAVE FUNCTION

Let us consider a system of n identical indistinguishable particles. The wave function of the system consisting of n particles is Ψ(1,2,3,4……….n, t). The Schrödinger equation for the above system of particles is written as

$$\hat{H}(1,2,3\ldots\ldots\ldots\ldots\ldots n)\,\Psi(1,2,3\ldots\ldots\ldots\ldots n,\,t) = i\hbar\frac{\partial}{\partial t}\,\Psi(1,2,3\ldots\ldots\ldots\ldots\ldots,\,t)$$

where each of the numbers represents all the position and spin coordinates of one of the particles. As the particles are identical, Hamiltonian $\hat{H}$ of the system is symmetrical in its arguments. Two types of solutions of equation (1) are possible for the wave function of Ψ; namely

(i) Symmetric wave function Ψ_S)

(ii) anti-symmetric wave function. (Ψ_A)

Symmetric wave function (ΨS): A wave function is said to be symmetric if the interchange between any pair of particles among its arguments do not change the sign of the wave function.

Anti-symmetric wave function (ΨA): A wave function is said to be anti-symmetric if the interchange between any pair of particles among its arguments change the sign of the wave function. This may be seen as follows:

Let $\Psi_S = \Psi(1,2) + \Psi(2,1)$ and $\Psi_A = \Psi(1,2) - \Psi(2,1)$.

Therefore

$$\hat{P}_{12}\,\Psi_S = \hat{P}_{12}\,[\Psi(1,2) + \Psi(2,1)] = \hat{P}_{12}\,\Psi(1,2) + \hat{P}_{12}\Psi(2,1$$

$$= \Psi(2,1) + \Psi(1,2) = \Psi(1,2) + \Psi(2,1) = \Psi_S$$

$$\text{Or, } \hat{P}_{12}\,\Psi_S = \Psi_S$$

Similarly

$$\hat{P}_{12}\,\Psi_A = \hat{P}_{12}\,[\Psi(1,2) - \Psi(2,1)] = \hat{P}_{12}\,\Psi(1,2) - \hat{P}_{12}\Psi(2,1$$

$$= \Psi(2,1) - \Psi(1,2) = -\,[\Psi(1,2) - \Psi(2,1)] = -\,\Psi_A$$

$$\text{Or, } \hat{P}_{12}\,\Psi_A = -\,\Psi_A$$

If we apply such an interchange operator ($\hat{P}_{12}$) twice on the wave function of the system consisting two particles, brings back to their original configuration and hence produces no change in the wave function.

Commutation relation of $\hat{P}_{12}$ with $\hat{H}$:

We know that

$$\hat{P}_{12}\,\Psi(1,2) = \Psi(2,1)$$

$$\text{Therefore } \hat{P}_{12}\,\hat{H}(1,2)\,\Psi(1,2) = \hat{H}(2,1)\,\Psi(2,1) = \hat{H}(1,2)\,\Psi(2,1) \qquad \text{As } \hat{H}(1,2) = \hat{H}(2,1)$$

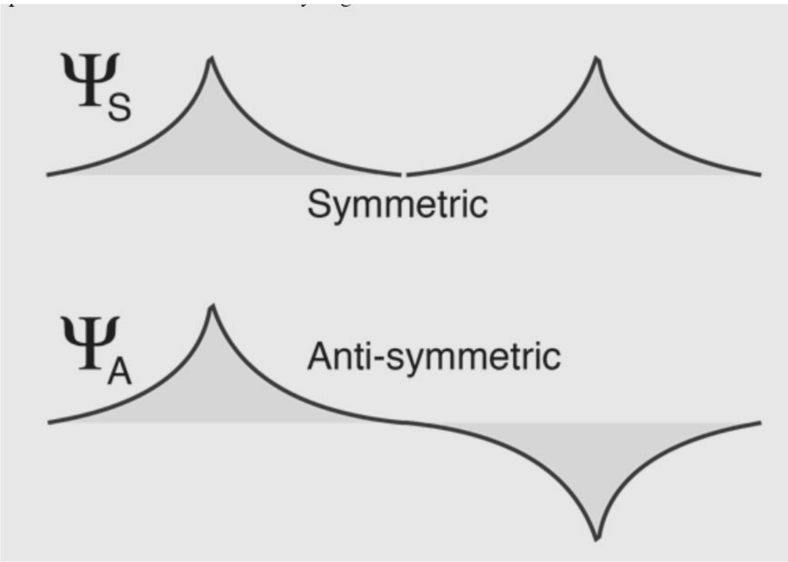
$$= \hat{H}(1,2)\,\hat{P}_{12}\,\Psi(1,2)$$

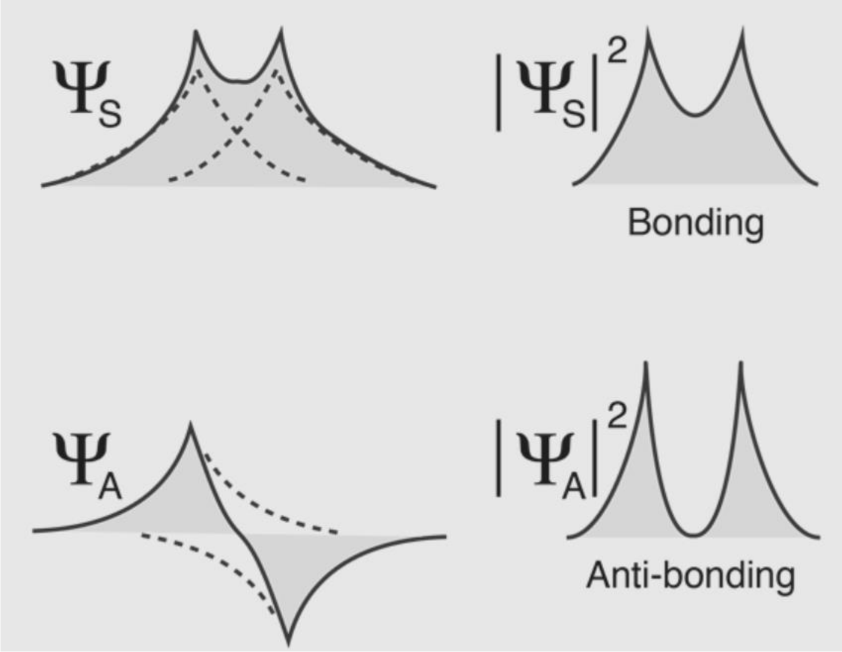
$$\text{Or } [\hat{P}_{12}\,\hat{H}(1,2) - \hat{H}(1,2)\,\hat{P}_{12}]\,\Psi(1,2) = 0$$

$$\text{Or } [\hat{P}_{12}\,\hat{H}(1,2) - \hat{H}(1,2)\,\hat{P}_{12}] = 0$$

$$\text{Or } [\hat{P}_{12}\,,\hat{H}(1,2)] = 0$$

Thus the particle exchange operator commutes with the Hamiltonian of the system.





6.5 CONCEPT OF SPIN

S.A. Goudsmit and **G.E. Uhlenbeck**, in 1925, recommended that an electron has an inherent angular momentum that is a magnetic moment that is recognized as **spin**. In atomic physics, the inherent angular momentum of a particular particle is parametrized by spin quantum numbers. The spin quantum number is the fourth number. The rest three are a principal quantum number, azimuthal, and magnetic quantum number. The spin quantum number explains the unique quantum state of an electron. This is nominated as ‘s’.

The spins play a noteworthy role in quantum mechanics in computing the characteristics of elementary units like electrons. The spin direction of the particle regulates several things like the spin quantum number, angular momentum, the degree of freedom, etc.

What is Electron Spin?

The electron spin is one of the three inherent properties of the electrons; the others are the mass and charge of the electron. The electron spin is described as the electron spinning around its axis.

It is articulated as:

$$\|S\| = \sqrt{s(s+1)h}$$

Where,

- **s** is equivalent to a quantized spin vector.
- The spin vector is articulated as **||s||.**
- The spin quantum number **(s)** is associated with the spin angular momentum and h is Planck's constant.

The spin quantum number can be articulated as:

$$S = \frac{n}{2}$$

Any non-negative integer can be n.

The permitted values of the spins are 0, 1/2, 1, 3/2, 2, etc.

The intrinsic angular momentum of the Electron is signified by quantum number 1/2

The total angular momentum **s** is articulated by:

$$s = \sqrt{n(n+1)h}$$
$$s = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)h}$$

$$S = \sqrt{\frac{3}{4}\bar{h}}$$

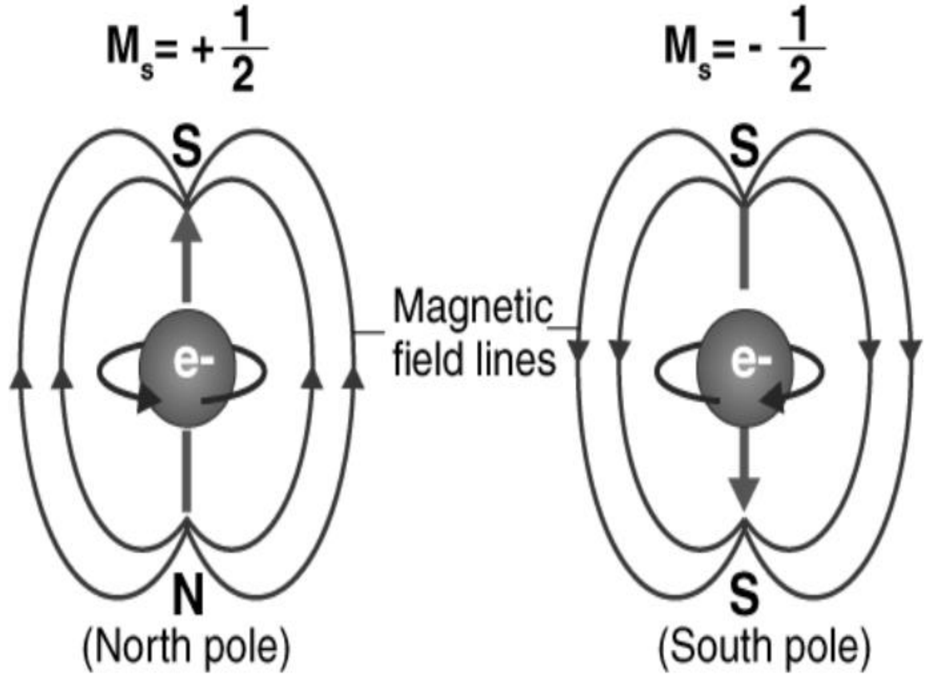
Where,
the reduced Planck's constant is *ħ*

ħ = h/2π.

Electron Spin Theory

As in classical theory, the electron spin theory describes the electron as a quantum particle instead of a simple sphere.

The theory says that "the electron spin direction and its influence on certain properties like the atom's magnetic properties".



The electron can spin in two directions:

1. Spin up
2. Spin down

The spin up and spin down directions correspond to the spinning in the **"+z"** or **"–z" direction**. These spins **(spin up and spin down)** are the particles that have spin "**s**" equal to 1/2, i.e. for electrons.

In quantum theory, the electron is thought of as the minute magnetic bar, and its spin points to the north pole of the minute bar. If two proximate electrons have a similar spin direction, the magnetic field formed by them strengthens each other, and therefore a strong magnetic field is gained. If the proximate electrons have an opposite spin direction, the magnetic field formed by them cancels each other, and no magnetic field is existent.

6.6 PAULI SPIN MATRICES

The **Pauli spin matrices** (named after physicist Wolfgang Ernst Pauli) are a set of unitary Hermitian matrices which form an orthogonal basis (along with the identity matrix) for the real Hilbert space of 2 × 2 Hermitian matrices and for the complex Hilbert spaces of all 2 × 2 matrices. They are usually denoted:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Algebraic properties

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I$$

For $i = 1, 2, 3$:

$$\det(\sigma_i) = -1$$
$$\mathrm{Tr}(\sigma_i) = 0$$
$$\text{eigenvalues} = \pm 1$$

Commutation relations

$$\sigma_1\sigma_2 = i\sigma_3$$
$$\sigma_3\sigma_1 = i\sigma_2$$
$$\sigma_2\sigma_3 = i\sigma_1$$
$$\sigma_i\sigma_j = -\sigma_j\sigma_i \text{ for } i \neq j$$

The Pauli matrices obey the following commutation and anticommutation relations:

$$[\sigma_i, \sigma_j] = 2i\,\varepsilon_{ijk}\,\sigma_k$$
$$\{\sigma_i, \sigma_j\} = 2\delta_{ij} \cdot I$$

where ε_{ijk} is the Levi-Civita symbol, δ_{ij} is the Kronecker delta, and I is the identity matrix.

The above two relations can be summarized as:

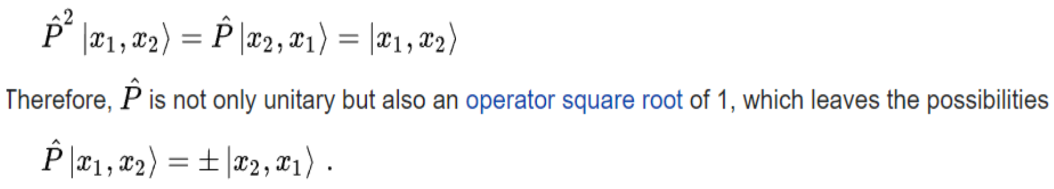
$$\sigma_i\sigma_j = \delta_{ij} \cdot I + i\varepsilon_{ijk}\sigma_k.$$

6.7 EXCHANGE OPERATOR

In quantum mechanics, the exchange operator $\hat{P}$, also known as permutation operator, is a quantum mechanical operator that acts on states in Fock space. The exchange operator acts by switching the labels on any two identical particles described by the joint position quantum state $|x_1, x_2\rangle$.

Since the particles are identical, the notion of exchange symmetry requires that the exchange operator be unitary.

In three or higher dimensions, the exchange operator can represent a literal exchange of the positions of the pair of particles by motion of the particles in an adiabatic process, with all other particles held fixed. Such motion is often not carried out in practice. Rather, the operation is treated as a "what if" similar to a parity inversion or time reversal operation. Consider two repeated operations of such a particle exchange:



$$\hat{P}^2 |x_1, x_2\rangle = \hat{P} |x_2, x_1\rangle = |x_1, x_2\rangle$$

Therefore, $\hat{P}$ is not only unitary but also an operator square root of 1, which leaves the possibilities

$$\hat{P} |x_1, x_2\rangle = \pm |x_2, x_1\rangle \ .$$

Both signs are realized in nature. Particles satisfying the case of +1 are called *bosons*, and particles satisfying the case of −1 are called *fermions*. The spin–statistics theorem dictates that all particles with integer spin are bosons whereas all particles with half-integer spin are fermions.

6.8 PAULI EXCLUSION PRINCIPLE

Pauli's Exclusion principle is one of the important principles along with Aufbau's Principle and Hund's Rule in chemistry. Learning about it is crucial for students especially when they are studying about electrons. Pauli's Exclusion principle basically helps us to understand the electron arrangements in atoms and molecules and it also gives an explanation for the classification of elements in the periodic table. In this section, we shall study the Pauli exclusion principle in detail and learn about all the underlying concepts.

What is Pauli Exclusion Principle?

The Pauli exclusion principle states that in a single atom no two electrons will have an identical set or the same quantum numbers (n, l, m_l, and m_s). To put it in simple terms, every electron should have or be in its own unique state (singlet state). There are two salient rules that the Pauli Exclusion Principle follows:

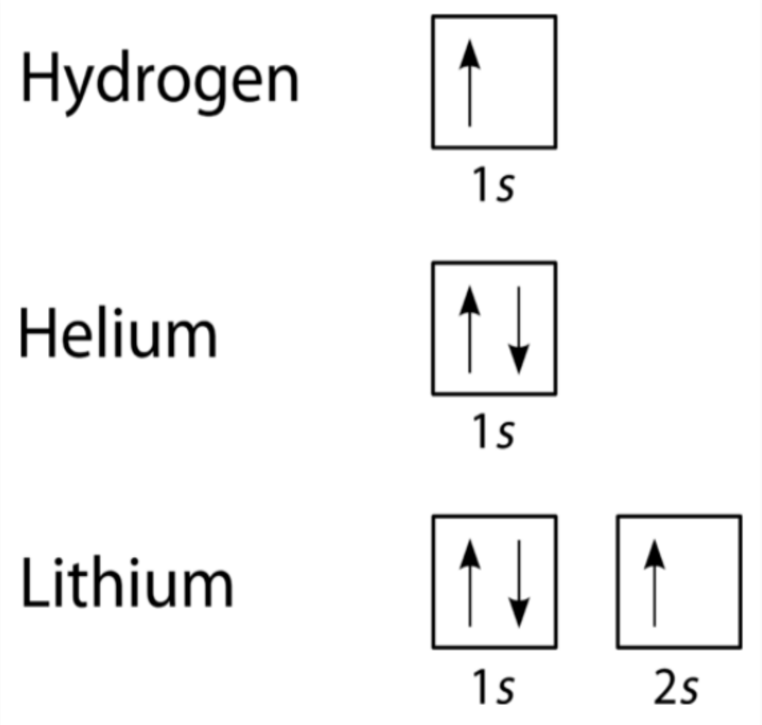
- Only two electrons can occupy the same orbital.
- The two electrons that are present in the same orbital must have opposite spins or they should be antiparallel.

However, Pauli's Exclusion Principle does not only apply to electrons. It applies to other particles of half-integer spin such as fermions. It is not relevant for particles with an integer spin such as bosons which have symmetric wave functions. Moreover, bosons can share or have the same quantum states, unlike fermions. As far as the nomenclature goes, fermions are named after the Fermi–Dirac statistical distribution that they follow. Bosons, on the other hand, get their name from the Bose-Einstein distribution function.

Formulation of the Principle

An Austrian physicist named Wolfgang Pauli formulated the principle in the year 1925. With this principle, he basically described the behaviour of the electrons. Later in the year 1940, he expanded on the principle to cover all fermions under his spin-statistics theorem. Meanwhile, fermions that are described by the principle include elementary particles such as quarks, electrons, neutrinos, and baryons.

Wolfgang Pauli was also awarded the Nobel prize in the year 1945 for the discovery of the Pauli Exclusion principle and his overall contribution to the field of quantum mechanics. He was even nominated by Albert Einstein for the award.



Formulation of the Pauli Exclusion Principle

Nuclear Stability and Pauli Exclusion Principle

The nuclei in an atom consist of neutrons and protons which are held together by the nuclear force. However, protons tend to repel each other via electromagnetic force as a result of their positive charge. Basically, these two forces are working against (competing) each other thereby leading to the stability of nuclei. Meanwhile, you will find only certain sets or combinations of protons and neutrons that form stable nuclei. The nucleus is mostly stabilized by the neutrons as attract each other and protons. This further helps counterbalance the electrical repulsion between protons. When this happens, the number of protons goes up. In essence, an increasing ratio of neutrons to protons is needed to form a stable nucleus.

In case if there are a larger number of (neutrons also obey the Pauli exclusion principle) or too few neutrons for a given number of protons, the nucleus of the atom is not stable. This will lead to radioactive decay. Meanwhile, Pauli's exclusion principle also has an effect on the critical energy of fissile and fissionable nuclei. For example, if we look at actinides that have an odd neutron number they are usually fissile or in other words fissionable with slow neutrons. On the other hand, actinides that have even neutron number they are usually not fissile or we can say that are fissionable with fast neutrons. Similarly, due to the Pauli exclusion principle, heavy nuclei with an even number of protons and neutrons are very stable due to the presence of 'paired spin'. Alternatively, nuclei with an odd number are unstable.

Importance And Applications of Pauli Exclusion Principle

- The Pauli exclusion principle helps to explain a wide variety of physical phenomena such as the electron shell structure of atoms and the way atoms share electrons.
- It helps in describing the various chemical elements and how they participate in forming chemical bonds.
- The periodic table can also be defined with the help of this principle.
- Solid-state Properties: Many electrical, optical, magnetic, mechanical and chemical properties of solids are the direct consequence of Pauli exclusion.
- The principle helps in describing the stability of large systems with many electrons and many nucleons.
- Apart from chemistry, the principle is a fundamental principle in quantum mechanics which is mainly studied in physics.
- It is also used in astrophysis

6.9 SUMMARY

The four sets of quantum numbers are:

Principal quantum number (n) – Signifies the size of the atomic orbital

Azimuthal quantum number (l) – signifies the shape of the atomic orbital

Magnetic quantum number (ml) – signifies the orientation of atomic orbitals in space.

Spin quantum number (ms) – signifies the electron’s spin in the atomic orbital.

1. Electrons are part of subatomic particles called fermions.
2. Fermions are particles with half-integer spin.
3. All fermions including neutrons and protons (derived particles) obey the Pauli exclusion principle.
4. Pauli exclusion principle states that no two identical electrons (fermions) can have the same quantum state.
5. Bosons, which have integer values of spin do not obey the Pauli exclusion principle. Photons, gravitons, gluons are an example of bosons.

6.10 TERMINAL QUESTIONS

1. Explain Distinguishable and Indistinguishable Particles.
2. Expalin Symmetric and Anti-symmetric Wave Function.
3. Discuss Pauli Exclusion Principle.

6.11 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 6.3
2. Section 6.4
3. Section 6.8

6.12 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

UNIT-7 APPROXIMATION METHODS

Structure

7.1 INTRODUCTION

There are three major approximation schemes: perturbation theory, variational methods and WKB approximation. Our interest is primarily in obtaining bound state energy and eigenstates. In perturbation theory, we deal with systems whose Hamiltonians are slightly different from systems which can be exactly solved. There are two distinct cases depending on whether the solution of the solvable Hamiltonian has degenerate eigenvalues. We will first consider the case where the exactly solvable problem has non-degenerate eigenvalues. Examples of systems where we employ non-degenerate perturbation theory are free particles in weak electric or magnetic field. The formalism is also known as Rayleigh Schrödinger perturbation theory

7.2 OBJECTIVES

After studying this unit, student should able to:

- Know about Perturbation Theory
- Discuss about Time Independent Perturbation Theory
- Explain the concept of Variation Method.
- Discuss about Time Dependent Perturbation Theory

7.3 STATIONARY PERTURBATION THEORY (NON-DEGENERATE CASE)

The stationary perturbation theory is concerned with finding the changes in the energy levels and eigen functions of a system when a shall disturbance is applied. In such cases, the Hamiltonian can be broken up into two parts, one of which is large and represents a system for which the Schroedinger equation can be solved exactly, while other part is small and can be treated as perturbation term. If the potential energy is disturbed by the influence of additional forces, the energy levels are shifted and for a weak perturbation, the amount of shift can be estimated if the original unperturbed states are known.

Consider a physical system subjected to a perturbation which shifts the energy levels slightly : of course the arrangement remains this same : Mathematically the effect of perturbation is to introduce additional terms in the Hamiltonian of the unperturbed system (or unchanged system). This additional term may be constant or it may be a function of both the space and momentum co-ordinates.

In other words, the Hamiltonian H in the Schroedinger equation can be written as the sum of two parts ; one of these parts H^0 corresponds to unperturbed system and other part H' corresponds to perturbation effect. Let us write Schroedinger wave equation

$$\hat{H}\,\psi = E\,\psi, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

in which Hamiltonian $\hat{H}$ represents the operator

$$\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 + V.$$

Let E be the eigen value and ψ is eigen function of operator $\hat{H}$. $\hat{H}$ is the sum of two H^0 and H' already defined

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

where H' is small perturbation term.

Let ψ_k^0 and E_k^0. be a particular orthonormal eigen function eigen value of unperturbed Hamiltonian H^0, i.e.,

$$H^0\,\psi_k^0 = E_k^0\,\psi_k^0$$

If we consider non-degenerate system that is the system for which there is one eigen function corresponding to each eigen value. In the stationary system, the Hamiltonian H does not depend upon time and it is possible to expand H in terms of some parameter λ yielding the expression

$$H = H^0 + \lambda H' + \lambda^2 H'' + \ldots$$

in which λ has been chosen in such a way that equation (1) for λ = 0 reduces to the form

$$H^0 \psi^0 - E^0 \psi^0 = 0 \qquad \text{...............................2}$$

It is to be remembered that there is one eigen function ψ and energy level E^0 corresponding to operator H^0. Equation (2) can be directly solved. This equation is said to be the “wave equation of unperturbed system” while the terms $\lambda H' + \lambda^2 H'' + \cdots$ are called the perturbation terms.

The unperturbed equation (2) has solutions

$$\psi_0^0, \psi_1^0, \psi_2^0, \ldots, \psi_k^0, \ldots$$

called the unperturbed eigen function and corresponding eigen values are

$$E_0^0, E_1^0; E_2^0, \ldots, E_k^0, \ldots$$

The function ψ_k^0 forma complete orthonormal set, i.e., they satisfy the condition

$$\int \psi_i^{0*} \psi_j^0 \, d\tau = \delta_{ij} \qquad \text{.................................3}$$

where δ_{ij} is Kronecker delta symbol defined as

$$\begin{aligned} \delta_{ij} &= 0 \text{ for } i \neq j \\ &= 1 \text{ for } i = j \end{aligned}$$

Now let us consider the effect of perturbation. The application of perturbation doe not cause large changes : hence the energy values and wave function for the perturbed system will be near to those for the unperturbed system. We can expand the energy E and the wave function ψ for the perturbed system in terms of λ, so

$$\psi_k = \psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + , \qquad \text{..............................4}$$

$$E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots \qquad \text{..............................5}$$

If the perturbation is small, then terms of the series (4) and (5) will become rapidly smaller i.e., the series will be convergent.

Now substituting (3), (4) and (5) in equation (1), we get

$$= (H^0 + \lambda H' + \lambda^2 H'' + \ldots)(\psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots) = (E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots)(\psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots)$$

On collecting the coefficients of like power of λ.

$$(H_0 \psi_k^0 - E_k^0 \psi_k) + (H^0 \psi_k' + H' \psi_k^0 - E_k^0 \psi_k' - E_k' \psi_k^0)\lambda + (H^0 \psi_k'' + H' \psi_k' + H'' \psi_k^0 - E_k^0 \psi_k'' - E_k' \psi_k' - E_k'' \psi_k^0)\lambda^2 + \ldots = 0.$$

If this series is properly convergent i.e., equal to zero for all possible values of λ, then coefficients of various powers of λ must vanish separately. This equation will have successively higher orders of the perturbation. The coefficient of λ^0 gives

$$(H^0 - E_k^0)\,\psi_k^0 = 0$$

……………………6a

The coefficient of λ gives the equation

$$(H^0\,\psi_k' + H'\,\psi_k^0 - E_k^0\,\psi_k' - E_k'\,\psi_k^0) = 0$$

or $$(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0$$ ……………6b

The coefficient of λ^2 gives the equation

$$(H^0\,\psi_k'' + H'\,\psi_k' + \psi_k' + H''\,\psi_k^0 - E_k^0\,\psi_k'' - E_k'\,\psi_k' - E_k''\,\psi_k^0) = 0$$

$$(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' + (H'' - E_k'')\,\psi_k^0 = 0$$

……………………..6c

Similarly, the coefficient of λ^3 yield

$$(H^0 - E_k^0)\,\psi_k''' + (H' - E_k')\,\psi_k'' + (H'' - E_k'')\,\psi_k' + (H''' - E_k''')\,\psi_k^0 = 0$$

………………6d

But is we limit the total Hamiltonian H upto $\lambda\,H'$, i.e., if we put $H = H^0 + \lambda\,H'$, then equations (7) will be modified as

$$\left.\begin{array}{ll} (H^0 - E_k^0)\,\psi_k^0 = 0 & \ldots(a) \\ (H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0 & \ldots(b) \\ (H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' - E_k''\,\psi_k^0 = 0 & \ldots(c) \\ (H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k'' - E_k''\,\psi_k' - E_k'''\,\psi_k^0 = 0 & \ldots(d) \end{array}\right]$$

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First order perturbation : Equation (7b) is

$$(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0$$

To solve this equation we use expansion theorem. As perturbation is very small, the deviations form unperturbed state are small, therefore the first order perturbation correction function ψ_k' can be expanded in terms of unperturbed functions $\psi_1^0, + \psi_2^0, \dots, \psi_1^0, \dots$., since ψ_1^0 form a normalized orthonormal set.

Hence we write

$$\psi_k' = \sum_{l=0}^{\infty} a_l\,\psi_l^0.$$

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Substituting ψ_k' from (8) in (7b), we get

$$(H^0 - E_k^0) \sum_l a_l \psi_l^0 + (H' - E_k') \psi_k^0 = 0$$

i.e.

$$\sum_l a_l H^0 \psi_l^0 - E_k^0 \sum_l a_l \psi_l^0 + (H' - E_k') \psi_k^0 = 0.$$

Using $H^0\psi^0 = E^0\,\psi^0$, we get

$$\sum_l a_l E_l^0 \psi_l^0 - E_k^0 \sum_l a_l \psi_l^0 + (H' - E_k') \psi_k^0 = 0.$$

$$\sum_l a_l (E_l^0 - E_k^0) \psi_k^0 = (E_k' - H') \psi_k^0$$

Multiplying above equation by ψ_m^{0*} and integrating over configuration space, we get

$$\sum_i a_l (E_l^0 - E_k^0) \int \psi_m^{0*} \psi_l^0 \, d\tau = \int \psi_m^{0*} (E_k' - H') \psi_k^0 \, d\tau$$

Using the condition of orthonormalization of $\psi_0{}'s$,

i.e.

$$\int \psi_i^{0*} \psi_j^0 \, d\tau = \delta_{ij} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

we get

$$\sum_i a_l (E_l^0 - E_k^0) \delta_{ml} = \int \psi_m^{0*} E_k' \psi_k^0 \, d\tau - \int \psi_m^{0*} H' \psi_k^0 \, d\tau$$

$$= E_k' \delta_{mk} - \int \psi_m^{0*} H' \psi_k^0 \, d\tau$$

Using the notations

$$\int \psi_m^{0*} H' \psi_k^0 \, d\tau = \langle m \mid H' \mid k \rangle.$$

we get

$$\sum_i a_l (E_l^0 - E_k^0) \delta_{ml} = E_k' \delta_{mk} - \langle m \mid H' \mid k \rangle. \qquad \ldots\ldots\ldots\ldots 9$$

Evaluation of first order energy E_k': Setting m = k in eqn. (9), we observe that

$$\sum_i a_l (E_l^0 - E_k^0) \delta_{kl} = 0 \text{ always.}$$

$$0 = E_k' - < km \mid H' \mid k >,$$

or $$E_k' = < k \mid H' \mid k > = \int \Psi_k^{0*} \, H' \, \Psi_k^0 \, d\tau.$$

This expression gives first order perturbation energy correction. Accordingly the "first order perturbation energy correction for a non-degenerate system is just the expectation value of first order perturbed Hamiltonian (H') over the unperturbed state of the system".

Evaluation of first order correction to wave function:

Equation (9) may be expressed as

$$a_m \, (E_m^0 - E_k^0) = E_k' \, \delta_{mk} - < m \mid H' \mid k >$$
$$\text{Since } \delta_{ml} \begin{cases} = 0 \text{ for } l \neq m \\ = 1 \text{ for } l = m \end{cases} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 10$$

For m ≠ k, equation (10) gives

$$a_m \, (E_m^0 - E_k^0) = - < m \mid H' \mid k >$$
$$a_m = - \frac{< m \mid H' \mid k >}{E_m^0 - E_k^0} = \frac{< m \mid H' \mid k >}{E_k^0 - E_m^0}$$

or

Setting $$m = l, \; a_l = \frac{< l \mid H' \mid k >}{E_k^0 - E_l^0}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots 11$$

If we retain only first order correction terms, then

$$\left. \begin{aligned} E_k &= E_k^0 + \lambda E_k' \quad \ldots(a) \\ \psi_k &= \psi_k^0 + \lambda \psi_k' \quad \ldots(b) \end{aligned} \right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 12$$

∴ Keeping in view equation (8) and (11), we get from (12b),

$$\psi_k = \psi_k^0 + \lambda \sum_l{}' \frac{< l \mid H' \mid k >}{E_k^0 - E_l^0} \, \psi_l^0 + \lambda \, a_k \, \psi_k^0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 13$$

where prime (or dash) on summation indicates that the term *l* = m has been omitted from the summation (or it reminds that *l* ≠ k).

The value of constant a_k may be evaluated by requiring that ψ_k is normalized, i.e.,

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

Substituting ψ_k from (13) and retaining only first order terms in λ we get

$$\int \psi_k^{0*}\,\psi_k^0\,d\tau + \lambda a_k \int \psi_k^{0*}\,\psi_k^0\,d\tau + \lambda a_k^* \int \psi_k^{0*}\,\psi_k^0\,d\tau + \lambda {\sum_l}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\delta_{lk} + \lambda {\sum_l}' \frac{[<l\,|\,H'\,|\,k>]^*}{E_k^0 - E_l^0}\,\delta_{lk} = 1$$

or $$\lambda a_k + \lambda a_k^* = 0 \quad i.e.\ a_k + a_k^* = 0$$

This equation indicates that the real part of a_k is zero and still it leaves an arbitrary choice for the imaginary part.

Let us take $a_k = i\,y$.

The wave function ψ_k can then be expressed as

$$\psi_k = \psi_k^0 + \lambda i \gamma \psi_k^0 + \lambda {\sum_l}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\psi_l^0$$
$$= \psi_k^0\,(1 + i\lambda\gamma) + \lambda {\sum_l}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 \qquad \text{…………………14}$$

The term containing y merely gives a phase shift in the unperturbed function ψ_k^0 and for normalization, this shift can be put equal to zero, so that equation (14) gives.

$$\psi_k = \psi_k^0 + \lambda \sum_l \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\psi_l^0$$

The arbitrary λ can be put equal to 1 and it may be included in symbols, i.e. λ H'→ H' ; then eigen values and eigen functions of the system upto first order perturbation correction terms are expressible as

$$\left.\begin{aligned} E_k &= E_k^0 + <k\,|H'\,|\,k> && \text{...}(a) \\ \text{and} \quad \psi_k &= \psi_k^0 + {\sum_l}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 && \text{...}(b) \end{aligned}\right\}$$

Second Order Perturbation : The second order perturbation equation (7c) is

$$(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' - E_k''\,\psi_k^0 = 0$$

Expanding second order wave functions ψ_k'' as a linear combination of unperturbed orthonormal wave functions ψ_m^0 by expansion theorem, i.e.,

$$\psi_k'' = \sum_m b_m\,\psi_m^0$$

Substituting $\psi_k' = {\sum_l}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\psi_l^0$; $\psi_k'' = \sum_m b_m\,\psi_m^0$

and $E_k' = <k\,|\,H'\,|\,k>$ in (11c); we get

$$(H^0 - E_k^0) \sum_m b_m\,\psi_m^0 + (H' - <k\,|\,H'\,|\,k>) {\sum_l}' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 - E_k''\,\psi_k^0 = 0$$

or $$\sum_m b_m\,H^0\,\psi_m^0 - E_k^0 \sum_m b_m\,\psi_m^0 + (H' - <k\,|H'|\,k>) {\sum_l}' \frac{<l\,|H'|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 - E_k''\,\psi_k^0 = 0$$

Using unperturbed Schroedinger equation

$H^0 \psi_m^0 = E_m^0 \psi_m^0$, we get

$$\sum_m b_m E_m^0 \psi_m^0 - E_k^0 \sum_m b_m \psi_m^0 + (H' - \langle k | H' | k \rangle) \sum_l{}' \frac{\langle l | H' | k \rangle}{E_k^0 - E_l^0} \psi_l^0 - E_k'' \psi_k^0 = 0$$

or $$\sum_m b_m (E_m^0 - E_k^0) \psi_m^0 + (H' - \langle k | H' | k \rangle) \Sigma' \frac{\langle l | H' | k \rangle}{E_k^0 - E_l^0} \psi_l^0 - E_k'' \psi_k^0 = 0$$

Multiplying by ψ_n^0 and integrating over all space, we get

$$\sum_m b_m (E_m^0 - E_k^0) \int \psi_n^{0*} \psi_m^0 \, d\tau + \int \psi_n^{0*} (H' - \langle k | H' | k \rangle) \Sigma' \frac{\langle l | H' | k \rangle}{E_k^0 - E_l^0} \psi_l^0 \, d\tau - E_k'' \int \psi_n^{0*} \psi_k^0 \, d\tau = 0$$

Using orthonormal property of unperturbed wave function ψ^0's, we get

$$\sum_m b_m (E_m^0 - E_k^0) \delta_{km} + \sum_l{}' \frac{\langle l | H' | k \rangle \langle k | H' | l \rangle}{E_k^0 - E_l^0} - \sum_l{}' \frac{\langle k | H' | k \rangle \langle l | H' | k \rangle}{E_k^0 - E_l^0} \delta_{kl} - E_k'' \delta_{nk} = 0$$

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Evaluation of second order energy correction :

Setting n = k in (15), we get

$$\sum_m b_m (E_m^0 - E_k^0) \delta_{km} + \sum_l{}' \frac{\langle l | H' | k \rangle \langle k | H' | l \rangle}{E_k^0 - E_l^0} - \sum_l{}' \frac{\langle k | H' | k \rangle \langle l | H' | k \rangle}{E_k^0 - E_l^0} \delta_{kl} - E_k'' \delta_{kk} = 0$$

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$$E_k'' = \sum_l{}' \frac{\langle l | H' | k \rangle \langle k | H' | l \rangle}{E_k^0 - E_l^0} - \sum_l{}' \frac{\langle k | H' | k \rangle \langle l | H' | k \rangle}{E_k^0 - E_l^0} \delta_{kl}$$

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Considering the second term in equation (17), we note that term is zero since ---- for all values of *l* except for *l* = k and this term is not included in the summation. Then equation (17) gives

$$E_k'' = \sum_l{}' \frac{\langle l | H' | k \rangle \langle k | H' | l \rangle}{E_k^0 - E_l^0}$$

If we assume that H' is *Hermitian operator*, we may write

$$E_k'' = \sum_l{}' \frac{|\langle k | H' | l \rangle|^2}{E_k^0 - E_l^0}$$

This equation gives second order energy correction term E_k''. The prime on summation reminds the omissional of the term l = k in the summation.

Evaluation of second order correction to wave function :

For m ≠ n, equation (15) gives.

For $m \neq n$, equation (20) gives

$$b_n (E_n^0 - E_k^0) + \sum_l{}' \frac{\langle l | H' | k\rangle \langle n | H' | l\rangle}{E_k^0 - E_l^0} - \sum_l{}' \frac{\langle l\, k | H' | k\rangle \langle l | H' | k\rangle}{E_k^0 - E_l^0}\,\delta_{nl} = 0$$

$$\text{or} \qquad b_n (E_n^0 - E_k^0) + \sum_l{}' \frac{\langle l | H' | k\rangle \langle n | H' | l\rangle}{E_k^0 - E_l^0} - \frac{\langle l\, k | H' | k\rangle \langle n | H' | k\rangle}{E_k^0 - E_n^0} = 0$$

This gives

$$b_n = \sum_l{}' \frac{\langle l | H' | k\rangle \langle n | H' | l\rangle}{(E_k^0 - E_l^0)\,(E_k^0 - E_n^0)^2} - \frac{\langle l\, k | H' | k\rangle \langle n | H' | k\rangle}{(E_k^0 - E_n^0)^2}$$

Setting n = m, we get

$$b_m = \sum_l{}' \frac{\langle l | H' | k\rangle \langle m | H' | l\rangle}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{\langle l\, k | H' | k\rangle \langle m | H' | k\rangle}{(E_k^0 - E_m^0)^2}$$

This equation determines all coefficients b_m's but not b_k. The coeffimient b_k is determined by the normalization condition for ψ_k retaining only terms upto second order in λ.

$$\begin{aligned}\psi_k &= \psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' = \psi_k^0 + \lambda \psi_k' + \lambda^2 \Sigma\, b_m \psi_m^0 \\ &= \psi_k^0 + \lambda \psi_k' + \lambda^2 b_k \psi_k^0 \\ &\quad + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{\langle l | H' | k\rangle \langle k | H' | l\rangle}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{\langle k | H' | k\rangle \langle m | H' | k\rangle}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0\end{aligned}$$

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The normalization condition for ψ_k gives

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

Substituting ψ_k from (18); we get

$$\begin{aligned}&\int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda \int \psi_k^{0*} \psi_k' \, d\tau + \lambda^2 b_k \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{\langle l | H' | k\rangle \langle k | H' | l\rangle}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} \right. \\ &\quad \left. - \frac{\langle k | H' | k\rangle \langle m | H' | k\rangle}{(E_k^0 - E_m^0)^2} \right\} \int \psi_k^{0*} \psi_m^0 \, d\tau + \lambda \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda^2 b_k^* \int \psi_k^{0*} \psi_k^0 \, d\tau \\ &\quad + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{\langle l | H' | k\rangle^* \langle k | H' | l\rangle^*}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{\langle k | H' | k\rangle^* \langle m | H' | k\rangle^*}{(E_k^0 - E_m^0)^2} \right\} \int \psi_m^{0*} \psi_m^0 \, d\tau \\ &\quad + \lambda^2 \int \psi_k'^* \psi_k' = 1\end{aligned}$$

$$d\tau + 0 + \lambda^2 b_k + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l|H'|k><k|H'|l>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} - \frac{<k|H'|k><m|H'|k>}{(E_k^0\ E_m^0)^2} \right\} \delta_{km}$$

$$+ 0 + \lambda^2 b_k^* + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l|H'|k>^*<k|H'|l>^*}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} - \frac{<k|H'|k>^*<m|H'|k>^*}{(E_k^0 - E_m^0)^2} \right\} \delta_{mk}$$

$$+ \lambda^2 \sum_l{}' \sum_m{}' \frac{<l|H'|k>^*<m|H'|k>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} \int \psi_l^{0*}\ \psi_m^*\ d\tau = 1$$

or

$$\lambda^2 b_k + \lambda^2 b_k^* + \lambda^2 \sum_l{}' \sum_m{}' \frac{<l|H'|k>^*<m|H'|k>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} \delta_{lm} = 0$$

or

$$\lambda^2 \left[b_k + b_k^* + \sum_l{}' \frac{<l|H'|k>^*<l|H'|k>}{(E_k^0 - E_l^0)(E_k^0 - E_l^0)} \right] = 0$$

As $\lambda^2 \neq 0$, therefore, we have

or

$$b_k + b_k^* = - \sum_l{}' \frac{|<l|H'|k>|^2}{(E_k^0 - E_l^0)^2}$$

The real part of b_k is fixed by this equation but the imaginary part is arbitrary. The choice of imaginary part simply affects the phase of the unperturbed wave function and it does not affect the energy of the system. Hence the imaginary part of b_k may be equal to zero. Thus, we have

$$b_k = - \sum_l{}' \frac{|<l|H'|k>|^2}{2(E_k^0 - E_l^0)^2}$$

Then

$$\psi_k'' = \sum_m b_m \psi_m^0 = b_k \psi_k^0 + \sum_m{}' b_m \psi_m^0$$

$$= - \sum_l{}' \frac{|<l|H'|k>|^2}{2(E_k^0 - E_l^0)^2} \psi_k^0 + \sum_m{}' \left\{ \sum_l{}' \frac{<l|H'|k><k|H'|l>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} - \frac{<k|H'|k><m|H'|k>}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0$$

Thus the complete eigen values and eigen function corrected upto second order perturbation terms are given by

$$E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k''$$

$$= E_k^0 + \lambda <k|H'|k>\ \lambda^2 \sum_l{}' \frac{|<k|H'|l>|^2}{E_k^0 - E_l^0}$$

and

$$\psi_k = \psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k''$$

$$= \psi_k^0 + \lambda \sum_l{}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0}\,\psi_l^0 + \lambda^2 \left[- \sum_l{}' \frac{|<l\,|\,H'\,|\,k>|^2}{2(E_k^0 - E_l^0)^2}\,\psi_k^0 + \sum_m{}' \left\{ \sum_l{}' \frac{<l\,|\,H'\,|\,k><k\,|\,H'\,|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|\,H'\,|\,k><m\,|\,H'\,|\,k>}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0 \right]$$

If we choose arbitrary λ = 1 or include λ in symbols, i.e. λH’ → H’ ; the above equations take the conventional form

$$E_k = E_k^0 + <k\,|\,H'\,|\,k> + \sum_l{}' \frac{|<k\,|\,H'\,|\,l>|^2}{(E_k^0 - (E_l^0)}$$

$$\psi_k = \psi_k^0 + \sum_l{}' \frac{<l\,|\,H'\,|\,k>}{2(E_k^0 - E_l^0)}\,\psi_l^0 - \sum_l{}' \frac{|<l\,|\,H'\,|\,k>|^2}{2(E_k^0 - E_l^0)^2}\,\psi_k^0 + \sum_m{}' \left\{ \sum_l{}' \frac{<l\,|\,H'\,|\,k><k\,|\,H'\,|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|\,H'\,|\,k><m\,|\,H'\,|\,k>}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0 .$$

7.4 THE VARIATION (RAYLEIGH-RITZ) METHOD

There are many problems of Quantum Mechanics which cannot be conveniently solved either by direct solution of wave equation or by the use of perturbation theory. The Helium atom is such a system. No direct method of solving the wave-equation has been found for this atom and the application of perturbation theory is unsatisfactory because the first order approximation is not accurate enough while it is troublesome to calculate the higher order approximations. An approximation method, which is conveniently used for such system is variation method. The variation method is specially applicable for the interest in chemical problems. In special cases variation method can be extended to the state of the system other than lowest one. The variation method may also be applied to the lowest to the lowest state of the given resultant angular momentum and of given electron spin multiplicity.

The expectation value of energy innormalised state ψ is given by

$$<E> = \int \psi^* \, H \psi \, d\tau \qquad \text{……………………………19}$$

If we choose the wave function ψ as variable function, then the integral (19) is known as variation integral and gives an upper limit to the energy E_0 of the lowest state of the system. The function ψ is the variation function and its choice may be quite arbitrary, but more wisely, it is chosen such that E approaches more closely to E_0.

If the variation function ψ equals the function ψ_0 of the lowest state, then energy E will be equal to E_0, i.e.,

$$< E > = \int \psi_0^* \, H \psi_0 \, d\tau = E_0$$

If $\psi \neq \psi_0$, then by expansion theorem ψ may be expanded in terms of a complete set of orthonormal functions ϕ_0, ϕ_1, ϕ_2 …. obtaining

$$= \sum_n a_n \phi_n \text{ with } \sum_n a_n a_n^* = 1 \text{ and } H\phi_n = E_n \phi_n \qquad \text{………………..20}$$

Substituting this in equation (1), we get

$$< E > = \sum_n a_n^* \, a_m \int \phi_n^* \, H\phi_m \, d\tau$$

But

$$H\phi_m = E_m \phi_m$$

we have

$$\begin{aligned} < E > &= \sum_n a_n^* \, a_m \int \phi_n^* E_m \phi_m \, d\tau \\ &= \sum_n a_n^* \, a_m \, E_m \int \phi_n^* \, \phi_m \, d\tau \\ &= \sum_n a_n^* \, a_m \, E_m \, \delta_{nm} \end{aligned}$$

$$\text{Therefore} < E > = \sum_n a_n^* . a_m \, E_n$$

$$\left[\begin{aligned} \text{Since } \delta_{mn} &= 1 \text{ for } m = n \\ &= 0 \text{ for } m \neq n \end{aligned} \right]$$

$$= \sum_n |a_n|^2 E_n \qquad \text{………………………21}$$

Subtracting ground state E_0 from both sides, we get

$$< E > - E_0 = \sum_n |a_n|^2 (E_n - E_0)$$

As $|a_n|^2$ is positive and $E_n \geq E_0$ (always) for all values of n; therefore right hand side is positive or zero. Thus we have proved that < E > is always an upper limit to E_0, i.e.

$$< E > \geq E_0$$

This theorem is the basis of the variation method for the calculation of the approximate eigen value of the system. If we choose a number of wave functions ψ_1, ψ_2, ψ_3, ……. and calculate the values E_1, E_2, E_3, …. corresponding to them, then each of these values of E is greater than the energy E_0, so that the lowest one is the nearest to E_0. Often the functions $\psi_1, \psi_2, \psi_3, \ldots\ldots$ are only distinguished by having different values of some parameter λ the process of minimizing E with respect to this parameter may then be carried out in order to obtain the best approximation to E_0, which from the trial function ψ will follow. If the trial function ψ is so chosen that it involves the variation parameter which may vary considerably, E_0 e.g. in the case of helium atom this been applied with great success.

If function ψ is not normalized, equation (19) can be written as

$$<E> = \frac{<\psi\,|H|\,\psi>}{<\psi\,|\,\psi>} \text{ or } \frac{\int \psi^* H\psi\, d\tau}{\int \psi^*\, \psi\, d\tau} \qquad \ldots\ldots\ldots\ldots\ldots\ldots..22$$

Evaluating the integral on R.H.S. of equation (19) or (22) with a trial function ψ that depends on the number of parameters and varying these parameters until the expectation value of the energy is minimum so that

$$E(\lambda_1, \lambda_2, \ldots \lambda_n) = \frac{<\psi(\lambda_1, \lambda_2, \ldots \lambda_n)\,|\,H\,|\,\psi(\lambda_1, \lambda_2, \ldots \lambda_n)>}{<\psi\,|\,\psi>}$$

These parameters are such that the expectation value of the energy takes a value

$$\frac{\partial E}{\partial \lambda_1} = 0, \frac{\partial E}{\partial \lambda_2} = 0, \ldots \frac{\partial E}{\partial \lambda_n} = 0.$$

Application to the Excited State : The variation method can also be used to calculate an upper limit for one of the higher energy level if the trial function is orthogonal to the eigen function of all the lower states. Taking the energy levels in ascending series $E_0, E_1, E_2, \ldots$, then if ψ is orthogonal to ϕ_i for i = 0; 1, ….. , n, it is easily seen from (20) that the corresponding coefficient's a_i are all zero and an inequality can be obtained from (21).

The technique of choosing the trial function for evaluation of energy for any excited is that this function must be orthogonal to the eigen functions of all the lower states (arranged in ascending order of energy). For nth excited state the trial function is chosen of the form

$$\psi = \chi - \sum_{n=0}^{n-1} a_n \int \phi_n^* \chi\, d\tau$$

where X is an arbitrary function and ϕ_n's (i.e. $\phi_0, \phi_1, \phi_2, \ldots \phi_n$ -1) represent the eigen function of lowest n-states. If we expand ψ in the complete of ϕ_n's we find that

$$a_n = 0 \quad \text{for} \quad n = 0, 1, 2, .. n-1$$

Then we have

$$<E> = \int \psi^* H\psi\, d\tau = <\psi\,|H|\,\psi> \geq E_n$$

This equation gives an upper limit to the energy of the nth state.

There are several cases in which such a situation may arise. The simplest example is a one-dimensional problem in which independent variable x goes from $-\infty\ to + \infty$ and the potential function is an even function of x, i.e.

$$V(-x) = V(x)$$

The wave function belonging to the lowest level of such a system is always an even function of x i.e.

$$\phi_0(-x) = \phi_0(x)$$

while the ϕ_1 odd function, i.e.

$$\phi_1(-x) = -\phi_1(x)$$

Therefore if we choose an even function for ψ we can only say that $E_n \geq E_0$; but if it is an odd function a0 will be zero and the relation $E \geq E_1$ will hold. For such a problem the variation method may be used to obtain the lowest energy levels.

7.5 PHYSICAL APPLICATIONS OF VARIATIN METHOD

Ground State of Helium: We use the variation method with a simple trial function to obtain an upper limit for the energy of the ground state of the helium atom. The helium atom consists of a nucleus of charge +2e and two electrons each of charge '-e'. If we consider the nucleus at rest the Hamiltonian will be

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}$$

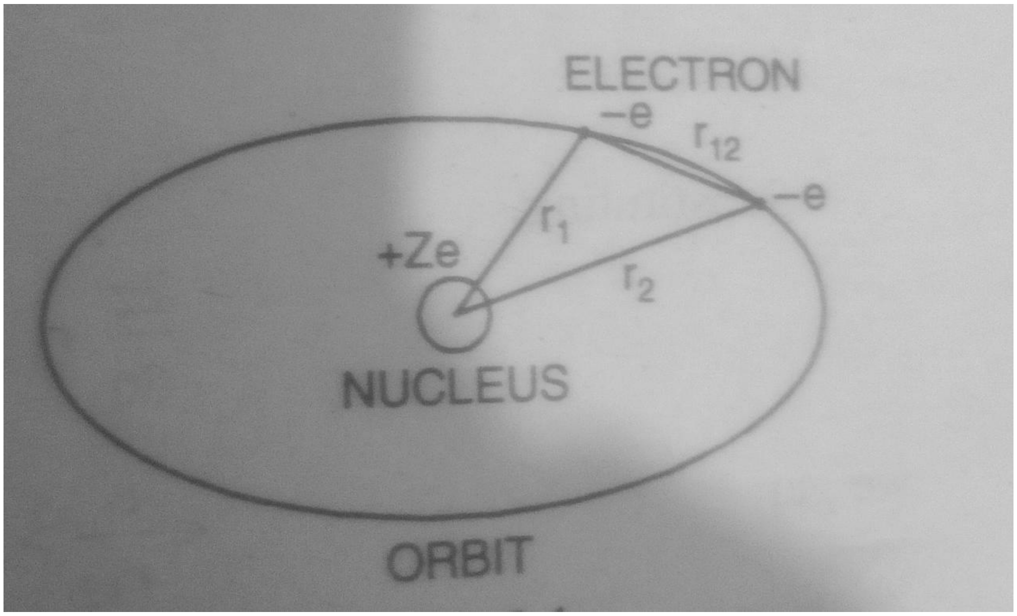
where ∇_1^2 and ∇_2^2 and Laplacian operators for the first and second electrons at a distance r_1 and r_2 from the nucleus, $r_{12} = |r_2 - r_1|$ is the distance between two electrons.

If the interaction energy $\frac{e^2}{r_{12}}$ between two electrons were not present, the ground state eigen function of he would be product of two normalized hydrogen like wave functions $u_{100}(r_1)\ u_{100}(r_2)$ given by

$$\psi(r_1 r_2) = u_{100}(r_1)\ u_{100}(r_2) = \frac{z^3}{\pi a_0^3} e^{-(z/a_0)\ (r_1 + r_2)}$$

with $z = 2$ and $a_0 = \frac{\hbar^2}{me^2}$.

We shall use $\psi(r_1, r_2)$ as a trial function and treat z to be the variation parameter, so that it is not necessarily equal to 2.



The expectation value of Hemitonian H is the sum expectation values of kinetic energy and potential energy individually.

H = K.E. + P.E.

$$= T + V + \text{interaction energy} \left(i.e. \ \frac{e^2}{r_{12}} \right) \text{of electrons.}$$

then $$\langle H \rangle = \langle T \rangle + \langle V \rangle + \langle \frac{e^2}{r_{12}} \rangle$$

Now the expectation values of hydrogen like atoms (having one electron) with z atomic number in general are

$$\langle T \rangle = \frac{z^2 e^2}{2a_0}, \ \langle V \rangle = -\frac{2ze^2}{a_0}. \ \text{Since } \frac{1}{r_1} = \frac{z}{a_0}.$$

But helium atom in ground state has two electrons, so will be twice of hydrogen like atom i.e.

$$\langle T \rangle = \frac{2 z^2 e^2}{2 a_0} = \frac{z^2 e^2}{a_0}$$

and $$\langle V \rangle = -2 \times \frac{2 ze^2}{a_0} = -\frac{4ze^2}{a_0}.$$

Hence $$\langle H \rangle = \frac{z^2 e^2}{a_0} - \frac{4ze^2}{a_0} + \langle \frac{e^2}{r_{12}} \rangle$$

Electron Interaction Energy : The expectation value of the interaction energy between the electrons is

$$< \frac{e^2}{r_{12}} > = \iint \psi^* (r_1 r_2) \frac{e^2}{r_{12}} \psi (r_1 r_2) \, d^3 r_1 \, d^3 r_2.$$

$$= \left(\frac{z^2}{\pi a_0^3} \right)^2 e^2 \iint \frac{1}{r_{12}} e^{-(2z/a_0)(r_1 + r_2)} d^3 r_1 \, d^3 r_2$$

Substituting,

$$\frac{2z}{a_0} r_1 = \rho_1 \text{ and } \frac{2z}{a_0} r_2 = \rho_2, \ \frac{2z}{a_0} r_{12} = \rho_{12}$$

we get

$$< \frac{e^2}{r_{12}} > = \frac{ze^2}{32\pi^2 a_0} \iint \frac{e^{-(\rho_1 + \rho_2)}}{\rho_{12}} d^3\rho_1 \, d^3\rho_2$$

Solving the spherically symmetric integral by knowledge of electrostatics as in perturbation theory, we get

∴

$$< \frac{e^2}{r_{12}} > = \frac{ze^2}{32\pi^2 a_0} 20\pi^2.$$

$$= \frac{5ze^2}{8a_0}$$

(i) By solving we get z=1.69

7.6 TIME DEPENDENT PERTURBATION THEORY

It is generally impossible to obtain exact solution of the Schrodinger equation when the Hamiltonian depends upon time. Therefore, such an equation is solved by time-dependent perturbation theory also called the method of variation of constants.

The total Hamiltonian is written as

$$H = H_0 + H' \quad \text{……………23}$$

where the unperturbed Hamiltonian H_0 can be solved for its normalized eigen function ϕ_n and its eigen value E_n i.e., we have

$$H_0 \phi_n = E_n \phi_n.$$

Time dependent perturbation term H' is small. Since H' depends upon time, the stationary solution of the actual Schroedinger equation does not exist. The time dependent Schroedinger equation is

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

…………………..24

The energy eigen states of such a system are stationary; the time enters only in the phases according to

$$\psi(t) = \Sigma a_n(t)\, \phi_n(\mathbf{r})\, e^{(-iE_n t/\hbar)}$$

……………25

where a_n's are time dependent constants and ϕ (r) is time independent.

This equation represents solution of (24), therefore substituting value of ψ and H from (23) and (25) in (24), we get

$$i\hbar \frac{\partial}{\partial t} [\sum_n a_n(t)\, \phi_n(\mathbf{r})\, e^{-iE_n t/\hbar)}] = (H_0 + H')[\sum_n a_n(t)\, \phi(\mathbf{r})\, e^{-iE_n t/\hbar)}]$$

or $$[\sum_n i\hbar \dot{a}_n(t)\, \phi_n(\mathbf{r})\, e^{(-iE_n t)/\hbar} + \sum_n a_n E_n\, \phi_n(\mathbf{r})\, e^{(-iE_n t)/\hbar}$$

$$= \sum_n a_n H_0\, \phi_n(\mathbf{r})\, e^{(-iE_n t)/\hbar} + \Sigma a_n H'\, \phi_n(\mathbf{r})\, e^{(-iE_n t)/\hbar}$$

where $$\frac{d}{dt} a_n(t) = \dot{a}_n$$

Using (2) *i.e.* $H_0 \phi_n = E_n \phi_n$, we get

$$\sum_n i\hbar \dot{a}_n \phi_n(\mathbf{r})\, e^{-iE_n t/\hbar} + \sum_n a_n E_n\, \phi_n(\mathbf{r})\, e^{-iE_n t/\hbar} = \sum_n a_n E_n\, \phi_n(\mathbf{r})\, e^{iE_n t/\hbar} + \sum_n a_n H'\, \phi_n(\mathbf{r})\, e^{-iE_n t/\hbar}$$

or $$\Sigma\, i\hbar \dot{a}_n \phi_n(\mathbf{r})\, e^{(-iE_n t)/\hbar} = \Sigma a_n H'\, \phi_n(\mathbf{r})\, e^{(-iE_n t)/\hbar}$$

Multiplying both sides by ϕ_k* and integrating over configuration space, we get

$$\Sigma\, i\hbar \dot{a}_n e^{-iE_n t/\hbar} \int \phi_k^* \phi_n^*\, d\tau = \sum_n a_n e^{-iE_n t/\hbar} \int \phi_k^* H' \phi_n\, d\tau$$

Now using orthonormality condition of ϕ's i.e.

$$\int \phi_k^* \phi_n\, d\tau = \delta_{kn} \begin{cases} = 0 \text{ for } n \neq k \\ = 1 \text{ for } n = k \end{cases}$$

we get $$i\hbar \dot{a}_n e^{(-iE_n t)/\hbar} \delta_{kn} = \sum_n a_n e^{(-iE_n)t/\hbar} \int \phi_k^* H' \phi_n\, d\tau.$$

Because in L.H.S. all terms will be zero excepted kth term due to the properties of Keonecker delta δ_{kn}, we have

$$i\hbar \dot{a}_k e^{-iE_n t/\hbar} = \sum_n a_n e^{-iE_n t/\hbar} \int \phi_k^* H' \phi_n\, d\tau$$

The integral $\int \phi_k^* H' \phi_n \, d\tau$ at right hand side is a matrix

$$< k \mid H' \mid n > = H'_{kn}$$

So $$i\hbar \, \dot{a}_k = \sum_n a_n \, e^{i(E_k - E_n)t/\hbar} \, H'_{kn}$$

But $$\frac{E_k - E_n}{\hbar} = \omega_{kn}.$$

is the Bohr's angular frequency.

∴ Time dependent constants a_n's are given by

$$\left.\begin{aligned} \dot{a}_k &= (i\hbar)^{-1} \sum_n a_n H'_{kn} \, e^{i\omega_{kn}t} \\ &= (i\hbar)^{-1} \sum_n a_n < k \mid H' \mid n > e^{i\omega_{kn}t} \end{aligned}\right\}$$

……….26

If we replace in equation (23) H' by λH' where λ is the parameter, then coefficient a's can be expressed in parameter λ as follows :

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

Substituting the value of a_n in equation (26) we get

$$\dot{a}_k^{(0)} + \lambda \dot{a}_k^{(1)} + \lambda^2 \dot{a}_k^{(2)} + ... = (i\hbar)^{-1} \sum_n (a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + ...) H'_{kn} \, e^{i\omega_{kn}t}$$

Comparing coefficients of different power of λ on both sides

Equating coefficient of λ^0, $i\hbar \dot{a}_k^{(0)} = 0$

Equating coefficient of λ, $i\hbar \dot{a}_k^{(1)} = \sum a_n^{(0)} H'_{kn} e^{i\omega_{kn}t}$

....

....

In general $$i\hbar \dot{a}_k^{(S+1)} = \sum_n a_n^{(S)} H_{kn}' e^{i\omega_{kn}t}$$

where S = 0, 1, 2, …… …………….. (27)

So we can get desired order in the perturbation.

Zeroth order calculation : from (27), we have

$$i\hbar \dot{a}_k^{(0)} = 0 \text{ or } \dot{a}_k^{(0)} = 0 \;\; i.e. \;\; \frac{d}{dt} a_k^{(0)} = 0.$$

Integrating, we obtain

$$a_k^{(0)} = constant \; in \; time.$$

For convenience without loss of generality, we may put

$$a_k^{(0)} = \langle k \mid m \rangle = \delta_{km}$$

according as the initial state m is one of a discrete or continuous set.

Accordingly $a_k^{(0)} = 1$ for $k = m$ i.e. $a_m^{(0)} = 1$

and $a_k^{(0)} = 0$ for $k \neq m$

Thus in the sum we have only one term and equation (26) may be expressed as

$$\dot{a}_k = (i\hbar)^{-1} \langle k \mid H' \mid m \rangle e^{i\omega_{km} t} \qquad \text{…..……………28}$$

Ist order perturbation.

Integration of (28), gives

$$a_k^{(1)}(t) = (i\hbar)^{-1} \int_{-\infty}^{t} \langle k \mid H' \mid m \rangle e^{i\omega_{km} t}\, dt. \qquad \text{…………………29}$$

The constant of integration is taken to be zero in order that $a_k^{(1)}$ be zero at $t = -\infty$ (before the perturbation is applied).

Perturbation constant in time : Let us consider a perturbation that is constant in time and that it operates only during the time o to t, i.e.

$$H'_{km} = \langle k \mid H' \mid m \rangle = \begin{cases} 0 & \text{for } -\infty < t' < 0 \\ \langle k \mid H' \mid m \rangle & \text{for } 0 \leq t' \leq t \\ 0 & \text{for } t' > t \end{cases} \qquad \text{……….30}$$

Substituting (30) in (29), we get

$$\begin{aligned} a_k^{(1)}(t) &= (i\hbar)^{-1} \int_0^t \langle k \mid H' \mid m \rangle e^{i\omega_{km} t'}\, dt' \\ &= (i\hbar)^{-1} \langle k \mid H' \mid m \rangle \int_0^t e^{i\omega_{km} t'}\, dt' \\ &= (i\hbar)^{-1} \langle k \mid H' \mid m \rangle \left[\frac{e^{i\omega_{km} t'}}{i\omega_{km}} \right]_0^t \\ &= (i\hbar)^{-1} \langle k \mid H' \mid m \rangle \left[\frac{e^{i\omega_{km} t} - 1}{i\omega_{km}} \right] \\ &= -\frac{\langle k \mid H' \mid m \rangle}{\omega_{km}\hbar} \left(e^{i\omega_{km} t} - 1\right) \end{aligned}$$

Thus, to first order, the probability of the system from mth state kth state is given by

$$|a_k^{(1)}(t)|^2 = \frac{|\langle k \mid H' \mid m \rangle|^2}{\omega_{km}^2 \hbar^2} \left|\left(e^{i\omega_{km} t} - 1\right)\right|^2 \qquad \text{…………31}$$

Using the relation

$$\lim_{x\to 0}\,(e^{ix}-1) = 2ie^{ix/2}\sin\frac{x}{2} = 2i\sin\frac{x}{2}$$

or

$$|(e^{ix}-1)|^2 = 4\sin^2\frac{x}{2}$$

i.e.

$$|(e^{i\omega_{km}t}-1)|^2 = 4\sin^2\left(\frac{\omega_{km}t}{2}\right).$$

equation (31) takes the form

$$|a_k^{(1)}(t)|^2 = \frac{4|<k|H'|m>|^2}{\hbar^2\omega_{km}^2}\sin^2\left(\frac{\omega_{km}t}{2}\right).$$

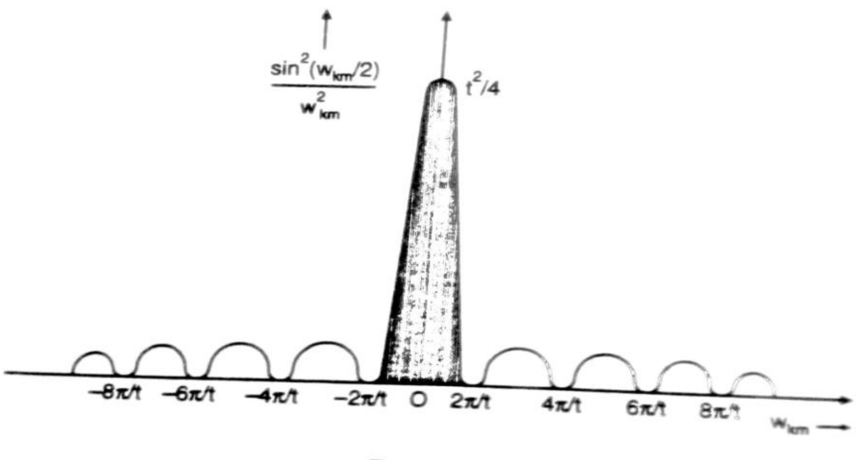
Physical Interpretation: In order to interpret equation (32) physically, we plot $\frac{sin^2(\omega_{km}t/2)}{\omega_{km}^2}$ as a function of ω_{km} and find the curve as shown is fig.

The major maxima of probability curve occur at $\omega_{km}=0$ i.e. for $E_k = E_m$ if we substitute $\omega_{km}=x$ in $\frac{sin^2\frac{\omega_{km}t}{2}}{\omega_{km}^2}$ we note that

$$\frac{\sin^2\frac{\omega_{km}t}{2}}{\omega_{km}^2} = \frac{\sin^2(xt/2)}{x^2} = \frac{1}{x^2}\left[\frac{xt}{2}-\frac{(xt/2)^3}{3}+\frac{(xt/2)^5}{5}-\dots\right]^2$$

$=\frac{}{x^2}\left(\frac{xt}{2}\right)^2$ if higher powers of $\left(\frac{xt}{2}\right)$ are neglected due to their smaller values $=\frac{t^2}{4}$.

$= \frac{}{4}\cdot$



7.7 SUMMARY

Though some simple problems in quantum mechanics can be solved analytically, those problems that most accurately represent the physical world almost invariably rely on approximation methods. For example, one can analytically solve for the eigenvalues and the eigenstates corresponding to the Hamiltonian of the finite square well potential, but this is not a very physically relevant problem. Instead, consider a system, like a hydrogen atom, and then expose this system to some outside force, like an electric field. The electric field alters the Hamiltonian of the initial system, which in turn alters the corresponding eigenenergies and eigenstates. To illustrate how this works, consider the simplified example of a finite square well potential in which there is a slight deviation (or perturbation) to the potential somewhere within the well. This perturbation alters the Hamiltonian and therefore the corresponding eigenvalues and eigenstates from what they were in the simple case of the unperturbed square well potential. Perturbation theory allows one to find approximate solutions to the perturbed eigenvalue problem by beginning with the known exact solutions of the unperturbed problem and then making small corrections to it based on the new perturbing potential. The limit of the infinite summation of corrections to the unperturbed solution is the exact solution to the perturbed problem. Of course, this infinite sum can never be calculated; the summation must be truncated at some point--hence the approximate nature of the solutions produced by perturbation theory. Luckily, subsequent corrections to the Hamiltonian become smaller and smaller, so the series can usually be truncated after only a few corrections.

One must be careful when using perturbation theory that the perturbing potential does not change the number of bound states in the system. As will be shown, perturbation theory relies on the assumption that the unperturbed states form a complete set, so the corrected states may be expressed as linear combinations of the unperturbed states. For example, if the perturbing potential changes the Hamiltonian of the system such that the number of bound states is increased by one, this new state must have come from the unbounded region.

Degeneracy in quantum mechanics refers to the situation when more than one eigenstate corresponds to the same energy. Conversely, non-degeneracy occurs when each eigenstate corresponds to a unique energy.

7.8 TERMINAL QUESTIONS

1. What do you mean by Perturbation Theory?
2. Discuss the Perturbation theory for non-degenerate levels in first and second orders.
3. Give the first order Perturbation theory for a non-degenerate case.
4. State and Prove the Variational Principle for Obtaining approximation energies.

5. Discuss the first order time independent perturbation theory for non-degenerate stationary state.
6. Discuss Time Dependent Perturbation theory.

7.9 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 7.3
2. Section 7.3
3. Section 7.3
4. Section 7.4
5. Section 7.3
6. Section 7.6

7.10 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

UNIT-8 ATOMIC SPECTRA

Structure

8.1 INTRODUCTION

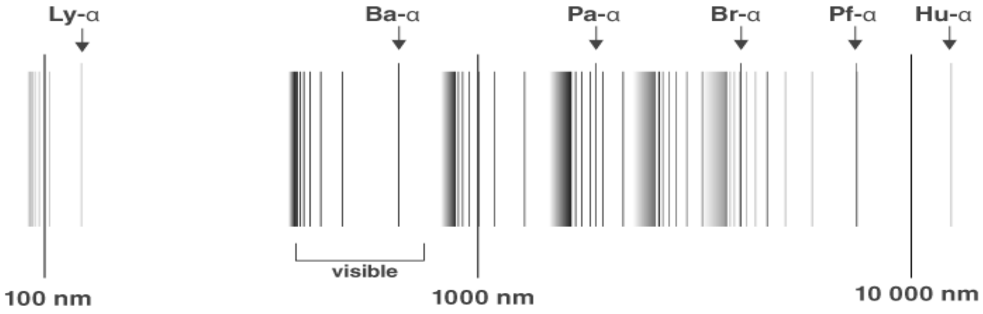
We know that in an atom, electrons have discrete and specific energies. There are more energy states in an atom than there are electrons. When an electron transitions from one energy level to another, it emits light or photon with a specific wavelength. In any given set of conditions, the collection of all these specific wavelengths is what constitutes the atomic spectrum. Hence, atomic spectra are the spectra of atoms. Here, in this short piece of article, we will be looking at atomic spectra more in detail along with the Rydberg formula and the spectral series of the hydrogen atom.

What are Atomic Spectra?

Atomic spectra are defined as

The spectrum of the electromagnetic radiation emitted or absorbed by an electron during transitions between different energy levels within an atom.

When an electron gets excited from one energy level to another, it either emits or absorbs light of a specific wavelength. The collection of all these specific wavelengths of the atom in a given set of conditions like pressure, temperature, etc is the atomic spectra of atoms. There are three types of atomic spectra and they are emission spectra, absorption spectra, and continuous spectra.



Hydrogen spectral series

From the image above, it is evident that the atomic hydrogen emission spectrum is divided into a number of spectral lines with wavelengths given by the Rydberg formula. The observed spectral lines in the hydrogen emission spectrum are due to the atomic transitions between different energy levels. The spectral series are important in astronomical spectroscopy.

Atomic Spectroscopy

Atomic spectroscopy is the study of the electromagnetic radiation absorbed or emitted by atoms. There are three types of atomic spectroscopy and they are:

- Atomic emission spectroscopy: This involves the transfer of energy from the ground state to an excited state. The electronic transition can be explained in atomic emission.
- Atomic absorption spectroscopy: For absorption to take place there should be identical energy differences between the lower and higher energy levels. The atomic absorption spectroscopy principle uses the fact that the free electrons generated in an atomizer can absorb radiation at a specific frequency. It quantifies the absorption of ground-state atoms in the gaseous state.
- Atomic fluorescence spectroscopy: This is a combination of atomic emission and atomic absorption as it involves radiation of both excitation and de-excitation.

Uses of Atomic Spectroscopy

- It is used for identifying the spectral lines of materials used in metallurgy.
- It is used in pharmaceutical industries to find the traces of materials used.
- It can be used to study multidimensional elements.

Characteristics of Atomic Spectra

There are various characteristics of atomic spectra, such as:

1. The atomic spectra should be a pure line spectrum.
2. It should be an emission band spectrum.
3. It should be an absorption line spectrum.
4. Also, it should be the absorption band spectrum.

8.2 OBJECTIVES

After studying this unit student should able to:

- Know about Atomic Spectra.
- State and derive Lande -G factor.
- Explain about Zeeman Effect.
- Define Stark Effect

8.3 LANDE-G-FACTOR

In physics, the **Landé *g*-factor** is a particular example of a *g*-factor, namely for an electron with both spin and orbital angular momenta. It is named after Alfred Landé, who first described it in 1921.[1]

In atomic physics, the Landé *g*-factor is a multiplicative term appearing in the expression for the energy levels of an atom in a weak magnetic field. The quantum states of electrons in atomic orbitals are normally degenerate in energy, with these degenerate states all sharing the same angular momentum. When the atom is placed in a weak magnetic field, however, the degeneracy is lifted.

In the weak field limit, we assume that the magnetic dipole moment due to the electron in an atom is proportional to the total angular momentum J:

$$\boldsymbol{\mu}_J = -\, g_J \frac{m_B}{\hbar} \boldsymbol{J}$$

where m_B is the Bohr magneton ($\frac{e\hbar}{2m_e}$) and g_J is the Landé g factor for $\boldsymbol{J}$. To find a value of g_J, we relate $\boldsymbol{J}$ to the known values of g_L and g_S and assume the following:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \qquad \boldsymbol{\mu}_J = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S$$

$$\boldsymbol{\mu}_L = -\, g_L \frac{m_B}{\hbar} \boldsymbol{L} \qquad \boldsymbol{\mu}_S = -\, g_S \frac{m_B}{\hbar} \boldsymbol{S}$$

$$\boldsymbol{\mu}_J = -\, g_J \frac{m_B}{\hbar} \boldsymbol{J} = -\, g_L \frac{m_B}{\hbar} \boldsymbol{L} + -g_S \frac{m_B}{\hbar} \boldsymbol{S}$$

$$g_J \boldsymbol{J} = g_L \boldsymbol{L} + g_S \boldsymbol{S}$$

We then take the dot product with **J** and get:

$$g_J \boldsymbol{J} \bullet \boldsymbol{J} = g_L \boldsymbol{L} \bullet \boldsymbol{J} + g_S \boldsymbol{S} \bullet \boldsymbol{J}$$

$$g_J J^2 = g_L \left(L^2 + \boldsymbol{L} \bullet \boldsymbol{S} \right) + g_S \left(S^2 + \boldsymbol{L} \bullet \boldsymbol{S} \right)$$

$$g_J J^2 = g_L \left(L^2 + 0.5 \left(J^2 - L^2 - S^2 \right) \right) + g_S \left(S^2 + 0.5 \left(J^2 - L^2 - S^2 \right) \right)$$

$$J^2 = \hbar^2 J(J+1) \qquad L^2 = \hbar^2 L(L+1) \qquad S^2 = \hbar^2 S(S+1)$$

$$g_J = \frac{g_L \left(J(J+1) + L(L+1) - S(S+1) \right) + g_S \left(J(J+1) - L(L+1) + S(S+1) \right)}{2J(J+1)}$$

For the case:

$g_L = 1$
$g_S = 2$

We get:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

And so, for the weak field limit:

$$W_z = -\boldsymbol{\mu}_J \bullet \boldsymbol{B} = g_J \omega_0 J_z$$

$$\omega_0 = -\frac{m_B}{\hbar} B_0 = -\frac{eB_0}{2m_e}$$

where ω_0 is the Larmor angular frequency.

$g_J = 4/3$ for 2p(j=3/2) state (L=1, S=1/2, J =3/2)

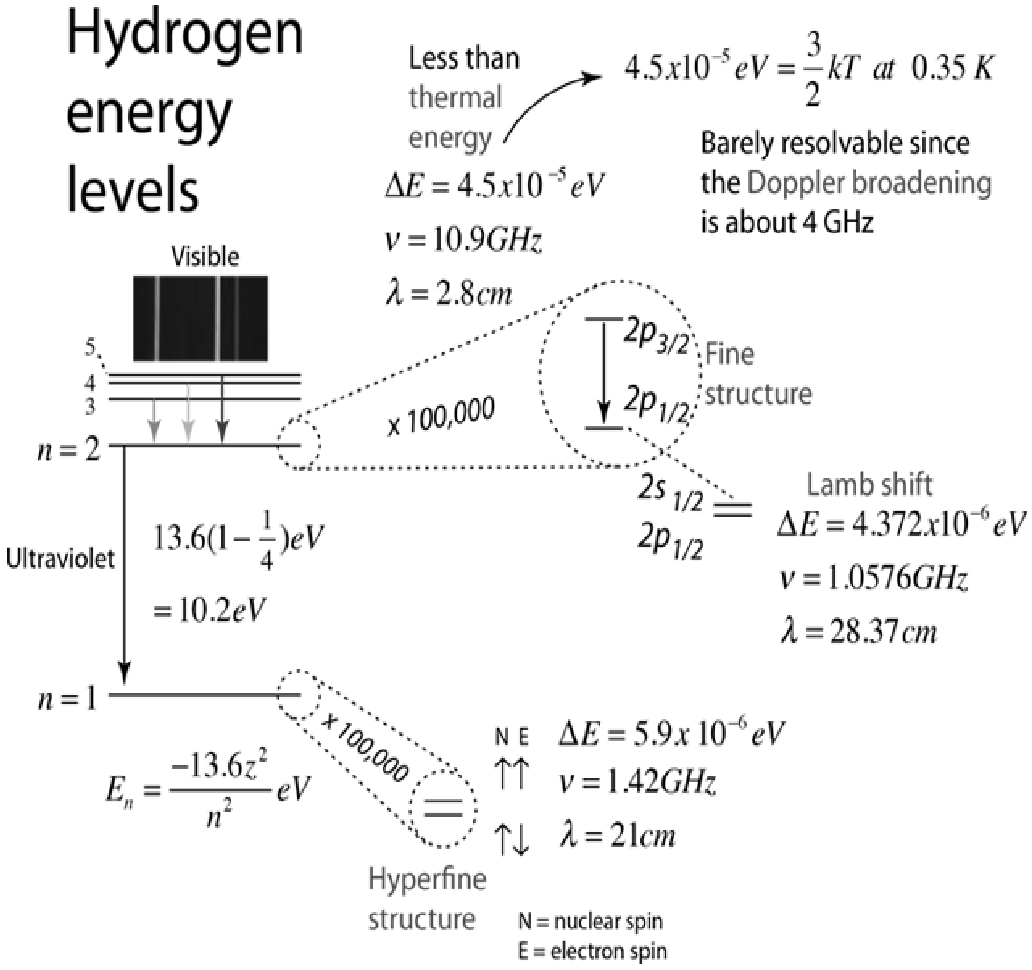
$g_J = 2/3$ for 2p(j=1/2) state (L=1, S=1/2, J =1/2)

8.4 SHIFT IN ENERGY OF ATOM

In physics, the **Lamb shift**, named after Willis Lamb, is a difference in energy between two energy levels ${}^2S_{1/2}$ and ${}^2P_{1/2}$ (in term symbol notation) of the hydrogen atom which was not predicted by the Dirac equation, according to which these states should have the same energy.

Interaction between vacuum energy fluctuations and the hydrogen electron in these different orbitals is the cause of the Lamb shift, as was shown subsequent to its discovery. The Lamb shift has since played a significant role through vacuum energy fluctuations in theoretical prediction of Hawking radiation from black holes.

This effect was first measured in 1947 in the **Lamb–Retherford experiment** on the hydrogen microwave spectrum[1] and this measurement provided the stimulus for renormalization theory to handle the divergences. It was the harbinger of modern quantum electrodynamics developed by Julian Schwinger, Richard Feynman, Ernst Stueckelberg, Sin-Itiro Tomonaga and Freeman Dyson. Lamb won the Nobel Prize in Physics in 1955 for his discoveries related to the Lamb shift.

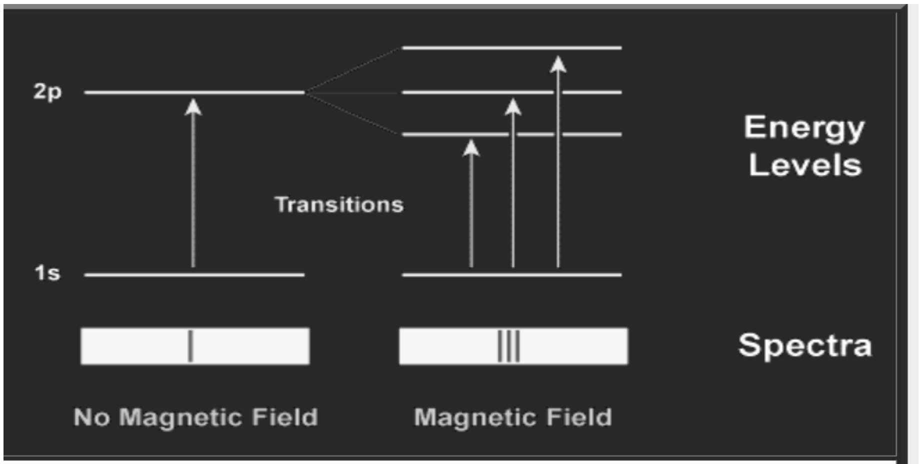


8.5 ZEEMAN EFFECT

The atomic energy levels, the transitions between these levels, and the associated spectral lines discussed to this point have implicitly assumed that there are no magnetic fields influencing the atom. If there are magnetic fields present, the atomic energy levels are split into a larger number of levels and the spectral lines are also split. This splitting is called the *Zeeman Effect*.

Zeeman Spectral Splitting:

The pattern and amount of splitting are a signature that a magnetic field is present, and of its strength. The splitting is associated with what is called the *orbital angular momentum quantum number* L of the atomic level. This quantum number can take non-negative integer values. The number of split levels in the magnetic field is 2 * L + 1. The following figure illustrates the Zeeman effect.

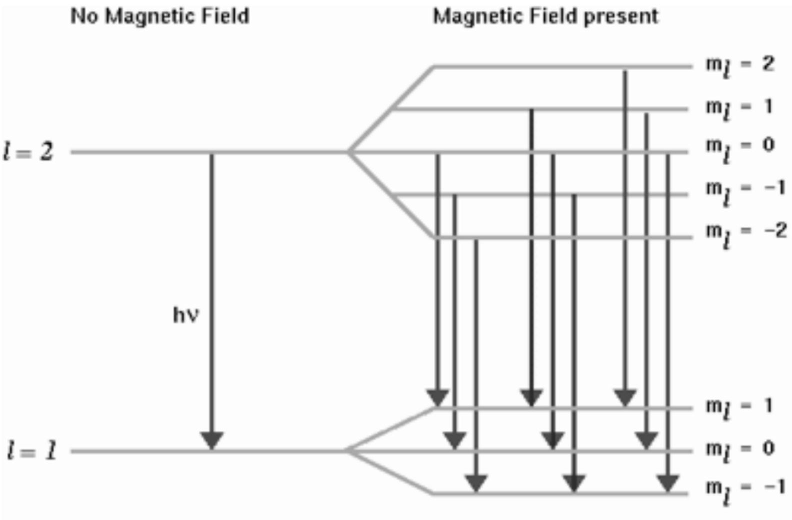


The Zeeman Effect

Atomic physicists use the abbreviation "s" for a level with L=0, "p" for L=1, and "d" for L=2, and so on (the reasons for these designations are of historical interest only). It is also common to precede this designation with the integer principal quantum number n. Thus, the designation "2p" means a level that has n=2 and L=1.

In the preceding example the lowest level is an "s" level, so it has L=0 and 2L + 1 = 1, so it isn't split in the magnetic field, while the first excited state has L=1 ("p" level), so it is split into 2L + 1 = 3 levels by the magnetic field. Thus, a single transition is split into 3 transitions by the magnetic field in this example.

The Zeeman effect can be interpreted in terms of the precession of the orbital angular momentum vector in the magnetic field, similar to the precession of the axis of a spinning top in a gravitational field.



Polarization of Spectral Lines :

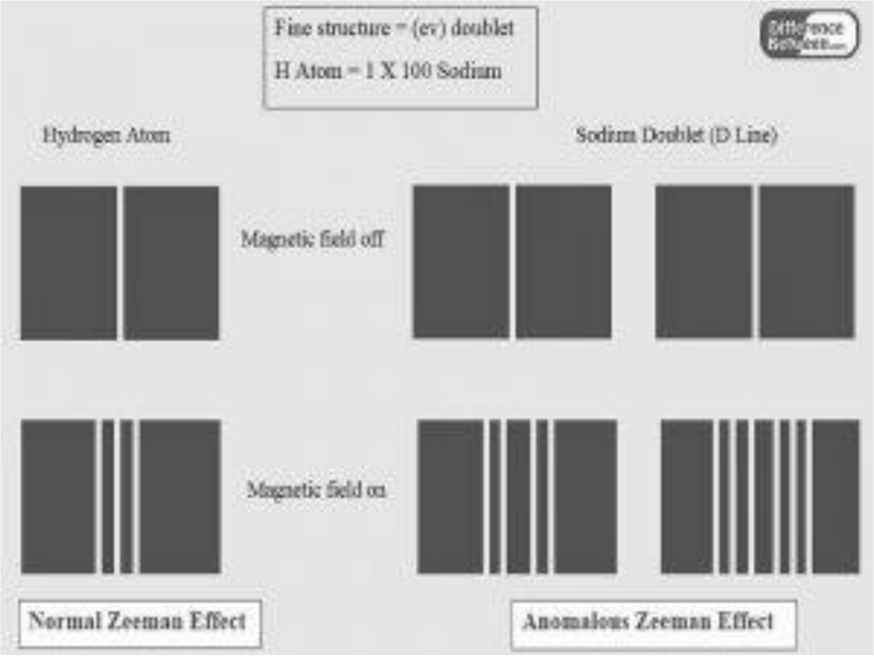
The lines corresponding to Zeeman splitting also exhibit *polarization effects*. Polarization has to do with the direction in which the electromagnetic fields are vibrating. This in turn, can have an effect on whether the spectral light can be observed. For example, polarizing sunglasses are often effective in suppressing ambiant glare because light reflected from surfaces has a particular polarization and polarizing sunglasses are designed to not pass that polarization of light.

One practical example in astronomy of such polarization effects is that in the preceding example the middle transition is polarized such that it cannot be easily be obverved from directly over a surface perpendicular to the magnetic field. As a consequence, when looking directly down on a sunspot (which have strong magnetic fields) typically only two of the three transitions shown above can be seen and the line is observed to split into two rather than three lines (the missing transition could be observed from a different angle where its light would not be suppressed by the polarization effect, but it is very weak when observed from directly overhead).

Types of Zeeman Effect

1. **Normal Zeeman Effect-** If the net spin of the optically active electron of an atom is equal to zero, then it exhibits a normal Zeeman effect. The normal Zeeman effect splits the spectral line of an atom into three major component lines. The explanation of the normal Zeeman effect is available in both Classical and quantum mechanics. In other words, when the splitting of a single spectral line of an atom into three component lines due to the action of the magnetic field is observed, then such a phenomenon is known as the normal Zeeman effect. For instance, if you consider the spectrum of a hydrogen atom, it consists of certain five spectral lines, namely, Lyman, Balmer, Paschen, Bracket, and Pfound. The Balmar line of the hydrogen spectrum lies in the visible range and can be observed when the electron jumps from n=3 to n=2 state. When the Balmar line of hydrogen atoms is placed under the influence of a magnetic field, it gets split into three component lines. The middle line is known as the pi component, while the other two lines, located on either side of the pi component line, denote the sigma components. The sigma components are equidistant from the pi component line. The vibration of the electric vector of the pi component of a spectral line is parallel to the applied magnetic field, while the vibration of the electric vector of the sigma component is perpendicular to the external magnetic field.
2. **Anomalous Zeeman Effect-** The net spin of the optically active electron of an atom exhibiting anomalous Zeeman effect is not equal to zero. The anomalous Zeeman effect causes the atomic spectral lines to get split into more than three component lines. This effect can be explained only with the help of quantum mechanics. The concept of spinning of electrons was not known when the Zeeman effect was discovered, which is why there was no perfect explanation available for the splitting of atomic spectral lines into multiple component lines at that time. Hence, the new elaborated theory

given by Thomas Preston in 1897 was named the anomalous Zeeman effect. In other words, the phenomenon of splitting the fine structure of an atom into its components by placing it under the influence of an external magnetic field is known as the anomalous Zeeman effect. For instance, if you observe the fine structure of a sodium atom, it consists of two spectral lines, namely D1 and D2 lines. The wavelengths corresponding to both the spectral lines are 5896 A° and 5890 A° respectively. When such a fine structure of sodium atom is placed under a magnetic field, the D1 spectral line gets split into four component lines, two of which are the pi component lines, and the other two are sigma component lines. In a similar manner, the D2 spectral line splits into six component lines out of which two are pi component lines, while four are sigma component lines. In the case of the anomalous Zeeman effect, the distance between the component lines may or may not be the same, i.e., the component lines are not necessarily equidistant.



Applications of Zeeman Effect

1. Zeeman effect helps the physicists to determine the energy levels of an atom and to study their angular momenta.

2. It also expands the scope of studying atomic nuclei and phenomena like electron paramagnetic resonance.

3. Zeeman effect is also used in the field of astronomy to study the magnetic field of the sun and other stars.

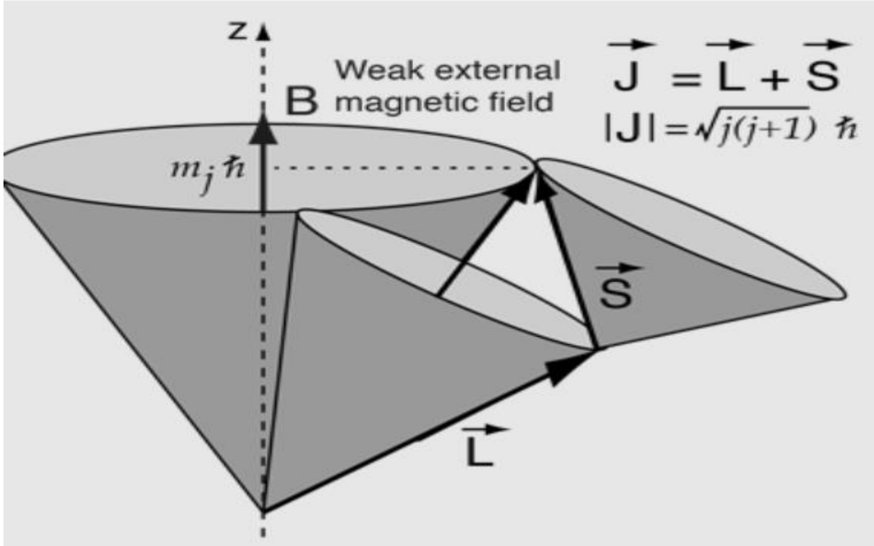
4. Zeeman effect finds its prime application in various spectroscopy techniques such as nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, Mössbauer spectroscopy, etc.

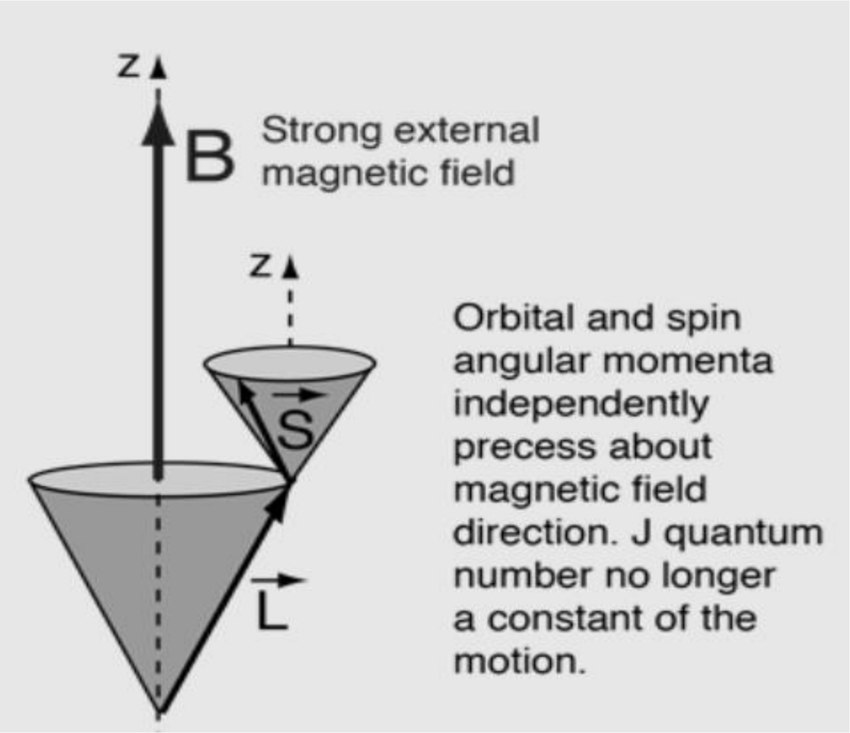
5. Some medical imaging techniques such as magnetic resonance imaging (MRI) also make use of the Zeeman effect.

6. Zeeman effect is also known to exhibit polarization effects. One of the best real-life examples of which are polarized sunglasses. The purpose of polarized sunglasses is to suppress ambient glare.

8.6 PASCHEN BACK EFFECT

In the presence of an external magnetic field, the energy levels of atoms are split. This splitting is described well by the Zeeman effect if the splitting is small compared to the energy difference between the unperturbed levels, i.e., for sufficiently weak magnetic fields. This can be visualized with the help of a vector model of total angular momentum. If the magnetic field is large enough, it disrupts the coupling between the orbital and spin angular momenta, resulting in a different pattern of splitting. This effect is called the Paschen-Back effect.



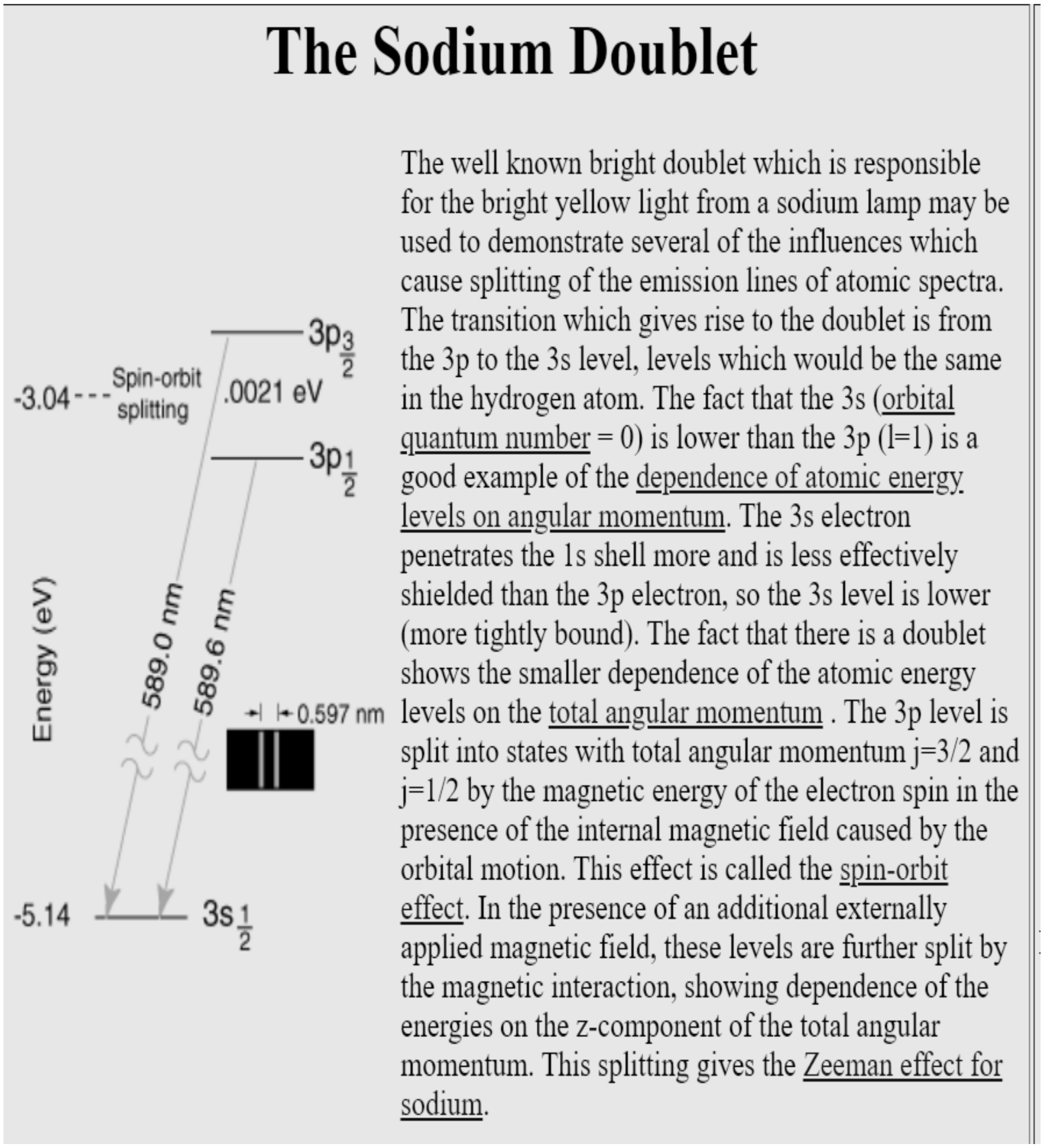


Orbital and spin angular momenta independently precess about magnetic field direction. J quantum number no longer a constant of the motion.

In the weak field case the vector model at left implies that the coupling of the orbital angular momentum L to the spin angular momentum S is stronger than their coupling to the external field. In this case where spin-orbit coupling is dominant, they can be visualized as combining to form a total angular momentum J which then precesses about the magnetic field direction.

In the strong-field case, S and L couple more strongly to the external magnetic field than to each other, and can be visualized as independently precessing about the external field direction.

8.7 ZEEMAN PATTERN FOR SODIUM LINES



The Sodium Doublet

The well known bright doublet which is responsible for the bright yellow light from a sodium lamp may be used to demonstrate several of the influences which cause splitting of the emission lines of atomic spectra. The transition which gives rise to the doublet is from the 3p to the 3s level, levels which would be the same in the hydrogen atom. The fact that the 3s (orbital quantum number = 0) is lower than the 3p (l=1) is a good example of the dependence of atomic energy levels on angular momentum. The 3s electron penetrates the 1s shell more and is less effectively shielded than the 3p electron, so the 3s level is lower (more tightly bound). The fact that there is a doublet shows the smaller dependence of the atomic energy levels on the total angular momentum . The 3p level is split into states with total angular momentum j=3/2 and j=1/2 by the magnetic energy of the electron spin in the presence of the internal magnetic field caused by the orbital motion. This effect is called the spin-orbit effect. In the presence of an additional externally applied magnetic field, these levels are further split by the magnetic interaction, showing dependence of the energies on the z-component of the total angular momentum. This splitting gives the Zeeman effect for sodium.

The magnitude of the spin-orbit interaction has the form $\mu_z B = \mu_B S_z L_z$. In the case of the sodium doublet, the difference in energy for the $3p_{3/2}$ and $3p_{1/2}$ comes from a change of 1 unit in the spin orientation with the orbital part presumed to be the same. The change in energy is of the form

$$\Delta E = \mu_B g B = 0.0021 \text{ eV}$$

where μ_B is the Bohr magneton and g is the electron spin g-factor with value very close to 2. This gives an estimate of the internal magnetic field needed to produce the observed splitting:

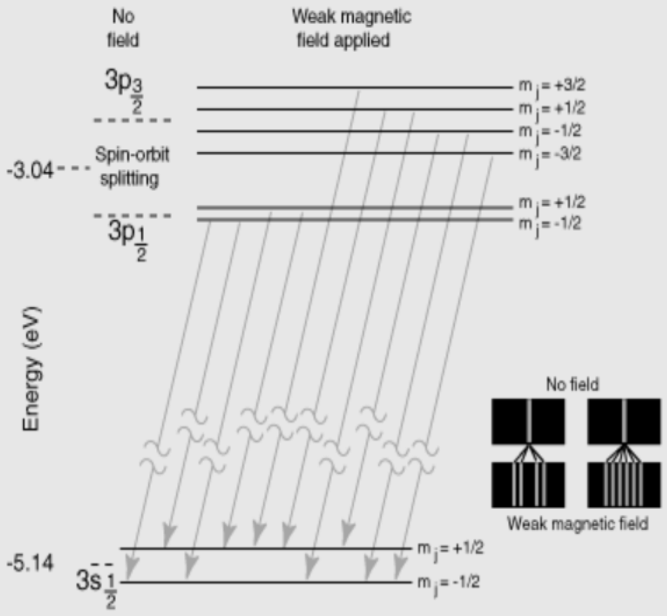
$$\mu_B g B = (5.79 \times 10^{-5} \text{ eV/T})2B = 0.0021 \text{ eV}$$

$$B = 18 \text{ Tesla}$$

This is a very large magnetic field by laboratory standards. Large magnets with dimensions over a meter, used for NMR and ESR experiments, have magnetic fields on the order of a Tesla.

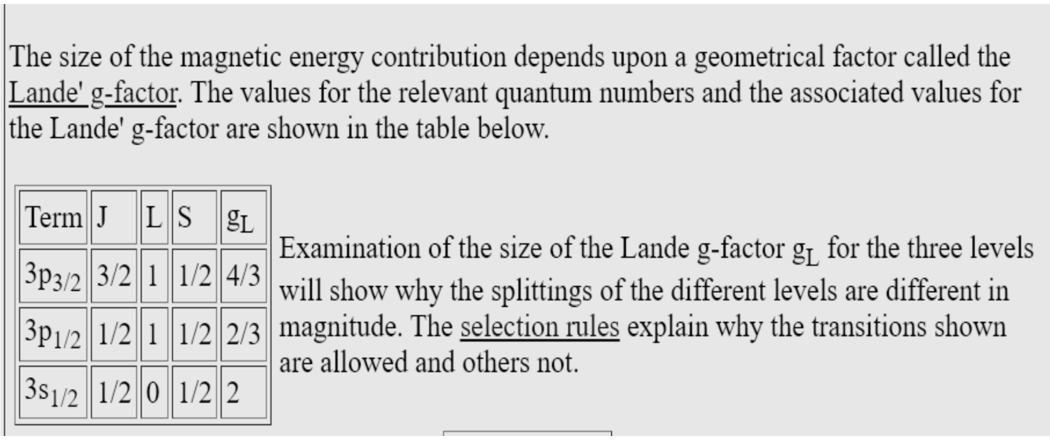
The Sodium Zeeman Effect

The sodium spectrum is dominated by the bright doublet known as the Sodium D-lines at 588.9950 and 589.5924 nanometers. From the energy level diagram it can be seen that these lines are emitted in a transition from the 3p to the 3s levels.



The sodium doublet is further spit by the application of an external magnetic field (Zeeman effect). Using the vector model for total angular momentum, the splitting is seen to produce one level for each possible value of the z-component of the total angular momentum J.

The size of the magnetic energy contribution depends upon a geometrical factor called the Lande' g-factor. The values for the relevant quantum numbers and the associated values for the Lande' g-factor are shown in the table below.



The size of the magnetic energy contribution depends upon a geometrical factor called the Lande' g-factor. The values for the relevant quantum numbers and the associated values for the Lande' g-factor are shown in the table below.

Term	J	L	S	g_L
$3p_{3/2}$	3/2	1	1/2	4/3
$3p_{1/2}$	1/2	1	1/2	2/3
$3s_{1/2}$	1/2	0	1/2	2

Examination of the size of the Lande g-factor g_L for the three levels will show why the splittings of the different levels are different in magnitude. The selection rules explain why the transitions shown are allowed and others not.

8.8 STARK EFFECT

The **Stark effect** is the shifting and splitting of spectral lines of atoms and molecules due to the presence of an external electric field. It is the electric-field analogue of the Zeeman effect, where a spectral line is split into several components due to the presence of the magnetic field. Although initially coined for the static case, it is also used in the wider context to describe the effect of time-dependent electric fields. In particular, the Stark effect is responsible for the pressure broadening (Stark broadening) of spectral lines by charged particles in plasmas. For most spectral lines, the Stark effect is either linear (proportional to the applied electric field) or quadratic with a high accuracy.

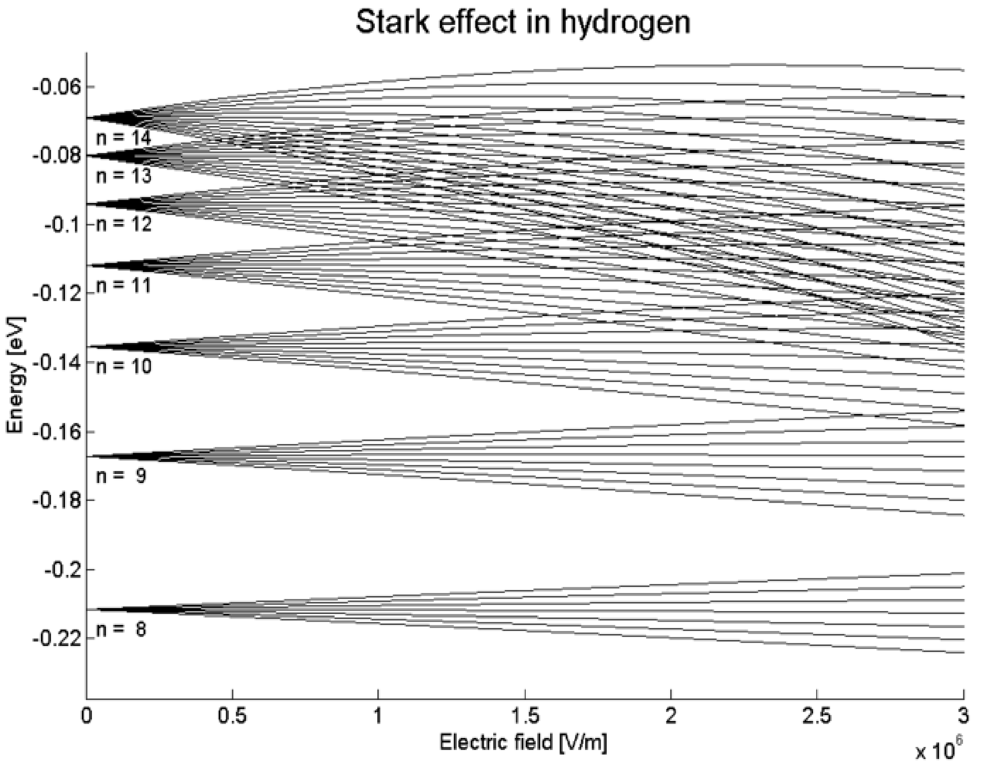
The Stark effect can be observed both for emission and absorption lines. The latter is sometimes called the **inverse Stark effect**, but this term is no longer used in the modern literature.

The effect is named after the German physicist Johannes Stark, who discovered it in 1913. It was independently discovered in the same year by the Italian physicist Antonino Lo Surdo, and in Italy it is thus sometimes called the **Stark–Lo Surdo effect**. The discovery of this effect contributed importantly to the development of quantum theory and Stark was awarded with the Nobel Prize in Physics in the year 1919.

An electric field pointing from left to right, for example, tends to pull nuclei to the right and electrons to the left. In another way of viewing it, if an electronic state has its electron disproportionately to the left, its energy is lowered, while if it has the electron disproportionately to the right, its energy is raised.

Other things being equal, the effect of the electric field is greater for outer electron shells, because the electron is more distant from the nucleus, so it travels farther left and farther right.

The Stark effect can lead to splitting of degenerate energy levels. For example, in the Bohr model, an electron has the same energy whether it is in the 2s state or any of the 2p states. However, in an electric field, there will be hybrid orbitals (also called quantum superpositions) of the 2s and 2p states where the electron tends to be to the left, which will acquire a lower energy, and other hybrid orbitals where the electron tends to be to the right, which will acquire a higher energy. Therefore, the formerly degenerate energy levels will split into slightly lower and slightly higher energy levels



The stark effect is the shifting and splitting (reduction of degeneracy) of spectral lines in atomic or molecular species under the influence of an externally applied electric field. It is sometimes considered the electric analog to the reduction of degeneracy in atomic and molecular species due to an externally applied magnetic field, the Zeeman effect. I'm not fond of that characterization since the two phenomena are quite different, but it is a reasonable viewpoint.

There are actually two types of stark effect: the linear stark effect and the quadratic version of the stark effect. As expected, the linear stark effect is linearly dependant on the applied electric field while the quadratic stark effect is smaller in the value of splitting and varies as the square of the applied electric field.

The splitting of spectral lines in an electric field is known as Stark effect.

The number of stark lines and the total width of the pattern increases with n.

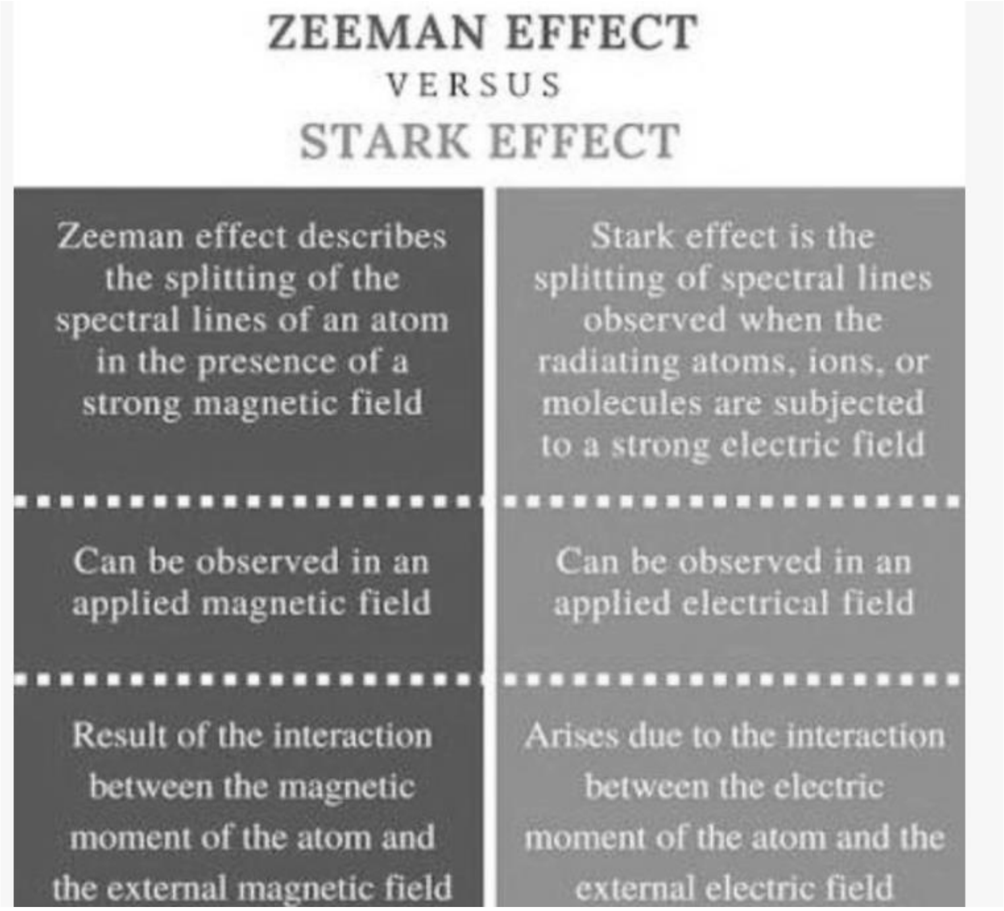
The π components show greater shift than the Sigma component.

8.9 SUMMARY

In this unit we discussed about different atomic spectra in brief.

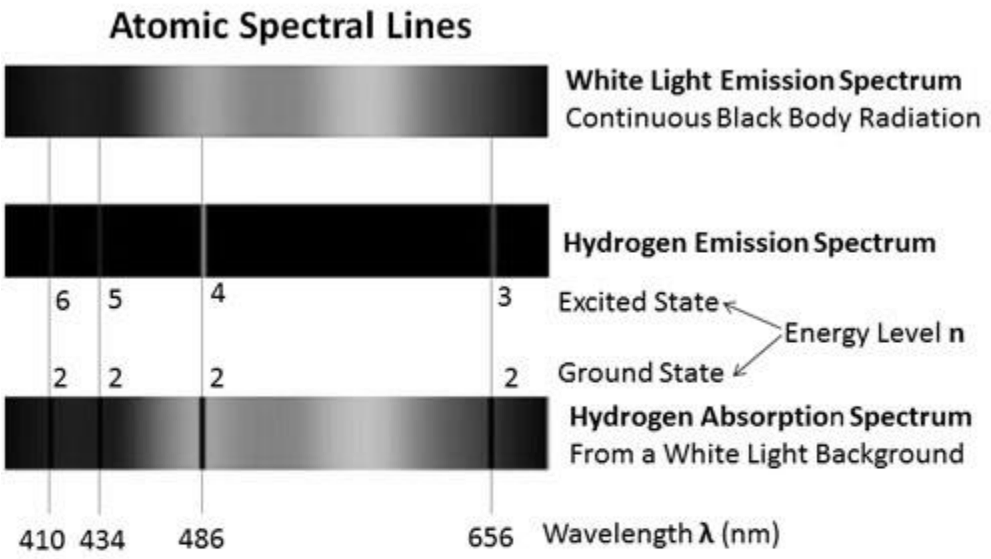
This splitting of the p-orbital (and of higher orbitals) within an atom in the presence of an external magnetic field is known as **Zeeman effect.**

The splitting of atomic spectral lines as a result of an externally applied electric field was discovered by **Stark**, and is called the **Stark effect**.



ZEEMAN EFFECT
VERSUS
STARK EFFECT

Zeeman effect describes the splitting of the spectral lines of an atom in the presence of a strong magnetic field	Stark effect is the splitting of spectral lines observed when the radiating atoms, ions, or molecules are subjected to a strong electric field
Can be observed in an applied magnetic field	Can be observed in an applied electrical field
Result of the interaction between the magnetic moment of the atom and the external magnetic field	Arises due to the interaction between the electric moment of the atom and the external electric field



8.10 TERMINAL QUESTIONS

1. State and prove Lande-g Factor.
2. Explain about Lamb Shift.

3. Discuss briefly about Zeeman Effect
4. What is Paschen Back Effect?
5. Explain Zeeman Pattern for Sodium Lines.
6. Discuss briefly about Stark Effect.

8.11 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 8.3
2. Section 8.4
3. Section 8.5
4. Section 8.6
5. Section 8.7
6. Section 8.8

8.12 SUGGESTED READINGS:

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

Uttar Pradesh Rajarshi Tandon
Open University

Bachelor of Science

DCEPHS-108

Quantum Mechanics And Spectroscopy

BLOCK

4

MOLECULAR SPECTROSCOPY

UNIT-9

Types of Spectroscopy

UNIT-10

Techniques of Spectroscopy

Course Design Committee

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ISBN :

Printed and Published by Vinay Kumar, Registrar, Uttar Pradesh Rajarshi Tandon Open University, 2023.

Printed By : Chandrakala Universal Pvt. 42/7 Jawahar Lal Neharu Road, Prayagraj.

UNIT-9 TYPES OF SPECTROSCOPY

Structure

9.1 INTRODUCTION

- Spectroscopy is the study of the interaction between light and matter where the absorption and emission of light or other radiation by the matter are studied and measured.

- Spectroscopy mainly deals with the dispersion of light and other radiations that is caused by an object which allows the study of various properties of the object.

- The measurement in spectroscopy is a function of the wavelength of the radiation being observed.

- Spectroscopy has been widely exploited as it allows the determination of composition, physical and electronic structure to be determined of various particles of molecular or atomic levels.

What is a spectrometer?

- The spectrometer is a scientific instrument that is used to measure the variation or differences in various properties caused by an object over a particular range.
- The property observed by a spectrometer varies with the type of spectrometer being used.
- NMR spectrometer measures the variation in nuclear resonance frequencies, mass spectrometer measure the difference in mass to charge ratio whereas an optical spectrometer measures the variation in the electromagnetic radiation.
- Based on the measurement of these variations, different properties of particles can be measured and observed.

What is a spectrophotometer?

- The spectrophotometer is a particular type of spectrometer that measures the interaction (absorption, reflection, scattering) of electromagnetic radiation from a sample or the emission (fluorescence, phosphorescence, electroluminescence) of electromagnetic radiation by various sample.
- It is also termed electromagnetic spectrometer as it deals with the measurement of different properties of light and its interaction with matter.
- These are commonly used in laboratories to measure the concentration of various samples on the basis of total light absorbed by the sample.

What is a spectroscope?

- A spectroscope or optical spectrometer is a device that measures different properties of light over a specific range in the spectrum used for the analysis of various objects.
- The property measured is mostly the intensity of light, although polarization of light is also measured under some conditions.
- Spectroscopes are commonly used in studies regarding astronomy and chemistry for the analysis of various samples.
- Traditionally, prisms were used as spectroscopes, however, nowadays, diffraction gratings, mobile slit, and photodetectors are used.
- These are mostly used to deduce the chemical composition of objects based on the radiation produced by different objects.

What is a spectrograph?

- The spectrograph is a scientific instrument that detects different light and separates them by their wavelength or frequencies which are recorded by multi detectors.
- These are mostly used for obtaining and recording the astronomical spectrum.
- Spectrographs are used for astronomical studies as telescopes.

- In a spectrograph, the light rays transfer into the spectrograph through the telescope which is provided with a mirror that functions to makes all light rays parallel to each other.
- The rays then reach the diffraction grating that disperses the light into different wavelengths which are passed to the detectors for the analysis of the individual wavelengths.
- These are highly useful to analyze the incoming light from various astronomical objects for the analysis of the chemical composition of those objects.

What are spectra?

- Spectra, singular spectrum, in optics, are the colors observed when white light is dispersed through a prism.
- Spectrum refers to the range of various variables associated with light and other waves.
- In light, the electromagnetic spectrum is the most commonly used. The electromagnetic spectrum includes the range of frequencies of electromagnetic radiation that are used to characterize the distribution of electromagnetic radiation absorbed or emitted by an object.
- Besides, the mass spectrum is also used in spectroscopy based on the ion abundance as a function of the mass to charge ratio.
- Electron spectrum is another spectrum used in physics that is the number or intensity of particle beam depending on the particle energy.

9.2 OBJECTIVES

After studying this unit student should able to:

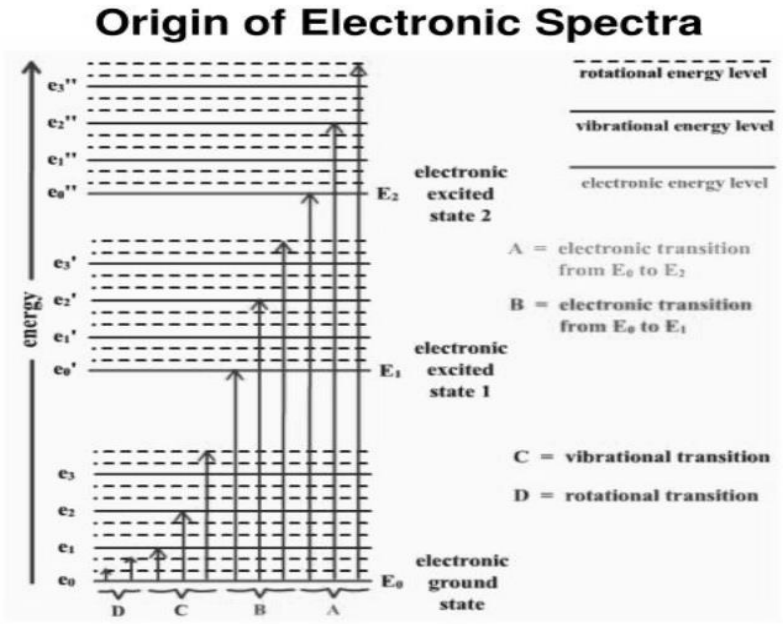
- Know about Spectroscopy.
- Different types of Spectroscopies.
- Discuss Raman effect.
- Explain Stokes and Anti stokes lines.
- Know about selection Rules

9.3 ELECTRONIC SPECTRO

Electron spectroscopy refers to a group formed by techniques based on the analysis of the energies of emitted electrons such as photoelectrons and Auger electrons. This group includes X-ray photoelectron spectroscopy (XPS), which also known as Electron Spectroscopy for Chemical Analysis (ESCA), Electron energy loss spectroscopy (EELS), Ultraviolet photoelectron spectroscopy (UPS), and Auger electron spectroscopy (AES). These analytical techniques are used to identify and determine the elements and their electronic structures from the surface of a test sample. Samples can be solids, gases or liquids.

Electronic Spectroscopy:

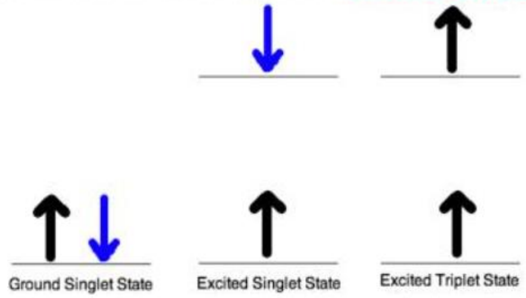
Transition energies between electronic states fall in the range of UV/vis photons. UV/vis or optical or electronic absorption spectroscopy determines the electronic energy levels and, therefore, electronic excited state structure and dynamics. Vibrational energy levels and structures of electronic excited states can be obtained from the Franck-Condon progression. We will also consider cases where the Franck- Condon principle breaks down and vibronic coupling must be taken into account.



ORIGIN OF ELECTRONIC SPECTRA

In the ground state electrons are paired

- If transition of electron from ground state to excited state takes place in such a way that spins of electrons are paired, it is known as **excited singlet state.**
- If electrons have parallel spins, it is known as **excited triplet state.**

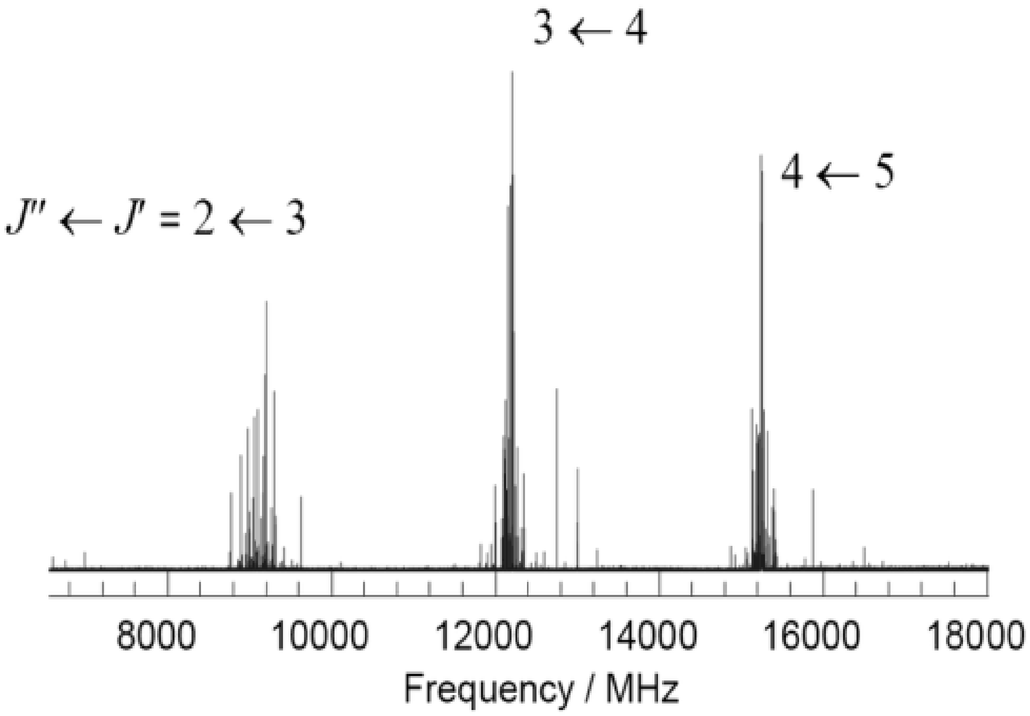


- Excitation of uv light results in excitation of electron from singlet ground state to singlet excited state
- Transition from singlet ground state to excited triplet state is **forbidden** due to symmetry consideration

9.4 ROTATIONAL SPECTRO SCOPY

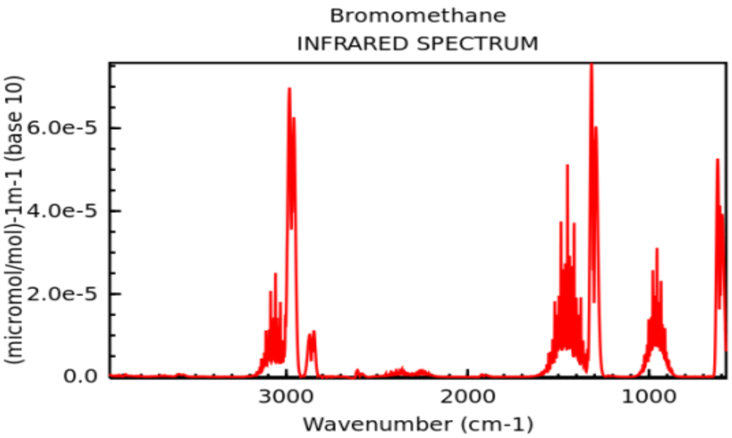
Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy or by far infrared spectroscopy. The rotational spectra of non-polar molecules cannot be observed by those methods, but can be observed and measured by Raman spectroscopy. Rotational spectroscopy is sometimes referred to as *pure* rotational spectroscopy to distinguish it from rotational-vibrational spectroscopy where changes in rotational energy occur together with changes in vibrational energy, and also from ro-vibronic spectroscopy (or just vibronic spectroscopy) where rotational, vibrational and electronic energy changes occur simultaneously.

For rotational spectroscopy, molecules are classified according to symmetry into spherical top, linear and symmetric top; analytical expressions can be derived for the rotational energy terms of these molecules. Analytical expressions can be derived for the fourth category, asymmetric top, for rotational levels up to J=3, but higher energy levels need to be determined using numerical methods. The rotational energies are derived theoretically by considering the molecules to be rigid rotors and then applying extra terms to account for centrifugal distortion, fine structure, hyperfine structure and Coriolis coupling. Fitting the spectra to the theoretical expressions gives numerical values of the angular moments of inertia from which very precise values of molecular bond lengths and angles can be derived in favorable cases. In the presence of an electrostatic field there is Stark splitting which allows molecular electric dipole moments to be determined.



9.5 VIBRATIONAL SPECTROSCOPY

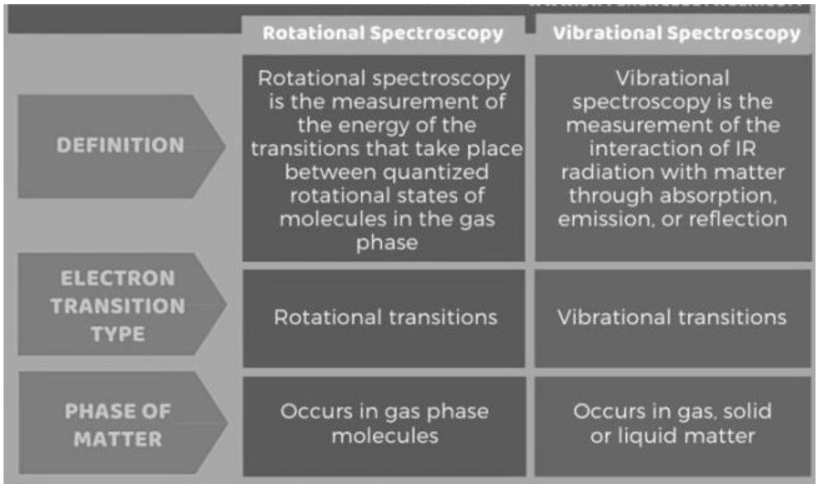
Vibrational spectroscopy is the measurement of the interaction of IR radiation with matter through absorption, emission, or reflection. This spectroscopic technique is useful in studying and identifying chemical substances or functional groups in solid, gas or liquid compounds. Vibrational spectroscopy is governed by vibrational transitions.



The vibrational transition of a molecule refers to the movement of the molecule from one vibrational energy level to another. We can also name it a vibronic transition. This type of transition occurs in between different vibrational levels of the same electronic state. In order to evaluate the vibrational transition of a particular molecule, we should know the dependence of the molecule-fixed components of the electric dipole moment on the molecular deformations. Generally, Raman spectroscopy is based on vibrational transitions.

What is the Difference Between Rotational and Vibrational Spectroscopy?

Rotational spectroscopy and vibrational spectroscopy are governed by electron transitions. The key difference between rotational and vibrational spectroscopy is that rotational spectroscopy is useful to measure the energy of the transitions that take place between quantized rotational states of molecules in the gas phase, whereas vibrational spectroscopy is useful in measuring the interaction of IR radiation with matter through absorption, emission, or reflection.



	Rotational Spectroscopy	Vibrational Spectroscopy
DEFINITION	Rotational spectroscopy is the measurement of the energy of the transitions that take place between quantized rotational states of molecules in the gas phase	Vibrational spectroscopy is the measurement of the interaction of IR radiation with matter through absorption, emission, or reflection
ELECTRON TRANSITION TYPE	Rotational transitions	Vibrational transitions
PHASE OF MATTER	Occurs in gas phase molecules	Occurs in gas, solid or liquid matter

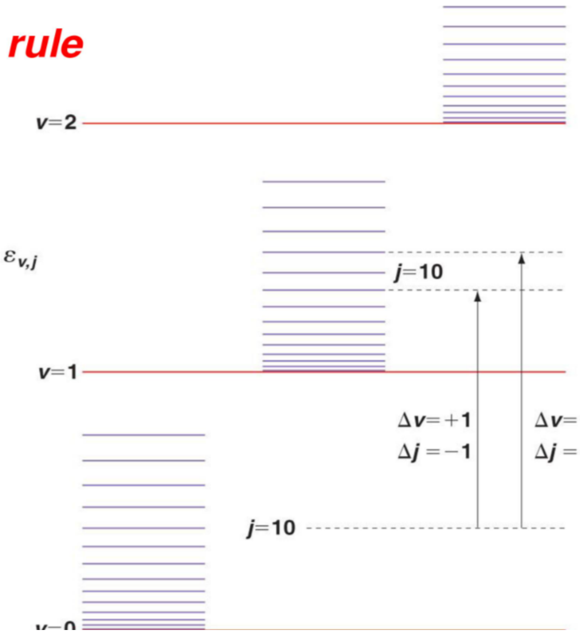
9.6 SELECTION RULES OF VIBRATIONAL SPECTRA

Vibrational selection rule

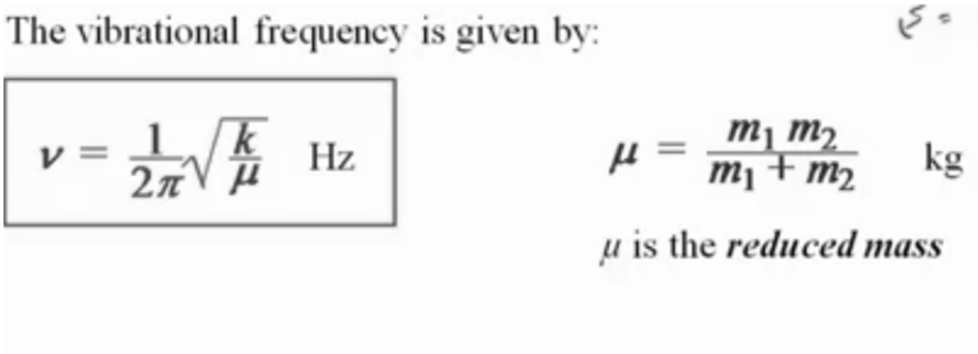
$$\Delta\upsilon = \pm 1$$

$$\Delta\upsilon = +1 \ (absorption)$$

$$\Delta\upsilon = -1 \ (emission)$$



9.7 ENERGY AND FREQUENCY OF VIBRATIONAL SPECTRA

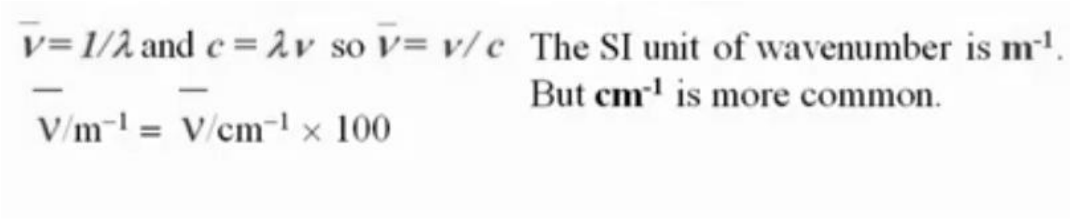


The vibrational frequency is given by:

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{Hz}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{kg}$$

μ is the ***reduced mass***

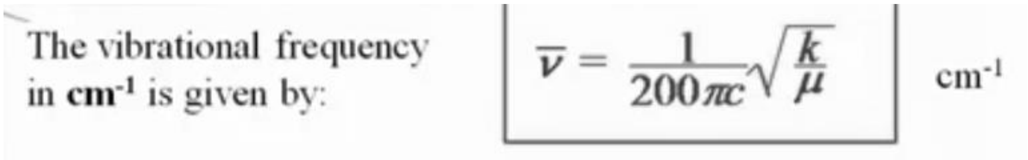
VIBRATION FREQUENCY IN cm^{-1}



$\bar{\nu} = 1/\lambda$ and $c = \lambda\nu$ so $\bar{\nu} = \nu/c$

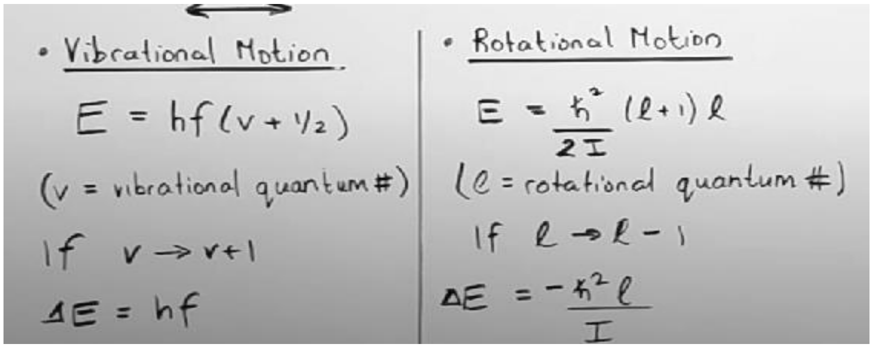
$\bar{\nu}/\text{m}^{-1} = \bar{\nu}/\text{cm}^{-1} \times 100$

The SI unit of wavenumber is m^{-1}. But $\textbf{cm}^{-1}$ is more common.



The vibrational frequency in $\textbf{cm}^{-1}$ is given by:

$$\boxed{\bar{\nu} = \frac{1}{200\pi c}\sqrt{\frac{k}{\mu}}} \quad \text{cm}^{-1}$$



- Vibrational Motion

$E = hf(v + 1/2)$

(v = vibrational quantum #)

If $v \rightarrow v+1$

$\Delta E = hf$

- Rotational Motion

$E = \frac{\hbar^2}{2I}(\ell+1)\ell$

(ℓ = rotational quantum #)

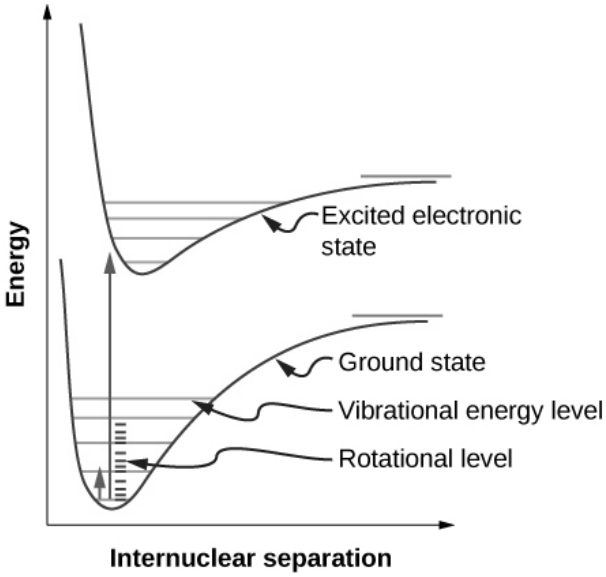
If $\ell \rightarrow \ell - 1$

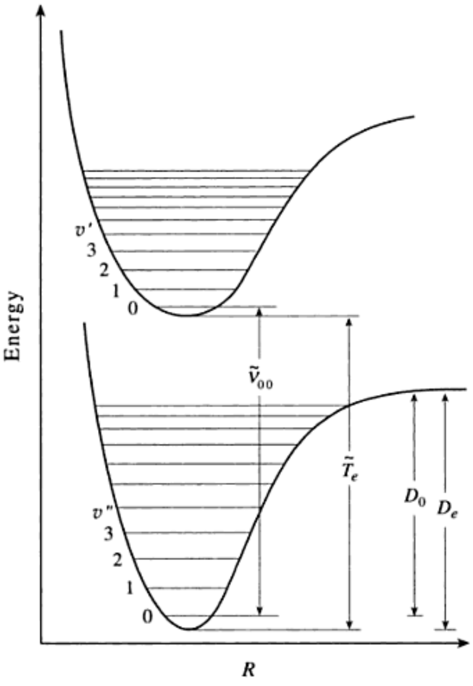
$\Delta E = -\frac{\hbar^2 \ell}{I}$

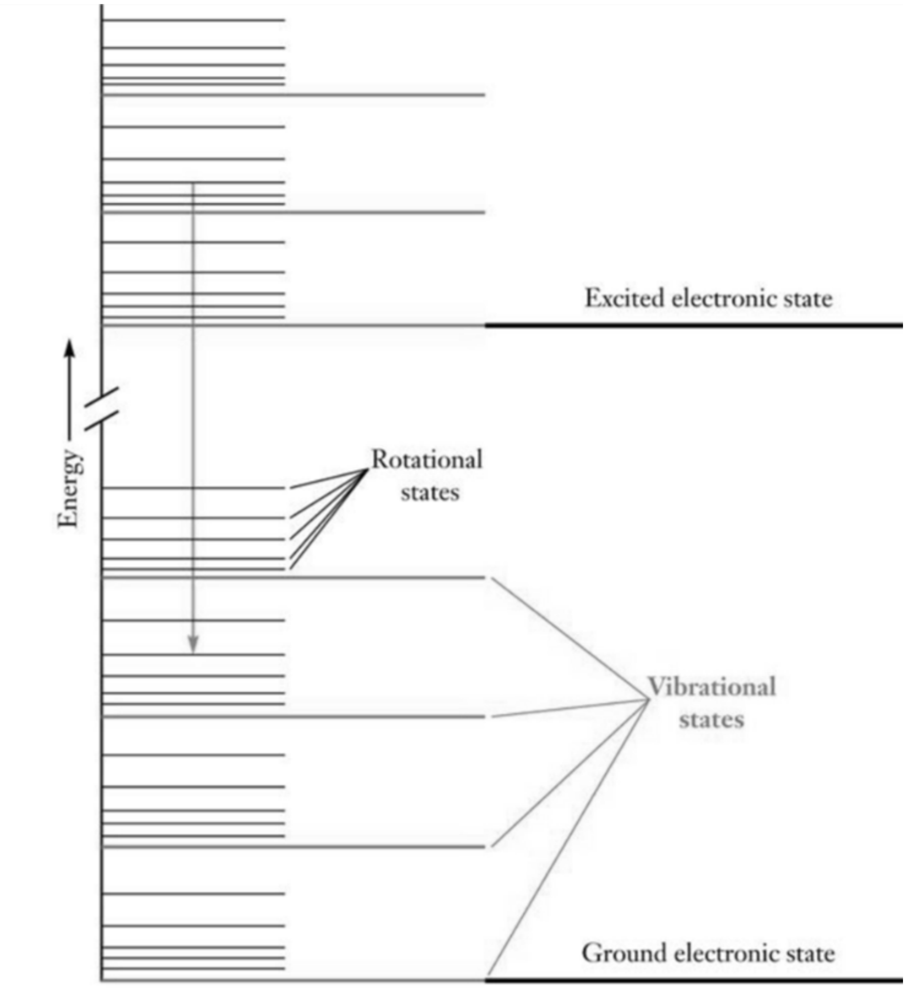
$$\boxed{\Delta E_{total} = hf - \frac{\hbar^2 \ell}{I}}$$

$\Delta \ell = -1$

$\ell \rightarrow \ell - 1$ ($\ell = 1, 2, 3, \dots$)







9.8 SELECTION RULES OF ROTATIONAL SPECTRA

(1) Bohr postulate

$$\Delta\varepsilon = h\nu = hc/\lambda$$

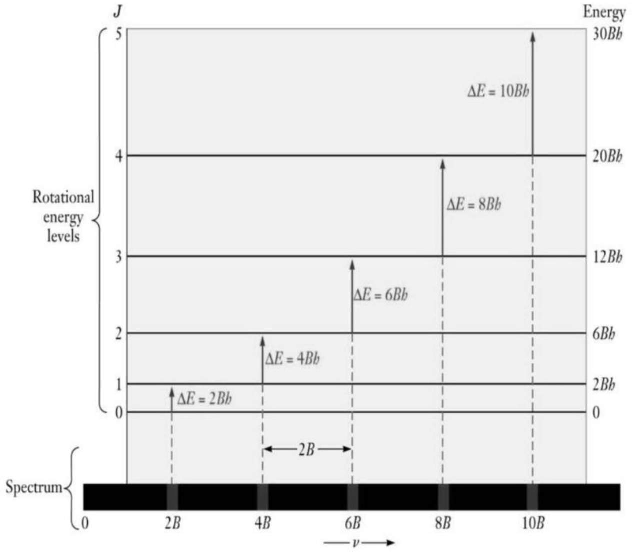
(2) Selection Rule

$\Delta j = \pm 1$

$\Delta j = +1$ (*absorption*)

$\Delta j = -1$ (*emission*)

$$\frac{\Delta\varepsilon_{j,\,j-1}}{hc} = 2Bj$$



9.9 RAMAN EFFECT

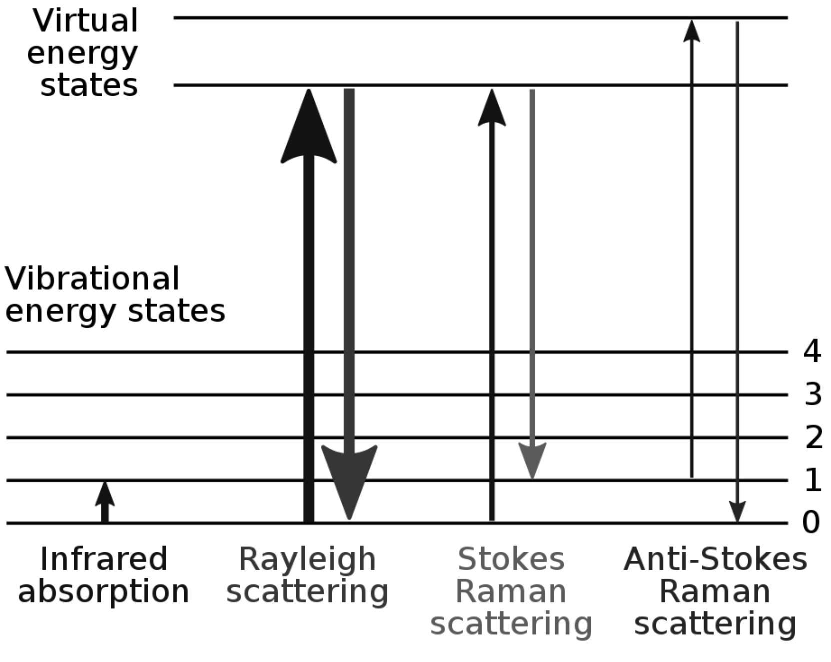
Raman spectroscopy is named after its discoverer 'Sir C.V. Raman', who discovered it in 1928. It is a Chemical analysis technique that provides detailed information about the molecular structure without causing any physical and chemical changes. It studies the vibrational modes along with translational and rotational modes of the molecule. In 1930, 'Sir C.V. Raman' received the Nobel prize in Physics for his work on the scattering of light and the discovery of the Raman effect.

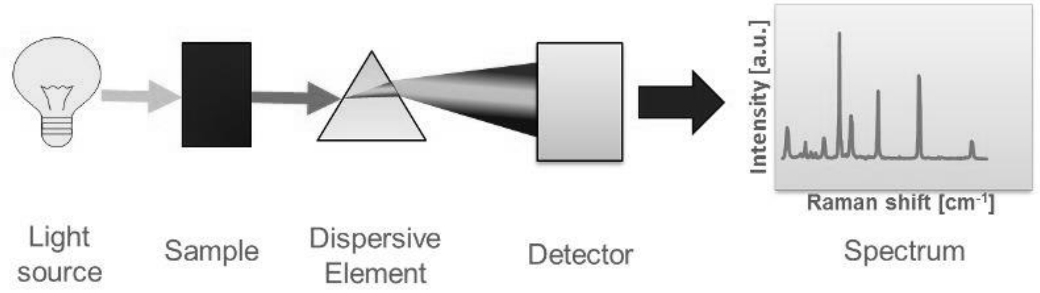
Raman scattering produces scattered photons with a different frequency depending on the source and the vibrational and rotational properties of the scattered molecules. Raman spectroscopy works on the principle of Raman scattering. It is used to study materials by chemists and physicists. In the olden days, to record spectra, a mercury lamp and photographic plates were used; in modern days, lasers are used. Sir CV Raman was awarded the Nobel Prize for Physics in the year 1930. C V Raman, along with his student K S Krishnan, discovered Raman's scattering.

What is Raman Scattering?

Raman scattering is defined as the scattering of photons by excited molecules at higher energy levels. It is also known as the Raman effect. The photons are inelastically scattered, which means that the kinetic energy of an incident particle is either lost or increased and is composed of Stokes and anti-Stokes portions.

Inelastic scattering of photons is similar to the concept of an inelastic collision, which states that the total microscopic kinetic energy is not conserved. In an elastic collision, the transfer of kinetic energy occurs, but the scattering will still be inelastic like in Compton scattering.





Types of Raman Spectroscopy

Following are the types:

1. Resonance Raman Spectroscopy (RRS)
2. Surface-enhanced Raman Spectroscopy (SERS)
3. Micro-Raman Spectroscopy
4. Non-linear Raman Spectroscopic Techniques

Applications of Raman Effect

- Raman amplification: this is based on the Raman scattering where the lower frequency photons are pumped to a high-frequency regime with a surplus amount of energy. This method is applicable to telecommunications.
- Supercontinuum generation: In optics, supercontinuum is formed using the Raman spectra, which results in smooth spectra as the initial spectra are built spontaneously which is later amplified to higher energy.
- Raman spectroscopy works on the basis of Raman effect and finds applications in various fields like in nanotechnology to understand the structure of nanowires, in biology and medicine where the low-frequency DNAs and proteins are studied and chemistry to understand the structure of molecules and their bonds.
- Raman scattering is used in remote sensing and planetary exploration.
- Raman scattering is used to sense the minerals in Mars.

9.10 STOKES AND ANTI STOKES LINES

The lines having frequencies lower than the incident frequency is called stokes lines and the lines having frequencies higher than the incident frequency are called Anti stokes lines.

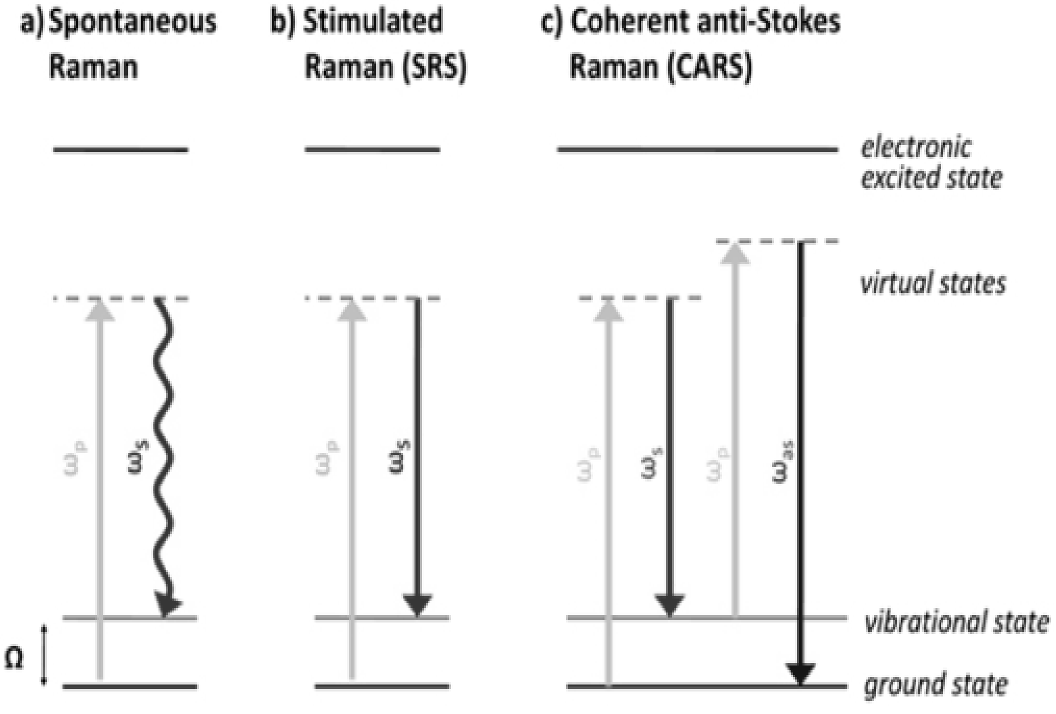
What are Stokes Lines?

Stokes lines represent radiation of particular wavelengths present in the line spectra associated with fluorescence (emission of light from a substance that has absorbed energy previously) and the Raman effect (change in the wavelength of light that happens when a light beam is deflected by molecules). This was named after the 19th-century British physicist Sir George Gabriel Stokes. These stokes lines are typically longer wavelengths than the wavelength of the exciting radiation responsible for fluorescence or the Raman effect.

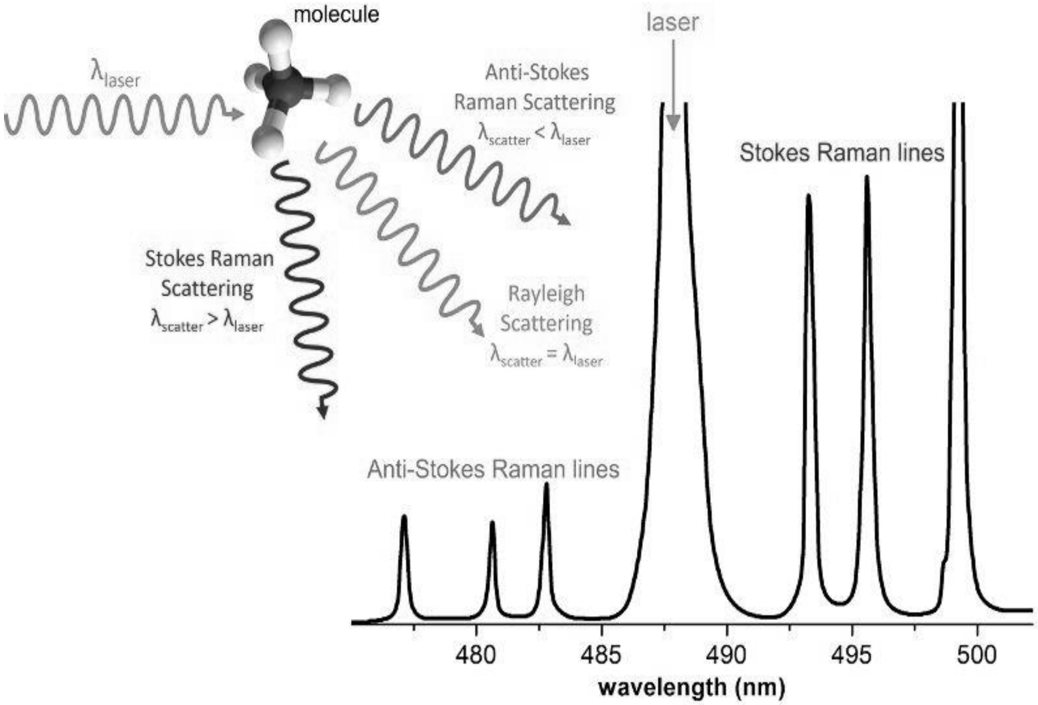
Stokes lines can be described as scattered photons that are reduced in energy relative to the incident photons that can interact with the molecule. Moreover, the reduction of energy of the scattered photons is usually proportional to the energy of vibrational levels of the molecule.

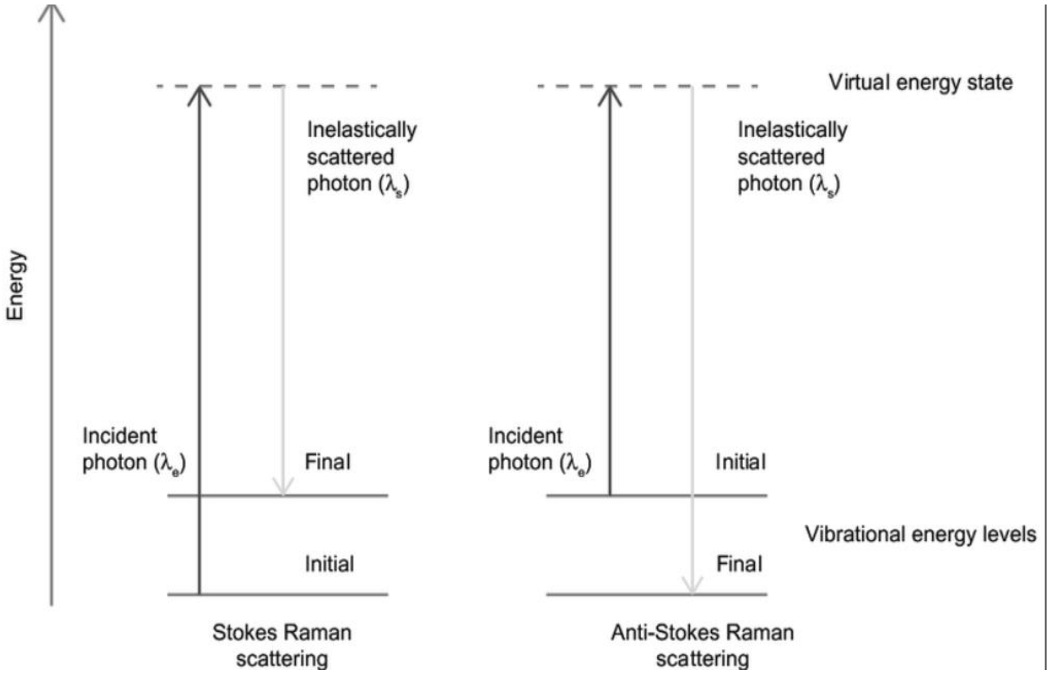
What are Anti-Stokes Lines?

Anti-stokes lines represent the radiation of particular wavelengths present in fluorescence and in Raman spectra when the atoms or molecules of the material exist in an excited state. Therefore, it is the opposite of stokes lines. Here, the radiated line energy gives the sum of the pre-excitation energy and the energy absorbed from the exciting radiation. Therefore, anti-stoke lines typically have a shorter wavelength compared to the light that produces them. Moreover, the difference between the frequency of the emitted light and absorbed light can be named the Stokes shift.



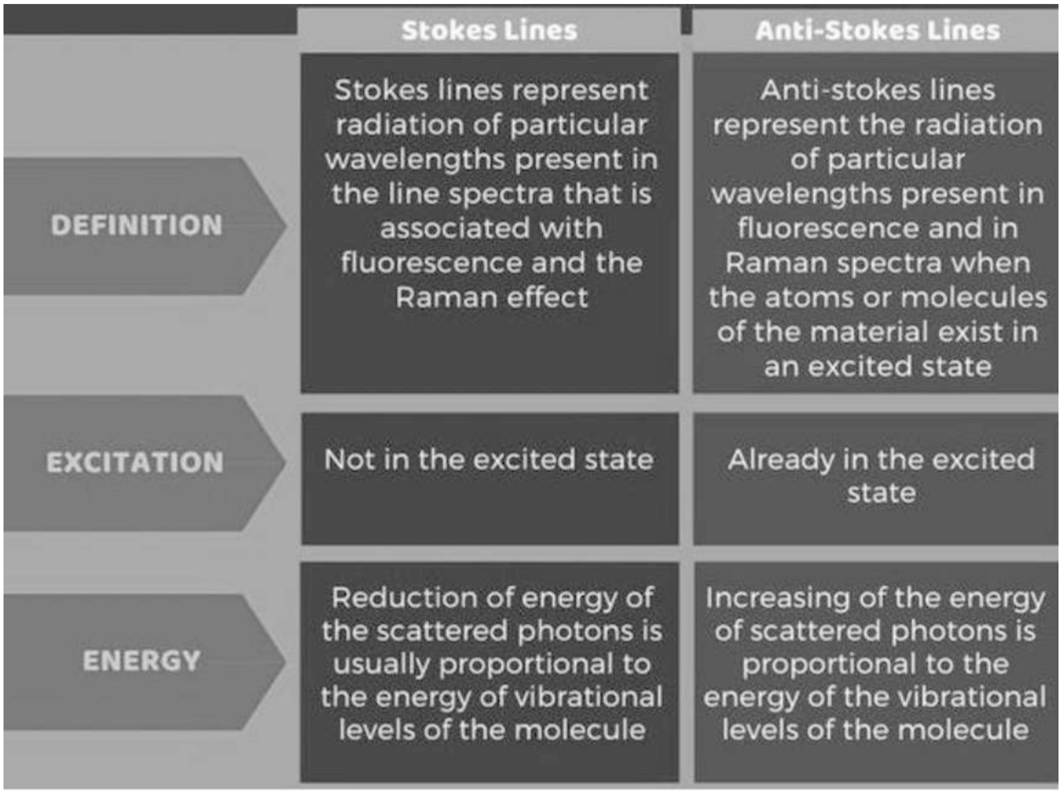
Raman spectroscopy works on the principle of Raman scattering. When a monochromatic radiation incident on the sample, the radiation gets reflected, absorbed, or scattered. The scattered light photons have a different frequency from the incident photon because of the change in the vibrational and rotational properties of the molecules, which results in the change of wavelength of the incident and the scattered light. This change in the frequencies of the incident photon and the scattered photon is known as the Raman shift. When the scattered photon has less energy, hence a longer wavelength than the incident photon, it is called Stokes scattering. When the scattered photon has more energy, hence a shorter wavelength than the incident photon, it is called anti-stokes scattering.





What is the Difference Between Stokes and Anti-Stokes Lines?

The terms Stokes lines and anti-stokes lines are important in spectroscopic detections. The key difference between stokes and anti-stokes lines is that stokes lines have a longer wavelength than the wavelength of exciting radiation that is responsible for the fluorescence or Raman effect, whereas Anti-stokes lines occur in fluorescence or Raman spectra when atoms or molecules are already in an excited state. While stokes lines are not in the excited state, anti-stokes lines are already in the excited state.



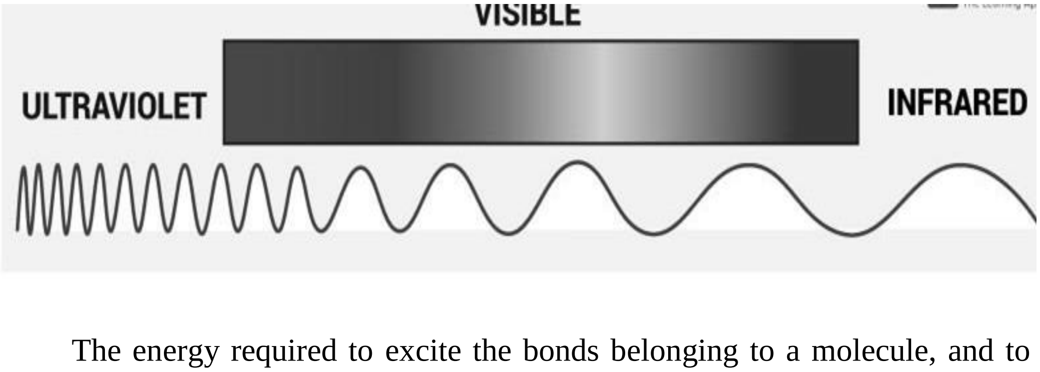
	Stokes Lines	Anti-Stokes Lines
DEFINITION	Stokes lines represent radiation of particular wavelengths present in the line spectra that is associated with fluorescence and the Raman effect	Anti-stokes lines represent the radiation of particular wavelengths present in fluorescence and in Raman spectra when the atoms or molecules of the material exist in an excited state
EXCITATION	Not in the excited state	Already in the excited state
ENERGY	Reduction of energy of the scattered photons is usually proportional to the energy of vibrational levels of the molecule	Increasing of the energy of scattered photons is proportional to the energy of the vibrational levels of the molecule

9.11 INFRARED SPECROSCOPY

Infrared spectroscopy, also termed vibrational spectroscopy, is a technique that utilizes the interaction between infrared and the sample.

An IR spectrum is essentially a graph plotted with the infrared light absorbed on the Y-axis against. frequency or wavelength on the X-axis. An illustration highlighting the different regions that light can be classified into is given below.

IR Spectroscopy detects frequencies of infrared light that are absorbed by a molecule. Molecules tend to absorb these specific frequencies of light since they correspond to the frequency of the vibration of bonds in the molecule.



The energy required to excite the bonds belonging to a molecule, and to make them vibrate with more amplitude, occurs in the Infrared region. A bond will only interact with the electromagnetic infrared radiation, however, if it is polar.

The presence of separate areas of partial positive and negative charge in a molecule allows the electric field component of the electromagnetic wave to excite the vibrational energy of the molecule.

The change in the vibrational energy leads to another corresponding change in the dipole moment of the given molecule. The intensity of the absorption depends on the polarity of the bond. Symmetrical non-polar bonds in N≡N and O=O do not absorb radiation, as they cannot interact with an electric field.

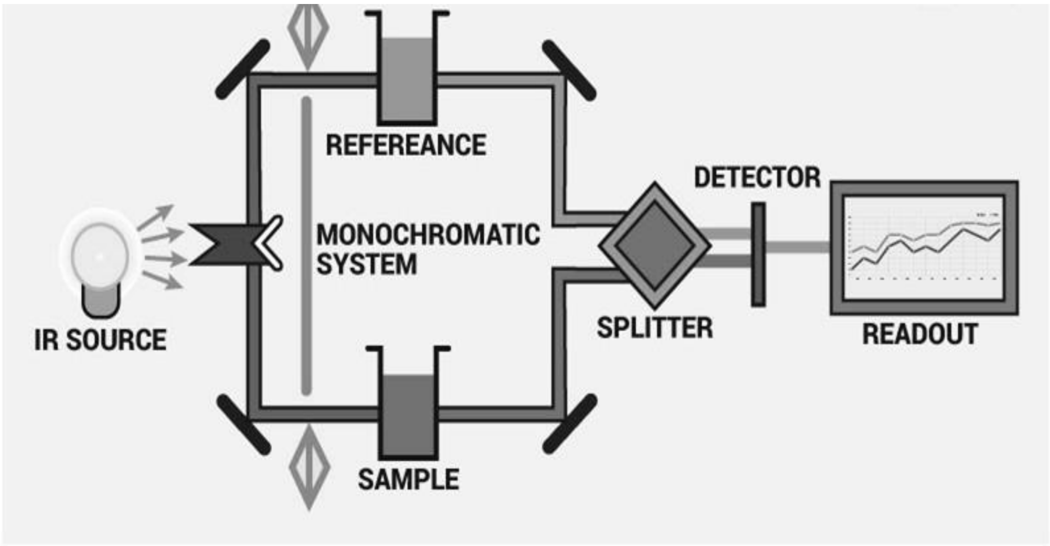
Regions of the Infrared spectrum

Most of the bands that indicate what functional group is present are found in the region from 4000 cm^{-1} to 1300 cm^{-1}. Their bands can be identified and used to determine the functional group of an unknown compound.

Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from 1300 cm^{-1} to 400 cm^{-1}. These bands are only used to compare the spectra of one compound to another.

IR Spectroscopy Instrumentation

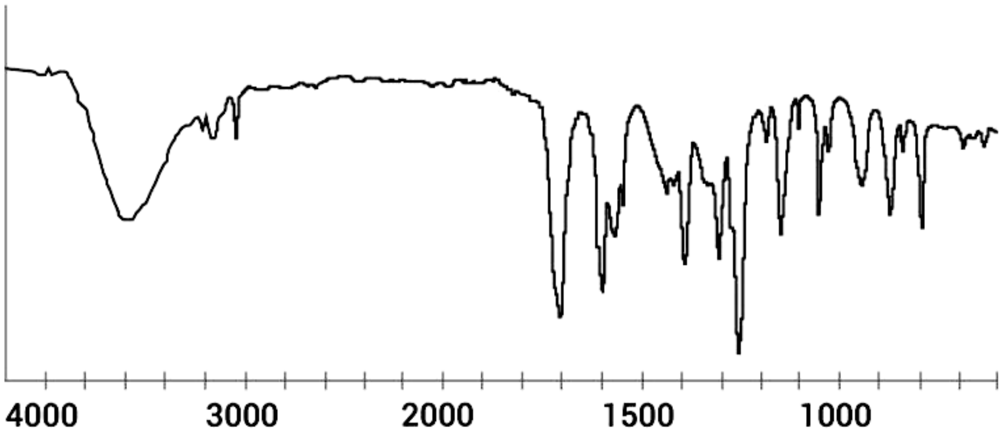
The instrumentation of infrared spectroscopy is illustrated below. First, a beam of IR light from the source is split into two and passed through the reference and the sample respectively.



Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.

Graph of the IR spectrum

Given below is a sample of typical Infrared Absorption Frequencies.



Thus, IR spectroscopy involves the collection of absorption information and its analysis in the form of a spectrum.

Principle of IR spectroscopy/ Vibrational spectroscopy

- The wavelength utilized for the analysis of organic compounds ranges from 2,500 to 16,000 nm, with a corresponding frequency range from 1.9×10^{13} to 1.2×10^{14} Hz.
- These rays don't have enough energy to excite the electrons, but they do, however, cause the vibrational excitation of covalently bonded atoms or groups.
- The vibration observed in the atoms is characteristic of these atoms and thus helps in the detection of the molecules.
- The infrared spectrum is the fundamental measurement obtained in infrared spectroscopy.
- The spectrum is a plot of measured infrared intensity versus wavelength (or frequency) of light.
- IR Spectroscopy measures the vibrations of atoms, and based on this; it is possible to determine the functional groups.

Steps of IR spectroscopy/ Vibrational spectroscopy

- The IR spectrometer is turned on and allowed to warm up for 30 minutes.
- The unknown sample is taken, and its appearance is recorded.
- The background spectrum is collected to remove the spectrum obtained from natural reasons.
- A small amount of sample is placed under the probe by using a metal spatula.
- The probe is set in place by twisting it.
- The IR spectrum of the unknown sample is obtained. The process is repeated, if necessary, to get a good quality spectrum.
- The absorption frequencies that indicate the functional groups present are recorded.
- The obtained spectrum is analyzed to determine the probable identification of the unknown sample.

Uses of IR spectroscopy/ Vibrational spectroscopy

- Infrared spectroscopy has been widely used for the characterization of proteins and the analysis of various solid, liquid, and gaseous samples.

- IR spectroscopy can be used for the detection of functional groups which helps in the identification of molecules and their composition.
- Applications of IR spectroscopic techniques allow identifying molecular changes due to bodily changes, understanding of the molecular mechanism of various diseases, and identifying specific spectral biomarkers that can be used in diagnosis.

9.12 FLUORESCENCE SPECTRO SCOPY

Fluorescence spectroscopy is a type of electromagnetic spectroscopy that utilizes the fluorescence produced by objects in a sample which is not necessarily in the visible range of the spectrum.

Principle of Fluorescence spectroscopy

- The principle of fluorescence spectroscopy is similar to emission spectroscopy, where the transition of electrons from one state to another causes the emission spectrum.
- Fluorescence is an emission phenomenon where a transition from a higher to a lower energy state is accompanied by radiation.
- Only molecules in their excited forms can emit fluorescence; thus, they have to be brought into a higher energy state prior to the emission phenomenon.
- The emitted radiation appears as a band spectrum because there are many closely related wavelength values dependent on the vibrational and rotational energy levels attained.
- The fluorescence spectrum of a molecule is independent of the wavelength of the exciting radiation and has a mirror image relationship with the absorption spectrum.
- The probability of the transition from the electronic excited to the ground state is proportional to the intensity of the emitted light.
- The fluorescence properties of a molecule are determined by features of the molecule itself and thus help in the determination of the composition of the molecules.

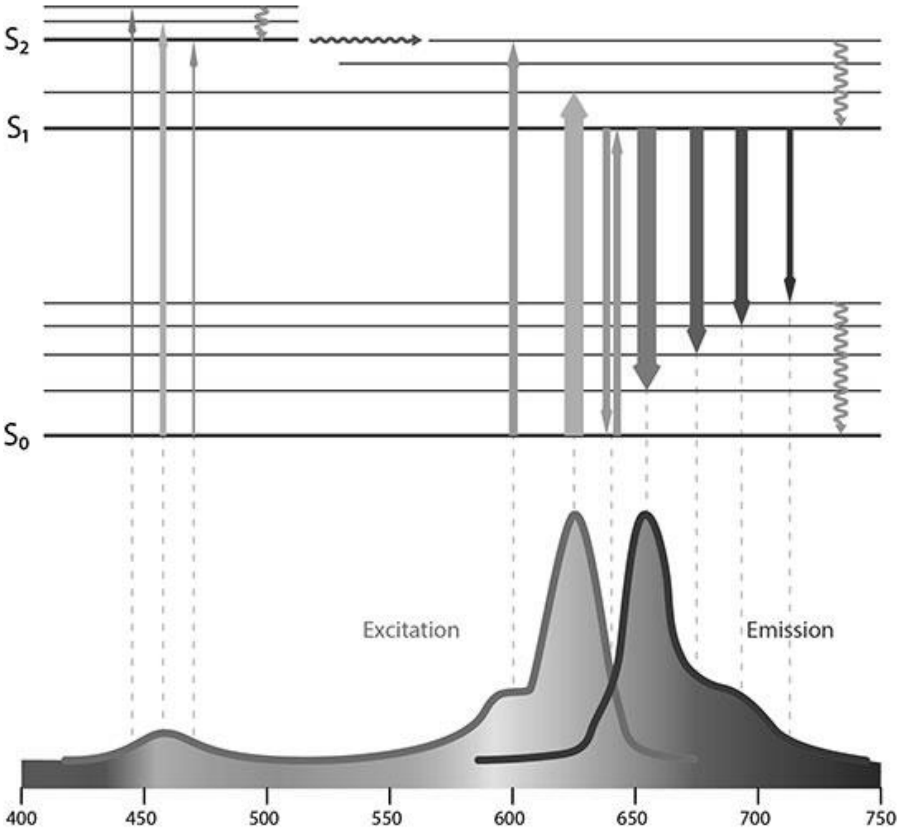
Steps of Fluorescence spectroscopy

- Two samples of known and unknown concentrations are taken in a transport vessel, also termed as a cuvette.
- The vessels are then placed, one after the other, in the spectrofluorometers that is provided with light source and detectors.
- The spectrofluorometers is operated that passes light of a particular wavelength through the sample.
- The photosensitive detectors present in the spectrophotometer detect the light passing through the sample, which is then converted into digital values.
- A graph of the fluorescence measured against the concentration of the sample is plotted, which can then be used for the determination of the unknown concentration of the sample.

Uses of Fluorescence spectroscopy

- Fluorescence spectroscopy is used in biomedical, medical, and chemical research for the analysis of organic compounds.

- This has also been used to differentiating malignant tumors from benign tumors.
- Atomic fluorescence spectroscopy can also be used for the detection of metals in various environmental samples like air, water, and soil.
- In analytical chemistry, fluorescence detectors are used along with **HPLC**.



The probability by which excitation and emission events occur at different wavelengths (depicted by arrow width) define the fluorescence spectra of a molecule.

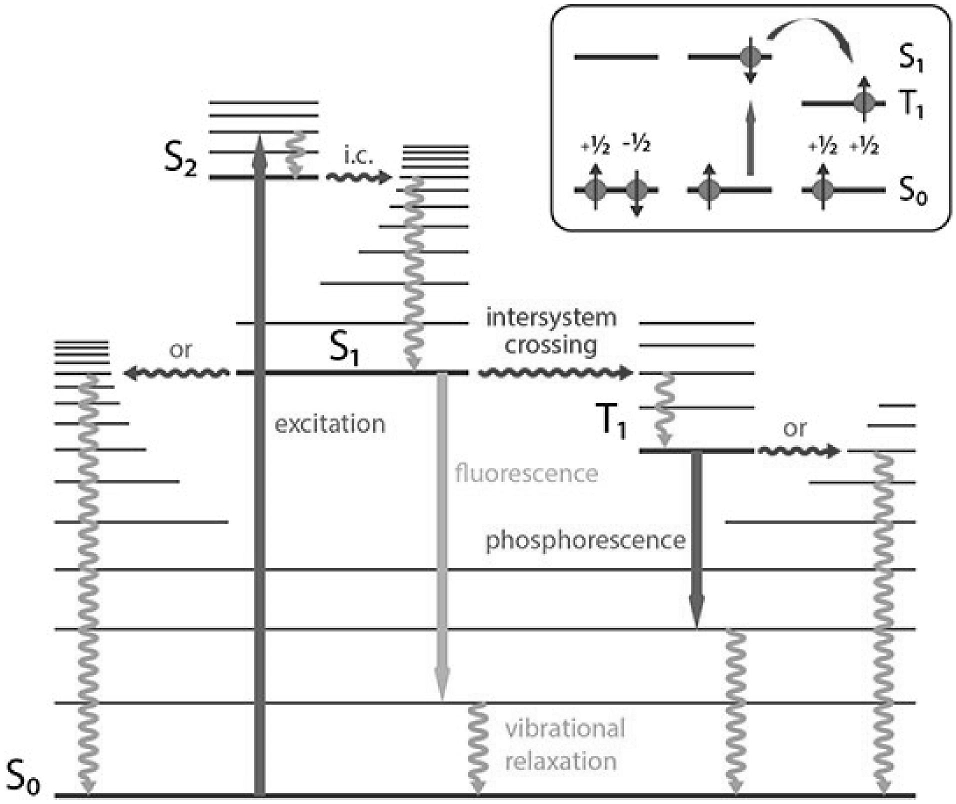
9.13 PHOSPHORESCENCE SPECTRO SCOPY

What is Phosphorescence?

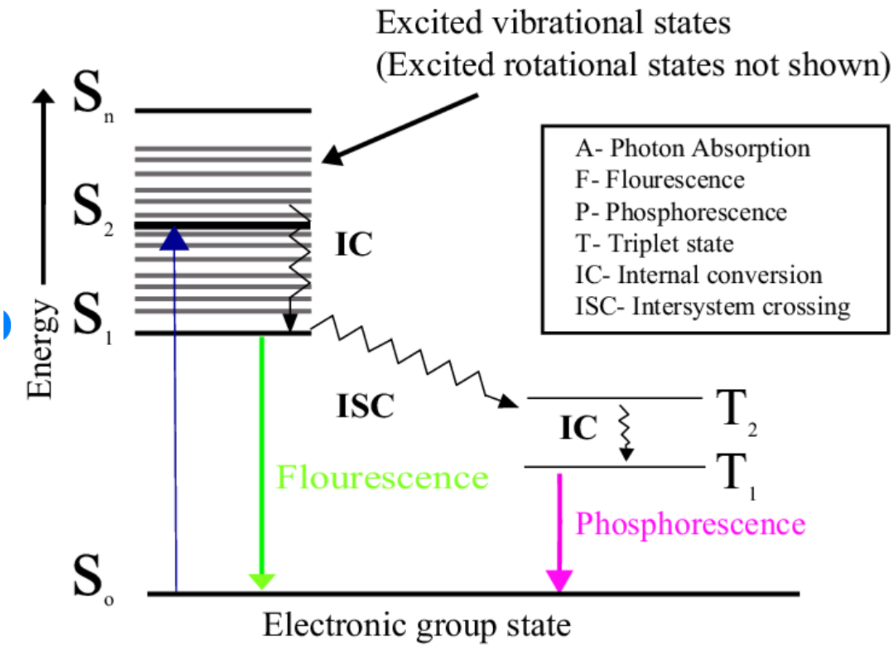
When molecules absorb light and go to the excited state, they have two options. They can either release energy and come back to the ground state immediately or undergo other non-radiative processes. If the excited molecule undergoes a non-radiative process, it emits some energy and come to a triplet state where the energy is somewhat lesser than the energy of the exited state, but it is higher than the ground state energy. Molecules can stay a bit longer in this less energy triplet state.

Unlike fluorescence, after excitation of a molecule, the excited electron first undergoes an intersystem crossing into a triplet state. In some cases an electron in a singlet excited state is transformed to a triplet excited state (the initial spin of the electron in its ground state is flipped in the opposite direction) in which its spin is no longer paired with the ground state. This means that the release of light from this excited state will now require a “spin-forbidden” transition from this triplet state to the singlet state. Emission between a triplet excited state and a singlet ground state—or between any two energy levels that differ in their respective spin states–is called *phosphorescence*. This type of emission process is much less likely to occur and is slower than the singlet-to-singlet transitions that led to light emission in fluorescence. Because the average lifetime for phosphorescence ranges from 10^{-4} – 10^{4} s (in the range of microseconds to minutes), phosphorescence may continue for some time after removing the excitation source. **A spectroscopic technique that utilizes phosphorescence to characterize or measure chemicals is called *phosphorescence spectroscopy*.**

As the measurement of phosphorescence requires low-temperature condition, which is usually maintained by liquid nitrogen, it is much more difficult to measure than fluorescence. The reason for the requirement of low temperature is that the lifetime of an excited triplet state (typically, 10^{-4} – 1 s or longer) is much greater than an excited singlet state (10^{-9} – 10^{-8} s). This longer lifetime means the probability of energy loss through collisions and heat loss is also much greater in phosphorescence than in fluorescence. Maintaining low temperatures for this measurement will minimize the molecular motion around the analyte and make its collisions with the solvent or other sample components less likely to occur.

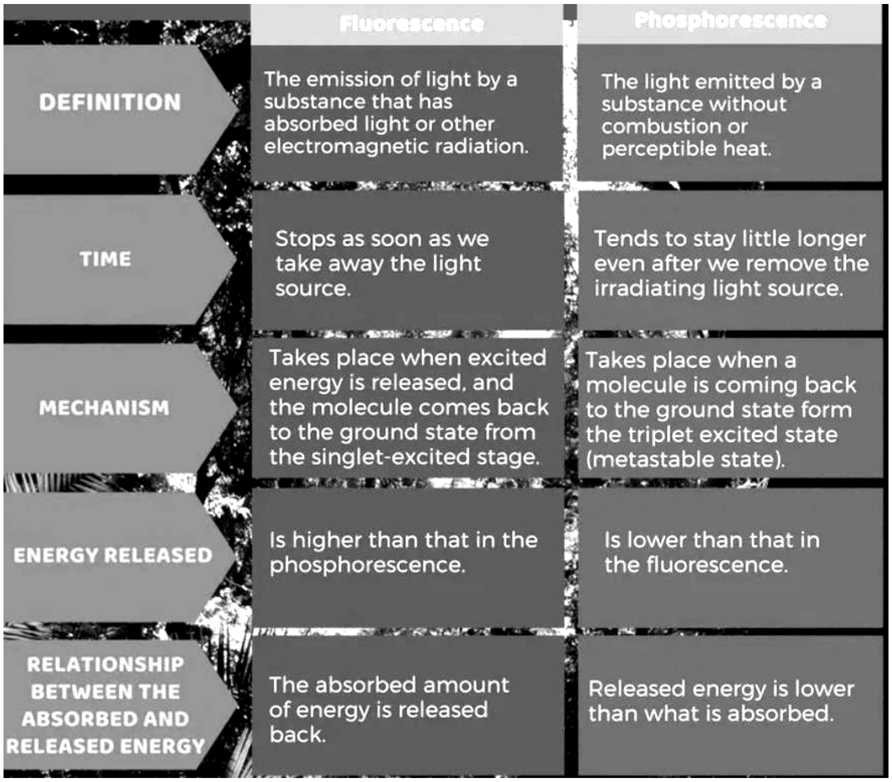


During intersystem crossing into excited triplet state (T1) the spin of the involved electron is flipped. Triplet states are metastable and relaxation by phosphorescence is delayed. The chance of alternative relaxation by non-radiative events defines the quantum yield for both fluorescence and phosphorescence



What is the Difference Between Fluorescence and Phosphorescence?

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation while phosphorescence refers to the light emitted by a substance without combustion or perceptible heat. When we supply light to a sample of molecules, we immediately see the fluorescence. Fluorescence stops as soon as we take away the light source. But phosphorescence tends to stay little longer even after we remove the irradiating light source.

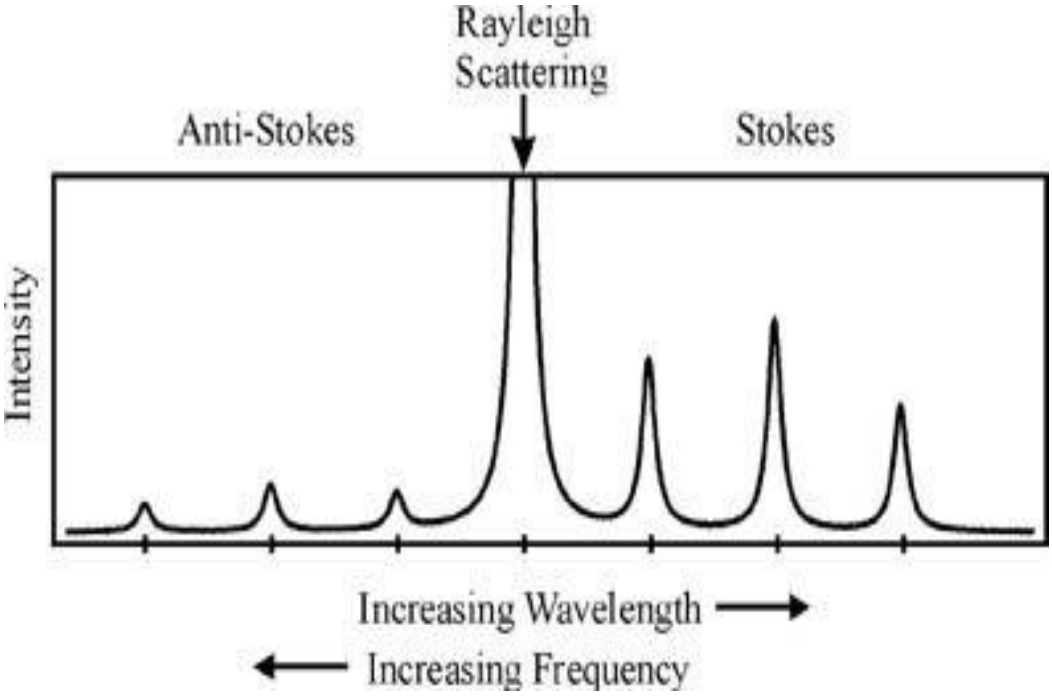


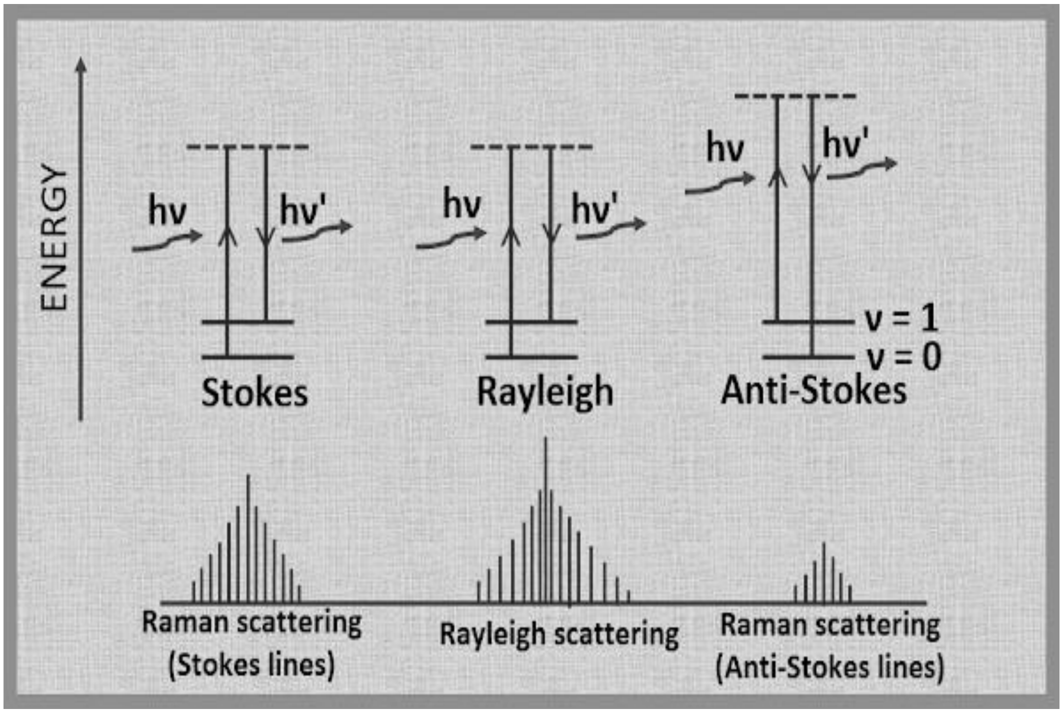
	Fluorescence	Phosphorescence
DEFINITION	The emission of light by a substance that has absorbed light or other electromagnetic radiation.	The light emitted by a substance without combustion or perceptible heat.
TIME	Stops as soon as we take away the light source.	Tends to stay little longer even after we remove the irradiating light source.
MECHANISM	Takes place when excited energy is released, and the molecule comes back to the ground state from the singlet-excited stage.	Takes place when a molecule is coming back to the ground state form the triplet excited state (metastable state).
ENERGY RELEASED	Is higher than that in the phosphorescence.	Is lower than that in the fluorescence.
RELATIONSHIP BETWEEN THE ABSORBED AND RELEASED ENERGY	The absorbed amount of energy is released back.	Released energy is lower than what is absorbed.

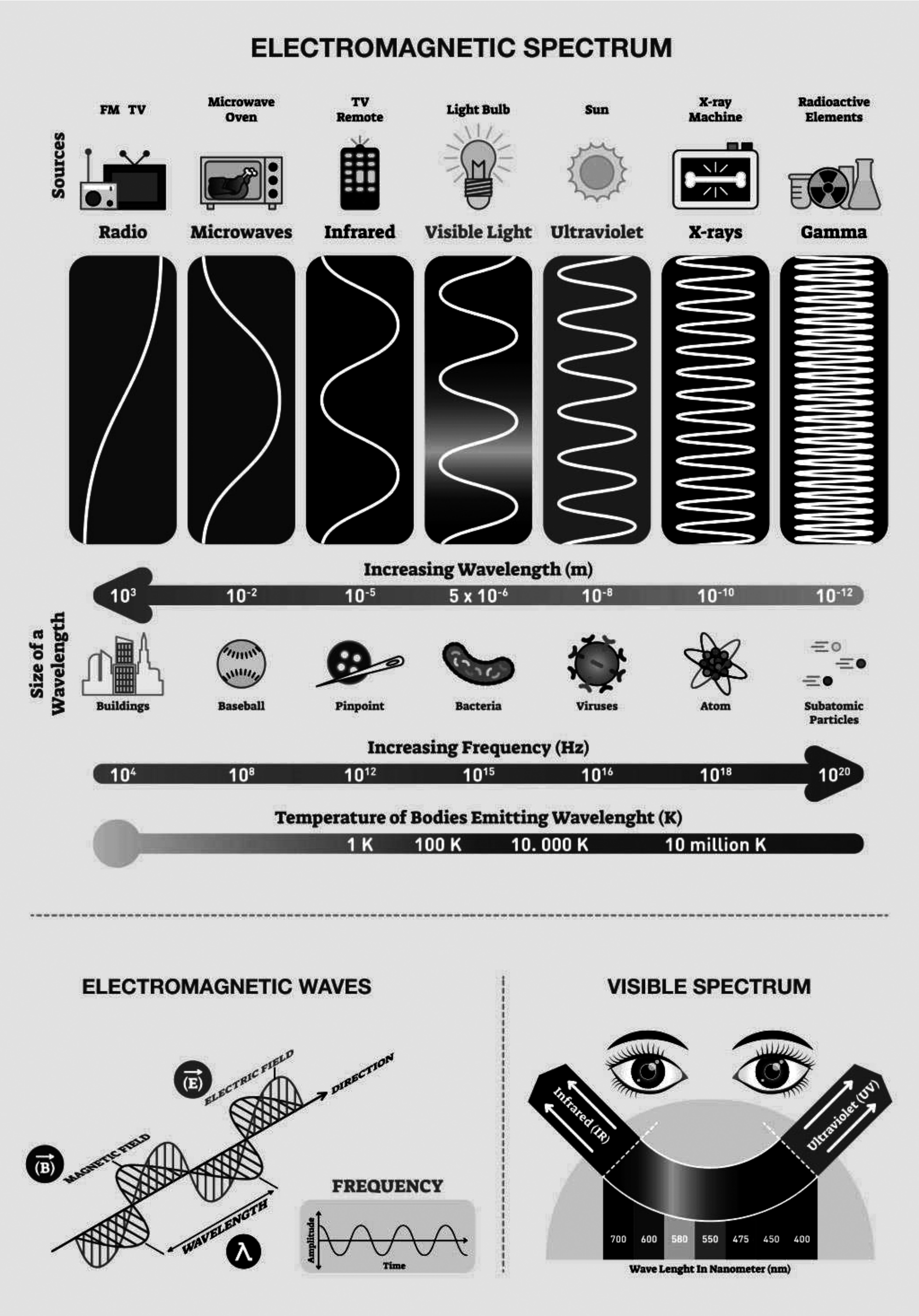
9.14 SUMMARY

In this unit we studied about spectroscopy and its different types.

Stokes lines and anti-stokes lines are also described in this unit. The key difference between stokes and anti-stokes lines is that stokes lines have a longer wavelength than the wavelength of exciting radiation that is responsible for the fluorescence or Raman effect, whereas Anti-stokes lines occur in fluorescence or Raman spectra when atoms or molecules are already in an excited state.







9.15 TERMINAL QUESTIONS

1. Define Rotational Spectroscopy.
2. Explain Raman Effect
3. Discuss Stokes and Anti Stokes Lines

4. Explain Infrared Spectroscopy
5. What is Fluorescence Spectroscopy?

9.16 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. Section 9.4
2. Section 9.9
3. Section 9.10
4. Section 9.11
5. Section 9.12

9.17 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

UNIT-10 TECGNIQUES OF SPECTRO SCOPY

Structure

10.1 INTRODUCTION

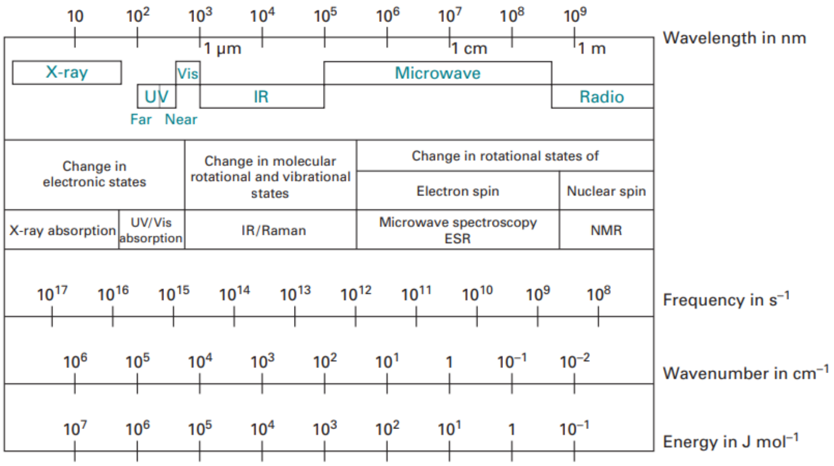
Spectroscopic techniques employ light to interact with matter and thus probe certain features of a sample to learn about its consistency or structure. Light is electromagnetic radiation, a phenomenon exhibiting different energies, and dependent on that energy, different molecular features can be probed. The basic principles of interaction of electromagnetic radiation with matter are treated in this chapter. There is no obvious logical dividing point to split the applications of electromagnetic radiation into parts treated separately. The justification for the split presented in this text is purely pragmatic and based on 'common practice'. The applications considered in this chapter use visible or UV light to probe consistency and conformational structure of biological molecules. Usually, these methods are the first analytical procedures used by a biochemical scientist.

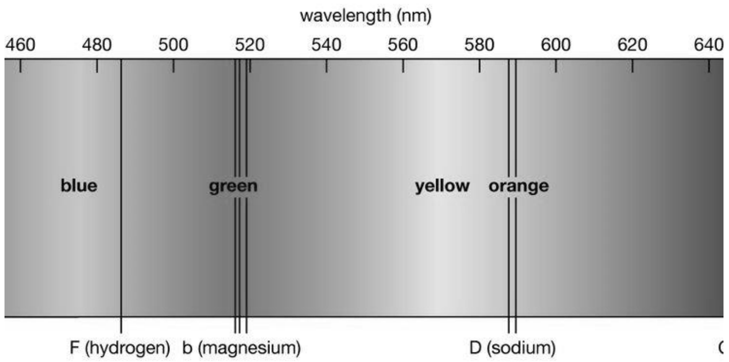
An understanding of the properties of electromagnetic radiation and its interaction with matter leads to an appreciation of the variety of types of spectra and, consequently, different spectroscopic techniques and their applications to the solution of biological problems.

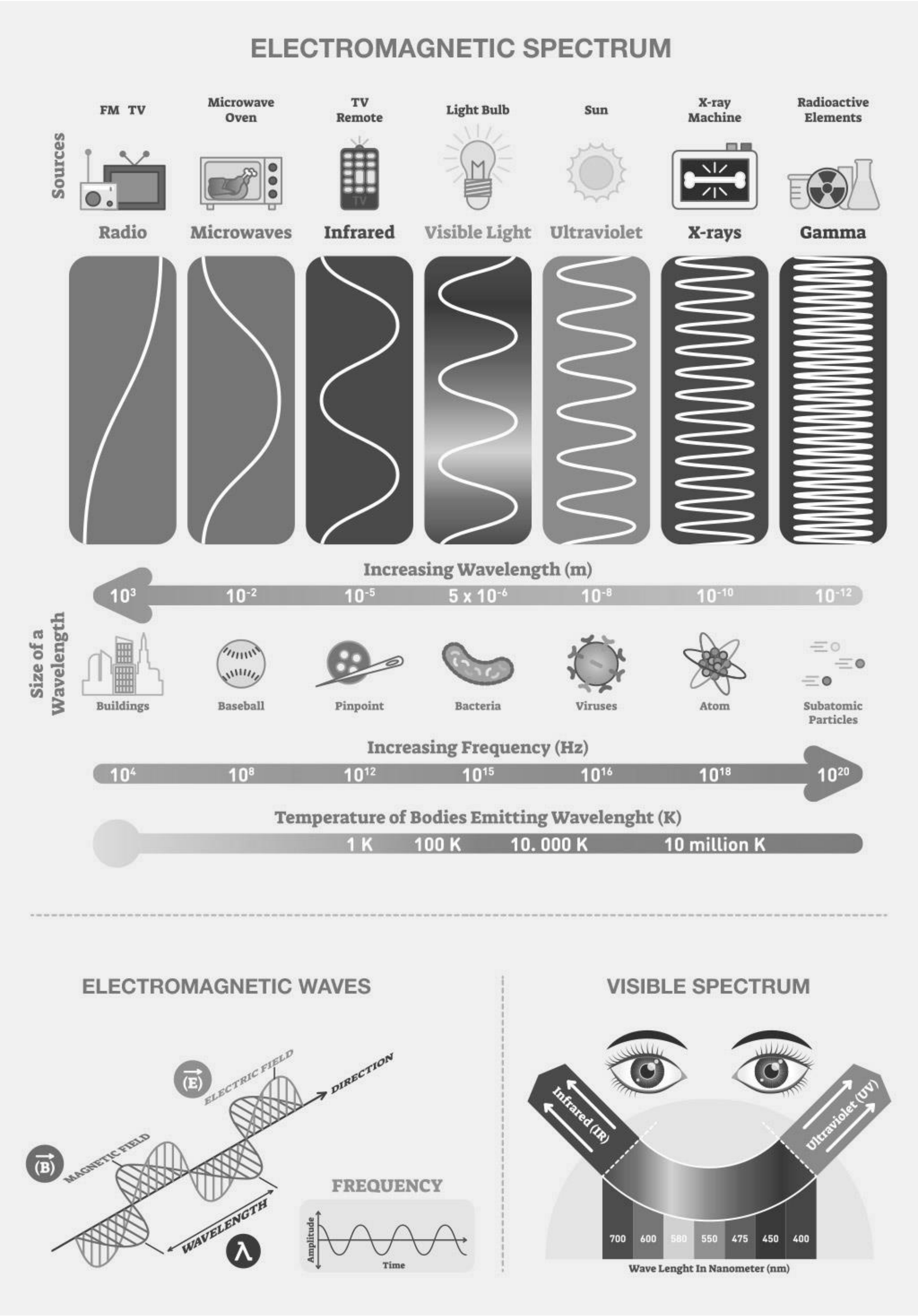
The spectrum of electromagnetic radiation organized by increasing wavelength, and thus decreasing energy, from left to right. Also annotated are the types of radiation and the various interactions with matter and the resulting spectroscopic applications, as well as the interdependent parameters of frequency and wavenumber. Electromagnetic phenomena are explained in terms of quantum mechanics. The photon is the elementary particle responsible for electromagnetic phenomena. It carries the electromagnetic radiation and has properties of a wave, as well as of a particle, albeit having a mass of zero. As a particle, it interacts with matter by transferring its energy E:

$$E = \frac{hc}{\lambda} = h\nu$$

In this unit we will discuss about **spectroscopy,** Study of the absorption and emission of light and other radiation by matter, as related to the dependence of these processes on the wavelength of the radiation. Usually, spectroscopy is devoted to identifying elements and compounds and elucidating atomic and molecular structure by measuring the radiant energy absorbed or emitted by a substance at characteristic wavelengths of the electromagnetic spectrum on excitation by an external energy source. However, spectroscopy also includes the study of particles (e.g., electrons, ions) that have been sorted or otherwise differentiated into a spectrum as a function of some property (such as energy or mass). The instruments used are spectrometers. Experiments involve a light source, a disperser to form the spectrum, detectors (visual, photoelectric, radiometric, or photographic) for observing or recording its details, devices for measuring wavelengths and intensities, and interpretation of the measured quantities to identify chemicals or give clues to the structure of atoms and molecules. Specialized techniques include Raman spectroscopy (*see* Chandrasekhara Venkata Raman), nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), microwave and gamma-ray spectroscopy, and electron spin resonance (ESR).







10.2 OBJECTIVES

After studying this unit, student should able to:

- Know about Electronic Spectra and Electronic Transitions
- Explain Frank-Condon Principles.
- Discuss about NMR.
- Define ESR.

10.3 WHAT IS SPECTROSCOPY?

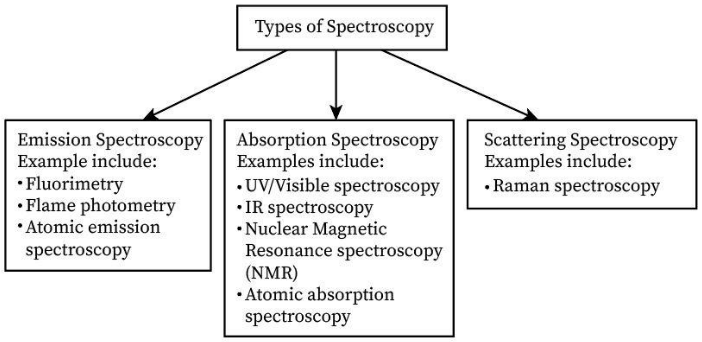
Spectroscopy is the investigation and measurement of spectra produced by matter interacting with or emitting electromagnetic radiation. Originally, spectroscopy was defined as the study of the interaction between radiation and matter as a function of wavelength. Now, spectroscopy is defined as any measurement of a quantity as a function of wavelength or frequency. During a spectroscopy experiment, electromagnetic radiation of a specified wavelength range passes from a source through a sample containing compounds of interest, resulting in absorption or emission. During absorption, the sample absorbs energy from the light source. During emission, the sample emits light of a different wavelength than the source's wavelength.

In absorption spectroscopy, the sample's compounds are excited by the electromagnetic radiation provided by a light source. Their molecules absorb energy from the electromagnetic radiation, become excited, and jump from a low energy ground state to a higher energy state of excitation. A detector, usually a photodiode, on the opposite side of the sample records the sample's absorption of wavelengths, and determines the extent of their absorption. The spectrum of a sample's absorbed wavelengths is known as its absorption spectrum, and the quantity of light absorbed by a sample is its absorbance.

Each molecule within a sample will only absorb wavelengths with energies corresponding to the energy difference of the present transition. In simpler terms, this means that a molecule that jumps from ground state 1 to excited state 2, with an energy difference of ΔE, will allow other wavelengths to pass through until it can absorb radiation from a wavelength that corresponds to ΔE. Light that passes through to the photodiode without any absorption is called Stray Radiant Energy, or stray light. Absorption that occurs due to an energy difference between the two states is called an absorption line, and a collection of absorption lines creates an absorption spectra. The frequency of each absorption line in an absorption spectra tells us about the sample's molecular structure, and can be influenced by factors such as stray light, environmental temperature, and electromagnetic fields.

Types of Spectroscopies

Since spectroscopy deals with the estimation of interaction between electromagnetic radiation and samples; hence, either absorption, emission, or the scattering process is observed, classifying spectroscopy into three types.



Absorption spectroscopy

Absorption spectroscopy is a spectroscopic method of absorbing electromagnetic radiation when the sample and the radiation display interaction. The wavelength or frequency is used as a function. The spectrum obtained from absorption is called an absorption spectrum.

The examples of absorption spectroscopy are as follows:

- Atomic Absorption (AA) Spectroscopy.
- Ultraviolet (UV)/ Visible Spectroscopy.
- Infrared (IR) Spectroscopy.
- Nuclear Magnetic Resonance (NMR) spectroscopy.

Emission spectroscopy

Emission spectroscopy is a spectroscopic method in which atoms/molecules emit photons while undergoing an electronic transition, that is, from a lower to a higher energy state. The photon's wavelength can be captured and examined to discover the sample's composition. The emission and absorption spectra differ from one another as the emission spectra consist of colored lines while the absorption spectra consist of dark lines.

The examples of emission spectroscopy are as follows:

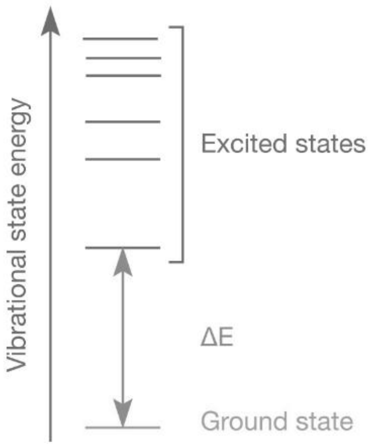
- Atomic Emission (AE) spectroscopy.
- Flame photometry.
- Fluorimetry.

Scattering spectroscopy

Scattering spectroscopy is a spectroscopic method by which a molecule's vibrational and rotational states are attained when light scattering occurs, leading to the excitement of the atoms. It rectifies the groups in the sample, which further helps to detect its composition. This process is the fastest compared to absorption and emission processes.

The example of scattering spectroscopy is as follows:

- Raman Spectroscopy.

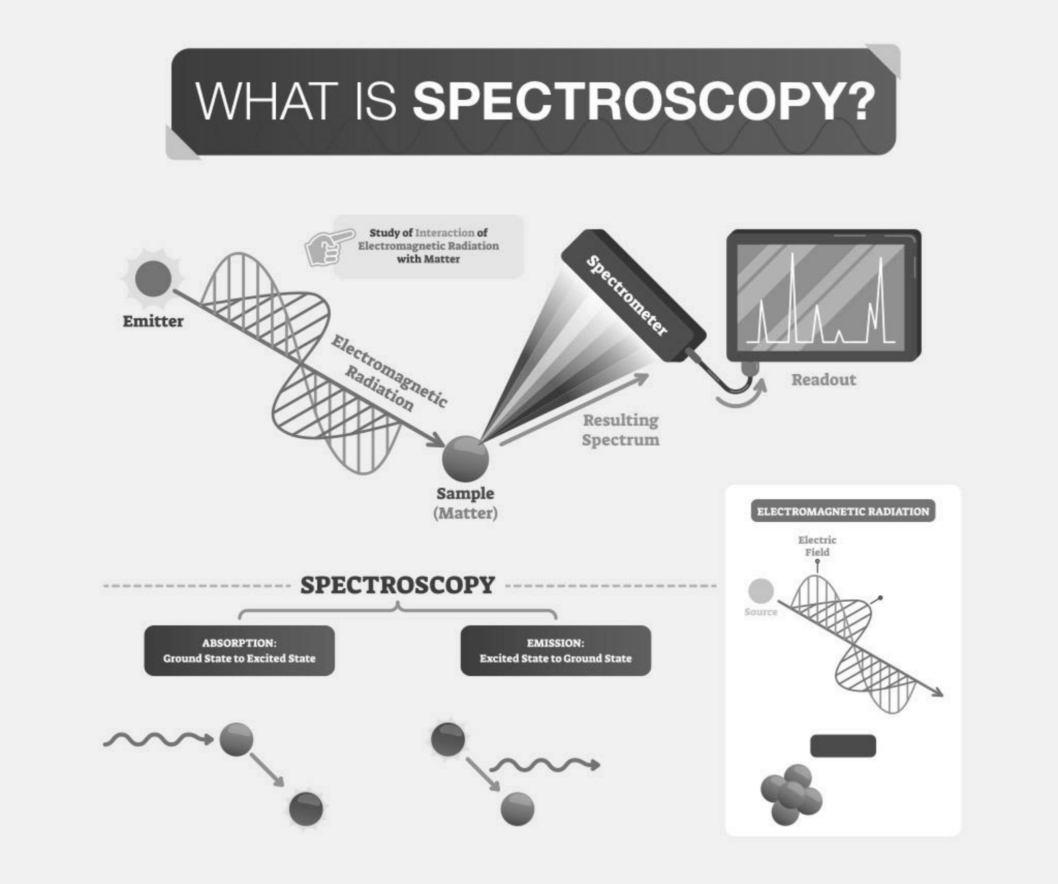


What is Spectroscopy Used For?

Spectroscopy is used in physical and analytical chemistry to detect, determine, or quantify the molecular and/or structural composition of a sample. Each type of molecule and atom will reflect, absorb, or emit electromagnetic radiation in its own characteristic way. Spectroscopy uses these characteristics to deduce and analyze the composition of a sample.

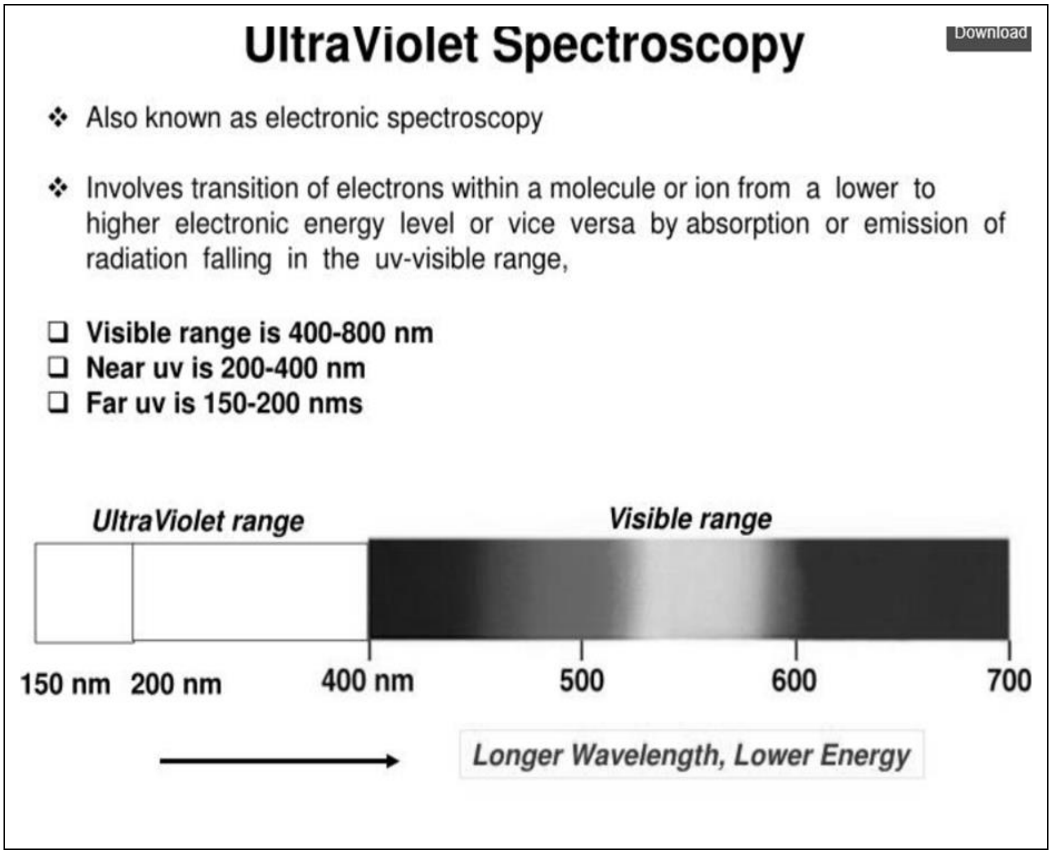
Examples of Spectroscopy Applications

- Determining the atomic structure of a sample
- Determining the metabolic structure of a muscle
- Monitoring dissolved oxygen content in freshwater and marine ecosystems
- Studying spectral emission lines of distant galaxies
- Altering the structure of drugs to improve effectiveness
- Characterization of proteins
- Space exploration
- Respiratory gas analysis in hospitals



10.3.1 ELECTRONIC SPECTRA

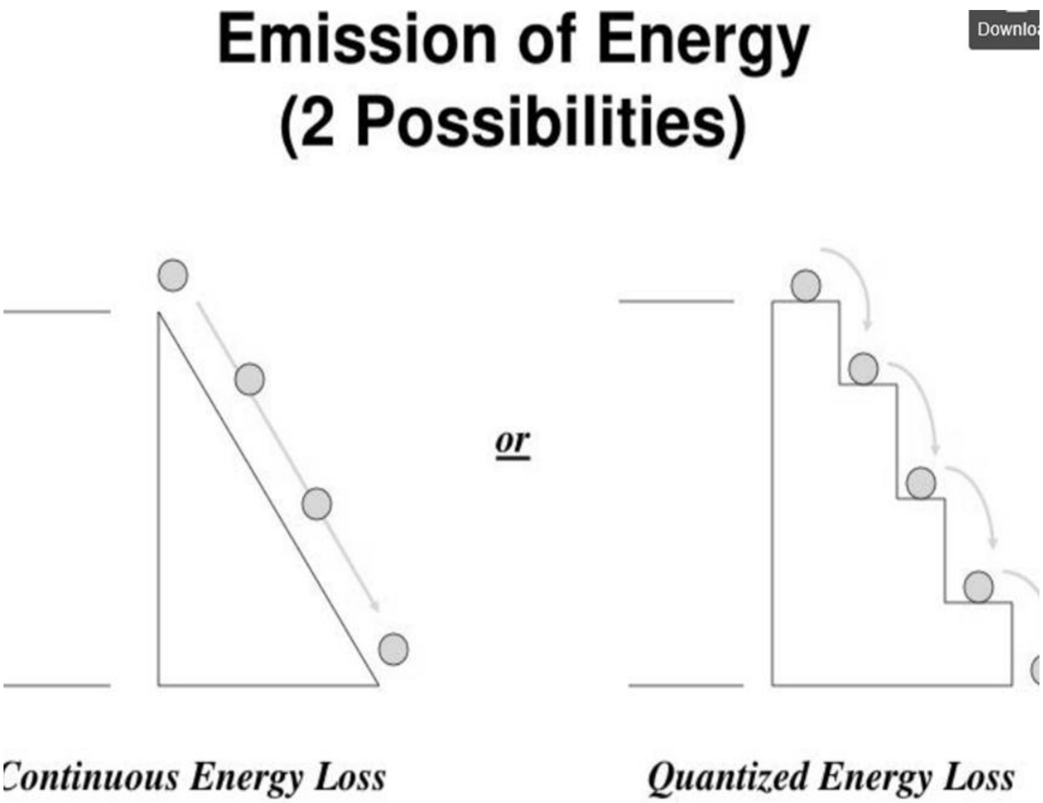
Electron spectroscopy is **an analytical technique to study the electronic structure and its dynamics in atoms and molecules**. In general, an excitation source such as x-rays, electrons or synchrotron radiation will eject an electron from an inner-shell orbital of an atom.



UltraViolet Spectroscopy

- ❖ Also known as electronic spectroscopy
- ❖ Involves transition of electrons within a molecule or ion from a lower to higher electronic energy level or vice versa by absorption or emission of radiation falling in the uv-visible range,

- ☐ **Visible range is 400-800 nm**
- ☐ **Near uv is 200-400 nm**
- ☐ **Far uv is 150-200 nms**



Emission of Energy (2 Possibilities)

Emission of Energy

Continuous Energy Loss

- Any and all energy values possible on way down
- Implies electron can be anywhere about nucleus of atom

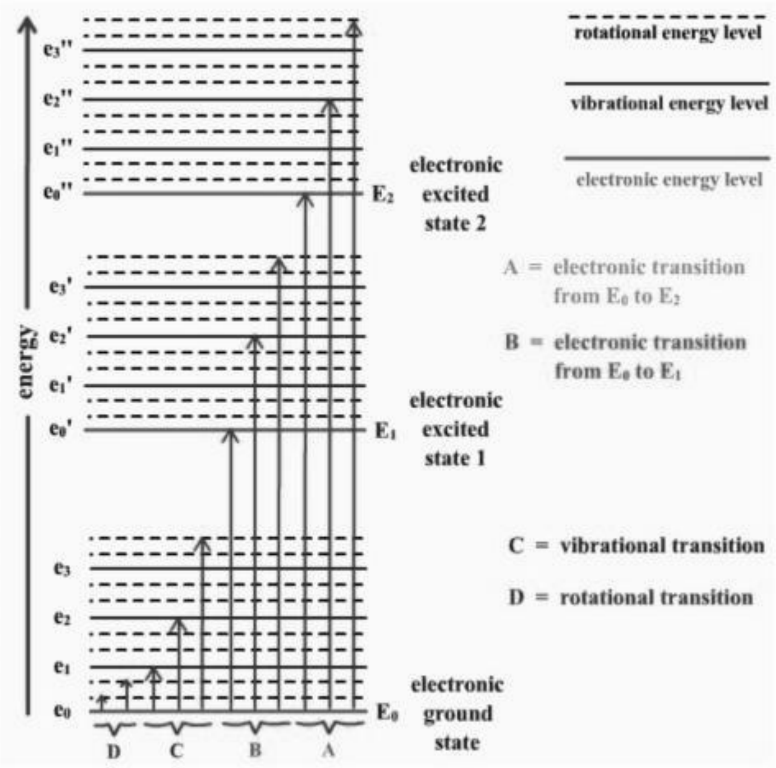
➢ Continuous emission spectra

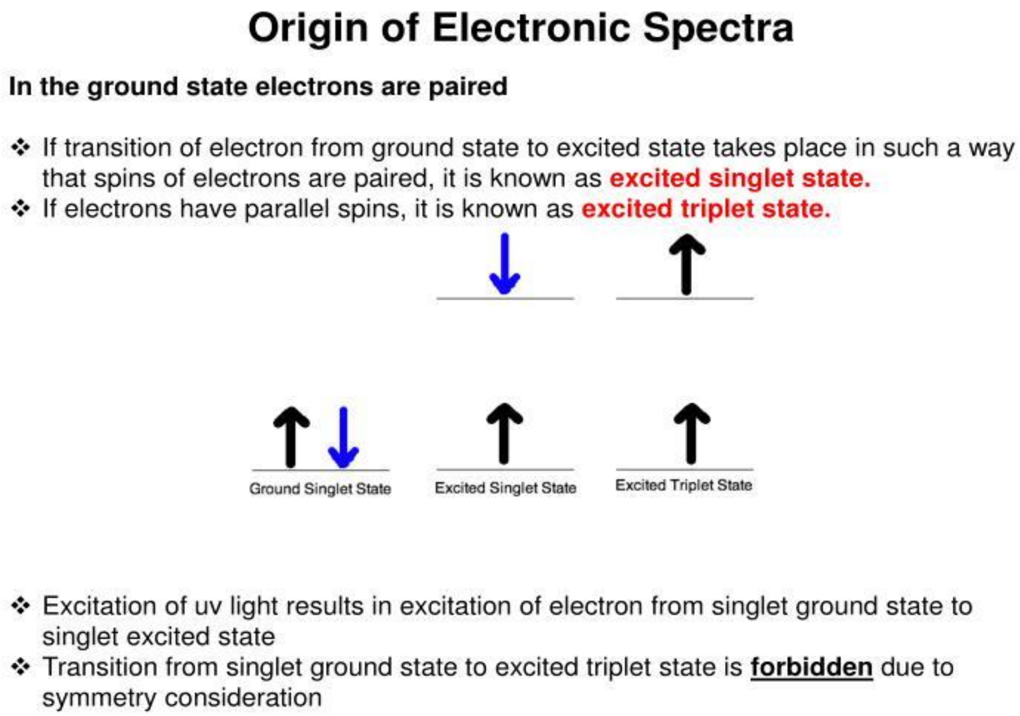
Quantized Energy Loss

- Only certain, restricted, quantized energy values possible on way down
- Implies an electron is restricted to quantized energy levels

➢ Line spectra

Origin of Electronic Spectra





Origin of Electronic Spectra

In the ground state electrons are paired

- If transition of electron from ground state to excited state takes place in such a way that spins of electrons are paired, it is known as **excited singlet state.**
- If electrons have parallel spins, it is known as **excited triplet state.**

- Excitation of uv light results in excitation of electron from singlet ground state to singlet excited state
- Transition from singlet ground state to excited triplet state is **forbidden** due to symmetry consideration

Electronic spectra of molecules

When the molecules possess sufficiently large amount of energy, the electronic states of the molecule can be excited. This gives rise to the most general type of transitions, rotation-vibration-electronic transitions. These produce photons of frequency

$$\nu = \frac{E_{e1} - E_{e2}}{h} + \frac{E_{v1} - E_{v2}}{h} + \frac{E_{r1} - E_{r2}}{h}$$

It is the outermost electrons of the atoms composing the molecule that are involved. These transitions are energetic enough that they produce electronic bands in the visible and ultraviolet regions. All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule.

Scattering of light

The phenomenon in which the particles of the medium deviate light in a lateral direction is called scattering of light. The particles of the medium absorb light and then emit light in all directions. **Types of scattering**

1. Coherent scattering or elastic scattering
2. Incoherent scattering or inelastic scattering

Coherent scattering - The phenomenon of scattering in which the scattered light has the same wavelength as that of incident light is called coherent scattering. In coherent scattering, the incident light does not suffer any change in its energy. Hence it is also called as elastic scattering. Eg. Rayleigh scattering and Tyndall scattering.

Rayleigh scattering - When the dimensions of the scattering particles is very small compared to the wavelength of the incident radiation, the scattering is called Raleigh scattering. According to Raleigh, the intensity of the scattered radiation is inversely proportional to the fourth power of the wavelength of the incident light. i.e,

$$I \, \alpha \, \frac{1}{\lambda^4}$$

Let a be the size of the particle scattering light and λ the wavelength of the incident light. If a << λ, Rayleigh's scattering takes place and light of shorter wavelengths get scattered to greater extent.

If a >> λ, Tyndall scattering takes place and light of all wavelengths get scattered nearly equal

Blue colour of sky:

The blue colour of the sky is due to Rayleigh scattering of sunlight by the air molecules in the atmosphere. Sunlight contains all colours, from violet to red. According to Raleigh, the intensity of the scattered radiation is inversely proportional to the fourth power of the wavelength of the incident light. Thus, in the daytime when sun light enters earth's atmosphere, violet and blue colours are the most scattered since wavelength is small. Red and orange are the least scattered since wavelength is large. When we look at the sky far away from the sun, the sky appears blue because we receive the most scattered colours, namely, violet and blue.

Note :

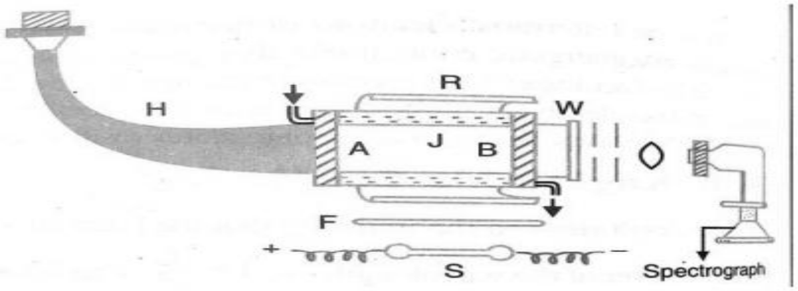
1. Near the sun it appears white because we get direct light from the sun.
2. The blue colour of the sea is due to reflection of light from the sky. Raman proved that the blue colour of sea water is due to the scattering of incident sunlight by water molecules.
3. In the absence of the atmosphere, the sky would appear black.

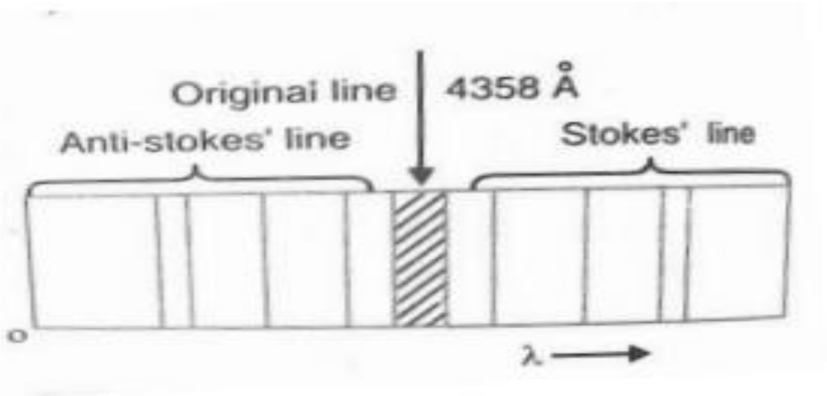
Red colour at sunrise and sunset - The orange red colour of the sky at sunrise and at sunset is due to Rayleigh scattering of light by air molecules in the atmosphere. According to Raleigh, the intensity of the scattered radiation is inversely proportional to the fourth power of the wavelength of the incident light. At sunrise and sunset, the light from the sun travels a longer distance through the earth's atmosphere before reaching the observer. Therefore, much of the blue is taken away by scattering. The light that reaches the earth 's surface is orange red colour. Thus, sky appears orange red colour.

Incoherent scattering: The phenomenon of scattering in which the scattered light has different wavelength compared to that of incident light is called incoherent scattering. In incoherent scattering, the incident light suffers a change in its energy. Hence it is also called as inelastic scattering. Eg. Raman scattering and Compton scattering.

Raman effect - The phenomenon in which there is a change in wavelength of the incident light due to scattering by particles of material medium is called Raman effect. Raman in the year 1928 observed that when a beam of monochromatic light is passed through organic liquids such as benzene, toluene etc, the scattered light was found to consist of lines corresponding to the higher wavelengths as well as lower wavelengths in addition to the incident wavelength. These lines are called Raman lines. When photons are scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering), such that the scattered photons have the same energy (frequency and wavelength) as the incident photons. A small fraction of the scattered photons (approximately 1 in 10 million) are scattered by an excitation, with the scattered photons having a frequency different from, and usually lower than, that of the incident photons. In a gas, Raman scattering can occur with a change in energy of a molecule due to a transition to another (usually higher) energy level. The spectrum of the scattered light is called Raman spectrum as shown

Experimental study of Raman Effect - The apparatus used for the study of Raman effect in liquids was first developed by Wood. It consists of a glass tube AB containing the pure liquid under study. The tube is closed at one end by an optically plane glass plate Wand at the other end end it is drawn into a horn Hand blackened on the outside.Light from a Mercury arc S is passed through a filter Fwhich allows only monochromatic radiation of λ = 4358 Å to pass through it. The tube is surrounded by a water jacket J through which water is circulated to prevent overheating of the liquid. A semi cylindrical aluminium reflector R is used to increase the intensity of illumination. The scattered light coming out of W is condensed on the slit of a spectrograph. A short focus camera is used to photograph the spectrum. The spectrum appears as shown





Features of Raman lines

1. The spectrum consists of intense central line of wavelength λ0 same as that of incident light called Raleigh line.
2. It consists of a number of low intensity lines of linger wavelength called stokes lines.
3. It also consists of very faint lines of lower wavelengths called anti stokes line.
4. The Raman lines are almost symmetrically placed wavelengths both above and below the incident light wavelengths.
5. Stokes lines were found to be more intense than the anti-stokes lines.
6. Raman lines are polarized.
7. The change in wavelength are characteristic of the scattering material and does not depend on the wavelength of incident light.

Quantum theory of Raman Effect

Raman effect is due to the interaction between a light photon and a molecule of the scatterer. Quantum theory is applied to explain Raman effect. Suppose a photon of frequency $\nu1$ is incident on a molecule and there is a collision between the two. Let m be the mass of the molecule, $\upsilon1$ and $\upsilon2$ its velocities before and after impact, $E1$ and $E2$ the intrinsic energies of the molecule before and after collision. Let $\nu2$ be the frequency of the scattered photon. Applying the principle of conservation of energy,

$$E_2 + \frac{1}{2}m\upsilon_2^2 + h\nu_2 = E_1 + \frac{1}{2}m\upsilon_1^2 + h\nu_1$$

Assuming that the kinetic energy of the molecule is unaltered during the process, the above equation becomes

$$E_2 + h\nu_2 = E_1 + h\nu_1 \qquad \text{or} \qquad \boldsymbol{\nu_1 = \nu_2 + \frac{E_2 - E_1}{h}}$$

Three cases arise

1. When the incident photons undergo elastic scattering with the molecules of the medium, the scattered photons have the same energy as that of the incident photons. This results in unmodified line of same wavelength as that of the incident light. Here

   $E_1 = E_2$. Thus $\nu_2 = \nu_2$.

2. Some photons are absorbed by molecules in the lower energy state. When the photons are reemitted, their energy will be less than that of the incident photons. This gives rise to lines having longer wavelength or shorter frequency called stokes lines. Here $E2 > E1$. The molecule gains energy from the photon and jumps to higher state so that $E2 - E1$ is positive.

Thus equation ( )

$$\nu_1 = \nu_2 + \frac{E_2 - E_1}{h}.$$

Thus, the frequency of the scattered photon is

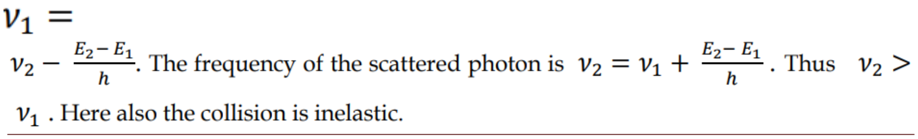
$$\nu_2 = \nu_1 - \frac{E_2 - E_1}{h}. \text{ Thus } \nu_2 < \nu_1.$$

The collision is inelastic.

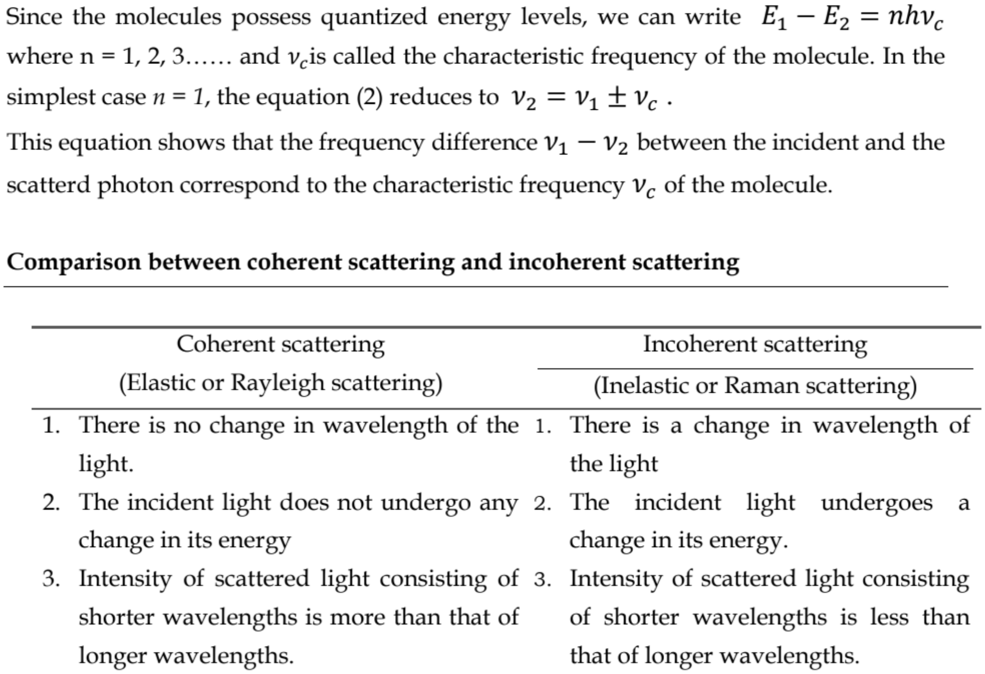
3. Some photons are absorbed by molecules which are already in the excited state. When the photons are reemitted, their energy will be more than that of the incident photons. This gives rise to lines having shorter wavelength or higher frequency called anti stokes lines.

Here $E_2 < E_1$.

The molecule loses energy to the photon and jumps to a lower energy state so that $E2 - E1$ is negative from equation (), we have



$\nu_1 = \nu_2 - \frac{E_2 - E_1}{h}$. The frequency of the scattered photon is $\nu_2 = \nu_1 + \frac{E_2 - E_1}{h}$. Thus $\nu_2 > \nu_1$. Here also the collision is inelastic.



Since the molecules possess quantized energy levels, we can write $E_1 - E_2 = nh\nu_c$ where n = 1, 2, 3…… and ν_c is called the characteristic frequency of the molecule. In the simplest case *n = 1*, the equation (2) reduces to $\nu_2 = \nu_1 \pm \nu_c$.

This equation shows that the frequency difference $\nu_1 - \nu_2$ between the incident and the scatterd photon correspond to the characteristic frequency ν_c of the molecule.

Comparison between coherent scattering and incoherent scattering

Coherent scattering (Elastic or Rayleigh scattering)	Incoherent scattering (Inelastic or Raman scattering)
1. There is no change in wavelength of the light.	1. There is a change in wavelength of the light
2. The incident light does not undergo any change in its energy	2. The incident light undergoes a change in its energy.
3. Intensity of scattered light consisting of shorter wavelengths is more than that of longer wavelengths.	3. Intensity of scattered light consisting of shorter wavelengths is less than that of longer wavelengths.

Applications of Raman effect

1. Raman effect is used in the study of molecular structure.

2. The geometrical configuration of a molecule of the substance can be determined using Raman spectra and infrared spectra of a substance,

3. The study of Raman spectra gives information about the nature of the chemical bond existing between the atoms.

4. Raman spectrum gives information about the structure of water (H2O) molecule which is nonlinear or bent having angle of bend as 120

5. Raman effect gives information about the binding forces in crystals.

10.4 ELECTRONIC TRANSITIONS

Electronic transitions **occur in atoms and molecules due to the absorption or emission of electromagnetic radiation** (typically UV or visible). The energy change associated with a transition is related to the frequency of the electromagnetic wave by Planck's equation,

$$E = h\nu$$

The term “electronic” connotes electron, and the term “transition” implies transformation. In a molecule, the electrons move from a lower to a higher energy state due to excitation. The two energy states, the ground state and the excited state are the lowest and the highest energy states, respectively. An energy change is observed with this transition, which depicts the various data related to the molecule.

What are the types of electronic transitions?

The three kinds of electrons responsible for electronic transitions are:

- Sigma (σ) electrons in saturated molecules
- Pi (π) electrons in unsaturated molecules
- Nonbonding (n) electrons in nonbonded elements

These electrons absorb ultraviolet radiation, which causes excitation. The movement from the ground state to a higher energy state is categorized into four types of electronic transitions. They are as follows:

σ→σ* transition

In this transition, the electrons in a molecule move from a bonding (σ) orbital to its comparable anti-bonding (σ*) orbital. This transition takes place due to the electromagnetic radiation that gets absorbed. The highest quantity of energy is needed to undergo this transition. It can be observed in the methane molecule due to the presence of only C-H bonds.

n→σ* transition

In this transition, the electrons from a nonbonding orbital (n) move to an anti-bonding (σ*) orbital. The lowest quantity of energy is needed to undergo this transition. Halogens and elements like sulfur, oxygen, and nitrogen display this transition.

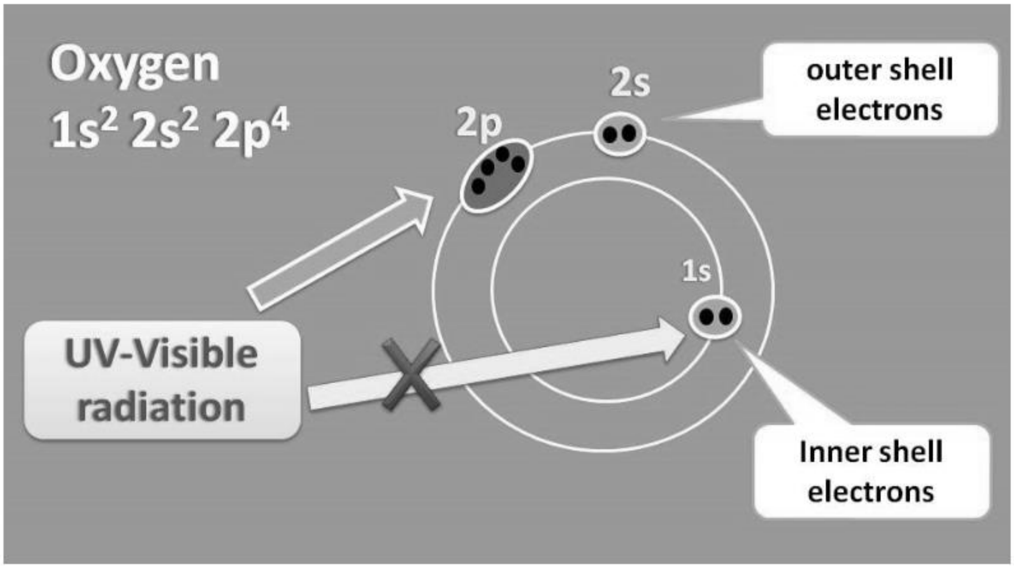
n→π* transition

In this transition, the electrons from a non-bonding orbital (n) move to an anti-bonding (π*) orbital. The lowest quantity of energy is needed to undergo this transition. Halogens and elements like sulfur, oxygen, or nitrogen display this transition.

π→π* transition

In this transition, the electrons move from a bonding orbital (π) to an anti-bonding (π*). Its energy requirement ranges in between the energies required for (n→π*) and (n→σ*). Organic compounds like the aromatic ones, alkenes, alkynes, nitriles, and carbonyl compounds display this transition.

Some transitions between energy levels are radiative, and some are nonradiative. The photon absorption involved between two energy levels is a radiative transition, whereas a transition involving no photons between two energy levels is a nonradiative transition.



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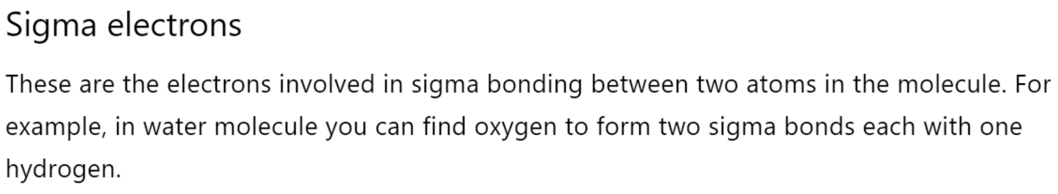
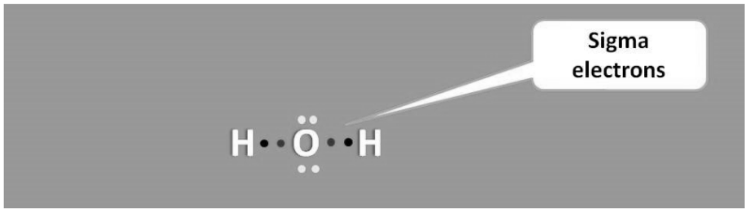


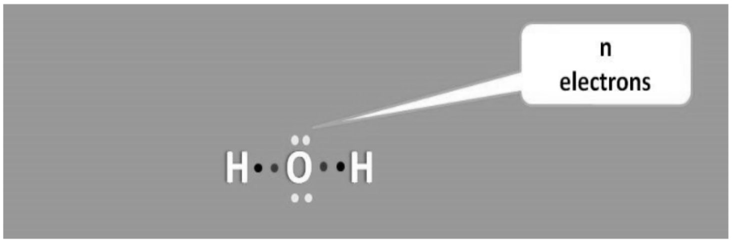
Sigma electrons

These are the electrons involved in sigma bonding between two atoms in the molecule. For example, in water molecule you can find oxygen to form two sigma bonds each with one hydrogen.



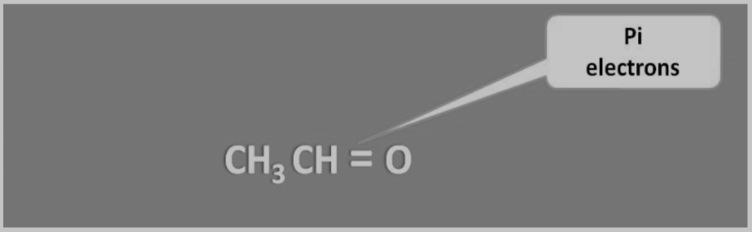
n electrons

These are the lone pair of electrons that are not involved in any bonding but still present in the outer shell. Hence these electrons can be easily excited.



Pi electrons

These are the electrons involved in lateral ways of overlapping in the molecule forming pi bond. For instance, in acetaldehyde, carbon forms a pi bond with oxygen.

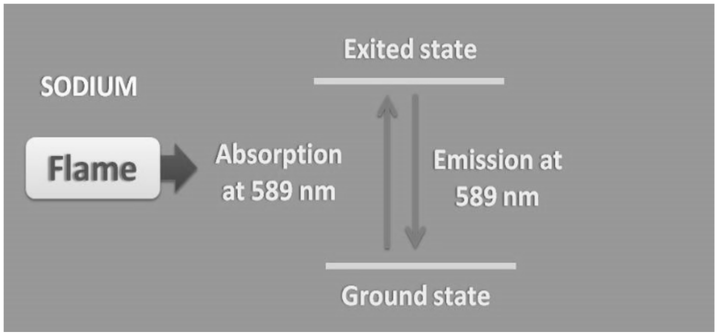


Again these electrons are stable but somewhat less than sigma electrons hence can be easily excited in UV-visible region.

Electronic transition in atoms

When light falls on the atom, the electrons in outer shell can go to excited state responsible for atomic absorption.

For example, sodium has electronic configuration $1s^2$ $2s^2$ $2p^6$ $3s^1$. When it is excited in flame, one of the electron from $3s^1$ is shifted to the next orbit. In this process if absorbs energy.



Now the electron is in a excited state which is not stable, therefore again jumps to $3s^1$ releasing energy. This is atomic emission.

Why sodium is golden yellow when burnt in flame?

Sodium when excited in flame electron jumps to excited level and then again jumps back to ground state releasing same amount of the energy as it absorbed. For sodium this falls at 589 nm which results in golden yellow colour in the flame.

Electronic transitions in molecules

As we have discussed above, in a molecule four types of electrons are involved among which only three types of electrons exist in outer shell. They are sigma, pi and n electrons.

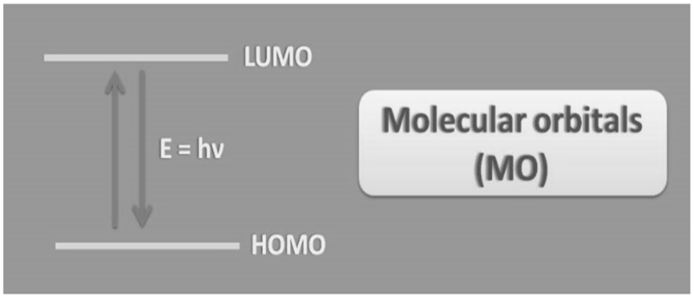
We already know that stability of these electrons is as follows.

Sigma > Pi > n electrons

Among these sigma and pi electrons are located in bonding molecular orbitals when they form chemical bond in the molecule. These molecular orbitals just like atomic orbitals can exist in two states,

- HOMO
- LUMO

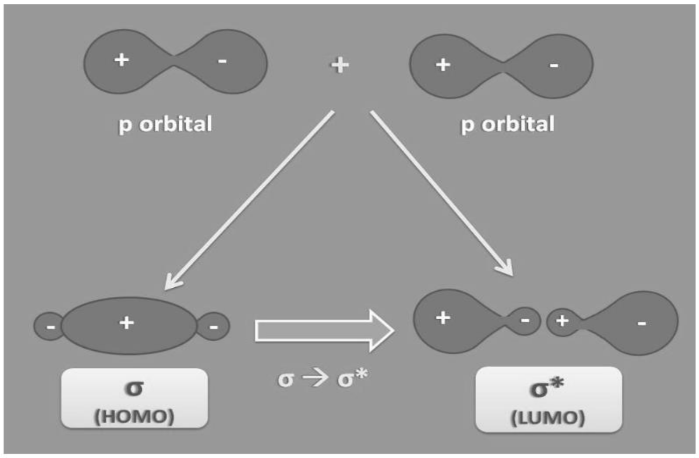
HOMO is the highest energy occupied molecular orbital that corresponds to ground state whereas LUMO is the Lowest energy unoccupied molecular orbital corresponds to excited state.



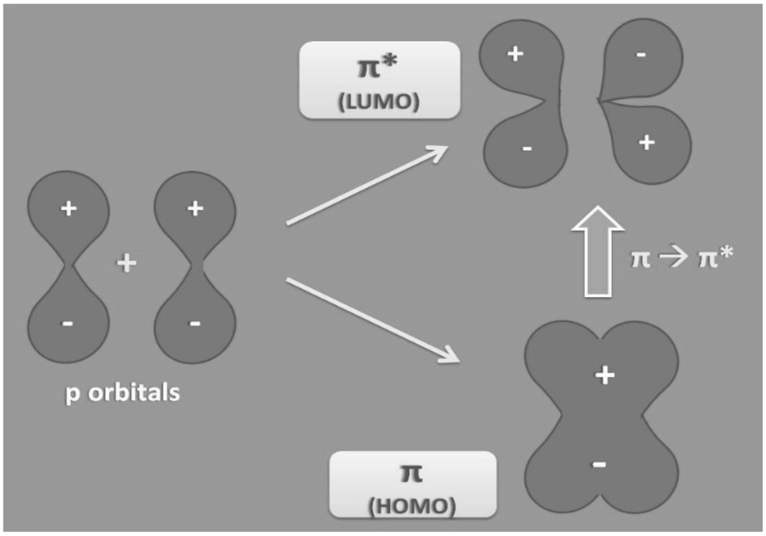
Therefore, an electron in HOMO can jump to LUMO when we supply energy in the form of electromagnetic radiation. This forms the basis for molecular absorption of EMR.

But here, unlike atoms, the situation is not so simple as different types of electrons present.

Suppose a sigma bond is formed between two p orbitals by sideways overlap. Two types of overlap may be possible. One is the bonding molecular orbital which is more stable acting as HOMO and another is the anti bonding molecular orbital acting as LUMO.



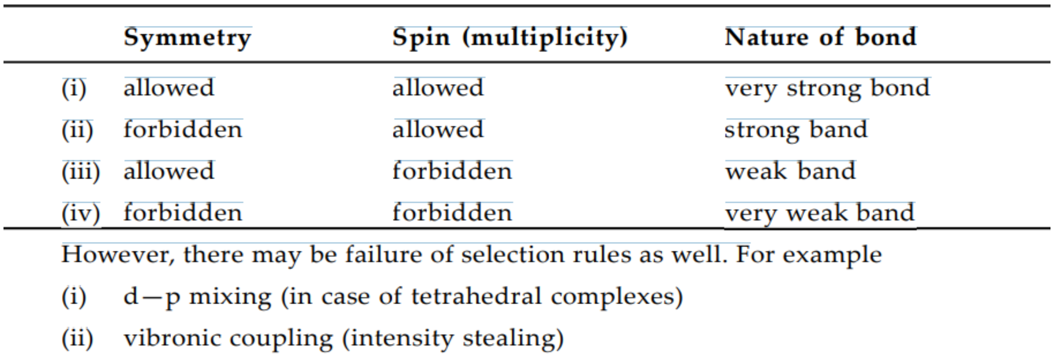
Similarly, when two p orbital overlap laterally to form pi bond, two types of molecular orbitals are formed one being bonding MO and another being antibonding MO.



The following selection rules are predicted for electronic transition in electron absorption spectroscopy.

1. Simultaneous excitation of more than one electron is forbidden.
2. **Spin selection rule:** Transition between states of different spin multiplicity (S.M. = 2S +1) is forbidden. That is, electronic transition in which the spin of an electron changes are forbidden. The selection rule is $\Delta S=0$ i.e., only states of same multiplicity combines with each other.
3. **Laporte rule:** In a molecule which has centre of symmetry, transition between two grade or two ungraded state (i.e. g → g or u → u) are Laporte forbidden.

The allowed transition is g → u and u → g. That for allowed electronic transition there must be change in parity. The allowed transition gives intense band where forbidden transition results in weak band. Thus, the conclusion may be drawn as table 1

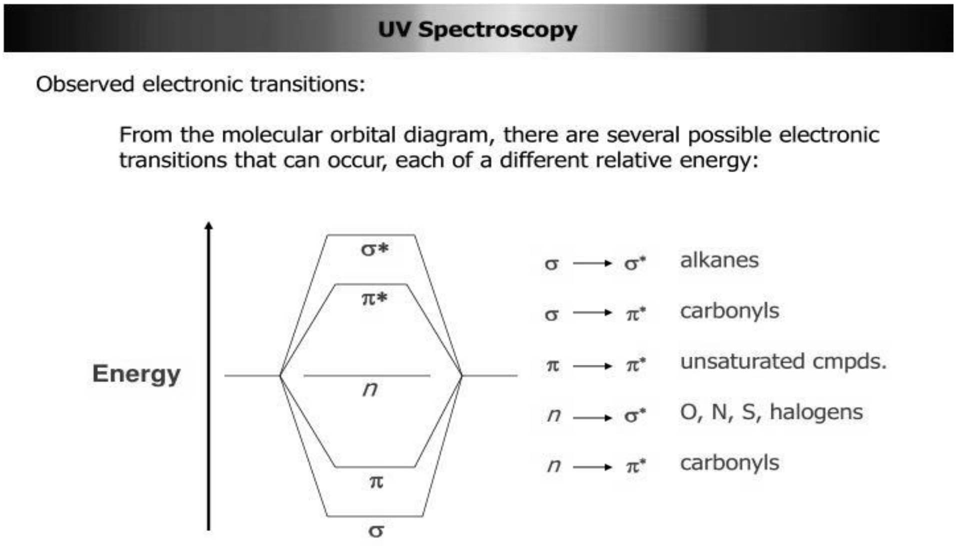


	Symmetry	Spin (multiplicity)	Nature of bond
(i)	allowed	allowed	very strong bond
(ii)	forbidden	allowed	strong band
(iii)	allowed	forbidden	weak band
(iv)	forbidden	forbidden	very weak band

However, there may be failure of selection rules as well. For example

(i) d—p mixing (in case of tetrahedral complexes)

(ii) vibronic coupling (intensity stealing)



UV Spectroscopy

Observed electronic transitions:

From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy:

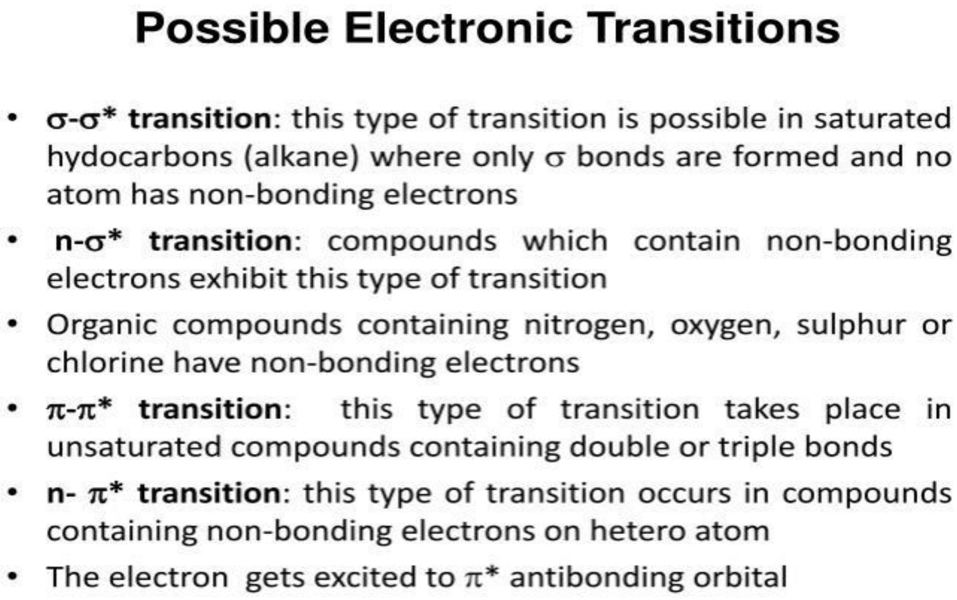
σ → σ* alkanes

σ → π* carbonyls

π → π* unsaturated cmpds.

n → σ* O, N, S, halogens

n → π* carbonyls



Possible Electronic Transitions

- **σ-σ* transition**: this type of transition is possible in saturated hydocarbons (alkane) where only σ bonds are formed and no atom has non-bonding electrons
- **n-σ* transition**: compounds which contain non-bonding electrons exhibit this type of transition
- Organic compounds containing nitrogen, oxygen, sulphur or chlorine have non-bonding electrons
- **π-π* transition**: this type of transition takes place in unsaturated compounds containing double or triple bonds
- **n- π* transition**: this type of transition occurs in compounds containing non-bonding electrons on hetero atom
- The electron gets excited to π* antibonding orbital

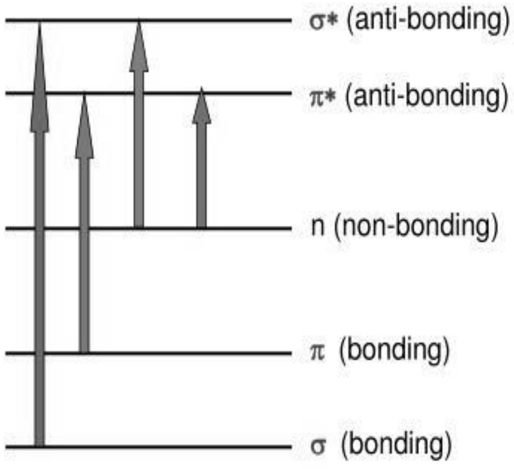
UV Spectroscopy

Observed electronic transitions:

- Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm
- Special equipment to study *vacuum* or *far UV* is required
- Routine organic UV spectra are typically collected from 200-700 nm
- This limits the transitions that can be observed:

$\sigma \longrightarrow \sigma^*$	alkanes	150 nm	
$\sigma \longrightarrow \pi^*$	carbonyls	170 nm	
$\pi \longrightarrow \pi^*$	unsaturated cmpds.	180 nm	**√ - if conjugated!**
$n \longrightarrow \sigma^*$	O, N, S, halogens	190 nm	
$n \longrightarrow \pi^*$	carbonyls	300 nm	√

The valence electrons are the only ones whose energies permit them to be excited by near UV/visible radiation.



Four types of transitions

$\sigma \rightarrow \sigma^*$

$\pi \rightarrow \pi^*$

$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$

$\sigma \rightarrow \sigma^*$ transition in vacuum UV (λ ~ 150 nm)

$n \rightarrow \sigma^*$ saturated compounds with non-bonding electrons

λ ~ 150-250 nm

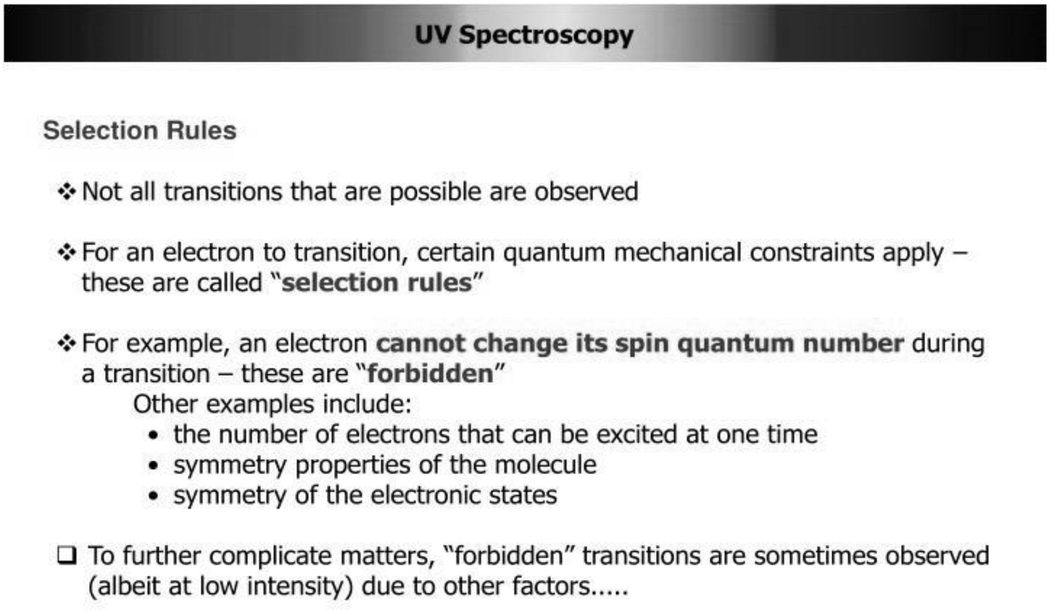
ε ~ 100-3000 (not strong)

$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ requires unsaturated functional groups most commonly used, energy good range for UV/Vis

λ ~ 200 - 700 nm

$n \rightarrow \pi^*$: ε ~ 10-100

$\pi \rightarrow \pi^*$: ε ~ 1000 – 10,000


UV Spectroscopy

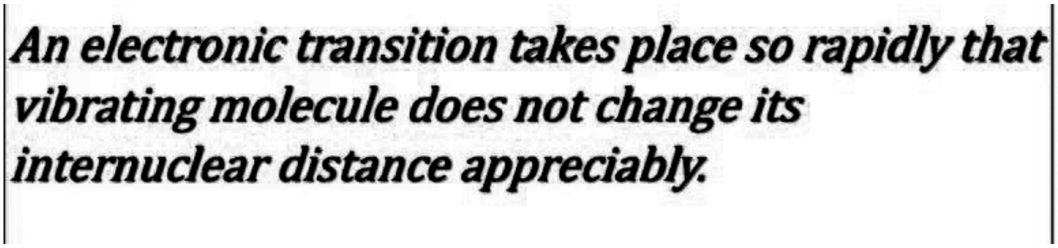
Selection Rules

- ❖ Not all transitions that are possible are observed
- ❖ For an electron to transition, certain quantum mechanical constraints apply – these are called "**selection rules**"
- ❖ For example, an electron **cannot change its spin quantum number** during a transition – these are "**forbidden**"
  Other examples include:
  - the number of electrons that can be excited at one time
  - symmetry properties of the molecule
  - symmetry of the electronic states
- ❑ To further complicate matters, "forbidden" transitions are sometimes observed (albeit at low intensity) due to other factors.....

10.5 FRANK-CONDON PRINCIPLES


Frank-Condon principle was proposed by German Physicist James Frank and U.S Physicist Edward U. Condon in 1926

STATEMENT OF FRANK-CONDON PRINCIPLES


An electronic transition takes place so rapidly that vibrating molecule does not change its internuclear distance appreciably.

The **Franck-Condon principle** is a rule in spectroscopy and quantum chemistry or Physics that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

The Franck-Condon principle has a well-established semiclassical interpretation based on the original contributions of James Franck [Franck

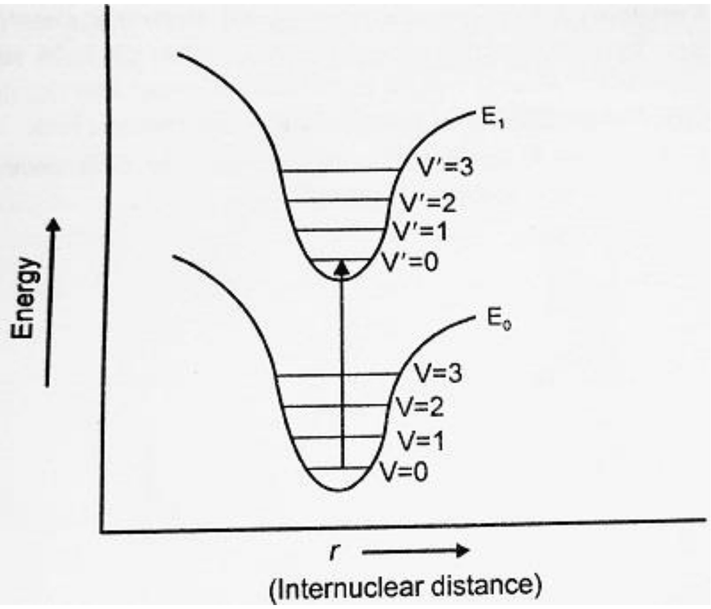
1927]. Electronic transitions are essentially instantaneous compared with the time scale of nuclear motions, therefore if the molecule is to move to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state. In the semiclassical picture of vibrations (oscillations) of a simple harmonic oscillator, the necessary conditions can occur at the turning points, where the momentum is zero.

Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

What is Franck Condon Principle?

The electronic transitions occur so quickly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

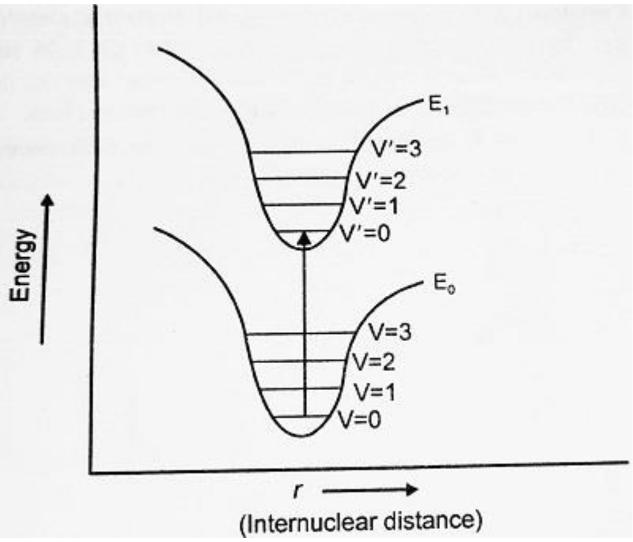
It can be explained as below-



Consider a potential energy diagram where E_0 is the energy of the ground state and E_1 of the excited electronic state. The two curves show the variation in electronic energy with internuclear separation in the two states. The vibrational energy levels are shown as horizontal lines.

If a molecule absorbs quantum in the ground state E_0, then its transition to excited state must occur along a straight line.

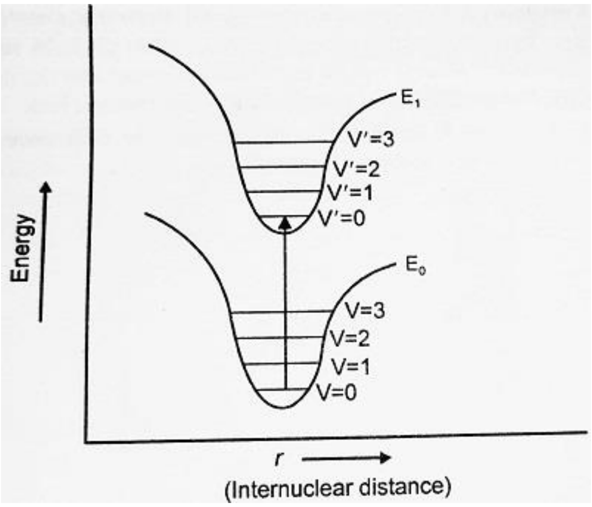
This is because nuclei are heavy and sluggish as compared to electrons. An electron undergoes a transition in about 10-16 sec, which is very short as compared to the period of vibration of atomic nuclei (i.e., 10-13 sec). So, the internuclear distance in the excited electronic state remains the same as it was in the initial ground state before the time of electronic transition. So the transition is shown by a vertical line. An upward arrow is drawn for absorption of energy and a downward arrow for emission of energy.

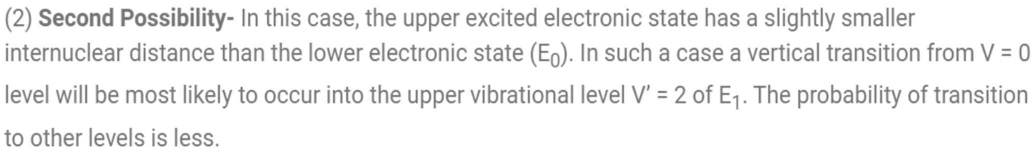


Now there are four possibilities w.r.t the internuclear distance.

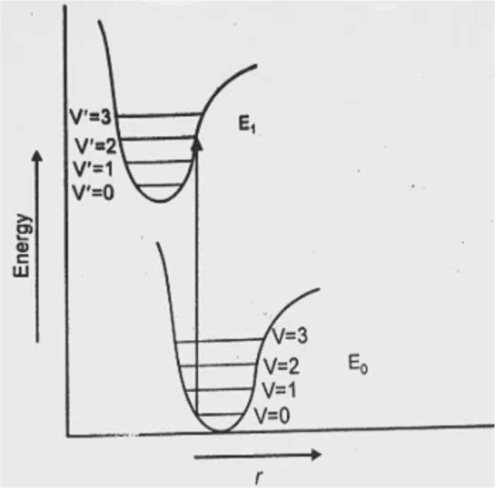
(1) **First Possibility-** In this case upper electronic state (E_1) has the same internuclear distance as the lower electronic state (E_0). Now according to Franck Condon Principle transition occurs vertically along a straight line. If the molecule is in V = 0 vibrational level of lower electronic state E_0, then the strongest spectral line will be obtained if the molecule undergoes a transition to $V' = 0$ of upper electronic state (E_1).

The transition of other levels gives rise to spectral lines that diminish rapidly in intensity.



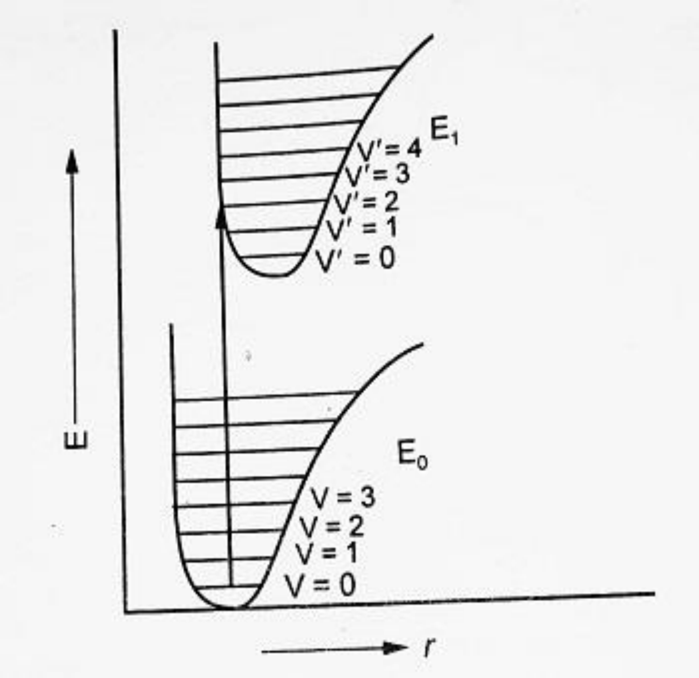


(2) **Second Possibility-** In this case, the upper excited electronic state has a slightly smaller internuclear distance than the lower electronic state (E_0). In such a case a vertical transition from V = 0 level will be most likely to occur into the upper vibrational level V' = 2 of E_1. The probability of transition to other levels is less.

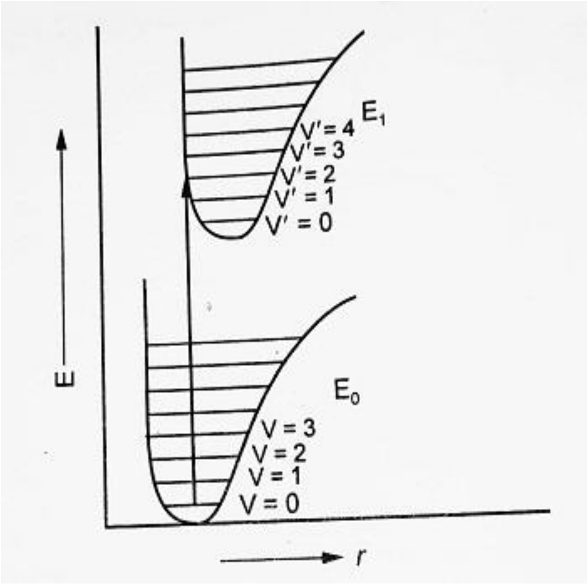


In general transitions to upper levels depend upon the difference between equilibrium separations in the lower and upper states.

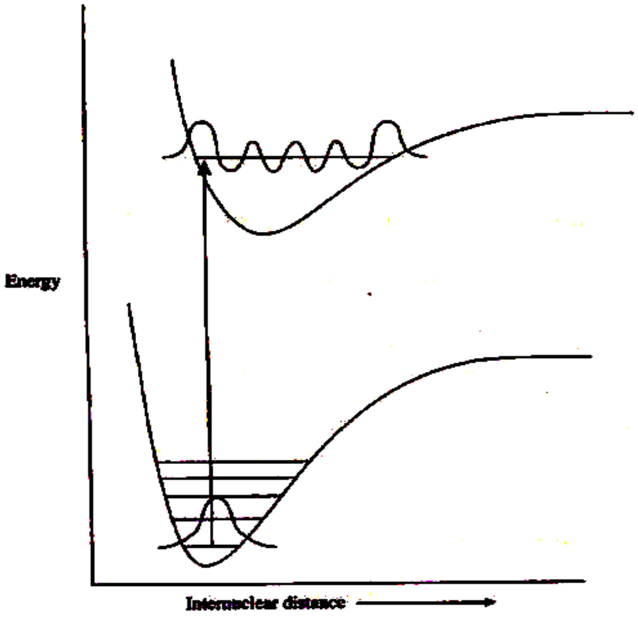
(3) **Third Possibility-** In this case, the upper excited state has a slightly larger internuclear separation than the ground state. The resulting transitions and spectrum are similar as above.



(4) **Fourth Possibility-** In this case, the upper excited electronic state has considerably greater separation than that in the lower electronic state. In such a case transition will occur to a higher vibrational level (V') of the upper electronic state (E_1) from the lower electronic state (E_0).

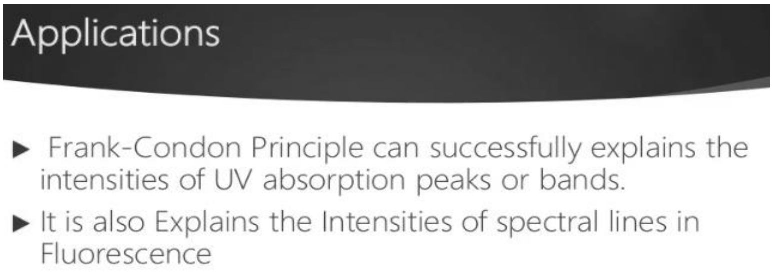


Prior to an electronic transition, most molecules are in the $n = 0$ vibrational state. Since an electron is much lighter than any nucleus, it subsequently moves much faster. Thus, during the time when an electronic transition occurs, there is no appreciable change in the internuclear distances in the molecule—this is called the **Franck-Condon Principle**. More precisely, the transition probability is given by the overlap integral of the initial and final vibrational wave functions at the same internuclear distance.



Recall the Boltzmann distribution for vibrational energy levels and explain why at room temperature the most likely electronic transition is from the $n = 0$ vibrational state of the ground electronic state (rather than $n = 1$).

Based on the Franck-Condon principle, explain why it is unlikely to observe a transition from the ground electronic $n = 0$ vibrational state to the $n' = 0$ vibrational state of the excited electronic state.



Applications

- ▶ Frank-Condon Principle can successfully explains the intensities of UV absorption peaks or bands.
- ▶ It is also Explains the Intensities of spectral lines in Fluorescence

10.6 SINGLET AND TRIPLET STATES

The terms singlet and triplet states are discussed under quantum mechanics. We can describe these terms regarding the spin of the system, i.e., atom. In quantum mechanics, spin is not a mechanical rotation. It is a concept that characterizes a particle's angular momentum.

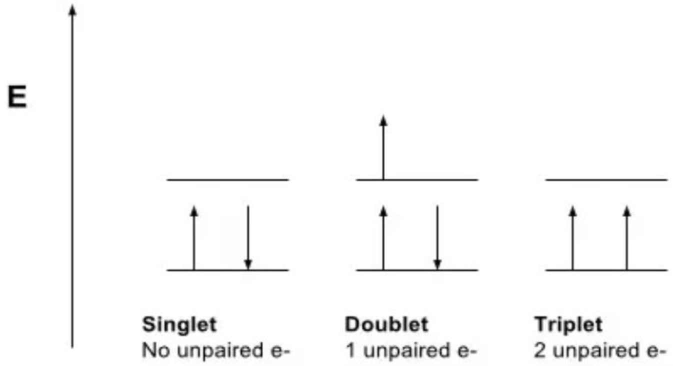
The electronic states of most organic molecules can be divided into singlet states and triplet states.

Singlet state: All electrons in the molecule are spin paired. It is called a singlet because there is only one possible orientation in space.

Triplet state: One set of electron spins is unpaired. It is called a triplet because there are three possible orientations in space with respect to the axis

What is Singlet State?

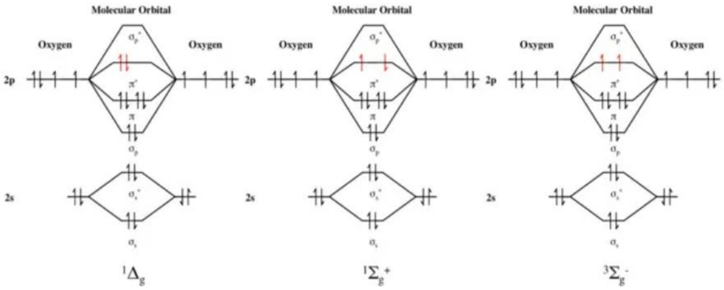
A singlet state is a system in which all the electrons are paired. The net angular momentum of the particles in this type of system is zero. Therefore, we can say that the overall spin quantum number, s is zero (s=0). Furthermore, if we take the spectrum of this system, it shows one spectral line, and thus, got the name "singlet state". Moreover, almost all the molecules that we know exist in the singlet state, but molecular oxygen is an exception.



As an example, the simplest possible bound particle pair having singlet state is positronium, which has an electron and positron. These two particles are bound by their opposite electrical charge. Moreover, the paired electrons of a system having a singlet state have parallel spin orientations.

What is Triplet State?

Triplet state of a system describes that the system has two unpaired electrons. The net angular momentum of the particles in this type of system is 1. Therefore, the spin quantum number is 1. Moreover, this allows three values of the angular momentum as -1, 0 and +1. Hence, the spectral lines that we obtain for this type of system split into three lines, and thus, got the name triplet state.

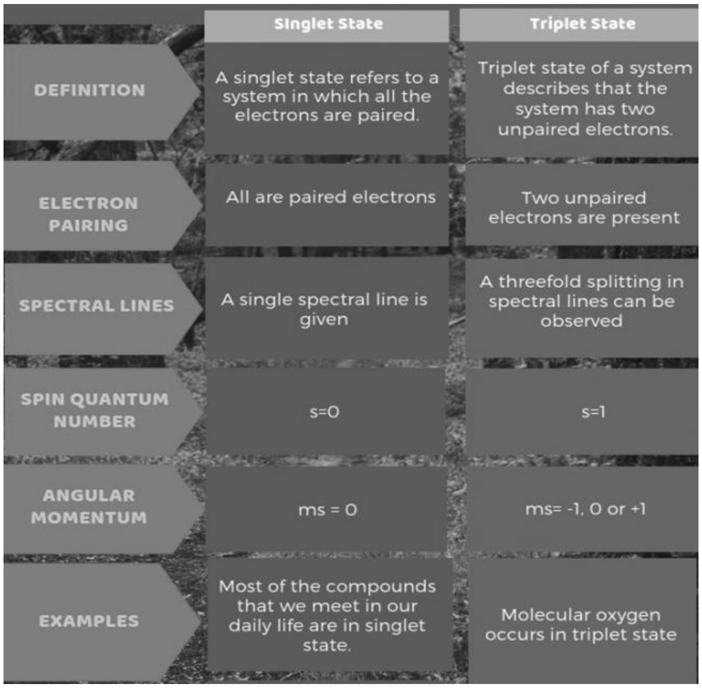


Shown are three electronic configurations of the molecular orbitals of molecular oxygen, O2. From left to right, the diagrams are for: 1Δg singlet oxygen (first excited state), 1Σ+ g singlet oxygen (second excited state), and 3Σ− g triplet oxygen (ground state).

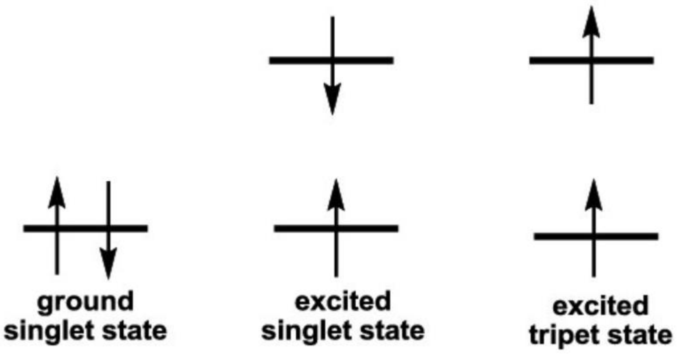
Difference Between Singlet and Triplet State

A singlet state refers to a system in which all the electrons are paired. Whereas, the triplet state of a system describes that the system has two unpaired electrons. The key difference between singlet and triplet state is that singlet state shows only one spectral line whereas triplet state shows the threefold splitting of spectral lines.

Moreover, a further difference between singlet and triplet state is that the spin quantum number of a singlet state is s=0 while it is s=1 for a triplet state. Besides, almost all the molecules that we know exist in singlet state except for the molecular oxygen. Whereas, molecular oxygen occurs at triplet state.



	Singlet State	Triplet State
DEFINITION	A singlet state refers to a system in which all the electrons are paired.	Triplet state of a system describes that the system has two unpaired electrons.
ELECTRON PAIRING	All are paired electrons	Two unpaired electrons are present
SPECTRAL LINES	A single spectral line is given	A threefold splitting in spectral lines can be observed
SPIN QUANTUM NUMBER	s=0	s=1
ANGULAR MOMENTUM	ms = 0	ms= -1, 0 or +1
EXAMPLES	Most of the compounds that we meet in our daily life are in singlet state.	Molecular oxygen occurs in triplet state



10.7 FINE STRUCTURE AND HYPER FINE STRUCTURE

Fine structure describes the splitting of the spectral lines of atoms due to electron spin and relativistic corrections to the non-relativistic Schrödinger equation. Hyperfine structure, with energy shifts typically orders of magnitudes smaller than those of a fine-structure shift, results from the interactions of the nucleus (or nuclei, in molecules) with internally generated electric and magnetic fields.

Spin–orbit coupling is an interaction of a particle's spin with its motion. This interaction leading to shifts in an electron's atomic energy levels, due to electromagnetic interaction between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus. This is detectable as a splitting of spectral lines, which can be thought of as a Zeeman effect due to the internal field.

The hyperfine structure is caused by interaction between magnetic field (from electron movement) and nuclear spin

Fine structure:

1. Spin orbit interaction
2. Relativistic kinetic energy correction

Hyperfine structure:

1. The lamb Shift
2. Nuclear Moments

In atomic physics and quantum effects on atoms, the study of the hydrogen atom and their spectrum plays an important role. When the hydrogen spectrum was studied, physics noticed that the familiar red spectral line of the hydrogen atom consists of two closely spaced lines. That means the spectral line was split into two closely spaced lines or closely spaced doublet. The splitting of spectral lines is known as the fine structure or fine structure of spectral lines and it is considered one of the first pieces of experimental evidence for the electron spin.

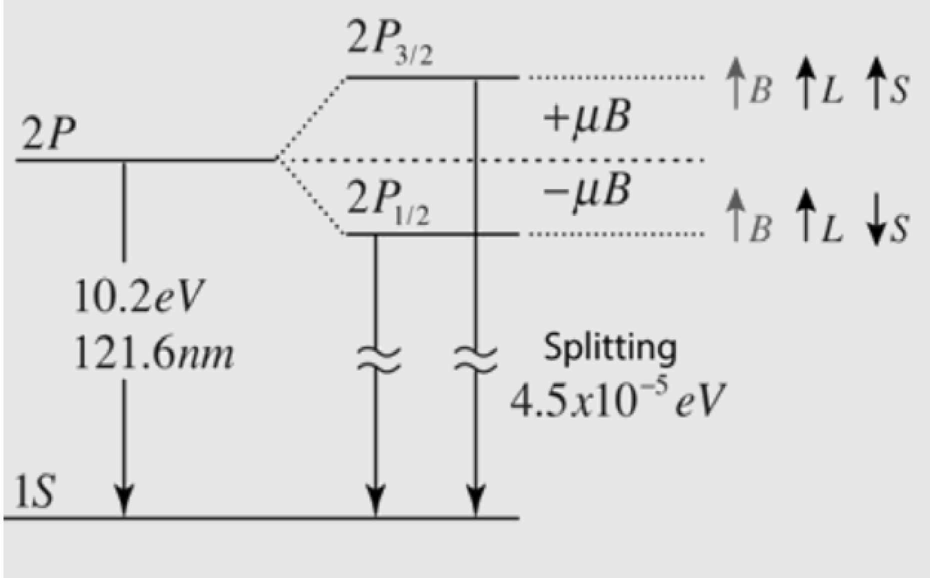
Fine Structure of Hydrogen Atom

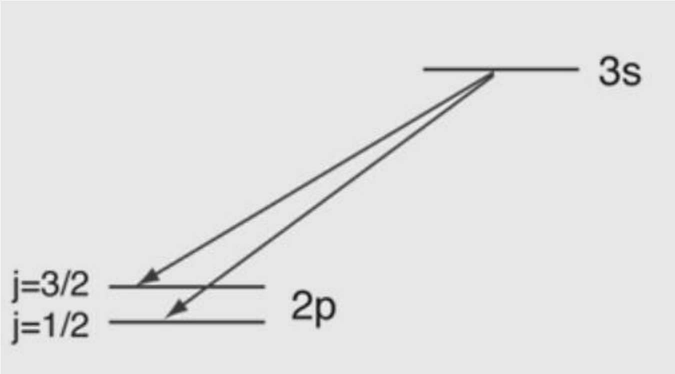
The fine structure of the hydrogen atom is also known as the hydrogen fine spectrum. We know that the hydrogen atom is one of the simplest forms of atom available, which consists of a single electron in its valence shell. Before we start with the fine structure of the hydrogen atom let us have a look at the spectrum of the hydrogen atom. The spectrum of a hydrogen atom consists of different series of spectral lines and these sets of spectral lines fall into a different region of the electromagnetic spectrum, for example, the Balmer series lies in the visible region of the electromagnetic spectrum.

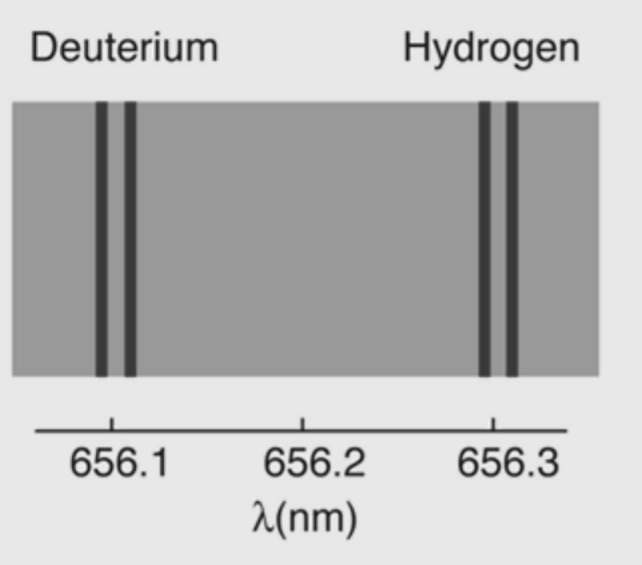
Fine structure, in spectroscopy, the splitting of the main spectral lines of an atom into two or more components, each representing a slightly different wavelength. Fine structure is produced when an atom emits light in making the transition from one energy state to another. The split lines, which are called the fine structure of the main lines, arise from the interaction of the orbital motion of an electron with the quantum mechanical “spin” of that electron. An electron can be thought of as an electrically charged spinning top, and hence it behaves as a tiny bar magnet. The spinning electron interacts with the magnetic field produced by the electron’s rotation about the atomic nucleus to generate the fine structure.

The amount of splitting is characterized by a dimensionless constant called the fine-structure constant. This constant is given by the equation $\alpha = \mathbf{ke^2/hc}$, where **k** is Coulomb’s constant, **e** is the charge of the electron, **h** is Planck’s constant, and **c** is the speed of light. The value of the constant $\boldsymbol{\alpha}$ is $7.29735254 \times 10^{-3}$, which is nearly equal to 1/137.

In the atoms of alkali metals such as sodium and potassium, there are two components of fine structure (called doublets), while in atoms of alkaline earths there are three components (triplets). This arises because the atoms of alkali metals have only one electron outside a closed core, or shell, of electrons, while the atoms of alkaline earths have two such electrons. Doublet separation for corresponding lines increases with atomic number; thus, with lithium (atomic number 3), a doublet may not be resolved by an ordinary spectroscope, whereas with rubidium (atomic number 37), a doublet may be widely separated.



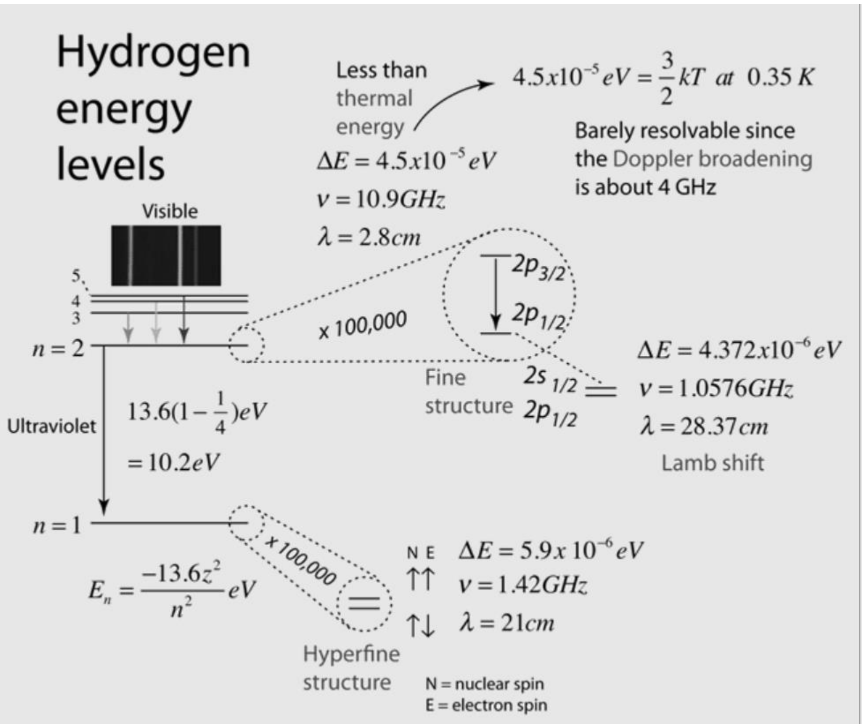


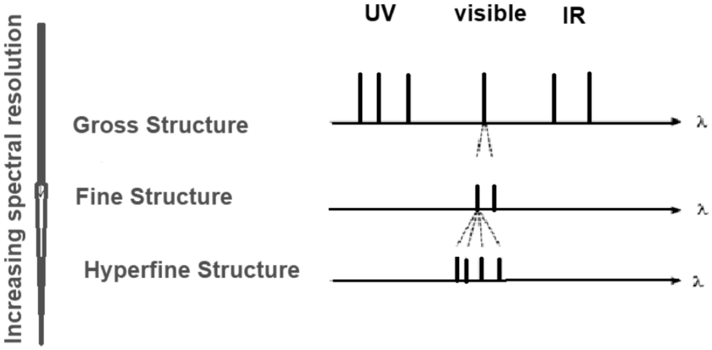


Hyperfine structure (HFS), in spectroscopy, the splitting of a spectral line into a number of components. The splitting is caused by nuclear effects and cannot be observed in an ordinary spectroscope without the aid of an optical device called an interferometer. In fine structure (***q.v.***), line splitting is the result of energy changes produced by electron spin–orbit coupling (***i.e.,*** interaction of forces from orbital and spin motion of electrons); but in hyperfine structure, line splitting is attributed to the fact that in addition to electron spin in an atom, the atomic nucleus itself spins about its own axis. Energy states of the atom will be split into levels corresponding to slightly different energies. Each of these energy levels may be assigned a quantum number, and they are then called quantized levels. Thus, when the atoms of an element radiate energy, transitions are made between these quantized energy levels, giving rise to hyperfine structure.

The spin quantum number is zero for nuclei of even atomic number and even mass number, and therefore no HFS is found in their spectral lines. The spectra of other nuclei do exhibit hyperfine structure. By observing HFS, it is possible to calculate nuclear spin.

A similar effect of line splitting is caused by mass differences (isotopes) of atoms in an element and is called isotope structure, or isotope shift. These spectral lines are sometimes referred to as hyperfine structure but may be observed in an element with spin-zero isotopes (even atomic and mass numbers). Isotope structure is seldom observed without true HFS accompanying it.





	Energy (eV)	Effects
Gross structure of spectral lines	1-10	electron-nuclear attraction Electron kinetic energy Electron-electron repulsion
Fine structure of spectral lines	0.001 - 0.01	Spin-orbit interaction Relativistic corrections
Hyperfine structure	10^{-6} - 10^{-5}	Nuclear interactions

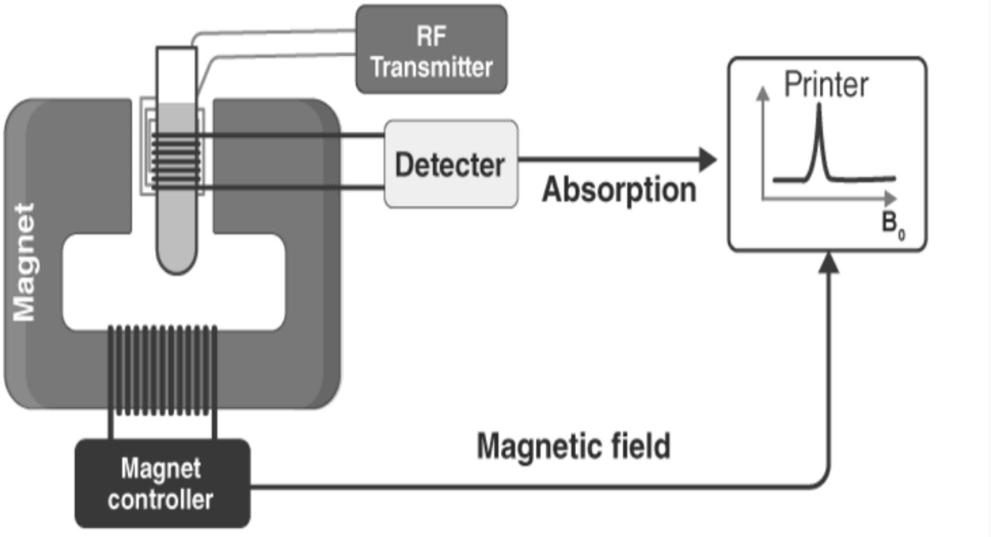
10.8 NMR

NMR Spectroscopy is abbreviated as *Nuclear Magnetic Resonance spectroscopy.*

Nuclear magnetic resonance (NMR) spectroscopy is the study of molecules by recording the interaction of radiofrequency (Rf) electromagnetic radiations with the nuclei of molecules placed in a strong magnetic field.

Zeeman first observed the strange behaviour of certain nuclei when subjected to a strong magnetic field at the end of the nineteenth century, but the practical use of the so-called *"Zeeman effect"* was only made in the 1950s when NMR spectrometers became commercially available.

It is a research technique that exploits the magnetic properties of certain atomic nuclei. The NMR spectroscopy determines the physical and chemical properties of atoms or molecules.



NMR Spectroscopy Instrumentation

Basis of NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) was first detected experimentally at the end of 1945, nearly concurrently with the work groups Felix Bloch, Stanford University and Edward Purcell, Harvard University. The first NMR spectrum was first published in the same issue of the Physical Review in January 1946. Bloch and Purcell were jointly awarded the 1952 Nobel Prize in Physics for their research of Nuclear Magnetic Resonance Spectroscopy.

Nuclear magnetic resonance (NMR) spectroscopy is a crucial analytical tool for organic chemists. The research in the organic lab has been significantly improved with the aid of the NMR. Not only can it provide information on the structure of the molecule, it can also determine the content and purity of the sample. Proton (1H) NMR is one of the most widely used NMR methods by organic chemists. The protons present in the molecule will behave differently depending on the surrounding chemical environment, making it possible to elucidate their structure.

NMR Spectroscopy Principle

Many nuclei have spin, and all nuclei are electrically charged, according to the NMR principle. An energy transfer from the base energy to a higher energy level is achievable when an external magnetic field is supplied.

- All nuclei are electrically charged, and many have spin.
- Transfer of energy is possible from base energy to higher energy levels when an external magnetic field is applied.
- The transfer of energy occurs at a wavelength that coincides with the radio frequency.
- Also, energy is emitted at the same frequency when the spin comes back to its base level.
- Therefore, by measuring the signal which matches this transfer the processing of the NMR spectrum for the concerned nucleus is yield.

NMR Spectroscopy Working

- Place the sample in a magnetic field.
- Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.
- These NMR signals are detected with sensitive radio receivers.
- The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.
- This gives details of a molecule’s individual functional groups and its electronic structure.
- Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.
- This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

Chemical Shift in NMR Spectroscopy

A spinning charge generates a magnetic field that results in a magnetic moment proportional to the spin. In the presence of an external magnetic field, two spin states exist; one spin up and one spin down, where one aligns with the magnetic field and the other opposes it.

Chemical shift is characterized as the difference between the resonant frequency of the spinning protons and the signal of the reference molecule. Nuclear magnetic resonance chemical change is one of the most important properties usable for molecular structure determination. There are also different nuclei that can be detected by NMR spectroscopy, 1H (proton), 13C (carbon 13), 15N (nitrogen 15), 19F (fluorine 19), among many more. 1H and 13C are the most widely used. The definition of 1H as it is very descriptive of the spectroscopy of the NMR. Both the nuts have a good charge and are constantly revolving like a cloud. Through mechanics, we learn that a charge in motion produces a magnetic field. In NMR, when we reach the radio frequency (Rf) radiation nucleus, it causes the nucleus and its magnetic field to turn (or it causes the nuclear magnet to pulse, thus the term NMR).

NMR Spectroscopy Instrumentation

This instrument consists of nine major parts. They are discussed below:

- **Sample holder –** It is a glass tube which is 8.5 cm long and 0.3 cm in diameter.
- **Magnetic coils –** Magnetic coil generates magnetic field whenever current flows through it
- **Permanent magnet –** It helps in providing a homogenous magnetic field at 60 – 100 MHZ
- **Sweep generator –** Modifies the strength of the magnetic field which is already applied.
- **Radiofrequency transmitter –** It produces a powerful but short pulse of the radio waves.
- **Radiofrequency –** It helps in detecting receiver radio frequencies.
- **RF detector –** It helps in determining unabsorbed radio frequencies.
- **Recorder –** It records the NMR signals which are received by the RF detector.
- **Readout system –** A computer that records the data.

NMR Spectroscopy Techniques

1. **Resonant Frequency -**It refers to the energy of the absorption, and the intensity of the signal that is proportional to the strength of the magnetic field. NMR active nuclei absorb electromagnetic radiation at a frequency characteristic of the isotope when placed in a magnetic field.
2. **Acquisition of Spectra -** Upon excitation of the sample with a radiofrequency pulse, a nuclear magnetic resonance response is obtained. It is a very weak signal and requires sensitive radio receivers to pick up.

NMR Spectroscopy Applications

1. NMR spectroscopy is a Spectroscopy technique used by chemists and biochemists to investigate the properties of organic molecules, although it is applicable to any kind of sample that contains nuclei possessing spin.
2. For example, the NMR can quantitatively analyze mixtures containing known compounds. NMR can either be used to match against spectral libraries or to infer the basic structure directly for unknown compounds.
3. Once the basic structure is known, NMR can be used to determine molecular conformation in solutions as well as in studying physical properties at the molecular level such as conformational exchange, phase changes, solubility, and diffusion.

10.9 ESR

ESR Full Form: Electron spin resonance (ESR) is a spectroscopic technique that is used to detect the transitions induced by electromagnetic radiation between the different energy levels of electron spins in the presence of a static magnetic field.

- Also called EPR Spectroscopy or Electron Paramagnetic Resonance Spectroscopy.
- Non-destructive technique
- Extensively used in transition metal complexes
- Deviated geometries in crystals

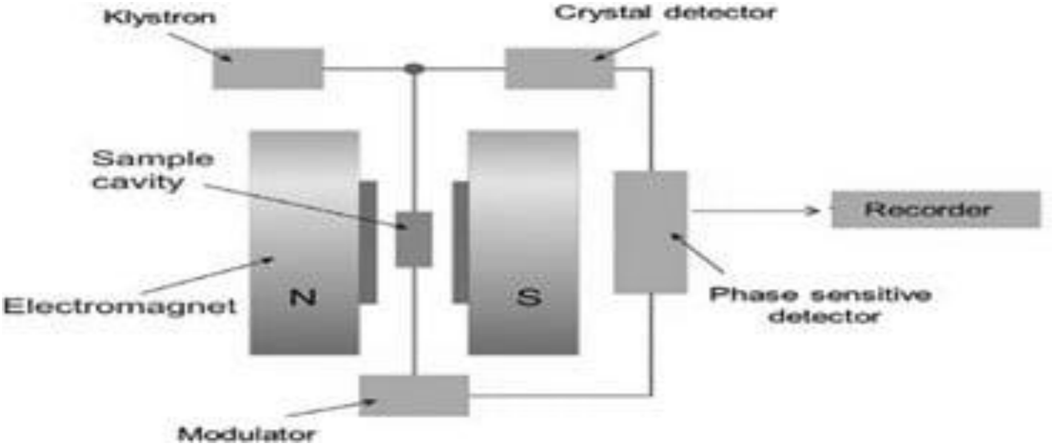
The full form of ESR is Electron Spin Resonance Spectroscopy. It is a branch of absorption spectroscopy in which radiation having a **frequency in the microwave region** is absorbed by the paramagnetic substances to induce a transition between the magnetic energy levels of electrons with unpaired spins. Magnetic energy splitting is done by applying a static magnetic field. Absorption spectroscopies operate at microwave frequency 10^4-10^6 MHz.

PRINCIPLE OF ESR

ESR spectroscopy is based upon the absorption of microwave radiation by an unpaired electron when exposed to a strong magnetic field.

- The electronic energy levels of the atom or molecules will split into different levels. Such excitation is called magnetic resonance absorption.
- With an ESR instrument, a static/magnetic field and microwave are used to observe the behavior of unpaired electrons in the material being studied.
- In principle, ESR finds paramagnetic centers (e.g., radicals) that may or may not be radiation-induced.

- A solid external magnetic field generates a difference between the energy levels of the electron spins, **ms = +½, and ms = –½**, which results in resonance absorption of an applied microwave energy figure below.



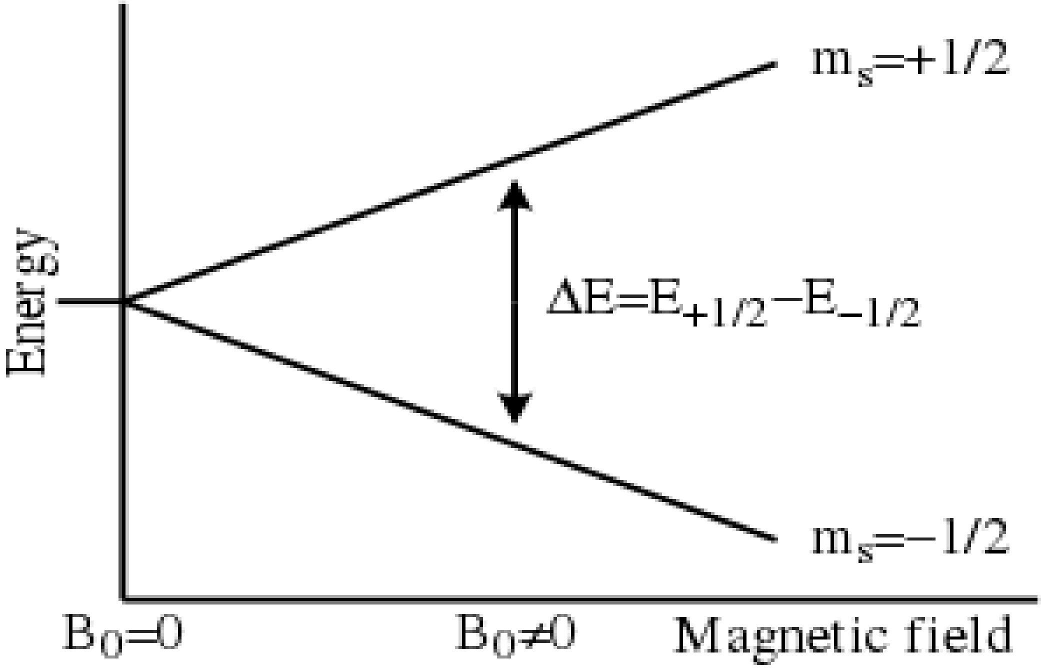


Fig. Showing a Strong external magnetic field generates a difference between the energy levels of the electron spins, ms = +½, and ms = –½

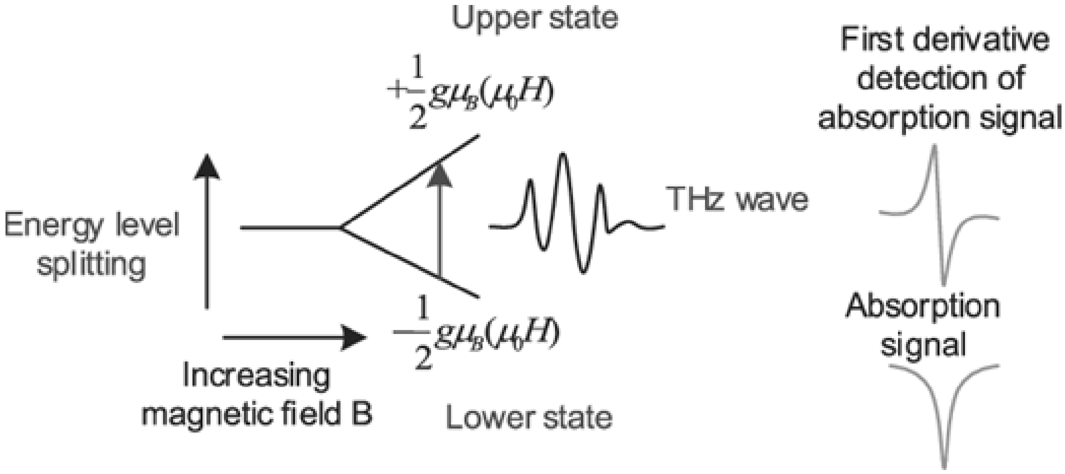
- The study of the behavior of electrons in a condition of the sample.
- ESR is used to observe and measure the absorption of microwave energy by unpaired electrons in a magnetic field as an electron's energy levels.

Working Principle of ESR

Electron Spin Resonance Spectroscopy working principle is explained in the points given below. For more understanding, check the points given here.

- The gap between the energy states is widened until it matches the energy of the microwaves. This is done by **increasing an external magnetic field.**

- At this point, the unpaired electrons can move between their two spin states.
- Absorption lines are detected when the separation energy level is equal to the energy of the incident light.
- It is this absorption that is monitored and converted into a spectrum.



ESR is Shown by the Following:

- An atom has an odd number of electrons.
- Ions have partly filled inner electron shells.
- Free radicals have unpaired electrons etc.

APPLICATIONS OF ESR SPECTROSCOPY

STUDY OF FREE RADICALS

- With the help of this, we can study free radicals. Even in low concentrations, we can check free radicals using ESR SPECTROSCOPY.
- The structure of organic and inorganic free radicals can be identified.
- We can also investigate molecules in the triplet state.
- The spin label gives information about the polarity of its environment.
- With the help of ESR Spectroscopy, several types of irradiated food can be identified.
- It can detect paramagnetic ions and free radicals in a variety of materials.

STRUCTURAL DETERMINATION

- In certain cases, ESR provides information about the shape of the radicals.

10.10 SUMMARY

In this unit we discussed about different techniques Spectroscopy.

Spectroscopy is the science of studying materials by measuring their response to different frequencies of radiation. It should be noted that while a few forms of spectroscopy use other forms of radiative energy, such as acoustic or matter waves, spectroscopy is virtually always understood to use *electromagnetic* radiation to probe matter.

Spectroscopy is a fundamental tool of scientific study, with applications ranging from materials characterization to astronomy and medicine. Spectroscopy techniques are commonly categorized according to the wavelength region used, the nature of the interaction involved, or the type of material studied.

10.11 TERMINAL QUESTIONS

Q1: Which type of electronic transition do aromatic compounds undergo?

(a) $(\sigma \rightarrow \sigma^*)$

(b) $(n \rightarrow \sigma^*)$

(c) $(n \rightarrow \pi^*)$

(d) $(\pi \rightarrow \pi^*)$

Q2: On which of the following factors does absorbance depend?

(a) Molar concentration of the sample

(b) Path length

(c) Molar absorption coefficient

(d) All of the above

Q3: Nuclear Magnetic Resonance (NMR) spectroscopy is an example of which type of spectroscopy?

(a) Absorption spectroscopy

(b) Emission spectroscopy

(c) Scattering spectroscopy

(d) None of the above

Q4: Which type of spectra display colored lines?

(a) Absorption spectra

(b) Emission spectra

(c) Scattering spectra

(d) All of the above

Q5: What is the unit of absorbance?

(a) Liters per mole per cm (L/mol.cm)

(b) Moles per liter (mol/L)

(c) Unitless

(d) Centimeters (cm)

10.12 ANSWER AND SOLUTION OF TERMINAL QUESTION

1. d
2. d
3. a
4. b
5. c

10.13 SUGGESTED READINGS

1. Introduction to Quantum Mechanics: David J. Griffiths.
2. Quantum Mechanics: Noureddine Zettili.
3. Elements of Quantum Mechanics: Kamal Singh, S.P.Singh
4. Quantum Mechanics: Chatwal and Anand

ROUGH WORK