



# ALAGAPPA UNIVERSITY

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(A State University Established by the Government of Tamil Nadu)

KARAIKUDI – 630 003



## Directorate of Distance Education

**M.Sc. [Physics]**

**II - Semester**

**345 21**

**QUANTUM MECHANICS-I**

**Authors:**

**Dr. Nikhil Ranjan Roy**, *Former Professor and Head, Department of Physics, Ranchi University*

Units (1 - 7)

**Mr VK Sarin**, *Retd. Senior Manager (Engineer), BHEL, Director - VARITECH*

Units (8 -14)

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E-28, Sector-8, Noida - 201301 (UP)

Phone: 0120-4078900 • Fax: 0120-4078999

Regd. Office: 7361, Ravindra Mansion, Ram Nagar, New Delhi 110 055

• Website: [www.vikaspublishing.com](http://www.vikaspublishing.com) • Email: [helpline@vikaspublishing.com](mailto:helpline@vikaspublishing.com)

**Work Order No. AU/DDE/DE1-291/Preparation and Printing of Course Materials/2018 Dated 19.11.2018 Copies - 500**

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## Quantum Mechanics - I

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## INTRODUCTION

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Quantum Mechanics (QM), also known as quantum physics, quantum theory, the wave mechanical model, matrix mechanics or quantum field theory, is a fundamental theory in physics which describes nature at the smallest scales of energy levels of atoms and subatomic particles. Principally, the quantum mechanics differs from classical physics in that energy, momentum, angular momentum and other quantities of a bound system are restricted to discrete values (quantization); objects have characteristics of both particles and waves (wave-particle duality); and there are limits to the precision with which quantities can be measured, uncertainty principle.

The foundations of quantum mechanics were established during the first half of the 20th century by Max Planck, Niels Bohr, Werner Heisenberg, Louis de Broglie, Arthur Compton, Albert Einstein, Erwin Schrödinger, Paul Dirac, David Hilbert, and others. The modern theory is formulated in various specially developed mathematical formalisms. In one of them, a mathematical function, the wave function, provides information about the probability amplitude of position, momentum, and other physical properties of a particle. The Schrödinger equation, applied to the free particle, predicts that the center of a wave packet will move through space at a constant velocity.

This book, *Quantum Mechanics-I*, is divided into four blocks, which are further subdivided into fourteen units. The topics discussed include wave particle duality, uncertainty principle, postulates of quantum mechanics, Schrödinger equation (time dependent and time independent), Ehrenfest's theorem, eigenfunction and eigenvectors, probability density, linear harmonic oscillator and tunnel effect, the free particle, particle in a box, three dimensional harmonic oscillator, rigid rotator, diatomic molecules, hydrogen atom, separation of variables, Dirac's ket and bra vectors, harmonic oscillator, solution using ladder operator, Schrödinger, Heisenberg and interaction pictures, perturbation theory (first order), time independent, Stark effect in hydrogen atom, variation method, ground state of helium atom and of deuteron, W.K.B approximation, time dependent perturbation theory, spontaneous emission and stimulated emission, Einstein's A & B coefficients, semi-classical and quantum theory of radiation, Rayleigh and Raman scattering and selection rules.

The book follows the self-instructional mode wherein each unit begins with an 'Introduction' to the topic. The 'Objectives' are then outlined before going on to the presentation of the detailed content in a simple and structured format. 'Check Your Progress' questions are provided at regular intervals to test the student's understanding of the subject. 'Answers to Check Your Progress Questions', a 'Summary', a list of 'Key Words', and a set of 'Self-Assessment Questions and Exercises' are provided at the end of each unit for effective recapitulation.

## NOTES

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**BLOCK - I**  
**FOUNDATIONS**

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*Postulates*

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**UNIT 1 POSTULATES**

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**NOTES**

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**1.0 INTRODUCTION**

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Quantum Mechanics (QM); also known as quantum physics, quantum theory, the wave mechanical model, or matrix mechanics, quantum field theory; is a fundamental theory in physics which describes nature at the smallest scales of energy levels of atoms and subatomic particles. In the mathematically rigorous formulation of quantum mechanics developed by Paul Dirac, David Hilbert, John von Neumann, and Hermann Weyl, the possible states of a quantum mechanical system are symbolized as unit vectors (called state vectors).

In order to understand the origin of quantum physics and the subsequent development of an altogether new and conceptually different mathematical theory of quantum mechanics, it is first of all necessary to understand the phenomena at micro-level that what was happening at the atomic and subatomic levels. The new aspects of nature and phenomena that were revealed at these levels are referred to as quantum phenomena, the word 'quantum' referring to peculiar aspects of nature that go against common sense. The study of quantum phenomena has come to be known as quantum physics.

## NOTES

Wave particle duality is the concept in quantum mechanics that every particle or quantum entity may be partly described in terms not only of particles, but also of waves. It expresses the inability of the classical concepts 'particle' or 'wave' to fully describe the behaviour of quantum scale objects.

In this unit, you will study about the wave particle duality, uncertainty principle and postulates of quantum mechanics.

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### 1.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand the significance of quantum mechanics
- Explain the wave particle duality
- Evaluate uncertainty principle
- Describe the various postulates of quantum mechanics

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### 1.2 ORIGIN AND SCOPE OF QUANTUM PHYSICS

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In order to understand the origin of quantum physics and the subsequent development of an altogether new and conceptually different mathematical theory of quantum mechanics, it is first of all necessary to understand the background of the crisis in physics which was witnessed in the beginning of the 20th century.

Towards the end of the 19th century and the beginning of the 20th century many new discoveries took place. The discovery of X-rays in 1895, the laws of radioactivity in 1896, electron in 1897, dependence of electron's mass on its velocity, the laws of photoelectric effect, the laws of Compton effect are a few in a very imposing list of discoveries. Many new experiments, such as Franck and Hertz experiment, Davisson-Germer experiment, Thomson's experiment were performed during the period. Many new aspects of nature were encountered while dealing with physical problems in the domain of small particles, namely atoms and subatomic particles. What was astonishing was that the new discoveries, the results of new experiments and the phenomena at atomic and subatomic levels could not be understood in terms of the then existing laws of classical physics. The phenomena at microlevel were found to be quite strange and one had to lose one's common sense in order to perceive what was happening at the atomic and subatomic levels. The new aspects of nature and phenomena that were revealed at these levels are referred to as *quantum phenomena*, the word 'quantum' referring to peculiar aspects of nature that go against common sense.

The study of quantum phenomena has come to be known as quantum physics.

Like classical physics, quantum physics also has been provided with a mathematical apparatus. The entirely new conceptual structure for dynamics in particular and physics in general, has been evolved during the last century. The currently accepted structure developed by Schrödinger, Heisenberg, Max Born, Jordan, Dirac and many others to deal with problems in the microdomain, i.e., at atomic and subatomic levels is termed as quantum mechanics.

## NOTES

### Scope of Quantum Mechanics

The laws of quantum physics that govern the elementary particles are, however, not unconcerned with the macroscopic world and instead represent generalization of classical laws including them as special cases. The laws of quantum physics have been found to be the most general laws of nature discovered so far.

We may note that just as theory of relativity extends the range of application of physical laws to the region of very high velocities and just as the universal constant of fundamental significance ' $c$ ' (speed of light in vacuum) characterizes relativity, so a universal constant of fundamental significance ' $h$ ' (Planck's constant) characterizes quantum physics which includes classical physics as a special case.

It is often said that 'revolution' was brought about through the discovery of quantum mechanics. The word revolution suggests that something has been overturned completely. We may note that the discovery of quantum mechanics has not overturned the laws of classical physics in any way. The motion of a simple pendulum is described in the same way even today as it was done prior to the discovery of quantum mechanics. Classical ideas embodied in the laws of classical physics have their own limits of applicability. The classical theories of physics do not find universal validity in the sense that they are only good phenomenological laws and are unable to tell us everything even about macroscopic bodies. There exists no comprehensive classical theory of matter. Classical physics does not provide answers to:

- Why the densities of materials are what they are?
- Why the elastic constants have the values they have?
- Why a rod breaks if the tension in the rod exceeds a certain limit?
- Why copper melts at  $1083^{\circ}\text{C}$ ?
- Why sodium vapour emits yellow light?
- Why copper conducts electricity but sulphur does not?
- Why uranium atom disintegrates spontaneously releasing energy?, etc.

## NOTES

We find a host of observation for which classical physics has to tell us very little or nothing at all. Besides, the facts of chemistry are not understood in terms of classical laws.

With the advent of quantum mechanics our knowledge has expanded enormously about the laws of physics in the realm of small particles which has consequently enabled us to build, if not comprehensive, at least a good theory of matter.

The theory of quantum mechanics has explained all kinds of details, such as why an oxygen atom combines with two hydrogen atoms to make one molecule of water, and so on. Quantum mechanics thus supplies the theory behind chemistry. It has been realized that fundamental theoretical chemistry is based on the theory of quantum mechanics.

### 1.2.1 Wave Nature of Microparticles: de-Broglie's Hypothesis

Around 1923, Louis de-Broglie suggested that the idea of duality should be extended not only to radiation but also to all microparticles. He hypothesized that just as a quantum of radiation has a wave associated with it which governs its motion in space, so also a quantity of matter has a corresponding wave (which may be called matter wave) that governs its motion in space.

The universe is essentially composed of only two entities namely matter and radiation. de-Broglie agreed that since one of the entities, namely radiation, has dual nature, the other entity matter must also exhibit dual character. His hypothesis is consistent with the symmetry principle of nature.

De-Broglie proposed to associate, with every microparticle, corpuscular characteristics namely energy  $E$  and momentum  $p$  on the one hand, and wave characteristics namely frequency  $\nu$  and wavelength  $\lambda$  on the other hand. According to de-Broglie, the mutual dependence between the characteristics of the two kinds was accomplished, through the Planck's constant  $h$  as

$$E = h\nu \quad \text{and} \quad p = \frac{h\nu}{c} = \frac{h}{\lambda} \quad \dots(1.1)$$

This relation is known as de-Broglie's equation.

The wavelength  $\lambda$  of matter wave associated with a microparticle is called de-Broglie wavelength of the particle. De-Broglie's hypothesis had profound importance from the fact that relation in Equation (1.1) was assumed to be satisfied not only for photons (zero rest mass), but for all microparticles, particularly for those which possess rest mass and which were associated with corpuscles.

### Confirmation of de-Broglie's Hypothesis

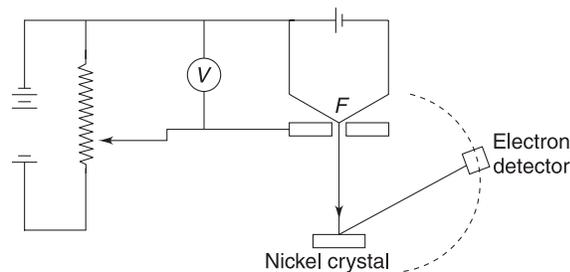
Walter Elsasser, for the first time in 1926, pointed out that the wave nature of matter could be tested by allowing a beam of electrons of appropriate

energy to be incident on a crystalline solid in which periodic arrangement of atoms might serve as a three-dimensional array of diffracting centres for the electron wave (if it at all exists), when diffraction peaks in characteristic directions might be observed.

The above idea was confirmed experimentally by Clinton Davisson and Lester Germer in the United States and George Thomson in Scotland.

### Davisson and Germer's Experiment

The experimental arrangement used by Davisson and Germer is schematically shown in the Figure 1.1.



**Fig. 1.1** Davisson and Germer Experiment

F is a filament which emits electrons when heated electrically.

The emitted electrons are accelerated through a potential  $V$  whose value can be adjusted as required by means of a potential divider arrangement. The accelerated electrons having kinetic energy  $E$  are then allowed to pass through a system of narrow slits so as to obtain a thin collimated beam of electrons. The beam of electrons thus obtained is then allowed to be incident normally on a single crystal C of nickel enclosed in a vacuum chamber. The crystal can be rotated about the incident beam as the axis. D is an electron detector which detects only elastically scattered electrons. The detector can be moved along an arc of a circle about the crystal so as to measure the intensity of elastic scattering in different directions in front of the crystal.

The intensities of the different beam at different angles  $\phi$  and for different values of the accelerating potential were determined. The results obtained are shown in the Figure 1.2 and Figure 1.3. A peak in the intensity was observed at  $\phi = 50^\circ$  for  $V = 54$  volts. Such an observation does not find explanation on the basis of particle motion. However, it finds explanation in terms of interference phenomenon which is characteristic of wave only.

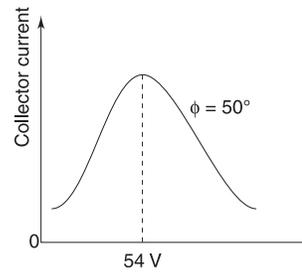
The wavelength of electrons impinging the crystal are given by  $\lambda = \frac{h}{p}$  according to de-Broglie's equation. We may assume Bragg reflections for electron wave to occur from certain families of atomic planes as in the case

## NOTES

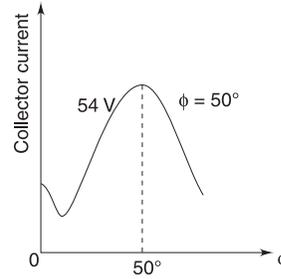
of X-ray diffraction from crystals. Bragg reflection obeying Bragg's equation is illustrated in the Figure 1.4. Bragg's equation is given by:

$$2d \sin \theta = m\lambda; \quad m = 1, 2, 3 \quad \dots(1.2)$$

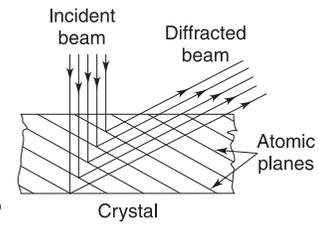
## NOTES



**Fig. 1.2**



**Fig. 1.3**



**Fig. 1.4**

Using X-ray analysis on the crystal it is found that at  $\phi = 50^\circ$ , a Bragg reflection occurs from atomic plane having interplanar spacing  $d = 0.91 \text{ \AA}$  and the corresponding Bragg angle of reflection or glancing angle is  $65^\circ$  (as indicated in the figure). Considering  $m = 1$  we obtain

$$2 \times (0.91 \text{ \AA}) \sin 65^\circ = \lambda$$

$$\text{or} \quad \lambda = 1.65 \text{ \AA} \quad \dots(1.3)$$

For electrons having kinetic energy  $E = 54 \text{ eV}$ , the de-Broglie wavelength is,

$$\lambda = \frac{h}{\sqrt{2mE}} \quad \dots(1.4)$$

Substituting  $h$ ,  $m$  and  $E$  we obtain,

$$\lambda = 1.65 \text{ \AA}. \quad \dots(1.5)$$

The existence of electron wave and the validity of de-Broglie equation are thus established.

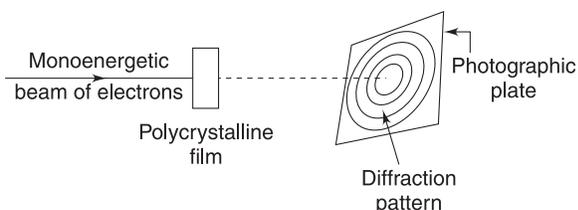
We may note that in the above calculations the value  $m = 1$  is used. If  $m = 2$  or more, then there should occur intensity peaks for different values of  $\phi$ . However, no such peaks are observed experimentally.

### GP Thomson's Experiment

Thomson's experiment is analogous to Debye-Scherrer X-ray diffraction method.

The experimental arrangement consisted of a glass envelope in which electrons were emitted from a heated filament. The emitted electrons were suitably accelerated and collimated to give a uni-directional, thin, monoenergetic beam of electrons. The beam thus obtained was allowed

to fall normally on a polycrystalline material as shown in Figure 1.5. The scattered (diffracted) electrons were recorded on a photographic film placed perpendicular to the incident beam.



**Fig. 1.5** GP Thomson Experiment

On the photographic plate a set of concentric circles were observed. The pattern of circles obtained was found to be a characteristic of the crystal used.

On replacing the electron beam by a monochromatic X-ray beam a similar circular pattern was observed on the photographic plate.

From the knowledge of the wavelength of the electron beam  $\left( \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \right)$  it was possible to determine the geometry of the crystal lattice which was found to be in complete agreement with that obtained using X-ray diffraction analysis of the crystal. It is thus clear that electron beam is diffracted by a crystal in the same way as X-rays.

It is important to note in the experiment of Davisson and Germer and of Thomson the following:

- In the process of acceleration, an electron behaves like a particle of charge  $-e$  and mass  $m$ .
- During the process of diffraction, the same electron behaves like a wave of wavelength  $\lambda = \frac{h}{p}$ .

Thus, the electron which shows wave-like property in one part of the experiment exhibits particle-like properties in two other parts of the same experiment. Clearly, for a complete description both the particle aspect as well as the wave aspect become necessary.

### Conclusion

The experiments of Davisson and Germer and Thomson give clear evidence of the existence of wave properties of electrons. Besides, the experiments confirm the validity of de-Broglie equation at least for the electron.

Experiments on diffraction of molecular beam of hydrogen and atomic beam of helium by the lithium fluoride crystal were performed by Estermann, Stern and Frisch. Hydrogen molecule and helium atom being

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very much different from each other as well as from electron, their successful experiments led to the *universality of matter waves*.

Fermi, Marshall and Zinn performed interference and diffraction experiments with slow neutrons and obtained results confirming de-Broglie's hypothesis. It is important to note that *neutron diffraction* is nowadays an important technique in crystal structure studies as a complement to X-ray and electron diffraction techniques.

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### 1.3 WAVE PARTICLE DUALITY

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In classical physics, energy is transported either by particles or by waves. Some macroscopic phenomena can be explained using a particle model while some other using a wave model. The radiation and matter of the observable universe exhibit both wave and particle characteristics. Radiation behaves as wave in its propagation but the same radiation exhibits particle behavior in its interaction with matter. Similarly entities of non-zero rest mass of which matter is made of requires wave model for understanding their diffraction effects. We are thus compelled to use both particle as well wave models for the same entity. Duality is thus established. We may, however, note that under given experimental conditions only one model is revealed.

Classical physics has acquainted us with two types of motion, namely corpuscular and wave. *Localization* of objects in space and definite path or trajectory of motion of objects in space are the two basic characteristics of corpuscular motion. The wave motion, on the other hand, is characterized by delocalization in space. The phenomena in the macroscopic world clearly distinguish the corpuscular motion and the wave motion. These classical concepts are, however, not revealed in the phenomena in the domain of microparticles. The motion of a microparticle shows both corpuscular as well as wave behaviours. If we consider corpuscular motion and wave motion as two separate cases of motion then microparticles occupy a place somewhere in between. They are neither purely corpuscular nor purely wave-like in the classical sense, instead, they are something qualitatively different. A microparticle to some extent is like a corpuscle and to some extent like a wave. The extents to which it is a corpuscle or a wave depends upon the conditions under which it is considered. In classical physics, corpuscle and wave are two mutually exclusive extremities, but at the level of microphenomena these extremities combine within the framework of a *single* microparticle. In this level we neither talk of particle nor of wave but only of microparticle. This is wave–particle duality.

**Check Your Progress**

1. What is quantum physics?
2. Define how the theory of relativity characterizes quantum physics.
3. Explain the Louis de-Broglie idea of duality.
4. What is mutual dependence according to de-Broglie?
5. What is the wavelength of electrons impinging the crystal according to de-Broglie's equation?
6. What does the radiation and matter of the observable universe exhibit?

**NOTES****1.4 THE UNCERTAINTY PRINCIPLE**

Equations of motion in classical mechanics (Newton's equation, Lagrange's equations, Hamilton's canonical equations) can be solved to find exactly the position and momentum (the two quantities that define the state of the system) of the system at all future and past instants of time from a knowledge of the position and momentum of the system at some given instant of time. This mechanics, as we know, is quite successful in the macroscopic world to predict future motion of objects in terms of their initial motion.

An observation or a measurement on a system involves an inherent interaction between the observer or the measuring instrument and the system, thereby producing disturbance in the system. In the case of a macroscopic system which obeys the laws of classical physics, disturbances, so caused are usually ignorable or controllable and can be taken into account accurately ahead of time by suitable calculation. The basic laws of physics are thus deterministic and the position and velocity (or momentum) of an object can be determined simultaneously with unlimited accuracy.

Such determinism is, however, lost in quantum physics which deals with problems in the domain of atomic and sub-atomic particles. The disturbances caused due to inherent interaction in the observations or measurements no longer remain ignorable and controllable irrespective of the skill of the observer and the improvements in measuring technique. *Precise and simultaneous measurement* of position and velocity of matter or of radiation by actual experiment becomes fundamentally impossible.

Heisenberg, in 1927, stated the uncertainty principle (also called indeterminacy principle) in the following two parts:

- (i) Experiment cannot determine simultaneously the component of momentum say  $p_x$  of a particle and its corresponding coordinate position

$x$  with unlimited accuracy; instead, the precision of measurement is inherently limited by the measurement process itself, such that

$$\Delta p_x \Delta x \geq \frac{\hbar}{2} \quad \dots(1.6)$$

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In the above,  $\Delta p_x$  is the uncertainty within which the momentum  $p_x$  is known and the position  $x$  in the same experiment is known within an accuracy  $\Delta x$ . There are exactly similar relations for the other two components.

$$\Delta p_y \Delta y \geq \frac{\hbar}{2} \quad \dots(1.7)$$

$$\Delta p_z \Delta z \geq \frac{\hbar}{2} \quad \dots(1.8)$$

- (ii) The uncertainties involved in simultaneous measurement of energy and time are given by,

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad \dots(1.9)$$

The above relation means that an energy determination that has an uncertainty  $\Delta E$  must occupy at least a time interval  $\Delta t = \frac{\hbar}{2\Delta E}$ .

Alternatively, if a system is in a given state for not longer than  $\Delta t$ , the energy of the system in that state is uncertain, at least by an amount  $\Delta E = \frac{\hbar}{2\Delta t}$ .

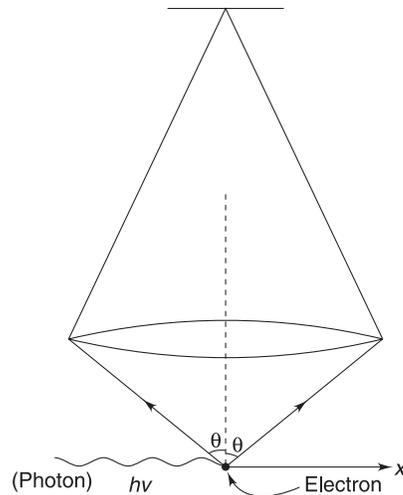
*It is important to note that position–momentum uncertainty relation given by the Equations (1.6), (1.7) and (1.8) and the time energy uncertainty relation given by the Equation (1.9) are quite different because the position and momentum variables can be measured at a given time and they play symmetric roles, whereas energy and time play different roles, the energy being a variable and the time being a parameter.*

### 1.4.1 Physical Origin of the Uncertainty Principle

Bohr proposed a *thought experiment* which is aimed at measuring the position of an electron accurately by observing it through a microscope. For viewing, the electron needs to be illuminated by light. In the process of illumination, the electron recoils because of Compton effect in a way that cannot be determined completely. Hence, the electron gets disturbed from its position. The disturbance can be decreased by using light of very weak intensity. The weakest that can be used is to assume that the electron is observable if only one scattered photon enters the objective lens of the microscope. The momentum of the incident photon for the light of frequency  $\nu$  is,

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

If  $2\theta$  be the angle subtended by the objective lens at the electron then the electron can be viewed provided a photon of the incident light gets scattered within the angular range  $2\theta$  as illustrated in the Figure 1.6.



**Fig. 1.6**

Clearly, the  $x$ -component of the momentum of the photon can have any value from  $-p \sin \theta$  to  $+p \sin \theta$ . After, scattering, the momentum becomes uncertain by an amount  $\Delta p_x$  given by,

$$\Delta p_x = p \sin \theta - (-p \sin \theta) = 2p \sin \theta$$

or 
$$\Delta p_x = \frac{2h}{\lambda} \sin \theta \quad \dots(1.10)$$

In the photon-electron collision, the linear momentum remains conserved and hence the electron receives a recoil momentum in the  $x$ -direction equal to the  $x$ -momentum change in the photon. Thus, the uncertainty of the  $x$ -component of the momentum of the electron is,

$$\Delta p_x = 2 \frac{h}{\lambda} \sin \theta.$$

It is possible to reduce  $\Delta p_x$  by using light of longer wavelength and/or using microscope with an objective lens subtending a smaller angle at the electron.

We know that the image of a point object formed by a convex lens is not a point; instead, it is a diffraction pattern. It is the resolving power of the microscope which determines the accuracy with which the electron can be located. Thus, the uncertainty in the position of the electron is equal to the linear separation between two point objects just resolvable in the image which is given by,

$$\Delta x = \frac{\lambda}{\sin \theta} \quad \dots(1.11)$$

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such that the one scattered photon at our disposal must originate somewhere within this range of the axis of the microscope.

Using the above results we get the product of the uncertainties in  $p_x$  and  $x$  to be given by,

$$\Delta p_x \Delta x = 2 \frac{h}{\lambda} \sin \theta \times \frac{\lambda}{\sin \theta} = 2h > \frac{\hbar}{2} \quad \dots(1.12)$$

If we use light of short wavelength, say gamma rays, to reduce  $\Delta x$ , we simultaneously increase the Compton recoil and hence increase the  $\Delta p_x$  and conversely. Similarly, if we use a lens of small aperture to reduce  $\theta$ ,  $\Delta p_x$  is reduced but  $\Delta x$  increases and conversely. Thus it is not possible to simultaneously make  $\Delta p_x$  and  $\Delta x$  as small as we may wish because the procedure that makes one small makes the other large.

Let us consider the electron to move freely along the  $x$ -axis, then its energy is given by,

$$E = \frac{p_x^2}{2m} \quad \dots(1.13)$$

If  $p_x$  is uncertain by  $\Delta p_x$ , then the uncertainty in the energy is,

$$\Delta E = 2 \frac{p_x}{2m} \Delta p_x = v_x \Delta p_x \quad \dots(1.14)$$

In the above,  $v_x \left( = \frac{p_x}{m} \right)$  is the recoil velocity of the electron along the  $x$ -axis which is illuminated with light. If  $\Delta t$  is the time interval required for the observation of the electron then the uncertainty in the portion of the electron is,

$$\Delta x = v_x \Delta t \quad \dots(1.15)$$

From the above, we have

$$\Delta p_x = \frac{\Delta E}{v_x} = \frac{\Delta E \Delta t}{\Delta x}$$

or

$$\Delta p_x \Delta x = \Delta E \Delta t \quad \dots(1.16)$$

Using  $\Delta p_x \Delta x \geq \frac{\hbar}{2}$ , we obtain

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad \dots(1.17)$$

### Discussions

Heisenberg's uncertainty relations have their roots in experiments.

If uncertainty principle is considered to be the fundamental principle of nature then wave particle duality of matter and radiation becomes obvious as can be understood from the following.

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The corpuscular description of an entity (matter or radiation) gives information about momentum and energy while the wave description of the same entity provides information about place and time. From uncertainty principle of Heisenberg we find that every determination of exact position carries with it large uncertainty in the momentum and vice-versa. Similarly, every determination of exact time involves a large uncertainty in energy and vice-versa. Thus, an experiment that aims the radiation to reveal its wave character strongly suppresses its particle character. Similarly, an experiment aiming to reveal particle character of radiation, strongly suppresses the wave character. Thus experiments do not allow the wave and particle characters to come face to face under the same experimental situation which could make duality obvious.

We also see that the de-Broglie relation  $p = \frac{h}{\lambda}$  and Einstein's relation  $E = h\nu$  which hold for both matter and radiation when combined with properties universal to wave give the uncertainty relations of Heisenberg. We can thus say that Heisenberg's uncertainty relations stem from wave-particle duality.

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### 1.5 POSTULATES OF QUANTUM MECHANICS

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The foundation of any physical theory rests on some hypotheses or postulates which are regarded as fundamental to the theory. The theory thus founded provides a logical as well as mathematical connection between the postulates and their observational consequences which are usually the predictions of the theory.

The basic elements (constructs) of the modern theory as developed by Schrödinger, Heisenberg, Jordan, Max Born, Dirac and many others, are (i) Physical System (ii) Observable (iii) Operator and (iv) State of Physical System.

Before we state and discuss the basic postulates of quantum theory in relation to these elements it is desirable to discuss these elements briefly.

- (i) **Physical System:** A physical system will be generally defined as an object of interest to the experimentalist. Thus, it may be an electron, a photon, a nucleus, or any combination of these which can be made the object of systematic study. The results of such systematic study will, in general, be represented by sets of real numbers which have been obtained from specific measurements or operations performed on the system.
- (ii) **Observable:** The operations will have been performed to determine certain properties of the system, such as its mass, size, energy, momentum, position or, in general, any function of the coordinates and momenta. Such properties of the system are called its observables.

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In this sense, the observables of a physical system are actually more representative of certain operations which can be performed on the system rather than they are of the system itself.

- (iii) **Operator:** Operator are associated with each measurable parameter in a physical system and are termed as quantum mechanical operator.
- (iv) **The State of Physical System:** It is possible to prepare systems in such a way that there will, in general, be one or more observables which yield identical results upon repeated measurements. For any particular method of preparation, the observable which exhibits this type of behaviour is said to have sharp values. The state of a physical system will then be defined in terms of the observables which are sharp, together with their particular values. The method of preparation of the system will determine which of its observables are sharp. Hence, the method of preparation determines the state of a physical system.

### 1.5.1 Basic Postulates of Quantum Mechanics

The purpose of the basic postulates of the quantum theory is to correlate the constructs defined above in such a way that the result of the correlation becomes physically meaningful in terms of the results of experiments. Thus, the postulates should provide an explicit definition for the constructs of states, in a mathematically meaningful fashion.

**Postulate 1:** To every quantum mechanical state of a physical system of 's' degree of freedom, there corresponds a function  $\psi$ , called the **wave function**. In general,  $\psi$  is a complex-valued function of generalized coordinates  $q_1, q_2, \dots, q_s$  and time 't'. The function  $\psi$  and its derivatives are single-valued, continuous and quadratically integrable over the entire domain of definition.

The representation in which the wave functions are functions of coordinates and time is called *coordinate representation*, while the representation in which the wave functions are functions of the momentum components and time is called the *momentum representation*. In order to extract physically meaningful information from wave functions, the second, third and fourth postulates have been made.

**Postulate 2:** For every observable of a physical system, there corresponds a Hermitian operator.

In the Table 1.1 below are given classical representations and corresponding quantum mechanical operators for the observables of a single particle.

*Table 1.1 Quantum Mechanical Operators*

Observable	Classical Representation	Operator
x-Coordinate	x	x
y-Coordinate	y	y
z-Coordinate	z	z

x-Component of Momentum	$p_x = m\dot{x}$	$-i\hbar \frac{\partial}{\partial x}$
y-Component of Momentum	$p_y = m\dot{y}$	$-i\hbar \frac{\partial}{\partial y}$
z-Component of Momentum	$p_z = m\dot{z}$	$-i\hbar \frac{\partial}{\partial z}$
Total Linear Momentum	$\vec{p} = m\dot{\vec{r}}$	$-i\hbar \vec{\nabla}$
Total Angular Momentum	$\vec{M}$	$-i\hbar \vec{r} \times \vec{\nabla}$
Kinetic Energy	$\frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$	$-\frac{\hbar^2}{2m} \nabla^2$
Potential Energy	$V(x, y, z)$	$V(x, y, z)$
Energy	$E$	$-i\hbar \frac{\partial}{\partial t}$
Time	$t$	$t$

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**Postulate 3:** The only possible result of a precise measurement of an observable  $A$  whose corresponding operator is  $\hat{A}$  are the eigenvalues  $a_n$  which are the solutions of the eigenvalue equation,

$$\hat{A}\psi_n = a_n\psi_n$$

where  $\{\psi_n\}$  forms a *complete set* of functions called eigenfunctions of  $\hat{A}$ . This means that any arbitrary state function can be expressed as a linear combination of the eigenfunctions.

**Postulate 4:** When a system is in a state described by the wave function  $\psi$ , the expected mean or expectation value, of a series of measurement of an observable, say  $A$ , is

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau}$$

where  $\hat{A}$  is the operator corresponding to the observable  $A$  and the integration is carried over the entire domain of definition.

It is usual to consider any state function, namely the wave function  $\psi$  to be normalized, i.e.,

$$\int \psi^* \psi d\tau = 1$$

With normalized wave function, Eq. (ii) gives

$$\langle A \rangle = \int \psi^* \hat{A} \psi d\tau$$

To study the development of the state of a quantum system, a fifth postulate has been introduced.

**Postulate 5:** The state function  $\psi(\vec{r}, t)$  of a physical system are solutions of the differential equation

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

where the operator  $\hat{H}$  corresponds to the total energy of the physical system at time  $t$ . It is, in general, a function of the operators for  $\vec{r}$ ,  $\vec{p}$  and time  $t$ .

### 1.5.2 Consequences of the Postulates

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The postulates stated in the last section have consequences which serve to establish the fundamental properties of the quantum theory. Besides, they tell us how these properties differ from those of classical theory. In the sub-sections which follow we discuss the general properties of the states of physical systems at a given instant of time (Quantum Statics).

#### Eigenstates

It is usual to assume any state function, say  $\phi$ , to be normalized. As such the expectation value of an observable  $A$  in that state is,

$$\langle A \rangle = \int \phi^* \hat{A} \phi d\tau \quad \dots(1.18)$$

Let us now suppose that the state function  $\phi$  is an eigenfunction of  $\hat{A}$ , say  $\psi_n$ , belonging to eigenvalue  $a_n$ . Equation can then be written as

$$\langle A \rangle = \int \psi_n^* \hat{A} \psi_n d\tau \quad \dots(1.19)$$

But we have the eigenvalue equation,

$$\hat{A} \psi_n = a_n \psi_n$$

And hence

$$\langle A \rangle = a_n \int \psi_n^* \psi_n d\tau = a_n \quad \dots(1.20)$$

Thus if the state of a system is an eigenfunction of the operator corresponding to a certain observable of the system then the expectation value of the observable is that eigenvalue of the operator which belongs to the given eigenfunction.

The observable then exhibits a sharp value. If a system exists in a state such that an observable exhibits a sharp value then that state is called an **eigenstate** of that observable. For example, if a physical system exists in a state such that repeated measurement of the total energy yields the same value  $W$ , then the system is considered to be in an eigenstate of energy, or in an energy eigenstate corresponding to the sharp value  $W$ , i.e., corresponding to the energy eigenvalue  $W$ .

#### Superposition States

Consider the system in a state described by the state function  $\phi$  in which the observable  $A$  does not exhibit a sharp value. The repeated measurement of the observable  $A$  then results in a spectrum of values, However, the result of any one measurement remains unpredictable, except within certain limits.

To illustrate this, let us suppose that the system is in an energy eigenstate, say  $\phi$ , and the observable to be measured be the linear momentum  $\vec{p}$ . Let the momentum operator  $\hat{p}$  have a complete set of momentum eigenfunctions say  $\{\psi_n\}$ . We can then express  $\phi$  as the linear superposition,

$$\phi = \sum a_n \psi_n \quad \dots(1.21)$$

The expectation value of the momentum of the system in state  $\phi$  is, by definition,

$$\langle p \rangle = \int \phi^* \hat{p} \phi d\tau$$

or

$$\langle p \rangle = \sum_n \sum_m a_n^* a_m \int \psi_n^* \hat{p} \psi_m d\tau$$

or

$$\langle p \rangle = \sum_n \sum_m a_n^* a_m p_m \int \psi_n^* \psi_m d\tau$$

or

$$\langle p \rangle = \sum_n \sum_m a_n^* a_m p_m \delta_{nm}$$

or

$$\langle p \rangle = \sum_n |a_n|^2 p_n \quad \dots(1.22)$$

The above result needs interpretation.

According to Postulate 2, the only possible result of a measurement of the momentum is one of the eigenvalues of the momentum operator. Let a series of measurements of the momentum of the system yield the various eigenvalues  $p_n$  with corresponding relative frequencies  $\omega_n$ . The mean value of the momentum can then be expressed mathematically as,

$$\langle p \rangle = \sum_n \omega_n p_n \quad \dots(1.23)$$

In view of Equations (1.22) and (1.23) it is reasonable to assume that  $|a_n|^2$  of Equation (1.22) are exactly the  $\omega_n$  of Equation (1.23). Since  $\phi$  is normalized, we have,

$$\int \phi^* \phi d\tau = 1$$

Using Equation (1.21) the above gives,

$$\sum_n \sum_m a_n^* a_m \int \psi_n^* \psi_m d\tau = 1$$

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Whence we get

$$\sum |a_n|^2 = 1$$

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Thus,  $|a_n|^2 \leq 1$ , for all  $n$ , as they should be, if the  $|a_n|^2$  are equal to  $\omega_n$ .

If an observable  $A$  of a system on measurement exhibits a range of values  $a_n$  together with a given frequency distribution  $\omega_n$ , the system is said to be in a superposition of eigenstates of  $\hat{A}$  or simply in a superposition state of  $\hat{A}$ .

*It is important to note that while  $\phi$  represents a superposition state relative to one operator, it is, in general, an eigenstate of some other operator.*

### Check Your Progress

7. What will be the momentum of the incident photon for the light of frequency  $\nu$ ?
8. What is the uncertainty in the position of the electron for the linear separation?
9. What are the basic elements (constructs) of the modern theory?
10. What are observables?
11. What is the purpose of the basic postulates of the quantum theory?
12. When an observable is called an eigenstate?

## 1.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The study of quantum phenomena has come to be known as quantum physics.
2. The theory of relativity extends the range of application of physical laws to the region of very high velocities and just as the universal constant of fundamental significance 'c' (speed of light in vacuum) characterizes relativity, so a universal constant of fundamental significance 'h' (Planck's constant) characterizes quantum physics.
3. Louis de-Broglie suggested that the idea of duality should be extended not only to radiation but also to all microparticles. He hypothesized that just as a quantum of radiation has a wave associated with it which governs its motion in space, so also a quantity of matter has a corresponding wave (which may be called matter wave) that governs its motion in space.

The universe is essentially composed of only two entities namely matter and radiation. De-Broglie agreed that since one of the entities, namely radiation, has dual nature, the other entity matter must also exhibit dual character. His hypothesis is consistent with the symmetry principle of nature.

4. De-Broglie proposed to associate, with every microparticle, corpuscular characteristics namely energy  $E$  and momentum  $p$  on the one hand, and wave characteristics namely frequency  $\nu$  and wavelength  $\lambda$  on the other hand. According to de-Broglie, the mutual dependence between the characteristics of the two kinds was accomplished, through the Planck's constant  $h$  as

$$E = h\nu \quad \text{and} \quad p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

This relation is known as de-Broglie's equation.

The wavelength  $\lambda$  of matter wave associated with a microparticle is called de-Broglie wavelength of the particle.

5. The wavelength of electrons impinging the crystal are given by  $\lambda = \frac{h}{p}$  according to de-Broglie's equation.
6. The radiation and matter of the observable universe exhibit both wave and particle characteristics. Radiation behaves as wave in its propagation but the same radiation exhibits particle behavior in its interaction with matter.
7. The momentum of the incident photon for the light of frequency  $\nu$  is,
- $$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

If  $2\theta$  be the angle subtended by the objective lens at the electron then the electron can be viewed provided a photon of the incident light gets scattered within the angular range  $2\theta$

8. The uncertainty in the position of the electron is equal to the linear separation between two point objects just resolvable in the image which is given by,

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

such that the one scattered photon at our disposal must originate somewhere within this range of the axis of the microscope.

9. The basic elements (constructs) of the modern theory as developed by Schrödinger, Heisenberg, Jordan, Max Born, Dirac and many others, are (i) Physical System (ii) Observable (iii) Operator and (iv) State of Physical System.
10. The operations will have been performed to determine certain properties of the system, such as its mass, size, energy, momentum, position or, in

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general, any function of the coordinates and momenta. Such properties of the system are called its observables.

11. The purpose of the basic postulates of the quantum theory is to correlate the constructs defined above in such a way that the result of the correlation becomes physically meaningful in terms of the results of experiments. Thus, the postulates should provide an explicit definition for the constructs of states, in a mathematically meaningful fashion.
12. If a system exists in a state such that an observable exhibits a sharp value then that state is called an **eigenstate** of that observable.

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## 1.7 SUMMARY

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- The study of quantum phenomena has come to be known as quantum physics.
- Like classical physics, quantum physics also has been provided with a mathematical apparatus. The currently accepted structure developed by Schrödinger, Heisenberg, Max Born, Jordan, Dirac and many others to deal with problems in the microdomain, i.e., at atomic and subatomic levels is termed as quantum mechanics.
- The theory of relativity extends the range of application of physical laws to the region of very high velocities and just as the universal constant of fundamental significance 'c' (speed of light in vacuum) characterizes relativity, so a universal constant of fundamental significance 'h' (Planck's constant) characterizes quantum physics which includes classical physics as a special case.
- Around 1923, Louis de-Broglie suggested that the idea of duality should be extended not only to radiation but also to all microparticles. He hypothesized that just as a quantum of radiation has a wave associated with it which governs its motion in space, so also a quantity of matter has a corresponding wave (which may be called matter wave) that governs its motion in space.
- The universe is essentially composed of only two entities namely matter and radiation. De-Broglie agreed that since one of the entities, namely radiation, has dual nature, the other entity matter must also exhibit dual character. His hypothesis is consistent with the symmetry principle of nature.
- De-Broglie proposed to associate, with every microparticle, corpuscular characteristics namely energy  $E$  and momentum  $p$  on the one hand, and wave characteristics namely frequency  $\nu$  and wavelength  $\lambda$  on the other hand. According to de-Broglie, the mutual dependence between

the characteristics of the two kinds was accomplished, through the Planck's constant  $h$  as

$$E = h\nu \quad \text{and} \quad p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

This relation is known as de-Broglie's equation.

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- The wavelength  $\lambda$  of matter wave associated with a microparticle is called de-Broglie wavelength of the particle.
- The wavelength of electrons impinging the crystal are given by  $\lambda = \frac{h}{p}$  according to de-Broglie's equation.
- In the process of acceleration, an electron behaves like a particle of charge  $-e$  and mass  $m$ .

During the process of diffraction, the same electron behaves like a wave of wavelength  $\lambda = \frac{h}{p}$ .

- In classical physics, energy is transported either by particles or by waves. Some macroscopic phenomena can be explained using a particle model while some other using a wave model.
- A microparticle to some extent is like a corpuscle and to some extent like a wave. The extents to which it is a corpuscle or a wave depends upon the conditions under which it is considered.
- Equations of motion in classical mechanics (Newton's equation, Lagrange's equations, Hamilton's canonical equations) can be solved to find exactly the position and momentum (the two quantities that define the state of the system) of the system at all future and past instants of time from a knowledge of the position and momentum of the system at some given instant of time.
- Bohr proposed a *thought experiment* which is aimed at measuring the position of an electron accurately by observing it through a microscope.
- In the photon-electron collision, the linear momentum remains conserved and hence the electron receives a recoil momentum in the  $x$ -direction equal to the  $x$ -momentum change in the photon.
- The uncertainty in the position of the electron is equal to the linear separation between two point objects just resolvable in the image which is given by,

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

such that the one scattered photon at our disposal must originate somewhere within this range of the axis of the microscope.

- The corpuscular description of an entity (matter or radiation) gives information about momentum and energy while the wave description of the same entity provides information about place and time.

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- From uncertainty principle of Heisenberg we find that every determination of exact position carries with it large uncertainty in the momentum and vice-versa.
- The de-Broglie relation  $p = \frac{h}{\lambda}$  and Einstein's relation  $E = h\nu$  which hold for both matter and radiation when combined with properties universal to wave give the uncertainty relations of Heisenberg.
- The foundation of any physical theory rests on some hypotheses or postulates which are regarded as fundamental to the theory. The theory thus founded provides a logical as well as mathematical connection between the postulates and their observational consequences which are usually the predictions of the theory.
- The basic elements (constructs) of the modern theory as developed by Schrödinger, Heisenberg, Jordan, Max Born, Dirac and many others, are (i) Physical System (ii) Observable (iii) Operator and (iv) State of Physical System.
- A physical system will be generally defined as an object of interest to the experimentalist. Thus, it may be an electron, a photon, a nucleus, or any combination of these which can be made the object of systematic study.
- The operations will have been performed to determine certain properties of the system, such as its mass, size, energy, momentum, position or, in general, any function of the coordinates and momenta. Such properties of the system are called its observables.
- The purpose of the basic postulates of the quantum theory is to correlate the constructs defined above in such a way that the result of the correlation becomes physically meaningful in terms of the results of experiments. Thus, the postulates should provide an explicit definition for the constructs of states, in a mathematically meaningful fashion.
- To every quantum mechanical state of a physical system of 's' degree of freedom, there corresponds a function  $\psi$ , called the wave function.
- For every observable of a physical system, there corresponds a Hermitian operator.
- If the state of a system is an eigenfunction of the operator corresponding to a certain observable of the system then the expectation value of the observable is that eigenvalue of the operator which belongs to the given eigenfunction.
- If an observable  $A$  of a system on measurement exhibits a range of values  $a_n$  together with a given frequency distribution  $\omega_n$ , the system is said to be in a superposition of eigenstates of  $\hat{A}$  or simply in a superposition state of  $\hat{A}$ .

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## 1.8 KEY WORDS

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- **Quantum physics:** The study of quantum phenomena has come to be known as quantum physics.
- **Bohr thought experiment:** It was proposed by Bohr which is aimed at measuring the position of an electron accurately by observing it through a microscope.
- **Uncertainty principle:** It is considered to be the fundamental principle of nature then wave particle duality of matter and radiation becomes evident.
- **Physical system:** It may be an electron, a photon, a nucleus, or any combination of these which can be made the object of systematic study, and the results of the study is generally represented by sets of real numbers which have been obtained from specific measurements or operations performed on the system.
- **Observable:** The operations will have been performed to determine certain properties of the system, such as its mass, size, energy, momentum, position or, in general, any function of the coordinates and momenta. Such properties of the system are called its observables.
- **Operator:** Operators in quantum mechanics are associated with each measurable parameter in a physical system and are also termed as the quantum mechanical operator.
- **Postulates:** It provides an explicit definition for the constructs of states, in a mathematically meaningful fashion.

## NOTES

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## 1.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### Short Answer Questions

1. When was quantum mechanics developed?
2. Name the areas where the quantum mechanics is used.
3. What is wave particle duality?
4. What dose GP Thomson's experiment state?
5. Define the term uncertainty principle.
6. What are postulates in quantum mechanics?
7. What are the basic elements (constructs) of the modern theory for postulates?

**NOTES**

**Long Answer Questions**

1. Briefly discuss about the origin, history and significance of quantum mechanics.
2. Discuss the wave nature of microparticles as stated by de-Broglie's hypothesis.
3. Briefly explain Davisson and Germer's experiment with the help of a diagrams.
4. Prove that the Thomson's experiment is analogous to Debye-Scherrer X-ray diffraction method.
5. Explain wave particle duality.
6. Briefly explain the uncertainty principle. What is the Heisenberg explanations for the uncertainty principle?
7. Discuss in detail about the physical origin of the uncertainty principle.
8. Briefly explain the basic postulates of quantum mechanics. What is the purpose of these postulates?

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**1.10 FURTHER READINGS**

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
- Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.
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## UNIT 2    SCHRÖDINGER EQUATION

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### Structure

- 2.0 Introduction
- 2.1 Objectives
- 2.2 Schrödinger Equation
  - 2.2.1 Dynamical State of a Microparticle: Concept of Wave Function
  - 2.2.2 Concept of Wave Packet
- 2.3 Time Dependent Schrödinger Equation
  - 2.3.1 Operators Corresponding to Energy and Linear Momentum
  - 2.3.2 Time-Dependent Schrödinger Equation for a Particle Moving in a Force Field
  - 2.3.3 Stationary States
- 2.4 Time Independent Schrödinger Equation
- 2.5 Ehrenfest's Theorem
- 2.6 Eigenfunctions and Eigen Vectors
  - 2.6.1 Eigenfunctions and Eigenvalues of a Linear Operator
  - 2.6.2 Eigenvalue Equation
  - 2.6.3 Discrete and Continuous Spectra of Eigenvalues of Operators
  - 2.6.4 Hermitian Operator
  - 2.6.5 Important Theorems on Operators
- 2.7 Probability Density
  - 2.7.1 Normalized Wave Function
  - 2.7.2 Probability Current Density
  - 2.7.3 Normalization Integral, a Constant of Motion
  - 2.7.4 Expectation Value of a Physical Quantity
  - 2.7.5 Acceptable Wave Functions for a Physical System
- 2.8 Answers to Check Your Progress Questions
- 2.9 Summary
- 2.10 Key Words
- 2.11 Self Assessment Questions and Exercises
- 2.12 Further Readings

### NOTES

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## 2.0    INTRODUCTION

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In physics, the Schrödinger equation is a linear partial differential equation that describes the wave function or state function of a quantum-mechanical system. It is a key result in quantum mechanics, and its discovery was a significant landmark in the development of the subject. The equation is named after Erwin Schrödinger, who derived the equation in 1925, and published it in 1926, forming the basis for the work that resulted in his Nobel Prize in Physics in 1933. Schrödinger's equation can be derived from the fact that the time-evolution operator must be unitary, and must therefore be generated by the exponential of a self-adjoint operator, which is the quantum Hamiltonian.

## NOTES

The theory of Schrödinger equation was 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 behaviour of matter wave. 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 computed within the framework of the theory.

The Schrödinger 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 particles. Schrödinger's time-independent equation can be solved analytically for a number of simple systems. The time-dependant equation is of the first order in time but of the second order with respect to the co-ordinates, hence it is not consistent with relativity.

Max Born and Jordan in 1926 gave a probabilistic interpretation of the wave function which is characteristic of and fundamental to the Schrödinger theory. This interpretation of the wavefunction is found to be both convenient and physically transparent enabling us to make precise computations regarding the behaviour of the particle. According to Max Born and Jordan, the wavefunction describes the probability distribution of the particle in space and time.

In this unit, you will study about the Schrödinger equation, wave packet, group velocity and wave packet, time dependent Schrödinger equation, time independent Schrödinger equation, Ehrenfest's theorem, eigenfunction and eigen vectors, Hermitian operator and probability density.

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## 2.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand and use the Schrödinger equations
- Explain about the wave packet and group velocity
- Interpret time dependent Schrödinger equation
- Explain time independent Schrödinger equation
- Define Ehrenfest's theorem
- Calculate the eigenfunction and eigen vectors
- Evaluate Hermitian operator
- Understand the probability density for the Schrödinger wavefunction

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## 2.2 SCHRODINGER EQUATION

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The theory of Schrödinger equation was formulated by Erwin Schrödinger 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 behaviour of matter wave.

The main assumptions made in the theory of Schrödinger equation 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.

In spite 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 computed within the framework of the theory.

The Schrödinger 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 particles.

### 2.2.1 Dynamical State of a Microparticle: Concept of Wave Function

The trajectory of a particle becomes known if the coordinate and momentum of the particle are known at every moment of time. In other words, the trajectory is known if  $x$  and  $\frac{dx}{dt}$  are known at all time  $t$ .

According to Heisenberg's uncertainty relation, a microparticle cannot simultaneously possess a definite coordinate, say,  $x$  and a definite projection of momentum  $p_x$ . Thus, the concept of trajectory of a microparticle, strictly speaking, is not applicable.

The rejection of trajectory concept is related to the existence of wave properties in microparticles which do not permit us to consider a microparticle as a classical corpuscle. The motion of a microparticle along the  $x$ -axis cannot be associated with the differentiable function  $x(t)$  which is so widely used in dealing with the motion of classical objects. From a known value of  $x$  of the microparticle at an instant of time  $t$ , it is impossible to predict the value of  $x$  at the time  $t + dt$ . A microparticle is fundamentally different from a classical corpuscle primarily because (i) it does not have a trajectory which is an essential attribute of a classical corpuscle, (ii) the use of coordinate,

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momentum, angular momentum, energy when considering microparticle become restricted to the framework of uncertainty relations.

Wave concepts are radically different from corpuscular concepts. Hence it is not surprising that the striking contrast between classical corpuscles and microparticle is explained by the existence of wave properties in the latter. It is the wave properties which account for the uncertainty relations and all the consequences resulting from them. We must, however, note that while a microparticle is not a classical corpuscle on one hand, it is not a classical wave on the other hand.

Thus, certain questions, unknown to classical physics, arise about the state and the method of describing the state of a microparticle in a new light.

We know that a classical wave possesses a characteristic frequency ( $\nu$ ), a wavelength ( $\lambda$ ) and the phase velocity ( $v_p$ ) related according to,

$$v_p = \nu\lambda (= \omega/k) \quad \dots(2.1)$$

Besides, any wave motion is described by a quantity which is a continuous function of position in space and of time. For example, an electromagnetic wave propagating along the  $x$ -axis is described by electric and magnetic fields varying with position and time, such as,

$$\begin{aligned} E &= E_0 \sin(\omega t - kx) \\ B &= B_0 \sin(\omega t - kx) \end{aligned} \quad \dots(2.2)$$

Similarly, a sound wave passing through an extended medium is described by the variation of pressure in the medium with position and time. By analogy, the wave belonging to a microparticle may be described by some entity which varies with position in space and time. This variable entity (function) is usually denoted as  $\psi(\vec{r}, t)$  and is called *wave displacement function* or *wave function*. For generality, unlike for a classical wave motion, the wave function which may be used to describe the wave character and the state of a microparticle is taken as a *complex valued* function of position of space and time.

The wave associated with a microparticle is of infinite extent because according to Heisenberg's uncertainty principle, the position of the particle becomes completely unknown if its momentum is taken to be well defined.

The infinite plane wave corresponding to a microparticle of mass ' $m$ ' moving freely along the  $x$ -axis with a well defined momentum  $p_x$  can be described by the wave function  $\psi(x, t)$  given by,

$$\Psi(x, t) = Ae^{i(kx - \omega t)} \quad \dots(2.3)$$

Where  $A$  is the constant amplitude,

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p_x}{h} = \frac{p_x}{\hbar} \quad \dots(2.4)$$

$$\text{And} \quad \omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar} \quad \dots(2.5)$$

In the above,  $E$  is the energy of the particle. Writing  $E = mc^2$ , according to Einstein's mass–energy relation, we obtain,

$$\omega = \frac{mc^2}{\hbar} \quad \dots(2.6)$$

The velocity  $u$  of the de-Broglie wave is thus,

$$u = \nu\lambda = \frac{\omega}{2\pi} \frac{h}{mv} = \frac{mc^2}{\hbar} \times \frac{\hbar}{mv} = \frac{c^2}{v} \quad \dots(2.7)$$

Since  $c$  is the maximum speed that can be attained by any material particle according to Einstein's special theory of relativity, we must have  $v < c$  so that the speed of the de-Broglie wave  $u$  is greater than  $c$  and hence greater than  $v$ . The de-Broglie wave associated with the particle thus travels faster than the particle itself which is a contradictory result. *We thus find that a microparticle cannot be described by a single wave train.*

### 2.2.2 Concept of Wave Packet

An important question that arises and that needs to be settled is about a mathematical description of a microparticle which jointly displays particle as well as wave characteristics. The mathematical scheme must embody the two features simultaneously.

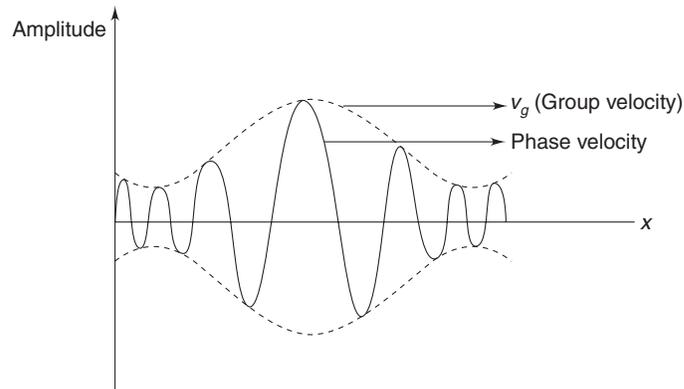
In classical physics, a particle is well localized in space by which we mean that the position and velocity (momentum) of the particle can be simultaneously determined with unlimited accuracy. As seen earlier, a microparticle is described by a wave function corresponding to the matter wave associated with it. A wave function, however, depends on the whole space and hence cannot be localized. A wave function may, however, describe the dynamical state of the particle if it vanishes everywhere except in the immediate neighbourhood of the particle or the neighbourhood of the classical trajectory. In other words, a particle which is localized within a certain region of space can be described by a matter wave function whose amplitude is large in that region and zero outside it. Such matter wave will then be localized around the region of space within which the particle is confined.

A *localized wave function* is called a *wave packet*. A wave packet representing a particle is formed as a result of superposition of a group of waves each having slightly different velocities and wavelengths, the phases and amplitudes of waves at any instant of time being so chosen that they interfere constructively over that small region where the particle is most likely to be located at that instant and destructively elsewhere so that the amplitude reduces to zero. This has been illustrated in Figure (2.1).

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## NOTES

Wave packets find application in describing isolated particles which are confined in a certain region. The concept of wave function is a mathematical representation of particle-like as well as wave-like behaviours of microparticles and hence provides a link between quantum mechanics and classical mechanics.



**Fig. 2.1** Group and Phase Velocity

A one-dimensional wave packet which may describe a classical particle confined to a one-dimensional region, say, a particle moving along the  $x$ -axis can be mathematically constructed by superposing an infinite number of plane waves with slightly different wave number  $k$ , all moving along the  $x$ -axis, by means of Fourier transforms. The wave, packet thus obtained is represented by the wave function  $\psi(x, t)$  given by

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i[kx - \omega t]} dk \quad \dots(2.8)$$

Where  $\phi(k)$  is the amplitude and the frequency  $\omega$  is a function of  $k$ ,

$$\omega = \omega(k) \quad \dots(2.9)$$

### Group Velocity of a Wave Packet

Since our interest lies with localized particles, we need such superposition which leads to a wave group travelling without change of shape. This becomes possible if  $\phi(k)$  is zero for all values of  $k$  excepting those within a small range  $\Delta k$  given by,

$$\left(k_0 - \frac{\Delta k}{2}\right) < k < \left(k_0 + \frac{\Delta k}{2}\right), \Delta k \ll k_0 \quad \dots(2.10)$$

It is then possible to expand  $\omega(k)$  as a power series in  $(k - k_0)$  about  $k_0$  as,

$$\omega(k) = \omega(k_0) + (k - k_0) \left( \frac{d\omega}{dk} \right)_{k=k_0} + \dots \text{smaller terms}$$

or 
$$\omega(k) = \omega_0 + (k - k_0) \frac{d\omega}{dk} \quad \dots(2.11)$$

Where we have written,

$$\omega(k_0) = \omega_0 \quad \dots(2.12)$$

And 
$$\left( \frac{d\omega}{dk} \right)_{k=k_0} = \frac{d\omega}{dk} \quad \dots(2.13)$$

We then obtain,

$$\begin{aligned} \psi(x, t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx - i\omega_0 t - i(k - k_0) \frac{d\omega}{dk} t} dk \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx - ik_0 x + ik_0 x - i\omega_0 t - i(k - k_0) \frac{d\omega}{dk} t} dk \\ &= \frac{1}{\sqrt{2\pi}} \int_{k_0 - \frac{\Delta k}{2}}^{k_0 + \frac{\Delta k}{2}} \phi(k) e^{i(k_0 x - \omega_0 t)} e^{i(k - k_0)x - i(k - k_0) \frac{d\omega}{dk} t} dk \end{aligned}$$

or 
$$\psi(x, t) = e^{i(k_0 x - \omega_0 t)} F(x, t) \quad \dots(2.14)$$

Where 
$$F(x, t) = \frac{1}{\sqrt{2\pi}} \int \phi(k) e^{i(k - k_0) \left[ x - \frac{d\omega}{dk} t \right]} dk \quad \dots(2.15)$$

$\psi(x, t)$  given by Equation (2.14) which represents the wave packet is a plane wave having propagation constant  $k_0$ , angular frequency  $\omega_0$ , propagating along the  $x$ -axis with amplitude  $F(x, t)$  which varies with position  $x$  and time  $t$  through the term  $\left[ x - \left( \frac{d\omega}{dk} \right) t \right]$ . Clearly the wave packet propagates with a velocity called the group velocity given by,

$$v_g = \frac{d\omega}{dk} \quad \dots(2.16)$$

We may note that while the wave packet as a whole moves with group velocity  $v_g$ , the individual waves, whose superposition makes the wave packet, travel with velocity called phase velocity or wave velocity.

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**Equality of Group Velocity and Particle Velocity**

The group velocity is given by,

**NOTES**

$$v_g = \frac{d\omega}{dk}$$

or 
$$v_g = \frac{d\omega}{dp} \frac{dp}{dk} \quad \dots(2.17)$$

Using  $E = \hbar\omega$  and  $p = \hbar k$  we get

$$\omega = \frac{E}{\hbar} \quad \text{and} \quad \frac{dp}{dk} = \hbar \quad \dots(2.18)$$

So that  $v_g$  becomes

$$v_g = \frac{d}{dp} \left( \frac{E}{\hbar} \right) \hbar = \frac{dE}{dp} \quad \dots(2.19)$$

Let the wavepacket under consideration represent a freely moving particle of mass  $m$  moving with a non-relativistic velocity  $v$ . We then have,

$$E = \frac{p^2}{2m} \quad \dots(2.20)$$

So that 
$$\frac{dE}{dp} = \frac{p}{m} = v \quad \dots(2.21)$$

We find from Equations (2.19) and (2.21),

$$v_g = v \quad \dots(2.22)$$

Let us now consider a relativistic particle of rest mass  $m_0$  moving with momentum  $p$ . We then have the energy  $E$  of the particle given by,

$$E^2 = m_0^2 c^4 + c^2 p^2 \quad \dots(23)$$

On differentiation with respect to  $p$ , the above gives

$$2E \frac{dE}{dp} = 2c^2 p$$

or 
$$\frac{dE}{dp} = \frac{c^2 p}{E} = \frac{c^2 \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} v}{m_0 c^2 / \sqrt{1 - \frac{v^2}{c^2}}}$$

or 
$$\frac{dE}{dp} = v \quad \dots(2.24)$$

In view of Equations (2.19) and (2.24) we find that the wave packets corresponding to both relativistic as well as non-relativistic particles have group velocity equal to particle velocity.

### 2.3 TIME DEPENDENT SCHRODINGER EQUATION

The wavelength  $\lambda$  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,

$$\lambda = \frac{h}{p_x} \quad \dots(2.25)$$

The wave-vector  $k$  is related to the wavelength  $\lambda$  as,

$$k = \frac{2\pi}{\lambda} \quad \dots(2.26)$$

From the above two equations, we get,

$$p_x = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k \quad \dots(2.27)$$

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

$$E = \hbar\omega \quad \dots(2.28)$$

Further, we have,

$$E = \frac{p_x^2}{2m} \quad \dots(2.29)$$

So that Equations (2.27), (2.28) and (2.29) yield,

$$\omega = \frac{E}{\hbar} = \frac{p_x^2}{\hbar 2m} = \frac{\hbar^2 k^2}{\hbar 2m} = \frac{\hbar k^2}{2m} \quad \dots(2.30)$$

The wave function  $\psi(x, t)$  which describes the free particle localized in the region of the  $x$ -axis [refer to Equation (2.8)] is given by,

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k) e^{i(kx - \omega t)} dk \quad \dots(2.31)$$

Using  $\omega$  given by Equation (2.30), the above becomes,

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k) e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk \quad \dots(2.32)$$

Differentiating Equation (2.32) with respect to time  $t$ , we get,

### NOTES

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{-i\hbar}{2m} \int_{-\alpha}^{+\alpha} k^2 A(k) e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk \quad \dots(2.33)$$

## NOTES

Further, differentiation of Equation (2.32) 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,

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = - \int_{-\alpha}^{+\alpha} k^2 A(k) e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk \quad \dots(2.34)$$

Multiplying Equation (2.33) by  $i\hbar$  we obtain,

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = \frac{\hbar^2}{2m} \int_{-\alpha}^{+\alpha} k^2 A(k) e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk \quad \dots(2.35)$$

In view of Equations (2.34) and (2.35) we obtain,

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = - \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} \quad \dots(2.36)$$

Equation (2.36) is the *one-dimensional time-dependent Schrödinger equation for a particle of mass  $m$  localized in the region of the  $x$ -axis and described by the wavefunction  $\psi(x, t)$ .*

Equation (2.36) can be extended to three dimensions in a straightforward manner. In three dimensions the wavefunction that describes the state of the particle is a function of position  $\vec{r}$  in space and time  $t$ . It is obtained by generalizing Equation (2.8), whence we get,

$$\begin{aligned} \psi(\vec{r}, t) &= \iiint A(k) e^{i\left[\vec{k} \cdot \vec{r} - \frac{\hbar k^2}{2m} t\right]} dk_x dk_y dk_z \\ &= \iiint A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z \quad \dots(2.37) \end{aligned}$$

Differentiating Equation (2.37) with respect to  $t$  we obtain,

$$\frac{\partial \psi(\vec{r}, t)}{\partial t} = - \frac{i\hbar}{2m} \iiint k^2 A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z$$

The above gives,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \frac{\hbar^2}{2m} \iiint k^2 A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z \quad \dots(2.38)$$

Differentiating Equation (2.37) with respect to  $x$  we get,

$$\frac{\partial \psi(\vec{r}, t)}{\partial x} = i \iiint A(k) k_x e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z$$

The above gives on differentiating with respect to  $x$ ,

$$\frac{\partial^2 \psi(\vec{r}, t)}{\partial x^2} = - \iiint k_x^2 A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z \quad \dots(2.39)$$

We similarly obtain,

$$\frac{\partial^2 \psi(\vec{r}, t)}{\partial y^2} = - \iiint k_y^2 A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z \quad \dots(2.40)$$

And

$$\frac{\partial^2 \psi(\vec{r}, t)}{\partial z^2} = - \iiint k_z^2 A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z \quad \dots(2.41)$$

Adding Equations (2.39), (2.40) and (2.41), we get,

$$\nabla^2 \psi(\vec{r}, t) = - \iiint k^2 A(k) e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x dk_y dk_z \quad \dots(2.42)$$

Equations (2.38) and (2.42) give,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) \quad \dots(2.43)$$

Equation (2.43) is the three-dimensional time-dependent Schrödinger equation for a free particle described by the wavefunction  $\psi(\vec{r}, t)$ . Equations (2.36) and (2.43) give the *causal development* or the *time evolution* of the wavefunctions describing the states of one-dimensional and three-dimensional motions of a *free* particle, respectively, *undisturbed by any measurement*.

### 2.3.1 Operators Corresponding to Energy and Linear Momentum

It is possible to write the one-dimensional Schrödinger equation for a free particle given by Equation (2.36) as,

$$\left(i\hbar \frac{\partial}{\partial t}\right) \psi(x, t) = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x, t) \quad \dots(2.44)$$

## NOTES

## NOTES

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

$$E = \frac{1}{2m} p_x^2 = \frac{1}{2m} (p_x) (p_x) \quad \dots(2.45)$$

Comparison of Equations (2.44) and (2.45) allows us to associate differential operators with the energy  $E$  and the momentum component  $p_x$ , which operate on the wavefunction  $\psi(x, t)$ , as,

$$(E)_{op} = \hat{E} \rightarrow i\hbar \frac{\partial}{\partial t} \quad \dots(2.46)$$

And

$$(p_x)_{op} = \hat{p}_x \rightarrow -i\hbar \frac{\partial}{\partial x} \quad \dots(2.47)$$

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

$$\left. \begin{aligned} \hat{p}_x &\rightarrow -i\hbar \frac{\partial}{\partial x} \\ \hat{p}_y &\rightarrow -i\hbar \frac{\partial}{\partial y} \\ \hat{p}_z &\rightarrow -i\hbar \frac{\partial}{\partial z} \end{aligned} \right\} \quad \dots(2.48)$$

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.,

$$\hat{\vec{p}} \rightarrow -i\hbar \vec{\nabla} \quad \dots(2.49)$$

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

### 2.3.2 Time-Dependent Schrödinger 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,

$$E = \frac{p^2}{2m} + V(\vec{r}, t) \quad \dots(2.50)$$

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

$$\hat{r} = \vec{r} \quad \dots(2.51)$$

And  $\hat{t} = t \quad \dots(2.52)$

Replacing  $E$ ,  $p$ ,  $r$  and  $t$  by their respective operators given by Equations (2.46), (2.49), (2.50) and (2.51) in Equation (2.50) we obtain,

$$i\hbar \frac{\partial}{\partial t} \rightarrow -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \quad \dots(2.53)$$

Allowing the operator Equation (2.53) to operate on the wave function  $\psi(\vec{r}, t)$  describing the state of the particle, we get,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t) \quad \dots(2.54)$$

Equation (2.54) is the time-dependent Schrödinger equation for a particle of mass  $m$  moving in space in a force field described 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  $\hat{H}$  so that the Schrödinger Equation (2.54) can be written in its usual form as,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \hat{H} \psi(\vec{r}, t) \quad \dots(2.55)$$

### 2.3.3 Stationary States

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

$$\begin{aligned} i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} &= \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t) \\ &= \hat{H} \psi(\vec{r}, t) \end{aligned} \quad \dots(2.56)$$

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 systems, that is, systems for which  $\hat{H}$  does not depend explicitly on time. If such is the case, the above equation becomes,

## NOTES

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}, t) \quad \dots(2.57)$$

**NOTES**

Since the operator  $\left( i\hbar \frac{\partial}{\partial t} \right)$  on the left is independent of coordinates while the operator  $\left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right]$  on the right is independent of time, it is reasonable to use, as a trial solution of Equation (2.57), one in the separated form:

$$\psi(\vec{r}, t) = \psi(\vec{r})T(t) \quad \dots(2.58)$$

Substituting Equation (2.56) in Equation (2.57) 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

$$\frac{1}{T(t)} i\hbar \frac{dT(t)}{dt} = \frac{1}{\psi(\vec{r})} \left[ \frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) \right] \quad \dots(2.59)$$

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,

$$(a) \frac{i\hbar}{T(t)} \frac{dT(t)}{dt} = E \quad \text{or} \quad i\hbar \frac{dT(t)}{dt} = ET(t) \quad \dots(2.60)$$

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

$$\text{or} \quad \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad \dots(2.61)$$

Solution of Equation (2.60) is given by,

$$T(t) = e^{\frac{-i}{\hbar} Et} \quad \dots(2.62)$$

Using Equation (2.62) in Equation (2.58) we may write the solution of the Schrödinger Equation (2.57) as,

$$\Psi(\vec{r}, t) = \Psi(\vec{r}) e^{\frac{-i}{\hbar} E t} \quad \dots(2.63)$$

Equation (2.61) can be written as,

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \quad \dots(2.64)$$

Where 
$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) = \frac{\hat{p}^2}{2m} + V(\vec{r}) \quad \dots(2.65)$$

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 (2.64) is the energy eigenvalue equation and the constant is thus identified as the energy eigenvalue. In general, Equation (2.64) has a complete set of solutions  $\Psi_n(\vec{r})$  such that,

$$\hat{H}\Psi_n(\vec{r}) = E_n\Psi_n(\vec{r}) \quad \dots(2.66)$$

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

$$\Psi_n(\vec{r}, t) = \Psi_n(\vec{r}) e^{\frac{-i}{\hbar} E_n t} \quad \dots(2.67)$$

Equation (2.67) gives the time-dependent states of the system.

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

$$\begin{aligned} P_n(\vec{r}, t) &= |\Psi_n(\vec{r}, t)|^2 \\ &= \Psi_n^*(\vec{r}) e^{\frac{i}{\hbar} E_n t} \Psi_n(\vec{r}) e^{\frac{-i}{\hbar} E_n t} \\ &= |\Psi_n(\vec{r})|^2 \end{aligned} \quad \dots(2.68)$$

We find that  $P_n(\vec{r}, t) = \text{constant in time.} \quad \dots(2.69)$

The states described by wavefunction such as  $\Psi_n(\vec{r}, t)$  given by Equation (2.67) for which the probability density is constant in time are called stationary or steady states of the system.

## NOTES

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 described by the wavefunction  $\psi_n(\vec{r}, t)$  is given by,

**NOTES**

$$\begin{aligned}\langle A \rangle &= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}, t) \hat{A} \psi_n(\vec{r}, t) d^3(\vec{r}) \\ &= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}, t) e^{\frac{iE_n}{\hbar}t} \hat{A} \psi_n(\vec{r}) e^{-\frac{iE_n}{\hbar}t} d^3(\vec{r}) \\ &= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}) \hat{A} \psi_n(\vec{r}) d^3(\vec{r}) = \text{Constant in time} \quad \dots(2.70)\end{aligned}$$

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

$$\frac{\partial P(\vec{r}, t)}{\partial t} + \vec{\nabla} \cdot \vec{J}(\vec{r}, t) = 0 \quad \dots(2.71)$$

For stationary states, probability density  $P(\vec{r}, t)$  is independent of time so that  $\frac{\partial P(\vec{r}, t)}{\partial t} = 0$ . Clearly, for stationary states, the current density  $\vec{J}(\vec{r}, t)$ , according to Equation (2.71), satisfies

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

or

$$\text{div } \vec{J}(\vec{r}, t) = 0 \quad \dots(2.72)$$

**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 wavefunctions which vanish at infinity. Clearly, for bound states, the probability density also vanishes at infinity.

**Superposition States**

As we have seen, the particular solutions of Equation (2.57) are of the form,

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r}) e^{-\frac{iE_n}{\hbar}t} \quad \dots(2.73)$$

The general solutions of Equation (2.57) are of the form,

$$\psi_n(\vec{r}, t) = \sum_n a_n \psi_n(\vec{r}, t) = \sum_n a_n \psi_n(\vec{r}) e^{-\frac{iE_n}{\hbar}t} \quad \dots(2.74)$$

where  $a_n$  are constants and, in particular, do not depend on time. The state of the system described by the wavefunction  $\psi(\vec{r}, t)$  [Equation (2.74)] is called a superposition state.

The probability density corresponding to the superposition state is given by,

$$\begin{aligned} P(\vec{r}, t) &= |\psi(\vec{r}, t)|^2 = \left| \sum_n a_n \psi_n(\vec{r}) e^{\frac{-iE_n t}{\hbar}} \right|^2 \\ &= \sum_m \sum_n a_m^* a_n \psi_m^*(\vec{r}) \psi_n(\vec{r}) e^{\frac{i(E_m - E_n)t}{\hbar}} \quad \dots(2.75) \end{aligned}$$

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

$$\begin{aligned} \langle A \rangle &= \int \psi^*(\vec{r}, t) \hat{A} \psi(\vec{r}, t) d^3 \vec{r} \\ &= \sum_m \sum_n a_m^* a_n e^{\frac{i(E_m - E_n)t}{\hbar}} \int \psi_m^*(\vec{r}) \hat{A} \psi_n(\vec{r}) d^3(\vec{r}) \quad \dots(2.76) \end{aligned}$$

As we have seen earlier  $\psi_n$ 's are the energy eigenfunctions, i.e., the eigenfunctions of the Hamiltonian operator  $\hat{H}$ .

If  $\hat{A}$  commutes with  $\hat{H}$ , then  $\psi_n$ 's are also the eigenfunctions of  $\hat{A}$ . In such a case we may write,

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

$$\begin{aligned} \text{Where } \delta_{mn} &= \int \psi_m^*(\vec{r}) \psi_n(\vec{r}) d^3(\vec{r}) = 1, \quad \text{if } m = n \\ &= 0, \quad \text{if } m \neq n \end{aligned}$$

Hence, we obtain,

$$\langle A \rangle = \sum |a_m|^2 A_m \quad \dots(2.77)$$

Clearly  $\langle A \rangle$  is constant in time in a superposition state provided  $\hat{A}$  commutes with  $\hat{H}$ . If  $\hat{A}$  does not commute with  $\hat{H}$ ,  $\langle A \rangle$  is time-dependent in general as indicated by Equation (2.76).

## NOTES

## 2.4 TIME INDEPENDENT SCHRODINGER EQUATION

### NOTES

Consider a particle of mass  $m$  moving freely in space. Let  $\psi(\vec{r}, t)$  or  $\psi(x, y, z, t)$  be the wavefunction 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 wavefunction 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  $u$  is 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 
$$\nabla^2 \psi(\vec{r}, t) = \frac{1}{u^2} \frac{\partial^2 \psi(\vec{r}, t)}{\partial t^2} \quad \dots(2.78)$$

The solution of Equation (2.78) in its most general form is given by,

$$\psi(\vec{r}, t) = \psi(\vec{r}) e^{-i\omega t} \quad \dots(2.79)$$

Where 
$$\omega = 2\pi\nu \quad \dots(2.80)$$

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

We get from Equation (2.79) 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,

$$\frac{\partial^2 \psi(\vec{r}, t)}{\partial t^2} = -\omega^2 \psi(\vec{r}) e^{-i\omega t} \quad \dots(2.81)$$

Using Equation (2.81) in Equation (2.78) we get,

$$\nabla^2 \psi(\vec{r}, t) = -\frac{\omega^2}{u^2} \psi(\vec{r}, t) \quad \dots(2.82)$$

We have,

$$\omega = 2\pi\nu = 2\pi \frac{u}{\lambda} \quad \dots(2.83)$$

Where  $\lambda$  is the wavelength of the de-Broglie wave. Equation (2.83) gives,

$$\frac{\omega}{u} = \frac{2\pi}{\lambda} \quad \dots(2.84)$$

Use of Equation (2.84) in Equation (2.82) 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 
$$\nabla^2 \psi(\vec{r}) + \frac{4\pi^2}{\lambda^2} \psi(\vec{r}) = 0 \quad \dots(2.85)$$

If  $v$  the velocity of the particle, we have,

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

Substituting the above in Equation (2.85) we obtain,

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

or 
$$\nabla^2 \psi(r) + \frac{m^2 v^2}{\hbar^2} \psi(\vec{r}) = 0 \quad \dots(2.86)$$

If  $E$  be the total energy of the particle and  $V$  be its potential energy then we have the kinetic energy of the particle,

$$\frac{1}{2} m v^2 = E - V$$

So that

$$m^2 v^2 = 2m (E - V) \quad \dots(2.87)$$

Substituting Equation (2.87) in Equation (2.86) we obtain,

$$\nabla^2 \psi(\vec{r}) + \frac{2m}{\hbar^2} (E - V) \psi(\vec{r}) = 0 \quad \dots(2.88)$$

Equation (2.88) is the time-independent Schrödinger equation for a particle of mass  $m$ , total energy  $E$  moving in a force field described by the potential energy function  $V$ .

## NOTES

For a freely moving particle in space,  $V = 0$ , so that Equation (2.88) reduces to,

$$\nabla^2 \psi(\vec{r}) + \frac{2m}{\hbar^2} E \psi(\vec{r}) = 0 \quad \dots(2.89)$$

**NOTES**

For one-dimensional motion localized in the region along the  $x$ -axis, Equation (2.88) gives,

$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad \dots(2.90)$$

**Check Your Progress**

1. Define the theory of Schrödinger equation.
2. What are the main assumptions made in the theory of Schrödinger equation?
3. When the trajectory of a particle becomes known?
4. Give the equation for classical wave.
5. What is a wave packet?
6. Give equation for group velocity.
7. What is the kinetic energy  $E$  of the particle?
8. Explain the time-dependent states of a quantum system.
9. According to classical mechanics, give the differential equation for the wavefunction.

**2.5 EHRENFEST'S THEOREM**

P. Ehrenfest in 1927 stated, in regard to the correspondence between the motion of a classical particle and the motion of a wave packet representing the particle, the following theorem.

The averages or the expectation values of the quantum mechanical variables satisfy the same equations of motion as the corresponding classical variables in the corresponding classical description. Specifically the theorem states that,

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle$$

$$\frac{d}{dt} \langle p_x \rangle = \left\langle -\frac{dV(x)}{dx} \right\rangle$$

provided that the wavefunction  $\psi(x, t)$  with respect to which averages are computed satisfies the time-dependent Schrödinger equation,

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

or

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

### Proof of Ehrenfest's Theorem

Consider a particle of mass  $m$  moving along the  $x$ -axis under the action of a force-field described by the potential energy  $V(x)$  for the particle. If  $\psi(x, t)$  be the wave function describing the state of the particle at the instant  $t$  we have the expectation value of the coordinate  $x$  of the particle in the state given by,

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

The time derivative of  $\langle x \rangle$  is,

$$\frac{d\langle x \rangle}{dt} = \frac{\partial}{\partial t} \int_{-\infty}^{+\infty} \psi^*(x, t) x \psi(x, t) dx \quad \dots(2.91)$$

The Schrödinger equation satisfied by  $\psi(x, t)$  is,

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x, t) \quad \dots(2.92)$$

The above gives,

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{-i}{\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x, t) \quad \dots(2.93)$$

Taking complex conjugate of Equation (2.93), we get,

$$\frac{\partial \psi^*(x, t)}{\partial t} = \frac{-i}{\hbar} \left[ \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi^*(x, t) \quad \dots(2.94)$$

Equation (2.91) gives,

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \frac{\partial \psi^*(x, t)}{\partial t} x \psi(x, t) dx + \int_{-\infty}^{+\infty} \psi^*(x, t) x \frac{\partial \psi(x, t)}{\partial t} dx$$

### NOTES

Using Equations (2.93) and (2.94) in the above, we get,

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \frac{i}{\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi^*(x, t) x \psi(x, t) dx$$

## NOTES

$$+ \int_{-\infty}^{+\infty} \psi^*(x, t) x \left( \frac{-i}{\hbar} \right) \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x, t) dx$$

Simplifying, we get,

$$\frac{d\langle x \rangle}{dt} = \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \left[ x \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} - x \psi(x, t) \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \right] dx \quad \dots(2.95)$$

Let,

$$I = \int_{-\infty}^{+\infty} x \psi(x, t) \frac{\partial^2 \psi^*(x, t)}{\partial x^2} dx$$

Integrating by parts, we get,

$$I = \left\{ x \psi(x, t) \frac{\partial \psi^*(x, t)}{\partial x} \right\}_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{\partial \psi^*(x, t)}{\partial x} \frac{\partial}{\partial x} [x \psi(x, t)] dx \quad \dots(2.96)$$

For a localized wave packet we have the boundary conditions,

$$\left. \begin{aligned} \psi(x, t) &\rightarrow 0 && \text{as } x \rightarrow \pm\infty \\ \frac{\partial \psi(x, t)}{\partial x} \text{ and } \frac{\partial \psi^*(x, t)}{\partial x} &\rightarrow 0 && \text{as } x \rightarrow \pm\infty \end{aligned} \right\} \quad \dots(2.97)$$

Use of conditions given by Equation (2.97) in Equation (2.96), we obtain,

$$I = - \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} [x \psi(x, t)] \frac{\partial \psi^*(x, t)}{\partial x} dx$$

Integrating once again by parts, we get

$$I = - \int_{-\infty}^{+\infty} \left\{ \frac{\partial}{\partial x} [x \psi(x, t)] \psi^*(x, t) \right\}_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial^2}{\partial x^2} [x \psi(x, t)] dx$$

Using condition given by Equation (2.97), the above becomes,

$$\begin{aligned} I &= \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial^2}{\partial x^2} [x \psi(x, t)] dx \\ &= \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial}{\partial x} \left[ \psi(x, t) + x \frac{\partial \psi(x, t)}{\partial x} \right] dx \end{aligned}$$

$$= \int_{-\infty}^{+\infty} \psi^*(x, t) \left[ \frac{\partial \psi(x, t)}{\partial x} + x \frac{\partial^2 \psi(x, t)}{\partial x^2} + \frac{\partial \psi(x, t)}{\partial x} \right] dx$$

or

$$I = \int_{-\infty}^{+\infty} \psi^*(x, t) \left[ 2 \frac{\partial \psi(x, t)}{\partial x} + x \frac{\partial^2 \psi(x, t)}{\partial x^2} \right] dx \quad \dots(2.98)$$

Using Equation (2.98) in Equation (2.95) we obtain,

$$\frac{d\langle x \rangle}{dt} = \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \left[ x \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} - 2 \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} - \psi^*(x, t) x \frac{\partial^2 \psi(x, t)}{\partial x^2} \right] dx$$

or

$$\frac{d\langle x \rangle}{dt} = \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} -2 \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} dx$$

or

$$\frac{d\langle x \rangle}{dt} = \frac{1}{m} \int_{-\infty}^{+\infty} \psi^*(x, t) \left( -i\hbar \frac{\partial}{\partial x} \right) \psi(x, t) dx$$

or

$$\frac{d\langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}, \quad \text{since } \langle p_x \rangle = \int_{-\infty}^{+\infty} \psi^*(x, t) \hat{p}_x \psi(x, t) dx$$

or

$$\langle p_x \rangle = m \frac{d\langle x \rangle}{dt} \quad \dots(2.99)$$

In the limiting case if the wave packet reduces to a point, i.e., the particle becomes *completely localized*, we get,

$$\langle x \rangle = x \text{ and } \langle p_x \rangle = p_x \quad \dots(2.100)$$

so that Equation (2.96) reduces to the classical definition,

$$p_x = m \frac{dx}{dt} \quad \dots(2.101)$$

We have the expectation value of  $p_x$  in the state described by the wavefunction  $\psi(x, t)$  given by,

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

Taking time derivative of the above we obtain,

**NOTES**

$$\frac{d\langle p_x \rangle}{dt} = \frac{\partial}{\partial t} \int_{-\infty}^{+\infty} \psi^*(x, t) \left( -i\hbar \frac{\partial}{\partial x} \right) \psi(x, t) dx$$

or

$$\begin{aligned} \frac{d\langle p_x \rangle}{dt} &= -i\hbar \int_{-\infty}^{+\infty} \frac{\partial \psi^*(x, t)}{\partial t} \frac{\partial \psi(x, t)}{\partial x} dx \\ &\quad - i\hbar \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial}{\partial x} \left( \frac{\partial \psi(x, t)}{\partial t} \right) dx \end{aligned}$$

Substituting for  $\frac{\partial \psi^*(x, t)}{\partial t}$  and  $\frac{\partial \psi(x, t)}{\partial t}$  from Equations (2.94) and (2.93) in the above we obtain,

$$\begin{aligned} \frac{d\langle p_x \rangle}{dt} &= -i\hbar \int_{-\infty}^{+\infty} \frac{i}{\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} dx \\ &\quad - i\hbar \int_{-\infty}^{+\infty} \psi^*(x, t) \left( \frac{-i}{\hbar} \right) \frac{\partial}{\partial x} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x, t) dx \\ &= \frac{-\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[ \frac{\partial^2}{\partial x^2} + V(x) \right] \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} dx \\ &\quad + \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial}{\partial x} \left[ \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x, t) dx \\ &= \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \frac{\partial \psi(x, t)}{\partial x} dx + \int_{-\infty}^{+\infty} V(x) \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} dx \\ &\quad + \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial}{\partial x} \left( \frac{\partial^2 \psi(x, t)}{\partial x^2} \right) dx - \int_{-\infty}^{+\infty} \psi^*(x, t) \frac{\partial}{\partial x} [V(x) \psi(x, t)] dx \\ &= \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[ \psi^*(x, t) \frac{\partial}{\partial x} \left( \frac{\partial^2 \psi(x, t)}{\partial x^2} \right) - \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \frac{\partial \psi(x, t)}{\partial x} \right] dx \\ &\quad + \int_{-\infty}^{+\infty} \left[ V(x) \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} - \psi^*(x, t) \frac{\partial}{\partial x} [V(x) \psi(x, t)] \right] dx \\ &= \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[ \frac{\partial}{\partial x} \left( \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} \right) - \frac{\partial \psi^*(x, t)}{\partial x} \frac{\partial^2 \psi(x, t)}{\partial x^2} - \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \frac{\partial \psi(x, t)}{\partial x} \right] dx \\ &\quad + \int_{-\infty}^{+\infty} \psi^*(x, t) \left[ \frac{-\partial V(x)}{\partial x} \right] \psi(x, t) dx \end{aligned}$$

## NOTES

$$= \frac{-\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[ \frac{\partial}{\partial x} \left( \psi^*(x, t) \frac{\partial^2 \psi(x, t)}{\partial x^2} \right) - \frac{\partial}{\partial x} \left[ \frac{\partial \psi^*(x, t)}{\partial x} \frac{\partial \psi(x, t)}{\partial x} \right] \right] dx + \left\langle \frac{-\partial V}{\partial x} \right\rangle$$

Using the condition given by Equation (2.97) in the above we find the first term in the above equation to vanish to yield,

$$\frac{d\langle p_x \rangle}{dt} = \left\langle \frac{-\partial V(x)}{\partial x} \right\rangle$$

The force  $F_x$  corresponding to the potential energy function  $V(x)$  is,

$$F_x = \frac{-\partial V}{\partial x}$$

The above two equations give,

$$\frac{d\langle p_x \rangle}{dt} = \langle F_x \rangle \quad \dots(2.102)$$

In the limiting case of the wave packet reducing to a point, i.e., the particle being completely localized we get,

$$\langle p_x \rangle = p_x \quad \text{and} \quad \langle F_x \rangle = F_x$$

and Equation (2.102) in that case takes the form,

$$F_x = \frac{dp_x}{dt}$$

Which is Newton's second law of motion.

## 2.6 EIGENFUNCTIONS AND EIGEN VECTORS

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  $\hat{A}$  defined in a certain domain of definition. Let  $\psi_1$  and  $\psi_2$  be any two arbitrary functions defined in the domain of definition of  $\hat{A}$ .

If on operating on the sum of the functions  $\psi_1$  and  $\psi_2$  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,

$$\hat{A}(\psi_1 + \psi_2) = \hat{A}\psi_1 + \hat{A}\psi_2 \quad \dots(2.103)$$

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

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

## NOTES

$$\hat{A}(c\psi_2) = c\hat{A}\psi_2 \quad \dots(2.104)$$

Where  $c$  is a number.

## NOTES

The properties of linear operator expressed by the Equations (2.103) and (2.104) will be useful in later developments of quantum mechanics.

### 2.6.1 Eigenfunctions and Eigenvalues of a Linear Operator

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

$$\hat{A}\psi = \phi \quad \dots(2.105)$$

However, for every linear operator  $\hat{A}$ , there exists a set of functions  $\psi_1, \psi_2, \dots, \psi_n$ , such that,

$$\begin{aligned} \hat{A}\psi_1 &= a_1\psi_1 \\ \hat{A}\psi_2 &= a_2\psi_2 \\ &\vdots \\ \hat{A}\psi_n &= a_n\psi_n \end{aligned} \quad \dots(2.106)$$

where  $a_1, a_2, \dots, a_n$  are constants with respect to the variables of which  $\psi_i$ 's ( $i = 1, \dots, n$ ) are functions. The set of functions  $\psi_1, \psi_2, \dots, \psi_n$  are called eigenfunctions of the operator  $\hat{A}$  and the constant  $a_1, a_2, \dots, a_n$  are called the eigenvalues belonging to the eigenfunctions  $\psi_1, \psi_2, \dots, \psi_n$ , respectively.

### 2.6.2 Eigenvalue Equation

The equation,

$$\hat{A}\psi_i = a_i\psi_i \quad (i = 1, 2, \dots, n) \quad \dots(2.107)$$

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

### 2.6.3 Discrete and Continuous Spectra of Eigenvalues of Operators

Consider the differential equation,

$$i \frac{d\psi(x)}{dx} = \lambda\psi(x) \quad \dots(2.108)$$

where  $\psi(x)$  is an arbitrary function of  $x$ ,  $\lambda$  is a constant (independent of  $x$ ) real number and  $\sqrt{-1} = \pm i$ .

Equation (2.108) is a special case of the general operator equation,

$$\hat{A}\psi(x) = a\psi(x) \quad \dots(2.109)$$

where  $\hat{A}$  is an operator and  $a$  is a real number. The general solutions of Equation (2.108) are,

$$\psi(x) = \psi_\lambda(x) = c_\lambda e^{-i\lambda x} \quad \dots(2.110)$$

with  $c_\lambda$  as an arbitrary constant. There exists a function  $\psi_\lambda(x)$  for each value of  $\lambda$  and each satisfies Equation (2.108).

In a sense then, the set of functions,  $\psi_\lambda(x)$  characterizes the operator,

$$\hat{A} \equiv i \frac{d}{dx}$$

and are the **eigenfunctions** or **characteristic functions** of the operator. In general, from Equation (2.109), one obtains a set of such characteristic functions  $\psi_i$  for any operator such that,

$$\hat{A}\psi_i = a_i\psi_i \quad \dots(2.111)$$

We thus find that, in general, an operator possesses a set of eigenfunctions, each of which is characterized by a number  $a_i$  through Equation (2.111). As has been mentioned in the beginning, the numbers  $a_i$  are the eigenvalues or characteristic values of the operator  $\hat{A}$ . The totality of these numbers for a given operator is called the **eigenvalue spectrum** of the operator.

The spectrum of eigenvalues of an operator can be **discrete, continuous** or **discrete-continuous**, depending on the form of the operator and possibly on certain other requirements which may have to be made on the eigenfunctions for physical reasons.

### Example of an Operator with a Continuous Spectrum of Eigenvalues

Consider the operator used in Equation (2.108)  $\hat{A} \int i \frac{d}{dx}$

The eigenfunctions, as we have seen earlier in the section, are

$$\psi_\lambda = c_\lambda e^{-i\lambda x} \quad \dots(2.112)$$

Equation (2.112) defines one eigenfunction for each value of  $\lambda$  which may vary continuously from a minimum to a maximum value. The spectrum of  $\lambda$  is evidently continuous.

### Example of an operator with discrete spectrum of eigenvalues:

Let us consider the second order differential equation,

$$\frac{d^2\psi(x)}{dx^2} + \lambda\psi(x) = \alpha(x) \quad \dots(2.113)$$

Subject to conditions,

## NOTES

$$\alpha(x) = 0 \quad \text{for } 0 < x < a \quad \dots(2.114)$$

$$= \infty \quad \text{for } x \leq 0 \text{ and } x \geq a$$

**NOTES**

In Equation (2.113),  $\psi(x)$  is some arbitrary function of the variable  $x$  and  $\lambda$  is a constant real number.

In view of the condition  $\alpha(x) = \infty$  for  $x \leq 0$  and  $x \geq a$ , we obtain the solution of Equation (2.113) in these two regions to be,

$$\psi(x) = 0$$

Clearly,

$$\text{And} \quad \left. \begin{array}{l} \psi(x) = 0 \quad \text{at } x = 0 \\ \psi(x) = 0 \quad \text{at } x = a \end{array} \right\}$$

In the region  $0 \leq x \leq a$ , Equation (2.113) becomes,

$$\frac{d^2\psi(x)}{dx^2} + \lambda\psi(x) = 0$$

or

$$-\frac{d^2\psi(x)}{dx^2} = \lambda\psi(x) \quad \dots(2.115)$$

The above equation can be identified as the eigenvalue equation,

$$\hat{A}\psi(x) = \lambda\psi(x) \quad \dots(2.116)$$

Where  $\hat{A}$  is the differential operator,

$$\hat{A} \int -\frac{d^2}{dx^2} \quad \dots(2.117)$$

And  $\lambda$  is the eigenvalue of  $\hat{A}$  corresponding to the eigenfunction  $\psi(x)$ .

The most general solution of Equation (2.115) is,

$$\psi(x) = A \sin \sqrt{\lambda}x + B \cos \sqrt{\lambda}x \quad \dots(2.118)$$

Where  $\hat{A}$  and  $\hat{B}$  are constants.

Boundary condition given by Equation (2.116) requires,

$$\psi(x) = 0 \quad \text{at } x = 0$$

The above when used in Equation (2.118) yields,

$$B = 0$$

So that the solution given by Equation (2.118) becomes,

$$\psi(x) = A \sin \sqrt{\lambda}x \quad \dots(2.119)$$

We also have the boundary condition,

$$\psi(x) = 0 \quad \text{at } x = a$$

which when used in Equation (2.119) gives,

$$A \sin \sqrt{\lambda} a = 0$$

or  $\sin \sqrt{\lambda} a = 0 \quad (\because A \neq 0)$

or  $\sin \sqrt{\lambda} a = \sin n\pi \quad (n = 0, \pm 1, \pm 2, \dots)$

or  $\sqrt{\lambda} a = n\pi$

$\therefore \lambda = \frac{n^2 \pi^2}{a^2}$

The possible values of  $\lambda$  from the above equation are given as,

$$0, \frac{\pi^2}{a^2}, \frac{4\pi^2}{a^2}, \frac{9\pi^2}{a^2}, \text{ etc.} \quad \dots(2.120)$$

We find the eigenvalues to be discrete. The eigenfunctions belonging to the possible eigenvalues are,

$$\psi(x) = A \sin \sqrt{\lambda} x = A \sin \left( \frac{n\pi}{a} x \right) \quad \dots(2.121)$$

#### 2.6.4 Hermitian Operator

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

$$\hat{A}\psi = \phi \quad \dots(2.122)$$

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

$$\hat{A}^*\psi^* = \phi^* \quad \dots(2.123)$$

In the domain of definition  $V$  in which the operator  $\hat{A}$  is defined, 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,

$$\int_V u^* \hat{A}v d\tau = \int_V (\hat{A}u)^* v d\tau = \int_V \hat{A}^* u^* v d\tau \quad \dots(2.124)$$

## NOTES

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  $\tilde{A}$  and is defined according to the relation,

**NOTES**

$$\int_v v(\hat{A}u)d\tau = \int_v u(\tilde{A}v)d\tau \quad \dots(2.125)$$

The transposed operator  $\tilde{A}^*$  for the operator  $\tilde{A}$  is, according to Equation (2.125), given by,

$$\int v(\hat{A}^*u)d\tau = \int u(\tilde{A}^*v)d\tau \quad \dots(2.126)$$

It is usual to denote  $\tilde{A}^*$  as  $\hat{A}^\dagger$  (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,

$$\hat{A} = \hat{A}^\dagger \quad \dots(2.127)$$

We may note that in mathematics the terms adjoint, conjugate and associate operator are used for  $\hat{A}^\dagger$ .

**Properties of Hermitian Operator**

Eigenfunctions and eigenvalues of Hermitian operator possess certain very general and useful properties.

**(i) Eigenvalues of Hermitian Operators are Real Numbers****Proof:**

Consider a Hermitian operator  $\hat{A}$ . Let  $\psi_n$  be an eigenfunction of  $\hat{A}$  belonging to the eigenvalue  $a_n$ . We then have the eigenvalue equation,

$$\hat{A}\psi_n = a_n\psi_n \quad \dots(2.128)$$

Taking complex conjugate of Equation (2.128), we get

$$\hat{A}^*\psi_n^* = a_n^*\psi_n^* \quad \dots(2.129)$$

Multiplying Equation (2.128) by  $\psi_n^*$  from the left and integrating over the entire domain of definition we obtain,

$$\int \psi_n^* \hat{A} \psi_n d\tau = \int \psi_n^* a_n \psi_n d\tau = a_n \int \psi_n^* \psi_n d\tau \quad \dots(2.130)$$

Since  $\hat{A}$  is Hermitian we may write Equation (2.130) as,

$$\int \hat{A}^* \psi_n^* \psi_n d\tau = a_n \int \psi_n^* \psi_n d\tau \quad \dots(2.131)$$

Multiplying Equation (2.129) by  $\psi_n$  from the right and integrating over the entire domain of definition we obtain,

$$\int \hat{A}^* \psi_n^* \psi_n d\tau = \int a_n^* \psi_n^* \psi_n d\tau = a_n^* \int \psi_n^* \psi_n d\tau \quad \dots(2.132)$$

The L.H.S of Equations (2.131) and (2.132) are the same and hence we get,

$$a_n \int \psi_n^* \psi_n d\tau = a_n^* \int \psi_n^* \psi_n d\tau$$

or

$$(a_n - a_n^*) \int \psi_n^* \psi_n d\tau = 0$$

Since  $\int \psi_n^* \psi_n d\tau \neq 0$ , the above gives,

$$a_n - a_n^* = 0$$

or

$$a_n = a_n^* \quad \dots(2.133)$$

Thus, the eigenvalues of the Hermitian operator  $\hat{A}$  are real.

**(ii) Any Two Eigenfunctions of a Hermitian Operator that belong to Different Eigenvalues are Orthogonal.**

**Proof:**

Two arbitrary functions  $u$  and  $v$  defined in the same domain of definition are said to be orthogonal to each other if,

$$\int u^* v d\tau = 0 \quad \dots(2.134)$$

where  $*$  indicates complex conjugate and the integration is carried over the entire domain of definition.

Consider a Hermitian operator  $\hat{A}$ . Let  $\psi_n$  and  $\psi_m$  be two eigenfunctions of  $\hat{A}$  belonging to eigenvalues  $a_n$  and  $a_m$ , respectively. We then have,

$$\hat{A}\psi_n = a_n \psi_n \quad \dots(2.135)$$

$$\hat{A}\psi_m = a_m \psi_m \quad \dots(2.136)$$

Multiplying Equation (2.135) by  $\psi_m^*$  from the left and integrating over the entire domain of definition, we get,

$$\int \psi_m^* \hat{A}\psi_n d\tau = \int \psi_m^* a_n \psi_n d\tau = a_n \int \psi_m^* \psi_n d\tau \quad \dots(2.137)$$

Taking complex conjugate of Equation (2.136), we obtain,

$$\hat{A}^* \psi_m^* = a_m^* \psi_m^* = a_m \psi_m^* \quad [\text{since } a_m \text{ is real}] \quad \dots(2.138)$$

Multiplying Equation (2.138) by  $\psi_m$  from the right and integrating over the entire domain of definition, we obtain,

$$\int \hat{A}^* \psi_m^* \psi_m d\tau = a_m \int \psi_m^* \psi_n d\tau \quad \dots(2.139)$$

Since  $\hat{A}$  is Hermitian, Equation (2.139) can be rewritten as,

$$\int \psi_m^* \hat{A}\psi_n d\tau = a_m \int \psi_m^* \psi_n d\tau \quad \dots(2.140)$$

From Equations (2.137) and (2.140), we get,

**NOTES**

$$a_n \int \psi_m^* \psi_n d\tau = a_m \int \psi_m^* \psi_n d\tau$$

or

$$(a_n - a_m) \int \psi_m^* \psi_n d\tau = 0 \quad \dots(2.141)$$

Since  $a_n$  and  $a_m$  are two different eigenvalues,

$$(a_n - a_m) \int \psi_m^* \psi_n d\tau = 0$$

and hence Equation (2.141) yields,

$$\int \psi_m^* \psi_n d\tau = 0 \quad \dots(2.142)$$

In view of Equation (2.134), we thus find that eigenfunctions of the Hermitian operator  $\hat{A}$  belonging to different eigenvalues are orthogonal to each other.

### 2.6.5 Important Theorems on Operators

**(i) If two operators have simultaneous eigenfunctions, i.e., if all the eigenfunctions of two operators are common, then the operators commute with each other.**

**Proof:**

Consider two operators  $\hat{A}$  and  $\hat{B}$  which have simultaneous eigenfunctions. Let  $\psi_n$  be one such eigenfunction of both  $\hat{A}$  and  $\hat{B}$  belonging to eigenvalues  $a_n$  and  $b_n$  respectively. We then have

$$\hat{A}\psi_n = a_n \psi_n \quad \dots(2.143)$$

and

$$\hat{B}\psi_n = b_n \psi_n \quad \dots(2.144)$$

Operating Equation (2.143) by the operator  $\hat{B}$  from the left, we get

$$\hat{B}(\hat{A}\psi_n) = \hat{B}(a_n \psi_n) = a_n \hat{B}\psi_n$$

Using Equation (2.144) the above becomes,

$$\hat{B}\hat{A}\psi_n = a_n b_n \psi_n \quad \dots(2.145)$$

Operating Equation (2.144) by the operator  $\hat{A}$  from the left, we get,

$$\hat{A}(\hat{B}\psi_n) = \hat{A}(b_n \psi_n) = b_n \hat{A}\psi_n$$

Using Equation (2.143) in the above we get,

$$\hat{A}\hat{B}\psi_n = b_n a_n \psi_n \quad \dots(2.146)$$

Combining Equations (2.145) and (2.146) we obtain,

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi_n = 0$$

and hence we have,

## NOTES

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0 \quad \dots(2.147)$$

Thus the operators  $\hat{A}$  and  $\hat{B}$  commute with each other.

**(ii) Commuting operators have common set of eigenfunctions.**

**Proof:**

Consider two operators  $\hat{A}$  and  $\hat{B}$  which commute with each other, i.e., consider

$$\hat{A}\hat{B} = \hat{B}\hat{A} \quad \dots(2.148)$$

Let  $\psi_i$  be an eigenfunction of  $\hat{A}$  belonging to eigenvalue  $a_i$ . We then have the eigenvalue equation for  $\hat{A}$ ,

$$\hat{A}\psi_i = a_i\psi_i \quad \dots(2.149)$$

Operating Equation (2.149) by  $\hat{B}$  from the left we get,

$$\hat{B}\hat{A}\psi_i = \hat{B}(a_i\psi_i) = a_i\hat{B}\psi_i$$

In view of Equation (2.148) the above can be written as,

$$\hat{A}(\hat{B}\psi_i) = a_i(\hat{B}\psi_i) \quad \dots(2.150)$$

We find  $\hat{B}\psi_i$  to be an eigenfunction of  $\hat{A}$  with the same eigenvalue  $a_i$ . If  $\hat{A}$  has only **nondegenerate** eigenvalue,  $\hat{B}\psi_i$  differs from  $\psi_i$  only by a multiplicative constant, say  $b_i$ , i.e.,

$$\hat{B}\psi_i = b_i\psi_i \quad \dots(2.151)$$

Clearly,  $\psi_i$  is also an eigenfunction of  $\hat{A}$ . In other words,  $\psi_i$  is a simultaneous eigenfunction of both  $\hat{A}$  as well as  $\hat{B}$ .

**(iii) If  $\hat{A}$  and  $\hat{B}$  are two Hermitian operators, then their product operator  $\hat{A}\hat{B}$  is Hermitian if and only if  $\hat{A}$  and  $\hat{B}$  commute with each other.**

**Proof:**

Consider two operators  $\hat{A}$  and  $\hat{B}$  defined in a certain domain of definition. Consider two arbitrary functions  $\psi$  and  $\phi$  in the domain in which  $\hat{A}$  and  $\hat{B}$  are defined. Using the definition of transposed operator we can write,

$$\begin{aligned} \int \psi (\hat{A}\hat{B})\phi d\tau &= \int \psi \hat{A}(\hat{B}\phi) d\tau \\ &= \int (\hat{B}\phi) \tilde{\hat{A}}\psi d\tau \\ &= \int (\hat{B}\phi) (\tilde{\hat{A}}\psi) d\tau \\ &= \int (\tilde{\hat{A}}\psi) \hat{B}\phi d\tau \\ &= \int (\phi \tilde{\hat{B}}\tilde{\hat{A}}\psi) d\tau \end{aligned} \quad \dots(2.152)$$

We also have,

$$\int \psi (\hat{A}\hat{B})\phi d\tau = \int \phi (\tilde{\hat{A}}\tilde{\hat{B}})\psi d\tau \quad \dots(2.153)$$

**NOTES**

Comparing Equations (2.152) and (2.153) we get,

$$\int \phi (\widehat{A}\widehat{B})\psi d\tau = \int \phi \widetilde{A}\widetilde{B}\psi d\tau$$

## NOTES

The above gives,

$$\widetilde{A}\widetilde{B} = \widetilde{B}\widetilde{A} \quad \dots(2.154)$$

Taking complex conjugate of Equation (2.154), we obtain

$$(\widehat{A}\widehat{B})^* = (\widetilde{B})^* (\widetilde{A})^*$$

$$\text{or} \quad (\widehat{A}\widehat{B})^\dagger = \widehat{B}^\dagger \widehat{A}^\dagger \quad \dots(2.155)$$

Since  $\widehat{A}$  and  $\widehat{B}$  are Hermitian we have,

$$\widehat{A}^\dagger = \widehat{A} \quad \text{and} \quad \widehat{B}^\dagger = \widehat{B}$$

and Equation (2.155) thus becomes,

$$(\widehat{A}\widehat{B})^\dagger = \widehat{B}\widehat{A} \quad \dots(2.156)$$

For the operator  $\widehat{A}\widehat{B}$  to be Hermitian the condition that must be satisfied is,

$$(\widehat{A}\widehat{B})^\dagger = \widehat{A}\widehat{B} \quad \dots(2.157)$$

In view of Equations (2.156) and (2.157) we find that the product  $\widehat{A}\widehat{B}$  is Hermitian if,

$$\widehat{A}\widehat{B} = \widehat{B}\widehat{A}$$

$$\text{or} \quad \widehat{A}\widehat{B} - \widehat{B}\widehat{A} = 0$$

$$\text{or} \quad [\widehat{A}, \widehat{B}] = 0$$

**(iv) If  $\widehat{A}$  and  $\widehat{B}$  are two non-commuting Hermitian operators then  $i(\widehat{A}\widehat{B} - \widehat{B}\widehat{A})$  is Hermitian.**

Consider two Hermitian operators defined in some domain of definition. We then have,

$$\widehat{A}^\dagger = \widehat{A}$$

$$\widehat{B}^\dagger = \widehat{B} \quad \dots(2.158)$$

Consider the operator  $\widehat{C} = i(\widehat{A}\widehat{B} - \widehat{B}\widehat{A})$ . Taking transpose, we obtain,

$$\begin{aligned} \widetilde{C} &= i(\widetilde{A}\widetilde{B} - \widetilde{B}\widetilde{A}) = i\widetilde{A}\widetilde{B} - i\widetilde{B}\widetilde{A} \\ &= i\widetilde{B}\widetilde{A} - i\widetilde{A}\widetilde{B} \end{aligned} \quad \dots(2.159)$$

Taking complex conjugate of Equation (2.159), we get

$$\begin{aligned} (\widetilde{C})^* &= -i(\widetilde{B})^* (\widetilde{A})^* + i(\widetilde{A})^* (\widetilde{B})^* \\ &= -i\widehat{B}^\dagger \widehat{A}^\dagger + i\widehat{A}^\dagger \widehat{B}^\dagger \end{aligned}$$

$$\text{or} \quad \hat{C}^\dagger = -i\hat{B}^\dagger\hat{A}^\dagger + i\hat{A}^\dagger\hat{B}^\dagger \quad \dots(2.160)$$

Using Equation (2.158) in Equation (2.160), we get

$$\hat{C}^\dagger = -i\hat{B}\hat{A} + i\hat{A}\hat{B} = i(\hat{A}\hat{B} - \hat{B}\hat{A}) \quad \dots(2.161)$$

In view of Equations (2.159) and (2.161), we find

$$\hat{C}^\dagger = \hat{C}$$

Clearly,  $\hat{C} = i(\hat{A}\hat{B} - \hat{B}\hat{A})$  is Hermitian.

**(v) The eigenvalues of the operator  $(\hat{f})^p$  are equal to the  $p$ th power of the eigenvalues of  $\hat{f}$ ,  $p$  being any positive integer.**

Let  $\psi_n$  be an eigenfunction of  $\hat{f}$  belonging to the eigenvalue  $f_n$ . We then have the eigenvalue equation,

$$\hat{f}\psi_n = f_n\psi_n \quad \dots(2.162)$$

Operating Equation (2.162) by  $\hat{f}$  from the left we obtain,

$$\hat{f}(\hat{f}\psi_n) = \hat{f}(f_n\psi_n) = f_n\hat{f}\psi_n$$

or

$$\hat{f}^2\psi_n = f_n^2\psi_n \quad [\text{using Equation (2.162)}] \dots(2.163)$$

Operating Equation (2.163) by  $\hat{f}$  from the left we get,

$$\hat{f}(\hat{f}^2\psi_n) = \hat{f}f_n^2\psi_n = f_n^2\hat{f}\psi_n$$

or

$$\hat{f}^3\psi_n = f_n^3\psi_n \quad [\text{using Equation (2.162)}] \dots(2.164)$$

Generalizing the above procedure we obtain,

$$\hat{f}^p\psi_n = f_n^p\psi_n$$

**Example 1:** Find the eigenvalues of the inverse of an operator.

**Solution:** Let  $\hat{A}$  be an operator and  $\hat{A}^{-1}$  be the inverse of the operator  $\hat{A}$ . We then have,

$$\hat{A}^{-1}\hat{A} = 1 \quad \dots(\text{i})$$

Let  $\psi$  be an eigenfunction of  $\hat{A}$  belonging to the eigenvalue  $a$ . We then have,

$$\hat{A}\psi = a\psi \quad \dots(\text{ii})$$

Operating Equation (ii) by  $\hat{A}^{-1}$  from the left we get,

$$\hat{A}^{-1}\hat{A}\psi = a\hat{A}^{-1}\psi \quad \dots(\text{iii})$$

Using Equation (i) we get,

$$\hat{A}^{-1}\hat{A}\psi = \psi \quad \dots(\text{iv})$$

## NOTES

In view of Equations (iii) and (iv) we obtain,

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

or

$$\hat{A}^{-1} \psi = \frac{1}{a} \psi$$

Clearly, the eigenvalue of  $\hat{A}^{-1}$  is  $\frac{1}{a}$  which is the reciprocal of the eigenvalue of  $\hat{A}$ .

## NOTES

### 2.7 PROBABILITY DENSITY

Schrödinger wavefunction  $\psi(x, t)$  or  $\psi(\vec{r}, t)$  is the amplitude of the de-Broglie wave for a particle. A rough interpretation of the wavefunction 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 wavefunction  $\psi(x, t)$  or  $\psi(\vec{r}, t)$  being a *complex valued* function of position and time cannot as such have any physical existence. However, the wavefunction 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 behaviour of the particle should become completely known if the wavefunction is known at all possible positions at all possible instants 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 Schrödinger theory. This interpretation of the wavefunction is found to be both convenient and physically transparent enabling us to make precise computations regarding the behaviour of the particle. According to Max Born and Jordan, the wavefunction 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  $\vec{r}$  in space is given by,

$$\begin{aligned} P(\vec{r}, t) d^3(\vec{r}) &= \psi^*(\vec{r}, t) \psi(\vec{r}, t) d^3(\vec{r}) \\ &= |\psi(\vec{r}, t)|^2 d^3(\vec{r}) \end{aligned} \quad \dots(2.165)$$

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 wavefunction.

**(b) The Schrödinger Wavefunction:** It is a complex valued function of position and time which satisfies the linear Schrödinger equation [Equation (2.117) in one dimension and Equation (2.123) in three-dimensions].

Every definite wavefunction describes a definite state of motion of the particle.

It is important to note that if  $\psi(\vec{r}, t)$  is a possible wavefunction then  $\psi(\vec{r}, t) = e^{i\theta}\psi(\vec{r}, t)$  is also a possible wavefunction if  $\theta$  is an arbitrary real constant. The probability distribution defined by  $\psi$  and  $\psi$  are exactly identical [ $\because |\psi(\vec{r}, t)|^2 d^3(\vec{r}) = |e^{i\theta}\psi(\vec{r}, t)|^2 d^3(\vec{r}) = |\psi(\vec{r}, t)|^2 d^3(\vec{r})$ ]. This means that two wavefunctions  $\psi$  and  $\psi$  describe the same state of motion of the particle.

From the above we find:

to every wavefunction 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 wavefunction. The wavefunction corresponding to a given state is known only to within a constant complex factor (phase factor) of modulus unity.

### 2.7.1 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 that space is unity, i.e.,

$$P = 1$$

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

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

$$\text{or} \quad \int |\psi(\vec{r}, t)|^2 d^3(\vec{r}) = 1 \quad \dots(2.166)$$

The wave functions which satisfy Equation (2.166) are called normalized wavefunctions. Equation (2.166) is usually referred to as the normalization integral.

Normalization of wavefunction can be understood from the following:

The Schrödinger equation given by Equation (2.123) is linear and homogeneous in the wavefunction  $\psi(\vec{r}, t)$  and its derivatives. Hence, if the solution of Equation (2.123) is multiplied by a constant the resulting function is also a solution. Let  $\psi(\vec{r}, t)$  be a solution of the Schrödinger 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,

$$\int |\psi(\vec{r}, t)|^2 d^3(\vec{r}) = N^2 \quad \dots(2.167)$$

The number  $N^2$  is called the norm of the wavefunction  $\psi(\vec{r}, t)$ .

Let us define,

$$\psi(\vec{r}, t) = \frac{1}{N} \psi(\vec{r}, t) \quad \dots(2.168)$$

## NOTES

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 Schrödinger equation.

**NOTES**

We get,

$$\int |\psi(\vec{r}, t)|^2 d^3(\vec{r}) = \int \frac{1}{N^2} |\psi'(\vec{r}, t)|^2 d^3(\vec{r})$$

In view of Equation (2.167), the above gives,

$$\int |\psi(\vec{r}, t)|^2 d^3(\vec{r}) = 1 \quad \dots(2.169)$$

The wave function  $\psi(\vec{r}, t)$  satisfies Equation (2.166) and is hence a normalized wavefunction. Comparing Equation (2.169) with Equation (2.167) we find that the norm of the wavefunction  $\psi(\vec{r}, t)$  is unity.

We can thus define a normalized wavefunction as one which has *unit norm*.

In Equation (2.168), through which normalized wavefunction is defined,  $N$  must be finite. In other words, normalizable wavefunctions must have finite norms. For  $N$  and hence  $N^2$  to be finite we get according to Equation (2.167),

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

$$\text{or} \quad \psi'(\vec{r}, t) \rightarrow 0 \quad \text{as} \quad r \rightarrow \pm\infty \quad \dots(2.170)$$

Equation (2.170) is the boundary condition that must be satisfied by normalizable wavefunctions.

**2.7.2 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 Schrödinger equation,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t) \quad \dots(2.171)$$

Taking complex conjugate of Equation (2.171) we get

$$-i\hbar \frac{\partial \psi^*(\vec{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \psi^*(\vec{r}, t) \quad \dots(2.172)$$

Multiplying Equation (2.171) by  $\psi^*(\vec{r}, t)$  from the left, and Equation (2.172) by  $\psi(\vec{r}, t)$  from the left and subtracting we obtain,

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

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

$$\text{or } \frac{\partial}{\partial t} [\psi^* \psi] = \frac{i\hbar}{2m} [\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*] \quad \dots(2.173)$$

Writing the Laplacian operator  $\Delta^2$  in terms of derivatives we get according to Equation (2.173),

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

$$\begin{aligned} \text{or } \frac{\partial}{\partial t} [\psi^* \psi] = & -\frac{i\hbar}{2m} \frac{\partial}{\partial x} \left[ \psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right] - \frac{i\hbar}{2m} \frac{\partial}{\partial y} \left[ \psi \frac{\partial \psi^*}{\partial y} - \psi^* \frac{\partial \psi}{\partial y} \right] \\ & - \frac{i\hbar}{2m} \frac{\partial}{\partial z} \left[ \psi \frac{\partial \psi^*}{\partial z} - \psi^* \frac{\partial \psi}{\partial z} \right] \quad \dots(2.174) \end{aligned}$$

Let us define,

$$J_x = \frac{i\hbar}{2m} \left[ \psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right] \quad \dots(2.175)$$

$$J_y = \frac{i\hbar}{2m} \left[ \psi \frac{\partial \psi^*}{\partial y} - \psi^* \frac{\partial \psi}{\partial y} \right] \quad \dots(2.176)$$

$$J_z = \frac{i\hbar}{2m} \left[ \psi \frac{\partial \psi^*}{\partial z} - \psi^* \frac{\partial \psi}{\partial z} \right] \quad \dots(2.177)$$

Then using Equations (2.175), (2.176) and (2.177) in Equation (2.174) we obtain,

$$\frac{\partial}{\partial t} [\psi^* \psi] + \left[ \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} \right] = 0 \quad \dots(2.178)$$

Equation (2.178) can alternatively be expressed as,

$$\frac{\partial}{\partial t} [\rho(\vec{r}, t)] + \vec{\nabla} \cdot \vec{J}(\vec{r}, t) = 0 \quad \dots(2.179)$$

$$\text{Where } \vec{J}(\vec{r}, t) = \frac{i\hbar}{2m} [\psi \vec{\nabla} \psi^* - \psi^* \vec{\nabla} \psi] \quad \dots(2.180)$$

$$\rho(\vec{r}, t) = \psi^* \psi \quad \dots(2.181)$$

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

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0 \quad \dots(2.182)$$

Where

$\rho$  = Number of fluid particles per unit volume or particle density

## NOTES

$\vec{j}$  = 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.

## NOTES

Comparing Equation (2.179) with Equation (2.182) we may interpret  $\rho(\vec{r}, t) = \psi^* \psi$  as the position probability density so that  $\psi^* \psi d^3(\vec{r})$  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

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

### 2.7.3 Normalization Integral, a Constant of Motion

Integrating Equation (2.173) over the entire volume of space we get,

$$\frac{\partial}{\partial t} \int_{-\infty}^{+\infty} \psi^* \psi d^3(\vec{r}) = \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} [\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*] d^3(\vec{r})$$

$$\text{or } \frac{\partial}{\partial t} \int \psi^* \psi d^3(\vec{r}) = \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) d^3(\vec{r})$$

$$\text{or } \frac{\partial}{\partial t} \int \psi^* \psi d^3(\vec{r}) = \frac{i\hbar}{2m} \{ \psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \}_{-\infty}^{+\infty} \quad \dots(2.183)$$

In most of the physical problems, the wave packet representing a particle is localized so that we get, (as seen earlier, Equation (2.174)),

$$\psi \rightarrow 0 \quad \text{and} \quad \psi^* \rightarrow 0 \quad \text{as } r \rightarrow \pm\infty$$

Using the above result in Equation (2.183) we obtain,

$$\frac{\partial}{\partial t} \int \psi^* \psi d^3(\vec{r}) = 0$$

Which gives,

$$\int \psi^* \psi d^3(\vec{r}) = \text{Constant in time, i.e., constant of motion.}$$

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.

### 2.7.4 Expectation Value of a Physical Quantity

Let us consider a particle in a definite state described by the normalized wavefunction  $\psi(\vec{r}, t)$ . 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 wavefunction to the

original form before any observation is made. Even if we ensure that before any measurement the wavefunction is restored to its original form, we do not get the same result each time. The average of the values obtained in these measurements is called the *measured value* or the *expectation value* and is denoted as  $\langle \vec{r} \rangle$ . Since  $\psi^*(\vec{r}, t) \psi(\vec{r}, t)$  represents the probability with which the value  $\vec{r}$  occurs in the measurement we get,

$$\langle \vec{r} \rangle = \int \vec{r} \psi^* \psi d^3(\vec{r}) = \int \psi^* \vec{r} \psi d^3(\vec{r}) \quad \dots(2.184)$$

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

$$\langle \vec{r} \rangle = \frac{\int \psi^* \vec{r} \psi d^3(\vec{r})}{\int \psi^* \psi d^3(\vec{r})} \quad \dots(2.185)$$

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

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

$$\text{or} \quad \langle f(\vec{r}) \rangle = \int \psi^*(\vec{r}, t) f(\vec{r}) \psi(\vec{r}, t) d^3(\vec{r}) \quad \dots(2.186)$$

### 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 described by the potential energy function  $V(\vec{r}, t)$ . Let  $\psi(\vec{r}, t)$  be the normalized wavefunction that describes the state of the particle. The time evolution of the wavefunction is given by the Schrödinger equation,

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

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

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

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

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

Using the definition of expectation value given above we obtain,

$$\left\langle i\hbar \frac{\partial}{\partial t} \right\rangle = \left\langle \frac{-\hbar^2}{2m} \nabla^2 \right\rangle + \langle V(\vec{r}, t) \rangle \quad \dots(2.187)$$

## NOTES

In view of Equation (2.126) and Equation (2.129), Equation (2.187) gives,

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle. \quad \dots(2.188)$$

## NOTES

Classically, the total energy is,

$$E = \text{Kinetic energy} + \text{Potential energy} = \frac{p^2}{2m} + V$$

Equation (2.188) tells that the expectation value of the total energy is the sum of the expectation values of the kinetic energy and the potential energy.

### General Result

From the above discussions, we get the following important recipe for the calculation of expectation values of physical quantities for a system in a state described by a known wave function.

Let  $A$  be any dynamical variable of a quantum system. Let the system be in a given state described by normalized wave function  $\psi(\vec{r}, t)$ . If  $\hat{A}$  be operator corresponding to the quantity  $A$  in the domain of definition of the wave function then the expectation values of  $A$  is

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

Since the above integration is carried over the entire space,  $\langle A \rangle$  is, in general, a function of time only.

### 2.7.5 Acceptable Wave Functions for a Physical System

The dynamical state of a physical system, say, a particle moving in space, is defined by the wavefunction  $\psi(\vec{r}, t)$  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 of finding the particle within a unit volume about the position  $\vec{r}$  at the time  $t$ . This probabilistic interpretation of the wavefunction necessitates some conditions that must be satisfied by it for its physical acceptability. These conditions are:

- (i) Wavefunction 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) Wavefunction must be single valued at any position at all instants of time. This requirement of single valuedness arises from the fact that at any given position, the wavefunction must be unique so that the

probability density at the position be uniquely defined at all instants of time.

- (iii) Wavefunction  $\psi(\vec{r}, t)$  must be a continuous function of position  $\vec{r}$  and time  $t$ . Further, the gradient of the wavefunction  $\vec{\nabla}\psi(\vec{r}, t)$  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 defined through  $\psi(\vec{r}, t)$  and  $\vec{\nabla}\psi(\vec{r}, t)$ . The Schrödinger equation satisfied by the wavefunction contains the term  $\nabla^2\psi$  which can exist provided  $\vec{\nabla}\psi$  is a continuous function at all points in space.
- (iv) The wavefunction must be quadratically integrable, i.e., we must have,

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

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

### Check Your Progress

10. What are the averages or the expectation values of the quantum mechanical variables that satisfy the same equations of motion as the corresponding classical variables?
11. What is linear operator?
12. What are the eigenfunctions and eigenvalues of a linear operator?
13. Explain the spectrum of eigenvalues of an operator.
14. When the operator  $\hat{A}$  is said to be Hermitian operator?
15. Define the Schrödinger wavefunction as the amplitude of the de-Broglie wave for a particle.
16. Explain the wavefunction that describes the probability distribution according to Max Born and Jordan.
17. What is normalized wave function?

## 2.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The theory of Schrödinger equation was formulated by Erwin Schrödinger 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 behaviour of matter wave.

## NOTES

## NOTES

2. The main assumptions made in the theory of Schrödinger equation 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.

3. The trajectory of a particle becomes known if the coordinate and momentum of the particle are known at every moment of time. In other words, the trajectory is known if  $x$  and  $\frac{dx}{dt}$  are known at all time  $t$ .

4. a classical wave possesses a characteristic frequency ( $\nu$ ), a wavelength ( $\lambda$ ) and the phase velocity ( $v_p$ ) related according to,

$$v_p = \nu\lambda (= \omega/k)$$

5. A *localized wave function* is called a *wave packet*. A wave packet representing a particle is formed as a result of superposition of a group of waves each having slightly different velocities and wavelengths, the phases and amplitudes of waves at any instant of time being so chosen that they interfere constructively over that small region where the particle is most likely to be located at that instant and destructively elsewhere so that the amplitude reduces to zero.

6. The group velocity is given by,

$$v_g = \frac{d\omega}{dk}$$

or 
$$v_g = \frac{d\omega}{dp} \frac{dp}{dk}$$

7. The kinetic energy  $E$  of the particle is related to the angular frequency  $\omega$  of the wave associated with it as,

$$E = \hbar\omega$$

8. The time-dependent states of a quantum system are the solutions of the general time-dependent Schrödinger equation,

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

$$= \hat{H}\psi(\vec{r}, t)$$

the operator  $\hat{H}$  being the Hamiltonian for the system.

9. In analogy with classical mechanics, the differential equation for the wavefunction 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  $u$  is the wave velocity of the de-Broglie wave.

10. The averages or the expectation values of the quantum mechanical variables satisfy the same equations of motion as the corresponding classical variables in the corresponding classical description. Specifically the theorem states that,

$$\frac{d}{dt} \langle x \rangle = \frac{i}{\hbar} \langle p_x \rangle$$

$$\frac{d}{dt} \langle p_x \rangle = \left\langle -\frac{dV(x)}{dx} \right\rangle$$

provided that the wavefunction  $\psi(x, t)$  with respect to which averages are computed satisfies the time-dependent Schrödinger equation,

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

11. If on operating on the sum of the functions  $\psi_1$  and  $\psi_2$  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.
12. Consider a linear operator  $\hat{A}$  defined in a certain domain of definition. If  $\psi$  is any function defined in the domain of the definition of  $\hat{A}$ , then in general, we have,

$$\hat{A}\psi = \phi$$

However, for every linear operator  $\hat{A}$ , there exists a set of functions  $\psi_1, \psi_2, \dots, \psi_n$ , such that,

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

$$\hat{A}\psi_2 = a_2\psi_2$$

$$\vdots \quad \quad \quad \vdots$$

$$\hat{A}\psi_n = a_n\psi_n$$

where  $a_1, a_2, \dots, a_n$  are constants with respect to the variables of which  $\psi_i$ 's ( $i = 1, \dots, n$ ) are functions. The set of functions  $\psi_1, \psi_2, \dots, \psi_n$  are

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called eigenfunctions of the operator  $\hat{A}$  and the constant  $a_1, a_2, \dots, a_n$  are called the eigenvalues belonging to the eigenfunctions  $\psi_1, \psi_2, \dots, \psi_n$ , respectively.

13. The spectrum of eigenvalues of an operator can be **discrete, continuous** or **discrete-continuous**, depending on the form of the operator and possibly on certain other requirements which may have to be made on the eigenfunctions for physical reasons.

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

$$\int_V u^* \hat{A} v d\tau = \int_V (\hat{A} u)^* v d\tau = \int_V \hat{A} u^* v d\tau$$

15. Schrödinger wavefunction  $\psi(x, t)$  or  $\psi(\vec{r}, t)$  is the amplitude of the de-Broglie wave for a particle. A rough interpretation of the wavefunction 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.

16. According to Max Born and Jordan, the wavefunction 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  $\vec{r}$  in space is given by,

$$\begin{aligned} P(\vec{r}, t) d^3(\vec{r}) &= \psi^*(\vec{r}, t) \psi(\vec{r}, t) d^3(\vec{r}) \\ &= |\psi(\vec{r}, t)|^2 d^3(\vec{r}) \end{aligned}$$

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

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

$$P = 1$$

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## 2.9 SUMMARY

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- The theory of Schrödinger equation was formulated by Erwin Schrödinger 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 behaviour of matter wave.
- The main assumptions made in the theory of Schrödinger equation 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.

- The Schrödinger 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 particles.
- The trajectory of a particle becomes known if the coordinate and momentum of the particle are known at every moment of time. In other words, the trajectory is known if  $x$  and  $\frac{dx}{dt}$  are known at all time  $t$ .
- According to Heisenberg's uncertainty relation, a microparticle cannot simultaneously possess a definite coordinate, say,  $x$  and a definite projection of momentum  $p_x$ . Thus, the concept of trajectory of a microparticle, strictly speaking, is not applicable.
- A microparticle is fundamentally different from a classical corpuscle primarily because (i) it does not have a trajectory which is an essential attribute of a classical corpuscle, (ii) the use of coordinate, momentum, angular momentum, energy when considering microparticle become restricted to the framework of uncertainty relations.
- A classical wave possesses a characteristic frequency ( $\nu$ ), a wavelength ( $\lambda$ ) and the phase velocity ( $v_p$ ) related according to,

$$v_p = \nu\lambda (= \omega/k)$$

- The wave associated with a microparticle is of infinite extent because according to Heisenberg's uncertainty principle, the position of the particle becomes completely unknown if its momentum is taken to be well defined.
- In classical physics, a particle is well localized in space by which we mean that the position and velocity (momentum) of the particle can be simultaneously determined with unlimited accuracy.
- A *localized wave function* is called a *wave packet*. A wave packet representing a particle is formed as a result of superposition of a group of waves each having slightly different velocities and wavelengths, the phases and amplitudes of waves at any instant of time being so chosen that they interfere constructively over that small region where the particle is most likely to be located at that instant and destructively elsewhere so that the amplitude reduces to zero.
- A one-dimensional wave packet which may describe a classical particle confined to a one-dimensional region, say, a particle moving along the  $x$ -axis can be mathematically constructed by superposing an infinite

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number of plane waves with slightly different wave number  $k$ , all moving along the  $x$ -axis, by means of Fourier transforms.

- The wavelength  $\lambda$  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,

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

- The operators which play important role in quantum mechanics can be further specialized. They are not only linear, they are Hermitian.
- Two arbitrary functions  $u$  and  $v$  defined in the same domain of definition are said to be orthogonal to each other if,

$$\int u^* v d\tau = 0$$

where \* indicates complex conjugate and the integration is carried over the entire domain of definition.

- (i) If two operators have simultaneous eigenfunctions, i.e., if all the eigenfunctions of two operators are common, then the operators commute with each other.

- Consider two operators  $\hat{A}$  and  $\hat{B}$  which have simultaneous eigenfunctions. Let  $\psi_n$  be one such eigenfunction of both  $\hat{A}$  and  $\hat{B}$  belonging to eigenvalues  $a_n$  and  $b_n$  respectively.
- If  $\hat{A}$  and  $\hat{B}$  are two Hermitian operators, then their product operator  $\hat{A}\hat{B}$  is Hermitian if and only if  $\hat{A}$  and  $\hat{B}$  commute with each other.
- If  $\hat{A}$  and  $\hat{B}$  are two non-commuting Hermitian operators then  $i(\hat{A}\hat{B} - \hat{B}\hat{A})$  is Hermitian.
- The eigenvalues of the operator  $(\hat{f})^p$  are equal to the  $p$ th power of the eigenvalues of  $\hat{f}$ ,  $p$  being any positive integer.
- Schrödinger wavefunction  $\psi(x, t)$  or  $\psi(\vec{r}, t)$  is the amplitude of the de-Broglie wave for a particle. A rough interpretation of the wavefunction 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 wavefunction  $\psi(x, t)$  or  $\psi(\vec{r}, t)$  being a *complex valued* function of position and time cannot as such have any physical existence. However, the wavefunction must, in some way, be related to the presence of the particle at the position  $x$  or  $\vec{r}$  at the instant of time  $t$ .

- Max Born and Jordan in 1926 gave a probabilistic interpretation of the wave function which is characteristic of and fundamental to the Schrödinger theory.
- According to Max Born and Jordan, the wavefunction 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  $\vec{r}$  in space is given by,

$$\begin{aligned} P(\vec{r}, t) d^3(\vec{r}) &= \psi^*(\vec{r}, t) \psi(\vec{r}, t) d^3(\vec{r}) \\ &= |\psi(\vec{r}, t)|^2 d^3(\vec{r}) \end{aligned}$$

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 wavefunction.
- Every definite wavefunction describes a definite state of motion of the particle.
- If  $\psi(\vec{r}, t)$  is a possible wavefunction then  $\psi(\vec{r}, t) = e^{i\theta} \psi(\vec{r}, t)$  is also a possible wavefunction if  $\theta$  is an arbitrary real constant. The probability distribution defined by  $\psi$  and  $\psi$  are exactly identical [ $\because |\psi(\vec{r}, t)|^2 d^3(\vec{r}) = |e^{i\theta} \psi(\vec{r}, t)|^2 d^3(\vec{r}) = |\psi(\vec{r}, t)|^2 d^3(\vec{r})$ ]. This means that two wavefunctions  $\psi$  and  $\psi$  describe the same state of motion of the particle.
- If the motion of the particle takes place in a space of finite extent then the total probability  $P$  of finding the particle in that space is unity, i.e.,

$$P = 1$$

- 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 Schrödinger equation,

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

- The dynamical state of a physical system, say, a particle moving in space, is defined by the wavefunction  $\psi(\vec{r}, t)$  which is a complex valued function of position  $\vec{r}$  in space and time  $t$ .
- The quantity  $\psi^*(\vec{r}, t) \psi(\vec{r}, t) d^3(\vec{r})$ , i.e., the quantity  $|\psi(\vec{r}, t)|^2 d^3(\vec{r})$  gives the probability of finding the particle within a volume element

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$d^3(\vec{r})$  about the position  $\vec{r}$ . In other words,  $|\psi(\vec{r}, t)|^2$  is the probability density, i.e., the probability of finding the particle within a unit volume about the position  $\vec{r}$  at the time  $t$ .

- Wavefunction 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.
- Wavefunction must be single valued at any position at all instants of time. This requirement of single valuedness arises from the fact that at any given position, the wavefunction must be unique so that the probability density at the position be uniquely defined at all instants of time.
- Wavefunction  $\psi(\vec{r}, t)$  must be a continuous function of position  $\vec{r}$  and time  $t$ . Further, the gradient of the wavefunction  $\vec{\nabla}\psi(\vec{r}, t)$  should be continuous at all points in space.

- The wavefunction must be quadratically integrable, i.e., we must have,

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

- If the above condition is satisfied then we may define a normalized wavefunction that corresponds to a total probability equal to unity.

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## 2.10 KEY WORDS

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- **Schrödinger equation:** The theory of Schrödinger equation was formulated by Erwin Schrödinger in the year 1926, the formulation is based on de-Broglie's concept of matter wave.
- **Wave packet:** A localized wave function is called a wave packet.
- **Bound states:** The probability density vanishes at infinity.
- **Probability density:** For Schrödinger wavefunction the probability density is proportional to the square modulus of the wavefunction.
- **Schrödinger wavefunction:** It is a complex valued function of position and time which satisfies the linear Schrödinger equation in one dimension.

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## 2.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### Short Answer Questions

1. What is Schrödinger equation?
2. Define the term wave packet and group velocity.
3. Explain the term dependent Schrödinger equation.
4. What is linear momentum?
5. Define about independent Schrödinger equation.
6. What does Ehrenfest's theorem state?
7. Explain the terms eigenfunction and eigen vectors.
8. What is Hermitian operator?
9. Explain probability density function.
10. What is normalized wave function?
11. What is the expectation value of a physical quantity?

### Long Answer Questions

1. Briefly discuss the theory of Schrödinger equation giving the assumptions.
2. Explain the dynamical state of a microparticle concept of wave function.
3. Discuss wave packet with reference to classical physics. Also explain about the group velocity for wave packet.
4. Explain the time dependent Schrödinger equation giving relevant equations.
5. Explain the operators that correspond to energy and linear momentum.
6. Derive the time-dependent Schrödinger equation for a particle moving in a force field.
7. What is the significance of time independent Schrödinger equation?
8. Explain and prove the Ehrenfest's theorem.
9. Discuss the properties and characteristic equations for eigenfunction and eigen vectors.
10. Prove that the linear operators are of prime interest in the mathematical formulation of quantum theory. Justify your answer.
11. Explain the significance of Hermitian operator.

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12. Briefly explain the probability density for the Schrödinger wavefunction.
13. Explain the Max Born and Jordan's probabilistic interpretation of the wave function for the Schrödinger theory.
14. Give the standard equations for calculating the probability current density that satisfies the time dependent Schrödinger equation.

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**2.12 FURTHER READINGS**

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
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## UNIT 3 ONE DIMENSIONAL PROBLEM

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### NOTES

#### Structure

- 3.0 Introduction
- 3.1 Objectives
- 3.2 One Dimensional Motion
- 3.3 Linear Harmonic Oscillator and Tunnel Effect
  - 3.3.1 Time-Independent Schrödinger Equation for An Oscillator
  - 3.3.2 Solution of the Wave Equation
  - 3.3.3 Energy Eigenvalues of the Oscillator
  - 3.3.4 Energy Eigenfunctions of the Oscillator
  - 3.3.5 Alternative Approach for Linear Harmonic Oscillator Problem
  - 3.3.6 Potential Barrier Problem
  - 3.3.7 Alpha-Particle Emission
- 3.4 Answers to Check Your Progress Questions
- 3.5 Summary
- 3.6 Key Words
- 3.7 Self Assessment Questions and Exercises
- 3.8 Further Readings

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### 3.0 INTRODUCTION

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Oscillations are found throughout nature as electromagnetic waves, vibrating molecules, and the gentle back-and-forth sway of a tree branch. A simple harmonic oscillator is a particle or system that undergoes harmonic motion about an equilibrium position, such as an object with mass vibrating on a spring.

A linear harmonic oscillator is a particle which is bound to an equilibrium position by a force which is proportional to the displacement from that position. The quantum harmonic oscillator is the quantum-mechanical analog of the classical harmonic oscillator. Because an arbitrary potential can usually be approximated as a harmonic potential at the vicinity of a stable equilibrium point, it is one of the most important model systems in quantum mechanics. The allowed energy in quantum mechanics is not continuous but discrete (step-like). Such discrete energies are called the eigenvalues and the corresponding states are called the eigenstates.

In this unit, you will study about the oscillating systems using quantum mechanics, one dimensional problems, linear harmonic oscillator and tunnel effect.

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### 3.1 OBJECTIVES

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## NOTES

After going through this unit, you will be able to:

- Understand the oscillating systems using quantum mechanics
  - Calculate one dimensional problems
  - Explain linear harmonic oscillator and tunnel effect
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### 3.2 ONE DIMENSIONAL MOTION

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Consider a particle of mass  $m$  having a total energy  $E$  moving in a one-dimensional potential  $V(x)$ . The state of the particle described by the wavefunction  $\psi(x)$  satisfies the time-independent Schrödinger equation,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad \dots(3.1)$$

The solutions of the above equation give the energy eigenfunctions  $\psi_n(x)$  belonging to different energy eigenvalues  $E_n$  for the particle.

Equation (3.1) can be solved exactly only when (i) the potential function  $V(x)$  is stated explicitly and (ii) the boundary conditions imposed on the system, i.e., on the wavefunction  $\psi(x)$  are known exactly.

The nature of the states of the particle is determined completely by the energy of the particle and the nature of the potential function  $V(x)$ . We encounter the following results with respect to the energy eigenvalues and states:

- (i) The eigenvalues form a *discrete-spectrum* corresponding to *bound* states.
- (ii) The eigenvalues form a *continuous spectrum* corresponding to unbound states.
- (iii) The eigenvalues form a mixed spectrum consisting of a discrete spectrum for some range of energy  $E$  and a continuous spectrum outside that range.

In the sections to follow we shall illustrate the above results by considering some important problems of one-dimensional motion.

The important properties of one-dimensional motion that we find are:

- (i) In case of bound states, the energy spectrum is not only discrete but is non-degenerate also.
- (ii) The eigenfunction  $\psi_n(x)$  for a bound state has ' $n$ ' number of nodes if the ground state corresponds to  $n = 0$  and  $(n - 1)$  number of nodes if the ground state corresponds to  $n = 1$ .

### 3.3 LINEAR HARMONIC OSCILLATOR AND TUNNEL EFFECT

Consider a particle of mass  $m$  undergoing simple harmonic oscillation along the  $x$ -axis with a frequency  $\nu_0$  (angular frequency  $\omega_0 = 2\pi\nu_0$ ). If  $x_0$  is the amplitude of the oscillator, its displacement  $x$  from the mean or the equilibrium position varies with time according to,

$$x = x_0 \sin \omega_0 t \quad \dots(3.2)$$

The force constant  $k$  (restoring force acting on the particle per unit displacement) is related to the frequency  $\omega_0$  as

$$k = m \omega_0^2 \quad \dots(3.3)$$

The kinetic energy of the oscillator is,

$$\begin{aligned} T &= \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 = \frac{1}{2} m x_0^2 \omega_0^2 \cos^2 \omega_0 t \\ &= \frac{1}{2} m \omega_0^2 x_0^2 (1 - \sin^2 \omega_0 t) \end{aligned}$$

or

$$T = \frac{1}{2} m \omega_0^2 (x_0^2 - x^2) \quad \dots(3.4)$$

The potential energy of the oscillator is,

$$V(x) = \frac{1}{2} kx^2 = \frac{1}{2} m \omega_0^2 x^2 \quad \dots(3.5)$$

We may note that the potential energy of the oscillator is not a constant and instead varies parabolically with the displacement  $x$  of the oscillator.

The total energy  $E$  of the oscillator is,

$$E = T + V$$

Using the expressions for  $T$  and  $V$  given respectively by Equations (3.4) and (3.5) we obtain,

$$E = \frac{1}{2} m \omega_0^2 x_0^2 \quad \dots(3.6)$$

We find for an oscillator of given frequency and given amplitude the total energy to be a constant.

#### 3.3.1 Time-Independent Schrödinger Equation for An Oscillator

Let  $\psi(x)$  represent the time-independent wave function which describes the state of the oscillator at some given instant of time.  $\psi(x)$  then satisfies the time-independent Schrödinger equation,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad \dots(3.7)$$

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Using the expression for  $V(x)$  given by Equation (3.5), Equation (3.6) becomes,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} \left[ E - \frac{1}{2} m \omega_0^2 x^2 \right] \psi(x) = 0 \quad \dots(3.8)$$

**NOTES**

For the convenience of solving Equation (3.8), we define a new variable  $y$  and a new parameter  $\lambda$  as,

$$y = \left( \frac{m\omega_0}{\hbar} \right)^{\frac{1}{2}} x \quad \dots(3.9)$$

and

$$\lambda = \frac{2E}{\hbar\omega_0} \quad \dots(3.10)$$

In view of the definition of the variable  $y$  in terms of the variable  $x$ , we may consider the wave function for the oscillator to be a function of  $y$  and write the wave function as  $\psi(y)$ .

Now,

$$\frac{d\psi(x)}{dx} = \frac{d\psi(y)}{dy} \frac{dy}{dx} = \left( \frac{m\omega_0}{\hbar} \right)^{\frac{1}{2}} \frac{d\psi(y)}{dy} \quad \text{[using Equation (3.9)]}$$

and

$$\frac{d^2\psi(x)}{dx^2} = \frac{d}{dx} \frac{d\psi(x)}{dx} = \frac{d}{dx} \left[ \left( \frac{m\omega_0}{\hbar} \right)^{\frac{1}{2}} \frac{d\psi(y)}{dy} \right]$$

$$= \left( \frac{m\omega_0}{\hbar} \right)^{\frac{1}{2}} \frac{d}{dx} \left( \frac{d\psi(y)}{dy} \right) \frac{dy}{dx}$$

$$\text{or} \quad \frac{d^2\psi(x)}{dx^2} = \frac{m\omega_0}{\hbar} \frac{d^2\psi(y)}{dy^2} \quad \dots(3.11)$$

Using Equations (3.9), (3.10) and (3.11) in Equation (3.8) we get,

$$\frac{m\omega_0}{\hbar} \frac{d^2\psi(y)}{dy^2} + \left[ \frac{2m}{\hbar^2} E - \frac{2m}{\hbar^2} \times \frac{1}{2} m \omega_0^2 \frac{\hbar}{m\omega_0} y^2 \right] \psi(y) = 0$$

$$\text{or} \quad \frac{d^2\psi(y)}{dy^2} + \left[ \frac{2E}{\hbar\omega_0} - y^2 \right] \psi(y) = 0$$

$$\text{or} \quad \frac{d^2\psi(y)}{dy^2} + [\lambda - y^2] \psi(y) = 0 \quad \dots(3.12)$$

Equation (3.12) is the time independent Schrödinger equation for the oscillator.

The solution of Equation (3.12) yields  $\psi(y)$  and hence the wave function  $\psi(x)$  for the oscillator.

### 3.3.2 Solution of the Wave Equation

#### Asymptotic Solution

Asymptotic solution of the wave equation is the solution of Equation (3.12) in the limit  $y \rightarrow \infty$  or  $x \rightarrow \infty$ . In this limit,

$$\lambda - y^2 \approx -y^2$$

so that Equation (3.12) reduces to

$$\frac{d^2\psi(y)}{dy^2} - y^2 \psi(y) = 0$$

or 
$$\frac{d^2\psi(y)}{dy^2} = y^2 \psi(y) \quad \dots(3.13)$$

The general solution of Equation (3.13) may be taken as,

$$\psi(y) = e^{\frac{+y^2}{2}} \text{ and } \psi(y) = e^{\frac{-y^2}{2}}$$

i.e., as

$$\psi(y) = e^{\pm \frac{y^2}{2}} \quad \dots(3.14)$$

The above can be easily seen. We get from Equation (3.14),

$$\frac{d\psi(y)}{dy} = \pm y e^{\pm \frac{y^2}{2}}, \quad \frac{d^2\psi(y)}{dy^2} = (y^2 + 1) e^{\pm \frac{y^2}{2}} = y^2 e^{\pm \frac{y^2}{2}} = y^2 \psi(y)$$

because  $y$  is being considered large tending to infinity. One of the asymptotic solutions namely  $\psi(y) = e^{\frac{+y^2}{2}}$  is not physically acceptable because it diverges as  $|y|$  and hence  $|x| \rightarrow \infty$ . We thus have the asymptotic solution for the oscillator,

$$\psi(y) = e^{-\frac{y^2}{2}} \quad \dots(3.15)$$

In terms of the variable  $x$ , the asymptotic solution can be expressed as,

$$\psi(x) = e^{-\frac{m\omega_0}{2h} x^2} \quad \dots(3.16)$$

#### Exact Solution: Recursion Formula

In view of the asymptotic solution given by Equation (3.15), we may express the exact solution of the wave equation for the oscillator given by Eq. (3.12) as

$$\psi(y) = e^{-\frac{y^2}{2}} H(y) \quad \dots(3.17)$$

where  $H(y)$  is a function of  $y$  such that the product  $e^{-\frac{y^2}{2}} H(y)$  tends to zero as  $|y| \rightarrow \infty$  or  $|\infty|$  as is required by the asymptotic solutions given by Equation (3.15) or Equation (3.16).

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From Equation (3.17) we obtain

$$\begin{aligned} \frac{d\psi(y)}{dy} &= e^{-\frac{y^2}{2}} \frac{dH(y)}{dy} - y e^{-\frac{y^2}{2}} H(y) \\ &= \left[ \frac{dH(y)}{dy} - y H(y) \right] e^{-\frac{y^2}{2}} \end{aligned}$$

and

$$\frac{d^2\psi(y)}{dy^2} = \frac{d^2H(y)}{dy^2} e^{-\frac{y^2}{2}} - y e^{-\frac{y^2}{2}} \frac{dH(y)}{dy} + y^2 H(y) e^{-\frac{y^2}{2}} - y e^{-\frac{y^2}{2}} \frac{dH(y)}{dy} - H(y) e^{-\frac{y^2}{2}}$$

$$\text{or} \quad \frac{d^2\psi(y)}{dy^2} = \left[ \frac{d^2H(y)}{dy^2} - 2y \frac{dH(y)}{dy} + (y^2 - 1) H(y) \right] e^{-\frac{y^2}{2}} \quad \dots(3.18)$$

Substituting Equations (3.17) and (3.18) in Equation (3.12) we get

$$\left[ \frac{d^2H(y)}{dy^2} - 2y \frac{dH(y)}{dy} + (y^2 - 1) H(y) \right] e^{-\frac{y^2}{2}} + (\lambda - y^2) H(y) e^{-\frac{y^2}{2}} = 0$$

$$\text{or} \quad \frac{d^2H(y)}{dy^2} - 2y \frac{dH(y)}{dy} + (\lambda - 1) H(y) = 0 \quad \dots(3.19)$$

We find that the function  $H(y)$  in the exact solution of the Schrödinger equation for the oscillator given by Equation (3.17) satisfies the *Hermite differential equation*.

### Power Series Solution

We now assume a power series solution of Equation (3.17) of the type

$$H(y) = \sum_{r=0}^{\infty} a_r y^{s+r} \quad \dots(3.20)$$

Where  $r$  takes integral values including zero. Equation (3.20) gives

$$\frac{dH(y)}{dy} = \sum_{r=0}^{\infty} a_r (s+r) y^{s+r-1} \quad \dots(3.21)$$

and

$$\frac{d^2H(y)}{dy^2} = \sum_{r=0}^{\infty} a_r (s+r)(s+r-1) y^{s+r-2} \quad \dots(3.22)$$

Substituting Equations (3.20), (3.21) and (3.22) in Equation (3.19) we obtain,

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

Dividing throughout by  $y^{s-2}$ , the above becomes,

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

or

$$a_0 s(s-1) y^0 + a_1 s(s+1) y^1 + \sum_{r=2}^{\infty} [a_r (s+r)(s+r-1) - a_{r-2} (2s+2r-3-\lambda)] y^r = 0 \quad \dots(3.23)$$

For Equation (3.23) to hold for all values of  $y$ , it is necessary that the coefficients of different powers of  $y$  must separately be equal to zero. We hence obtain

$$a_0 s(s-1) = 0 \quad \dots(3.24(a))$$

$$a_1 s(s+1) = 0 \quad \dots(3.24(b))$$

$$a_r (s+r)(s+r-1) - a_{r-2} (2s+2r-3-\lambda) = 0 \quad \dots(3.25)$$

Equation (3.25) gives

$$a_r = \frac{2s+2r-3-\lambda}{(s+r)(s+r-1)} a_{r-2}; \quad (r \geq 2) \quad \dots(3.26)$$

Equation (3.26) is called the *recurrence relation*.

As  $a_0 \neq 0$ , we have according to Equation (3.24(a))

$$s = 0 \quad \text{or} \quad s = 1$$

According to Equation (3.24(b)) we may have,

$$a_1 = 0 \quad \text{or} \quad s = 0 \quad \text{or} \quad s = -1 \quad \dots(3.27)$$

Since  $s \neq -1$  we get either  $a_1 = 0$  or  $s = 0$  or both.

The recurrence relation given by Equation (3.26) allows us to calculate all the even coefficients in terms of  $a_0$  and all odd coefficients in terms of  $a_1$ . Equation (3.20) will have only odd coefficients if  $a_0 = 0$  and only even coefficients if  $a_1 = 0$ . We thus have two independent solutions of Equation (3.20). A linear combination of these two solutions gives the most general solution of Equation (3.26).

Considering the root  $s = 0$ , Equation (3.26) gives,

$$a_r = \frac{2r-3-\lambda}{r(r-1)} a_{r-2} \quad (r \geq 2) \quad \dots(3.28)$$

The above equation yields the even coefficients as,

$$\left. \begin{aligned} a_2 &= \frac{1-\lambda}{2 \times 1} a_0 = \frac{1-\lambda}{2!} a_0 \\ a_4 &= \frac{5-\lambda}{4 \times 3} a_2 = \frac{(5-\lambda)(1-\lambda)}{4!} a_0 \end{aligned} \right\} \text{etc.} \quad \dots(3.29)$$

## NOTES

**NOTES**

and the odd coefficients as,

$$\left. \begin{aligned} a_3 &= \frac{3-\lambda}{3 \times 2} a_1 = \frac{3-\lambda}{3!} a_1 \\ a_5 &= \frac{7-\lambda}{5 \times 4} a_3 = \frac{(7-\lambda)(3-\lambda)}{5 \times 4 \times 3!} a_1 = \frac{(7-\lambda)(3-\lambda)}{5!} a_1 \end{aligned} \right\} \text{etc.} \quad \dots(3.30)$$

With  $s = 0$ , the solution given by Equation (3.20) becomes

$$H(y) = \sum_{r=0}^{\infty} a_r y^r$$

The above can be written conveniently as

$$H(y) = (a_0 + a_2 y^2 + a_4 y^4 + \dots) + (a_1 y + a_3 y^3 + a_5 y^5 + \dots)$$

Using the results given by Equations (3.29) and (3.30), the above gives

$$H(y) = \alpha^0 \left[ 1 + \frac{5i}{1-y} \lambda_3 + \frac{4i}{(2-y)(1-y)} \lambda_4 + \dots \right] + \alpha^1 \left[ \lambda + \frac{3i}{3-y} \lambda_3 + \frac{2i}{(1-y)(3-y)} \lambda_2 + \dots \right] \quad \dots(3.31)$$

An inspection of Equation (3.31) shows the following:

- (1) For  $\lambda = 1, 5, 9$ , etc., the first series in Equation (3.31) becomes a polynomial while the second series remains an infinite series.
- (ii) For  $\lambda = 3, 7, 11$ , etc., while the first series is an infinite series, the second one reduces to a polynomial. From the above we can conclude that when,

$$\lambda = (2n + 1), \quad n = 0, 1, 2, \dots \quad \dots(3.32)$$

one of the solutions is a polynomial.

**3.3.3 Energy Eigenvalues of the Oscillator**

Equation (3.28) gives for large  $r$

$$a_r = \frac{2r-3-\lambda}{r(r-1)} a_{r-2} \rightarrow \frac{2r}{r^2} a_{r-2}$$

or 
$$\frac{a_r}{a_{r-2}} \rightarrow \frac{2}{r} \quad \dots(3.33)$$

From the above we obtain

$$\text{Lt}_{r \rightarrow \infty} \frac{a_r}{a_{r-2}} = 0 \quad \dots(3.34)$$

Thus under the condition given by Equation (3.32), both the infinite series in Equation (3.31) converge for all values of  $y$ .

We have the Taylor series expansion of  $e^{y^2}$  as

$$e^{y^2} = 1 + y^2 + \frac{y^4}{2!} + \frac{y^6}{3!} + \dots$$

$$= \sum_{r=0,2,4,\dots} \frac{1}{(r/2)!} y^r$$

Writing

$$b_r = \frac{1}{(r/2)!} \dots \quad \dots(3.35)$$

we get

$$e^{y^2} = \sum_{r=0,2,4,\dots} b_r y^r \quad \dots(3.36)$$

The ratio of the coefficients of the successive terms in Equation (3.36) is

$$\frac{b_r}{b_{r-2}} = \frac{\frac{1}{(r/2)!}}{\frac{1}{\left(\frac{r}{2}-1\right)!}} = \frac{\left(\frac{r}{2}-1\right)!}{\left(\frac{r}{2}\right)!} = \frac{2}{r} \quad \dots(3.37)$$

In view of Equation (3.33) and (3.37) we may write

$$\frac{a_r}{a_{r-2}} = \frac{b_r}{b_{r-2}} \quad (\text{for large } r) \quad \dots(3.38)$$

We find that for large values of  $r$ , the wave function  $\psi(y) = e^{-y^2/2} H(y)$  will behave like  $e^{y^2/2}$  if  $H(y)$  is given by the first (or even) series in Equation (3.31) while it will behave like  $y e^{y^2/2}$  if  $H(y)$  is given by the second (or odd) series in Equation (3.31). This is not physically acceptable. This unrealistic situation is resolved if the infinite series in Equation (3.20) terminates after a certain number of terms so that  $\psi(y) \rightarrow 0$  as  $y \rightarrow \pm \infty$  because of the factor  $E^{-y^2/2}$ . Thus for the wave function of the oscillator to satisfy the boundary condition, the infinite series must be terminated by selecting  $\lambda$  in such a way that  $(2r + 1 - \lambda)$  vanishes for  $r = n$ . Thus one of the series becomes a polynomial and the other can be eliminated by setting the first coefficient to zero. Thus, we obtain

$$2n + 1 - \lambda = 0$$

or

$$\lambda = 2n + 1,$$

$$n = 0, 1, 2, \dots \quad \dots(3.39)$$

Using  $\lambda$  given by Equation (3.10) in Equation (3.39) we get

$$\frac{2E}{\hbar\omega_0} = 2n + 1$$

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$$\text{or} \quad E = \frac{2n+1}{2} \hbar\omega_0 = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad \dots(3.40)$$

**NOTES**

We observe that integral values of  $n$  including 0 value leads to a *discrete set of energy values* for the oscillator. It is important to note that the oscillator possesses equi-spaced energy levels, the spacing between successive energy levels being  $\hbar\omega_0$ .

**3.3.4 Energy Eigenfunctions of the Oscillator**

For the wave function of the oscillator to satisfy the boundary conditions ( $\psi(y) \rightarrow 0$  as  $y \rightarrow \pm\infty$ ), the parameter  $\lambda$  should take the value  $(2n + 1)$  where  $n$  is a positive integer including zero.

When  $\lambda = (2n + 1)$ ,  $H(y)$  in Equation (3.19) can be conveniently replaced by  $H_n(y)$  to get,

$$\frac{d^2 H_n(y)}{dy^2} - 2y \frac{dH_n(y)}{dy} + (2n + 1 - 1) H_n(y) = 0$$

$$\text{or} \quad \frac{d^2 H_n(y)}{dy^2} - 2y \frac{dH_n(y)}{dy} + 2n H_n(y) = 0 \quad \dots(3.41)$$

The solution of Equation (3.41) is the well known Hermite polynomial of degree  $n$  given by,

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} (e^{-y^2}) \quad \dots(3.42)$$

We may note the following recurrence relation that holds between  $H_{n-1}(y)$ ,  $H_n(y)$  and  $H_{n+1}(y)$

$$H_{n+1}(y) = 2y H_n(y) - 2n H_{n-1}(y) \quad \dots(3.43)$$

Hermite polynomials of different degrees may be obtained from Equation (3.42)

$$\begin{aligned} n = 0, & \quad H_0(y) = 1 \\ n = 1, & \quad H_1(y) = 2y \\ n = 2, & \quad H_2(y) = 4y^2 - 2 \\ n = 3, & \quad H_3(y) = 8y^3 - 12y, \quad \text{etc.} \end{aligned} \quad \dots(3.44)$$

We may obtain the Hermite polynomials of higher degrees using Equation (3.44) and the Equation (3.43).

The energy eigenfunctions of the oscillator given by Equation (3.15) can now be expressed in the most general form as,

$$\psi_n(y) = N_n H_n(y) e^{-y^2/2} \quad \dots(3.45)$$

or 
$$\psi_n(x) = N_n e^{-\frac{m\omega_0}{2\hbar} x^2} H_n\left(\sqrt{\frac{m\omega_0}{\hbar}} x\right) \quad \dots(3.46)$$

In the above,  $N_n$  is the normalization constant which can be evaluated from the normalization condition,

$$\int_{-\infty}^{+\infty} \psi_n^*(x) \psi_n(x) dx = 1$$

or 
$$\int_{-\infty}^{+\infty} |\psi_n(y)|^2 \left(\frac{\hbar}{m\omega_0}\right)^{1/2} dy = 1$$

Using Equation (3.45) in the above we get

$$|N_n|^2 \left(\frac{\hbar}{m\omega_0}\right)^{1/2} \int_{-\infty}^{+\infty} H_n^2(y) e^{-y^2} dy = 1$$

or 
$$|N_n|^2 \left(\frac{\hbar}{m\omega_0}\right)^{1/2} \pi^{1/2} 2^n (n!) = 1$$

The above gives

$$N_n = \left[ \left(\frac{m\omega_0}{\hbar\pi}\right)^{1/2} \frac{1}{2^n (n!)} \right]^{1/2} \quad \dots(3.47)$$

Using  $N_n$  given by Equation (3.47) in Equation (3.48), we obtain the normalized energy eigenfunctions of the oscillator to be given as,

$$\psi_n(x) = \left[ \left(\frac{m\omega_0}{\hbar\pi}\right)^{1/2} \frac{1}{2^n (n!)} \right]^{1/2} e^{-\frac{m\omega_0}{2\hbar} x^2} H_n\left(\sqrt{\frac{m\omega_0}{\hbar}} x\right) \quad \dots(3.48)$$

In the following Table are given the energy eigenfunctions, representing the quantized states of the oscillator and the corresponding energy eigenvalues.

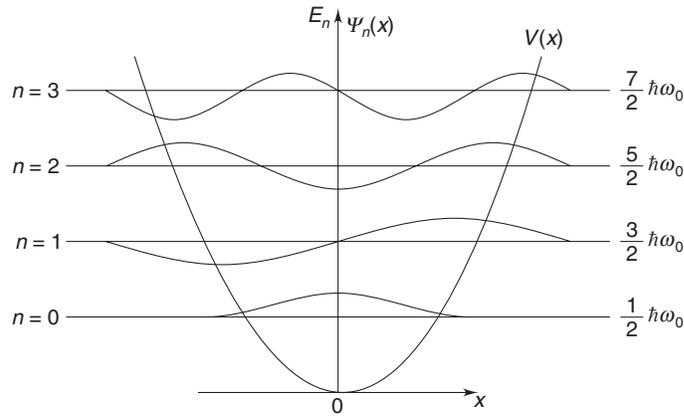
**Table 3.1** Energy Eigenfunctions and Energy Eigenvalues

State	Energy eigenfunctions	Energy eigenvalue
Ground state	$\psi_0(x) = \left(\frac{m\omega_0}{\hbar\pi}\right)^{1/4} e^{-\frac{m\omega_0}{2\hbar} x^2}$	$\frac{1}{2} \hbar\omega_0$
First excited state	$\psi_1(x) = \left[\frac{4m^2\omega_0^2}{\hbar^2\pi}\right]^{1/4} x e^{-\frac{m\omega_0}{2\hbar} x^2}$	$\frac{3}{2} \hbar\omega_0$
Second excited state	$\frac{\psi_2(x)}{2^{3/2}} \left[\frac{m\omega_0}{\pi\hbar}\right]^{1/4} \left(\frac{4m\omega_0}{\hbar} x^2 - 2\right) e^{-\frac{m\omega_0}{2\hbar} x^2}$	$\frac{5}{2} \hbar\omega_0$ , etc.

**NOTES**

Some of the energy eigenfunctions  $\psi_n(x)$ , the corresponding energy eigenvalues  $E_n$ , the potential energy function  $V(x)$  are shown in the Figure (3.1).

**NOTES**

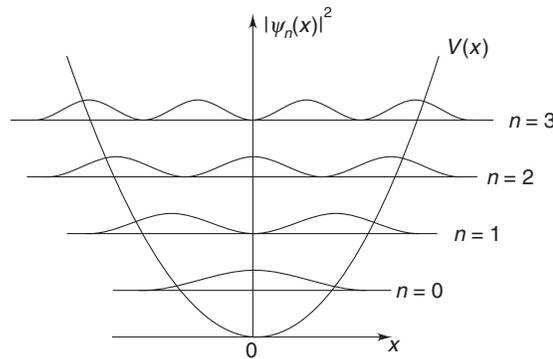


**Fig. 3.1** Normalized Wave Functions  $\psi_n(x)$  for  $n = 0, 1, 2, 3$   
 Energy Eigenvalues  $E_n$  for  $n = 0, 1, 2, 3$   
 The Potential Energy Function  $V(x)$

The probability of finding the oscillating particle between  $x$  and  $x + dx$  when the oscillator is in the  $n^{\text{th}}$  state described by the wavefunction  $\psi_n(x)$  and according to the definition is given by,

$$P_n(x) dx = \psi_n^*(x) \psi_n(x) dx = |\psi_n(x)|^2 dx \quad \dots(3.49)$$

Using Equation (3.48) in Equation (3.49) we can find the probability  $P_n(x)$ . The plots of probability density  $|\psi_n(x)|^2$  for some of the states along with that of the potential energy function are shown in Figure (3.2).



**Fig. 3.2** Probability Density  $|\psi_n(x)|^2$  for  $n = 0, 1, 2, 3$ .  
 Potential Energy Function  $v(x)$

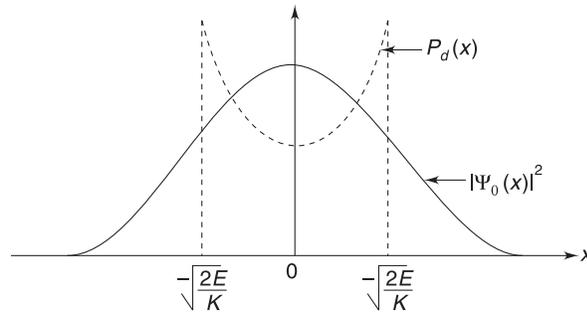


Fig. 3.3 Probability Curve

### Discussions

From the wave mechanical treatment of linear harmonic oscillator presented in the preceding sections we observe the following:

- (i) While a harmonic oscillator treated classically possesses constant total energy depending upon the frequency and the amplitude, a wave mechanical treatment of the oscillator yields a discrete set of equispaced energy eigenvalues given by,

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega_0, \quad n = 0, 1, 2, \dots \quad \dots(3.50)$$

In the lowest or the ground state, which corresponds to  $n = 0$ , the oscillator has the finite energy,

$$E_0 = \frac{1}{2} \hbar \omega_0 \quad \dots(3.51)$$

Which is called the *zero-point energy*.

According to old quantum theory, the energy values of the oscillator are given by,

$$E_n = n \hbar \omega_0, \quad n = 0, 1, 2, \dots \quad \dots(3.52)$$

A comparison of the result given by Equation (3.52) with that given by Equation (3.50) shows that each of the equispaced energy levels obtained in the old quantum theory are raised by an amount equal to half the energy gap between the successive energy levels, i.e., by an amount equal to the zero point energy to give the energy levels of the oscillator in wave mechanical treatment. According to classical mechanics and old quantum theory, while the harmonic oscillator possesses zero energy in the lowest state corresponding to the state at absolute zero (0K), the oscillator when treated wave mechanically possesses the energy  $\frac{1}{2} \hbar \omega_0$  even at absolute zero.

The existence of zero point energy is in agreement with experiments and is found to be consistent with the uncertainty principle also.

### NOTES

**NOTES**

(ii) The function  $e^{-y^2/2}$  is always an even function,  $H_n(y)$  is an even function for  $n$  even and an odd function for  $n$  odd, we find the oscillator energy eigenfunctions given by Eq. (49) are even function for  $n$  even and odd functions for  $n$  odd.

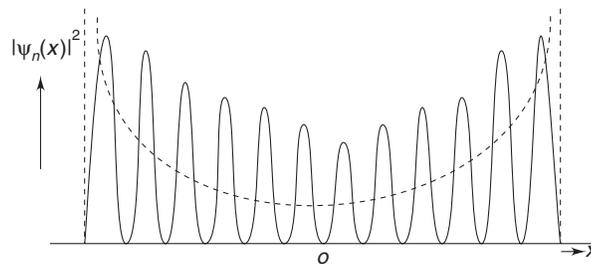
(iii) Since the oscillator energy eigenfunctions  $\psi_n(x)$  do not become zero at the classical turning points  $x = \pm x_0$ , the oscillator can be found outside the parabolic potential barrier  $\left(V = \frac{1}{2} kx^2\right)$ . The oscillator in all its quantum state is thus able to penetrate the potential barrier. This fact becomes evident from Figure (3.4).

(iv) The total energy of the oscillator at the position corresponding to the displacement  $\pm x$  from the mean position is,

$$E = \frac{1}{2} mv^2 + \frac{1}{2} kx^2$$

We obtain from the above, the velocity of the oscillator at the position  $\pm x$  to be,

$$v = \left[ \frac{2E - kx^2}{m} \right]^{1/2} \dots(3.53)$$



**Fig. 3.4** Solid Curve Represents the Variation of  $|\psi_{10}(x)|^2$  with  $x$ .

Dotted curve represents the probability density of a classical oscillator of the same total energy.

Classically, the probability of finding the oscillator at the position  $\pm x$  is inversely proportional to the velocity, i.e.,

$$P_{cl}(x) \propto \sqrt{\frac{m}{2E - kx^2}} \dots(3.54)$$

We find the probability to be the minimum at the mean position ( $x = 0$ ) and maximum at the two extreme positions  $\left(x_0 = \pm \sqrt{\frac{2E}{k}}\right)$ . This is shown by the dotted curve in Figure 3.3. Quantum mechanically, for the ground state of the oscillator ( $n = 0$ ), the probability density

given by  $|\psi_0(x)|^2$  is maximum at  $x = 0$  and becomes zero at positions outside the classical turning points ( $x = \pm x_0$ ). This result is shown by full line curve in Figure (3.3). Figure (3.2) shows the plot of  $|\psi_n(x)|^2$  against  $x$  for different values of  $n$  corresponding to different quantum states of the oscillator.

- (v) As we move towards higher and higher excited states ( $n$  increasing), the maximum value of probability density moves towards the extreme positions as illustrated in the Figure (3.4) by the full line curve. The dotted curve in this figure shows the variation of classical probability density with position for the same energy.

It is important to remark that though the classical and quantum mechanical probability distributions become closer and closer for larger and larger  $n$ , the theory of oscillator described above cannot take account of the rapid oscillations of  $|\psi_n(x)|^2$ .

### 3.3.5 Alternative Approach for Linear Harmonic Oscillator Problem

#### Abstract Operator Method

The Schrödinger method for solving the energy eigenvalue problem of linear harmonic oscillator as presented in the previous sections consists in replacing the position  $x$  and the linear momentum  $p$  in the expression for total energy by the corresponding Hermitian operator  $\hat{x}$  for  $x$  and  $\hat{p} = -i\hbar \frac{d}{dx}$ , respectively, to obtain the Hamiltonian operator  $\hat{H}$  for the oscillator and then to solve for the energy eigenvalue equation,

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

We may, however, note that one of the fundamental features of quantum mechanics is that operators  $\hat{x} = x$  and  $\hat{p}$  satisfy the commutation relation,

$$[\hat{x}, \hat{p}] = i\hbar \quad \dots(3.55)$$

There exist many problems which can be exactly and elegantly solved using the method of abstract operator algebra, i.e., using the commutation relations between operators without considering specific forms for the operators.

In the following, we use this method to solve the energy eigenvalue problem for linear harmonic oscillator. As we shall see, the method allows us to find, with simplicity not only the expectation values of various physical quantities for the oscillator but also the energy eigenfunctions of the oscillator.

The Hamiltonian operator of a harmonic oscillator of mass  $m$  oscillating along the  $x$ -axis under a force constant  $k$  is,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} k x^2 \quad \dots(3.56)$$

## NOTES

Let us introduce two operators  $\hat{a}$  and  $\hat{a}^\dagger$  according to,

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}} x + i\sqrt{\frac{1}{2m\hbar\omega_0}} \hat{p} \quad \dots(3.57)$$

And

$$\hat{a}^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}} x - i\sqrt{\frac{1}{2m\hbar\omega_0}} \hat{p} \quad \dots(3.58)$$

In the above  $\hat{a}^\dagger$  is the Hermitian adjoint of  $\hat{a}$  and  $\omega_0$  is the natural angular frequency of the oscillator. From Equations (3.57) and (3.58) we obtain

$$\begin{aligned} \hat{a}\hat{a}^\dagger &= \left( \sqrt{\frac{m\omega_0}{2\hbar}} x + i\sqrt{\frac{1}{2m\hbar\omega_0}} \hat{p} \right) \left( \sqrt{\frac{m\omega_0}{2\hbar}} x - i\sqrt{\frac{1}{2m\hbar\omega_0}} \hat{p} \right) \\ &= \frac{m\omega_0}{2\hbar} x^2 + \frac{1}{2m\hbar\omega_0} \hat{p}^2 + \frac{i}{2\hbar} (\hat{p}x - x\hat{p}) \end{aligned}$$

Using Equation (3.55) in the above we obtain

$$\hat{a}\hat{a}^\dagger = \frac{m\omega_0}{2\hbar} x^2 + \frac{1}{2m\hbar\omega_0} \hat{p}^2 + \frac{i}{2\hbar} (-i\hbar)$$

or 
$$\hat{a}\hat{a}^\dagger = \frac{1}{\hbar\omega_0} \left[ \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega_0^2 x^2 \right] + \frac{1}{2}$$

or 
$$\hat{a}\hat{a}^\dagger = \frac{\hat{H}}{\hbar\omega_0} + \frac{1}{2} \quad [\text{using Equation (3.56)}] \quad \dots(3.59)$$

Similarly, we obtain

$$\hat{a}^\dagger \hat{a} = \frac{\hat{H}}{\hbar\omega_0} - \frac{1}{2} \quad \dots(3.60)$$

Adding Equations (3.59) and (3.60) we obtain,

$$2 \frac{\hat{H}}{\hbar\omega_0} = \hat{a}\hat{a}^\dagger + \hat{a}^\dagger \hat{a}$$

or 
$$\hat{H} = \frac{1}{2} \hbar\omega_0 (\hat{a}\hat{a}^\dagger + \hat{a}^\dagger \hat{a}) \quad \dots(3.61)$$

Subtracting Equation (3.60) from Equation (3.59) we get,

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

Clearly, the operators  $\hat{a}$  and  $\hat{a}^\dagger$  satisfy the commutation relation,

$$[\hat{a}, \hat{a}^\dagger] = 1 \quad \dots(3.62)$$

## NOTES

We may also express the Hamiltonian operator  $\hat{H}$  as,

$$\hat{H} = \hbar\omega_0 \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \quad \dots(3.63)$$

We observe that the Hamiltonian operator  $\hat{H}$  and the operator  $\hat{a}^\dagger \hat{a}$  are related to each other by numbers only. Clearly, the eigenvalues  $\hat{H}$  and that of  $\hat{a}^\dagger \hat{a}$  bear the same relationship.

## NOTES

### **Eigenvalues of $\hat{a}^\dagger \hat{a}$**

We have

$$[\hat{a}^\dagger \hat{a}, a] = \hat{a}^\dagger \hat{a}a - \hat{a}\hat{a}^\dagger a = (\hat{a}^\dagger \hat{a} - \hat{a}\hat{a}^\dagger) a = -(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a}) a$$

Using the result given by Equation (3.62) in the above we obtain

$$[\hat{a}^\dagger \hat{a}, \hat{a}] = -\hat{a} \quad \dots(3.64)$$

Also we have

$$[\hat{a}^\dagger \hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger \hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a}^\dagger \hat{a} = \hat{a}^\dagger (\hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a}) = \hat{a}^\dagger \quad \dots(3.65)$$

Let  $\psi$  be an eigenfunction of the operator  $\hat{a}^\dagger \hat{a}$  belonging to eigenvalue  $\lambda$ , i.e.,

$$\hat{a}^\dagger \hat{a}\psi = \lambda\psi \quad \dots(3.66)$$

We now have

$$\begin{aligned} (\hat{a}^\dagger \hat{a})(\hat{a}\psi) &= (\hat{a}\hat{a}^\dagger - 1)(\hat{a}\psi) && \text{[using Equation (3.62)]} \\ &= \hat{a}\hat{a}^\dagger \hat{a}\psi - \hat{a}\psi \\ &= \hat{a}\lambda\psi - \hat{a}\psi && \text{[using Equation (3.66)]} \end{aligned}$$

$$\text{or} \quad (\hat{a}^\dagger \hat{a})(\hat{a}\psi) = (\lambda - 1) \hat{a}\psi \quad \dots(3.67)$$

Similarly, we get

$$(\hat{a}^\dagger \hat{a})(\hat{a}^\dagger \psi) = (\lambda + 1) \hat{a}^\dagger \psi \quad \dots(3.68)$$

Equations (3.67) and (3.68) show:

- (i)  $\hat{a}\psi$  is an eigenfunction of  $\hat{a}^\dagger \hat{a}$  belonging to the eigenvalue  $(\lambda - 1)$ .
- (ii)  $\hat{a}^\dagger \psi$  is an eigenfunction of  $\hat{a}^\dagger \hat{a}$  belonging to the eigenvalue  $(\lambda + 1)$ .

From the above, we find that given the eigenfunction  $\psi$  of  $\hat{a}^\dagger \hat{a}$  it is possible to construct eigenfunctions  $\hat{a}^\dagger \psi$ ,  $(\hat{a}^\dagger)^2 \psi$ ,  $(\hat{a}^\dagger)^3 \psi$ , etc., belonging respectively to eigenvalues  $(\lambda + 1)$ ,  $(\lambda + 2)$ ,  $(\lambda + 3)$ , etc. Similarly, we can construct eigenfunctions  $\hat{a}\psi$ ,  $(\hat{a})^2 \psi$ ,  $(\hat{a})^3 \psi$ , etc. belonging to eigenvalues  $(\lambda - 1)$ ,  $(\lambda - 2)$ ,  $(\lambda - 3)$ , etc.

Now  $\hat{a}^\dagger \hat{a}$  is self-adjoint irrespective of whether  $\hat{a}$  is self-adjoint or not. The expectation value of  $\hat{a}^\dagger \hat{a}$  is positive in all states, i.e., the operator

does not possess negative eigenvalues. Hence the sequence of eigenvalues  $(\lambda - 1), (\lambda - 2), \dots$  must terminate before the negative value is reached and also the sequence  $\hat{a}\psi, \hat{a}^2\psi, \dots$  must terminate.

## NOTES

Denoting the limiting eigenfunction (the last of the eigenfunctions) in the sequence as  $\psi_0$  we obtain,

$$\hat{a}\psi_0 = 0 \quad \dots(3.69)$$

The above gives,

$$\hat{a}^\dagger \hat{a}\psi_0 = 0 = 0 \times \psi_0 \quad \dots(3.70)$$

indicating that  $\psi_0$  is an eigenfunction of the operator  $\hat{a}^\dagger \hat{a}$  belonging to the eigenvalue 0.

In view of Equation (3.68) we then obtain

$$\begin{aligned} \hat{a}^\dagger \hat{a} (\hat{a}^\dagger \psi_0) &= 1 \times (\hat{a}^\dagger \psi_0) \\ \hat{a}^\dagger \hat{a} [(\hat{a}^\dagger)^2 \psi_0] &= 2 \times (\hat{a}^\dagger)^2 \psi_0 \\ \hat{a}^\dagger \hat{a} [(\hat{a}^\dagger)^3 \psi_0] &= 3(\hat{a}^\dagger)^3 \psi_0, \quad \text{etc.} \end{aligned} \quad \dots(3.71)$$

or generalizing, we get

$$\hat{a}^\dagger \hat{a} [(\hat{a}^\dagger)^n \psi_0] = n(\hat{a}^\dagger)^n \psi_0 \quad \dots(3.72)$$

We observe that the eigenvalue spectrum of the operator  $\hat{a}^\dagger \hat{a}$  consists of a set of positive integers  $n$ . Equation (3.72) when applied to Equation (3.63) gives

$$\hat{H}[(\hat{a}^\dagger)^n \psi_0] = \hbar\omega_0 \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right) [(\hat{a}^\dagger)^n \psi_0] = \hbar\omega_0 \left( n + \frac{1}{2} \right) (\hat{a}^\dagger)^n \psi_0 \quad \dots(3.73)$$

Thus the energy eigenvalues of the oscillator are

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega_0, \quad n = 0, 1, 2, \dots \quad \dots(3.74)$$

The operator  $\hat{a}^\dagger$  and  $\hat{a}$  are, respectively, called the raising and lowering operators. Further, since the eigenvalues of  $\hat{a}^\dagger \hat{a}$  are positive integers it is usual to call the operator  $\hat{a}^\dagger \hat{a}$  as the number operator. The lowest energy eigenvalue is,

$$E_0 = \frac{1}{2} \hbar\omega_0$$

Which is the zero point energy of the oscillator.

Replacing  $\hat{p}$  by  $-i\hbar \frac{d}{dx}$  in Equation (3.57) and (3.58) we obtain

$$\hat{a} = \frac{1}{(2m\hbar\omega_0)^{1/2}} \left( m\omega_0 x + \hbar \frac{d}{dx} \right)$$

$$\hat{a}^\dagger = \frac{1}{(2m\hbar\omega_0)^{1/2}} \left( m\omega_0 x - \hbar \frac{d}{dx} \right)$$

Using the above in Equation (3.69) we obtain,

$$\frac{1}{(2m\hbar\omega_0)^{1/2}} \left( m\omega_0 x + \hbar \frac{d}{dx} \right) \Psi_0 = 0$$

or 
$$m\omega_0 x \Psi_0 + \hbar \frac{d\Psi_0}{dx} = 0$$

or 
$$\frac{d\Psi_0}{\Psi_0} = \frac{-m\omega_0 x}{\hbar} dx$$

Integrating we obtain,

$$\Psi_0 = N_0 e^{-\frac{m\omega_0 x^2}{2\hbar}}, \quad N_0 = \text{A constant.} \quad \dots(3.75)$$

The above is the energy eigenfunction of the oscillator belonging to the lowest energy eigenvalue  $\frac{1}{2} \hbar\omega_0$ . The eigenfunction corresponding to the first excited state belonging to energy eigenvalue  $\frac{3}{2} \hbar\omega_0$  is,

$$\Psi_1 = \hat{a}^\dagger \Psi_0 = \frac{1}{(2m\hbar\omega_0)^{1/2}} \left( m\omega_0 x - \hbar \frac{d}{dx} \right) N_0 e^{-\frac{m\omega_0 x^2}{2\hbar}}$$

or 
$$\begin{aligned} \Psi_1 &= \frac{N_0}{(2m\hbar\omega_0)^{1/2}} \left( m\omega_0 x - \hbar \frac{d}{dx} \right) e^{-\frac{m\omega_0 x^2}{2\hbar}} \\ &= N_1 \left( m\omega_0 x - \hbar \frac{d}{dx} \right) e^{-\frac{m\omega_0 x^2}{2\hbar}} \end{aligned} \quad \dots(3.76)$$

The eigenfunction corresponding to the second excited state belonging to the energy eigenvalue  $\frac{5}{2} \hbar\omega_0$  is,

$$\Psi_2 = \hat{a}^\dagger \Psi_1 = \frac{N_1}{(2m\hbar\omega_0)^{1/2}} \left( m\omega_0 x - \hbar \frac{d}{dx} \right)^2 e^{-\frac{m\omega_0 x^2}{2\hbar}}$$

or 
$$\Psi_2 = N_2 \left( m\omega_0 x - \hbar \frac{d}{dx} \right)^2 e^{-\frac{m\omega_0 x^2}{2\hbar}}$$

Repeating the operation by  $\hat{a}^\dagger$  from the left we get the energy eigenfunction belonging to energy eigenvalue  $\left( n + \frac{1}{2} \right) \hbar\omega_0$  as,

$$\Psi_n = N_n \left( m\omega_0 x - \hbar \frac{d}{dx} \right)^n e^{-\frac{m\omega_0 x^2}{2\hbar}} \quad \dots(3.77)$$

## NOTES

$\psi_n$  given by Equation (3.77) is the same as the eigenfunction for the oscillator obtained using the previous method.

### 3.3.6 Potential Barrier Problem

#### NOTES

A one-dimensional potential barrier of height  $V_0$  and width  $a$  is defined by potential function  $V(x)$  given by,

$$\begin{aligned} V(x) &= 0 \quad \text{for } x < 0 \\ &= V_0 \quad \text{for } 0 < x < a \\ &= 0 \quad \text{for } x > a \end{aligned}$$

The above potential function is shown in the Figure (3.5).

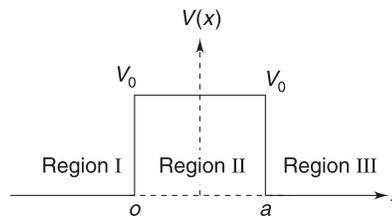


Fig. 3.5 Potential Function

Let us consider a particle of mass  $m$  moving from the left, encounter the barrier at  $x = 0$  with energy  $E$ . We limit our discussion to energies of the particles such that  $E < V_0$ , that is, energies such that no penetration of the barrier would occur according to classical physics.

In the Region I ( $x < 0$ ) the Schrödinger equation is,

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

or 
$$\frac{d^2\psi_1(x)}{dx^2} + k^2 \psi_1(x) = 0, \quad k = \sqrt{\frac{2m}{\hbar^2} E} \quad \dots(3.78)$$

In the Region II, i.e., inside the barrier we have the equation,

$$\frac{d^2\psi_2(x)}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_2(x) = 0$$

Putting

$$\sqrt{\frac{2m}{\hbar^2} (V_0 - E)} = \alpha \quad (\text{A positive quantity}) \quad \dots(3.79)$$

The above equation becomes,

$$\frac{d^2\psi_2(x)}{dx^2} - \alpha^2 \psi_2(x) = 0 \quad \dots(3.80)$$

In the Region III ( $x \geq a$ ), we have the equation,

$$\frac{d^2 \psi_3(x)}{dx^2} + k^2 \psi_3(x) = 0 \quad \dots(3.81)$$

The general solutions of Equation (3.78), (3.80) and (3.81) are given respectively by,

$$\psi_1(x) = A_1 e^{ikx} + B_1 e^{-ikx} \quad \dots(3.82)$$

$$\psi_2(x) = A_2 e^{\alpha x} + B_2 e^{-\alpha x} \quad \dots(3.83)$$

$$\psi_3(x) = A_3 e^{ikx} + B_3 e^{-ikx} \quad \dots(3.84)$$

In the above  $A_1, A_2, A_3, B_1, B_2, B_3$  are constants.

The first term in Equation (3.82) which represents a plane wave travelling along the positive  $x$ -axis in Region I can be considered as the wave *incident* on the barrier at  $x = 0$ . The second term representing a wave travelling along the negative  $x$ -axis in the region can be interpreted as the wave reflected from the barrier at  $x = 0$ .

The first and second terms in Equation (3.83) can similarly be interpreted as the wave transmitted into the barrier at  $x = 0$  and the wave reflected from the barrier at  $x = a$ . In Equation (3.84) the first term can be interpreted as the wave transmitted into the region III from the barrier at  $x = a$ . In this region the only wave that can exist is a wave travelling along the positive  $x$ -axis. Hence, the coefficient  $B_3$  in the second term of the Equation (3.85) is identically zero.

Considering the amplitude of the incident wave as unity we may write the solutions in the three regions as,

$$\psi_1(x) = e^{ikx} + B_1 e^{-ikx} \quad \dots(3.85)$$

$$\psi_2(x) = A_2 e^{\alpha x} + B_2 e^{-\alpha x} \quad \dots(3.86)$$

$$\psi_3(x) = A_3 e^{ikx} \quad \dots(3.87)$$

Single valuedness and continuity of the wavefunctions at the boundaries at  $x = 0$  and at  $x = a$  give the following boundary conditions:

and

$$\left. \begin{aligned} \psi_1(0) &= \psi_2(0) \\ \frac{\partial \psi_1(x)}{\partial x} &= \frac{\partial \psi_2(x)}{\partial x} \text{ at } x = 0 \\ \psi_2(a) &= \psi_3(a) \\ \frac{\partial \psi_2(x)}{\partial x} &= \frac{\partial \psi_3(x)}{\partial x} \text{ at } x = a \end{aligned} \right\} \dots(3.88)$$

## NOTES

Using these boundary conditions we obtain,

$$I + B_1 = A_2 + B_2 \quad \dots(3.89)$$

$$ik(I - B_1) = \alpha(A_2 - B_2) \quad \dots(3.90)$$

$$A_2 e^{\alpha a} + B_2 e^{-\alpha a} = A_3 e^{ika} \quad \dots(3.91)$$

$$\alpha[A_2 e^{\alpha a} - B_2 e^{-\alpha a}] = ik A_3 e^{ika} \quad \dots(3.92)$$

Solving the simultaneous Equations [(3.89) to (3.92)] we obtain,

$$A_3 = \frac{2ik \alpha e^{-ika}}{(\alpha^2 - k^2) \sin h(\alpha a) - 2i\alpha k \cos h(\alpha a)} \quad \dots(3.93)$$

$A_3$  being the amplitude of wave transmitted into the Region III. We get the transmission coefficient under the condition  $E < V_0$  as,

$$T = A_3 A_3^* = |A_3|^2 = \frac{2ik \alpha e^{-ika}}{(\alpha^2 - k^2) \sin h(\alpha a) - 2i\alpha k \cos h(\alpha a)} \times \frac{-2ik \alpha e^{ika}}{(\alpha^2 - k^2) \sin h(\alpha a) + 2i\alpha k \cos h(\alpha a)}$$

or

$$T = \frac{4k^2 \alpha^2}{(\alpha^2 - k^2)^2 \sin^2 h(\alpha a) + 4\alpha^2 k^2 \cos^2 h(\alpha a)} \quad \dots(3.94)$$

Since both  $k$  as well as  $\alpha$  are real quantities, the transmission coefficient has a finite value.

When  $E \rightarrow 0$ ,  $k \rightarrow 0$  and hence  $T \rightarrow 0$ .

As the energy  $E$  of the incident particle increases, remaining less than  $V_0$ , both  $k$  as well as  $\alpha$  increase and the transmission coefficient increases.

Under the condition  $E < V_0$ ,  $\alpha \neq 0$ , we obtain from Equation (3.94)

$$T = \frac{4k^2 \alpha^2}{k^4 \alpha^2 a^2 + 4\alpha^2 k^2} = \frac{1}{1 + \left(\frac{ka}{2}\right)^2} \quad \dots(3.95)$$

Under the condition of the barrier height  $V_0$  large and the barrier width  $a$  also large we get  $\alpha a$  large, so that

$$\sin h(\alpha a) = \frac{1}{2} e^{\alpha a}$$

$$\cos h(\alpha a) = \frac{1}{2} e^{\alpha a}$$

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The transmission coefficient given by Equation (3.94) then yields

$$T = \frac{16k^2 \alpha^2}{(\alpha^2 - k^2) + 4\alpha^2 k^2} e^{-2\alpha a}$$

or 
$$T = \frac{16k^2 \alpha^2}{(\alpha^2 + k^2)^2} e^{-2\alpha a}$$

Using the values of  $k$  and  $\alpha$  in the above we obtain for such a barrier,

$$T = \frac{16E(V_0 - E)}{V_0^2} e^{-2 \left[ \frac{2m}{\hbar^2} (V_0 - E) \right]^{1/2} a} \quad \dots(3.96)$$

We observe that transmission does occur even though the energy lies below the top of the barrier. This is a wave phenomenon and in quantum mechanics it is also exhibited by the particle. This *tunneling* of a particle through a barrier is frequently encountered. We note that when  $\alpha a$  is large, the ratio of the transmitted flux to incident flux is,

$$T \approx \left( \frac{2k\alpha}{\alpha^2 + k^2} \right)^2 e^{-4\alpha a} \quad \dots(3.97)$$

We find the flux ratio to be an extremely sensitive function of the width  $a$  of the barrier, and of the amount by which the barrier height  $V_0$  exceeds the incident energy.

The phenomenon of particle tunneling is quite common in atomic and nuclear physics. Some examples are thermionic emission, field emission,  $\alpha$ -particle emission from a heavy nucleus.

### 3.3.7 Alpha-Particle Emission

It is observed that some radioactive nuclei disintegrate by the emission of alpha ( $\alpha$ ) particle which is the nucleus of a helium atom having charge of  $+2e$  and a mass 4 units.

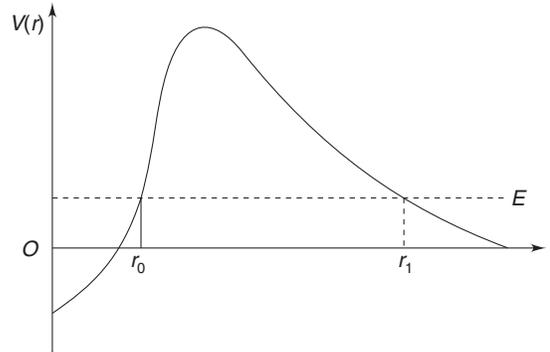
An  $\alpha$ -particle remains bound within the nucleus by a strong, attractive, short range nuclear force. This attractive nuclear force acts upto a distance which is approximately equal to the radius of the nucleus. When the  $\alpha$ -particle comes out of the nucleus then it experiences a long range coulomb repulsive force due to the residual nucleus (the nucleus that remains after the emission of the  $\alpha$ -particle). The variation of the potential energy of the  $\alpha$ -particle with distance from the centre of the nucleus is qualitatively as shown in the Figure (3.6).

If  $r_0$  be the radius of the nucleus and  $Ze$  be the charge of the residual nucleus then the coulomb potential energy of the  $\alpha$ -particle just beyond the surface of the nucleus becomes  $\frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_1}$ . For the  $\alpha$ -emitting nuclides

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this energy is several times larger than the energy of the  $\alpha$ -particles. The question thus arises how the  $\alpha$ -particles of energy much less than the potential barrier cross the barrier? The answer is provided by the quantum mechanical tunneling of a particle through a potential barrier as discussed in the previous section.



**Fig. 3.6** Potential Energy of the  $\alpha$ -Particle

Let  $E$  be the energy of the  $\alpha$ -particle emitted from the nucleus. Let the repulsive coulomb potential energy of the nucleus be equal to  $E$  at a distance  $r_1$  from the centre of the nucleus. We then have,

$$E = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_1} \quad \dots(3.98)$$

or 
$$r_1 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{E} \quad \dots(3.99)$$

We may, for some qualitative understanding of the phenomenon of  $\alpha$ -emission, consider the potential  $V(r)$  in the region  $r_0 \leq r \leq r_1$  as a one-dimensional square potential barrier and use the result of the last section to write the transmission coefficient from the barrier as,

$$T = \frac{16E(V_0 - E)}{V_0^2} e^{-\left[\sqrt{\frac{8m}{\hbar^2}(V_0 - E)}\right](r_1 - r_0)} \quad \dots(3.100)$$

Where 
$$V_0 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_0} = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_1} \quad \dots(3.101)$$

A rigorous treatment yields the transmission coefficient to be,

$$T = e^{-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2m(V(r) - E)} dr}$$

or 
$$T = e^{-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2m \left[ \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r} - E \right]} dr} \quad \dots(3.102)$$

The speed of an  $\alpha$ -particle in a heavy nucleus has been estimated to be of the order of  $10^7 \text{ ms}^{-1}$ . Considering the nucleus's radius to be  $10^{-14} \text{ m}$  we find that the time taken by the  $\alpha$ -particle to move once across the nucleus to be  $10^{-21}$ . Clearly the  $\alpha$ -particle strikes the coulomb barrier at the surface of the nucleus  $10^{21}$  times per second. The probability that the  $\alpha$ -particle crosses the barrier and comes out of the nucleus per sec is,

$$P = T \times 10^{21}$$

The reciprocal of  $P$  gives the life time  $\tau$  of the  $\alpha$ -decaying nucleus, i.e.,

$$\tau = \frac{1}{P} = \frac{1}{T \times 10^{21}} \quad \dots(3.103)$$

If  $\lambda$  be the disintegration constant of the nucleus we get,

$$\lambda = \frac{1}{\tau} = T \times 10^{21} = 10^{21} e^{-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2m \left[ \frac{1}{4\pi\epsilon_0} \frac{2ze^2}{r} - E \right]} dr}$$

Taking its logarithm we get from the above,

$$\log \lambda = A + BE, \quad A \text{ and } B \text{ Constants} \quad \dots(3.104)$$

which is the well-known Geiger-Nuttal law.

**Example 1:** Find the probability density at the position  $x$  of a linear harmonic oscillator of mass  $m$  and natural angular frequency  $\omega_0$  if the oscillator is in its ground state. Find also the position at which the probability density is the maximum. What is the maximum probability density?

**Solution:** The ground state of the given oscillator is described by the wavefunction,

$$\Psi_0(x) = \left( \frac{m\omega_0}{\hbar\pi} \right)^{1/4} e^{-\frac{m\omega_0}{2\hbar} x^2}$$

The probability density at the position  $x$  is given by,

$$P(x) = \Psi_0^*(x) \Psi_0(x) = \left( \frac{m\omega_0}{\hbar\pi} \right)^{1/2} e^{-\frac{m\omega_0}{\hbar} x^2}$$

We find  $P(x)$  to be a function of  $x$ . Hence, for  $P(x)$  to be maximum we have,

$$\frac{dP(x)}{dx} = 0$$

$$\text{or} \quad \left( \frac{m\omega_0}{\hbar\pi} \right)^{1/2} e^{-\frac{m\omega_0}{\hbar} x^2} x \left( -\frac{m\omega_0}{\hbar} \right) 2x = 0$$

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The above gives  $x = 0$ . Thus the probability density is the maximum at the mean position ( $x = 0$ ). The maximum probability density is clearly,

$$P_{\max} = P(0) = \left( \frac{m\omega_0}{\hbar\pi} \right)^{1/2}$$

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**Example 2:** A linear harmonic oscillator is described at some instant of time by the wavefunction  $\psi = a\psi_0 + b\psi_1$ , where  $\psi_0$  and  $\psi_1$  are, respectively, the real, normalized ground state and first excited state energy eigenfunctions of the oscillator with  $a$  and  $b$  real numbers.

- (a) Show that the average value of position  $x$  is in general different from zero.
- (b) Find the values of  $a$  and  $b$  for which  $\langle x \rangle$  is maximum.
- (c) Find the values of  $a$  and  $b$  for which  $\langle x \rangle$  is minimum.

**Solution:** (a) The normalization condition of the wavefunction gives,

$$\int \psi^* \psi dx = 1$$

or 
$$\int (a\psi_0 + b\psi_1)^2 dx = 1$$

or 
$$\int a^2\psi_0^2 dx + \int b^2\psi_1^2 dx + 2ab \int \psi_0\psi_1 dx = 1$$

The above gives,

$$a^2 + b^2 = 1 \tag{... (i)}$$

since  $\int \psi_0^2 dx = 1$ ;  $\int \psi_1^2 dx = 1$  and  $\int \psi_0\psi_1 dx = 0$  ( $\psi_0$  and  $\psi_1$  being orthogonal)

Now

$$\begin{aligned} \langle x \rangle &= \int (a\psi_0 + b\psi_1) x (a\psi_0 + b\psi_1) dx \\ &= \int x (a\psi_0 + b\psi_1)^2 dx \end{aligned}$$

or 
$$\langle x \rangle = 2ab \int \psi_0 x \psi_1 dx \tag{... (ii)}$$

Since  $a$  and  $b$  are not zero, in general, we get  $\langle x \rangle \neq 0$ .

(b) We may write the result given by Equation (ii), in view of Equation (i) as

$$\langle x \rangle = [1 - (a^2 + b^2 - 2ab)] \int \psi_0 x \psi_1 dx$$

or 
$$\langle x \rangle = [1 - (a - b)^2] \int \psi_0 x \psi_1 dx \tag{... (iii)}$$

From the above we find for  $\langle x \rangle$  to be the maximum,

$$a - b = 0$$

or 
$$a = b = \frac{1}{\sqrt{2}} \quad (\text{using Equation (i)})$$

(c) From Equation (iii) we find for  $\langle x \rangle$  to be the minimum

$$a = b = \frac{1}{\sqrt{2}}$$

**Example 3:** A particle of rest mass  $0.51 \text{ eV}$  undergoes harmonic oscillation of angular frequency  $\omega_0$  along the  $x$ -axis. If the particle is confined to the ground state of the oscillator such that  $\sqrt{\langle (x - \langle x \rangle)^2 \rangle} = 0$ , find the energy required to excite it to its first excited state.

**Solution:** For a one-dimensional harmonic oscillator the average kinetic energy  $\langle T \rangle$  is equal to the average potential energy  $\langle V \rangle$ . Thus the total energy of the oscillator is,

$$E = \langle T \rangle + \langle V \rangle = 2\langle V \rangle = 2 \times \frac{1}{2} m_0 \omega_0^2 \langle x^2 \rangle \quad \dots(\text{i})$$

Since the particle is confined in the ground state we have,

$$E = \frac{1}{2} \hbar \omega_0 \quad \dots(\text{ii})$$

From Equations (i) and (ii) we have,

$$\frac{1}{2} \hbar \omega_0 = m_0 \omega_0^2 \langle x^2 \rangle$$

or 
$$\omega_0 = \frac{\hbar}{2m_0 \langle x^2 \rangle} \quad \dots(\text{iii})$$

We know that for the harmonic oscillator  $\langle x \rangle = 0$ . We have according to the problem,

$$\sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\langle x^2 \rangle} = 10^{-10} \text{ m} \quad \dots(\text{iv})$$

The energy difference between the ground state and the first excited state is  $\hbar \omega_0$ . Clearly, the energy required to excite the particle from the ground to the first excited state is,

$$\begin{aligned} \Delta E = \hbar \omega_0 &= \hbar \frac{\hbar}{2m_0 \langle x^2 \rangle} = \frac{\hbar^2}{2m_0 \langle x^2 \rangle} \\ &= \frac{(6.58 \times 10^{-16})^2 \times c^2}{2m_0 10^{-20} \times c^2} \\ &= \frac{(6.58 \times 10^{-16})^2 \times (3 \times 10^8)^2}{2 \times 0.51 \times 10^{-20}} \\ &= 3.8 \text{ eV.} \end{aligned}$$

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**Example 4:** A particle of mass  $m$  undergoes simple harmonic motion along the  $x$ -axis with an angular frequency  $\omega$ . Considering the uncertainty relation

$$\Delta x \Delta p = \frac{\hbar}{2}, \text{ where,}$$

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$$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle \text{ and } (\Delta p)^2 = \langle (p - \langle p \rangle)^2 \rangle,$$

Find the minimum energy of the oscillator.

**Solution:** We know that for the linear harmonic oscillator,

$$\langle x \rangle = 0 \text{ and } \langle p \rangle = 0 \quad \dots(i)$$

We hence get

$$(\Delta x)^2 = \langle x^2 \rangle \text{ and } (\Delta p)^2 = \langle p^2 \rangle \quad \dots(ii)$$

The Hamiltonian of the oscillator is given by,

$$H = \text{Kinetic Energy } (T) + \text{Potential Energy } (V)$$

Clearly

$$\begin{aligned} \langle H \rangle &= \langle T \rangle + \langle V \rangle \\ &= \left\langle \frac{p^2}{2m} \right\rangle + \left\langle \frac{1}{2} m \omega^2 x^2 \right\rangle \\ &= \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} m \omega^2 \langle x^2 \rangle \quad \dots(iii) \end{aligned}$$

Since both terms on the right hand side of Equation (iii) are real and positive, we get,

$$\langle H \rangle = \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} m \omega^2 \langle x^2 \rangle \geq 2 \sqrt{\frac{1}{2m} \langle p^2 \rangle \times \frac{1}{2} m \omega^2 \langle x^2 \rangle}$$

$$\text{or } \langle H \rangle \geq 2 \sqrt{\frac{1}{4} \omega^2 \langle p^2 \rangle \langle x^2 \rangle} = \omega \sqrt{(\Delta x)^2 (\Delta p)^2}$$

(using Equation (iii))

$$\text{or } \langle H \rangle \geq \omega \Delta x \Delta p$$

$$\text{or } \langle H \rangle \geq \frac{\hbar \omega}{2}$$

Clearly, the minimum energy is given by,

$$\langle H \rangle_{\min} = \frac{1}{2} \hbar \omega$$

**Example 5:** A particle of mass  $m$  is undergoing harmonic oscillation of angular frequency  $\omega$ . If the wavefunction describing the state of the particle be,

$$\Psi = x e^{\frac{-m\omega}{2\hbar} x^2}$$

Find the energy of the particle.

**Solution:** The wavefunction  $\Psi$  satisfies the Schrödinger equation,

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} [E - V] \Psi = 0 \quad \dots(i)$$

In the above,  $E$  is the energy eigenvalue in the state under consideration,  $V$  is the potential energy given by,

$$V = \frac{1}{2} m\omega^2 x^2 \quad \dots(ii)$$

We have

$$\Psi = x e^{\frac{-m\omega}{2\hbar} x^2}$$

Clearly,

$$\begin{aligned} \frac{d\Psi}{dx} &= e^{\frac{-m\omega}{2\hbar} x^2} - x \frac{m\omega}{2\hbar} 2x e^{\frac{-m\omega}{2\hbar} x^2} \\ &= e^{\frac{-m\omega}{2\hbar} x^2} \left[ 1 - \frac{m\omega}{\hbar} x^2 \right] \end{aligned}$$

Further, we get

$$\frac{d^2\Psi}{dx^2} = e^{\frac{-m\omega}{2\hbar} x^2} \left[ -\frac{m\omega}{\hbar} 2x \right] - \left[ 1 - \frac{m\omega}{\hbar} x^2 \right] \times \frac{m\omega}{2\hbar} 2x e^{\frac{-m\omega}{2\hbar} x^2}$$

$$\text{or } \frac{d^2\Psi}{dx^2} = e^{\frac{-m\omega}{2\hbar} x^2} \left[ \frac{-m\omega}{\hbar} 2x - \frac{m\omega}{\hbar} x + \frac{m^2\omega^2}{\hbar^2} x^3 \right]$$

$$\text{or } \frac{d^2\Psi}{dx^2} = \frac{m\omega x}{\hbar} e^{\frac{-m\omega}{2\hbar} x^2} \left[ \frac{m\omega}{\hbar} x^2 - 3 \right] \quad \dots(iii)$$

Substituting Equations (ii) and (iii) in Equation (i) we get,

$$\frac{m\omega}{\hbar} x e^{\frac{-m\omega}{2\hbar} x^2} \left[ \frac{m\omega}{\hbar} x^2 - 3 \right] + \frac{2m}{\hbar^2} \left[ E - \frac{1}{2} m\omega^2 x^2 \right] x e^{\frac{-m\omega}{2\hbar} x^2} = 0$$

$$\text{or } \frac{2m}{\hbar^2} x e^{\frac{-m\omega}{2\hbar} x^2} \left[ E - \frac{1}{2} m\omega^2 x^2 + \frac{m\omega^2 x^2}{2} - \frac{3}{2} \hbar\omega \right] = 0$$

## NOTES

The above gives,

$$E - \frac{3}{2} \hbar \omega = 0$$

or 
$$E = \frac{3}{2} \hbar \omega .$$

## NOTES

**Example 6:** Find the probability of finding a particle undergoing simple harmonic oscillations outside the classical limits if the oscillator is in its ground state.

**Solution:** Consider a linear harmonic oscillator of mass  $m$  and angular frequency  $\omega$ .

If  $a$  be the amplitude of oscillation, the total energy of the particle when we treat the oscillator classically is,

$$E = \frac{1}{2} m \omega^2 a^2$$

According to the problem, the oscillator is in its ground state and hence its energy is,

$$E = \frac{1}{2} \hbar \omega$$

Thus, we have

$$\frac{1}{2} m \omega^2 a^2 = \frac{1}{2} \hbar \omega$$

or 
$$a^2 = \frac{\hbar}{m \omega}$$

or 
$$a = \sqrt{\frac{\hbar}{m \omega}}$$

The wavefunction describing the ground state of the oscillator is given by,

$$\Psi_0 = \left( \frac{\alpha}{\sqrt{\pi}} \right)^{1/2} e^{-\frac{\alpha^2 x^2}{2}}$$

Where

$$\alpha = \sqrt{\frac{m \omega}{\hbar}} = \frac{1}{a}$$

The probability of finding the oscillator within the classical limits ( $x = -a$  to  $x = +a$ ) is given by,

$$p = \int_{-a}^{+a} \Psi_0^* \Psi_0 dx$$

$$= \int_{-a}^{+a} \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 x^2} dx$$

$$= \int_{-\frac{1}{\alpha}}^{+\frac{1}{\alpha}} \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 x^2} dx$$

Let us introduce a new variable  $y$  as,

$$y = \alpha x$$

We then get,

$$p = \int_{-1}^{+1} \frac{1}{\sqrt{\pi}} e^{-y^2} dy$$

$$= 2 \int_0^1 \frac{1}{\sqrt{\pi}} e^{-y^2} dy$$

or 
$$p = \frac{2}{\sqrt{\pi}} \left[ \int_0^1 dy - \int_0^1 y^2 dy + \int_0^1 \frac{y^4}{2!} dy - \int_0^1 \frac{y^6}{3!} dy + \dots \right]$$

or 
$$p = \frac{2}{\sqrt{\pi}} \left[ 1 - \frac{1}{3} + \frac{1}{10} - \frac{1}{42} + \dots \right]$$

or 
$$p = 0.84$$

Thus, the probability of finding the oscillator within the classical limits is 0.84 or 84% when the oscillator is in its ground state. Clearly in the ground state the probability of finding the particle outside the classical limits of the oscillator is  $(1 - 0.84) = 0.16$  or 16%.

**Example 7:** Show that the existence of zero point energy of a linear harmonic oscillator is a consequence of the uncertainty principle.

**Solution:** Consider a harmonic oscillator of mass  $m$  capable of oscillating along the  $x$ -axis with an angular frequency  $\omega$ . If at any time  $t$ ,  $x$  be the displacement and  $p$  the linear momentum, the Hamiltonian of the oscillator is given by,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} kx^2 \quad \dots(i)$$

where  $k$  is the force constant equal to  $m\omega^2$ . Classically, the average displacement and the average linear momentum of the oscillator are zero, i.e.,

$$\langle x \rangle = 0 \quad \text{and} \quad \langle p \rangle = 0 \quad \dots(ii)$$

## NOTES

According to Ehrenfest's theorem, Equation (ii) also holds for the quantum mechanical oscillator. If  $\Delta x$  and  $\Delta p$  be the uncertainties in the measured values of  $x$  and  $p$  then by definition we get,

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2$$

and

$$(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2$$

Using Equation (ii), the above become

$$\left. \begin{aligned} (\Delta x)^2 &= \langle x^2 \rangle \\ (\Delta p)^2 &= \langle p^2 \rangle \end{aligned} \right\} \dots(\text{iii})$$

The average value of the total energy is given by

$$\langle E \rangle = \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} k \langle x^2 \rangle$$

Hence, using Equation (iii) we get,

$$\langle E \rangle = \frac{1}{2m} (\Delta p)^2 + \frac{1}{2} k (\Delta x)^2 \dots(\text{iv})$$

We have the uncertainty relation,

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

or  $(\Delta p)^2 (\Delta x)^2 \geq \frac{\hbar^2}{4} \dots(\text{v})$

Using Equation (v), Equation (iv) can be written as,

$$\langle E \rangle \geq \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2} k (\Delta x)^2 \dots(\text{vi})$$

For  $\langle E \rangle$  to be the minimum we must have,

$$\frac{d\langle E \rangle}{d(\Delta x)^2} = 0$$

or  $\frac{-\hbar^2}{8m(\Delta x)_{\min}^4} + \frac{1}{2} k = 0$

or  $(\Delta x)_{\min}^4 = \frac{\hbar^2}{4mk} = \frac{\hbar^2}{4m m \omega^2}$

or  $(\Delta x)_{\min}^2 = \frac{\hbar}{2m\omega} \dots(\text{vii})$

Clearly

**NOTES**

$$\begin{aligned}\langle E \rangle_{\min} &= \frac{\hbar^2}{8m(\Delta x)_{\min}^2} + \frac{1}{2} m\omega^2 (\Delta x)_{\min}^2 \\ &= \frac{\hbar^2 2m\omega}{8m\hbar} + \frac{1}{2} m\omega^2 \frac{\hbar}{2m\omega}\end{aligned}$$

or 
$$\langle E \rangle_{\min} = \frac{1}{2} \hbar\omega$$

**Example 8:** A particle of mass  $m$  undergoes simple harmonic motion along the  $x$ -axis with an angular frequency  $\omega$ . The wavefunction describing the state of the particle at  $t = 0$  is given by,

$$\psi(x, 0) = A \sum_n \left( \frac{1}{\sqrt{2}} \right)^n \psi_n(x)$$

where  $\psi_n(x)$  are the energy eigenfunctions of the oscillator belonging to eigenvalues  $\left(n + \frac{1}{2}\right)$ . Find:

- The normalization constant  $A$
- An expression for  $\psi(x, t)$ .
- Expectation value of the energy at  $t = 0$  and
- Show that the probability density  $|\psi(x, t)|^2$  is a periodic function of time.

**Solution:** (a) The normalization condition of the wavefunction is,

$$\int \psi^*(x, 0) \psi(x, 0) dx = 1$$

Using the expression for  $\psi(x, 0)$  in the above we get,

$$|A|^2 \int \sum_n \left( \frac{1}{\sqrt{2}} \right)^n \psi_n^*(x) \sum_m \left( \frac{1}{\sqrt{2}} \right)^m \psi_m(x) dx = 1$$

or 
$$|A|^2 \sum_{n,m} \int \left( \frac{1}{\sqrt{2}} \right)^{n+m} \psi_n^*(x) \psi_m(x) dx = 1 \quad \dots(i)$$

The orthonormality property of eigenfunctions gives,

$$\int \psi_n^*(x) \psi_m(x) dx = \delta_{nm}$$

Using the above in Equation (i) we get,

$$|A|^2 \sum_n \left( \frac{1}{\sqrt{2}} \right)^{2n} = 1$$

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or 
$$|A|^2 \sum_n \left(\frac{1}{2}\right)^{\frac{2n}{2}} = 1$$

or 
$$|A|^2 2 = 1$$

or 
$$|A| = \frac{1}{\sqrt{2}} \quad \dots(\text{ii})$$

(b)  $\psi(x, t)$  and  $\psi(x, 0)$  are related according to,

$$\begin{aligned} \psi(x, t) &= \psi(x, 0) e^{\frac{-i\hat{H}t}{\hbar}} \\ &= \sum_n \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}}\right)^n \psi_n(x) e^{\frac{-i\hbar\omega\left(n+\frac{1}{2}\right)t}{\hbar}} \end{aligned}$$

or 
$$\psi(x, t) = \sum_n \left(\frac{1}{\sqrt{2}}\right)^{n+1} e^{-i\omega\left(n+\frac{1}{2}\right)t} \psi_n(x) \quad \dots(\text{iii})$$

(c) By definition, the expectation value of energy at  $t = 0$  is given by,

$$\begin{aligned} \langle E \rangle &= \int \psi^*(x, 0) \hat{H} \psi(x, 0) dx \\ &= \sum_{n,m} \left(\frac{1}{2}\right)^{\frac{n+m}{2}+1} \int \psi_n^*(x) \psi_m(x) dx \\ &= \sum_{n,m} \left(\frac{1}{2}\right)^{\frac{n+m}{2}+1} \left(n + \frac{1}{2}\right) \hbar\omega \delta_{nm} \\ &= \sum_{n=0}^{\infty} \left(\frac{1}{2}\right)^{n+1} \left(n + \frac{1}{2}\right) \hbar\omega \\ &= \sum \frac{1}{2^{n+1}} \left(n + \frac{1}{2}\right) \hbar\omega \\ &= \sum \frac{n}{2^{n+1}} \hbar\omega + \sum \frac{1}{2^{n+2}} \hbar\omega \\ &= 1 \times \hbar\omega + \frac{1}{2} \hbar\omega \end{aligned}$$

or 
$$\langle E \rangle = \frac{3}{2} \hbar\omega$$

(d) The probability density is given by,

$$|\psi(x, t)|^2 = \psi^*(x, t) \psi(x, t)$$

$$= \sum_{n,m} \left(\frac{1}{2}\right)^{\frac{n+m}{2}+1} e^{-i\omega(n-m)t} \psi_n^*(x) \psi_m(x)$$

The time factor, namely  $e^{-i\omega(n-m)t}$  is a function of time with period  $\frac{2\pi}{(n-m)\omega}$ .

**Example 9:** The Hamiltonian operator for a harmonic oscillator of angular frequency  $\omega$  in terms of raising and lowering operators  $\hat{a}^+$  and  $\hat{a}$  is given by,

$$\hat{H} = \hbar\omega \left( \hat{a}^+ \hat{a} + \frac{1}{2} \right).$$

$$\text{where } \hat{a} = \left( \frac{m\omega}{2\hbar} \right)^{\frac{1}{2}} x + i \left( \frac{1}{2m\hbar\omega} \right)^{\frac{1}{2}} \hat{p}$$

$$\hat{a}^\dagger = \left( \frac{m\omega}{2\hbar} \right)^{\frac{1}{2}} x - i \left( \frac{1}{2m\hbar\omega} \right)^{\frac{1}{2}} \hat{p}$$

Unnormalized energy eigenfunction of the oscillator is,

$$\psi = (2x^3 - 3x) e^{-\frac{x^2}{2}}$$

Considering dimensionless units ( $m = 1, \omega = 1, \hbar = 1$ ), find the eigenfunctions which are closest to  $\psi$  in energy.

**Solution:** If we take  $m = 1, \omega = 1$  and  $\hbar = 1$  we get,

$$\left. \begin{aligned} \hat{a} &= \frac{1}{\sqrt{2}} (x + i\hat{p}) \\ \hat{a}^\dagger &= \frac{1}{\sqrt{2}} (x - i\hat{p}) \end{aligned} \right\} \dots(\text{i})$$

Let  $\psi_n$  be an energy eigenfunction of the oscillator belonging to the energy eigenvalue,

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega = \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \dots(\text{ii})$$

We have

$$\hat{a} \psi_n = \sqrt{n} \psi_{n-1}$$

And

$$\hat{a}^\dagger \psi_n = \sqrt{n+1} \psi_{n+1}$$

So that

$$\hat{a} \hat{a}^\dagger \psi_n = \hat{a} (\sqrt{n+1}) \psi_{n+1} = (n+1) \psi_n \dots(\text{iii})$$

Using Equation (i) we have,

## NOTES

**NOTES**

$$\hat{a}\hat{a}^\dagger \psi = \frac{1}{2}(x + i\hat{p})(x - i\hat{p}) \psi$$

Replacing  $\hat{p}$  by  $-i\hbar \frac{d}{dx} = -i \frac{d}{dx}$ , the above becomes,

$$\hat{a}\hat{a}^\dagger \psi = \frac{1}{2} \left( x + \frac{d}{dx} \right) \left( x - \frac{d}{dx} \right) \psi$$

Using  $\psi$  given in the problem we get,

$$\hat{a}\hat{a}^\dagger \psi = \frac{1}{2} \left( x + \frac{d}{dx} \right) \left( x - \frac{d}{dx} \right) (2x^3 - 3x) e^{-\frac{x^2}{2}}$$

or 
$$\hat{a}\hat{a}^\dagger \psi = 4(2x^3 - 3x) e^{-\frac{x^2}{2}} = (3 + 1) \psi \quad \dots(\text{iv})$$

Comparing Equation (iv) with Equation (iii) we get,

$$n = 3$$

Hence, the eigenfunctions closest in energy to  $\psi$  belong to  $n = 2$  and  $n = 4$ .

The eigenfunction corresponding to  $n = 2$  is,

$$\Psi_2 = \frac{1}{\sqrt{3}} \hat{a} \psi = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{2}} \left( x + \frac{d}{dx} \right) (2x^3 - 3x) e^{-\frac{x^2}{2}}$$

or 
$$\Psi_2 = \frac{1}{\sqrt{6}} \left( x + \frac{d}{dx} \right) (2x^3 - 3x) e^{-\frac{x^2}{2}}$$

The eigenfunction corresponding to  $n = 4$  is,

$$\Psi_4 = \frac{1}{2} \hat{a}^\dagger \psi = \frac{1}{2\sqrt{2}} \left( x - \frac{d}{dx} \right) (2x^3 - 3x) e^{-\frac{x^2}{2}}$$

**Example 10:** The ground state eigenfunction and the first excited state eigenfunction of a linear harmonic oscillator along the  $x$ -axis are given, respectively, by,

$$\Psi_0(x) = \left[ \frac{\alpha}{\sqrt{\pi}} \right]^{1/2} e^{-\frac{\alpha^2 x^2}{2}}$$

and 
$$\Psi_1(x) = 2 \left[ \frac{\alpha}{2\sqrt{\pi}} \right]^{1/2} \alpha x e^{-\frac{\alpha^2 x^2}{2}}$$

Find the expectation value of the energy of the oscillator if its state is described by the wavefunction,

$$\psi(x) = \frac{1}{\sqrt{2}} [\Psi_0(x) + \Psi_1(x)]$$

**Solution:** Let  $\hat{H}$  be the Hamiltonian operator for the oscillator. We then have according to the problem,

$$\hat{H} \psi_0(x) = \frac{1}{2} \hbar \omega \psi_0(x) \quad \dots(i)$$

$$\hat{H} \psi_1(x) = \frac{3}{2} \hbar \omega \psi_1(x) \quad \dots(ii)$$

We also have the following orthonormal properties of  $\psi_0(x)$  and  $\psi_1(x)$ ,

$$\int_{-\infty}^{+\infty} \psi_0^*(x) \psi_0(x) dx = \int_{-\infty}^{+\infty} |\psi_0(x)|^2 dx = \int_{-\infty}^{+\infty} \psi_0^2(x) dx = 1 \quad \dots(iii)$$

$$\int_{-\infty}^{+\infty} \psi_1^*(x) \psi_1(x) dx = \int_{-\infty}^{+\infty} |\psi_1(x)|^2 dx = \int_{-\infty}^{+\infty} \psi_1^2(x) dx = 1 \quad \dots(iv)$$

$$\int_{-\infty}^{+\infty} \psi_0^*(x) \psi_1(x) dx = \int_{-\infty}^{+\infty} \psi_0(x) \psi_1(x) dx = 0 \quad \dots(v)$$

The expectation value of energy in the state described by the wavefunction  $\psi(x)$  is given by,

$$\begin{aligned} \langle E \rangle &= \int_{-\infty}^{+\infty} \psi^*(x) \hat{H} \psi(x) dx \\ &= \int_{-\infty}^{+\infty} \left[ \frac{1}{\sqrt{2}} \{\psi_0(x) + \psi_1(x)\}^* \hat{H} \frac{1}{\sqrt{2}} \{\psi_0(x) + \psi_1(x)\} \right] dx \\ &= \frac{1}{2} \left[ \int_{-\infty}^{+\infty} \{\psi_0(x) + \psi_1(x)\} \hat{H} \{\psi_0(x) + \psi_1(x)\} dx \right] \end{aligned}$$

or

$$\begin{aligned} \langle E \rangle &= \frac{1}{2} \left[ \int_{-\infty}^{+\infty} \psi_0(x) \hat{H} \psi_0(x) dx + \int_{-\infty}^{+\infty} \psi_1(x) \hat{H} \psi_1(x) dx \right. \\ &\quad \left. + \int_{-\infty}^{+\infty} \psi_0(x) \hat{H} \psi_1(x) dx + \int_{-\infty}^{+\infty} \psi_1(x) \hat{H} \psi_0(x) dx \right] \end{aligned}$$

Using Equations (i) and (ii) the above becomes,

$$\begin{aligned} \langle E \rangle &= \frac{1}{2} \left[ \int_{-\infty}^{+\infty} \frac{1}{2} \hbar \omega \psi_0^2(x) dx + \int_{-\infty}^{+\infty} \frac{3}{2} \hbar \omega \psi_1^2(x) dx \right. \\ &\quad \left. + \int_{-\infty}^{+\infty} \frac{3}{2} \hbar \omega \psi_0(x) \psi_1(x) dx + \int_{-\infty}^{+\infty} \frac{1}{2} \hbar \omega \psi_1(x) \psi_0(x) dx \right] \end{aligned}$$

## NOTES

Using Equations (iii), (iv) and (v) the above gives,

$$\langle E \rangle = \frac{1}{2} \left[ \frac{1}{2} \hbar \omega + \frac{3}{2} \hbar \omega \right] = \hbar \omega$$

## NOTES

### Check Your Progress

1. What are the two important properties of one-dimensional motion?
2. How is force constant related to the frequency?
3. What is the total energy of the oscillator?
4. In terms of the variable  $x$ , express the asymptotic solution.
5. Why the infinite series must be terminated for the wave function of the oscillator to satisfy the boundary condition?
6. What is the condition for the wave function of the oscillator to satisfy the boundary conditions?
7. What is zero-point energy?
8. What is the total energy of the oscillator? How will you obtain velocity from it?
9. Give the Hamiltonian operator of a harmonic oscillator.
10. Explain the energy eigenvalues of the oscillator.

## 3.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The important properties of one-dimensional motion that we find are:
  - (i) In case of bound states, the energy spectrum is not only discrete but is non-degenerate also.
  - (ii) The eigenfunction  $\psi_n(x)$  for a bound state has ' $n$ ' number of nodes if the ground state corresponds to  $n = 0$  and  $(n - 1)$  number of nodes if the ground state corresponds to  $n = 1$ .
2. The force constant  $k$  (restoring force acting on the particle per unit displacement) is related to the frequency  $\omega_0$  as
 
$$k = m \omega_0^2$$
3. The total energy  $E$  of the oscillator is,
 
$$E = T + V$$

4. In terms of the variable  $x$ , the asymptotic solution can be expressed as,

$$\psi(x) = e^{-\frac{m\omega_0}{2\hbar}x^2}$$

5. For the wave function of the oscillator to satisfy the boundary condition, the infinite series must be terminated by selecting  $\lambda$  in such a way that  $(2r + 1 - \lambda)$  vanishes for  $r = n$ . Thus one of the series becomes a polynomial and the other can be eliminated by setting the first coefficient to zero.
6. For the wave function of the oscillator to satisfy the boundary conditions ( $\psi(y) \rightarrow 0$  as  $y \rightarrow \pm \infty$ ), the parameter  $\lambda$  should take the value  $(2n + 1)$  where  $n$  is a positive integer including zero.
7. In the lowest or the ground state, which corresponds to  $n = 0$ , the oscillator has the finite energy,

$$E_0 = \frac{1}{2} \hbar \omega_0$$

Which is called the *zero-point energy*.

8. The total energy of the oscillator at the position corresponding to the displacement  $\pm x$  from the mean position is,

$$E = \frac{1}{2} mv^2 + \frac{1}{2} kx^2$$

We obtain from the above, the velocity of the oscillator at the position  $\pm x$  to be,

$$v = \left[ \frac{2E - kx^2}{m} \right]^{1/2}$$

9. The Hamiltonian operator of a harmonic oscillator of mass  $m$  oscillating along the  $x$ -axis under a force constant  $k$  is,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} kx^2$$

10. The energy eigenvalues of the oscillator are

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega_0, \quad n = 0, 1, 2, \dots$$

The operator  $\hat{a}^\dagger$  and  $\hat{a}$  are, respectively, called the raising and lowering operators. Further, since the eigenvalues of  $\hat{a}^\dagger \hat{a}$  are positive integers it is usual to call the operator  $\hat{a}^\dagger \hat{a}$  as the number operator.

## NOTES

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### 3.5 SUMMARY

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- The nature of the states of the particle is determined completely by the energy of the particle and the nature of the potential function  $V(x)$ .

**NOTES**

- The important properties of one-dimensional motion that we find are:
  - (i) In case of bound states, the energy spectrum is not only discrete but is non-degenerate also.
  - (ii) The eigenfunction  $\psi_n(x)$  for a bound state has 'n' number of nodes if the ground state corresponds to  $n = 0$  and  $(n - 1)$  number of nodes if the ground state corresponds to  $n = 1$ .

- If  $x_0$  is the amplitude of the oscillator, its displacement  $x$  from the mean or the equilibrium position varies with time according to,
 
$$x = x_0 \sin \omega_0 t$$

- The potential energy of the oscillator is,

$$V(x) = \frac{1}{2} kx^2 = \frac{1}{2} m \omega_0^2 x^2$$

- The total energy  $E$  of the oscillator is,

$$E = T + V$$

- One of the asymptotic solutions namely  $\psi(y) = e^{+\frac{y^2}{2}}$  is not physically acceptable because it diverges as  $|y| \rightarrow \infty$ . We thus have the asymptotic solution for the oscillator,

$$\psi(y) = e^{-\frac{y^2}{2}}$$

- For the wave function of the oscillator to satisfy the boundary condition, the infinite series must be terminated by selecting  $\lambda$  in such a way that  $(2r + 1 - \lambda)$  vanishes for  $r = n$ . Thus one of the series becomes a polynomial and the other can be eliminated by setting the first coefficient to zero.

- The oscillator possesses equi-spaced energy levels, the spacing between successive energy levels being  $\hbar\omega_0$ .

- For the wave function of the oscillator to satisfy the boundary conditions ( $\psi(y) \rightarrow 0$  as  $y \rightarrow \pm \infty$ ), the parameter  $\lambda$  should take the value  $(2n + 1)$  where  $n$  is a positive integer including zero.

- The probability of finding the oscillating particle between  $x$  and  $x + dx$  when the oscillator is in the  $n^{\text{th}}$  state described by the wavefunction  $\psi_n(x)$  and according to the definition is given by,

$$P_n(x) dx = \psi_n^*(x) \psi_n(x) dx = |\psi_n(x)|^2 dx$$

- In the lowest or the ground state, which corresponds to  $n = 0$ , the oscillator has the finite energy,

$$E_0 = \frac{1}{2} \hbar\omega_0$$

Which is called the *zero-point energy*.

- The function  $e^{-y^2/2}$  is always an even function,  $H_n(y)$  is an even function for  $n$  even and an odd function for  $n$  odd, we find the oscillator energy eigenfunctions are even function for  $n$  even and odd functions for  $n$  odd.
- Since the oscillator energy eigenfunctions  $\psi_n(x)$  do not become zero at the classical turning points  $x = \pm x_0$ , the oscillator can be found outside the parabolic potential barrier  $\left(V = \frac{1}{2} kx^2\right)$ . The oscillator in all its quantum state is thus able to penetrate the potential barrier.
- The total energy of the oscillator at the position corresponding to the displacement  $\pm x$  from the mean position is,

$$E = \frac{1}{2} mv^2 + \frac{1}{2} kx^2$$

We obtain from the above, the velocity of the oscillator at the position  $\pm x$  to be,

$$v = \left[ \frac{2E - kx^2}{m} \right]^{1/2}$$

- The Hamiltonian operator of a harmonic oscillator of mass  $m$  oscillating along the  $x$ -axis under a force constant  $k$  is,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} kx^2$$

- $\hat{a}^\dagger \hat{a}$  is self-adjoint irrespective of whether  $\hat{a}$  is self-adjoint or not. The expectation value of  $\hat{a}^\dagger \hat{a}$  is positive in all states, i.e., the operator does not possess negative eigenvalues. Hence the sequence of eigenvalues  $(\lambda - 1), (\lambda - 2), \dots$  must terminate before the negative value is reached and also the sequence  $\hat{a}\psi, \hat{a}^2\psi, \dots$  must terminate.
  - The energy eigenvalues of the oscillator are
- $$E_n = \left( n + \frac{1}{2} \right) \hbar\omega_0, \quad n = 0, 1, 2, \dots$$
- The operator  $\hat{a}^\dagger$  and  $\hat{a}$  are, respectively, called the raising and lowering operators. Further, since the eigenvalues of  $\hat{a}^\dagger \hat{a}$  are positive integers it is usual to call the operator  $\hat{a}^\dagger \hat{a}$  as the number operator.
  - A one-dimensional potential barrier of height  $V_0$  and width  $a$  is defined by potential function  $V(x)$  given by,

$$\begin{aligned} V(x) &= 0 \quad \text{for } x < 0 \\ &= V_0 \quad \text{for } 0 < x < a \\ &= 0 \quad \text{for } x > a \end{aligned}$$

## NOTES

**NOTES**

- As the energy  $E$  of the incident particle increases, remaining less than  $V_0$ , both  $k$  as well as  $\alpha$  increase and the transmission coefficient increases.

- It is observed that some radioactive nuclei disintegrate by the emission of alpha ( $\alpha$ ) particle which is the nucleus of a helium atom having charge of  $+2e$  and a mass 4 units.

- An  $\alpha$ -particle remains bound within the nucleus by a strong, attractive, short range nuclear force. This attractive nuclear force acts upto a distance which is approximately equal to the radius of the nucleus.

- If  $r_0$  be the radius of the nucleus and  $Ze$  be the charge of the residual nucleus then the coulomb potential energy of the  $\alpha$ -particle just beyond the surface of the nucleus becomes  $\frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_1}$ .

- The speed of an  $\alpha$ -particle in a heavy nucleus has been estimated to be of the order of  $10^7 \text{ ms}^{-1}$ .

- The probability that the  $\alpha$ -particle crosses the barrier and comes out of the nucleus per sec is,

$$P = T \times 10^{21}$$

- The reciprocal of  $P$  gives the life time  $\tau$  of the  $\alpha$ -decaying nucleus, i.e.,

$$\tau = \frac{1}{P} = \frac{1}{T \times 10^{21}}$$

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**3.6 KEY WORDS**

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- **Nature of the states of the particle:** It is determined completely by the energy of the particle and the nature of the potential function  $V(x)$ .
- **Bound states:** In bound state the energy spectrum is not only discrete but is non-degenerate also.
- **Total energy E of the oscillator:** The total energy  $E$  of the oscillator is given as  $E = T + V$ .
- **Alpha-particle emission:** Some radioactive nuclei disintegrate by the emission of alpha ( $\alpha$ ) particle which is the nucleus of a helium atom having charge of  $+2e$  and a mass 4 units.

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### 3.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

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#### Short Answer Questions

1. What is one dimensional motion?
2. How the nature of the states of the particle is determined?
3. Define the term linear harmonic oscillator.
4. What is kinetic energy of the oscillator?
5. Give the equation for the asymptotic solution of the wave equation.
6. What is the recurrence relation for the oscillator?
7. What is abstract operator method?
8. Differentiate between eigenvalues and eigenfunction.
9. What is potential barrier problem?
10. Define the term tunnel effect.

#### Long Answer Questions

1. Discuss the one dimensional problems in quantum mechanics giving appropriate examples.
2. Briefly explain the linear harmonic oscillator and tunnel effect in quantum mechanics giving appropriate examples.
3. Explain the equations for the time-independent Schrödinger equation for an oscillator.
4. Briefly discuss the exact solution/recursion formula of the wave equation for the oscillator.
5. Discuss the energy eigenfunctions of the oscillator giving equations and figures.
6. Explain the abstract operator method for linear harmonic oscillator problem.
7. Write a detailed note on one-dimensional potential barrier.
8. Discuss about the alpha-particle emission giving appropriate examples.

#### NOTES

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### 3.8 FURTHER READINGS

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#### NOTES

Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.

Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.

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**BLOCK - II**

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**DISCRETE EIGEN VALUE PROBLEMS**

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**NOTES**

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**UNIT 4 THE FREE PARTICLE**

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**Structure**

- 4.0 Introduction
- 4.1 Objectives
- 4.2 The Free Particle
  - 4.2.1 The Potential Step
  - 4.2.2 Asymmetric Square Well
  - 4.2.3 Symmetric Square-Well Potential of Infinite Depth
  - 4.2.4 Symmetric Square-Well Potential of Finite Depth
- 4.3 Particle in a Box
- 4.4 Answers to Check Your Progress Questions
- 4.5 Summary
- 4.6 Key Words
- 4.7 Self Assessment Questions and Exercises
- 4.8 Further Readings

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**4.0 INTRODUCTION**

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In physics, a free particle is a particle that, in some sense, is not bound by an external force, or equivalently not in a region where its potential energy varies. In classical physics, this means the particle is present in a ‘field-free’ space. In quantum mechanics, it means a region of uniform potential, usually set to zero in the region of interest since potential can be arbitrarily set to zero at any point (or surface in three dimensions) in space. By a free particle we mean a particle which moves freely in space without the influence of any force. Hence, for a free particle the potential energy is zero.

In quantum mechanics, the particle in a box model, also known as the infinite potential well or the infinite square well, describes a particle free to move in a small space surrounded by impenetrable barriers. The particle may only occupy certain positive energy levels. The particle in a box model is one of the very few problems in quantum mechanics which can be solved analytically, without approximations.

In this unit, you will study about the free particle and particle in a box.

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**4.1 OBJECTIVES**

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After going through this unit, you will be able to:

- Understand what free particle is
- Define the particle in a box

## 4.2 THE FREE PARTICLE

### NOTES

By a free particle we mean a particle which moves freely in space without the influence of any force. Hence, for a free particle the potential energy is zero.

Restricting our discussion to motion in one-dimension, say, along the  $x$ -axis, we have  $V(x) = 0$  for all values of  $x$  so that the wavefunction  $\psi(x)$  describing the state of the particle of mass  $m$  and a total energy  $E$  satisfies the Schrödinger equation,

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

$$\text{or} \quad \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\psi(x) = 0$$

$$\text{or} \quad \frac{d^2\psi(x)}{dx^2} + k^2 \psi(x) = 0 \quad \dots(4.1)$$

$$\text{Where} \quad k^2 = \frac{2m}{\hbar^2} E \quad \dots(4.2)$$

The most general solution of Equation (4.1) is a combination of two linearly independent plane wave solutions  $e^{ikx}$  and  $e^{-ikx}$

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx} \quad \dots(4.3)$$

where  $A$  and  $B$  are arbitrary constants. The complete wavefunction is given by,

$$\psi_k(x, t) = Ae^{i(kx - \omega t)} + Be^{-i(kx + \omega t)} \quad \dots(4.4)$$

$$\text{Where} \quad \omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m} \quad \dots(4.5)$$

The first term in Equation (4.3)  $\psi_+(x, t) = Ae^{i(kx - \omega t)}$  is a wave travelling along the positive  $x$ -axis while the second term  $\psi_-(x, t) = Be^{-i(kx + \omega t)}$  represents a wave travelling along the negative  $x$ -axis. Both the waves  $\psi_+(x, t)$  and  $\psi_-(x, t)$  travelling along opposite directions are associated with the motion of the free particle having well defined momentum and energy. The momentum associated with  $\psi_+(x, t)$  is  $p_+ = \hbar k$  while that with  $\psi_-(x, t)$  is  $p_- = -\hbar k$ . Both  $\psi_+(x, t)$  and  $\psi_-(x, t)$  belong to the energy  $\frac{\hbar^2 k^2}{2m}$ . Since for free particle motion there are no boundary conditions, there exist no restrictions on the values of  $k$  and  $E$ . Clearly the states of the free particle are continuous or unbound.

It is important to discuss some of the physical subtleties present in the free particle motion:

(1) The probability density corresponding to the solution  $\psi_+(x, t)$  is,

$$P_+(x, t) = |\psi_+(x, t)|^2 = |A|^2 = \text{Constant independent of } x \text{ and } t$$

The probability density corresponding to the solution  $\psi_-(x, t)$  is,

$$P_-(x, t) = |\psi_-(x, t)|^2 = |B|^2 = \text{Constant independent of } x \text{ and } t.$$

The above result is a purely quantum mechanical result having no explanation according to classical mechanics. Since the particle represented by the waves  $\psi_+(x, t)$  and  $\psi_-(x, t)$  have well defined momenta and energy we have the uncertainty in momentum  $\Delta p = 0$  and uncertainty in energy  $\Delta E = 0$ . According to Heisenberg's uncertainty principle we get the uncertainty in the position  $\Delta x \rightarrow \infty$  and the uncertainty in the time  $\Delta t \rightarrow \infty$ . Thus there is complete loss of information about the position and time for any state of the particle.

(2) The speed of the plane waves  $\psi_+(x, t)$  and  $\psi_-(x, t)$  is given by

$$v_{\text{wave}} = \frac{\omega}{k} = \frac{E}{\hbar k} = \frac{\hbar^2 k^2 / 2m}{\hbar k} = \frac{\hbar k}{2m} \quad \dots(4.6)$$

The speed of the particle according to classical mechanics is given by,

$$v_{\text{particle}} = \frac{p}{m} = \frac{\hbar k}{m} \quad \dots(4.7)$$

We thus observe,

$$v_{\text{particle}} = 2v_{\text{wave}} \quad \dots(4.8)$$

The above means that the particle travels with a speed which is double the speed of the waves representing the particle.

(3) The wavefunction representing the particle is not normalizable. This is because,

$$\int_{-\infty}^{+\infty} \psi_+^*(x, t) \psi_+(x, t) dx = |A|^2 \int_{-\infty}^{+\infty} dx = \infty \quad \dots(4.9)$$

$$\text{And} \quad \int_{-\infty}^{+\infty} \psi_-^*(x, t) \psi_-(x, t) dx = |B|^2 \int_{-\infty}^{+\infty} dx = \infty \quad \dots(4.10)$$

We may conclude from the above result that the solutions of the Schrödinger equation  $\psi_+(x, t)$  and  $\psi_-(x, t)$  do not represent physical situation because wavefunction representing the state of any system must be quadratically integrable. We may make a formal conclusion that a free particle described by the laws of quantum mechanics cannot have sharply defined momentum and energy. We may further conclude that a free particle cannot be represented by single (monochromatic) plane wave. Physically acceptable representation of a free particle is a wave packet. We may further conclude

## NOTES

that solutions of the Schrödinger equation which are physically acceptable cannot be plane waves.

### 4.2.1 The Potential Step

#### NOTES

Consider a particle of mass  $m$  moving in a one-dimensional potential specified in the Figure (4.1). Mathematically, the potential function  $V(x)$  is of the form,

$$\begin{aligned} V(x) &= 0 & x < 0 & \text{(Region I)} \\ &= V_0 & x > 0 & \text{(Region II)} \end{aligned}$$

The particle moving freely in Region I encounters the potential  $V_0$  at  $x = 0$ .

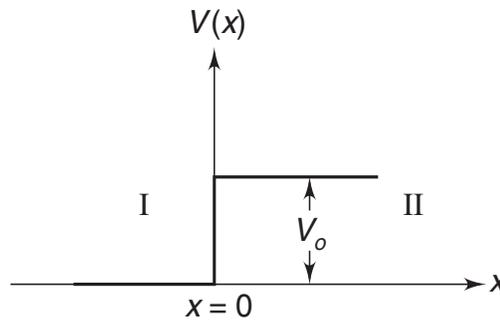


Fig. 4.1 The Potential Step

The wavefunction  $\psi(x)$  describing the state of the particle in general satisfies the Schrödinger equation,

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

or 
$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad \dots(4.11)$$

In the above,  $E$  is the total energy of the particle.

In the Region I, if  $\psi_1(x)$  is the wavefunction, Equation (4.11) takes the form

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2m}{\hbar^2} E \psi_1(x) = 0 \quad \dots(4.12)$$

or 
$$\frac{d^2\psi_1(x)}{dx^2} + k^2 \psi_1(x) = 0$$

where 
$$k^2 = \frac{2m}{\hbar^2} E \quad \dots(4.13)$$

If  $\psi_2(x)$  be the wavefunction of the particle in Region II, Equation (4.11) gives,

$$\frac{d^2 \psi_2(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V_o] \psi_2(x) = 0$$

or 
$$\frac{d^2 \psi_2(x)}{dx^2} + \alpha^2 \psi_2(x) = 0 \quad \dots(4.14)$$

Where 
$$\alpha^2 = \frac{2m}{\hbar^2} [E - V_o] \quad \dots(4.15)$$

Most general solutions of Equations (4.12) and (4.15) can be written as,

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \quad \dots(4.16)$$

$$\psi_2(x) = Ce^{i\alpha x} + De^{-i\alpha x} \quad \dots(4.17)$$

In the above  $A, B, C$  and  $D$  are constants which may be determined using the boundary conditions on the wavefunctions. The first term in Equation (4.16),  $\psi_{1+}(x) = Ae^{ikx}$  represents a plane wave travelling along the positive  $x$ -axis in the Region I and can be considered as an *incident wave*, while the second term  $\psi_{1-}(x) = Be^{-ikx}$  representing a plane wave in Region I travelling along the negative  $x$ -axis can be considered as the wave *reflected* at the potential step at  $x = 0$ . The first term in Equation (4.17)  $\psi_{2+}(x) = Ce^{i\alpha x}$  represents a plane wave travelling in Region II along the positive  $x$ -axis and can be considered as the wave *transmitted* in Region II from the potential step at  $x = 0$ , while the second term  $\psi_{2-}(x) = De^{-i\alpha x}$  represents a plane wave in Region II travelling along the negative  $x$ -axis. Since throughout the Region II there exists no potential boundary from which reflection can occur,  $\psi_{2-}(x)$  must vanish which requires  $D$  to be equal to zero so that Equation (4.17) reduces to,

$$\psi_2(x) = C e^{i\alpha x} \quad \dots(4.18)$$

We have the following boundary conditions in view of single valuedness and continuity of wavefunction at a potential boundary:

(i) 
$$\psi_1(x) = \psi_2(x) \quad \text{at } x = 0 \quad \dots(4.19)$$

Using the above we obtain from Equations (4.16) and (4.18)

$$A + B = C \quad \dots(4.20)$$

(ii) 
$$\frac{d\psi_1(x)}{dx} = \frac{d\psi_2(x)}{dx} \quad \text{at } x = 0 \quad \dots(4.21)$$

From Equation (4.16) we have

$$\frac{d\psi_1(x)}{dx} = ikAe^{ikx} - ikBe^{-ikx} \quad \dots(4.22)$$

From Equation (4.18) we have

$$\frac{d\psi_2(x)}{dx} = i\alpha C e^{i\alpha x} \quad \dots(4.23)$$

## NOTES

Using Equations (4.22) and (4.23) we get using Equation (4.21)

$$k(A - B) = \alpha C \quad \dots(4.24)$$

Solving Equations (4.20) and (4.24) we obtain,

$$C = \frac{2k}{k + \alpha} A \quad \dots(4.25)$$

$$B = \frac{k - \alpha}{k + \alpha} A \quad \dots(4.26)$$

If we consider the constant  $A$  as the amplitude of the incident wave, constants  $B$  and  $C$  can respectively be interpreted as the reflected and the transmitted amplitudes. We now consider the results on reflection and transmission in two cases, namely when  $E > V_0$  and when  $E < V_0$ .

**Case 1:**  $E > V_0$

The wavefunction in Region I is,

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \quad \dots(4.27)$$

We get on differentiating Equation (4.27) with respect to  $x$

$$\frac{d\psi_1(x)}{dx} = ik[Ae^{ikx} - Be^{-ikx}] \quad \dots(4.28)$$

Taking complex conjugate, Equation (4.27) becomes

$$\psi_1^*(x) = A^* e^{-ikx} + B^* e^{ikx} \quad \dots(4.29)$$

Taking complex conjugate, Equation (4.28) we get

$$\frac{d\psi_1^*(x)}{dx} = -ik[A^* e^{-ikx} - B^* e^{ikx}] \quad \dots(4.30)$$

The general expression for probability current density is given by

$$J = \frac{-i\hbar}{2m} [\psi^* \nabla \psi - \psi \nabla \psi^*] \quad \dots(4.31)$$

Since we are considering one-dimensional motion we get from Equation (4.31) the probability current density in Region I to be

$$J_1 = \frac{-i\hbar}{2m} \left[ \psi_1^*(x) \frac{d\psi_1(x)}{dx} - \psi_1(x) \frac{d\psi_1^*(x)}{dx} \right]$$

Substituting from Equations (4.27), (4.28), (4.29), and (4.30) in the above we obtain

$$J_1 = \frac{\hbar k}{m} (|A|^2 - |B|^2) \quad \dots(4.32)$$

The first term on the right hand side of Equation (4.32) gives the probability current density of the incident wave/beam

## NOTES

$$(J_1)_{\text{incident}} = \frac{\hbar k}{m} |A|^2 \quad \dots(4.33)$$

while the second term gives the probability current density of the reflected wave/beam

$$(J_1)_{\text{reflected}} = \frac{\hbar k}{m} |B|^2 \quad \dots(4.34)$$

Let us now consider Region II in which the wavefunction is given by

$$\psi_2(x) = C e^{i\alpha x} \quad \dots(4.35)$$

The above gives

$$\frac{d\psi_2(x)}{dx} = i\alpha C e^{i\alpha x} \quad \dots(4.36)$$

Taking complex conjugate of Equation (4.36) we get

$$\psi_2^*(x) = C^* e^{-i\alpha x} \quad \dots(4.37)$$

and taking complex conjugate of Equation (4.36) we get

$$\frac{d\psi_2^*(x)}{dx} = -i\alpha C^* e^{-i\alpha x} \quad \dots(4.38)$$

The probability current density in Region II by definition is given by

$$J_2 = \frac{-i\hbar}{2m} \left[ \psi_2^*(x) \frac{d\psi_2}{dx} - \psi_2 \frac{d\psi_2^*}{dx} \right] \quad \dots(4.39)$$

Substituting from Equations (4.35), (4.36), (4.37) and (4.38) in Equation (4.39) we obtain

$$J_2 = \frac{\hbar\alpha}{m} |C|^2 \quad \dots(4.40)$$

Since in Region II, there exists only the transmitted wave we get the probability current density of the transmitted wave/beam,

$$(J_2)_{\text{transmitted}} = \frac{\hbar\alpha}{m} |C|^2 \quad \dots(4.41)$$

The *reflectance* or the *reflection coefficient* is, by definition, given by

$$\begin{aligned} R &= \frac{\text{Probability current density for reflected beam}}{\text{Probability current density for incident beam}} \\ &= \frac{(J_1)_{\text{reflected}}}{(J_1)_{\text{incident}}} \end{aligned}$$

Using Equations (4.33) and (4.34) we obtain

$$R = \frac{\frac{\hbar k}{m} |B|^2}{\frac{\hbar k}{m} |A|^2} = \frac{|B|^2}{|A|^2}$$

## NOTES

Using Equation (4.26) in the above we obtain

$$R = \left( \frac{k - \alpha}{k + \alpha} \right)^2 \quad \dots(4.42)$$

## NOTES

Similarly, the transmittance or transmission coefficient is

$$T = \frac{(J_2)_{\text{transmitted}}}{(J_1)_{\text{incident}}}$$

Using Equations (4.33) and (4.41), the above gives

$$T = \frac{\frac{\hbar\alpha}{m} |C|^2}{\frac{\hbar k}{m} |A|^2} = \frac{\alpha}{k} \frac{|C|^2}{|A|^2}$$

Using Equation (4.25) in the above we get

$$T = \frac{\alpha}{k} \left( \frac{2k}{k + \alpha} \right)^2$$

or 
$$T = \frac{4k\alpha}{(k + \alpha)^2} \quad \dots(4.43)$$

We note the following:

1. We have  $k = \sqrt{\frac{2m}{\hbar^2} E}$ , a real positive quantity

$$\alpha = \sqrt{\frac{2m}{\hbar^2} (E - V_0)}, \text{ a real positive quantity under the condition } E > V_0$$

Equation (4.42) then shows that  $R$  is a real positive quantity, meaning that a certain fraction of the incident particles gets reflected on encountering the potential step at  $x = 0$ . This result is in contrast to classical mechanics, according to which a particle going over a potential step, under the condition  $E > V_0$ , would slow down in order to conserve energy but would never be reflected. The observed result is a consequence of the wave properties of the particle. In other words, we can say that reflection under the condition  $E > V_0$  is a *quantum mechanical effect*.

2. For  $E \gg V_0$ , that is for  $\alpha \rightarrow k$  from below, the ratio of the reflected flux to the incident flux, that is,  $|R|^2$  approaches zero. This agrees with intuition which tells us that at very high incident energies, the presence of the step is but a small perturbation on the propagation of the wave.

**Case 2:  $E < V_0$** 

In this case,  $\alpha$  given by  $\alpha = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$  becomes imaginary. We may write

$$\alpha = \sqrt{-\frac{2m}{\hbar^2}(V_0 - E)} = i\sqrt{\frac{2m}{\hbar^2}(V_0 - E)} = i\beta \quad \dots(4.44)$$

hence  $\beta = \sqrt{\frac{2m}{\hbar}(V_0 - E)}$  is real positive. ...(4.45)

The solution of the Schrödinger equation in Region II is now given by

$$\psi_2(x) = C e^{i\beta x} = C e^{-\beta x} \quad \dots(4.46)$$

We find that  $\psi_2(x)$  does not blow up at  $x = +\infty$

The reflection coefficient given by Equation (4.42), in this case becomes

$$R = \left(\frac{k - i\beta}{k + i\beta}\right) \left(\frac{k - i\beta}{k + i\beta}\right)^* = \left(\frac{k - i\beta}{k + i\beta}\right) \left(\frac{k + i\beta}{k - i\beta}\right) \quad \dots(4.47)$$

or  $R = 1$

Thus, when  $E < V_0$ , as in classical mechanics there is total reflection.

It can, however, be seen that the transmission coefficient given by Equation (4.43) does not vanish. Clearly, a part of the incident wave penetrates into the classically forbidden region, *Such penetration phenomenon again is characteristic of waves permitting a 'tunneling' through barriers that would totally block particles in classical description.*

**4.2.2 Asymmetric Square Well**

Consider a particle of mass  $m$  moving in a one-dimensional infinitely deep asymmetric potential well as shown in the Figure (4.2), the potential function  $V(x)$  being of the form,

$$\begin{aligned} & V(x) = +\infty \\ \text{for } x < 0 & \quad \text{[Region I]} \\ & = 0 \\ \text{for } 0 \leq x \leq a & \quad \text{[Region II]} \\ & = +\infty \\ \text{for } x > a & \quad \text{[Region III]} \end{aligned}$$

**NOTES**

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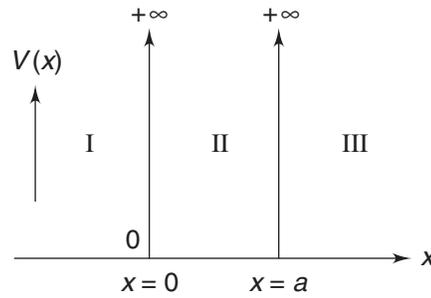


Fig. 4.2 Asymmetric Square Well

Classically, the particle remains confined within the well and moves with constant momentum back and forth as a result of repeated reflections from the walls of the well at  $x = 0$  and at  $x = a$ .

Since  $V(x) = +\infty$  for  $x < 0$  (i.e., in Region I) as well as for  $x > a$  (i.e., in Region III), the wavefunctions of the particle in these two regions are zero, i.e.,

$$\psi(x = 0) = 0 = \psi(x = a) \quad \dots(4.48)$$

If  $\psi(x)$  represents the wavefunction for the particle inside the well ( $0 \leq x \leq a$ ), we have the Schrödinger equation

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

or 
$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \quad \dots(4.49)$$

Where  $k = \sqrt{\frac{2m}{\hbar^2} E} \quad \dots(4.50)$

The general solutions of Equation (4.49) are

$$\psi(x) = C e^{ikx} + D e^{-ikx}$$

or 
$$\psi(x) = A \sin kx + B \cos kx \quad \dots(4.51)$$

where  $A$  and  $B$  are constants.

Using the boundary condition given by Equation (4.48), namely  $\psi(0) = 0$  in Equation (4.51) we get

$$B = 0$$

so that the solution becomes

$$\psi(x) = A \sin kx \quad \dots(4.52)$$

Further, applying the other boundary condition namely  $\psi(a) = 0$ , we get from Equation (4.52)

$$A \sin ka = 0$$

The above gives either  $A = 0$  or  $\sin ka = 0$ . However,  $A = 0$  leads to  $\psi(x) = 0$  everywhere which is not possible. Hence, we obtain

$$\sin ka = 0$$

The above gives

$$\begin{aligned} ka &= n\pi, \quad n = \text{A positive integer} \\ &= 1, 2, 3, \dots \end{aligned} \quad \dots (4.53)$$

We may note that  $n$  cannot be 0 because that would make  $k = 0$  so that wavefunction would vanish everywhere.

From Equation (4.53) we thus get

$$k = \frac{n\pi}{a} \quad \dots(4.54)$$

Using Equation (4.54) in Equation (4.52) we get the energy eigenfunctions of the particle to be given by

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right) \quad ; n = 1, 2, \dots \quad \dots(4.55)$$

Constant  $A$  can be determined from the requirement that the eigenfunctions are normalized, i.e.,

$$\int_0^a \psi_n^*(x) \psi_n(x) dx = 1$$

The above gives,

$$A^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx = 1$$

or  $A^2 \frac{a}{2} = 1$

or  $A = \sqrt{\frac{2}{a}} \quad \dots(4.56)$

The energy eigenfunctions are thus

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right); \quad n = 1, 2, \dots \quad \dots(4.57)$$

Using Equation (4.50) in Equation (4.54) we get the energy eigenvalues of the particle to be given by

$$\sqrt{\frac{2m}{\hbar^2}} E_n = \frac{n\pi}{a}$$

## NOTES

$$\text{or} \quad E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2, \quad n = 1, 2, \dots \quad \dots(4.58)$$

**NOTES**

We find the energy to be quantized, only certain values of energy are permitted. This is as expected because the states of a particle which are confined within a limited region of space are bound states and the energy eigenvalue spectrum is discrete. This result is in sharp contrast to the result in classical physics in which the energy of the particle given by  $E = \frac{p^2}{2m}$  ( $p$  being the momentum of the particle) can assume any value continuously from a minimum to a maximum.

From Equation (4.58) we get

$$E_{n+1} - E_n = \frac{\hbar^2 \pi^2}{2ma^2} (2n + 1) \quad \dots(4.59)$$

Clearly, the energy levels are not equispaced.

We have

$$\frac{E_{n+1} - E_n}{E_n} = \frac{2n + 1}{n^2} = \frac{2}{n} + \frac{1}{n^2}$$

Clearly, in the classical limit, the above gives,

$$\text{Lt}_{n \rightarrow \infty} \left( \frac{E_{n+1} - E_n}{E_n} \right) = \text{Lt}_{n \rightarrow \infty} \left( \frac{2}{n} + \frac{1}{n^2} \right) = 0 \quad \dots(4.60)$$

meaning that the levels become so close together that they become practically indistinguishable forming a continuum.

The lowest energy state or the ground state corresponds to  $n = 1$ . The ground state energy is given by,

$$E_1 = \frac{\hbar^2 \pi^2}{2ma^2} \quad \dots(4.61)$$

And the ground state wavefunction is given by,

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a} x\right) \quad \dots(4.62)$$

Energy given by Equation (4.61) is called the zero point energy because there exists no state with zero energy.

The plot of some of the eigenfunctions with  $x$  are shown in Figure (4.3). We observe from the plots that the eigenfunction  $\psi_n(x)$  has  $(n - 1)$  nodes.

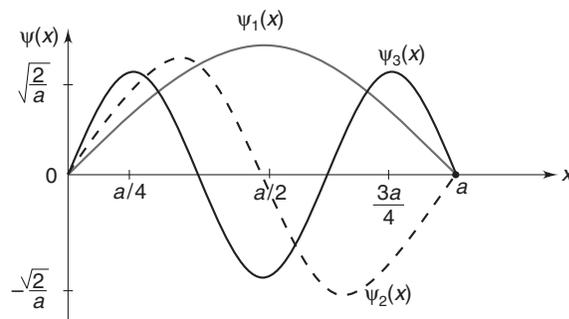


Fig. 4.3 Plot of Eigenfunctions

### Discussion on Zero Point Energy

If the particle inside the well has zero energy then it will come to rest and will be localized within the limited region defining the well. Heisenberg's uncertainty relation then will require the particle to acquire a finite momentum and hence a minimum kinetic energy. Since the particle is confined in the region  $0 < x < a$ , it has a maximum position uncertainty  $\Delta x = a$  and hence a minimum momentum uncertainty  $\Delta p \sim \frac{\hbar}{a}$  which in turn corresponds to a minimum kinetic energy  $\frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2ma^2}$  which is in qualitative agreement with the exact value  $E_1 = \frac{\pi^2 \hbar^2 m}{2ma^2}$ .

The minimum momentum uncertainty given by  $\Delta p \sim \frac{\hbar}{a}$ , is inversely proportional to the width of the well. Smaller the width, more the particle becomes localized, and  $\Delta p$  increases. This causes the particle to move faster thereby increasing the zero point energy. If on the other hand, width of the well increases, the zero point energy decreases but never becomes zero. Thus localization of a particle forces a minimum motion and hence a minimum energy to the particle.

#### 4.2.3 Symmetric Square-Well Potential of Infinite Depth

A symmetric infinite square well potential is defined as

$$\begin{aligned} V(x) &= +\infty & \text{for } x < -a \\ &= 0 & \text{for } -a \leq x \leq a \\ &= +\infty & \text{for } x > a \end{aligned}$$

and is represented in the Figure (4.4)

Consider the motion of a particle of mass  $m$  in the one-dimensional potential described above.

## NOTES

NOTES

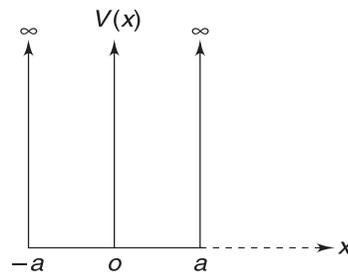


Fig. 4.4 Symmetric Infinite Square

If  $\psi(x)$  is the wavefunction describing the state of the particle in the region  $-a \leq x \leq a$  then it satisfies the time-independent Schrödinger equation,

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

or 
$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \quad \dots(4.63)$$

Where 
$$k = \sqrt{\frac{2m}{\hbar^2} E} \quad \dots(4.64)$$

The most general solution of Equation (4.63) is given by,

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad \dots(4.65)$$

Where  $A$  and  $B$  are constants.

Since  $V(x) = \infty$  for  $x < -a$  and  $x > a$ , the wavefunctions in these two regions vanish giving,

$$\psi(-a) = 0 \quad \text{and} \quad \psi(+a) = 0 \quad \dots(4.66)$$

Using the conditions given by Equation (4.66) in Equation (4.65) we get

$$A \sin ka + B \cos ka = 0 \quad \dots(4.67)$$

and

$$-A \sin ka + B \cos ka = 0 \quad \dots(4.68)$$

For the above two equations to hold simultaneously we must have

$$A \sin ka = 0 \quad \dots(4.69)$$

and 
$$B \cos ka = 0 \quad \dots(4.70)$$

In view of Equations (4.69) and (4.70) we may have  $A = 0$  and  $B = 0$  but these are physically unacceptable because  $\psi(x)$  given by Equation (4.65) would then vanish.

Since  $B \neq 0$ , we have from Equation (4.70),

$$\cos ka = 0 = \cos \frac{n\pi}{2}, \quad n = 1, 3, 5, \dots$$

$$\text{or} \quad ka = \frac{n\pi}{2} \quad \text{or} \quad k = \frac{n\pi}{2a} \quad \dots(4.71)$$

Using Equation (4.64) in the above we obtain the energy eigenvalues

$$E_n = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{a^2} = \frac{\pi^2 \hbar^2}{8ma^2} n^2, \quad n = 1, 3, 5, \dots \quad \dots(4.72)$$

The energy eigenfunctions corresponding to the above energy eigenvalues are

$$\psi_n(x) = B \cos kx = B \cos\left(\frac{n\pi}{2a} x\right), \quad n = 1, 3, 5 \quad \dots(4.73)$$

The condition given by Equation (4.69) gives

$$\sin ka = 0 = \sin n\pi \quad (\text{since } A \neq 0)$$

$$\text{or} \quad ka = n\pi \quad \text{or} \quad k = \frac{n\pi}{a}, \quad n = 2, 4, 6 \quad \dots(4.74)$$

Using the above value of  $k$  in Equation (4.64) we get the energy eigenvalues

$$E_n = \frac{\hbar^2}{2m} k^2 = \frac{\pi^2 \hbar^2 n^2}{8ma^2}, \quad n = 2, 4, 6, \dots \quad \dots(4.75)$$

The corresponding energy eigenfunctions are

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{2a}\right), \quad n = 2, 4, 6, \dots \quad \dots(4.76)$$

The normalization conditions of the wavefunctions,

$$\int_{-a}^{+a} \psi_n^*(x) \psi_n(x) dx = 1$$

lead to

$$A = \frac{1}{\sqrt{a}}, \quad B = \frac{1}{\sqrt{a}} \quad \dots(4.77)$$

We can thus write the set of energy eigenfunctions for the particle in the symmetric infinite square well potential as,

$$\psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a} x\right), \quad n = 2, 4, \dots \quad \dots(4.78)$$

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi}{2a} x\right), \quad n = 1, 3, 5, \dots \quad \dots(4.79)$$

## NOTES

and the discrete set of energy eigenvalues as

$$E_n = \frac{\pi^2 \hbar^2}{8ma^2} n^2, \quad n = 1, 2, 3, \dots \quad \dots(4.80)$$

**NOTES**

**Discussion**

The wavefunctions corresponding to  $n = 1, 3, 5, \dots$ , i.e., corresponding to odd quantum numbers are symmetric,  $\psi(-x) = \psi(x)$ .

- The wavefunctions corresponding to  $n = 2, 4, 6, \dots$  i.e., corresponding to even quantum numbers are antisymmetric,  $\psi(-x) = -\psi(x)$
- In other words, for symmetric potentials  $V(-x) = V(x)$ , the wavefunctions of bound states are either even (symmetric) or odd (antisymmetric).
- The energy spectrum for the particle is discrete and non-degenerate.
- The ground state energy or the zero point energy is,

$$E_1 = \frac{\pi^2 \hbar^2}{8ma^2}$$

Corresponding to the eigenfunction,

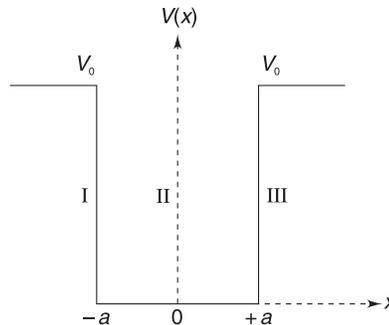
$$\psi_1(x) = \frac{1}{\sqrt{a}} \cos \frac{\pi x}{2a}$$

**4.2.4 Symmetric Square-Well Potential of Finite Depth**

A symmetric square well potential of finite depth is described by potential function  $V(x)$  of the form

$$\begin{aligned} V(x) &= V_0 && \text{for } x < -a && \text{(Region I)} \\ &= 0 && \text{for } -a \leq x \leq a && \text{(Region II)} \\ &= V_0 && \text{for } x > a && \text{(Region III)} \end{aligned}$$

The potential function is shown in the Figure (4.5)



**Fig. 4.5** Potential Function

Consider the motion of a particle of mass  $m$  in the potential well described above.

The Schrödinger equation in Regions I and III is,

$$\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x)$$

or 
$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi(x) = 0 \quad \dots(4.81)$$

In Region II the Schrödinger equation is

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

which can be put in the form

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \quad \dots(4.82)$$

where 
$$k = \sqrt{\frac{2m}{\hbar^2} E} \quad \dots(4.83)$$

Let us consider the cases where:  $E < V_0$ , and  $E > V_0$

**Case  $E < V_0$ :** We may write Equation (4.81) in the form

$$\frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) = 0 \quad \dots(4.84)$$

where 
$$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$
 is real positive  $\dots(4.85)$

The most general solution of Equation (4.84) is

$$\psi(x) = Ae^{+\alpha x} + Be^{-\alpha x}, \quad A \text{ and } B \text{ are constants} \quad \dots(4.86)$$

Specific solution in Region I  $\psi_1(x) = A e^{+\alpha x} \quad \dots(4.87)$

Specific solution in Region III  $\psi_3(x) = B e^{-\alpha x} \quad \dots(4.88)$

Solution of Equation (4.82) gives the wavefunction in region II

$$\psi_2(x) = C \sin(kx) + D \cos(kx) \quad \dots(4.89)$$

$\psi_2(x)$  is either symmetric or antisymmetric about  $x = 0$ . The first term in Equation (4.89) is antisymmetric because  $\sin(kx) = -\sin(-kx)$ . The second term is symmetric because  $\cos(kx) = \cos(-kx)$ .

For the *symmetric function* in Region II, the coefficient  $C = 0$  so that we may write the symmetric wavefunction in Region II as

## NOTES

$$(\psi_2(x))_{\text{symmetric}} = D \cos(kx) \quad \dots(4.90)$$

At  $x = \pm a$ , we have, using the single valuedness of wavefunction

$$Ae^{-\alpha a} = D \cos ka \quad \dots(4.91)$$

$$Be^{-\alpha a} = D \cos ka \quad \dots(4.92)$$

Similarly, using the continuity of wavefunction at  $x = \pm a$  gives

$$\alpha A e^{-\alpha a} = +D k \sin(ka) \quad \dots(4.93)$$

$$+ \alpha B e^{-\alpha a} = D k \sin(ka) \quad \dots(4.94)$$

The above equations give

$$A = B \quad \dots(4.95)$$

$$\text{and} \quad k \tan ka = \alpha \quad \dots(4.96)$$

Let us now consider the antisymmetric wavefunctions in Region II. In the case  $D = 0$  so that we may write the antisymmetric wavefunction in Region II as

$$(\psi_2(x))_{\text{antisymmetric}} = C \sin(kx) \quad \dots(4.97)$$

Using the single valuedness and continuity of wavefunction at the boundaries at  $x = \pm a$  we get

$$A e^{-\alpha a} = -C \sin(ka) \quad \dots(4.98)$$

$$B e^{-\alpha a} = C \sin(ka) \quad \dots(4.99)$$

$$\alpha A e^{-\alpha a} = -C k \cos(ka) \quad \dots(4.100)$$

$$- \alpha B e^{-\alpha a} = C k \cos(ka) \quad \dots(4.101)$$

From the above four equations, we obtain

$$A = -B \quad \dots(4.102)$$

and

$$k \cot ka = -\alpha \quad \dots(4.103)$$

The energy eigenvalues for the particle can be obtained by solving Equations (4.96) and (4.103) graphically as explained in the following:

$$\text{Let us put} \quad ka = x \quad \dots(4.104)$$

$$\alpha a = y \quad \dots(4.105)$$

From the above we get

$$x^2 + y^2 = (k^2 + \alpha^2) a^2$$

Substituting for  $k$  and  $\alpha$  from Equations (4.83) and (4.85), the above becomes

## NOTES

$$x^2 + y^2 = \left[ \frac{2m}{\hbar^2} E + \frac{2m}{\hbar^2} (V_0 - E) \right] a^2$$

$$\text{or} \quad x^2 + y^2 = \frac{2ma^2}{\hbar^2} V_0 \quad \dots(4.106)$$

Substituting Equations (4.104) and (4.105) in Equations (4.96) and (4.103), respectively, we obtain

$$x \tan x = y \quad \dots(4.107)$$

$$-x \cot x = y \quad \dots(4.108)$$

We plot  $x \tan x$  against  $x$ ,  $x \cot x$  against  $x$  and  $x^2 + y^2$  for different values of  $V_0 a^2$  (which are circles of different radii). Since both  $x$  and  $y$  can take only positive values, the sections of the circles have been shown in the first quadrant only in Figure (4.6).

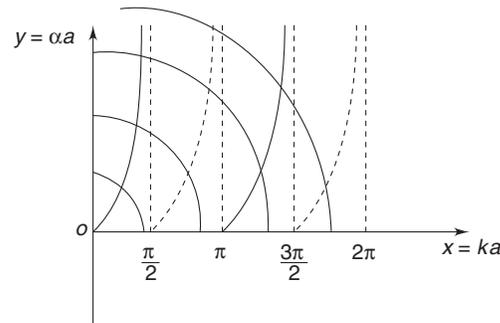


Fig. 4.6 Graph

In the Figure 4.6,

Full line curves  $\rightarrow x \tan x$  against  $x$  plots

Dashed curves  $\rightarrow -x \cot x$  against  $x$  plots

Circular sections  $\rightarrow$  Different values of  $V_0 a^2$

The energy levels and the energy eigenvalues for the symmetric wavefunction are given by the intersections of the  $x \tan x$  against  $x$  curves and the circular sections. Similarly, the energy eigenfunctions and the energy eigenvalues when the wavefunction in the well is antisymmetric are given by the intersections of  $-x \cot x$  against  $x$  curves and the circular sections.

If the intersections of  $x \tan x$  against  $x$  curves and circles occur at values of  $x$  equal to  $x_1, x_2, \dots, x_n, \dots$  then we get

$$x_n^2 = k^2 a^2 = \frac{2m E_n}{\hbar^2} a^2$$

$$\text{or} \quad E_n = \frac{\hbar^2}{2ma^2} x_n^2, \quad n = 1, 3, 5, \dots$$

## NOTES

Similarly, if the intersections of  $-x \cot x$  against  $x$  curves and the circles occur at values of  $x$  equal to  $x_1, x_2, \dots, x_{n'} \dots$ , then we get

$$x_{n'}^2 = k^2 a^2 = \frac{2mE_{n'}}{\hbar^2} a^2$$

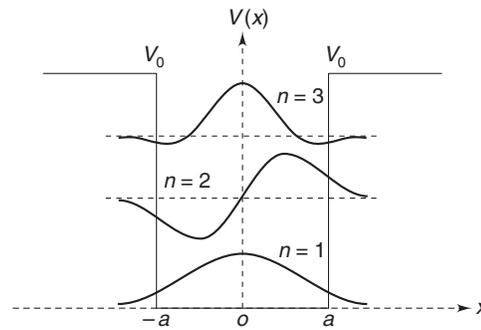
or 
$$E_{n'} = \frac{\hbar^2}{2ma^2} x_{n'}^2; \quad n' = 2, 4, 6, \dots$$

**NOTES**

The number of bound states are seen to depend upon the height  $V_0$  and the width  $a$  of the well through the factor  $V_0 a^2$ . From the Figure (4.6) we find the following

- (i) Only one energy level of symmetric type, if  $0 < V_0 a^2 < \frac{\pi^2 \hbar^2}{8m}$
- (ii) Two energy levels of which one is of symmetric type and the other of antisymmetric type, if  $\frac{\pi^2 \hbar^2}{8m} < V_0 a^2 < \frac{4\pi^2 \hbar^2}{8m}$
- (iii) Three energy levels of which two are of symmetric type and one of antisymmetric type, if  $\frac{4\pi^2 \hbar^2}{8m} < V_0 a^2 < \frac{9\pi^2 \hbar^2}{8m}$  and so on.

Some of the energy eigenfunctions corresponding to bound states are shown in the Figure (4.7).



**Fig. 4.7 Eigenfunctions for Bound State**

Unlike in the case of infinite potential well, both the symmetric as well as the antisymmetric eigenfunctions extend beyond the well, i.e., in the regions  $x < -a$  and  $x > a$  which define the classical turning points. Clearly, there exists finite probability of finding the particle outside the well. This is a quantum mechanical effect.

**Case  $E > V_0$ :**

The Schrodinger equation in Regions I and III is given by,

$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi(x) = 0$$

Since  $E$  is greater than  $V_0$ ,  $\frac{2m}{\hbar^2} (E - V_0)$  is a real positive quantity. As such the solution of the above equation is sinusoidal in nature. The probability

density for the particle is distributed over all space in regions I and III. It is also distributed in Region II, i.e., within the well. Thus we do not get bound state for the particle.

### 4.3 PARTICLE IN A BOX

Consider a particle of mass  $m$  moving within a rectangular box. Let us choose a Cartesian coordinate system with  $x$ ,  $y$  and  $z$  axes parallel to the three adjacent edges of the box. Let the lengths of the box parallel to the  $x$ ,  $y$  and  $z$  axes be respectively,  $a$ ,  $b$  and  $c$ . Let  $p_x$ ,  $p_y$  and  $p_z$  be the components of the linear momentum of the particle along  $x$ ,  $y$  and  $z$  axes, respectively. Let us consider the motion of the particle to be force-free and the collision of the particle with the walls to be perfectly elastic. Under such a force-free motion  $p_x$ ,  $p_y$ ,  $p_z$  are constants of motion and they only change sign on collision with the walls perpendicular to the  $x$ -axis,  $y$ -axis and  $z$ -axis, respectively. Further, one cycle of motion parallel to the  $x$ -axis is  $2a$ , that parallel to the  $y$ -axis is  $2b$  and that parallel to the  $z$ -axis is  $2c$ .

We now have, according to the Wilson–Sommerfeld quantization rule,

$$\oint p_x dx = \int_0^{2a} p_x dx = p_x 2a = n_x h \quad \dots(4.109)$$

$$\oint p_y dy = \int_0^{2b} p_y dy = p_y 2b = n_y h \quad \dots(4.110)$$

$$\oint p_z dz = \int_0^{2c} p_z dz = p_z 2c = n_z h \quad \dots(4.111)$$

The total energy of the particle is given by,

$$E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

The motion being force-free, potential energy of the particle is zero. Using Equations (4.109), (4.110) and (4.111) in the above, it becomes

$$E = \frac{1}{2m} \left[ \frac{n_x^2 h^2}{4a^2} + \frac{n_y^2 h^2}{4b^2} + \frac{n_z^2 h^2}{4c^2} \right]$$

or 
$$E = \frac{h^2}{8m} \left[ \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \quad \dots(4.112)$$

In the above equations,  $n_x$ ,  $n_y$  and  $n_z$  are zero or integers. Equation (4.112) shows that the energy of the particle within the box is quantized.

### NOTES

## NOTES

**Check Your Progress**

1. What is free particle?
2. Define the Heisenberg's uncertainty principle.
3. Explain potential function  $V(x)$ .
4. What is reflection coefficient?
5. What happens if the particle inside the well has zero energy?

---

#### 4.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

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1. By a free particle we mean a particle which moves freely in space without the influence of any force. Hence, for a free particle the potential energy is zero.
2. According to Heisenberg's uncertainty principle we get the uncertainty in the position  $\Delta x \rightarrow \infty$  and the uncertainty in the time  $\Delta t \rightarrow \infty$ . Thus there is complete loss of information about the position and time for any state of the particle.

3. Mathematically, the potential function  $V(x)$  is of the form,

$$\begin{aligned} V(x) &= 0 & x < 0 & & \text{(Region I)} \\ &= V_0 & x > 0 & & \text{(Region II)} \end{aligned}$$

The particle moving freely in Region I encounters the potential  $V_0$  at  $x = 0$ .

4. The *reflectance* or the *reflection coefficient* is, by definition, given by

$$\begin{aligned} R &= \frac{\text{Probability current density for reflected beam}}{\text{Probability current density for incident beam}} \\ &= \frac{(J_1)_{\text{reflected}}}{(J_1)_{\text{incident}}} \end{aligned}$$

5. If the particle inside the well has zero energy then it will come to rest and will be localized within the limited region defining the well. Heisenberg's uncertainty relation then will require the particle to acquire a finite momentum and hence a minimum kinetic energy.

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#### 4.5 SUMMARY

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- By a free particle we mean a particle which moves freely in space without the influence of any force. Hence, for a free particle the potential energy is zero.

- The probability density corresponding to the solution  $\psi_+(x, t)$  is,

$$P_+(x, t) = |\psi_+(x, t)|^2 = |A|^2 = \text{Constant independent of } x \text{ and } t$$

The probability density corresponding to the solution  $\psi_-(x, t)$  is,

$$P_-(x, t) = |\psi_-(x, t)|^2 = |B|^2 = \text{Constant independent of } x \text{ and } t.$$

- Mathematically, the potential function  $V(x)$  is of the form,

$$V(x) = 0 \quad x < 0 \quad (\text{Region I})$$

$$= V_0 \quad x > 0 \quad (\text{Region II})$$

The particle moving freely in Region I encounters the potential  $V_0$  at  $x = 0$ .

- The *reflectance* or the *reflection coefficient* is, by definition, given by

$$R = \frac{\text{Probability current density for reflected beam}}{\text{Probability current density for incident beam}}$$

$$= \frac{(J_1)_{\text{reflected}}}{(J_1)_{\text{incident}}}$$

- For  $E \gg V_0$ , that is for  $\alpha \rightarrow k$  from below, the ratio of the reflected flux to the incident flux, that is,  $|R|^2$  approaches zero.
- If the particle inside the well has zero energy then it will come to rest and will be localized within the limited region defining the well. Heisenberg's uncertainty relation then will require the particle to acquire a finite momentum and hence a minimum kinetic energy.
- The minimum momentum uncertainty given by  $\Delta p \sim \frac{\hbar}{a}$ , is inversely proportional to the width of the well.
- The wavefunctions corresponding to  $n = 1, 3, 5, \dots$ , i.e., corresponding to odd quantum numbers are symmetric,  $\psi(-x) = \psi(x)$ .
- The energy levels and the energy eigenvalues for the symmetric wavefunction are given by the intersections of the  $x \tan x$  against  $x$  curves and the circular sections.

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## 4.6 KEY WORDS

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- **Free particle:** It means a particle which moves freely in space without the influence of any force. Hence, for a free particle the potential energy is zero.
- **Heisenberg's uncertainty principle:** It states that the uncertainty in the position  $\Delta x \rightarrow \infty$  and the uncertainty in the time  $\Delta t \rightarrow \infty$ .

## NOTES

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## 4.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### NOTES

#### Short Answer Questions

1. What is free particle?
2. Define Heisenberg's uncertainty principle.
3. What is potential step?
4. What does particle in a box state?

#### Long Answer Questions

1. Discuss the concept of free particle giving appropriate examples.
2. Briefly explain the potential function  $V(x)$  with relevant equations.
3. Discuss asymmetric square well and symmetric square well with relevant examples.
4. Explain the concept of particle in a box.

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## 4.8 FURTHER READINGS

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
- Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.
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- Schiff, Leonard L. 1968. *Quantum Mechanics*, 3rd Edition. New York: McGraw Hill.

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## UNIT 5 THREE DIMENSIONAL PROBLEM

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### NOTES

#### Structure

- 5.0 Introduction
- 5.1 Objectives
- 5.2 Three Dimensional Harmonic Oscillator
- 5.3 Rigid Rotator
  - 5.3.1 Schrödinger Equation for a Rigid Rotator with Free-Axis
  - 5.3.2 Solution of the Wave Equation: Energy Eigenvalues and Energy Eigenfunctions for the Rotator
  - 5.3.3 Rigid Rotator with Fixed Axis
- 5.4 Answers to Check Your Progress Questions
- 5.5 Summary
- 5.6 Key Words
- 5.7 Self Assessment Questions and Exercises
- 5.8 Further Readings

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### 5.0 INTRODUCTION

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In physics, the one and three-dimensional particle in a box are prototypes of bound systems. The harmonic oscillator is the most basic model with which we treat the vibrations of molecules. The rigid rotor is a mechanical model of rotating systems. An arbitrary rigid rotor is a 3-dimensional rigid object, such as a top. A special rigid rotor is the linear rotor requiring only two angles to describe, for example of a diatomic molecule. More general molecules are 3-dimensional, such as water (asymmetric rotor), ammonia (symmetric rotor), or methane (spherical rotor).

In this unit, you will study about the three dimensional harmonic oscillator and rigid rotator.

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### 5.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand what three dimensional harmonic oscillator is
- Define the rigid rotator

---

### 5.2 THREE DIMENSIONAL HARMONIC OSCILLATOR

---

A general three-dimensional harmonic oscillator consists of a particle, of mass say  $m$ , bound to the origin  $O$  of a rectangular coordinate system ( $XYZ$ )

by a restoring force  $\vec{F} = -k\vec{r}$  where  $\vec{r}$  is the position vector of the particle with respect to the origin  $O$  and  $k$  is the force constant. We may consider the force  $\vec{F}$  to have cartesian components

**NOTES**

$$F_x = -k_x x, \quad F_y = -k_y y, \quad F_z = -k_z z \quad \dots(5.1)$$

where  $x, y, z$  are respectively the components of  $\vec{r}$  along  $x, y$  and  $z$  axes. For generality, the force constants  $k_x, k_y$  and  $k_z$  along the three axes have been considered to be different.

If  $\nu_x, \nu_y, \nu_z$  be respectively the components of the natural frequency  $\nu_0$  of the oscillator along the  $x, y$  and  $z$  axes then we have

$$\left. \begin{aligned} k_x &= m\omega_x^2 = m(2\pi\nu_x)^2 = 4\pi^2 m\nu_x^2 \\ k_y &= m\omega_y^2 = m(2\pi\nu_y)^2 = 4\pi^2 m\nu_y^2 \\ k_z &= m\omega_z^2 = m(2\pi\nu_z)^2 = 4\pi^2 m\nu_z^2 \end{aligned} \right\} \dots(5.2)$$

$$k = m\omega_0^2 = m(2\pi\nu_0)^2 = 4\pi^2 m\nu_0^2 \quad \dots(5.3)$$

The potential energy function of the oscillator is spherically symmetric and is given by

$$V = V(r) = \frac{1}{2}kr^2 = \frac{1}{2}m\omega_0^2 r^2 \quad \dots(5.4)$$

Alternatively, we may write the potential energy function as

$$V(x, y, z) = \frac{1}{2}m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) \quad \dots(5.5)$$

The Schrödinger equation for the oscillator given by

$$\Delta^2\psi + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0$$

can be expressed in Cartesian coordinates as

$$\frac{\partial^2\psi(x, y, z)}{\partial x^2} + \frac{\partial^2\psi(x, y, z)}{\partial y^2} + \frac{\partial^2\psi(x, y, z)}{\partial z^2} + \frac{2m}{\hbar^2}[E - m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)]\psi(x, y, z) = 0 \quad \dots(5.6)$$

**Solution of the Schrödinger Equation**

Equation (5.6) can be solved using the method of separation of variables. We write  $\psi(x, y, z)$  as a product of a function of only  $x$ , a function of only  $y$ , and a function of only  $z$ ,

$$\psi(x, y, z) = X(x) Y(y) Z(z) \quad \dots(5.7)$$

Using Equation (5.7) in Equation (5.6) we get

$$YZ \frac{d^2 X}{dx^2} + XZ \frac{d^2 Y}{dy^2} + XY \frac{d^2 Z}{dz^2} + \frac{2m}{\hbar^2}[E - m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)]XYZ = 0$$

Dividing by  $XYZ$  and rearranging the terms the above becomes

$$\left[ \frac{1}{x} \frac{d^2 X}{dx^2} - \frac{2m^2}{\hbar^2} \omega_x^2 x^2 \right] + \left[ \frac{1}{y} \frac{d^2 Y}{dy^2} - \frac{2m^2}{\hbar^2} \omega_y^2 y^2 \right] + \left[ \frac{1}{z} \frac{d^2 Z}{dz^2} - \frac{2m^2}{\hbar^2} \omega_z^2 z^2 \right] = -\frac{2mE}{\hbar^2} \quad \dots(5.8)$$

We find

- (i) The sum of the three terms on the left hand side of Equation (5.8) is a constant because the total energy  $E$  of the harmonic oscillator is a constant.
- (ii) The first term in the left hand side of Equation (5.8) is a function of only  $x$ , the second term is a function of only  $y$  while the third term is a function of only  $z$ .

These facts require each term on the left hand side of Equation (5.8) to be equal to a separate constant, we put

$$\frac{1}{X} \frac{d^2 X}{dx^2} - \frac{2m^2}{\hbar^2} \omega_x^2 x^2 = \frac{-2m}{\hbar^2} E_x, \quad E_x = \text{A constant}$$

$$\text{or} \quad \frac{1}{X} \frac{d^2 X}{dx^2} + \frac{2m^2}{\hbar^2} [E_x - m\omega_x^2 x^2] = 0$$

$$\text{or} \quad \frac{d^2 X}{dx^2} + \frac{2m^2}{\hbar^2} [E_x - m\omega_x^2 x^2] X = 0 \quad \dots(5.9)$$

Similarly, writing the second term and the third term on the left hand side of Equation (5.8) equal to  $\frac{-2m}{\hbar^2} E_y$  and  $\frac{-2m}{\hbar^2} E_z$  respectively, we obtain

$$\frac{d^2 Y}{dy^2} + \frac{2m}{\hbar^2} [E_y - m\omega_y^2 y^2] Y = 0 \quad \dots(5.10)$$

$$\frac{d^2 Z}{dz^2} + \frac{2m}{\hbar^2} [E_z - m\omega_z^2 z^2] Z = 0 \quad \dots(5.11)$$

We also find

$$-\frac{2m}{\hbar^2} E_x - \frac{2m}{\hbar^2} E_y - \frac{2m}{\hbar^2} E_z = \frac{-2m}{\hbar^2} E$$

or

$$E_x + E_y + E_z = E \quad \dots(5.12)$$

Equations (5.9), (5.10) and (5.11) are mathematically identical with the time-independent Schrödinger equation for linear harmonic oscillator.

The results (A) and (B) as below:

$$(A) \quad \left. \begin{aligned} E_x &= \left( n_x + \frac{1}{2} \right) \hbar \omega_x \\ E_y &= \left( n_y + \frac{1}{2} \right) \hbar \omega_y \\ E_z &= \left( n_z + \frac{1}{2} \right) \hbar \omega_z \end{aligned} \right\} \quad \dots(5.13)$$

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where  $n_x, n_y, n_z$  are positive integers including zero.

In view of the results given by Equations (5.12) and (5.13) we get the energy eigenvalues of the three-dimensional harmonic oscillator to be

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$$E_{n_x, n_y, n_z} = E_x + E_y + E_z = \left[ \left( n_x + \frac{1}{2} \right) \omega_x + \left( n_y + \frac{1}{2} \right) \omega_y + \left( n_z + \frac{1}{2} \right) \omega_z \right] \hbar \quad \dots(5.14)$$

(B) The normalized solutions of Equations (5.9), (5.10) and (5.11) to be given respectively by

$$X_{n_x}(x) = N_{n_x} H_{n_x}(\xi) e^{-\frac{\xi^2}{2}}$$

or 
$$X_{n_x}(x) = \left[ \frac{\gamma_x}{2^{n_x} n_x! \sqrt{\pi}} \right]^{1/2} H_{n_x}(\xi) e^{-\frac{\xi^2}{2}} \quad \dots(5.15)$$

where 
$$\gamma_x = \sqrt{\frac{m\omega_x}{\hbar}} \quad \text{and} \quad \xi = \gamma_x x \quad \dots(5.16)$$

$$Y_{n_y}(y) = \left[ \frac{\gamma_y}{2^{n_y} n_y! \sqrt{\pi}} \right]^{1/2} H_{n_y}(\eta) e^{-\eta^2} \quad \dots(5.17)$$

where 
$$\gamma_y = \sqrt{\frac{m\omega_y}{\hbar}} \quad \text{and} \quad \eta = \gamma_y y$$

and

$$Z_{n_z}(z) = \left[ \frac{\gamma_z}{2^{n_z} n_z! \sqrt{\pi}} \right]^{1/2} H_{n_z}(\zeta) e^{-\zeta^2/2} \quad \dots(5.18)$$

$$\gamma_z = \sqrt{\frac{m\omega_z}{\hbar}} \quad \text{and} \quad \zeta = \gamma_z z \quad \dots(5.19)$$

Substituting Equations (5.15), (5.17) and (5.18) in Equation (5.19) we get the normalized eigenfunctions of the three-dimensional oscillator to be given by

$$\Psi_{n_x, n_y, n_z}(x, y, z) = \left[ \frac{\gamma_x \gamma_y \gamma_z}{2^{n_x} n_x! n_y! n_z! \pi^{3/2}} \right]^{1/2} H_{n_x}(\xi) H_{n_y}(\eta) H_{n_z}(\zeta) \times e^{-\frac{1}{2}(\xi^2 + \eta^2 + \zeta^2)} \quad \dots(5.20)$$

In the above,

$$n = n_1 + n_2 + n_3 \quad \dots(5.21)$$

**Special Case**

In the following we consider a three-dimensional harmonic oscillator for which the natural frequencies of oscillations  $n_x, n_y, n_z$  along  $X, Y$  and  $Z$  axes respectively are equal. The angular frequencies  $\omega_x, \omega_y,$  and  $\omega_z$  then are also equal. Let us assume

$$\omega_x = \omega_y = \omega_z = \omega_0 \quad \dots(5.22)$$

Equation (5.14) then gives the energy eigenvalues of the oscillator to be

$$E_{n_x, n_y, n_z} = \left[ (n_x + n_y + n_z) \omega_0 + \frac{3}{2} \omega_0 \right] \hbar$$

or

$$E_n = \left( n + \frac{3}{2} \right) \hbar \omega_0; \quad n = n_x + n_y + n_z = 0, 1, 2, \dots \quad \dots(5.23)$$

In view of Equation (5.22) we find

$$\gamma_x = \gamma_y = \gamma_z = \sqrt{\frac{m\omega_0}{\hbar}} \quad \dots(5.24)$$

$$\xi = \sqrt{\frac{m\omega_0}{\hbar}} x; \quad \eta = \sqrt{\frac{m\omega_0}{\hbar}} y; \quad \zeta = \sqrt{\frac{m\omega_0}{\hbar}} z \quad \dots(5.25)$$

Substituting Equations (5.24) and (5.25) in Equation (5.20) we get the eigenfunctions of the oscillator to be given by

$$\Psi_{n_x, n_y, n_z}(x, y, z) = \left[ \frac{\left( \frac{m\omega_0}{\hbar} \right)^3}{2^{(n_x + n_y + n_z)} n_x! n_y! n_z! \pi^{3/2}} \right]^{1/2} H_{n_x}(\xi) H_{n_y}(\eta) H_{n_z}(\zeta) \times e^{-\frac{1}{2} \frac{m\omega_0}{\hbar} (x^2 + y^2 + z^2)} \quad \dots(5.26)$$

The *ground state of the oscillator* corresponds to

$$n_x = n_y = n_z = 0 \quad \dots(5.27)$$

From Equation (5.23) we get the energy of the ground state to be given by

$$E_0 = \frac{3}{2} \hbar \omega_0$$

and the ground state eigenfunction from Equation (5.26) to be

$$\Psi_{000}(x, y, z) = \left( \frac{m\omega_0}{\hbar\pi^{1/2}} \right)^{3/2} e^{-\frac{1}{2} \frac{m\omega_0}{\hbar} (x^2 + y^2 + z^2)} \quad \dots(5.28)$$

The first excited state corresponds to

$$n = 1$$

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so that we may have

$$\left. \begin{aligned} n_x = 1, \quad n_y = 0, \quad n_z = 0 \\ n_x = 0, \quad n_y = 1, \quad n_z = 0 \\ n_x = 0, \quad n_y = 0, \quad n_z = 1 \end{aligned} \right\} \quad \dots(5.29)$$

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Equation (5.23) gives the energy eigenvalues corresponding to this state to be

$$E_1 = \frac{5}{2} \hbar \omega_0 \quad \dots(5.30)$$

The corresponding eigenfunctions are

$$\Psi_{010}, \quad \Psi_{010} \quad \text{and} \quad \Psi_{001}$$

We find that there are 3 different eigenfunctions corresponding to the same energy eigenvalue  $\frac{5}{2} \hbar \omega_0$ .

Consider the *first excited state of the three-dimensional isotropic oscillator to be 3-fold degenerate.*

The second excited state of the oscillator corresponds to

$$n = 2$$

so that we may have the following sets of values of  $n_x$ ,  $n_y$ , and  $n_z$

$$\left. \begin{aligned} n_x = 2, n_y = 0, n_z = 0 \\ n_x = 0, n_y = 2, n_z = 0 \\ n_x = 0, n_y = 0, n_z = 2 \\ n_x = 1, n_y = 1, n_z = 0 \\ n_x = 1, n_y = 0, n_z = 1 \\ n_x = 0, n_y = 1, n_z = 1 \end{aligned} \right\} \quad \dots(5.31)$$

The energy eigenvalue for this state from Equation (5.23) is given by

$$E_2 = \frac{7}{2} \hbar \omega_0 \quad \dots(5.32)$$

Corresponding to this energy eigenvalue there exist 6 different energy eigenfunctions, namely

$$\Psi_{200}, \quad \Psi_{020}, \quad \Psi_{002}, \quad \Psi_{110}, \quad \Psi_{101}, \quad \Psi_{011}$$

Thus the second excited state is six-fold degenerate.

In general, the degeneracy of the energy eigenstate of the three-dimensional isotropic oscillator is

$$\text{Degree of degeneracy} = \frac{1}{2} (n + 1) (n + 2) \quad \dots(5.33)$$

### 5.3 RIGID ROTATOR

A rigid rotator consists of two mass points attached at the two ends of a massless rod. The system is capable of rotating about an axis passing through its centre of mass and perpendicular to the length of the rod. If the rotator is constrained to rotate in plane, it can be described by an angle coordinate  $\theta$  at any instant of time.

The potential energy of the rotator is zero because the masses are rigidly connected to the ends of the rod of constant length.

The kinetic energy of the rotator is given by

$$T = \frac{1}{2} I \omega^2 = \frac{1}{2} I \dot{\theta}^2$$

where  $I$  is the moment of inertia of the rotator about the axis of rotation and  $\omega = \dot{\theta}$  is the angular velocity of rotation. Clearly, the total energy of the classical rotator is

$$E = T = \frac{1}{2} I \dot{\theta}^2 = \frac{1}{2} I \omega^2 \quad \dots(5.34)$$

The phase integral of the rotator can be written in terms of the total angular momentum  $p_\theta$  and the angular coordinate  $\theta$  as

$$J = \oint p_\theta d\theta \quad \dots(5.35)$$

According to Wilson–Sommerfeld quantization rule we have

$$J = nh, \quad n = 0, 1, 2, \dots \quad \dots(5.36)$$

Using Equation (5.35) in Equation (5.36) we obtain

$$\oint p_\theta d\theta = nh$$

Since the total angular momentum  $p_\theta = I\omega$  is a constant of motion, the above equation gives

$$p_\theta \int_0^{2\pi} d\theta = nh$$

or 
$$p_\theta = I\omega = \frac{nh}{2\pi} \quad \dots(5.37)$$

The above equation gives

$$\omega = \frac{nh}{2\pi I} = \frac{n\hbar}{I} \quad \dots(5.38)$$

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Substituting the value of  $\omega$  in Equation (5.34) we obtain

$$E = \frac{1}{2} I \frac{n^2 \hbar^2}{I^2}$$

## NOTES

or

$$E = \frac{1}{2} \frac{n^2 \hbar^2}{I} \quad \dots(5.39)$$

We find that the energy of the rigid rotator is discrete and not continuous.

### Problem of Rigid Rotator

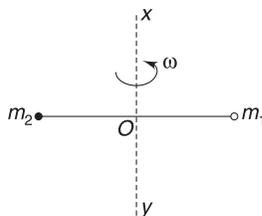
Rigid rotator is a system of two spherical particles separated by a fixed distance. The system can rotate about an axis through the centre of mass and perpendicular to the plane containing the particles. If the plane containing the particles can take any arbitrary orientation, the axis of rotation can assume any orientation in space and the system is then referred to as a rigid rotator with *free axis*. On the other hand, if the particles are confined within a given plane then the axis of rotation has a fixed direction in space and the system is then referred to as a rigid rotator with fixed axis.

A quantum mechanical treatment of rigid rotator with free axis is helpful in understanding the behaviour of a diatomic molecule which can be considered as a rigid rotator with free axis at least as a first approximation.

#### 5.3.1 Schrödinger Equation for a Rigid Rotator with Free-Axis

In order to arrive at the Schrödinger equation, let us first calculate the total energy of the oscillator which is the sum of the kinetic energies of the two particles constituting the rotator and the potential energy of the system.

Let the rotator consist of two particles of masses  $m_1$  and  $m_2$  separated by a fixed distance  $r_0$ . Let the system of particles rotate with an angular velocity ' $\omega$ ' about the axis  $XY$  passing through the centre of mass  $O$  and normal to the line joining the particles as shown in the Figure (5.1).



**Fig. 5.1** Rigid Rotator

Let for any arbitrary position of the plane containing the particles, i.e., for an arbitrary orientation of the axis  $XY$  in space, the cartesian coordinates of  $m_1$  and  $m_2$  with respect to  $O$  which is considered as the origin of a rectangular

coordinate system be respectively  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ . Let  $(r_1, \theta, \phi)$  and  $(r_2, \theta + \pi, \phi + \pi)$  be respectively the spherical polar coordinates of  $m_1$  and  $m_2$ . We then have the transformation equations given by

$$\left. \begin{aligned} x_1 &= r_1 \sin \theta \cos \phi \\ y_1 &= r_1 \sin \theta \sin \phi \\ z_1 &= r_1 \cos \theta \end{aligned} \right\} \dots(5.40)$$

and

$$\left. \begin{aligned} x_2 &= r_2 \sin (\theta + \pi) \cos (\phi + \pi) = r_2 \sin \theta \cos \phi \\ y_2 &= r_2 \sin (\theta + \pi) \sin (\phi + \pi) = r_2 \sin \theta \sin \phi \\ z_2 &= r_2 \cos (\theta + \pi) = -r_2 \cos \theta \end{aligned} \right\} \dots(5.41)$$

The kinetic energy of the particle of mass  $m_1$  is

$$T_1 = \frac{1}{2} m_1 (\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) \dots(5.42)$$

Obtaining the time derivatives  $\dot{x}_1$ ,  $\dot{y}_1$  and  $\dot{z}_1$  from Equation (5.40), substituting them in Equation (5.42) and simplifying we obtain

$$T_1 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \dots(5.43)$$

Similarly, the kinetic energy of the particle of mass  $m_2$  is found to be

$$T_2 = \frac{1}{2} m_2 (\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) = \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \dots(5.44)$$

The total kinetic energy of the rotator is thus

$$T = T_1 + T_2 = \left( \frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 \right) (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \dots(5.45)$$

Since for the rigid rotator the distance  $r_0$  between the two particles is fixed ( $r_0 = \text{constant}$ ), we can say that there exists no mutual force between the particles. As a consequence, the potential energy of the rotator is zero ( $V = 0$ ).

The total energy of the rotator is thus

$$\begin{aligned} E = T &= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \\ E &= \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \end{aligned} \dots(5.46)$$

$$\text{where,} \quad I = m_1 r_1^2 + m_2 r_2^2 \dots(5.47)$$

is the moment of inertia of the rotator about the axis of rotation  $XY$ .

To gain physical insight into the rotator problem, we now express Equation (5.46) in a different form using the definition of centre of mass of a system of particles. Let with respect to the origin  $O$ ,  $\vec{r}_1$  and  $\vec{r}_2$  be respectively the position vectors of the particles of masses  $m_1$  and  $m_2$ . The position vector of the centre of mass with respect to the origin is then given by

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$$\vec{r} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \quad \dots(5.48)$$

Since the origin has been chosen as the centre of mass itself we have

$$\vec{r} = 0, \quad \vec{r}_1 \text{ and } \vec{r}_2 \text{ oppositely directed}$$

We thus obtain from Equation (5.48)

$$O = \frac{m_1 r_1 - m_2 r_2}{m_1 + m_2}$$

The above gives

$$m_1 r_1 = m_2 r_2 \quad \dots(5.49)$$

We may write Equation (5.49) as

$$m_1 r_1 = m_2 (r_0 - r_1)$$

or

$$r_1 = \frac{m_2}{m_1 + m_2} r_0 \quad \dots(5.50)$$

Similarly, we obtain

$$r_2 = \frac{m_1}{m_1 + m_2} r_0 \quad \dots(5.51)$$

Substituting Equations (5.50) and (5.51) in Equation (5.47) we get

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

or

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

or

$$I = \mu r_0^2 \quad \dots(5.52)$$

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  in the reduced mass of the two particles.

Using Equation (5.52) in Equation (5.46) we get the total energy of the rotator as

$$E = \frac{1}{2} \mu r_0^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \quad \dots(5.53)$$

If for convenience, we set the distance between the particles equal to unity, i.e.,  $r_0 = 1$ , we get

$$\mu r_0^2 = \mu = I_0 (\text{say}) \quad \dots(5.54)$$

We can then write the total energy of the rotator as

$$E = \frac{1}{2} I_0 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \quad \dots(5.55)$$

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which is the kinetic energy of a particle of mass  $\mu = I_0$  moving on the surface of a sphere of radius unity.

Thus the motion of the rigid rotator is the same as that of a single particle of mass  $I_0$ , equal to the reduced mass of the two particles forming the rotator, over the surface of a sphere of radius unity.

The wavefunction  $\psi(x, y, z)$  describing the state of a particle of mass  $m$  having a total energy  $E$  moving in a potential field  $V$  satisfies the Schrödinger equation,

$$\Delta^2 \psi(x, y, z) + \frac{2m}{\hbar^2} [E - V] \psi(r, \theta, \phi) = 0 \quad \dots(5.56)$$

In spherical polar coordinates the above becomes

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) \\ + \frac{1}{r^2 \sin^2 \theta} \frac{\partial \psi(r, \theta, \phi)}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V] \psi(r, \theta, \phi) = 0 \quad \dots(5.57) \end{aligned}$$

As seen above, the rigid rotator behaves as a single particle of mass  $\mu = I_0$  over a sphere of unit radius. We thus have  $r = 1$  so that we get

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial \phi^2} \right) = 0 \quad \dots(5.58)$$

Equation (5.57) then becomes

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2I_0}{\hbar^2} [E - V] \psi = 0 \quad \dots(5.59)$$

Further for the rigid rotator  $V = 0$ , so that Equation (5.59) reduces to

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2I_0}{\hbar^2} E \psi = 0 \quad \dots(5.60)$$

In the above,  $\psi$  is a function of only  $\theta$  and  $\phi$  since  $r = \text{constant}$  i.e.,  $\psi = \psi(\theta, \phi)$

### 5.3.2 Solution of the Wave Equation: Energy Eigenvalues and Energy Eigenfunctions for the Rotator

The wave equation given by Equation (5.60) can be solved using the method of separation of variables. We do this by writing

$$\psi(\theta, \phi) = \Theta(\theta) \Phi(\phi) \quad \dots(5.61)$$

where  $\Theta$  and  $\Phi$  are respectively functions of  $\theta$  alone and  $\phi$  alone.

Using Equation (5.61) in Equation (5.60) we obtain

$$\Phi \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \Theta \frac{1}{\sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} + \frac{2I_0 E}{\hbar^2} \Theta \Phi = 0$$

## NOTES

## NOTES

Dividing the above throughout by  $\frac{\Theta\Phi}{\sin^2 \theta}$ , we get

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2I_0 E}{\hbar^2} \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad \dots(5.62)$$

The left hand side of Equation (5.62) depends only on  $\theta$  while the right hand side depends only on  $\phi$ . Hence for the Equation (5.62) to be valid, each side of it must separately be equal to a constant. For convenience we set

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2 \quad (m = \text{constant})$$

$$\text{or} \quad \frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \quad \dots(5.63)$$

Let us call it  $\Phi$  equation.

We also have

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2I_0 E}{\hbar^2} \sin^2 \theta = m^2$$

Dividing the above by  $\frac{\sin^2 \theta}{\Theta}$  we obtain

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2I_0 E}{\hbar^2} \Theta = \frac{m^2}{\sin^2 \theta} \Theta$$

or

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( \frac{2I_0 E}{\hbar^2} - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots(5.64)$$

Let us call it  $\Theta$  equation.

### Solution of the $\Phi$ Equation

The most general solution of Equation (5.63) is given by

$$\Phi = A e^{\pm im\phi} \quad \dots(5.65)$$

where  $A$  is an arbitrary constant, and can be evaluated using the requirement of the normalization of  $\Phi$

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

Using Equation (5.65) in the above we obtain

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

or

$$|A|^2 2\pi = 1$$

or

$$|A|^2 = \frac{1}{2\pi}$$

or

$$A = \frac{1}{\sqrt{2\pi}} \quad \dots(5.66)$$

For  $\Phi$  to be a factor in the total wavefunction of the rotator, the single valuedness of  $\Phi$  demands

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

Using Equation (5.65) in the above we get

$$Ae^{\pm im\phi} = Ae^{\pm im(\phi+2\pi)}$$

or

$$e^{\pm im\phi} = e^{\pm im\phi} e^{\pm 2\pi mi}$$

or

$$e^{\pm 2\pi mi} = 1$$

or

$$\cos 2\pi m \pm i \sin 2\pi m = 1$$

The above demands  $m$  to be zero or an integer positive as well as negative, i.e.,

$$m = 0, \pm 1, \pm 2, \dots \quad \dots(5.67)$$

Using the results given in Equations (5.66) and (5.67), we obtain from Equation (5.66)

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad \dots(5.68)$$

The integer  $m$  can be identified as the *magnetic quantum number*.

**Note:** The Lagrangian function  $L$  for the rigid rotator is by definition given by

$$L = T - V.$$

or

$$L = E \quad (\because V = 0 \text{ and } E = T)$$

Using the expression for the total energy  $E$  given by Equation (5.46) we get

$$L = \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2)$$

We observe that  $\phi$  does not appear explicitly in the Lagrangian function and hence  $\phi$  is a cyclic or ignorable coordinate.

### Solution of the $\Theta$ Equation

Putting 
$$\lambda = \frac{2I_0 E}{\hbar^2} \quad \dots(5.69)$$

## NOTES

the  $\Theta$  equation which is given by Equation (5.64) becomes

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( \lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots(5.70)$$

## NOTES

Let us introduce a new variable  $\xi$  as

$$\xi = \cos \theta \quad \dots(5.71)$$

Now

$$\frac{d\Theta}{d\theta} = \frac{d\Theta}{d\xi} \frac{d\xi}{d\theta} = -\sin \theta \frac{d\Theta}{d\xi} \quad (\text{using Equation 5.71})$$

or

$$\frac{d}{d\theta} = -\sin \theta \frac{d}{d\xi} \quad \dots(5.72)$$

Using Equations (5.71) and (5.72) in Equation (5.70) we get

$$-\frac{d}{d\xi} \left[ -(1-\xi^2)^2 \frac{d\Theta}{d\xi} \right] + \left[ \lambda - \frac{m^2}{1-\xi^2} \right] \Theta = 0$$

or

$$(1-\xi^2) \frac{d^2\Theta}{d\xi^2} - 2\xi \frac{d\Theta}{d\xi} + \left[ \lambda - \frac{m^2}{1-\xi^2} \right] \Theta = 0 \quad \dots(5.73)$$

For mathematical convenience let us substitute

$$\Theta = (1-\xi^2)^{\frac{m}{2}} X(\xi) \quad \dots(5.74)$$

where  $X(\xi)$  is a function of only  $\xi$ .

Substituting for  $\frac{d\Theta}{d\xi}$  and  $\frac{d^2\Theta}{d\xi^2}$  as obtained from Equation (5.74) in

Equation (5.73) and simplifying we obtain

$$(1-\xi^2) \frac{d^2X}{d\xi^2} - 2(m+1)\xi \frac{dX}{d\xi} + [\lambda - m(m+1)]X = 0 \quad \dots(5.75)$$

Equation (5.75) can be solved using power series method. For this we express the function  $X$  as a power series in  $\xi$  as

$$X = \sum_{n=0}^{\infty} a_n \xi^n, \quad n = 0, 1, 2, \dots \quad \dots(5.76)$$

The above gives

$$\frac{dX}{d\xi} = \sum_{n=0}^{\infty} n a_n \xi^{n-1} \quad \dots(5.77)$$

and

$$\frac{d^2X}{d\xi^2} = \sum_{n=2}^{\infty} n(n-1) \xi^{n-2} \quad \dots(5.78)$$

Substitution of Equations (5.76), (5.77) and (5.78) in Equation (5.75) yields

$$\sum_{n=2}^{\infty} n(n-1) a_n \xi^{n-2} - \sum_{n=2}^{\infty} n(n-1) a_n \xi^n - 2(m+1) \sum_{n=1}^{\infty} n a_n \xi^n + [\lambda - m(m+1)] \sum_{n=0}^{\infty} a_n \xi^n = 0 \quad \dots(5.79)$$

For Equation (5.79) to be valid for all possible values of  $\xi$ , the coefficients of the individual powers of  $\xi$  must separately vanish.

Thus we obtain, in general, for the coefficient of  $\xi^n$

$$(n+1)(n+2)a_{n+2} - n(n-1)a_n - 2(m+1)na_n + [\lambda - m(m+1)]a_n = 0$$

or

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

or

$$\frac{a_{n+2}}{a_n} = \frac{n(n-1) + 2n(m+1) + m(m+1) - \lambda}{(n+1)(n+2)} \quad \dots(5.80)$$

Equation (5.79) is referred to as the *Recursion formula* for the coefficients of the series for  $X(\xi)$ . In order that the polynomial  $X$  represents a satisfactory part of the total wavefunction of the rotator, the series for  $X$  must break off (terminate) after a finite number of terms (otherwise it diverges). Considering that polynomial breaks off after the  $n$ th term we get,

$$a_{n+2} = 0$$

and hence Equation (5.80) gives

$$n(n-1) + 2n(m+1) + m(m+1) - \lambda = 0$$

$$\text{or} \quad \lambda = (n+m)(n+m+1) \quad \dots(5.81)$$

In Equation (5.81)  $m = 0, 1, 2, \dots$  and  $n = 0, 1, 2, \dots$ , Hence we may write

$$n+m = l \text{ is an integer including } 0 \quad \dots(5.82)$$

We can thus write Equation (5.81) as

$$\lambda = l(l+1) \quad \dots(5.83)$$

Using the above values of  $\lambda$ , Equation (5.73) becomes

$$(1-\xi^2) \frac{d^2\Theta}{d\xi^2} - 2\xi \frac{d\Theta}{d\xi} + \left[ l(l+1) - \frac{m^2}{1-\xi^2} \right] \Theta = 0 \quad \dots(5.84)$$

It is well known that the associated Legendre function  $p_l^{(m)}(\xi)$  of degree  $l$  and order  $|m|$  where  $l = 0, 1, 2, \dots$  and  $m = 0, 1, 2, \dots, l$  is defined in terms of Legendre polynomial  $P_l(\xi)$  as

## NOTES

$$P_l^{(m)}(\xi) = (1 - \xi^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{d\xi^{|m|}} P_l(\xi) \quad \dots(5.85)$$

$P_l(\xi)$  satisfies the Legendre differential equation

$$\frac{d}{d\xi} \left[ (1 - \xi^2) \frac{dP_l(\xi)}{d\xi} \right] + l(l+1) P_l(\xi) = 0 \quad \dots(5.86)$$

Differentiating Equation (5.86)  $|m|$  times with respect to  $\xi$  and using Equation (5.85) we obtain,

$$(1 - \xi^2) \frac{d^2 P_l^{(m)}}{d\xi^2} - 2\xi \frac{d P_l^{(m)}(\xi)}{d\xi} + \left\{ l(l+1) - \frac{m^2}{1 - \xi^2} \right\} P_l^{(m)}(\xi) = 0 \quad \dots(5.87)$$

Comparing Equations (5.84) and (5.88) we identify

$$\Theta(\theta) = P_l^{(m)}(\xi) = P_l^{(m)}(\cos \theta) \quad \dots(5.88)$$

Thus we can express the general solution of the  $\Theta$  equation as,

$$\Theta(\theta) = B P_l^{(m)}(\cos \theta) \quad \dots(5.89)$$

In the above the constant  $B$  is determined by requiring  $\Theta(\theta)$  to be normalized, i.e.,

$$\int_0^\pi \Theta^*(\theta) \Theta(\theta) \sin \theta d\theta = 1$$

Using Equation (5.89) in the above we obtain,

$$B^2 \int_{-1}^{+1} \{P_l^{(m)}(\cos \theta)\}^* \{P_l^{(m)}(\cos \theta)\} d(\cos \theta) = 1$$

or

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

The above gives

$$B = \sqrt{\frac{2l+l(l-|m|)!}{2(l+|m|)!}} \quad \dots(5.90)$$

Thus the general solution of the  $\Theta$  equation given by Equation (5.90) becomes

$$\Theta(\theta) = \sqrt{\frac{2l+l(l-|m|)!}{2(l+|m|)!}} P_l^{(m)}(\cos \theta) \quad \dots(5.91)$$

In view of Equation (5.68) and Equation (5.91) we can now write the wavefunction  $\psi$  for the rigid rotator with free axis as

**NOTES**

$$\psi_{l,|m|} = \Theta(\theta)\Phi(\theta) = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{2l+l(|m|)!}{2(l+|m|)!}} P_l^{|m|}(\cos\theta)e^{im\phi} \dots(5.92)$$

Set of values of  $l$  and  $|m|$  give the different energy eigenfunctions for the rotator.

The corresponding energy eigenvalues are obtained from

$$\lambda = l(l+1)$$

or

$$\frac{2I_0 E_l}{\hbar^2} = l(l+1)$$

or

$$E_l = \frac{\hbar^2}{2I_0} [l(l+1)] \dots(5.93)$$

### 5.3.3 Rigid Rotator with Fixed Axis

For a rigid rotator with fixed axis,  $\theta$  becomes  $90^\circ$  so that the Schrödinger equation for the rotator given by Equation (5.60) becomes

$$\frac{\partial^2 \Psi}{\partial \phi^2} + \frac{2I_0}{\hbar^2} E \Psi = 0 \dots(5.94)$$

Writing  $\frac{2I_0}{\hbar^2} E = m^2$  as before, Equation (5.94) becomes

$$\frac{\partial^2 \Psi}{\partial \phi^2} + m^2 \Psi = 0 \dots(5.95)$$

The general solution of Equation (5.95) is given by

$$\Psi(\phi) = A e^{\pm im\phi}$$

As has been shown earlier, the requirement of normalization of  $\Psi(\phi)$  gives

$$A = \frac{1}{\sqrt{2\pi}}$$

and the requirement of single valuedness property  $\Psi(\phi)$  demands  $m$  to be zero or a positive or negative integer. Thus the normalized eigenfunctions of a rigid rotator with fixed axis are given by

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots$$

and the corresponding energy eigenvalues are

$$E_m = \frac{\hbar^2}{2I_0} m^2$$

**Note:** The total wave function describing the state of a rigid rotator with free axis as obtained above is

## NOTES

$$\psi = \Theta_{l,\pm m}(\theta) \Phi_{\pm m}(\phi) = Y_{l,\pm m}(\theta, \phi)$$

The functions  $Y_{l,\pm m}(\theta, \phi)$  are called spherical harmonics. They are the simultaneous eigenfunctions of angular momentum operators  $\hat{L}_z$  and  $\hat{L}^2$ , being solutions of the eigenvalue equations

**NOTES**

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

$$\hat{L}_z Y_{l,\pm m}(\theta, \phi) = \pm m \hbar Y_{l,\pm m}$$

We find that the quantum mechanical problems of rigid rotator and angular momentum are directly related.

**Check Your Progress**

1. What is three-dimensional harmonic oscillator?
2. Define the potential energy function of the oscillator.
3. Explain rigid rotator.
4. Give equation for the kinetic energy of the rotator.
5. What is the total energy of the rotator?

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## 5.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

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1. Three-dimensional harmonic oscillator. A general three-dimensional harmonic oscillator consists of a particle, of mass say  $m$ , bound to the origin  $O$  of a rectangular coordinate system ( $XYZ$ ) by a restoring force  $\vec{F} = -k\vec{r}$  where  $\vec{r}$  is the position vector of the particle with respect to the origin  $O$  and  $k$  is the force constant.
2. The potential energy function of the oscillator is spherically symmetric and is given by

$$V = V(r) = \frac{1}{2}kr^2 = \frac{1}{2}m\omega_0^2 r^2$$

3. A rigid rotator consists of two mass points attached at the two ends of a massless rod. The system is capable of rotating about an axis passing through its centre of mass and perpendicular to the length of the rod. If the rotator is constrained to rotate in plane, it can be described by an angle coordinate  $\theta$  at any instant of time.
4. The kinetic energy of the rotator is given by

$$T = \frac{1}{2}I\omega^2 = \frac{1}{2}I\dot{\theta}^2$$

where  $I$  is the moment of inertia of the rotator about the axis of rotation and  $\omega = \dot{\theta}$  is the angular velocity of rotation.

5. The total energy of the rotator is thus

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

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

where

$$I = m_1 r_1^2 + m_2 r_2^2$$

is the moment of inertia of the rotator about the axis of rotation  $XY$ .

## NOTES

### 5.5 SUMMARY

- Three-dimensional harmonic oscillator. A general three-dimensional harmonic oscillator consists of a particle, of mass say  $m$ , bound to the origin  $O$  of a rectangular coordinate system ( $XYZ$ ) by a restoring force  $\vec{F} = -k\vec{r}$  where  $\vec{r}$  is the position vector of the particle with respect to the origin  $O$  and  $k$  is the force constant.
- The potential energy function of the oscillator is spherically symmetric and is given by

$$V = V(r) = \frac{1}{2} kr^2 = \frac{1}{2} m\omega_0^2 r^2$$

- A rigid rotator consists of two mass points attached at the two ends of a massless rod. The system is capable of rotating about an axis passing through its centre of mass and perpendicular to the length of the rod. If the rotator is constrained to rotate in plane, it can be described by an angle coordinate  $\theta$  at any instant of time.
- The potential energy of the rotator is zero because the masses are rigidly connected to the ends of the rod of constant length.
- The kinetic energy of the rotator is given by

$$T = \frac{1}{2} I\omega^2 = \frac{1}{2} I\dot{\theta}^2$$

where  $I$  is the moment of inertia of the rotator about the axis of rotation and  $\omega = \dot{\theta}$  is the angular velocity of rotation.

- Rigid rotator is a system of two spherical particles separated by a fixed distance. The system can rotate about an axis through the centre of mass and perpendicular to the plane containing the particles.
- If the particles are confined within a given plane then the axis of rotation has a fixed direction in space and the system is then referred to as a rigid rotator with fixed axis.
- Any arbitrary position of the plane containing the particles, i.e., for an arbitrary orientation of the axis  $XY$  in space, the cartesian coordinates of  $m_1$  and  $m_2$  with respect to  $O$  which is considered as the origin of a rectangular coordinate system be respectively  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ . Let  $(r_1, \theta, \phi)$  and  $(r_2, \theta + \pi, \phi + \pi)$  be respectively the spherical polar coordinates of  $m_1$  and  $m_2$ .

## NOTES

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**5.6 KEY WORDS**


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- **Three-dimensional harmonic oscillator:** A general three-dimensional harmonic oscillator consists of a particle, of mass say  $m$ , bound to the origin  $O$  of a rectangular coordinate system ( $XYZ$ ) by a restoring force  $\vec{F} = -k\vec{r}$  where  $\vec{r}$  is the position vector of the particle with respect to the origin  $O$  and  $k$  is the force constant.
  - **Rigid rotator:** It consists of two mass points attached at the two ends of a massless rod. The system is capable of rotating about an axis passing through its centre of mass and perpendicular to the length of the rod.
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**5.7 SELF ASSESSMENT QUESTIONS AND EXERCISES**


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**Short Answer Questions**

1. Define three-dimensional harmonic oscillator.
2. Give the Schrödinger equation for the oscillator.
3. What is rigid rotator?

**Long Answer Questions**

1. Discuss the concept of three-dimensional harmonic oscillator giving appropriate examples.
  2. Briefly explain the concept of rigid rotator with relevant equations.
  3. Prove that the potential energy of the rotator is zero because the masses are rigidly connected to the ends of the rod of constant length.
  4. Explain the terms free axis and fixed axis for a rotator.
  5. Discuss Schrödinger equation for a rigid rotator with free-axis with relevant examples.
  6. Explain the energy eigenvalues and energy eigenfunctions for the rotator.
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**5.8 FURTHER READINGS**


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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
- Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.
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## UNIT 6 APPLICATION TO DIATOMIC MOLECULES

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### NOTES

#### Structure

- 6.0 Introduction
- 6.1 Objectives
- 6.2 Separation of Variables and Solution of  $R$ ,  $\theta$ ,  $\Phi$ , Equations
  - 6.2.1 Solution of the  $\Phi$ -Equation
  - 6.2.2 Solution of the  $\theta$ -Equation
  - 6.2.3 Normalized Angular Part of the Wavefunction
  - 6.2.4 Solution of the Radial Wave Equation
- 6.3 Application to Diatomic Molecules – Hydrogen Atom
  - 6.3.1 Properties of the Radial Wave Function of Hydrogen Atom
- 6.4 Discussion of Bound States and Parity
- 6.5 Answers to Check Your Progress Questions
- 6.6 Summary
- 6.7 Key Words
- 6.8 Self Assessment Questions and Exercises
- 6.9 Further Readings

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### 6.0 INTRODUCTION

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A potential depending only on the distance from a fixed point (centre of the force) is referred to as a spherically symmetric potential. Examples of spherically symmetric potential are: gravitational potential due to a mass point, electrostatic potential due to a point charge, etc. Diatomic molecules are molecules composed of only two atoms, of the same or different chemical elements. The prefix ‘*di-*’ is of Greek origin, meaning ‘two’. If a diatomic molecule consists of two atoms of the same element, such as hydrogen ( $H_2$ ) or oxygen ( $O_2$ ), then it is said to be homonuclear. Otherwise, if a diatomic molecule consists of two different atoms, such as carbon monoxide (CO) or nitric oxide (NO), the molecule is said to be heteronuclear. The only chemical elements that form stable homonuclear diatomic molecules at Standard Temperature and Pressure (STP) or typical laboratory conditions, of 1 bar and 25 °C, are the gases hydrogen ( $H_2$ ), nitrogen ( $N_2$ ), oxygen ( $O_2$ ), fluorine ( $F_2$ ), and chlorine ( $Cl_2$ ). The simplest molecule possible is the  $H_2^+$  molecular ion. It consists of two protons and one electron. The ground state energy of the system will be -13.6 eV, when the electron forms a hydrogen atom with one of the protons.

In this unit, you will study about the separation of variables and solution of  $R, \theta, \Phi$  equation, diatomic molecules - hydrogen atom, and bound states and parity.

NOTES

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## 6.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand separation of variables and solution of R,  $\theta$ ,  $\Phi$  equation
- Define diatomic molecules - hydrogen atom
- Discuss and solve for bound states and parity

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## 6.2 SEPARATION OF VARIABLES AND SOLUTION OF R, $\theta$ , $\Phi$ , EQUATIONS

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Consider a particle of mass  $m$  moving under a central force, i.e., a force whose magnitude depends only on the distance of the particle from a fixed point and whose the direction is always towards or away from the fixed point. Such a force  $\vec{F}(r)$  can always be derived from a potential function  $V$  according to

$$\vec{F}(r) = \frac{-dV}{dr} \quad \dots(6.1)$$

It is evident that the potential function depends only on the distance  $r$  and can be expressed as

$$V = V(r) \quad \dots(6.2)$$

Such a potential depending only on the distance from a fixed point (centre of the force) is referred to as a *spherically symmetric potential*. Examples of spherically symmetric potential are: gravitational potential due to a mass point, electrostatic potential due to a point charge, etc.

The wavefunction  $\psi$  which is a function of the coordinates of the particle in space and which describes the state of the particle satisfies the Schrödinger equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(r)] \psi = 0 \quad \dots(6.3)$$

For motion under spherically symmetric potential, it is advantageous to express the Schrödinger equation in terms of spherical polar coordinates  $r$ ,  $\theta$ ,  $\phi$  instead of Cartesian coordinates  $x$ ,  $y$ ,  $z$  because the potential is independent of the angular coordinates  $\theta$  and  $\phi$ .

The operator  $\nabla^2$  in spherical polar coordinates is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad \dots(6.4)$$

which when used in Equation (6.3) gives the Schrödinger equation in spherical polar coordinates

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

$$+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V(r)] \psi(r, \theta, \phi) = 0 \quad \dots(6.5)$$

The above equation can be separated into three independent equations corresponding to the three independent variables  $r$ ,  $\theta$  and  $\phi$  using the well known method of separation of variables. The method consists in writing

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad \dots(6.6)$$

where  $R(r)$ ,  $\Theta(\theta)$  and  $\Phi(\phi)$  are, respectively, functions of only  $r$ , only  $\theta$  and only  $\phi$ .

Substituting Equation (6.6) in Equation (6.5) we obtain

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

Multiplying throughout by  $\frac{r^2 \sin^2 \theta}{R \Theta \Phi}$ , the above equation gives

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

$$\text{or } \frac{\sin^2 \theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2m}{\hbar^2} [E - V(r)] r^2 \sin^2 \theta = \frac{-1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \dots(6.7)$$

Since the left hand side of the above equation is a function of  $r$  and  $\theta$  while the right hand side is a function of only  $\phi$ , we must have each side equal to some constant. For convenience let the constant be put equal to  $m^2$ . We then get

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2 \text{ or } \frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \quad \dots(6.8)$$

We also get

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

Dividing the above equation by  $\sin^2 \theta$  we obtain

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [E - V(r)] r^2 = \frac{-1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + m^2 / \sin^2 \theta = 0 \quad \dots(6.9)$$

## NOTES

In the above equation the left hand side is a function of only  $r$  while the right hand side is a function of  $\theta$  only. Hence each side of the equation must be equal to a constant. Considering the constant to be  $\lambda$ , we get

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

$$\text{or} \quad \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( \lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots(6.10)$$

$$\text{and} \quad \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [E - V(r)] r^2 = \lambda$$

Multiplying by  $\frac{R}{r^2}$  the above gives

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [E - V(r)] R = \frac{\lambda R}{r^2}$$

$$\text{or} \quad \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [E - V(r)] R = \frac{\lambda}{r^2} R = 0 \quad \dots(6.11)$$

Equation (6.11) is usually referred to as the radial wave equation. We have thus been able to separate the three-dimensional Schrödinger equation given by Equation (6.5) into three independent, one-dimensional equations involving the independent coordinate  $r$ ,  $\theta$  and  $\phi$  given by Equations (6.8), (6.10) and (6.11), respectively.

It is important to note that the equation involving the angular coordinates namely  $\theta$  and  $\phi$  do not contain the potential function and hence these two equations hold for all three-dimensional problems involving spherically symmetric potentials. The radial wave equation given by Equation (6.11), however, involves the potential function  $V(r)$  and hence it takes different forms for different types of  $V(r)$  as in hydrogen atom problem, three-dimensional oscillator problem, rigid rotator problem, etc.

### Solution of the Schrödinger Equation

Solutions of the Equations (6.8), (6.10) and (6.11), respectively, give the functions  $R(r)$ ,  $\Theta(\theta)$ ,  $\Phi(\phi)$ . We can then obtain the solution of the Schrödinger equation given by Equation (6.5) in terms of  $R(r)$ ,  $\Theta(\theta)$  and  $\Phi(\phi)$  as

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

#### 6.2.1 Solution of the $\Phi$ -Equation

The function  $\Phi(\phi)$  satisfies Equation (6.8)

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

The general solution of the above second-order differential equation is given by

$$\Phi(\phi) = Ae^{\pm im\phi} \quad \dots(6.12)$$

For  $\Phi(\phi)$  to be a factor of acceptable wavefunction  $\psi(r, \theta, \phi)$ , it must be single valued, i.e., it must satisfy the condition

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

or  $Ae^{\pm im\phi} = Ae^{\pm im(\phi + 2\pi)} = Ae^{\pm im\phi} e^{\pm i2\pi m}$

The above holds if

$$e^{\pm i2\pi m} = 1$$

or

$$\cos 2\pi m \pm i \sin 2\pi m = 1$$

The above requires  $m$  to be equal to 0 or an integer, i.e.,

$$m = 0, 1, 2, \dots(6.13)$$

$m$  is called the magnetic quantum number.

Further, the function  $\Phi(\phi)$  must be normalized requiring

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

Using Equation (6.12) in the above we obtain

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

or  $|A|^2 = \frac{1}{2\pi}$  or  $A = \frac{1}{\sqrt{2\pi}}$   $\dots(6.14)$

The normalized solution of the  $\Phi$ -equation is thus

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots \dots(6.15)$$

We find that the function  $\Phi(\phi)$  is, in general, a complex function which can be decomposed into a real part and an imaginary part, i.e.,

Real form  $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \cos m\phi$   $\dots(6.16)$

Imaginary from  $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \sin m\phi$   $\dots(6.17)$

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## 6.2.2 Solution of the $\Theta$ -Equation

We have the  $\Theta$ -equation given by Equation (6.10)

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

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Let us introduce a new variable  $\xi$  as

$$\xi = \cos \theta \quad \dots(6.18)$$

We then get

$$\frac{d\Theta}{d\theta} = \frac{d\Theta}{d\xi} \frac{d\xi}{d\theta} = -\sin \theta \frac{d\Theta}{d\xi} \quad \dots(6.19)$$

Further

$$\sin \theta = \sqrt{1 - \cos^2 \theta} = \sqrt{1 - \xi^2} \quad \dots(6.20)$$

Using Equation (6.20) in Equation (6.19) we get

$$\frac{d}{d\theta} = -\sqrt{1 - \xi^2} \frac{d}{d\xi} \quad \dots(6.21)$$

Using Equations (6.19), (6.20) and (6.21), the  $\Theta$  equation becomes

$$\frac{d}{d\xi} \left[ (1 - \xi^2) \frac{d\Theta(\xi)}{d\xi} \right] + \left[ \lambda - \frac{m^2}{1 - \xi^2} \right] \Theta(\xi) = 0 \quad \dots(6.22)$$

Equation (6.22) is the well known *associated Legendre equation*. Since  $\xi = \cos \theta$ , the above equation is physically meaningful only for values of  $\xi$  lying between  $-1$  and  $+1$ . Physically acceptable solutions of Equation (6.22) give

$$\lambda = l(l + 1); \quad l = 0, 1, 2, \dots \quad \dots(6.23)$$

$$m = 0, \pm 1, \pm 2, \dots \pm l \quad \dots(6.24)$$

When  $m = 0$ , Equation (6.22) reduces to the well known Legendre differential equation whose solution is the Legendre polynomial

$$P_l(\xi) = P_l(\cos \theta) \quad \dots(6.25)$$

For  $m \neq 0$ , the solutions are *associated Legendre polynomials*

$$P_l^{(m)}(\xi) = P_l^{(m)}(\cos \theta) \quad \dots(6.26)$$

The normalized solutions of Equation (6.22) are given by

$$\Theta_l^m(\theta) = (-1)^m \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta), \quad m > 0 \quad \dots(6.27)$$

$$\Theta_l^m(\theta) = \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta), \quad m \leq 0 \quad \dots(6.28)$$

### 6.2.3 Normalized Angular Part of the Wavefunction

The normalized angular part of the wavefunction is the product of  $\Theta(\theta)$  given by Equation (6.27) and  $\Phi(\phi)$  given by Equation (6.15)

$$\psi_{\text{angular}}(\theta, \phi) = \frac{1}{\sqrt{2\pi}} (-1)^m \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta), e^{im\phi} \quad \dots(6.29)$$

where

$$l = 0, 1, 2, \dots; \quad m = 0, \pm 1, \pm 2, \dots, \pm l \quad \dots(6.30)$$

The angular part of the wavefunction is called *spherical harmonic* and written as  $Y_{lm}(\theta, \phi)$ . We get

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta), e^{im\phi} \quad \dots(6.31)$$

We observe that the angular part of the wavefunction neither depends upon the total energy  $E$  nor upon the potential function  $V(r)$ .

### 6.2.4 Solution of the Radial Wave Equation

The radial wave equation is given by Equation (6.11)

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

The above equation can be solved exactly provided the potential function  $V(r)$  is stated explicitly. It is thus clear that the radial wavefunction  $R(r)$  depends upon the nature of the problem under consideration.

For solving the radial wavefunction it is usual to introduce a function  $u(r)$  according to

$$u(r) = rR(r) \quad \dots(6.32)$$

The above gives,

$$\frac{dR}{dr} = \frac{-u}{r^2} + \frac{1}{r} \frac{du}{dr} \quad \dots(6.33)$$

Using Equations (6.32) and (6.33) and  $\lambda = l(l+1)$  in the radial wave equation and simplifying we obtain

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2} \right] u = 0 \quad \dots(6.34)$$

The term  $\frac{l(l+1)\hbar^2}{2mr^2}$  is called the *centrifugal potential* because its first derivative with respect to  $r$  gives the classical centrifugal force when we

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use  $\sqrt{l(l+1)}\hbar$  as the orbital angular momentum. Since centrifugal force is a repulsive force, the term  $\frac{l(l+1)\hbar^2}{2mr^2}$  represents a repulsive potential. We

may note that the spherically symmetric potential  $V(r)$  may be attractive or repulsive. We may write Equation (6.34) as

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2} [E - V_{\text{eff}}]u = 0 \quad \dots(6.35)$$

where  $V_{\text{eff}}$  which may be called the effective potential under which the particle moves is given as

$$V_{\text{eff}} = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \quad \dots(6.35(a))$$

Equation (6.35) has the form of one-dimensional Schrödinger equation and can be solved from a knowledge of the spherically symmetric potential  $V(r)$ .

## 6.3 APPLICATION TO DIATOMIC MOLECULES – HYDROGEN ATOM

A hydrogen atom consists of an electron of charge  $-e$ , mass  $m_e$  and a nucleus having a proton of charge  $+e$  and mass  $m_p$ . By hydrogen-like atom we mean a one electron atom having a nucleus with  $Z$  protons (for example a singly ionized helium atom, a doubly-ionized lithium atom, etc.) For generality we consider a hydrogen-like atom.

If  $r$  be distance between the nucleus and the electron then the potential energy function  $V(r)$  is given by

$$V(r) = \frac{-1}{4\pi\epsilon_0} \frac{Ze^2}{r} = -k \frac{Ze^2}{r} \quad \left[ k = \frac{1}{4\pi\epsilon_0} \right] \quad \dots(6.36)$$

If  $E$  be the total energy of relative motion between the nucleus and the electron then the time independent Schrödinger equation for the atom in the centre of mass coordinate system is given by

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2} [E - V(r)]\psi(\vec{r}) = 0 \quad \dots(6.37)$$

where

$$m = \frac{m_e(Zm_p)}{m_e + (Zm_p)} \text{ is the reduced mass.}$$

Equation (6.37) expressed in spherical polar coordinate  $(r, \theta, \phi)$  is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V(r)]\psi = 0 \dots(6.38)$$

In the above,

$$\psi = \psi(r, \theta, \phi).$$

Using the method of separation of variables we may write

$$\psi = \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad \dots(6.39)$$

We obtain the following three equations

$$(i) \Phi \text{ equation: } \frac{d^2\Phi}{d\phi^2} m^2\Phi = 0 \quad \dots(6.40)$$

$$(ii) \Theta \text{ equation: } \frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \left( \lambda - \frac{m^2}{\sin^2\theta} \right) \Theta = 0 \quad \dots(6.41)$$

$$(iii) R \text{ (radial) equation: } \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [E - v(r)]R - \frac{\lambda}{r^2} R = 0 \quad \dots(6.42)$$

$$\text{In the above, } \lambda = l(l+1) \quad \dots(6.43)$$

Solution of the  $\Phi$  equation was obtained earlier and is given by

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots \quad \dots(6.44)$$

Solution of the  $\Theta$  equation was obtained in earlier and is given by

$$\Theta_{lm}(\theta) = (-1)^m \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta); \quad m > 0 \quad \dots(6.45)$$

$$\Theta_{lm}(\theta) = \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta); \quad m \leq 0 \quad \dots(6.46)$$

In the above,

$$l = 0, 1, 2, \dots \quad \dots(6.47)$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l \quad \dots(6.48)$$

The normalized angular part of the wavefunction is given by

$$\psi_{lm}(\theta, \phi) = \Theta_{lm}(\theta) \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} (-1)^m \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta) e^{im\phi} \quad \dots(6.49)$$

### Solution of the Radial Equation

Substituting for  $V(r)$  given by Equation (6.36) and  $\lambda$  given by Equation (6.43) the radial wave Equation (6.42) becomes

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ E - \frac{l(l+1)\hbar^2}{2mr^2} + k \frac{Ze^2}{r} \right] R = 0 \quad \dots(6.50)$$

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For solving Equation (6.50) let us introduce a dimensionless variable  $\rho$  as

$$\rho = \gamma r \quad \dots(6.51)$$

The parameter  $\gamma$  is chosen as

$$\gamma = \sqrt{\frac{-8mE}{\hbar^2}} \quad \dots(6.52)$$

Further let us introduce a constant  $\lambda$  as

$$\lambda = \frac{kZe^2}{\hbar} \sqrt{\frac{m}{-2E}} \quad \dots(6.53)$$

We may note that  $E$  is negative for bound states of the atom under consideration and hence both  $\rho$  and  $\lambda$  are real.

In terms of  $\rho$  and  $\lambda$ , Equation (6.50) becomes

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[ \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R = 0 \quad \dots(6.54)$$

Let us first find the *asymptotic solution* of Equation (6.54). It is the solution in the limit  $\rho$  (and hence  $r$ )  $\rightarrow \infty$ . In this limit Equation (6.54) reduces to

$$\frac{d^2 R}{d\rho^2} - \frac{1}{4} R = 0 \quad \dots(6.55)$$

The two independent solutions of the above equation are

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

and

$$R = e^{+\rho/2}$$

The second solution is not acceptable because as  $\rho \rightarrow \infty$   $R \rightarrow \infty$ . Hence the acceptable asymptotic solution is

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

In view of the above asymptotic solution, we may write the exact solution of Equation (6.54) as

$$R(\rho) = F(\rho)e^{-\rho/2} \quad \dots(6.56)$$

where  $F(\rho)$  is some function of  $\rho$ .

Using Equation (6.56) in Equation (6.54) we obtain

$$\rho^2 \frac{d^2 R(\rho)}{d\rho^2} + \rho(2 - \rho) \frac{dF(\rho)}{d\rho} + [\rho\lambda - \rho - l(l+1)]F(\rho) = 0 \quad \dots(6.57)$$

We find that when  $\rho = 0$

$$l(l+1) F(0) = 0$$

or

$$F(0) = 0, l \neq 0 \quad \dots(6.58)$$

Clearly, a power series solution for  $F(\rho)$  must not contain a constant term. Hence, we may write the power series solution as

$$F(\rho) = \sum_{k=0}^{\infty} C_k \rho^{s+k} \quad \dots(6.59)$$

The above gives

$$\frac{dF(\rho)}{d\rho} = \sum C_k (s+k) \rho^{s+k-1} \quad \dots(6.60)$$

$$\frac{d^2F(\rho)}{d\rho^2} = \sum C_k (s+k)(s+k-1) \rho^{s+k-2} \quad \dots(6.61)$$

Substituting Equations (6.59), (6.60), (6.61) in Equation (6.57) we obtain

$$\sum_k C_k (\lambda - 1 - s + k) \rho^{s+k-1} + \sum_k C_k (s^2 + 2sk + k^2 + s + k - l^2 - l) \rho^{s+k} = 0 \quad \dots(6.62)$$

For the above equation to be valid for all value of  $\rho$ , the coefficient of each power of  $\rho$  must separately vanish. Equating the coefficient of  $\rho^s$  to zero we get

$$C_0 (s^2 + s - l^2 - l) = 0$$

Since  $C_0 \neq 0$ , we get

$$s^2 + s - l^2 - l = 0$$

or

$$(s - l)(s + l + 1) = 0$$

The above gives

$$s = l \quad \text{or} \quad s = -(l + 1) \quad \dots(6.63)$$

If  $s = -(l + 1)$ , the first term in  $F(\rho)$  given by Equation (6.59) becomes  $C_0 \rho^{-(l+1)k} = \frac{C_0}{\rho^{(l+1)k}}$  which tends to infinity as  $\rho$  and hence  $r$  tends to zero. We hence get  $s = l$ . Equating the coefficient of  $\rho^{s+k+1} = \rho^{l+k+1}$  in Equation (6.62) to zero we obtain the recurrence relation

$$C_{k+1} = \frac{l + k + 1 - \lambda}{(k + 1)(k + 2l + 2)} C_k \quad \dots(6.64)$$

Using the above relation we can find the coefficients  $C_1, C_2, C_3, \dots$ , in terms of the coefficient  $C_0$ .

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For large values of  $k$ , Equation (6.64) gives

$$C_{k+1} = \frac{k}{k^2} C_k$$

or

$$\frac{C_{k+1}}{C_k} = \frac{1}{k} \quad \dots(6.65)$$

We have

$$e^\rho = \sum_{k=0}^{\infty} \frac{1}{k!} \rho^k = \sum_{k=0}^{\infty} b_k \rho^k \quad \dots(6.66)$$

where  $b_k = \frac{1}{k!}$

Clearly

$$b_{k+1} = \frac{1}{(k+1)!}$$

So that

$$\frac{b_{k+1}}{b_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1}$$

For large  $k$  we get

$$\frac{b_{k+1}}{b_k} = \frac{1}{k} \quad \dots(6.67)$$

$F(\rho)$  given by Equation (6.59) can be written as

$$F(\rho) = \rho^s \sum_{k=0}^{\infty} C_k \rho^k = \rho^l \sum_{k=0}^{\infty} C_k \rho^k \quad \dots(6.68)$$

Using Equation (6.66) we obtain

$$\rho^l e^\rho = \rho^l \sum b_k \rho^k \quad \dots(6.69)$$

In view of the results given by Equations (6.65), (6.67), (6.68) and (6.69) we get

$$F(\rho) = \rho^l e^\rho$$

So that

$$R(\rho) = \rho^l e^\rho e^{-\rho/2} = \rho^l e^{\rho/2} \quad \dots(6.70)$$

$R(\rho)$  given by Equation (6.70) is not acceptable because  $R(\rho) \rightarrow \infty$  as  $\rho \rightarrow \infty$  and hence  $r \rightarrow \infty$ . Thus the series governed by the recursion relation given by Equation (6.64) does not lead to an acceptable radial wavefunction unless the series breaks off after a finite number of terms.

**Energy Eigenvalues**

Let us assume the series to break off after the  $k^{\text{th}}$  term so that  $C_{k+1}$  becomes zero. The recursion formula given by Equation (6.64) then gives

$$l + k + 1 + \lambda = 0$$

or

$$\lambda = l + k + 1 = n \text{ (say)} \quad \dots(6.71)$$

In Equation (6.71), the number  $k$  is called the *radial quantum number* which can take values 0, 1, 2, 3, ... . The number  $n$  is called the total or principal quantum number which can take the values 1, 2, 3, ...

From Equation (6.53) we get

$$\lambda^2 = \frac{k^2 Z^2 e^4}{\hbar^2} \frac{m}{(-2E)}$$

Using Equation (6.71) in the above equation we obtain the energy eigenvalues for a hydrogen-like atom to be

$$E_n = \frac{-k^2 m Z^2 e^4}{2\hbar^2 n^2} - \frac{m e^4 Z^2}{32 \pi^2 \epsilon_0^2 \hbar^2 n^2} \quad \dots(6.72)$$

The energy eigenvalues for a hydrogen atom are obtained by putting  $Z = 1$  in Equation (6.72). We get

$$E_n = \frac{-m e^4}{32 \pi^2 \epsilon_0^2 \hbar^2 n^2} \quad \dots(6.73)$$

Substituting the values of  $m$ ,  $e$ ,  $\epsilon_0$  and  $\hbar$  we obtain the energy eigenvalues of hydrogen atom to be

$$E_1 = -13.6 \text{ eV}, \quad E_2 = -3.4 \text{ eV}, \quad E_3 = -1.51 \text{ eV}, \text{ etc.}$$

The above values are the same as obtained by Bohr on the basis of old quantum theory.

**Radial Wave Function**

The infinite series for  $F(\rho)$  becomes a polynomial due to the requirement of the series to break off after a finite number of terms.

Let us write

$$F(\rho) = \rho^l L(\rho) \quad \dots(6.74)$$

We then get

$$\frac{dF(\rho)}{d\rho} = \rho^l \frac{dL(\rho)}{d\rho} + l\rho^{l-1} L(\rho) \quad \dots(6.75)$$

$$\frac{d^2 F(\rho)}{d\rho^2} = \rho^l \frac{d^2 L(\rho)}{d\rho^2} + l\rho^{l-1} \frac{dL(\rho)}{d\rho} + l\rho^{l-1} \frac{dL(\rho)}{d\rho} + l(l-1)\rho^{l-2} L(\rho)$$

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$$= \rho^l \frac{d^2 L(\rho)}{d\rho^2} + 2l\rho^{l-1} \frac{dL(\rho)}{d\rho} + l(l-1)\rho^{l-2} L(\rho) \quad \dots(6.76)$$

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Substituting Equations (6.74), (6.75) and (6.76) in Equation (6.57) and simplifying we get

$$\rho \frac{d^2 L(\rho)}{d\rho^2} + (2l+2-\rho) \frac{dL(\rho)}{d\rho} + (n-l-1)L(\rho) = 0 \dots(6.77)$$

If  $L_q^p(\rho)$  be the associated Laguerre polynomial of the order  $p$  and degree  $(q-p)$  then it satisfies the differential equation

$$\rho \frac{d^2 L_q^p(\rho)}{d\rho^2} + (p+1-\rho) \frac{dL_q^p(\rho)}{d\rho} + (q-p)L_q^p(\rho) = 0 \quad \dots(6.78)$$

If we consider  $q = n+l$  and  $p = 2l+l$  then Equation (6.77) becomes identical with Equation (6.78) and we can identify  $L(\rho)$  as the associated Laguerre polynomial of the order  $(2l+1)$  and degree  $(n+l)$ , i.e., as  $L_{n+l}^{2l+1}(\rho)$ .

We thus obtain the radial wavefunction to be of the form

$$R_{nl}(r) = \rho^l L_{n+l}^{2l+1}(\rho) e^{-\rho/2}$$

The normalized radial wavefunction is then

$$R_{nl}(r) = N_{nl} \rho^l L_{n+l}^{2l+1}(\rho) e^{-\rho/2} \quad \dots(6.79)$$

The normalization constant  $N_{nl}$  can be obtained from the normalized integral

$$\int_0^{\infty} R_{nl}^2(r) r^2 dr = 1 \quad \dots(6.80)$$

Using  $R_{nl}(r)$  given by Equation (6.79) and the orthogonal properties of associated Laguerre polynomials we obtain

$$N_{nl} = \pm \left[ \left( \frac{2Zmke^2}{n\hbar^2} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} \quad \dots(6.81)$$

Using the result given by Equation (6.81) in Equation (6.79) we obtain

$$R_{nl}(r) = - \left[ \left( \frac{2Z}{na_H} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \quad \dots(6.82)$$

where

$$a_H = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad \dots(6.83)$$

Since the reduced mass  $m$  is almost the same as the electron mass  $m_e$  (for both hydrogen and hydrogen-like atoms), we get

$$a_H = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = a_0 \text{ (A constant)} \quad \dots(6.84)$$

$a_0$  is identified as the radius of the first circular orbit for the electron in the hydrogen atom called the Bohr radius.

In view of Equation (6.84), the radial wavefunction becomes

$$R_{ne}(r) = - \left[ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right] e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \quad \dots(6.85)$$

The negative sign for  $N$  has been used to make  $R_{10}$  positive.

$\rho$  and  $r$  are related according to  $\rho = \gamma r = \sqrt{\frac{-8mE}{\hbar^2}} r$

Substituting for  $E$  given by Equation (167) we get

$$\rho = \frac{2Z}{na_0} r \quad \dots(6.86)$$

Equation (6.86) used in Equation (6.82) gives the radial wavefunction for hydrogen-like atom as

$$R_{nl}(r) = - \sqrt{\left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{Z}{na_0} r} \left( \frac{2Zr}{na_0} \right)^l L_{n+l}^{2l+1} \left( \frac{2Zr}{na_0} \right) \dots(6.87)$$

Putting  $Z = 1$  in the above, the radial wavefunction for hydrogen atom is found to be

$$R_{nl}(r) = - \sqrt{\left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{na_0}} \left( \frac{2r}{na_0} \right)^l L_{n+l}^{2l+1} \left( \frac{2r}{na_0} \right) \dots(6.88)$$

### Complete Wavefunction

The complete wavefunction is given by

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi)$$

where

$$\Theta_{lm}(\theta) = \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} P_l^m(\cos \theta)$$

### NOTES

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

## NOTES

$$\text{and } R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

In the above

$$n = 1, 2, 3, \dots$$

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

$$m = 0, \pm 1, \pm 2, \dots \pm l.$$

The explicit forms of the complete wavefunctions  $\psi_{nlm}$ , for some of the values of  $n, l, m$  which describe stationary states of the hydrogen-like atom are given below along with the spectroscopic designations of the states.

n	l	m	Spectroscopic designation	Wave function $\psi_{nlm}$
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$
2	0	0	2s	$\psi_{200} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
2	1	0	2p	$\psi_{210} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{2a_0}\right)^{5/2} r e^{-\frac{Zr}{2a_0}} \cos \theta$
2	1	+1	2p	$\psi_{211} = \frac{1}{\sqrt{8\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-\frac{Zr}{2a_0}} \sin \theta e^{i\phi}$
2	1	-1	2p	$\psi_{21-1} = \frac{1}{\sqrt{8\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-\frac{Zr}{2a_0}} \sin \theta e^{-i\phi}$

Putting  $Z = 1$  in the above, we obtain the wavefunctions for the hydrogen atom.

### Degeneracy of the Energy Levels

The energy eigenvalues for the hydrogen-like or hydrogen atom depend only on the principal quantum numbers  $n$  as is seen from the Equations (6.72) and (6.73). The energy eigenfunctions, however, depend on the quantum numbers  $n, l$  and  $m$ . We have seen that for a given value of  $n, l$  can take values 0 to  $n-1$  and for each of these  $l$  values there are  $2l+1$  values of the  $m$  from  $-l$  to  $+l$ . Clearly the energy level defined by the energy eigenvalue  $E_n$  is degenerate. The degeneracy is given by

$$D = \sum_{l=0}^{n-1} (2l+1) = n^2 \quad \dots(6.89)$$

The ground state, i.e., the minimum energy state for which  $n = 1$  is clearly non-degenerate ( $n^2 = 1$ ). The first excited state for which  $n = 2$  is 4-fold degenerate, and so on.

### Probability Distribution Function

Let us consider the atom in the state described by the wavefunction  $\Psi_{nlm}(r, \theta, \phi)$ . The probability of finding the electron in the volume element  $d\tau = r^2 dr \sin \theta d\theta d\phi$  about the point  $(r, \theta, \phi)$  is then given by

$$\begin{aligned} P_{nlm} d\tau &= |\Psi_{nlm}|^2 d\tau = |\Psi_{nlm}|^2 r^2 dr \sin \theta d\theta d\phi \\ &= |R_{nl}(r)|^2 |Y_{lm}(\theta, \phi)|^2 r^2 dr \sin \theta d\theta d\phi \end{aligned}$$

Clearly, the probability of finding the electron within a spherical shell of radius  $r$  and thickness  $dr$  from the nucleus irrespective of its angular position is given by

$$P_{nl}(r) dr = |R_{nl}(r)|^2 r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$$

$$\text{or} \quad P_{nl}(r) dr = 4\pi |R_{nl}(r)|^2 r^2 dr \quad \dots(6.90)$$

In this case, the atom is in the ground state described by the wavefunction,

$$\Psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-\frac{r}{a_0}}$$

The probability of finding the electron at the distance  $r$  from the nucleus is according to Equation (6.90) given by

$$P_{10}(r) = \frac{4\pi}{(\pi a_0^3)} e^{-\frac{2r}{a_0}} r^2 = \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} r^2 \quad \dots(6.91)$$

For  $P_{10}(r)$  to be the maximum we have

$$\frac{d P_{10}(r)}{dr} = 0$$

or

$$\frac{d}{dr} \left[ \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} r^2 \right] = 0$$

or

$$e^{-\frac{2r}{a_0}} 2r - r^2 e^{-\frac{2r}{a_0}} \frac{2}{a_0} = 0$$

or

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$$2r - \frac{2r^2}{a_0} = 0$$

or

**NOTES**

$$1 - \frac{r}{a_0} = 0 \quad \text{or} \quad \frac{r}{a_0} = 1$$

or

$$r = a_0 \quad \dots(6.91)$$

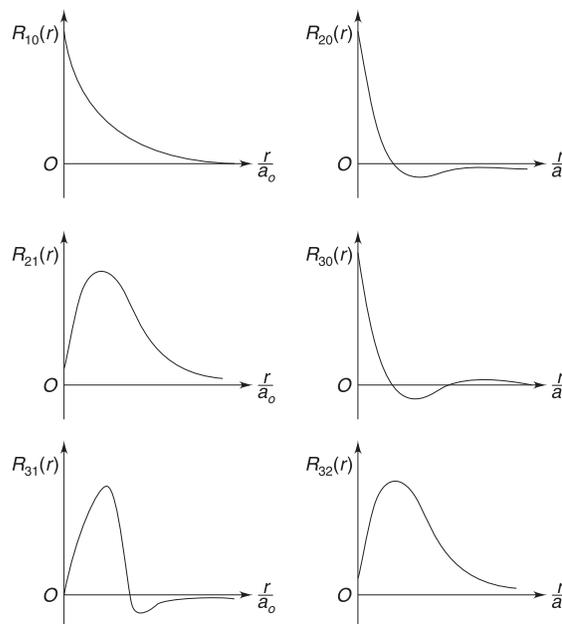
Thus the electron of the hydrogen atom in the ground state is found with maximum probability at a distance equal to the Bohr radius which is about 0.5 Å from the nucleus.

Equation (6.91) shows that  $P_{10} = 0$  at  $r = 0$  and also at  $r = \infty$ . We thus find from the theory of hydrogen atom based on Schrödinger wave mechanics that the position of the electron in the atom is not certain as opposed to Bohr's theory and instead we can say that the electron is found for most of the time around the Bohr radius. The result is consistent with Heisenberg's uncertainty principle.

**6.3.1 Properties of the Radial Wave Function of Hydrogen Atom**

The radial wavefunctions of the hydrogen atom have the properties shown in the Figure (6.1). We observe the following:

- (i) They behave like  $r^l$  for small  $r$
- (ii) They decrease exponentially for large value of  $r$  since  $L_{n+l}^{2l+1}$  is dominated by the highest power  $r^{n-l-1}$ .



**Fig. 6.1** Radial Wavefunctions of Hydrogen Atom

- (iii) The radial function  $R_{nl}(r)$  has  $n - l - 1$  radial nodes since  $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$  is a polynomial of degree  $n - l - 1$ .

## 6.4 DISCUSSION OF BOUND STATES AND PARITY

## NOTES

**Example 1:** A rigid rotator which rotates freely in the  $x$ - $y$  plane has a moment of inertia  $I$  about the axis of rotation.  $\phi$  is the angle between the  $x$ -axis and the axis of rotation. Find (a) the energy eigenvalues and the corresponding eigenfunctions. (b) If at  $t = 0$ , the rotator is described by the wavefunction  $\psi(0) = A \sin^2 \phi$ , find the wavefunction at the time  $t$  ( $t > 0$ ).

**Solution:**

- (a) For the given rotator, the Hamiltonian is given by

$$\hat{H} = \frac{-\hbar^2}{2I} \frac{d^2}{d\phi^2} \quad \dots(6.92)$$

If  $\psi$  be the energy eigenfunction belonging to the energy eigenvalue  $E$ , we have the eigenvalue equation

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

or

$$\frac{-\hbar^2}{2I} \frac{d^2\psi}{d\phi^2} = E\psi$$

or

$$\frac{d^2\psi}{d\phi^2} + \frac{2I}{\hbar^2} E\psi = 0$$

or

$$\frac{d^2\psi}{d\phi^2} + m^2\psi = 0 \quad \dots(6.93)$$

where

$$m^2 = \frac{2I}{\hbar^2} E \quad \dots(6.94)$$

The general solution of Equation (6.93) is

$$\psi(\phi) = Ae^{im\phi} \quad \dots(6.95)$$

where  $A$  is an arbitrary constant.

Single valuedness of  $\psi(\phi)$  requires

$$\psi(\phi) = \psi(\phi + 2\pi) \quad \dots(6.96)$$

Using Equation (6.95) in Equation (6.96) we get

$$m = 0, \pm 1, \pm 2, \dots \quad \dots(6.97)$$

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Thus, we may write the solution given by Equation (6.95) as

$$\psi(\phi) = A e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots \quad \dots(6.98)$$

Normalization of  $\psi(\phi)$  gives

$$\int_0^{2\pi} \psi^*(\phi)\psi(\phi)d\phi = 1$$

or

$$|A|^2 = \frac{1}{2\pi} \quad \text{or} \quad A = \frac{1}{\sqrt{2\pi}} \quad \dots(6.99)$$

We thus get energy eigenvalues, using Equation (6.94), as

$$E_m = \frac{\hbar^2}{2I} m^2, \quad m = 0, \pm 1, \pm 2, \dots \quad \dots(6.100)$$

and the energy eigenfunctions, using Equation (6.99) in Equation (6.98), as

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots \quad \dots(6.101)$$

(b) We have

$$\psi(0) = A \sin^2 \phi$$

We may express the above as

$$\psi(0) = \frac{A}{2} [1 - \cos 2\phi] = \frac{A}{2} - \frac{A}{4} (e^{i2\phi} + e^{-i2\phi}) \dots(6.102)$$

The first term corresponds to  $m = 0$ .

The term  $\frac{A}{4} e^{i2\phi}$  corresponds to  $m = +2$

The term  $\frac{A}{4} e^{-i2\phi}$  corresponds to  $m = -2$

Now we get  $\psi(t)$  from  $\psi(0)$  as

$$\psi(t) = \frac{A}{2} - \frac{A}{4} e^{i2\phi} e^{-iE_2t} - \frac{A}{4} e^{-i2\phi} e^{-iE_2t}$$

or

$$\psi(t) = \frac{A}{2} - \frac{A}{4} e^{i2\phi} e^{\frac{-i2\hbar^2}{I}t} - \frac{A}{4} e^{-i2\phi} e^{\frac{-i2\hbar^2}{I}t}$$

or

$$\psi(t) = \frac{A}{2} - \frac{A}{4} e^{2i\left(\phi - \frac{\hbar^2}{I}t\right)} - \frac{A}{4} e^{-2i\left(\phi - \frac{\hbar^2}{I}t\right)} \quad \dots(6.103)$$

**Example 2:** For a rigid hydrogen molecule ( $H_2$ ) calculate the energies of the stationary states corresponding to  $l = 1$  and  $l = 2$ . Find the bond length of the molecule in terms of the energy difference between the states.

**Solution:** A rigid hydrogen molecule can be considered as a rigid rotator with free axis. As such the energy eigenvalues are given by

$$E_l = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \dots \quad \dots(6.104)$$

where  $I$  = the moment of inertia of the molecule

$$= \mu a^2 = \frac{mm}{m+m} a^2 = \frac{m}{2} a^2 \quad \dots(6.105)$$

In the above  $m$  is the mass of each atom and  $a$  is the bond length.

We have from Equation (6.104)

$$\text{the energy corresponding to } l = 1 \text{ as } E_1 = \frac{\hbar^2}{I}$$

$$\text{the energy corresponding to } l = 2 \text{ as } E_2 = \frac{3\hbar^2}{I}$$

$$\text{We get} \quad E_2 - E_1 = \frac{2\hbar^2}{I}$$

$$\text{which gives} \quad I = \frac{2\hbar^2}{E_2 - E_1} \quad \dots(6.106)$$

From Equation (6.105) we have the bond length given by

$$a = \sqrt{\frac{2I}{m}}$$

Using Equation (6.107) in the above we get

$$a = \sqrt{\frac{2 \times 2\hbar^2}{(E_2 - E_1)m}} = 2\hbar \sqrt{\frac{1}{m(E_2 - E_1)}} \quad \dots(6.107)$$

**Example 3:** A particle of mass  $m$  is moving in a three-dimensional potential given by

$$V(x, y, z) = \frac{1}{2} m \omega^2 z^2 \quad \text{for } 0 < x < a, \quad 0 < y < a \\ = \infty \text{ elsewhere.}$$

Write down (a) the total energy (b) the wavefunction for the particle.

**Solution:** The given three-dimensional potential essentially consists of

- An infinite potential well along the  $x$ -axis
- An infinite potential well along the  $y$ -axis
- A harmonic oscillator potential along the  $z$ -axis.

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## NOTES

The energy due to the potential well along the  $x$ -axis =  $\frac{\pi^2 \hbar^2}{2ma^2} n_x^2$

The energy due to the potential well along the  $y$ -axis =  $\frac{\pi^2 \hbar^2}{2ma^2} n_y^2$

The energy due to the harmonic oscillator potential =  $\left(n_z + \frac{1}{2}\right) \hbar \omega$

(a) Clearly, the total energy of the particle is

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2) + \left(n_z + \frac{1}{2}\right) \hbar \omega$$

(b) The total wavefunction of the particle is

$$\Psi_{n_x n_y n_z}(x, y, z) = \frac{2}{a} \sin\left(\frac{\pi n_x}{a} x\right) \sin\left(\frac{\pi n_y}{a} y\right) Z_{n_z}(z)$$

where  $Z_{n_z}$  is given in terms of Hermite polynomial as

$$Z_{n_z}(z) = \frac{1}{[\sqrt{\pi} 2^{n_z} n_z! z_0]^{1/2}} e^{-\frac{z^2}{2z_0^2}} H_{n_z}\left(\frac{z}{z_0}\right)$$

$$z_0 = \sqrt{\frac{\pi \hbar}{m \omega}}$$

**Example 4:** Determine the expectation values for  $r$  and  $r^2$  when a hydrogen atom is in its ground state,  $r$  being the distance of the electron from the nucleus.

**Solution:** The wavefunction for the hydrogen atom in its ground state is

$$\Psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-\frac{r}{a_0}}$$

By definition we have the expectation value of  $r$  irrespective of its angular position with respect to the nucleus as given by

$$\langle r \rangle = \int \Psi_{100}^* r \Psi_{100} d\tau = \int_0^\infty |\Psi_{100}|^2 r r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$$

$$= 4\pi \int_0^\infty \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}} r^3 dr$$

or

$$\langle r \rangle = \frac{4}{a_0^3} \left(\frac{a_0}{2}\right)^4 3! = \frac{3}{2} a_0$$

The expectation value of  $r^2$  is similarly given by

$$\begin{aligned}\langle r^2 \rangle &= 4\pi \int_0^{\infty} \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}} r^4 dr \\ &= \frac{4}{a_0^3} \left( \frac{a_0}{2} \right)^5 4!\end{aligned}$$

or

$$\langle r^2 \rangle = 3a_0^2$$

**Example 5:** Obtain the expectation value of the potential energy  $v(r)$  of the electron in a hydrogen atom in its ground state.

**Solution:** The normalized wavefunction for the hydrogen atom in its ground state is

$$\Psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-\frac{r}{a_0}}$$

The potential energy of the electron in the Coulomb field of the nucleus is given by

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

By definition, we get

$$\begin{aligned}\langle V(r) \rangle &= \int |\Psi_{100}|^2 \left( -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \right) d\tau \\ &= \int_0^{\infty} |\Psi_{100}|^2 \left( -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \right) r^2 dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \\ &= -\frac{e^2}{4\pi\epsilon_0} 4\pi \times \frac{1}{\pi a_0^3} \int_0^{\infty} e^{-\frac{2r}{a_0}} r dr \\ &= -\frac{e^2}{\pi\epsilon_0 a_0^3} \times \frac{1}{\left(\frac{2}{a_0}\right)^2} = -\frac{e^2}{\pi\epsilon_0 a_0^3} \times \frac{a_0^2}{4}\end{aligned}$$

or

$$\langle V(r) \rangle = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{a_0}$$

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**Example 6:** Calculate  $\left\langle \frac{1}{r} \right\rangle$  for a singly-charged helium ion in its ground state.

**Solution:** The radial part of the wavefunction of a hydrogen-like atom in the ground state is

$$R_{10}(r) = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-\frac{Z}{a_0} r}$$

For  $H_c^+$  we have  $Z = 2$  so that the radial wavefunction becomes

$$\begin{aligned} R_{10}(r) &= 2 \left( \frac{2}{a_0} \right)^{3/2} e^{-\frac{2}{a_0} r} \\ &= \frac{4\sqrt{2}}{a_0^{3/2}} e^{-\frac{2}{a_0} r} \end{aligned}$$

The radial probability density is then given by

$$P_{10}(r) = r^2 |R_{10}(r)|^2 = \frac{32}{a_0^3} r^3 e^{-\frac{4r}{a_0}}$$

We thus get

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int_0^\infty \frac{1}{r} P(r) dr = \int_0^\infty \frac{1}{r} \frac{32}{a_0^3} r^3 e^{-\frac{4r}{a_0}} dr \\ &= \frac{32}{a_0^3} \int_0^\infty e^{-\frac{4r}{a_0}} r dr \\ &= \frac{32}{a_0^3} \times \frac{a_0^2}{16} \end{aligned}$$

or

$$\left\langle \frac{1}{r} \right\rangle = \frac{2}{a_0}$$

**Example 7:** Obtain the effective potential energy of the electron in a hydrogen atom. Under what condition does the bound state for the atom occur?

**Solution:** The radial wave equation for hydrogen atom is given by

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [E - V(r)] R - \frac{l(l+1)}{r^2} R = 0 \dots (6.108)$$

where  $R = R(r)$  is the radial wavefunction for the atom.

We can write Equation (6.108) as

$$\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] R - l(l+1) R = 0 \dots (6.109)$$

Let us introduce a function of  $r$ , namely  $u(r)$  as

$$u(r) = r R(r) \quad \dots(6.110)$$

The above gives

$$R(r) = \frac{u(r)}{r} \quad \dots(6.111)$$

Using Equation (6.111) in Equation (6.109) we get

$$\frac{d}{dr} \left[ r^2 \times \frac{1}{r} \frac{du(r)}{dr} - r^2 \times \frac{1}{r^2} u(r) \right] + \frac{2mr^2}{\hbar^2} [E - V(r)] \frac{u(r)}{r} - l(l+1) \frac{u(r)}{r} = 0$$

or

$$\frac{d}{dr} \left[ r^2 \frac{du(r)}{dr} - u(r) \right] + \frac{2m}{\hbar^2} r [E - V(r)] u(r) - l(l+1) \frac{u(r)}{r} = 0$$

or

$$r \frac{d^2 u(r)}{dr^2} + \frac{du(r)}{dr} - \frac{du(r)}{dr} + \frac{2m}{\hbar^2} [E - V(r)] r u(r) - \frac{l(l+1)}{r} u(r) = 0$$

Dividing throughout by  $r$ , we get

$$\frac{d^2 u(r)}{dr^2} + \frac{2m}{\hbar^2} [E - V(r)] u(r) - \frac{l(l+1)}{r^2} u(r) = 0$$

or

$$\frac{d^2 u(r)}{dr^2} + \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2} \right] u(r) = 0$$

or

$$\frac{d^2 u(r)}{dr^2} + \frac{2m}{\hbar^2} [E - V_{\text{effective}}] u(r) = 0 \quad \dots(6.112)$$

where

$$V_{\text{effective}} = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \quad \dots(6.113)$$

Equation (6.112) is the Schrödinger equation for a particle of mass  $m$  and total energy  $E$  moving in a potential field given by the potential energy function  $V_{\text{effective}}$  defined by Equation (6.113).

The first term in Equation (6.113) is the Coulomb potential energy given by

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

The second term can be recognized as the centrifugal potential energy function because its first derivative with respect to  $r$  gives the centrifugal force if we take the angular momentum of the electron as  $\sqrt{l(l+1)} \hbar$ .

## NOTES

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The plot of  $V_{\text{effective}}$  against  $r$  is as shown in the Figure (6.2).

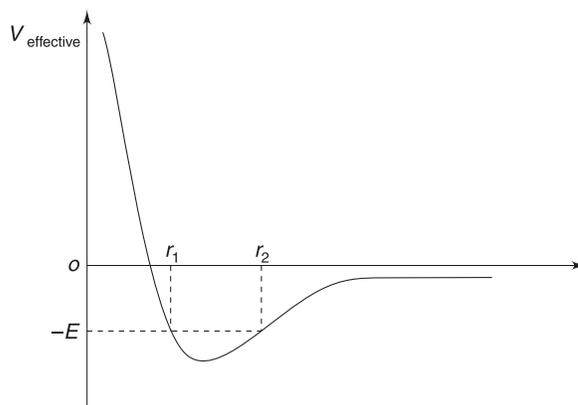


Fig. 6.2 Plot of  $V_{\text{effective}}$  against  $r$

For total energy positive,  $V_{\text{effective}}$  is positive corresponding to repulsive force and hence positive energy cannot correspond to bound state. On the other hand if the total energy is negative say  $-E$ , the effective potential remains negative corresponding to attractive force in the range  $r_1 < r < r_2$ . The state of the particle is clearly a bound state.

**Example 8:** A hydrogen atom is in its ground state. Find the root mean square deviation in the measurement of  $r$  (distance of the electron from the nucleus).

**Solution:** The root mean square deviation in the measurement of  $r$  is by definition given by

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$$

In the ground state of hydrogen atom, we have seen in Example 4

$$\langle r \rangle = \frac{3}{2} a_0$$

and

$$\langle r^2 \rangle = 3 a_0^2$$

We hence obtain

$$\Delta r = \sqrt{3a_0^2 - \frac{9}{4} a_0^2} = \sqrt{\frac{3}{4}} a_0.$$

**Check Your Progress**

1. What is spherically symmetric potential?
2. Define operator  $\nabla^2$  in spherical polar coordinates.
3. State the condition essential to be a factor of acceptable wavefunction.
4. What is centrifugal potential?
5. State the properties of hydrogen atom.
6. Explain the properties of the radial wave function of hydrogen atom.

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## 6.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

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1. The potential function depends only on the distance  $r$  and can be expressed as

$$V = V(r)$$

2. The operator  $\nabla^2$  in spherical polar coordinates is given by

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

3. For  $\Phi(\phi)$  to be a factor of acceptable wavefunction  $\psi(r, \theta, \phi)$ , it must be single valued, i.e., it must satisfy the condition

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

4. The term  $\frac{l(l+1)\hbar^2}{2mr^2}$  is called the *centrifugal potential* because its first derivative with respect to  $r$  gives the classical centrifugal force when we use  $\sqrt{l(l+1)}\hbar$  as the orbital angular momentum.

5. A hydrogen atom consists of an electron of charge  $-e$ , mass  $m_e$  and a nucleus having a proton of charge  $+e$  and mass  $m_p$ . By hydrogen-like atom we mean a one electron atom having a nucleus with  $Z$  protons (for example a singly ionized helium atom, a doubly-ionized lithium atom, etc.)

6. The radial wavefunctions of the hydrogen atom have the properties

- They behave like  $r^l$  for small  $r$
- They decrease exponentially for large value of  $r$  since  $L_{n+l}^{2l+1}$  is dominated by the highest power  $r^{n-l-1}$ .
- The radial function  $R_{nl}(r)$  has  $n - l - 1$  radial nodes since

$$L_{n+l}^{2l+1} \left( \frac{2r}{na_0} \right) \text{ is a polynomial of degree } n - l - 1.$$

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## 6.6 SUMMARY

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- The potential function depends only on the distance  $r$  and can be expressed as

$$V = V(r)$$

## NOTES

## NOTES

Such a potential depending only on the distance from a fixed point (centre of the force) is referred to as a *spherically symmetric potential*.

- The wavefunction  $\psi$  which is a function of the coordinates of the particle in space and which describes the state of the particle satisfies the Schrödinger equation

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

- For motion under spherically symmetric potential, it is advantageous to express the Schrödinger equation in terms of spherical polar coordinates  $r, \theta, \phi$  instead of Cartesian coordinates  $x, y, z$  because the potential is independent of the angular coordinates  $\theta$  and  $\phi$ .
- For  $\Phi(\phi)$  to be a factor of acceptable wavefunction  $\psi(r, \theta, \phi)$ , it must be single valued, i.e., it must satisfy the condition

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

- The normalized solution of the  $\Phi$ -equation is

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots$$

- The function  $\Phi(\phi)$  is, in general, a complex function which can be decomposed into a real part and an imaginary part, i.e.,

$$\text{Real form} \quad \Phi(\phi) = \frac{1}{\sqrt{2\pi}} \cos m\phi$$

$$\text{Imaginary from} \quad \Phi(\phi) = \frac{1}{\sqrt{2\pi}} \sin m\phi$$

- The angular part of the wavefunction is called *spherical harmonic* and written as  $Y_{lm}(\theta, \phi)$ .
- The term  $\frac{l(l+1)\hbar^2}{2mr^2}$  is called the *centrifugal potential* because its first derivative with respect to  $r$  gives the classical centrifugal force when we use  $\sqrt{l(l+1)}\hbar$  as the orbital angular momentum.

- A hydrogen atom consists of an electron of charge  $-e$ , mass  $m_e$  and a nucleus having a proton of charge  $+e$  and mass  $m_p$ . By hydrogen-like atom we mean a one electron atom having a nucleus with  $Z$  protons (for example a singly ionized helium atom, a doubly-ionized lithium atom, etc.)
- If  $E$  be the total energy of relative motion between the nucleus and the electron then the time independent Schrödinger equation for the atom in the centre of mass coordinate system is given by

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

where

$$m = \frac{m_e(Zm_p)}{m_e + (Zm_p)}$$

is the reduced mass.

- $E$  is negative for bound states of the atom under consideration and hence both  $\rho$  and  $\lambda$  are real.
- The infinite series for  $F(\rho)$  becomes a polynomial due to the requirement of the series to break off after a finite number of terms.
- The complete wavefunction is given by

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi)$$

- The energy eigenvalues for the hydrogen-like or hydrogen atom depend only on the principal quantum numbers  $n$ .
- The probability of finding the electron in the volume element  $d\tau = r^2 dr \sin \theta d\theta d\phi$  about the point  $(r, \theta, \phi)$  is then given by

$$\begin{aligned} P_{nlm} d\tau &= |\Psi_{nlm}|^2 d\tau = |\Psi_{nlm}|^2 r^2 dr \sin \theta d\theta d\phi \\ &= |R_{nl}(r)|^2 |Y_{lm}(\theta, \phi)|^2 r^2 dr \sin \theta d\theta d\phi \end{aligned}$$

- The electron of the hydrogen atom in the ground state is found with maximum probability at a distance equal to the Bohr radius which is about  $0.5 \text{ \AA}$  from the nucleus.
- The normalized wavefunction for the hydrogen atom in its ground state is

$$\Psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$$

- The potential energy of the electron in the Coulomb field of the nucleus is given by

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

## NOTES

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## 6.7 KEY WORDS

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- Spherically symmetric potential: The potential depending only on the distance from a fixed point (centre of the force) is referred to as a spherically symmetric potential.
- Spherical harmonic: The angular part of the wavefunction is called spherical harmonic and written as  $Y_{lm}(\theta, \phi)$ .
- Radial quantum number: The number  $k$  is called the radial quantum number which can take values  $0, 1, 2, 3, \dots$ .
- Complete wavefunction: The complete wavefunction is given by the equation,  $\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi)$ .

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## 6.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### NOTES

#### Short Answer Questions

1. Define the term spherically symmetric potential giving examples.
2. What are  $\theta$  equation and  $\Phi$  equation?
3. Define the angular part of the wavefunction spherical harmonic.
4. What is diatomic molecule?
5. Give the composition of hydrogen atom.
6. What is bound states and parity?

#### Long Answer Questions

1. Discuss the concept of separation of variables and solution of  $R, \theta, \Phi$  equation giving appropriate examples.
2. Explain the equations for Schrödinger equation in spherical polar coordinates.
3. Discuss the solution equations of the radial wave equation.
4. Briefly explain diatomic molecules with reference to hydrogen atom.
5. What is the significance of energy eigenvalues? Discuss with the help of examples.
6. Discuss about bound states and parity with the help of relevant examples.

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## 6.9 FURTHER READINGS

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
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**BLOCK - III**
**REPRESENTATION THEORIES**


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**NOTES**


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**UNIT 7 HARMONIC OSCILLATOR**


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**Structure**

- 7.0 Introduction
- 7.1 Objectives
- 7.2 Harmonic Oscillator
- 7.3 Dirac's Bra Ket Vectors
  - 7.3.1 Wavefunction as Vector; Ket Vector
  - 7.3.2 Scalar Product, Bra Vector
  - 7.3.3 Norm of a Ket
  - 7.3.4 Orthogonality of Kets and Bras
- 7.4 Solution using Ladder Operator and Matrix Representation
- 7.5 Answers to Check Your Progress Questions
- 7.6 Summary
- 7.7 Key Words
- 7.8 Self Assessment Questions and Exercises
- 7.9 Further Readings

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**7.0 INTRODUCTION**


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The harmonic oscillator is a model which has several important applications in both classical and quantum mechanics. It serves as a prototype in the mathematical treatment of such diverse phenomena as elasticity, acoustics, AC circuits, molecular and crystal vibrations, electromagnetic fields and optical properties of matter. In classical mechanics, a harmonic oscillator is a system that, when displaced from its equilibrium position, experiences a restoring force  $F$  proportional to the displacement  $x$ ,  $\vec{F} = -k\vec{x}$ , where,  $k$  is a positive constant.

If  $F$  is the only force acting on the system, the system is called a simple harmonic oscillator, and it undergoes simple harmonic motion: sinusoidal oscillations about the equilibrium point, with a constant amplitude and a constant frequency (which does not depend on the amplitude). A simple harmonic oscillator is an oscillator that is neither driven nor damped. It consists of a mass  $m$ , which experiences a single force  $F$ , which pulls the mass in the direction of the point  $x = 0$  and depends only on the mass's position  $x$  and a constant  $k$ .

Bra-ket notation is a notation for linear algebra, particularly focused on vectors, inner products, linear operators, Hermitian conjugation, and the dual space, for both finite-dimensional and infinite-dimensional complex

**NOTES**

vector spaces. It is specifically designed to ease the types of calculations that frequently come up in quantum mechanics. Its use in quantum mechanics is quite widespread. Many phenomena that are explained using quantum mechanics are usually explained using bra–ket notation.

In simple cases, a ket  $|m\rangle$  can be described as a column vector, a bra with the same label  $\langle m|$  is its conjugate transpose (which is a row vector), and writing bras, kets, and linear operators next to each other implies matrix multiplication. However, kets may also exist in uncountably-infinite-dimensional vector spaces, such that they cannot be literally written as a column vector. Also, writing a column vector as a list of numbers requires picking a basis, whereas one can write  $|m\rangle$  without committing to any particular basis. This is helpful because quantum mechanics calculations involve frequently switching between different bases, so it is better to have the basis vectors (if any) written out explicitly. In some situations involving two important basis vectors they will be referred to simply as  $|-\rangle$  and  $|+\rangle$ .

In this unit, you will study about harmonic oscillator, Dirac's bra ket vectors and solutions using ladder operator and matrix representation in detail.

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## 7.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand what harmonic oscillator is
- Discuss Dirac's bra ket vectors
- Explain solutions using ladder operator and matrix representation

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## 7.2 HARMONIC OSCILLATOR

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Bohr's theory based on the quantization of angular momentum and energy of the electron in hydrogen atom was successful in explaining broad features of hydrogen atom and of the spectral lines emitted by it. The concepts used in the theory were new but of fundamental importance and inspired further researches in atomic physics.

Bohr's theory was extended by Arnold Sommerfeld in the year 1915 by introducing elliptical orbits for the electrons in atoms.

In the same year Wilson and Sommerfeld postulated independently a more general statement of quantization rule for systems undergoing periodic motion.

If a periodic system of  $s$  degrees of freedom described by generalized coordinates  $q_1 \dots q_s$  and generalized momenta  $p_1, p_2, \dots, p_s$  then phase integrals of the system are defined as

$$J_i = \oint p_i dq_i, \quad i = 1, 2, \dots, s \quad \dots(7.1)$$

the integration being carried over one complete cycle of the variable  $q_i$ . Wilson and Sommerfeld stated that the stationary states (allowed orbits) for the system are those for which the phase integrals are integral multiples of Planck's constant  $h$ , i.e.,

$$J_i = \oint p_i dq_i = n_i h; \quad n_i = 0, 1, 2, \dots \quad \dots(7.2)$$

In the case of motion of electron in circular orbits, the number of degrees of freedom is only one and the angular momentum  $l = mvr$  is a constant of motion so that the quantization rule given by Equation (7.2) reduces to

$$\begin{aligned} \oint mvr d\phi &= nh \\ \text{or} \quad mvr 2\pi &= nh \\ \text{so that} \quad mvr &= \frac{nh}{2\pi} \quad \dots(7.3) \end{aligned}$$

We may note that Equation (7.3) is the quantization rule postulated by Bohr for the electron in hydrogen atom rotating in circular orbits.

The general quantization rule of Wilson and Sommerfeld was used in a number of problems of interest, particularly for finding out the energies that periodic systems could assume. In the following, we present a brief outline of some such systems in the microscopic domain.

### The Harmonic Oscillator

Consider a harmonic oscillator of mass  $m$  oscillating along the  $x$ -axis about the equilibrium position  $x = 0$ . The displacement of the particle from the equilibrium position at any instant  $t$  is given by

$$x = a \sin \omega_0 t \quad \dots(7.4)$$

where  $a$  is amplitude and  $\omega_0$  is the natural frequency related to the force constant according to

$$\omega_0 = \sqrt{\frac{k}{m}} \quad \dots(7.5)$$

The potential energy of the oscillator is given by

$$V = \frac{1}{2} kx^2 = \frac{1}{2} m\omega_0^2 a^2 \sin^2(\omega_0 t) \quad \dots(7.6)$$

The kinetic energy of the oscillator is

$$T = \frac{1}{2} mv^2 = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 = \frac{1}{2} ma^2 \omega_0^2 \cos^2(\omega_0 t) \quad \dots(7.7)$$

Thus, the total energy of the oscillator becomes

$$E = T + V = \frac{1}{2} m \omega_0^2 a^2 \quad \dots(7.8)$$

## NOTES

## NOTES

According to Wilson–Sommerfeld quantization rule, we get

$$\oint p_x dx = nh, \quad n = 0, 1, 2,$$

or 
$$m \oint \frac{dx}{dt} dx = nh.$$

Substituting for  $\frac{dx}{dt}$  and  $dx$ , the above equation becomes

$$ma^2 \omega_0^2 \int_0^{2\pi/\omega_0} \cos^2(\omega_0 t) dt = nh$$

Evaluating the integral, the above gives

$$ma^2 \omega_0^2 \times \frac{\pi}{\omega_0} = nh \quad \dots(7.9)$$

Using Equation (7.9) in Equation (7.8), the energy of the oscillator is

$$E = \frac{1}{2} \frac{nh\omega_0}{\pi} = n\hbar\omega_0, \quad n = 0, 1, 2 \quad \dots(7.10)$$

Thus the quantization rule applied to linear harmonic oscillator gives the energy of the oscillator to be zero or an integral multiple of  $\hbar\omega_0$  and not continuous.

### 7.3 DIRAC'S BRA KET VECTORS

According to the Schrödinger formulation of quantum mechanics, the physical state at any time  $t$ , say, of a particle of mass  $m$  moving in one dimension in a potential field  $V(q)$ ,  $q$  being the coordinate of the particle which can take values from  $-\infty$  to  $+\infty$ , is described, in general by a complex valued function  $\psi(q, t)$  called the wave function in the position or coordinate representation. Schrödinger *postulated* that if the particle is undisturbed by any measurement its state develops with time in a completely *causal* manner according to the equation

$$i\hbar \frac{\partial \psi(q, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + V(q) \right] \psi(q, t) \quad \dots(7.11)$$

According to Max Born and Jordan,  $|\psi(q, t)|^2 dq$  gives the probability of finding the particle between the position  $q$  and  $q+dq$  if a measurement is made.

It is possible to define a function  $\phi(p, t)$  called the wave function in the momentum representation ( $p$  representing the momentum of the particle) according to the Fourier transform,

$$\phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(q, t) e^{\frac{-ipq}{\hbar}} dq \quad \dots(7.12)$$

$\phi(p, t)$  which is completely determined by  $\psi(q, t)$  describes the state of the particle as does  $\psi(q, t)$ . In other words,  $\phi(p, t)$  represents the same dynamical state as  $\psi(q, t)$  while the expression  $|\phi(p, t)|^2 dp$  gives the probability that a measurement of momentum yields a value lying between  $p$  and  $p + dp$ .

Schrödinger theory has been developed in position as well as momentum representation in entirely equivalent way.

We know that problems in ordinary geometry may be solved using vectors without the necessity of using any coordinate system. A question thus arises—can quantum mechanics be formulated without using any particular representation? If the answer is yes, the results would then be independent of representation on the one hand, while on the other the obvious advantages of using a representation in such a formulation would not be lost. To carry out calculations we would be free to use any convenient representation, just like in geometry a coordinate system may be conveniently chosen when vectors are used.

In Dirac's formulation, quantum mechanics is developed without using any specific representation and instead it uses the concept of vectors in a space that may have a finite or an infinite dimension.

In the sections to follow a brief account of the essentials of Dirac's formulation is presented.

### 7.3.1 Wavefunction as Vector; Ket Vector

Let  $\psi(q)$  be the wavefunction that describes the state of a particle moving in one dimension at the time  $t$ . For each specific value of  $q$  (in the range  $-\infty$  to  $+\infty$ ), say  $q_1, q_2$ , etc., the wave function is  $\psi(q_1), \psi(q_2)$ , etc., respectively.

Let us imagine an infinite dimensional space having mutually perpendicular axes each labeled by one of the values of  $q$ . Let us now consider a vector in this space at the time  $t$  such that its projection on the  $q_i$  axis is  $\psi(q_1)$ , that on the  $q_2$ -axis is  $\psi(q_2)$  and so on. The vector thus considered then represents the state of the particle just as its components along the different axes do.

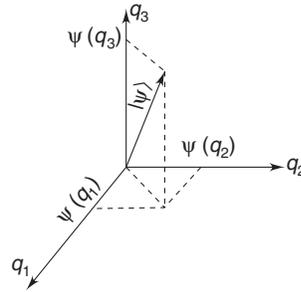
Since  $\psi$ 's are, in general, complex valued functions, the vector representing the state is not an ordinary vector in real space.

For Dirac, we call such a *state-vector* in a complex vector-space a *ket vector* or simply a *ket* and denote it by the symbol  $|\psi\rangle$ . The particular vector whose components are  $\psi(q_1), \psi(q_2)$ , etc., is called ket  $\psi$  and is written as  $|\psi\rangle$ .

In the Figure (7.1) is shown the ket vector  $|\psi\rangle$  and its components  $\psi(q_1), \psi(q_2)$ , etc., along the different axes (it is possible to show only three components).

## NOTES

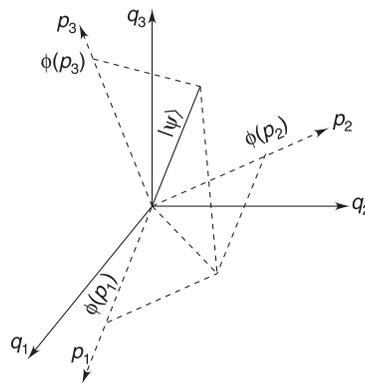
NOTES



**Fig. 7.1** Ket Vector  $|\psi\rangle$  and Three of its Coordinate Representatives

If  $A_x, A_y, A_z$  be the components of an ordinary vector  $\vec{A}$  along the axes of a Cartesian coordinate system  $XYZ$ , then the vector  $\vec{A}$  can be represented completely by these components, i.e.,  $\vec{A} = [A_x, A_y, A_z]$ . Likewise,  $|\psi\rangle$  may be completely represented by its components along the orthogonal  $q$ -axes, i.e.,  $|\psi\rangle = [\psi(q_1), \psi(q_2), \dots]$ . The vector  $|\psi\rangle$  thus represented is said to be given in the position representation.

If we now consider another Cartesian co-ordinate system  $X'Y'Z'$  rotated with respect to the system  $XYZ$  then the same vector  $\vec{A}$  may equally well be represented by its new components  $A'_x, A'_y$  and  $A'_z$  and we may write  $\vec{A} = [A'_x, A'_y, A'_z]$ . Exactly similarly, we may express  $|\psi\rangle$  in another representation, namely the momentum representation as  $|\psi\rangle = [\phi(p_1), \phi(p_2), \dots]$ . We may visualize  $\phi(p_1), \phi(p_2)$ , etc., as the components of  $|\psi\rangle$  on a rotated orthogonal set of axes  $p_1, p_2, \dots$  as shown in the Figure (7.2). The relation between the new  $p$ -axes and the old  $q$ -axes is given by Fourier transform.



**Fig. 7.2** Ket Vector  $|\psi\rangle$  and Three of its Momentum Representatives.

We note that by introducing the above concept of vector in complex vector space to describe physical state of a quantum system it is possible to visualize the possibility of an infinite number of equivalent representations in which quantum mechanics can be formulated.

### More About Ket-Vector

With each state of a dynamical system is associated a ket vector. A general ket is denoted by the symbol  $|\rangle$ . The ket vectors with labels inside such as  $|a\rangle$ ,  $|b\rangle$ , etc., designate particular states.

The state ket is postulated to contain complete information about the physical state.

The ket vector space is a linear vector space by which we mean that if  $C_1$  and  $C_2$  are two complex numbers and  $|a\rangle$  and  $|b\rangle$  are two ket vectors in a given space, the linear combination,

$$|\alpha\rangle = C_1 |a\rangle + C_2 |b\rangle \quad \dots(7.13)$$

is also a ket vector in the space of  $|a\rangle$  and  $|b\rangle$  and represents a state of the system.

If a ket depends on a parameter  $q'$  which may take any value in the range  $q'_1 < q' < q'_2$  then we may generalize Equation (7.13) as

$$|\beta\rangle = \int_{q'_1}^{q'_2} C(q') |q'\rangle dq' \quad \dots(7.14)$$

when  $C(q')$  is a complex function of  $q'$  and the vector  $|\beta\rangle$  is in ket space.

Kets  $|\alpha\rangle$  and  $|\beta\rangle$  defined by Equations (7.13) and (7.14), respectively are said to be linearly dependent on  $|a\rangle$  and  $|b\rangle$  and on  $|q'\rangle$ .

When  $C_1|a\rangle$  and  $C_2|a\rangle$  are added, the result is

$$C_1|a\rangle + C_2|a\rangle = (C_1 + C_2)|a\rangle \quad \dots(7.15)$$

In the above,  $C_1|a\rangle$ ,  $C_2|a\rangle$  and  $(C_1 + C_2)|a\rangle$  represent the same dynamical state of the system. If, however,  $C_1 + C_2 = 0$ , the result is no state at all.

From the above, it follows that dynamical state of a system is specified entirely by the direction of the ket vector representing the state in the ket space. In other words, there exists a one-to-one correspondence between the state of a system and a direction in ket vector space.  $|a\rangle$  and  $-|a\rangle$  represents the same state.

The above also shows that classical and quantum superposition principles are different. Quantum mechanically, there exists nothing that corresponds to classical amplitude. Instead, only the direction of ket is significant. Further, in quantum mechanics there is no state corresponding to no motion ( $C_1 + C_2 = 0$  in Equation 7.15); no motion is nothing at all. However, classically the state of rest (no motion) is a state of the system.

The dimensionality of ket space is determined by the number of linearly independent kets in the space, i.e., the number of independent states of the system under consideration.

### NOTES

## 7.3.2 Scalar Product, Bra Vector

## NOTES

With each ket  $|a\rangle$ , a complex number  $f$  is associated. The set of numbers associated with different  $|a\rangle$ 's is a linear function of  $|a\rangle$ . This means that the number associated with  $(|a_1\rangle + |a_2\rangle)$ , where  $|a_1\rangle$  and  $|a_2\rangle$  are two kets, is the sum of the numbers associated with  $|a_1\rangle$  and  $|a_2\rangle$  separately. Similarly, the number associated with  $C|a\rangle$ , where  $C$  is a complex number, is  $C$  times the number associated with  $|a\rangle$ . The above results may be written as,

$$f(|a_1\rangle + |a_2\rangle) = f(|a_1\rangle) + f(|a_2\rangle) \quad \dots(7.16)$$

$$f(C|a\rangle) = Cf|a\rangle \quad \dots(7.17)$$

The number  $f$  associated with all the kets in ket space may be visualized as defining a vector in another space (dual space) denoted, following Dirac, by the symbol  $\langle f|$ , and called the *bra* vector.

The scalar product of  $\langle f|$  and  $|a\rangle$  is written as  $\langle f|a\rangle$  and it is a complex number.

In view of the above, we may re-write Equations (7.16) and (7.17) as

$$\langle f|(|a_1\rangle + |a_2\rangle) = \langle f|a_1\rangle + \langle f|a_2\rangle \quad \dots(7.18)$$

$$\langle f|(C|a\rangle) = C\langle f|a\rangle \quad \dots(7.19)$$

If  $\langle b|a\rangle = 0$  for all  $|a\rangle$ , we may conclude that  $\langle b| = 0$ , i.e.,  $\langle b|$  is a *null bra*.

$$\text{If,} \quad \langle b_1|a\rangle = \langle b_2|a\rangle \text{ for all } |a\rangle \quad \dots(7.20)$$

$$\text{then} \quad \langle b_1| = \langle b_2| \quad \dots(7.21)$$

The sum of two bras  $\langle b_1|$  and  $\langle b_2|$  is defined by its scalar product with  $|a\rangle$ . Thus

$$(\langle b_1| + \langle b_2|)|a\rangle = \langle b_1|a\rangle + \langle b_2|a\rangle \quad \dots(7.22)$$

It is *assumed* that each ket is associated with a single bra in a unique way. Hence bra is given the same status as the ket to which it is associated.  $\langle a|$  is the bra associated with the ket  $|a\rangle$ .

Consider the ket

$$|\alpha\rangle = |a\rangle + |b\rangle \quad \dots(7.23)$$

The bra associated with  $|\alpha\rangle$  is then

$$\langle \alpha| = \langle a| + \langle b| \quad \dots(7.24)$$

With the ket,

$$|\beta\rangle = C|a\rangle, \quad C = \text{A complex number} \quad \dots(7.25)$$

is associated the bra,

$$\langle\beta| = C^* \langle a|, \quad C^* = \text{Complex conjugate of } C \dots(7.26)$$

From the above, it is reasonable to call the bra  $\langle\alpha|$  associated with a ket  $|\alpha\rangle$  as the hermitian adjoint of  $|\alpha\rangle$  and vice-versa, i.e.,

$$\langle\alpha| = (|\alpha\rangle)^\dagger, \quad |\alpha\rangle = (\langle\alpha|)^\dagger \quad \dots(7.27)$$

Since there exists unique correspondence between bras and kets, the direction of a bra vector represents the state of a quantum system as does the direction of the associated ket. Hence, they are said to be *dual* of one another.

### 7.3.3 Norm of a Ket

Consider two kets  $|a\rangle$  and  $|b\rangle$  and the bras  $\langle a|$  and  $\langle b|$  associated with them, respectively. We can form four numbers, namely

$$\langle a|a\rangle, \quad \langle a|b\rangle, \quad \langle b|b\rangle \quad \text{and} \quad \langle b|a\rangle$$

In general,  $\langle a|b\rangle$  and  $\langle b|a\rangle$  are complex, and it is assumed that they are related as

$$\langle a|b\rangle = \langle b|a\rangle^* \quad \dots(7.28)$$

Replacing  $|b\rangle$  by  $|a\rangle$  in Equation (7.28) we get

$$\langle a|a\rangle = \langle a|a\rangle^* \quad \dots(7.29)$$

Clearly,  $\langle a|a\rangle$  is real and is called the length or norm of  $|a\rangle$ .

It is assumed that the norm of a ket vector is either positive or zero, i.e.,

$$\langle a|a\rangle \geq 0 \quad \dots(7.30)$$

Equality sign holds in the above if  $|a\rangle = 0$ .

The assumption given by Equations (7.28) and (7.29) are motivated from a consideration of wave function  $\psi(q, t)$  and its complex conjugate  $\psi^*(q, t)$ . As seen earlier,  $\psi(q, t)$  is visualized as components of  $|\psi\rangle$  in ket space. Likewise, we may visualize  $\psi^*(q, t)$  as the components of  $\langle\psi|$  in the bra space. We know from wave mechanics that the complex numbers  $\psi^*(q, t)$   $\chi(q, t)$  and  $\chi^*(q, t)$   $\psi(q, t)$  are related as

$$\psi^*(q, t) \chi(q, t) = [\chi^*(q, t) \psi(q, t)]^* \quad \dots(7.31)$$

We also know that

$$\int |\psi(q, t)|^2 dq \geq 0 \quad \dots(7.32)$$

Since bras and kets are intimately related to wave functions, relations similar to those given by Equations (7.31) and (7.32) should hold also for them. Such relations are given by Equations (7.28) and (7.30).

## NOTES

### 7.3.4 Orthogonality of Kets and Bras

In wave mechanics, the wave functions  $\psi(q)$  and  $\phi(q)$  are orthogonal, if

$$\int \psi^*(q) \phi(q) dq = 0 \quad \dots(7.33)$$

#### NOTES

In the case of kets and bras, the vectors  $|a\rangle$  and  $|b\rangle$  are orthogonal if their scalar product is zero, i.e., if

$$\langle a|b\rangle = 0 \quad \dots(7.34)$$

The orthogonality involved with ket/bra vector is different from the orthogonality of two ordinary vectors, say,  $\vec{A}$  and  $\vec{B}$  in the real space. If  $\vec{A}$  and  $\vec{B}$  are orthogonal, i.e., if  $\vec{A} \cdot \vec{B} = 0$ ,  $\vec{A}$  and  $\vec{B}$  are at right angles to each other and they lie in the same vector space. In the orthogonality condition given by Equation (7.34), we may note that  $\langle a|$  and  $|b\rangle$  are in different vector spaces. Further, if  $\langle a|b\rangle = 0$  we may say that not only  $|a\rangle$  and  $|b\rangle$  are orthogonal but also  $\langle a|$  and  $\langle b|$  are orthogonal. When  $\langle a|b\rangle = 0$  it may also be said that the associated quantum states of the system they represent are orthogonal.

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## 7.4 SOLUTION USING LADDER OPERATOR AND MATRIX REPRESENTATION

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If with each ket  $|a\rangle$  in the ket space we can associate another ket  $|b\rangle$ , then this association may be used to define an operator say  $\hat{\alpha}$  which we may write in the form

$$|b\rangle = \hat{\alpha}|a\rangle \quad \dots(7.35)$$

$\hat{\alpha}$  in the above might mean multiplication, differentiation, integration, etc., operations.

An operator always appears to the left of the ket on which it operates.

A class of operators used extensively in the formulation of quantum mechanics is the *linear operators*. A linear operator in ket space is defined as given in the following; if  $|a_1\rangle$ ,  $|a_2\rangle$  and  $|a\rangle$  are any three kets in the space and  $C$  is a number then an operator  $\hat{\alpha}$  is said to be linear if

$$\hat{\alpha} ( |a_1\rangle + |a_2\rangle ) = \hat{\alpha} |a_1\rangle + \hat{\alpha} |a_2\rangle \quad \dots(7.36)$$

And  $\hat{\alpha}(C |a\rangle) = C \hat{\alpha} |a\rangle \quad \dots(7.37)$

### Equal Linear Operators

A linear operator is completely defined when its effect on every ket in the ket space is known. Hence, two linear operators  $\hat{\alpha}_1$  and  $\hat{\alpha}_2$  are equal ( $\hat{\alpha}_1 = \hat{\alpha}_2$ ) if

$$\hat{\alpha}_1 |a\rangle = \hat{\alpha}_2 |a\rangle \quad \text{for all } |a\rangle \quad \dots(7.38)$$

**Null Operator**

A linear operator  $\hat{\alpha}$  is a *null operator* if

$$\hat{\alpha}|a\rangle = 0 \quad \text{for all } |a\rangle \quad \dots(7.39)$$

**Identity operator**

A linear Operator  $\hat{\alpha}$  is said to be an *identity operator* if

$$\hat{\alpha}|a\rangle = |a\rangle \quad \text{for all } |a\rangle \quad \dots(7.40)$$

**Algebra of Linear Operators**

(i) **Sum** of two linear operators  $\hat{\alpha}_1$  and  $\hat{\alpha}_2$ , i.e.,  $(\hat{\alpha}_1 + \hat{\alpha}_2)$  is defined according to

$$(\hat{\alpha}_1 + \hat{\alpha}_2)|a\rangle = \hat{\alpha}_1|a\rangle + \hat{\alpha}_2|a\rangle \quad \dots(7.41)$$

(ii) **Product** of two linear operators  $\hat{\alpha}_1$  and  $\hat{\alpha}_2$ , i.e.,  $(\hat{\alpha}_1 \hat{\alpha}_2)$  is defined according to

$$(\hat{\alpha}_1 \hat{\alpha}_2)|a\rangle = \hat{\alpha}_1(\hat{\alpha}_2|a\rangle) \quad \dots(7.42)$$

From Equation (7.42) it is possible to define powers of a linear operator.

We further find the following relations to hold

$$(\hat{\alpha}_1 + \hat{\alpha}_2)|a\rangle = (\hat{\alpha}_2 + \hat{\alpha}_1)|a\rangle \quad \dots(7.43)$$

$$[(\hat{\alpha}_1 + \hat{\alpha}_2) + \hat{\alpha}_3]|a\rangle = [\hat{\alpha}_1 + (\hat{\alpha}_2 + \hat{\alpha}_3)]|a\rangle \quad \dots(7.44)$$

$$[\hat{\alpha}_1(\hat{\alpha}_2 + \hat{\alpha}_3)]|a\rangle = \hat{\alpha}_1\hat{\alpha}_2|a\rangle + \hat{\alpha}_1\hat{\alpha}_3|a\rangle \quad \dots(7.45)$$

(iii) **Commutator** of two linear operators  $\hat{\alpha}_1$  and  $\hat{\alpha}_2$  is written as  $[\hat{\alpha}_1, \hat{\alpha}_2]$  and is defined as

$$[\hat{\alpha}_1, \hat{\alpha}_2] = \hat{\alpha}_1\hat{\alpha}_2 - \hat{\alpha}_2\hat{\alpha}_1 \quad \dots(7.46)$$

The operator  $\hat{\alpha}_1$  and  $\hat{\alpha}_2$  are said to be *non-commutative* if

$$\hat{\alpha}_1\hat{\alpha}_2 \neq \hat{\alpha}_2\hat{\alpha}_1, \text{ i.e., } [\hat{\alpha}_1, \hat{\alpha}_2] \neq 0 \quad \dots(7.47)$$

We may note that the above properties hold with matrices.

It is seen that the algebra of  $N$ -dimensional square matrices is the same as the algebra of linear operators.

We may further note that the algebra of quantum mechanics is a non-commutative algebra.

Multiplication by a constant is linear operation. A constant operator commutes with all linear operators.

(iv) **Inverse of an Operator:** If two linear operators  $\hat{\alpha}_1$  and  $\hat{\alpha}_2$  satisfy the equation

$$\hat{\alpha}_1\hat{\alpha}_2 = \hat{\alpha}_2\hat{\alpha}_1 = \hat{I} \text{ (Identity operator)} \quad \dots(7.48)$$

then  $\hat{\alpha}_2$  is said to be the *inverse* of  $\hat{\alpha}_1$  and vice-versa, provided the inverse exists and we write

**NOTES**

$$\hat{\alpha}_2 = \hat{\alpha}_1^{-1}, \quad \hat{\alpha}_1 = \hat{\alpha}_2^{-1} \quad \dots(7.49)$$

The inverse of a product of operators ( $\hat{\alpha}_1, \hat{\alpha}_2, \hat{\alpha}_3$ ) is

$$(\hat{\alpha}_1 \hat{\alpha}_2 \hat{\alpha}_3)^{-1} = \hat{\alpha}_3^{-1} \hat{\alpha}_2^{-1} \hat{\alpha}_1^{-1} \quad \dots(7.50)$$

## NOTES

As mentioned earlier, the above properties of linear operators are common to finite square matrices. This fact allows us to *represent operators by matrices*.

### Operation of Linear Operator on Bra

By operating a linear operator (say  $\hat{\alpha}$ ) on a bra (say  $\langle c |$ ) we obtain, in general, another bra (say  $\langle d |$ ) in the same bra space. It is a convention to write the operator to the right of the bra on which it operates. Hence we write,

$$\langle d | = \langle c | \hat{\alpha} \quad \dots(7.51)$$

The operation is defined through the equation,

$$\langle c | (\hat{\alpha} | a \rangle) = (\langle c | \hat{\alpha} | a \rangle). \quad \dots(7.52)$$

Thus,  $\hat{\alpha}$  may first operate on  $\langle c |$  and the result applied to  $| a \rangle$  or vice-versa.

We may note that operator properties given above are equally valid whether they are applied to kets or to bras.

### An Example of a Linear Operator

A simple example of a linear operator that occurs frequently in quantum theory is,

$$| a \rangle \langle b | = \hat{P} \quad \dots(7.53)$$

$\hat{P}$  may operate as a ket, say,  $| c \rangle$  to give

$$\hat{P} | c \rangle = | a \rangle \langle b | c \rangle$$

The above is the ket  $| a \rangle$  multiplied by the number  $\langle b | c \rangle$

$\hat{P}$  may operate on the bra  $\langle c |$  to give

$$\langle c | \hat{P} = \langle c a \rangle \langle b. \quad \dots(7.54)$$

The above is the bra  $\langle b |$  multiplied by the number  $\langle c | a \rangle$ .

The operator  $\hat{P}$  defined above is seen to satisfy the requirements of a linear operator.

### Hermitian Operators

As discussed earlier, the linear operators which represent dynamical variables of a quantum system are real linear operators. Such operators are said to be

Hermitian. In the following we define Hermitian operator in the space of ket and bra vectors.

Consider the ket  $|q\rangle$  to be the result of operation of the linear operator  $\hat{\alpha}$  on a ket  $|p\rangle$ , i.e.,

$$|q\rangle = \hat{\alpha} |p\rangle$$

The bra associated with ket  $|q\rangle$  is then given by,

$$\langle q| = \langle p| \hat{\alpha}^\dagger = \hat{\alpha}^\dagger |p\rangle^\dagger = (|q\rangle)^\dagger$$

The symbol  $\hat{\alpha}^\dagger$  is called the Hermitian adjoint of  $\hat{\alpha}$ . Thus, the bra  $\langle q|$  which is hermitian adjoint of  $|q\rangle$  may be considered as the result of some linear operator operating on  $\langle p|$  which is designated by  $\hat{\alpha}^\dagger$ .

If in Equation (7.28) we take  $\langle a| = \langle p| \hat{\alpha}^\dagger$  and  $|a\rangle = \hat{\alpha} |p\rangle$ , then we get

$$\langle p| \hat{\alpha}^\dagger |b\rangle = \langle b| \hat{\alpha} |p\rangle^* \quad \dots(7.55)$$

Equation (7.55) is a general result that applies to any two kets  $|p\rangle$  and  $|b\rangle$  and any linear operator  $\hat{\alpha}$ .

We may replace  $\hat{\alpha}$  by  $\hat{\alpha}^\dagger$  in Equation (7.55) to obtain

$$\langle p| \hat{\alpha}^{\dagger\dagger} |b\rangle = \langle b| \hat{\alpha}^\dagger |p\rangle^* \quad \dots(7.56)$$

Let us now replace  $|a\rangle$  in Equation (7.28) by  $|a\rangle = \hat{\alpha}^\dagger |p\rangle$

and  $\langle a| = \langle p| \hat{\alpha}$ . We then get

$$\langle p| \hat{\alpha} |b\rangle = \langle b| \hat{\alpha}^\dagger |p\rangle^* \quad \dots(7.57)$$

Comparing Equations (7.56) and (7.57) we obtain

$$\langle p| \hat{\alpha}^\dagger |b\rangle = \langle p| \hat{\alpha} |b\rangle. \quad \dots(7.58)$$

Since in Equation (7.58) ket  $|b\rangle$  and bra  $\langle p|$  are arbitrary, we find that

$$\hat{\alpha}^{\dagger\dagger} = \hat{\alpha} \quad \dots(7.59)$$

If the linear operator  $\hat{\alpha}$  is self adjoint, i.e., if

$$\hat{\alpha} = \hat{\alpha}^\dagger$$

then  $\hat{\alpha}$  is said to be Hermitian. From Equation (7.55) we find that if  $\hat{\alpha}$  is Hermitian, it must satisfy

$$\langle p| \hat{\alpha}^\dagger |b\rangle = \langle b| \hat{\alpha} |p\rangle^* \quad \dots(7.60)$$

for arbitrary  $|b\rangle$  and  $|p\rangle$ .

## NOTES

## Eigenvalue Problem for Operators in Ket and Bra Space

Let us consider a linear operator  $\hat{\alpha}$ . In general,  $\hat{\alpha}$  operating on a ket gives another ket in the same space.

### NOTES

However, for every linear operator there exists a set of kets such that the result of operation of the operator on any such ket is the same ket multiplied by a number. If  $|a\rangle$  be such a ket for the operator  $\hat{\alpha}$  then we obtain

$$\hat{\alpha} |a\rangle = \alpha_a |a\rangle \quad \dots(7.61)$$

$\alpha_a$  being a number.

Equation (7.61) is referred to as the eigenvalue problem for the operator  $\hat{\alpha}$ ,  $|a\rangle$  is said to be the eigen ket of  $\hat{\alpha}$  and  $\alpha_a$  the associated eigenvalue.

It is customary to label an eigenket with the associated eigenvalue. With this convention, we may rewrite the eigenvalue problem (eigenvalue equation) as

$$\hat{\alpha} |\alpha_a\rangle = \alpha_a |\alpha_a\rangle \quad \dots(7.61a)$$

If  $|\alpha_a\rangle$  is an eigenket of  $\hat{\alpha}$ , then by Equation (7.62) any constant  $c$  times  $|\alpha_a\rangle$  is also an eigenket of  $\hat{\alpha}$  with the same eigenvalue  $\alpha_a$ . The states represented by  $|\alpha_a\rangle$  and  $c|\alpha_a\rangle$  are one and the same state.

Eigenvalue problem formulated in terms of bras is

$$\langle\beta_a| \hat{\beta} = \beta_a \langle\beta_a|. \quad \dots(7.61b)$$

In the above  $\langle\beta_a|$  is an eigenbra of the linear operator  $\hat{\beta}$  belonging to the eigenvalue  $\beta_a$ .

### Theorems Valid for All Linear Hermitian Operators

Earlier we discussed the following two theorems related to linear Hermitian operators. We once again state the theorems and prove them using Dirac's bra and ket notations.

**Theorem 1:** The eigenvalues of a linear Hermitian operator are real.

**Proof:** Consider a linear hermitian operator  $\hat{\alpha}$ . The eigenvalues of  $\hat{\alpha}$  satisfy the equation

$$\hat{\alpha} |\alpha_k\rangle = \alpha_k |\alpha_k\rangle$$

Forming scalar product of both sides of the above equation with  $\langle\alpha_k|$ , we get

$$\langle\alpha_k| \hat{\alpha} |\alpha_k\rangle = \alpha_k \langle\alpha_k| \alpha_k\rangle \quad \dots(7.62)$$

Taking complex conjugate of both sides we obtain

$$\langle\alpha_k| \hat{\alpha} |\alpha_k\rangle^* = \langle\alpha_k| \hat{\alpha}^\dagger |\alpha_k\rangle = \alpha_k^* \langle\alpha_k| \alpha_k\rangle \quad \dots(7.63)$$

But since  $\hat{\alpha}^\dagger = \hat{\alpha}$  and  $\langle \alpha_k | \alpha_k \rangle \neq 0$ , comparing Equations (7.62) and (7.63) we get

$$\alpha_k = \alpha_k^* \quad \dots(7.64)$$

Clearly the eigenvalue  $\alpha_k$  is real.

**Theorem 2:** Two eigenvectors of a linear Hermitian operator belonging to different eigenvalues are orthogonal.

**Proof:** Consider a linear Hermitian operator  $\hat{\alpha}$ .

Let  $|\alpha_j\rangle$  be the eigenvector of  $\hat{\alpha}$  belonging to eigenvalue  $\alpha_j$  and  $|\alpha_k\rangle$  be the eigenvector of  $\alpha$  belonging to eigenvalue  $\alpha_k$ .

We then have according to our considerations

$$\left. \begin{aligned} \hat{\alpha} &= \hat{\alpha}^\dagger \\ \alpha_j &= \alpha_j^* ; \alpha_k = \alpha_k^* \end{aligned} \right\} \quad \dots(7.65)$$

Let  $\langle \alpha_k |$  be the eigenbra associated with the eigenket  $|\alpha_k\rangle$ .

We then have the eigenvalue equations

$$\hat{\alpha} |\alpha_j\rangle = \alpha_j |\alpha_j\rangle \quad \dots(7.66)$$

$$\langle \alpha_k | \hat{\alpha} = \alpha_k \langle \alpha_k | \quad \dots(7.67)$$

Forming scalar product of Equation (7.65) with  $\langle \alpha_k |$ , we get

$$\langle \alpha_k | \hat{\alpha} |\alpha_j\rangle = \alpha_j \langle \alpha_k | \alpha_j\rangle \quad \dots(7.68)$$

Similarly, forming scalar product of Equation (7.67) with  $|\alpha_j\rangle$  we obtain

$$\langle \alpha_k | \hat{\alpha} |\alpha_j\rangle = \alpha_k \langle \alpha_k | \alpha_j\rangle \quad \dots(7.69)$$

Subtracting Equation (7.69) from Equation (7.68), we get

$$(\alpha_j - \alpha_k) \langle \alpha_k | \alpha_j\rangle = 0 \quad \dots(7.70)$$

Since  $\alpha_j$  and  $\alpha_k$  are two different eigenvalues, Equation (7.70) gives

$$\langle \alpha_k | \alpha_j\rangle = 0 \quad \dots(7.71)$$

Clearly, the eigenvectors  $|\alpha_j\rangle$  and  $|\alpha_k\rangle$  are orthogonal to each other.

We may note from Equations (7.66) and (7.67) that the eigenvalues associated with eigenkets are the same as those associated with the corresponding bras.

**Physical Interpretation to Eigenvalues; Completeness, Expansion in Eigenkets**

Any dynamical variable of a system that can be measured is called an observable of that system.

**NOTES**

## NOTES

According to a basic postulate of quantum mechanics, with every observable there is associated a Hermitian operator and the result of measurement of an observable is an eigenvalue of the corresponding operator.

Consider an observable  $\hat{\alpha}$  of a quantum system. Let  $\hat{\alpha}$  be the corresponding Hermitian operator. If the system is in a particular eigen state of  $\hat{\alpha}$ , say  $|\alpha_k\rangle$ , then if we measure  $\alpha$  we obtain the value  $\alpha_k$ . We assume that if we measure  $\alpha$  and in each measurement we obtain the value  $\alpha_k$  with certainty, that is, if we measure  $\alpha$  for a large number of systems each prepared in an identical way and always get the value  $\alpha_k$ , then we say that the system is in the state  $|\alpha_k\rangle$ .

Furthermore, when a single measurement of  $\alpha$  is made on the system in an arbitrary state, we obtain one of the eigen values of  $\hat{\alpha}$ . In such a measurement the measurement process disturbs the system and causes it to jump into one of the eigen states of  $\hat{\alpha}$ .

The eigenkets of the operator  $\hat{\alpha}$  corresponding to the observable  $\alpha$  form an orthonormal set,

$$\langle l_i | l_j \rangle = \delta_{ij} \quad \dots(7.72)$$

where  $\delta_{ij}$  is the Kronecker delta,

$$\left. \begin{aligned} \delta_{ij} &= 0 & \text{if } i \neq j \\ &= 1 & \text{if } i = j \end{aligned} \right\} \quad \dots(7.73)$$

It is postulated that any state of the system is linearly dependent on the eigenkets  $|\alpha_k\rangle$ . In other words eigenkets of  $\hat{\alpha}$  form a complete set. Any arbitrary state described by the ket  $|P\rangle$  can thus be written in terms of the eigenkets of  $\hat{\alpha}$  as

$$|P\rangle = \sum_k a_k |\alpha_k\rangle \quad \dots(7.74)$$

If a measurement of  $\alpha$  is made in the state described by  $|P\rangle$  then  $|a_k|^2$  gives the probability of obtaining the value  $\alpha_k$ .

If the system is in a state described by the normalized ket

$$|P\rangle = a_1 |\alpha_1\rangle + a_2 |\alpha_2\rangle \quad \dots(7.75)$$

then a measurement of  $\alpha$  gives either the value  $\alpha_1$  with probability  $|a_1|^2$  or the value  $\alpha_2$  with probability  $|a_2|^2$ . Since  $\langle P|P\rangle = 1$ , we obtain

$$|P\rangle = \sum_k a_k |\alpha_k\rangle \quad \dots(7.74) \quad |a_1|^2 + |a_2|^2 = 1. \quad \dots(7.76)$$

We know that the eigenkets of  $\hat{\alpha}$  form an orthonormal set so that

$$\langle \alpha_i | \alpha_j \rangle = \delta_{ij}$$

We have

$$\langle \alpha_i | P \rangle = \sum_k C_k \langle \alpha_i | \alpha_k \rangle = \sum_k C_k \delta_{ik} = C_i \quad \dots(7.77)$$

Thus,  $|P\rangle = \sum_k |\alpha_k\rangle C_k = \{ \sum_k |\alpha_k\rangle \langle \alpha_k | P \rangle \}$

$$(\because C_k = \langle \alpha_k | P \rangle \text{ from Equation (7.76)})$$

Since the above result holds for all arbitrary kets we must have

$$\sum_k |\alpha_k\rangle \langle \alpha_k| = 1. \quad \dots(7.78)$$

The above equation is referred to as the completeness condition of eigenkets of the operator corresponding to an observable of a quantum system.

**Classical Definition of Angular Momentum**

Let us first consider the angular momentum classically. For this, let us consider a particle of mass  $m$  moving along a path  $AB$  about some fixed point  $O$  as shown in the Figure (7.3). Let at some instant of time, the particle be at the position  $P$ . The position  $P$  of the particle with respect to the point  $O$  is defined by the position vector  $\vec{OP}$  or  $\vec{r}$ . Let the linear momentum of the particle at the position  $P$  be  $\vec{p}$ . The direction of  $\vec{p}$  is along the tangent to the path  $AB$  at  $P$ .

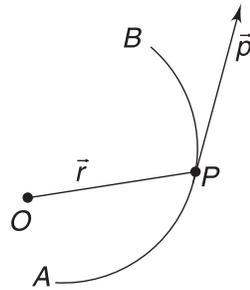


Fig. 7.3 Angular Momentum

Classically, the angular momentum (which is a vector quantity) of the particle about the point  $O$  when it is at  $P$  is defined as

$$\vec{L} = \vec{r} \times \vec{p} \quad \dots(7.79)$$

With the point  $O$  as the origin, let us consider a rectangular coordinate system  $(XYZ)$ . If  $x, y, z$  be the coordinates of the point  $P$  then

$$\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z \quad \dots(7.80)$$

Further, if  $p_x, p_y$  and  $p_z$  be respectively the components of  $\vec{p}$  along  $X, Y$  and  $Z$  axes then

$$\vec{p} = \hat{i}p_x + \hat{j}p_y + \hat{k}p_z \quad \dots(7.81)$$

**NOTES**

If  $L_x$ ,  $L_y$  and  $L_z$  be respectively the X, Y and Z components of  $\vec{L}$ , then using equations (7.80) and (7.81) in Equation (7.79), we get

**NOTES**

$$\hat{i}L_x + \hat{j}L_y + \hat{k}L_z = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

Evaluating the right hand side of the above equation and comparing the coefficients of  $\hat{i}$ ,  $\hat{j}$  and  $\hat{k}$  on both sides we obtain

$$L_x = yp_z - zp_y \quad \dots(7.82)$$

$$L_y = zp_x - xp_z \quad \dots(7.83)$$

$$L_z = xp_y - yp_x \quad \dots(7.84)$$

**Quantum Mechanical Description of Angular Momentum**

In order to treat angular momentum quantum mechanically, we replace the physical quantities  $\vec{L}$ ,  $\vec{r}$ ,  $\vec{p}$ ,  $L_x$ ,  $L_y$ ,  $L_z$ ,  $x$ ,  $y$ ,  $z$ ,  $p_x$ ,  $p_y$  and  $p_z$  by corresponding linear Hermitian operators,

$$x \rightarrow \hat{x} = x$$

$$y \rightarrow \hat{y} = y$$

$$z \rightarrow \hat{z} = z$$

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

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

$$p_z \rightarrow \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \quad \dots(7.85)$$

Substituting the above in Equations (7.79), (7.82), (7.83) and (7.84) we obtain the quantum mechanical operators corresponding to the quantities  $\vec{L}$ ,  $L_x$ ,  $L_y$ ,  $L_z$  as

$$\hat{\vec{L}} = -i\hbar \vec{r} \times \vec{\nabla} \quad \dots(7.86)$$

$$\hat{L}_x = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad \dots(7.87)$$

$$\hat{L}_y = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad \dots(7.88)$$

$$\hat{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad \dots(7.89)$$

## Step-Up (Raising) and Step-Down (Lowering) Operators or Ladder Operators

Instead of  $\hat{L}_x$  and  $\hat{L}_y$  it is often convenient and more instructive to use their complex combinations  $\hat{L}_x \pm i\hat{L}_y$ .

$$\text{The operator } \hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \dots(7.90)$$

is called the step-up operator.

$$\text{The operator } \hat{L}_- = \hat{L}_x - i\hat{L}_y \quad \dots(7.91)$$

is called the step-down operator.

$$\text{We find } \hat{L}_z \hat{L}_+ = \hat{L}_z (\hat{L}_x + i\hat{L}_y) = \hat{L}_z \hat{L}_x + i\hat{L}_z \hat{L}_y \quad \dots(7.92)$$

Using the commutation relations Equation (7.92) becomes

$$\begin{aligned} \hat{L}_z \hat{L}_+ &= \hat{L}_x \hat{L}_z + i\hat{L}_y \hat{L}_z + i(\hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y) \\ &= (\hat{L}_x + i\hat{L}_y) \hat{L}_z + (\hat{L}_x + i\hat{L}_y) \\ &= \hat{L}_+ \hat{L}_z + \hat{L}_+ \end{aligned}$$

or

$$\hat{L}_z \hat{L}_+ = \hat{L}_+ (\hat{L}_z + 1) \quad \dots(7.93)$$

Similarly, we obtain

$$\hat{L}_z \hat{L}_- = \hat{L}_- (\hat{L}_z + 1) \quad \dots(7.94)$$

Let  $Y_{lm}$  be a simultaneous eigenfunction of  $\hat{L}^2$  and  $\hat{L}_z$  belonging to eigenvalue  $m$  of  $\hat{L}_z$ . We obtain

$$\begin{aligned} \hat{L}_z \hat{L}_+ Y_{lm} &= \hat{L}_+ (\hat{L}_z + 1) Y_{lm} \quad [\text{using Equation (7.93)}] \\ &= \hat{L}_+ \hat{L}_z Y_{lm} + \hat{L}_+ Y_{lm} \\ &= \hat{L}_+ m Y_{lm} + \hat{L}_+ Y_{lm} \end{aligned}$$

or

$$\hat{L}_z (\hat{L}_+ Y_{lm}) = (m + 1) (\hat{L}_+ Y_{lm}) \quad \dots(7.95)$$

Similarly, we get

$$\hat{L}_z (\hat{L}_- Y_{lm}) = (m - 1) (\hat{L}_- Y_{lm}) \quad \dots(7.96)$$

Equation (7.95) shows that  $\hat{L}_+ Y_{lm}$  is an eigenfunction of  $\hat{L}_z$  belonging to eigenvalue  $(m + 1)$ , i.e., an eigenvalue one unit greater while Equation (7.96) shows that  $\hat{L}_- Y_{lm}$  is an eigenfunction of  $\hat{L}_z$  with eigenvalue  $(m - 1)$ , i.e., an eigenvalue one unit less than the eigenvalue  $m$  belonging to the eigenfunction  $Y_{lm}$ . For the above reasons, the operators  $\hat{L}_+$  and  $\hat{L}_-$  are Respectively, called the step-up and step-down operators or ladder operators.

## NOTES

## NOTES

**Check Your Progress**

1. Why was Bohr's theory extended?
2. Give the displacement equation of the particle from the equilibrium position at any instant  $t$ .
3. According to the Schrödinger formulation of quantum mechanics, explain the physical state at any time  $t$ .
4. What is ket vector? How it is represented?
5. How is a dynamical system associated with a ket vector? How is a general ket denoted?
6. Explain that each ket is associated with a single bra.
7. When the ket and bra said to be dual of one another?
8. When a linear operator is a null operator?

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### 7.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

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1. Bohr's theory was extended by Arnold Sommerfeld in the year 1915 by introducing elliptical orbits for the electrons in atoms.
2. The displacement of the particle from the equilibrium position at any instant  $t$  is given by

$$x = a \sin \omega_0 t$$

where  $a$  is amplitude and  $\omega_0$  is the natural frequency related to the force constant according to

$$\omega_0 = \sqrt{\frac{k}{m}}$$

3. According to the Schrödinger formulation of quantum mechanics, the physical state at any time  $t$ , say, of a particle of mass  $m$  moving in one dimension in a potential field  $V(q)$ ,  $q$  being the coordinate of the particle which can take values from  $-\infty$  to  $+\infty$ , is described, in general by a complex valued function  $\psi(q, t)$  called the wave function in the position or coordinate representation.
4. Since  $\psi$ 's are, in general, complex valued functions, the vector representing the state is not an ordinary vector in real space.

For Dirac, we call such a *state-vector* in a complex vector-space a *ket vector* or simply a *ket* and denote it by the symbol  $|\rangle$ . The particular vector whose components are  $\psi(q_1)$ ,  $\psi(q_2)$ , etc., is called ket  $\psi$  and is written as  $|\psi\rangle$ .

5. With each state of a dynamical system is associated a ket vector. A general ket is denoted by the symbol  $|\rangle$ . The ket vectors with labels inside such as  $|a\rangle$ ,  $|b\rangle$ , etc., designate particular states.

The state ket is postulated to contain complete information about the physical state.

6. It is *assumed* that each ket is associated with a single bra in a unique way. Hence bra is given the same status as the ket to which it is associated.  $\langle a|$  is the bra associated with the ket  $|a\rangle$ .
7. Since there exists unique correspondence between bras and kets, the direction of a bra vector represents the state of a quantum system as does the direction of the associated ket. Hence, they are said to be *dual* of one another.
8. A linear operator  $\hat{a}$  is a *null operator* if

$$\hat{a}|a\rangle = 0 \quad \text{for all } |a\rangle$$

## NOTES

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## 7.6 SUMMARY

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- Bohr's theory was extended by Arnold Sommerfeld in the year 1915 by introducing elliptical orbits for the electrons in atoms.
- In the case of motion of electron in circular orbits, the number of degrees of freedom is only one and the angular momentum  $l = mvr$  is a constant of motion.
- The displacement of the particle from the equilibrium position at any instant  $t$  is given by  $x = a \sin \omega_0 t$

where  $a$  is amplitude and  $\omega_0$  is the natural frequency related to the force constant according to  $\omega_0 = \sqrt{\frac{k}{m}}$

- The potential energy of the oscillator is given by

$$V = \frac{1}{2} kx^2 = \frac{1}{2} m\omega_0^2 a^2 \sin^2(\omega_0 t) \quad \dots(7.6)$$

- The kinetic energy of the oscillator is

$$T = \frac{1}{2} mv^2 = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 = \frac{1}{2} ma^2 \omega_0^2 \cos^2(\omega_0 t)$$

- Thus the quantization rule applied to linear harmonic oscillator gives the energy of the oscillator to be zero or an integral multiple of  $\hbar\omega_0$  and not continuous.
- According to the Schrödinger formulation of quantum mechanics, the physical state at any time  $t$ , say, of a particle of mass  $m$  moving in one dimension in a potential field  $V(q)$ ,  $q$  being the coordinate of the

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particle which can take values from  $-\infty$  to  $+\infty$ , is described, in general by a complex valued function  $\psi(q, t)$  called the wave function in the position or coordinate representation.

- According to Max Born and Jordan,  $|\psi(q, t)|^2 dq$  gives the probability of finding the particle between the position  $q$  and  $q + dq$  if a measurement is made.
- In Dirac's formulation, quantum mechanics is developed without using any specific representation and instead it uses the concept of vectors in a space that may have a finite or an infinite dimension.
- Since  $\psi$ 's are, in general, complex valued functions, the vector representing the state is not an ordinary vector in real space.
- For Dirac, we call such a *state-vector* in a complex vector-space a *ket vector* or simply a *ket* and denote it by the symbol  $|\rangle$ . The particular vector whose components are  $\psi(q_1)$ ,  $\psi(q_2)$ , etc., is called ket  $\psi$  and is written as  $|\psi\rangle$ .
- With each state of a dynamical system is associated a ket vector. A general ket is denoted by the symbol  $|\rangle$ . The ket vectors with labels inside such as  $|a\rangle$ ,  $|b\rangle$ , etc., designate particular states.
- The state ket is postulated to contain complete information about the physical state.
- The dimensionality of ket space is determined by the number of linearly independent kets in the space, i.e., the number of independent states of the system under consideration.
- The scalar product of  $\langle f|$  and  $|a\rangle$  is written as  $\langle f|a\rangle$  and it is a complex number.
- It is *assumed* that each ket is associated with a single bra in a unique way. Hence bra is given the same status as the ket to which it is associated.  $\langle a|$  is the bra associated with the ket  $|a\rangle$ .
- Since there exists unique correspondence between bras and kets, the direction of a bra vector represents the state of a quantum system as does the direction of the associated ket. Hence, they are said to be *dual* of one another.
- Consider two kets  $|a\rangle$  and  $|b\rangle$  and the bras  $\langle a|$  and  $\langle b|$  associated with them, respectively. We can form four numbers, namely  $\langle a|a\rangle$ ,  $\langle a|b\rangle$ ,  $\langle b|b\rangle$  and  $\langle b|a\rangle$
- In the case of kets and bras, the vectors  $|a\rangle$  and  $|b\rangle$  are orthogonal if their scalar product is zero, i.e., if  $\langle a|b\rangle = 0$ .
- If with each ket  $|a\rangle$  in the ket space we can associate another ket  $|b\rangle$ , then this association may be used to define an operator say  $\hat{\alpha}$  which we may write in the form

$$|b\rangle = \hat{\alpha}|a\rangle$$

$\hat{\alpha}$  in the above might mean multiplication, differentiation, integration, etc., operations.

- An operator always appears to the left of the ket on which it operates.
- A linear Operator  $\hat{\alpha}$  is said to be an *identity operator* if

$$\hat{\alpha} |a\rangle = |a\rangle \quad \text{for all } |a\rangle$$

- Eigenvalue problem formulated in terms of bras is

$$\langle \beta_a | \hat{\beta} = \beta_a \langle \beta_a |.$$

- Any dynamical variable of a system that can be measured is called an observable of that system.
- When a single measurement of  $\alpha$  is made on the system in an arbitrary state, we obtain one of the eigen values of  $\hat{\alpha}$ .

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### 7.7 KEY WORDS

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- **Dirac's Formulation:** In quantum mechanics it is developed without using any specific representation and instead it uses the concept of vectors in a space that may have a finite or an infinite dimension.
- **Ket Vector:** With each state of a dynamical system is associated a ket vector. A general ket is denoted by the symbol  $|\rangle$ .
- **Duality of Ket and Bra:** Since there exists unique correspondence between bras and kets, the direction of a bra vector represents the state of a quantum system as does the direction of the associated ket. Hence, they are said to be dual of one another.

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### 7.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

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#### Short Answer Questions

1. Define the term harmonic oscillator.
2. What is the total energy of the oscillator?
3. What are Dirac's bra ket vectors?
4. When ket and bra are dual of one another?
5. How the linear operator is completely defined?
6. What is Hermitian operator?
7. Define angular momentum.

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**Long Answer Questions**

1. Discuss the concept of harmonic oscillator giving appropriate examples.
2. Briefly explain Dirac's bra ket vectors.
3. Explain the wavefunction that describes the state of a particle moving in one dimension at the time  $t$ .
4. Discuss the norms essential for a ket.
5. Explain linear operator in ket space.
6. Discuss the operation of linear operator performed on bra.
7. Prove that the eigenvalues of a linear Hermitian operator are real.
8. Explain angular momentum with the help of examples.

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**7.9 FURTHER READINGS**

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
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## UNIT 8 QUANTUM DYNAMICS

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### Structure

- 8.0 Introduction
- 8.1 Objectives
- 8.2 Schrödinger, Heisenberg and Interaction Pictures
  - 8.2.1 Schrödinger Picture
  - 8.2.2 Heisenberg Picture
  - 8.2.3 Interaction Picture
- 8.3 Answers to Check Your Progress Questions
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- 8.5 Key Words
- 8.6 Self Assessment Questions and Exercises
- 8.7 Further Readings

### NOTES

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## 8.0 INTRODUCTION

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In physics, quantum dynamics is the quantum version of classical dynamics. Quantum dynamics deals with the motions, and energy and momentum exchanges of systems whose behavior is governed by the laws of quantum mechanics.

In quantum mechanics, the interaction picture, also known as the Dirac picture named after Paul Dirac, is an intermediate representation between the Schrödinger picture and the Heisenberg picture. However in the other two pictures either the state vector or the operators carry time dependence, in the interaction picture both carry part of the time dependence of observables. The interaction picture is advantageous since it considers the changes to the wave functions and observables due to interactions. Most field-theoretical calculations typically use the interaction representation because they provide the solution to the various Schrödinger equations as the solution to the free-particle problem and also for some unknown interaction parts.

In this unit, you will learn about the Schrödinger, Heisenberg and interaction pictures.

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## 8.1 OBJECTIVES

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After going through this unit, you will be able to:

- Explain what quantum dynamics is
- Discuss Schrödinger picture
- Understand Heisenberg picture
- Define interaction picture

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## 8.2 SCHRÖDINGER, HEISENBERG AND INTERACTION PICTURES

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In physics, quantum dynamics is referred as the quantum version of classical dynamics. Quantum dynamics deals with the motions, and energy and momentum exchanges of systems whose behaviour is governed by the laws of quantum mechanics. Quantum dynamics is significant for fields, such as quantum computing and atomic optics.

Pictures in quantum mechanics are different points of view in describing a quantum system. In the general Schrödinger picture, the operators are time independent and the state vectors (wave functions) are time dependent. In Heisenberg picture, the operators are rendered time dependent and the state vectors become time independent. The Interaction (Dirac) picture, is a hybrid view-point where both operators and state vectors are time dependent, evolving in time by different unitary operators.

Quantum systems are considered as wave functions which solve the Schrödinger equation. Observables are represented by Hermitian operators which act on the wave function. In the Schrödinger picture, the operators stay fixed while the Schrödinger equation changes the basis with time.

In the Dirac or interaction picture, both the basis and the operators carry time-dependence. The interaction picture allows for operators to act on the state vector at different times and forms the basis for quantum field theory and many other newer methods.

In the Heisenberg picture, it is the operators which change in time while the basis of the space remains fixed. Heisenberg's matrix mechanics actually came before Schrödinger's wave mechanics but were too mathematically different to catch on. A fixed basis is, in some ways, more mathematically pleasing. This formulation also generalizes more easily to relativity - it is the nearest analog to classical physics.

### 8.2.1 Schrödinger Picture

In physics, the Schrödinger picture, also termed as the Schrödinger representation is a formulation of quantum mechanics in which the state vectors evolve in time, but the operators (observables and others) are constant with respect to time. This differs from the Heisenberg picture which keeps the states constant while the observables evolve in time, and from the interaction picture in which both the states and the observables evolve in time. The Schrödinger and Heisenberg pictures are related as active and passive transformations and commutation relations between operators are preserved in the passage between the two pictures.

In the Schrödinger picture, the state of a system evolves with time. The evolution for a closed quantum system is brought about by a unitary operator, the time evolution operator.

For time evolution from a state vector  $|\psi(t_0)\rangle$  at time  $t_0$  to a state vector  $|\psi(t)\rangle$  at time  $t$ , the time-evolution operator is commonly written  $U(t, t_0)$ , and one has,  $|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle$ .

In the case where the Hamiltonian of the system does not vary with time, the time-evolution operator has the form,

$$U(t, t_0) = e^{-iH(t-t_0)/\hbar}$$

Where the exponent is evaluated via its Taylor series.

The Schrödinger picture is useful when dealing with a time-independent Hamiltonian  $H$ ; that is,  $\partial_t H = 0$ .

In elementary quantum mechanics, the state of a quantum-mechanical system is represented by a complex-valued wavefunction  $\psi(x, t)$ . More abstractly, the state may be represented as a state vector, or ket  $|\psi\rangle$ . This ket is an element of a Hilbert space, a vector space containing all possible states of the system. A quantum-mechanical operator is a function which takes a ket  $|\psi\rangle$  and returns some other ket  $|\psi'\rangle$ .

The differences between the Schrödinger and Heisenberg pictures of quantum mechanics revolve around how to deal with systems that evolve in time: the time-dependent nature of the system must be carried by some combination of the state vectors and the operators. For example, a quantum harmonic oscillator may be in a state  $|\psi\rangle$  for which the expectation value of the momentum,  $\langle\psi|\hat{p}|\psi\rangle$ , oscillates sinusoidally in time. One can then ask whether this sinusoidal oscillation should be reflected in the state vector  $|\psi\rangle$ , the momentum operator  $\hat{p}$ , or both. All three of these choices are valid; the first gives the Schrödinger picture, the second the Heisenberg picture, and the third the interaction picture.

### The Time Evolution Operator

The time-evolution operator  $U(t, t_0)$  is defined as the operator which acts on the ket at time  $t_0$  to produce the ket at some other time  $t$ :

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle.$$

For Bras, we instead have,

$$\langle\psi(t)| = \langle\psi(t_0)|U^\dagger(t, t_0).$$

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**Properties**

**Unitarity:** The time evolution operator must be unitary. This is because we demand that the norm of the state ket must not change with time. That is,

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger(t, t_0) U(t, t_0) | \psi(t_0) \rangle = \langle \psi(t_0) | \psi(t_0) \rangle$$

Therefore,

$$U^\dagger(t, t_0) U(t, t_0) = I.$$

**Identity:** When  $t = t_0$ ,  $U$  is the identity operator, since

$$|\psi(t_0)\rangle = U(t_0, t_0) |\psi(t_0)\rangle.$$

**Closure:** Time evolution from  $t_0$  to  $t$  may be viewed as a two-step time evolution, first from  $t_0$  to an intermediate time  $t_1$ , and then from  $t_1$  to the final time  $t$ . Therefore,

$$U(t, t_0) = U(t, t_1) U(t_1, t_0).$$

**8.2.2 Heisenberg Picture**

In physics, the Heisenberg picture, also called the Heisenberg representation, is a formulation given by Werner Heisenberg in 1925, of quantum mechanics in which the operators (observables and others) incorporate a dependency on time, but the state vectors are time-independent, an arbitrary fixed basis rigidly underlying the theory.

It stands in contrast to the Schrödinger picture in which the operators are constant, instead, and the states evolve in time. The two pictures only differ by a basis change with respect to time-dependency, which corresponds to the difference between active and passive transformations. The Heisenberg picture is the formulation of matrix mechanics in an arbitrary basis, in which the Hamiltonian is not necessarily diagonal. It further serves to define a third hybrid picture, the interaction picture.

In the Heisenberg picture of quantum mechanics the state vectors,  $|\psi(t)\rangle$ , do not change with time, while observables  $A$  satisfy,

$$\frac{d}{dt} A(t) = \frac{i}{\hbar} [H, A(t)] + \left( \frac{\partial A}{\partial t} \right)_H$$

Where  $H$  is the Hamiltonian and  $[\bullet, \bullet]$  denotes the commutator of two operators (in this case  $H$  and  $A$ ). Taking expectation values automatically yields the Ehrenfest theorem, featured in the correspondence principle.

By the Stone–von Neumann theorem, the Heisenberg picture and the Schrödinger picture are unitarily equivalent, just a basis change in Hilbert space. In some sense, the Heisenberg picture is more natural and convenient than the equivalent Schrödinger picture, especially for relativistic theories. Lorentz invariance

is manifest in the Heisenberg picture, since the state vectors do not single out the time or space.

This approach also has a more direct similarity to classical physics: by simply replacing the commutator above by the Poisson bracket, the Heisenberg equation reduces to an equation in Hamiltonian mechanics.

### Equivalence of Heisenberg's Equation to the Schrödinger Equation

For the sake of pedagogy, the Heisenberg picture is introduced here from the subsequent, but more familiar, Schrödinger picture.

The expectation value of an observable  $A$ , which is a Hermitian linear operator, for a given Schrödinger state  $|\psi(t)\rangle$ , is given by,

$$\langle A \rangle_t = \langle \psi(t) | A | \psi(t) \rangle$$

In the Schrödinger picture, the state  $|\psi(t)\rangle$  at time  $t$  is related to the state  $|\psi(0)\rangle$  at time 0 by a unitary time-evolution operator,  $U(t)$ ,

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle.$$

In the Heisenberg picture, all state vectors are considered to remain constant at their initial values  $|\psi(0)\rangle$ , whereas operators evolve with time according to,

$$A(t) := U^\dagger(t) A U(t).$$

The Schrödinger equation for the time-evolution operator is,

$$\frac{d}{dt} U(t) = -\frac{iH}{\hbar} U(t)$$

Where  $H$  is the Hamiltonian and  $\hbar$  is the reduced Planck constant.

It follows that,

$$\begin{aligned} \frac{d}{dt} A(t) &= \frac{i}{\hbar} U^\dagger(t) H A U(t) + U^\dagger(t) \left( \frac{\partial A}{\partial t} \right) U(t) + \frac{i}{\hbar} U^\dagger(t) A (-H) U(t) \\ &= \frac{i}{\hbar} U^\dagger(t) H U(t) U^\dagger(t) A U(t) + U^\dagger(t) \left( \frac{\partial A}{\partial t} \right) U(t) - \frac{i}{\hbar} U^\dagger(t) A U(t) U^\dagger(t) H U(t) \\ &= \frac{i}{\hbar} (H(t) A(t) - A(t) H(t)) + U^\dagger(t) \left( \frac{\partial A}{\partial t} \right) U(t), \end{aligned}$$

Where differentiation was carried out according to the product rule. Note that the Hamiltonian that appears in the final line above is the Heisenberg Hamiltonian  $H(t)$ , which may differ from the Schrödinger Hamiltonian.

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**8.2.3 Interaction Picture**

In quantum mechanics, the interaction picture, also known as the Dirac picture named after Paul Dirac, is an intermediate representation between the Schrödinger picture and the Heisenberg picture. While the other two pictures either the state vector or the operators carry time dependence, the interaction picture carry both the part of the time dependence of observables (probability amplitudes). The interaction picture is advantageous since it consider the changes to the wave functions and observables due to interactions. Most field-theoretical calculations typically use the interaction representation because they provide the solution to the various Schrödinger equations as the solution to the free-particle problem and also for some unknown interaction parts.

Equations that include operators at different times, which hold in the interaction picture, do not necessarily hold either in the Schrödinger picture or in the Heisenberg picture. This is because time dependent unitary transformations relate operators in one picture to the analogous operators in the others.

Operators and state vectors in the interaction picture are related by a change of basis (unitary transformation) to those same operators and state vectors in the Schrödinger picture.

To switch into the interaction picture, we divide the Schrödinger picture Hamiltonian into two parts:

$$H_S = H_{0,S} + H_{1,S}.$$

Any possible choice of parts will yield a valid interaction picture; but in order for the interaction picture to be useful in simplifying the analysis of a problem, the parts will typically be chosen so that  $H_{0,S}$  is well understood and exactly solvable, while  $H_{1,S}$  contains some harder-to-analyze perturbation to this system.

If the Hamiltonian has explicit time-dependence (for example, if the quantum system interacts with an applied external electric field that varies in time), it will usually be advantageous to include the explicitly time-dependent terms with  $H_{1,S}$  leaving  $H_{0,S}$  time-independent. We proceed assuming that this is the case. If there is a context in which it makes sense to have  $H_{0,S}$  be time-dependent, then one can proceed by replacing  $e^{\pm iH_{0,S}t/\hbar}$  by the corresponding time-evolution operator in the definitions below.

**State Vectors**

A state vector in the interaction picture is defined as,

$$|\psi_I(t)\rangle = e^{iH_{0,S}t/\hbar} |\psi_S(t)\rangle,$$

Where  $|\psi_S(t)\rangle$  is the state vector in the Schrödinger picture.

## Operators

An operator in the interaction picture is defined as,

$$A_I(t) = e^{iH_0s t/\hbar} A_S(t) e^{-iH_0s t/\hbar}.$$

Note that  $A_S(t)$  will typically not depend on  $t$  and can be rewritten as just  $A_S$ . It only depends on  $t$  if the operator has ‘explicit time dependence’, for example, due to its dependence on an applied external time-varying electric field.

## Hamiltonian Operator

For the operator  $H_0$  itself, the interaction picture and Schrödinger picture coincide:

$$H_{0,I}(t) = e^{iH_0s t/\hbar} H_{0,S} e^{-iH_0s t/\hbar} = H_{0,S}$$

This is easily seen through the fact that operators commute with differentiable functions of themselves. This particular operator then can be called  $H_0$  without ambiguity.

For the perturbation Hamiltonian  $H_{1,P}$  however,

$$H_{1,I}(t) = e^{iH_0s t/\hbar} H_{1,S} e^{-iH_0s t/\hbar}$$

Where the interaction picture perturbation Hamiltonian becomes a time-dependent Hamiltonian, unless  $[H_{1,S}, H_{0,S}] = 0$ .

It is possible to obtain the interaction picture for a time-dependent Hamiltonian  $H_{0,S}(t)$  as well, but the exponentials need to be replaced by the unitary propagator for the evolution generated by  $H_{0,S}(t)$ , or more explicitly with a time-ordered exponential integral.

## Expectation Values

For a general operator  $A$ , the expectation value in the interaction picture is given by,

$$\langle A_I(t) \rangle = \langle \psi_I(t) | A_I(t) | \psi_I(t) \rangle = \langle \psi_S(t) | e^{-iH_0s t} e^{iH_0s t}$$

$$A_S e^{-iH_0s t} e^{iH_0s t} | \psi_S(t) \rangle = \langle A_S(t) \rangle.$$

Using the density-matrix expression for expectation value, we will get,

$$\langle A_I(t) \rangle = \text{Tr} (\rho_I(t) A_I(t)).$$

The purpose of the interaction picture is to shunt all the time dependence due to  $H_0$  onto the operators, thus allowing them to evolve freely, and leaving only  $H_{1,I}$  to control the time-evolution of the state vectors.

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The interaction picture is convenient when considering the effect of a small interaction term,  $H_{1,p}$ , being added to the Hamiltonian of a solved system,  $H_{0,S}$ . By utilizing the interaction picture, one can use time-dependent perturbation theory to find the effect of  $H_{1,p}$ , for example, in the derivation of Fermi's golden rule, or the Dyson series in quantum field theory: in 1947, Shin'ichirō Tomonaga and Julian Schwinger appreciated that covariant perturbation theory could be formulated elegantly in the interaction picture, since field operators can evolve in time as free fields, even in the presence of interactions, now treated perturbatively in such a Dyson series.

**Comparison of Evolution in all the Three Pictures**

Table 8.1 illustrates the comparative evaluation of all the three pictures, viz., Schrödinger, Heisenberg and interaction pictures for a time-independent Hamiltonian  $H_S$ .

Table 8.1 Comparative Evaluation of Schrödinger, Heisenberg and Interaction Pictures

Evolution	Picture		
of:	Heisenberg	Interaction	Schrödinger
Ket state	constant	$ \psi_I(t)\rangle = e^{iH_{0,S} t/\hbar}  \psi_S(t)\rangle$	$ \psi_S(t)\rangle = e^{-iH_S t/\hbar}  \psi_S(0)\rangle$
Observable	$A_H(t) = e^{iH_S t/\hbar} A_S e^{-iH_S t/\hbar}$	$A_I(t) = e^{iH_{0,S} t/\hbar} A_S e^{-iH_{0,S} t/\hbar}$	constant
Density matrix	constant	$\rho_I(t) = e^{iH_{0,S} t/\hbar} \rho_S(t) e^{-iH_{0,S} t/\hbar}$	$\rho_S(t) = e^{-iH_S t/\hbar} \rho_S(0) e^{iH_S t/\hbar}$

**Check Your Progress**

1. Define the term quantum dynamics.
2. What are pictures in quantum mechanics?
3. What are quantum systems?
4. Define the term the Schrödinger picture.
5. When is Schrödinger picture useful?
6. In elementary quantum mechanics, how is the state of a quantum-mechanical system represented?
7. Explain the term the Heisenberg picture.
8. What are the state vectors in the Heisenberg picture of quantum mechanics?
9. What is Schrödinger picture? When it is useful?
10. Give the Schrödinger equation for the time-evolution operator.
11. Define the term the interaction picture.

### 8.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. In physics, quantum dynamics is referred as the quantum version of classical dynamics. Quantum dynamics deals with the motions, and energy and momentum exchanges of systems whose behaviour is governed by the laws of quantum mechanics.
2. Pictures in quantum mechanics are different points of view in describing a quantum system. In the general Schrödinger picture, the operators are time independent and the state vectors (wave functions) are time dependent. In Heisenberg picture, the operators are rendered time dependent and the state vectors become time independent. The Interaction (Dirac) picture, is a hybrid view-point where both operators and state vectors are time dependent, evolving in time by different unitary operators.
3. Quantum systems are considered as wave functions which solve the Schrödinger equation. Observables are represented by Hermitian operators which act on the wave function. In the Schrödinger picture, the operators stay fixed while the Schrödinger equation changes the basis with time.
4. In physics, the Schrödinger picture, also termed as the Schrödinger representation is a formulation of quantum mechanics in which the state vectors evolve in time, but the operators (observables and others) are constant with respect to time. In the Schrödinger picture, the state of a system evolves with time. The evolution for a closed quantum system is brought about by a unitary operator, the time evolution operator.
5. The Schrödinger picture is useful when dealing with a time-independent Hamiltonian  $H$ ; that is,  $\partial_t H = 0$ .
6. In elementary quantum mechanics, the state of a quantum-mechanical system is represented by a complex-valued wavefunction  $\psi(x, t)$ . More abstractly, the state may be represented as a state vector, or ket  $|\psi\rangle$ . This ket is an element of a Hilbert space, a vector space containing all possible states of the system. A quantum-mechanical operator is a function which takes a ket  $|\psi\rangle$  and returns some other ket  $|\psi\rangle$ .
7. In physics, the Heisenberg picture, also called the Heisenberg representation, is a formulation given by Werner Heisenberg in 1925, of quantum mechanics in which the operators (observables and others) incorporate a dependency on time, but the state vectors are time-independent, an arbitrary fixed basis rigidly underlying the theory. The Heisenberg picture is the formulation of matrix mechanics in an arbitrary basis, in which the Hamiltonian is not

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necessarily diagonal. It further serves to define a third hybrid picture, the interaction picture.

8. In the Heisenberg picture of quantum mechanics the state vectors,  $|\psi(t)\rangle$ , do not change with time, while observables  $A$  satisfy,

$$\frac{d}{dt}A(t) = \frac{i}{\hbar}[H, A(t)] + \left(\frac{\partial A}{\partial t}\right)_H$$

Where  $H$  is the Hamiltonian and  $[\bullet, \bullet]$  denotes the commutator of two operators (in this case  $H$  and  $A$ ). Taking expectation values automatically yields the Ehrenfest theorem, featured in the correspondence principle.

9. In the Schrödinger picture, the state of a system evolves with time. The evolution for a closed quantum system is brought about by a unitary operator, the time evolution operator. The Schrödinger picture is useful when dealing with a time-independent Hamiltonian  $H$ ; that is,  $\partial_t H = 0$ .

10. The Schrödinger equation for the time-evolution operator is,

$$\frac{d}{dt}U(t) = -\frac{iH}{\hbar}U(t)$$

Where  $H$  is the Hamiltonian and  $\hbar$  is the reduced Planck constant.

11. In quantum mechanics, the interaction picture, also known as the Dirac picture named after Paul Dirac, is an intermediate representation between the Schrödinger picture and the Heisenberg picture. While the other two pictures either the state vector or the operators carry time dependence, the interaction picture carry both the part of the time dependence of observables (probability amplitudes). The interaction picture is advantageous since it consider the changes to the wave functions and observables due to interactions.

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## 8.4 SUMMARY

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- In physics, quantum dynamics is referred as the quantum version of classical dynamics. Quantum dynamics deals with the motions, and energy and momentum exchanges of systems whose behaviour is governed by the laws of quantum mechanics. Quantum dynamics is significant for fields, such as quantum computing and atomic optics.
- Pictures in quantum mechanics are different points of view in describing a quantum system. In the general Schrödinger picture, the operators are time independent and the state vectors (wave functions) are time dependent.
- In Heisenberg picture, the operators are rendered time dependent and the state vectors become time independent.

- The Interaction (Dirac) picture, is a hybrid view-point where both operators and state vectors are time dependent, evolving in time by different unitary operators.
- Quantum systems are considered as wave functions which solve the Schrödinger equation. Observables are represented by Hermitian operators which act on the wave function. In the Schrödinger picture, the operators stay fixed while the Schrödinger equation changes the basis with time.
- In the Dirac or interaction picture, both the basis and the operators carry time-dependence. The interaction picture allows for operators to act on the state vector at different times and forms the basis for quantum field theory and many other newer methods.
- In the Heisenberg picture, it is the operators which change in time while the basis of the space remains fixed. Heisenberg's matrix mechanics actually came before Schrödinger's wave mechanics but were too mathematically different to catch on.
- In physics, the Schrödinger picture, also termed as the Schrödinger representation is a formulation of quantum mechanics in which the state vectors evolve in time, but the operators (observables and others) are constant with respect to time. This differs from the Heisenberg picture which keeps the states constant while the observables evolve in time, and from the interaction picture in which both the states and the observables evolve in time.
- The Schrödinger and Heisenberg pictures are related as active and passive transformations and commutation relations between operators are preserved in the passage between the two pictures.
- In the Schrödinger picture, the state of a system evolves with time. The evolution for a closed quantum system is brought about by a unitary operator, the time evolution operator.
- The Schrödinger picture is useful when dealing with a time-independent Hamiltonian  $H$ ; that is,  $\partial_t H = 0$ .
- In elementary quantum mechanics, the state of a quantum-mechanical system is represented by a complex-valued wavefunction  $\psi(x, t)$ . More abstractly, the state may be represented as a state vector, or ket  $|\psi\rangle$ . This ket is an element of a Hilbert space, a vector space containing all possible states of the system.
- A quantum-mechanical operator is a function which takes a ket  $|\psi\rangle$  and returns some other.

## NOTES

## NOTES

- In physics, the Heisenberg picture, also called the Heisenberg representation, is a formulation given by Werner Heisenberg in 1925, of quantum mechanics in which the operators (observables and others) incorporate a dependency on time, but the state vectors are time-independent, an arbitrary fixed basis rigidly underlying the theory.
- It stands in contrast to the Schrödinger picture in which the operators are constant, instead, and the states evolve in time. The two pictures only differ by a basis change with respect to time-dependency, which corresponds to the difference between active and passive transformations.
- In the Heisenberg picture of quantum mechanics the state vectors,  $|\psi(t)\rangle$ , do not change with time, while observables  $A$  satisfy,

$$\frac{d}{dt} A(t) = \frac{i}{\hbar} [H, A(t)] + \left( \frac{\partial A}{\partial t} \right)_H$$

Where  $H$  is the Hamiltonian and  $[\bullet, \bullet]$  denotes the commutator of two operators (in this case  $H$  and  $A$ ). Taking expectation values automatically yields the Ehrenfest theorem, featured in the correspondence principle.

- By the Stone–von Neumann theorem, the Heisenberg picture and the Schrödinger picture are unitarily equivalent, just a basis change in Hilbert space.
- The expectation value of an observable  $A$ , which is a Hermitian linear operator, for a given Schrödinger state  $|\psi(t)\rangle$ , is given by,

$$\langle A \rangle_t = \langle \psi(t) | A | \psi(t) \rangle.$$

- In the Schrödinger picture, the state  $|\psi(t)\rangle$  at time  $t$  is related to the state  $|\psi(0)\rangle$  at time 0 by a unitary time-evolution operator,  $U(t)$ ,

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle.$$

- In the Heisenberg picture, all state vectors are considered to remain constant at their initial values  $|\psi(0)\rangle$ , whereas operators evolve with time according to,  $A(t) := U^\dagger(t)AU(t)$ .
- The Schrödinger equation for the time-evolution operator is,

$$\frac{d}{dt} U(t) = -\frac{iH}{\hbar} U(t)$$

Where  $H$  is the Hamiltonian and  $\hbar$  is the reduced Planck constant.

- In quantum mechanics, the interaction picture, also known as the Dirac picture named after Paul Dirac, is an intermediate representation between the Schrödinger picture and the Heisenberg picture.
- While the other two pictures either the state vector or the operators carry time dependence, the interaction picture carry both the part of the time dependence of observables (probability amplitudes).
- The interaction picture is advantageous since it consider the changes to the wave functions and observables due to interactions.
- Equations that include operators at different times, which hold in the interaction picture, do not necessarily hold either in the Schrödinger picture or in the Heisenberg picture. This is because time dependent unitary transformations relate operators in one picture to the analogous operators in the others.
- Operators and state vectors in the interaction picture are related by a change of basis (unitary transformation) to those same operators and state vectors in the Schrödinger picture.

## NOTES

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### 8.5 KEY WORDS

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- **Quantum dynamics:** It deals with the motions, and energy and momentum exchanges of systems whose behaviour is governed by the laws of quantum mechanics.
- **Quantum systems:** These are considered as wave functions which solve the Schrödinger equation.
- **Schrödinger picture:** Also termed as the Schrödinger representation, it is a formulation of quantum mechanics in which the state vectors evolve in time, but the operators (observables and others) are constant with respect to time.
- **Heisenberg picture:** Also called the Heisenberg representation, is a formulation given by Werner Heisenberg in 1925, of quantum mechanics in which the operators (observables and others) incorporate a dependency on time, but the state vectors are time-independent, an arbitrary fixed basis rigidly underlying the theory.
- **Interaction picture:** Also known as the Dirac picture named after Paul Dirac, is an intermediate representation between the Schrödinger picture and the Heisenberg picture, as the interaction picture carry both the part of the time dependence of observables (probability amplitudes).

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## 8.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### NOTES

#### Short Answer Questions

1. What is the significance of quantum dynamics?
2. Define the terms picture, observables and operators.
3. Explain Schrödinger picture.
4. What is Heisenberg picture?
5. How Schrödinger and Heisenberg pictures are related?
6. What is interaction picture?

#### Long Answer Questions

1. Briefly discuss the significance of quantum dynamics and quantum systems giving appropriate examples.
2. Explain the how the three pictures Schrödinger, Heisenberg and interaction are related to each other.
3. Discuss the Schrödinger picture giving its relevance in quantum physics.
4. Analyse the Heisenberg picture and state that how it is different from the Schrödinger picture.
5. Briefly discuss the differences between the Schrödinger and Heisenberg pictures of quantum mechanics giving appropriate examples.
6. Explain the significance of interaction pictures in quantum mechanics.
7. Give the equations for state vector, operator and Hamiltonian operator for the interaction pictures.

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## 8.7 FURTHER READINGS

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
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## **UNIT 9 TIME INDEPENDENT PERTURBATION THEORY**

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### **NOTES**

#### **Structure**

- 9.0 Introduction
- 9.1 Objectives
- 9.2 Time Independent Perturbation Theory
- 9.3 Answers to Check Your Progress Questions
- 9.4 Summary
- 9.5 Key Words
- 9.6 Self Assessment Questions and Exercises
- 9.7 Further Readings

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### **9.0 INTRODUCTION**

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In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a ‘small’ term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated. This is only approximate because the sum of a Coulomb potential with a linear potential is unstable (has no true bound states) although the tunneling time (decay rate) is very long. Time independent perturbation theory is observed to be useful because of its importance in experimental solid state physics in general and transport properties in particular.

In this unit, you will study about the perturbation theory (first order), the time independent perturbation theory and stark effect in hydrogen atom.

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### **9.1 OBJECTIVES**

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After going through this unit, you will be able to:

- Explain the time independent perturbation theory
- Discuss the perturbation theory of first order
- Understand the stark effect in hydrogen atom

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## 9.2 TIME INDEPENDENT PERTURBATION THEORY

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### NOTES

In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a ‘small’ term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated. This is only approximate because the sum of a Coulomb potential with a linear potential is unstable (has no true bound states) although the tunneling time (decay rate) is very long.

The expressions produced by perturbation theory are not exact, but they can lead to accurate results as long as the expansion parameter, say  $\alpha$ , is very small. Typically, the results are expressed in terms of finite power series in  $\alpha$  that seem to converge to the exact values when summed to higher order. After a certain order  $n \sim 1/\alpha$  however, the results become increasingly worse since the series are usually divergent (being asymptotic series). There exist ways to convert them into convergent series, which can be evaluated for large expansion parameters, most efficiently by the variational method.

Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence. The time independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In this paper Schrödinger referred to earlier work of Lord Rayleigh, who investigated harmonic vibrations of a string perturbed by small in-homogeneities. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.

### First Order Corrections

Consider an unperturbed Hamiltonian,  $H_0$ , which is also assumed to have no time dependence. It has known energy levels and eigenstates, arising from the time independent Schrödinger equation of the form:

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle, \quad n = 1, 2, 3, \dots$$

For simplicity, assume that the energies are discrete. The (0) superscripts denote that these quantities are associated with the unperturbed system. Note the use of bra–ket notation.

We now introduce a perturbation to the Hamiltonian. Let  $V$  be a Hamiltonian representing a weak physical disturbance, such as a potential energy produced by an external field. Thus,  $V$  is formally a Hermitian operator. Let  $\lambda$  be a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (the full perturbation). The perturbed Hamiltonian is represented as,

$$H = H_0 + \lambda V$$

The energy levels and eigenstates of the perturbed Hamiltonian are again given by the Schrödinger equation:

$$(H_0 + \lambda V) |n\rangle = E_n |n\rangle$$

The objective is to express  $E_n$  and  $|n\rangle$  in terms of the energy levels and eigenstates of the old Hamiltonian. If the perturbation is sufficiently weak, we can write them as a (Maclaurin) power series in  $\lambda$ :

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

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots$$

Where,

$$E_n^{(k)} = \left. \frac{1}{k!} \frac{d^k E_n}{d\lambda^k} \right|_{\lambda=0}$$

$$|n^{(k)}\rangle = \left. \frac{1}{k!} \frac{d^k |n\rangle}{d\lambda^k} \right|_{\lambda=0}$$

When  $k = 0$ , these reduce to the unperturbed values, which are the **first term** in each series. Since the perturbation is weak, the energy levels and eigenstates should not deviate too much from their unperturbed values, and the terms should rapidly become smaller as we go to higher order.

Substituting the power series expansion into the Schrödinger equation, we obtain,

$$(H_0 + \lambda V) (|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \dots) (|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots)$$

Expanding this equation and comparing coefficients of each power of  $\lambda$  results in an infinite series of simultaneous equations. The zeroth-order equation is simply the Schrödinger equation for the unperturbed system. The first order equation is,

$$H_0 |n^{(1)}\rangle + V |n^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle$$

## NOTES

## NOTES

Operating through by  $\langle n^{(0)} |$ , the first term on the left-hand side cancels the first term on the right-hand side as per the unperturbed Hamiltonian is Hermitian. This leads to the first order energy shift:

$$E_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle$$

This is simply the expectation value of the perturbation Hamiltonian while the system is in the unperturbed state.

### The Stark Effect for $n = 2$ Hydrogen

The Stark effect for the  $n = 2$  states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of  $E_0$ . That is  $H_0 \phi_{2\ell m} = E_0 \phi_{2\ell m}$ .

The degenerate states are  $\phi_{200}$ ,  $\phi_{211}$ ,  $\phi_{210}$  and  $\phi_{21(-1)}$ .

The perturbation due to an electric field in the  $z$  direction is  $H_1 = +e\mathcal{E}z$ .

So the first order degenerate state perturbation theory equation is,

$$\sum_i \alpha_i \langle \phi^{(j)} | H_0 + e\mathcal{E}z | \phi^{(i)} \rangle = (E_0 + E^{(1)}) \alpha_j.$$

This is essentially a 4 x 4 matrix eigenvalue equation. There are 4 eigenvalues  $(E_0 + E^{(1)})$ , distinguished by the index  $n$ .

Because of the exact degeneracy ( $H_0 \phi^{(j)} = E_0 \phi^{(j)}$ ), the  $H_0$  and  $E_0$  can be eliminated from the equation.

$$\begin{aligned} \sum_i \alpha_i (E_0 \delta_{ij} + \langle \phi^{(j)} | e\mathcal{E}z | \phi^{(i)} \rangle) &= (E_0 + E^{(1)}) \alpha_j \\ E_0 \alpha_j + \sum_i \alpha_i \langle \phi^{(j)} | e\mathcal{E}z | \phi^{(i)} \rangle &= E_0 \alpha_j + E^{(1)} \alpha_j \\ \sum_i \alpha_i \langle \phi^{(j)} | e\mathcal{E}z | \phi^{(i)} \rangle &= E^{(1)} \alpha_j \end{aligned}$$

This is just the eigenvalue equation for  $H_1$  which we can write in (pseudo) matrix form as follows,

$$\begin{pmatrix} H_1 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

Now, in fact, most of the matrix elements of  $H_1$  are zero. We can define that because  $[L_z, z] = 0$ , hence all the matrix elements between states of unequal  $m$  are zero. Another way of saying this is that the operator  $z$  does not 'change'  $m$ . Here is a little proof.

$$\langle Y_{lm} | [L_z, z] | Y_{l'm'} \rangle = 0 = (m - m') \langle Y_{lm} | z | Y_{l'm'} \rangle$$

This implies that  $\langle Y_{lm} | z | Y_{l'm'} \rangle = 0$  unless  $m = m'$ .

Let us define the one remaining nonzero (real) matrix element to be  $\gamma$ .

$$\gamma = e\mathcal{E} \langle \phi_{200} | z | \phi_{210} \rangle$$

The equation that is labelled with the basis states to define the order is.

$$\begin{matrix} \phi_{200} \\ \phi_{211} \\ \phi_{210} \\ \phi_{21-1} \end{matrix} \begin{pmatrix} 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & 0 \\ \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

We can see by inspection that the eigenfunctions of this operator are  $\phi_{211}$ ,  $\phi_{21-1}$ , and  $\frac{1}{\sqrt{2}}(\phi_{200} \pm \phi_{210})$  with eigenvalues (of  $H_1$ ) of 0, 0, and  $\pm\gamma$ .

What remains is to compute  $\gamma$ . Recall  $Y_{00} = \frac{1}{\sqrt{4\pi}}$  and  $Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$ .

$$\begin{aligned} \gamma &= e\mathcal{E} \int (2a_0)^{-3/2} 2 \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00} z (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{10} d^3r \\ &= 2e\mathcal{E} (2a_0)^{-3} \frac{1}{\sqrt{3}} \int r^3 d^3r \left(1 - \frac{r}{2a_0}\right) \left(\frac{r}{a_0}\right) e^{-r/a_0} \int \frac{1}{\sqrt{4\pi}} \cos\theta Y_{10} d\Omega \\ &= 2eE(2)^{-3} \frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} \int_0^\infty \left(\frac{r^4}{a_0^4} - \frac{r^5}{2a_0^5}\right) e^{-r/a_0} dr \\ &= \frac{a_0 e\mathcal{E}}{12} \left[ \int_0^\infty x^4 e^{-x} dx - \frac{1}{2} \int_0^\infty x^5 e^{-x} dx \right] \\ &= \frac{a_0 e\mathcal{E}}{12} \left[ 4 \cdot 3 \cdot 2 \cdot 1 - \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{2} \right] \\ &= \frac{a_0 e\mathcal{E}}{12} (-36) \\ &= -3e\mathcal{E}a_0 \quad \Rightarrow \quad E^{(1)} = \mp 3e\mathcal{E}a_0 \end{aligned}$$

This is first order in the electric field, as we would expect in first order (degenerate) perturbation theory.

If the states are not exactly degenerate, we have to leave in the diagonal terms of  $H_0$ . Assume that the energies of the two (mixed) states are  $E_0 \pm \Delta$ , where  $\Delta$  comes from some other perturbation, like the hydrogen fine structure. The  $\phi_{211}$  and  $\phi_{21(-1)}$  are still not mixed by the electric field.

## NOTES

$$\begin{pmatrix} E_0 - \Delta & \gamma \\ \gamma & E_0 + \Delta \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

## NOTES

$$E = E_0 \pm \sqrt{\gamma^2 + \Delta^2}$$

This is correct in both limits,  $\Delta \gg \gamma$ , and  $\gamma \gg \Delta$ . It is also correct when the two corrections are of the same order.

### Check Your Progress

1. What is perturbation theory? When it is applied?
2. Explain the time independent perturbation theory.
3. What is first order equation?
4. What is stark effect?

## 9.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a 'small' term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated.
2. Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence.
3. The first order equation is,

$$H_0 |n^{(1)}\rangle + V |n^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle$$

4. The stark effect for the  $n = 2$  states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of  $E_0$ . That is  $H_0 \phi_{2\ell m} = E_0 \phi_{2\ell m}$ . The degenerate states  $\phi_{200}$ ,  $\phi_{211}$ ,  $\phi_{210}$  and  $\phi_{21(-1)}$ .

## 9.4 SUMMARY

- In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one.
- Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a ‘small’ term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated.
- The expressions produced by perturbation theory are not exact, but they can lead to accurate results as long as the expansion parameter, say  $\alpha$ , is very small.
- Typically, the results are expressed in terms of finite power series in  $\alpha$  that seem to converge to the exact values when summed to higher order. After a certain order  $n \sim 1/\alpha$  however, the results become increasingly worse since the series are usually divergent (being asymptotic series).
- Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence.
- The time independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In this paper Schrödinger referred to earlier work of Lord Rayleigh, who investigated harmonic vibrations of a string perturbed by small in-homogeneities. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.
- The first order equation is,

$$H_0 |n^{(1)}\rangle + V |n^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle$$

- The Stark effect for the  $n = 2$  states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of  $E_0$ . That is  $H_0 \phi_{2\ell m} = E_0 \phi_{2\ell m}$ . The degenerate states  $\phi_{200}$ ,  $\phi_{211}$ ,  $\phi_{210}$  and  $\phi_{21(-1)}$ .

## NOTES

## NOTES

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### 9.5 KEY WORDS

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- **Perturbation theory:** It is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one.
- **Time independent perturbation:** The theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence.

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### 9.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

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#### Short Answer Questions

1. What is perturbation theory?
2. What is perturbation theory of first order?
3. Explain the time independent perturbation theory.
4. What is stark effect in hydrogen atom?

#### Long Answer Questions

1. Discuss the significance of perturbation theory in quantum mechanics.
2. Explain the perturbation theory that specifies the first order corrections.
3. Discuss the time independent perturbation theory giving appropriate examples.
4. Explain the concept of stark effect in hydrogen atom.

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### 9.7 FURTHER READINGS

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
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## UNIT 10 VARIATIONAL PRINCIPLE

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### Structure

- 10.0 Introduction
- 10.1 Objectives
- 10.2 Variation Method
- 10.3 Answers to Check Your Progress Questions
- 10.4 Summary
- 10.5 Key Words
- 10.6 Self Assessment Questions and Exercises
- 10.7 Further Readings

### NOTES

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### 10.0 INTRODUCTION

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The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions, such as molecular orbitals. The basis for this method is the variational principle. The method consists of choosing a 'trial wavefunction' depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy. The emission spectra of helium (He) consists of a number of series in the visible region of the spectrum as well as in the near and far UV regions.

In this unit, you will study about the variation method, ground state of helium atom and the ground state of deuteron.

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### 10.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand the significance of variation method

- Discuss about the ground state of helium atom
- Explain the ground state of deuteron.

## NOTES

**10.2 VARIATION METHOD**

The variational method is the key approximate method/technique typically used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it is hard to determine a good unperturbed Hamiltonian, i.e., one which makes the perturbation small but is still solvable. On the other hand, in cases where there is a good unperturbed Hamiltonian, perturbation theory can be more efficient than the variational method.

The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions, such as molecular orbitals. The basis for this method is the variational principle. The method consists of choosing a ‘trial wavefunction’ depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.

Basically the ‘trial wavefunction’ for the problem consists of some adjustable parameters called termed as the ‘variational parameters’. These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.

Suppose we are given a Hilbert space and a Hermitian operator over it called the Hamiltonian,  $H$ . Ignoring complications about continuous spectra, consider the discrete spectrum of  $H$  and the corresponding eigenspaces of each eigenvalue »:

$$\langle \psi_{\lambda_1} | \psi_{\lambda_2} \rangle = \delta_{\lambda_1 \lambda_2}$$

Where  $\delta_{i,j}$  is the Kronecker delta,

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

And the Hamiltonian is related to  $\lambda$  through the typical eigenvalue relation,

$$\hat{H} |\psi_\lambda\rangle = \lambda |\psi_\lambda\rangle$$

Physical states are normalized, meaning that their norm is equal to 1. Once again ignoring complications involved with a continuous spectrum of  $H$ , suppose it is bounded from below and that its greatest lower bound is  $E_0$ . Suppose also that we know the corresponding state  $|\psi_0\rangle$ . The expectation value of  $H$  is then,

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \sum_{\lambda_1, \lambda_2 \in \text{Spec}(H)} \langle \psi | \psi_{\lambda_1} \rangle \langle \psi_{\lambda_1} | H | \psi_{\lambda_2} \rangle \langle \psi_{\lambda_2} | \psi \rangle \\ &= \sum_{\lambda \in \text{Spec}(H)} \lambda |\langle \psi_\lambda | \psi \rangle|^2 \geq \sum_{\lambda \in \text{Spec}(H)} E_0 |\langle \psi_\lambda | \psi \rangle|^2 = E_0 \end{aligned}$$

Evidently, in order to vary over all possible states with norm 1 trying to minimize the expectation value of  $H$ , the lowest value would be  $E_0$  and the corresponding state would be an eigenstate of  $E_0$ . Varying over the entire Hilbert space is usually too complicated for physical calculations, and a subspace of the entire Hilbert space is chosen, parametrized by some (real) differentiable parameters  $\alpha_i$  ( $i = 1, 2, \dots, N$ ). The choice of the subspace is called the ansatz. Some choices of ansatzes lead to better approximations than others, therefore the choice of ansatz is important.

Assume that there is some overlap between the ansatz and the ground state (otherwise, it is a bad ansatz). We still wish to normalize the ansatz, so we have the constraints,

$$\langle \psi(\alpha) | \psi(\alpha) \rangle = 1$$

And to minimize,

$$\varepsilon(\alpha) = \langle \psi(\alpha) | H | \psi(\alpha) \rangle$$

If  $\psi(\alpha)$  is expressed as a linear combination of other functions ( $\alpha_i$  being the coefficients), as in the Ritz method, there is only one minimum and the problem is straightforward.

Although generally limited to calculations of the ground state energy, this method can be applied in certain cases to calculations of excited states as well.

## NOTES

If the ground state wavefunction is known, either by the method of variation or by direct calculation, a subset of the Hilbert space can be chosen which is orthogonal to the ground state wavefunction.

## NOTES

$$|\psi\rangle = |\psi_{\text{test}}\rangle - \langle\psi_{\text{gr}}|\psi_{\text{test}}\rangle|\psi_{\text{gr}}\rangle$$

The resulting minimum is usually not as accurate as for the ground state, as any difference between the true ground state and  $\psi_{\text{gr}}$  results in a lower excited energy. This defect is worsened with each higher excited state.

In another formulation,

$$E_{\text{ground}} \leq \langle\phi|H|\phi\rangle$$

This holds for any trial  $\mathcal{A}$  since, by definition, the ground state wavefunction has the lowest energy, and any trial wavefunction will have energy greater than or equal to it.

**Proof:**  $\phi$  can be expanded as a linear combination of the actual eigenfunctions of the Hamiltonian (which we assume to be normalized and orthogonal):

$$\phi = \sum_n c_n \psi_n$$

Then, to find the expectation value of the Hamiltonian,

$$\begin{aligned} & \langle\phi|H|\phi\rangle \\ &= \left\langle \sum_n c_n \psi_n \left| H \right| \sum_m c_m \psi_m \right\rangle \\ &= \sum_n \sum_m \langle c_n^* \psi_n | E_m | c_m \psi_m \rangle \\ &= \sum_n \sum_m c_n^* c_m E_m \langle \psi_n | \psi_m \rangle \\ &= \sum_n |c_n|^2 E_n. \end{aligned}$$

Now, the ground state energy is the lowest energy possible, i.e.,  $E_n \geq E_g$ . Therefore, if the guessed wave function  $\mathcal{A}$  is normalized:

$$\langle\phi|H|\phi\rangle \geq E_g \sum_n |c_n|^2 = E_g$$

For a Hamiltonian  $H$  that describes the studied system and any normalizable function  $\psi$  with arguments appropriate for the unknown wave function of the system, we define the functional,

$$\varepsilon[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

The variational principle states that,

- $\varepsilon \geq E_0$ , where  $E_0$  is the lowest energy eigenstate (ground state) of the Hamiltonian.

- $\varepsilon = E_0$  if and only if  $\Psi$  is exactly equal to the wave function of the ground state of the studied system.

The variational principle formulated above is the basis of the variational method used in quantum mechanics and quantum chemistry to find approximations to the ground state.

Another feature in variational principles in quantum mechanics is that since  $\Psi$  and  $\Psi^*$  can be varied separately (a fact arising due to the complex nature of the wave function), the quantities can be varied in principle just one at a time.

### Helium Atom Ground State

The helium atom consists of two electrons with mass  $m$  and electric charge  $-e$ , around an essentially fixed nucleus of mass  $M \gg m$  and charge  $+2e$ . The Hamiltonian for it, neglecting the fine structure, is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

where  $\hbar$  is the reduced Planck constant,  $\epsilon_0$  is the vacuum permittivity,  $r_i$  (for  $i = 1, 2$ ) is the distance of the  $i$ th electron from the nucleus, and  $|\mathbf{r}_1 - \mathbf{r}_2|$  is the distance between the two electrons.

If the term  $V_{ee} = e^2/(4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|)$ , representing the repulsion between the two electrons, were excluded, the Hamiltonian would become the sum of two hydrogen-like atom Hamiltonians with nuclear charge  $+2e$ . The ground state energy would then be  $8E_1 = -109$  eV, where  $E_1$  is the Rydberg constant, and its ground state wavefunction would be the product of two wavefunctions for the ground state of hydrogen-like atoms:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$$

Where  $a_0$  is the Bohr radius and  $Z = 2$ , Helium's nuclear charge. The expectation value of the total Hamiltonian  $H$  (including the term  $V_{ee}$ ) in the state described by  $\psi_0$  will be an upper bound for its ground state energy.  $\langle V_{ee} \rangle$  is  $-5E_1/2 = 34$  eV, so  $\langle H \rangle$  is  $8E_1 - 5E_1/2 = -75$  eV.

### NOTES

## NOTES

A tighter upper bound can be found by using a better trial wavefunction with ‘tunable’ parameters. Each electron can be thought to see the nuclear charge partially ‘shielded’ by the other electron, so we can use a trial wavefunction equal with an ‘effective’ nuclear charge  $Z < 2$ : The expectation value of  $H$  in this state is:

$$\langle H \rangle = \left[ -2Z^2 + \frac{27}{4}Z \right] E_1$$

This is minimal for  $Z = 27/16$  implying shielding reduces the effective charge to  $\sim 1.69$ . Substituting this value of  $Z$  into the expression for  $H$  yields  $729E_1/128 = -77.5$  eV, within 2% of the experimental value,  $-78.975$  eV.

**Deuteron Ground State**

Deuterium or hydrogen-2, symbol D or  ${}^2\text{H}$ , also known as heavy hydrogen, is one of two stable isotopes of hydrogen (the other being protium, or hydrogen-1). The nucleus of deuterium, called a deuteron, contains one proton and one neutron, whereas the far more common protium has no neutron in the nucleus. Deuterium has a natural abundance in Earth’s oceans of about one atom in 6420 of hydrogen. Thus deuterium accounts for approximately 0.02% (or, on a mass basis, 0.03%) of all the naturally occurring hydrogen in the oceans, while protium accounts for more than 99.98%.

The deuteron has spin +1 ‘triplet state’ and is thus a boson. The NMR frequency of deuterium is significantly different from common light hydrogen. Infrared spectroscopy also easily differentiates many deuterated compounds, due to the large difference in IR absorption frequency seen in the vibration of a chemical bond containing deuterium, versus light hydrogen. The two stable isotopes of hydrogen can also be distinguished by using mass spectrometry.

The triplet deuteron nucleon is barely bound at  $E_B = 2.23$  MeV, and none of the higher energy states are bound. The singlet deuteron is a virtual state, with a negative binding energy of  $\sim 60$  keV. There is no such stable particle, but this virtual particle transiently exists during neutron-proton inelastic scattering, accounting for the unusually large neutron scattering cross-section of the proton.

Variation method – ground state of helium atom – ground state of Deuteron.

**Check Your Progress**

1. Define variational principle.
2. What is trial wavefunction?
3. What does variational principle state?
4. Explain the term variational parameters.
5. Explain the structure of helium atom.

## 10.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.
2. In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. The basis for this method is the variational principle. The method consists of choosing a 'trial wavefunction' depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy.
3. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.
4. Basically the 'trial wavefunction' for the problem consists of some adjustable parameters called termed as the 'variational parameters'. These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.
5. The helium atom consists of two electrons with mass  $m$  and electric charge  $-e$ , around an essentially fixed nucleus of mass  $M \gg m$  and charge  $+2e$ . The Hamiltonian for it, neglecting the fine structure, is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

where  $\hbar$  is the reduced Planck constant,  $\epsilon_0$  is the vacuum permittivity,  $r_i$  (for  $i = 1, 2$ ) is the distance of the  $i$ th electron from the nucleus, and  $|\mathbf{r}_1 - \mathbf{r}_2|$  is the distance between the two electrons.

## NOTES

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## 10.4 SUMMARY

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### NOTES

- The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions.
- Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.
- In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions, such as molecular orbitals. The basis for this method is the variational principle. The method consists of choosing a ‘trial wavefunction’ depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible.
- The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy.
- The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.
- Basically the ‘trial wavefunction’ for the problem consists of some adjustable parameters called termed as the ‘variational parameters’. These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.
- The variational principle states that,
  1.  $\epsilon \geq E_0$ , where  $E_0$  is the lowest energy eigenstate (ground state) of the Hamiltonian.
  2.  $\epsilon = E_0$  if and only if  $\psi$  is exactly equal to the wave function of the ground state of the studied system.
- The helium atom consists of two electrons with mass  $m$  and electric charge  $-e$ , around an essentially fixed nucleus of mass  $M \gg m$  and charge  $+2e$ . The Hamiltonian for it, neglecting the fine structure, is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

where  $\hbar$  is the reduced Planck constant,  $\epsilon_0$  is the vacuum permittivity,  $r_i$  (for  $i = 1, 2$ ) is the distance of the  $i$ th electron from the nucleus, and  $|\mathbf{r}_1 - \mathbf{r}_2|$  is the distance between the two electrons.

- Deuterium or hydrogen-2, symbol D or  ${}^2\text{H}$ , also known as heavy hydrogen, is one of two stable isotopes of hydrogen (the other being protium, or hydrogen-1).
- The nucleus of deuterium, called a deuteron, contains one proton and one neutron, whereas the far more common protium has no neutron in the nucleus.
- The deuteron has spin +1 ‘triplet state’ and is thus a boson. The NMR frequency of deuterium is significantly different from common light hydrogen.
- The triplet deuteron nucleon is barely bound at  $E_B = 2.23$  MeV, and none of the higher energy states are bound. The singlet deuteron is a virtual state, with a negative binding energy of  $\sim 60$  keV.

## NOTES

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### 10.5 KEY WORDS

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- **Variational principle:** It is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions.
- **Hermitian:** Any physical law which can be expressed as a variational principle describes a self-adjoint operator are also called Hermitian.
- **Variational parameters:** The trial wavefunction for the problem consists of some adjustable parameters called termed as the variational parameters.

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### 10.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

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#### Short Answer Questions

1. What is variation method?
2. Explain variational parameters.
3. Explain the ground state of helium atom.
4. Explain the ground state of deuteron.

NOTES

**Long Answer Questions**

1. Briefly discuss the variation method giving appropriate examples.
2. Explain the equations involved in expressing and evaluating the ground state.
3. Discuss the ground state of helium atom and deuteron.

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**10.7 FURTHER READINGS**

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# UNIT 11 WKB APPROXIMATION

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## Structure

- 11.0 Introduction
- 11.1 Objectives
- 11.2 WKB Approximation
- 11.3 Answers to Check Your Progress Questions
- 11.4 Summary
- 11.5 Key Words
- 11.6 Self Assessment Questions and Exercises
- 11.7 Further Readings

## NOTES

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### 11.0 INTRODUCTION

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In mathematical physics, the WKB approximation or WKB method is used for finding approximate solutions to linear differential equations with spatially varying coefficients. It is typically used for a semi-classical calculation in quantum mechanics in which the wavefunction is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.

The WKB approximation is named after Wentzel–Kramers–Brillouin. This method is specifically used for obtaining an approximate solution to a time independent one-dimensional differential equation, typically the Schrödinger equation. Its principal applications include the calculations of bound state energies and tunnelling rates through barriers.

In this unit, you will study about the WKB approximation and its application to bound states.

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### 11.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand the WKB approximation method
- Define the WKB approximation application to bound states

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### 11.2 WKB APPROXIMATION

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In mathematical physics, the WKB approximation or WKB method is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. It is typically used for a semi-classical calculation in quantum mechanics in which the wavefunction is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.

## NOTES

The abbreviation WKB approximation refers to Wentzel–Kramers–Brillouin, i.e., the WKB approximation method is named after physicists Gregor Wentzel, Hendrik Anthony Kramers, and Léon Brillouin, who all developed it in 1926. In 1923, mathematician Harold Jeffreys had developed a general method of approximating solutions to linear, second order differential equations, a class that includes the Schrödinger equation. Early texts in quantum mechanics contain any number of combinations of their initials, including WBK, BWK, WKBJ, JWKB and BWKJ.

The WKB approximation is specifically used for obtaining an approximate solution to a time independent one-dimensional differential equation, typically the Schrödinger equation. Its principal applications include the calculations of bound state energies and tunnelling rates through barriers.

**WKB Method**

The WKB theory is a method typically used for approximating the solution of a differential equation whose highest derivative is multiplied by a small parameter ‘ $\epsilon$ ’. The method of approximation is as follows.

For a differential equation,

$$\epsilon \frac{d^n y}{dx^n} + a(x) \frac{d^{n-1} y}{dx^{n-1}} + \cdots + k(x) \frac{dy}{dx} + m(x)y = 0,$$

Assume that following is the solution of the form of an asymptotic series expansion in the limit  $\delta \rightarrow 0$ ,

$$y(x) \sim \exp \left[ \frac{1}{\delta} \sum_{n=0}^{\infty} \delta^n S_n(x) \right]$$

The asymptotic scaling of  $\delta$  in terms of  $\epsilon$  will be determined by the equation,

$$\epsilon^2 \left[ \frac{1}{\delta^2} \left( \sum_{n=0}^{\infty} \delta^n S'_n \right)^2 + \frac{1}{\delta} \sum_{n=0}^{\infty} \delta^n S''_n \right] = Q(x).$$

WKB theory is a special case of multiple scale analysis.

**Precision or Exactness of the Asymptotic Series**

The asymptotic series for  $y(x)$  is typically considered as a divergent series, whose general term  $\delta^n S_n(x)$  starts to increase after a certain value  $n = n_{\max}$ . Therefore, the smallest error attained by the WKB method is the order of the last included term.

For the equation,

$$\epsilon^2 \frac{d^2 y}{dx^2} = Q(x)y$$

With  $Q(x) < 0$  an analytic function, the value  $n_{\max}$  and the magnitude of the last term can be estimated as follows:

$$n_{\max} \approx 2\epsilon^{-1} \left| \int_{x_0}^{x_*} \sqrt{-Q(z)} dz \right|,$$

$$\delta^{n_{\max}} S_{n_{\max}}(x_0) \approx \sqrt{\frac{2\pi}{n_{\max}}} \exp[-n_{\max}],$$

Where  $x_0$  is the point at which  $y(x_0)$  needs to be evaluated and  $x_*$  is the (complex) turning point where  $Q(x_*) = 0$ , closest to  $x = x_0$ .

The number  $n_{\max}$  can be interpreted as the number of oscillations between  $x_0$  and the closest turning point.

If  $\epsilon^{-1} Q(x)$  is a slowly changing function,

$$\epsilon \left| \frac{dQ}{dx} \right| \ll Q^2,$$

The number  $n_{\max}$  will be large, and the minimum error of the asymptotic series will be exponentially small.

### Derivation of the Schrödinger Equation

Solving the Schrödinger equation is one of the essential problems in quantum mechanics. Since a non-linear second order Ordinary Differential Equation (ODE) has, in general, no analytic solution, hence an approximation method is typically applied. Instead of starting with a simplified potential and adding small terms, which leads to perturbation theory, the WKB approximation makes an assumption of a slowly varying potential.

To derive the approximation, consider the Schrödinger equation,

$$\frac{d^2\psi}{dx^2} + k(x)^2\psi = 0 \quad \dots(11.1)$$

With the abbreviations,

$$k(x) = \left(\frac{2m}{\hbar^2}(E - V)\right)^{1/2} \quad \text{if } E > V(x)$$

$$k(x) = i\left(\frac{2m}{\hbar^2}(V - E)\right)^{1/2} = i\kappa(x) \quad \text{if } E < V(x) \quad \dots(11.2)$$

If  $k(x) = \text{Constant}$  is the function has the solution  $\Psi(x) = e^{\pm ikx}$ . If  $k$  is no longer constant but varies at a slow rate, then reasonably we can use the solution, with  $x$  dependent  $k$ ,

$$e^{\pm i \int k(t) dt} \quad \dots(11.3)$$

### NOTES

Substituting it in to the Schrödinger equation gives us,

$$\frac{d^2\psi}{dx^2} + k(x)^2\psi = \left(\frac{d^2}{dx^2} + k^2\right)e^{\pm i \int k(t)dt} = \pm i k'(x)e^{\pm i \int k(t)dt} \quad \dots(11.4)$$

## NOTES

Thus the solutions in Equation (11.3) solves the equation only when  $k'(x)$  is equal to 0. However, Equation (11.4) suggests that Equation (11.3) remains a good approximation, if  $k'$  is negligible, or, more precisely, if

$$|k'| \ll k^2 \quad \dots(11.5)$$

This is the condition used in the derivation of the WKB approximation.

### Application to Bound States

In quantum physics, a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space. The potential may be external or it may be the result of the presence of another particle; in the latter case, one can equivalently define a bound state as a state representing two or more particles whose interaction energy exceeds the total energy of each separate particle. One consequence is that, given a potential vanishing at infinity, negative-energy states must be bound. In general, the energy spectrum of the set of bound states is discrete, unlike free particles, which have a continuous spectrum.

In a bound state problem with potential  $V(x)$ , for a given energy  $E$ , we can divide space into classically allowed regions, for which  $E > V(x)$ , and classically forbidden regions for which  $E < V(x)$ . Assume that there are only three regions in total, classically forbidden for  $x < a$  and  $x > b$ , and classically allowed for  $a < x < b$ .

In the classically allowed region  $a < x < b$  the wave function will be oscillating and we can write it either as a superposition of right- and left-moving complex exponentials or as,

$$\psi(x) = A \cos \int_a^x k(x') dx' + \phi$$

For the particular case of a well with infinite sides the solution must vanish at the boundaries, so (taking the lower limit of integration as  $a$  for definiteness; any other choice just shifts  $\phi$ )  $\phi = (n' + 1/2)\pi$  and  $\int_a^b k(x') dx' + \phi = (n'' + 1/2)\pi$ ; in other words  $\int_a^b k(x') dx' = (n + 1)\pi$ , with integer  $n \geq 0$ . Evidently for constant  $k$  this gives  $k = n\pi/(b - a)$ , which is exact.

For a more general potential, outside the classically allowed region we will have decaying exponentials. If we approximate the potential as linear we can solve the Schrödinger equation exactly (in terms of Airy functions). For WKB solutions in the locality of  $x = a$  and  $x = b$  gives the surprisingly simple result that inside the well,

$$\psi(x) = A \cos \int_a^x k(x') dx' - \pi/4 \quad \text{and} \quad \psi(x) = A' \cos \int_b^x k(x') dx' + \pi/4$$

which can only be satisfied if  $A' = \pm A$  and  $\int_a^b k(x') dx' = (n + 1/2)\pi$ . This latter

is the quantisation condition for a finite well; it is different from the infinite well because the solution can leak into the forbidden region. For a semi-infinite well, the condition is that the integral equal  $(n + 3/4)\pi$ . This is the appropriate form for the  $l = 0$  solutions of a spherically symmetric well.

### Check Your Progress

1. What is WKB approximation?
2. What does abbreviation WKB approximation refers?
3. When is WKB approximation used?
4. Define WKB theory.
5. What is asymptotic series for  $y(x)$ ?
6. In quantum physics, what is a bound state?

### NOTES

## 11.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. In mathematical physics, the WKB approximation or WKB method is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. It is typically used for a semi-classical calculation in quantum mechanics in which the wavefunction is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.
2. The abbreviation WKB approximation refers to Wentzel–Kramers–Brillouin, i.e., the WKB approximation method is named after physicists Gregor Wentzel, Hendrik Anthony Kramers, and Léon Brillouin, who all developed it in 1926.
3. The WKB approximation is specifically used for obtaining an approximate solution to a time independent one-dimensional differential equation, typically the Schrödinger equation. Its principal applications include the calculations of bound state energies and tunnelling rates through barriers.
4. The WKB theory is a method typically used for approximating the solution of a differential equation whose highest derivative is multiplied by a small parameter ' $\epsilon$ '. The method of approximation is as follows.

For a differential equation,

$$\epsilon \frac{d^n y}{dx^n} + a(x) \frac{d^{n-1} y}{dx^{n-1}} + \cdots + k(x) \frac{dy}{dx} + m(x)y = 0,$$

Assume that following is the solution of the form of an asymptotic series expansion in the limit  $\delta \rightarrow 0$ ,

$$y(x) \sim \exp \left[ \frac{1}{\delta} \sum_{n=0}^{\infty} \delta^n S_n(x) \right]$$

**NOTES**

The asymptotic scaling of  $\delta$  in terms of  $\epsilon$  will be determined by the equation,

$$\epsilon^2 \left[ \frac{1}{\delta^2} \left( \sum_{n=0}^{\infty} \delta^n S'_n \right)^2 + \frac{1}{\delta} \sum_{n=0}^{\infty} \delta^n S''_n \right] = Q(x).$$

5. The asymptotic series for  $y(x)$  is typically considered as a divergent series, whose general term  $\delta^n S_n(x)$  starts to increase after a certain value  $n = n_{\max}$ . Therefore, the smallest error attained by the WKB method is the order of the last included term.
6. In quantum physics, a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space. The potential may be external or it may be the result of the presence of another particle; in the latter case, one can equivalently define a bound state as a state representing two or more particles whose interaction energy exceeds the total energy of each separate particle.

**11.4 SUMMARY**

- In mathematical physics, the WKB approximation or WKB method is a method for finding approximate solutions to linear differential equations with spatially varying coefficients.
- WKB approximation is typically used for a semi-classical calculation in quantum mechanics in which the wavefunction is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.
- The abbreviation WKB approximation refers to Wentzel–Kramers–Brillouin, i.e., the WKB approximation method is named after physicists Gregor Wentzel, Hendrik Anthony Kramers, and Léon Brillouin, who all developed it in 1926.
- The WKB approximation is specifically used for obtaining an approximate solution to a time independent one-dimensional differential equation, typically the Schrödinger equation. Its principal applications include the calculations of bound state energies and tunnelling rates through barriers.
- The WKB theory is a method typically used for approximating the solution of a differential equation whose highest derivative is multiplied by a small parameter ‘ $\epsilon$ ’.
- WKB theory is a special case of multiple scale analysis.
- The asymptotic series for  $y(x)$  is typically considered as a divergent series, whose general term  $\delta^n S_n(x)$  starts to increase after a certain value  $n = n_{\max}$ .

Therefore, the smallest error attained by the WKB method is the order of the last included term.

- Solving the Schrödinger equation is one of the essential problems in quantum mechanics. Since a non-linear second order Ordinary Differential Equation (ODE) has, in general, no analytic solution, hence an approximation method is typically applied.
- In quantum physics, a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space.
- The potential may be external or it may be the result of the presence of another particle; in the latter case, one can equivalently define a bound state as a state representing two or more particles whose interaction energy exceeds the total energy of each separate particle.
- In a bound state problem with potential  $V(x)$ , for a given energy  $E$ , we can divide space into classically allowed regions, for which  $E > V(x)$ , and classically forbidden regions for which  $E < V(x)$ . Assume that there are only three regions in total, classically forbidden for  $x < a$  and  $x > b$ , and classically allowed for  $a < x < b$ .

## NOTES

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### 11.5 KEY WORDS

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- **WKB approximation or WKB method:** It is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. The WKB approximation refers to Wentzel–Kramers–Brillouin.
- **Bound state:** A bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space.

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### 11.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

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#### Short Answer Questions

1. Define WKB approximation.
2. Who developed WKB approximation?
3. Which condition is used in the derivation of the WKB approximation?
4. What is bound state?

#### Long Answer Questions

1. Discuss the WKB approximation or WKB method giving appropriate examples.

**NOTES**

2. Briefly explain the WKB theory with relevant equations.
3. Explain the exactness of the asymptotic series.
4. Explain the derivation of the Schrödinger equation.
5. Discuss the bound state for WKB approximation.

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## **11.7 FURTHER READINGS**

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**BLOCK IV  
TIME EVOLUTION**

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**UNIT 12 TIME DEPENDENT  
PERTURBATION THEORY**

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**NOTES**

**Structure**

- 12.0 Introduction
- 12.1 Objectives
- 12.2 Time Dependent Perturbation Theory
- 12.3 Spontaneous and Stimulated Emission
- 12.4 Answers to Check Your Progress Questions
- 12.5 Summary
- 12.6 Key Words
- 12.7 Self Assessment Questions and Exercises
- 12.8 Further Readings

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**12.0 INTRODUCTION**

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In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The basic notion is to start with a simple system for which a mathematical solution is known, and then adding an additional ‘perturbing’ Hamiltonian representing a weak disturbance to the system. If the disturbance is not too large, the various physical quantities associated with the perturbed system, for example its energy levels and eigenstates, can be expressed as ‘corrections’ to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods, such as asymptotic series.

The time dependent perturbation theory was developed by Paul Dirac who proposed that the effect of a time dependent perturbation  $V(t)$  can be applied to a time independent Hamiltonian  $H_0$ . Since the perturbed Hamiltonian is time-dependent, so are its energy levels and eigenstates.

The emission of a single photon by an excited atom can be studied using the time dependent perturbation theory to find the transition probability for atom. The atoms those exist in higher energy state (by stimulated absorption) can make a transition to ground state (lower energy state) through the emission of electromagnetic radiation by two ways, the spontaneous emission and the stimulated emission.

In this unit, you will study about the time dependent perturbation theory, the golden rule and applications, spontaneous emission and stimulated emission.

## NOTES

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### 12.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand the time dependent perturbation theory
- Explain the golden rule and its applications for time dependent perturbation theory
- Discuss about the spontaneous emission and stimulated emission

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### 12.2 TIME DEPENDENT PERTURBATION THEORY

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In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The basic notion is to use a simple system for which a mathematical solution is known, and then adding an additional ‘Perturbing’ Hamiltonian representing a weak disturbance to the system. If the disturbance is not too large, then the various physical quantities associated with the perturbed system, for example its energy levels and eigenstates, can be expressed as ‘Corrections’ to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods, such as asymptotic series. The complicated system can consequently be studied based on the simpler one.

Time dependent perturbation theory, developed by Paul Dirac, typically explains the effect of a time dependent perturbation  $V(t)$  applied to a time independent Hamiltonian,  $H_0$ . Since the perturbed Hamiltonian is time dependent, accordingly are its energy levels and eigenstates. Thus, the goals of time dependent perturbation theory are slightly different from time independent perturbation theory. Following are the two significant quantities of the time dependent perturbation:

1. The time dependent expectation value of some observable  $A$ , for a given initial state.
2. The time dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

#### General Time Dependent Perturbations

Assume that the unperturbed energy eigenvalue problem is exactly of the form  $H_0\phi_n = E_n\phi_n$ .

To this is added a perturbation that depends on time,  $\nu(t)$ . To solve the time dependent problems we use the following time dependent Schrödinger equation.

$$(H_0 + \mathcal{V}(t)) \psi(t) = i\hbar \frac{\partial \psi(t)}{\partial t}$$

Then we expand  $\psi$  in terms of the eigenfunctions as,

$$\psi(t) = \sum_k c_k(t) \phi_k e^{-iE_k t/\hbar} \text{ with } c_k(t) e^{-iE_k t/\hbar} = \langle \phi_k | \psi(t) \rangle.$$

The time dependent Schrödinger equations is then given as,

$$\begin{aligned} \sum_k (H_0 + \mathcal{V}(t)) c_k(t) e^{-iE_k t/\hbar} \phi_k &= i\hbar \sum_k \frac{\partial c_k(t) e^{-iE_k t/\hbar}}{\partial t} \phi_k \\ \sum_k c_k(t) e^{-iE_k t/\hbar} (E_k + \mathcal{V}(t)) \phi_k &= \sum_k \left( i\hbar \frac{\partial c_k(t)}{\partial t} + E_k c_k(t) \right) e^{-iE_k t/\hbar} \phi_k \\ \sum_k \mathcal{V}(t) c_k(t) e^{-iE_k t/\hbar} \phi_k &= i\hbar \sum_k \frac{\partial c_k(t)}{\partial t} e^{-iE_k t/\hbar} \phi_k \end{aligned}$$

Now dot  $\langle \phi_n |$  into this equation to get the time dependence of one coefficient.

$$\begin{aligned} \sum_k \mathcal{V}_{nk}(t) c_k(t) e^{-iE_k t/\hbar} &= i\hbar \frac{\partial c_n(t)}{\partial t} e^{-iE_n t/\hbar} \\ \frac{\partial c_n(t)}{\partial t} &= \frac{1}{i\hbar} \sum_k \mathcal{V}_{nk}(t) c_k(t) e^{i(E_n - E_k)t/\hbar} \end{aligned}$$

Assuming that at  $t = 0$ , we are in an initial state  $\psi(t = 0) = \phi_i$  and hence all the other  $c_k$  are equal to zero as  $c_k = \delta_{ki}$ .

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar} \left( \mathcal{V}_{ni}(t) e^{i\omega_{ni}t} + \sum_{k \neq i} \mathcal{V}_{nk}(t) c_k(t) e^{i\omega_{nk}t} \right)$$

Next we calculate the transition rates. Considering that for the first order, all the  $c_k(t)$  are small in comparison to  $c_i(t) \approx 1$ , therefore the sum can be neglected.

$$\begin{aligned} \frac{\partial c_n^{(1)}(t)}{\partial t} &= \frac{1}{i\hbar} \mathcal{V}_{ni}(t) e^{i\omega_{ni}t} \\ c_n^{(1)}(t) &= \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni}t'} \mathcal{V}_{ni}(t') dt' \end{aligned}$$

This equation is used to calculate transition probabilities for a general time dependent perturbation. This can also be used as a basis to calculate the transition rates for the specific problem of harmonic potentials.

Assuming again that 't' is small enough hence the  $c_i$  may not have changed much.

Remember that, if there is a large energy difference between the initial and the final states, then a slowly varying perturbation can average to zero.

## NOTES

## NOTES

Subsequently we can find that the perturbation may require frequency components that are compatible with  $\omega_{ni}$  in order to cause transitions.

If the first order term is zero or higher accuracy is required, then the second order term can be calculated. In second order, first a transition is made to an intermediate state  $\phi_k$  and then a transition to  $\phi_n$ . We simply put the first order  $c_k^{(1)}(t)$  into the sum.

$$\begin{aligned}\frac{\partial c_n(t)}{\partial t} &= \frac{1}{i\hbar} \left( \mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k \neq i} \mathcal{V}_{nk}(t)c_k^{(1)}(t)e^{i\omega_{nk}t} \right) \\ \frac{\partial c_n(t)}{\partial t} &= \frac{1}{i\hbar} \left( \mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k \neq i} \mathcal{V}_{nk}(t) \frac{1}{i\hbar} e^{i\omega_{nk}t} \int_0^t e^{i\omega_{ki}t'} \mathcal{V}_{ki}(t') dt' \right) \\ c_n^{(2)}(t) &= \frac{-1}{\hbar^2} \sum_{k \neq i} \int_0^t dt'' \mathcal{V}_{nk}(t'') e^{i\omega_{nk}t''} \int_0^{t''} dt' e^{i\omega_{ki}t'} \mathcal{V}_{ki}(t') \\ c_n^{(2)}(t) &= \frac{-1}{\hbar^2} \sum_{k \neq i} \int_0^t dt'' \mathcal{V}_{nk}(t'') e^{i\omega_{nk}t''} \int_0^{t''} dt' e^{i\omega_{ki}t'} \mathcal{V}_{ki}(t')\end{aligned}$$

### The Golden Rule and its Applications

In quantum physics, Fermi's golden rule is a formula that describes the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system to a group of energy eigenstates in a continuum, as a result of a weak perturbation. This transition rate is effectively independent of time (so long as the strength of the perturbation is independent of time) and is proportional to the strength of the coupling between the initial and final states of the system, typically described by the square of the matrix element of the perturbation, along with the density of states. It is also applicable when the final state is not part of a continuum if there is some de-coherence in the process, like relaxation of the atoms or like noise in the perturbation, in which case the density of states is replaced by the reciprocal of de-coherence bandwidth.

Fermi's Golden Rule, also referred to as, the Golden Rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state  $|i\rangle$  to a final state  $|f\rangle$  that is part of a continuum of states.

Fermi's golden rule describes a system which begins in an eigenstate,  $|i\rangle$ , of an unperturbed Hamiltonian,  $H_0$  and considers the effect of a perturbing Hamiltonian,  $H'$  applied to the system. If  $H'$  is considered time independent, then the system goes only into those states in the continuum that have the same energy as the initial state. If  $H'$  is oscillating sinusoidally as a function of time, i.e., it is a harmonic perturbation, with an angular frequency  $\hat{E}$ , then the transition is into states with energies that differ by  $\hat{E}$  from the energy of the initial state.

In both cases, the transition probability per unit of time from the initial state  $|i\rangle$  to a set of final states  $|f\rangle$  is essentially constant. It is given, to first order approximation, by,

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \rho(E_f)$$

Where  $\langle f|H'|i\rangle$  is the matrix element (in bra-ket notation) of the perturbation  $H'$  between the final and initial states and  $\rho(E_f)$  is the density of states (number of continuum states in an infinitesimally small energy interval  $E + dE$  at the energy  $E_f$  of the final states. This transition probability is also called 'Decay Probability' and is related to the inverse of the mean lifetime. Thus, the probability of finding the system in state  $|f\rangle$  is proportional to  $e^{-\Gamma_{i \rightarrow f} t}$ .

The standard way to derive the equation is to start with time dependent perturbation theory and to take the limit for absorption under the assumption that the time of the measurement is much larger than the time needed for the transition.

#### Check Your Progress

1. What is time dependent perturbation theory?
2. Define the two significant quantities of the time dependent perturbation.
3. When the perturbation can average to zero?
4. What is Fermi's golden rule?
5. What does Fermi's golden rule describes?

### 12.3 SPONTANEOUS AND STIMULATED EMISSION

One of the most outstanding developments of science and technology in 20th century is laser. Laser first made in 1960. The term laser is the abbreviation of 'Light Amplification by Stimulated Emission of Radiation'. So the term reflects the crucial role of the technology of stimulated emission for quantum oscillators and amplifiers of coherent light source. This field of science and technology first came into light when Albert Einstein showed that the process stimulated emission must exist.

Any atomic system is characterized by different discrete energy state. Normally, the atoms are lying in the lowest energy state (say, ground state). An atom lying in a ground state may be excited by variety of processes to a higher energy state. It may occur by the collisions with other particles or through the absorption of electromagnetic radiation of particular frequencies; such a way is known as stimulated absorption.

#### NOTES

## NOTES

On the other hand, the atoms those exist in higher energy state (by stimulated absorption) can make a transition to ground state (lower energy state) through the emission of electromagnetic radiation by two ways — (a) Spontaneous Emission and (b) Stimulated Emission.

### Optical Coherence

If light waves from different sources, which are always in phase is called coherent light. Such waves are responsible for interference effects. Actual light waves consist of different photons with different states. So, the photons emitted from different sources have their different energy, different direction of momentum, and polarization. These light waves are made of ‘disordered’ photons. Only the waves from coherence sources can produce an interference pattern. The ability of a wave to produce an interference pattern may be measured by the fringe contrast, i.e., fringe visibility. The visibility of an interference pattern is defined by the relation,

$$V = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$

where  $I_{\max}$  is the maximum intensity of bright fringes and  $I_{\min}$  is the minimum intensity of dark fringe ( $\sim 0$ ). From the above relation we see that when  $I_{\min} = 0$ , the visibility is maximum, i.e.,  $V = 1$ . Visibility will be minimum when  $I_{\max} = I_{\min}$ , i.e., when simply no interference pattern is evident.

The ability of light waves to produce interference depends on the ‘Degree of Coherence’ of the light wave. An increase in the ‘Degree of Coherence’ of a light beam corresponds to a contrast interference pattern, i.e., visibility will be higher.

### Spontaneous and Stimulated Emission

The energy level of an atom or molecule has with definite (discrete) energy. The transition of an atom or molecule from one energy of lower and upper level to other happens by quantum transition. The transition occurs when atoms or molecules interact with molecular radiation.

Before the discussion of spontaneous and stimulated emission we must discuss about absorption (stimulated) of light. Let the energies of lower and upper level are  $E_1$  and  $E_2$ . If the atoms are in lower energy state, then one say that a photon having energy  $E_{12} = E_2 - E_1$  travels to the atoms. The atoms can absorb this photonic energy and jump from level  $E_1$  to  $E_2$  (Refer Figure (12.1)).

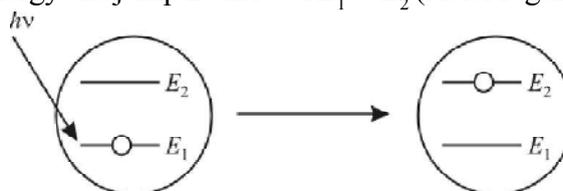


Fig. 12.1 Absorption of Photon

If  $W_{ab}$  be the probability of absorption of light (photon) from  $E_1$  to  $E_2$  transition in atoms per unit time, the probability is proportional to the numbers of incident photons and can be written as,

$$W_{ab} = BNE_{12} \quad \dots(12.1)$$

where  $N$  is the numbers of photons per unit volume and  $B$  is a constant.

**Spontaneous Emission:** When an atom that are in excited state (higher energy state) of energy  $E_2$  will tend to come to ground state (or lower energy state) of energy  $E_1$  spontaneously, i.e., without any stimulus. The photon emitted the energy  $E_{12} = E_2 - E_1$  spontaneously (Refer Figure (12.2)). If the probability of spontaneous emission is  $W_{sp}$ , then we can say,

$$W_{sp} = A \quad \dots(12.2)$$

The probability of spontaneous emission depends only on the properties of the transition.

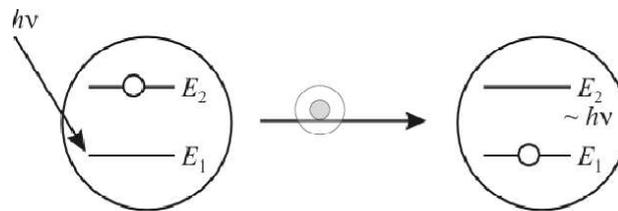


Fig. 12.2 Spontaneous Emission

**Stimulated Emission:** When the atoms that are in the excited state (higher energy level), then the same incident photon can play the role of a trigger, i.e., it can induce the atom to come back to lower energy state (or ground state). So, the transition takes place from  $E_2$  level to  $E_1$  level. Due to this transition photon emitted some energy of  $E_{12} = E_2 - E_1$ . Both the inducing and induced photon has the same energy  $E_{12}$ . This phenomenon is known as stimulated emission (Refer Figure (12.3)). The rate of stimulated emission (as well as absorption) depends on the intensity of the field applied (external) and on the numbers of atoms in the excited state (higher energy level). The total stimulated transition (stimulated emission and absorption) depends on the difference of atoms in the ground state (lower energy state) and excited state (higher energy state). But for the case of spontaneous emission, the transition depends on the numbers of atoms in the excited state (higher energy state).

If the probability of stimulated emission is  $W_{st}$  per unit time, then we have

$$W_{st} = BNE_{12} \quad \dots(12.3)$$

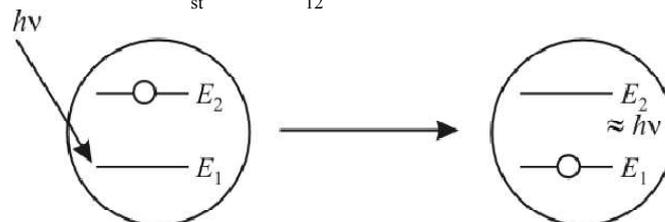


Fig. 12.3 Stimulated Emission

## NOTES

NOTES

**Check Your Progress**

6. How any atomic system is characterized?
7. Explain the ‘Degree of Coherence’.
8. What is spontaneous emission?
9. On what the probability of spontaneous emission depends?
10. Explain stimulated emission.

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**12.4 ANSWERS TO CHECK YOUR PROGRESS  
QUESTIONS**

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1. Time dependent perturbation theory, developed by Paul Dirac, typically explains the effect of a time dependent perturbation  $V(t)$  applied to a time independent Hamiltonian,  $H_0$ . Since the perturbed Hamiltonian is time dependent, accordingly are its energy levels and eigenstates.
2. Following are the two significant quantities of the time dependent perturbation:
  - The time dependent expectation value of some observable  $A$ , for a given initial state.
  - The time dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.
3. If there is a large energy difference between the initial and the final states, then a slowly varying perturbation can average to zero.
4. Fermi’s Golden Rule, also referred to as, the Golden Rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state  $|i\rangle$  to a final state  $|f\rangle$  that is part of a continuum of states.
5. Fermi’s golden rule describes a system which begins in an eigenstate,  $|i\rangle$ , of an unperturbed Hamiltonian,  $H_0$  and considers the effect of a perturbing Hamiltonian,  $H'$  applied to the system. If  $H'$  is considered time independent, then the system goes only into those states in the continuum that have the same energy as the initial state. If  $H'$  is oscillating sinusoidally as a function of time, i.e., it is a harmonic perturbation, with an angular frequency  $\dot{E}$ , then the transition is into states with energies that differ by  $\dot{E}$  from the energy of the initial state.

In both cases, the transition probability per unit of time from the initial state  $|i\rangle$  to a set of final states  $|f\rangle$  is essentially constant.

6. Any atomic system is characterized by different discrete energy state. Normally, the atoms are lying in the lowest energy state (say, ground state). An atom lying in a ground state may be excited by variety of processes to a higher energy state. It may occur by the collisions with other particles or through the absorption of electromagnetic radiation of particular frequencies; such a way is known as stimulated absorption.  
The atoms those exist in higher energy state (by stimulated absorption) can make a transition to ground state (lower energy state) through the emission of electromagnetic radiation by two ways, spontaneous emission and stimulated emission.
7. The ability of light waves to produce interference depends on the ‘Degree of Coherence’ of the light wave. An increase in the ‘Degree of Coherence’ of a light beam corresponds to a contrast interference pattern, i.e., visibility will be higher.
8. The spontaneous emission states that when an atom that are in excited state (higher energy state) of energy  $E_2$  will tend to come to ground state (or lower energy state) of energy  $E_1$  spontaneously, i.e., without any stimulus. The photon emitted the energy  $E_{12} = E_2 - E_1$  spontaneously.
9. The probability of spontaneous emission depends only on the properties of the transition.
10. The stimulated emission states that when the atoms that are in the excited state (higher energy level), then the same incident photon can play the role of a trigger, i.e., it can induce the atom to come back to lower energy state (or ground state). So, the transition takes place from  $E_2$  level to  $E_1$  level. Due to this transition photon emitted some energy of  $E_{12} = E_2 - E_1$ . Both the inducing and induced photon has the same energy  $E_{12}$ . This phenomenon is known as stimulated emission.

## NOTES

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### 12.5 SUMMARY

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- In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one.
- The basic notion is to use a simple system for which a mathematical solution is known, and then adding an additional ‘Perturbing’ Hamiltonian representing a weak disturbance to the system.
- If the disturbance is not too large, then the various physical quantities associated with the perturbed system, for example its energy levels and eigenstates, can be expressed as ‘Corrections’ to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods, such as asymptotic series.

## NOTES

- Time dependent perturbation theory, developed by Paul Dirac, typically explains the effect of a time dependent perturbation  $V(t)$  applied to a time independent Hamiltonian,  $H_0$ .
- Since the perturbed Hamiltonian is time dependent, accordingly are its energy levels and eigenstates. Thus, the goals of time dependent perturbation theory are slightly different from time independent perturbation theory.
- The time dependent expectation value of some observable  $A$ , for a given initial state.
- The time dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.
- If there is a large energy difference between the initial and the final states, then a slowly varying perturbation can average to zero.
- In quantum physics, Fermi's golden rule is a formula that describes the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system to a group of energy eigenstates in a continuum, as a result of a weak perturbation.
- Fermi's Golden Rule, also referred to as, the Golden Rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state  $|i\rangle$  to a final state  $|f\rangle$  that is part of a continuum of states.
- Fermi's golden rule describes a system which begins in an eigenstate,  $|i\rangle$ , of an unperturbed Hamiltonian,  $H_0$  and considers the effect of a perturbing Hamiltonian,  $H'$  applied to the system.
- If  $H'$  is considered time independent, then the system goes only into those states in the continuum that have the same energy as the initial state. If  $H'$  is oscillating sinusoidally as a function of time, i.e., it is a harmonic perturbation, with an angular frequency  $\omega$ , then the transition is into states with energies that differ by  $\pm\hbar\omega$  from the energy of the initial state. In both cases, the transition probability per unit of time from the initial state  $|i\rangle$  to a set of final states  $|f\rangle$  is essentially constant.
- The standard way to derive the equation is to start with time dependent perturbation theory and to take the limit for absorption under the assumption that the time of the measurement is much larger than the time needed for the transition.
- Any atomic system is characterized by different discrete energy state. Normally, the atoms are lying in the lowest energy state (say, ground state). An atom lying in a ground state may be excited by variety of processes to a higher energy state. It may occur by the collisions with other particles or through the absorption of electromagnetic radiation of particular frequencies; such a way is known as stimulated absorption.

- The atoms those exist in higher energy state (by stimulated absorption) can make a transition to ground state (lower energy state) through the emission of electromagnetic radiation by two ways, spontaneous emission and stimulated emission.
- The ability of light waves to produce interference depends on the ‘Degree of Coherence’ of the light wave. An increase in the ‘Degree of Coherence’ of a light beam corresponds to a contrast interference pattern, i.e., visibility will be higher.
- The energy level of an atom or molecule has with definite (discrete) energy. The transition of an atom or molecule from one energy of lower and upper level to other happens by quantum transition. The transition occurs when atoms or molecules interact with molecular radiation.
- The probability of spontaneous emission depends only on the properties of the transition.
- The spontaneous emission states that when an atom that are in excited state (higher energy state) of energy  $E_2$  will tend to come to ground state (or lower energy state) of energy  $E_1$  spontaneously, i.e., without any stimulus. The photon emitted the energy  $E_{12} = E_2 - E_1$  spontaneously.
- The stimulated emission states that when the atoms that are in the excited state (higher energy level), then the same incident photon can play the role of a trigger, i.e., it can induce the atom to come back to lower energy state (or ground state). So, the transition takes place from  $E_2$  level to  $E_1$  level. Due to this transition photon emitted some energy of  $E_{12} = E_2 - E_1$ . Both the inducing and induced photon has the same energy  $E_{12}$ . This phenomenon is known as stimulated emission.
- The total stimulated transition (stimulated emission and absorption) depends on the difference of atoms in the ground state (lower energy state) and excited state (higher energy state).

## NOTES

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### 12.6 KEY WORDS

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- **Time dependent perturbation theory:** It was developed by Paul Dirac that typically explains the effect of a time dependent perturbation  $V(t)$  applied to a time independent Hamiltonian,  $H_0$ .
- **Fermi’s golden rule:** It is also referred to as the golden rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state  $|i\rangle$  to a final state  $|f\rangle$  that is part of a continuum of states.
- **Degree of Coherence:** The ability of light waves to produce interference depends on the ‘Degree of Coherence’ of the light wave. An increase in the ‘Degree of Coherence’ of a light beam corresponds to a contrast interference pattern, i.e., visibility will be higher.

## NOTES

- **Spontaneous emission:** When an atom that are in excited state (higher energy state) of energy  $E_2$  will tend to come to ground state (or lower energy state) of energy  $E_1$  spontaneously, i.e., without any stimulus. The photon emitted the energy  $E_{12} = E_2 - E_1$  spontaneously.
- **Stimulated emission:** When the atoms that are in the excited state (higher energy level), then the same incident photon can play the role of a trigger, i.e., it can induce the atom to come back to lower energy state (or ground state). So, the transition takes place from  $E_2$  level to  $E_1$  level. Due to this transition photon emitted some energy of  $E_{12} = E_2 - E_1$ . Both the inducing and induced photon has the same energy  $E_{12}$ .

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## 12.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### Short Answer Questions

1. What dose time dependent perturbation theory state?
2. State Fermi's golden rule?
3. Differentiate between spontaneous emission and stimulated emission.

### Long Answer Questions

1. Discuss the significance of the time dependent perturbation theory giving appropriate examples.
2. Briefly explain the fields where the time dependent perturbation theory is used.
3. Explain the Fermi's golden rule and its applications for time dependent perturbation theory.
4. Discuss about the spontaneous emission and stimulated emission giving appropriate examples and derivations.

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## 12.8 FURTHER READINGS

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
- Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.
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- Devanathan, V. 2005. *Quantum Mechanics*. Oxford: Alpha Science International Ltd.
- Schiff, Leonard L. 1968. *Quantum Mechanics*, 3rd Edition. New York: McGraw Hill.

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# UNIT 13 QUANTUM THEORY OF RADIATION

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## NOTES

### Structure

- 13.0 Introduction
- 13.1 Objectives
- 13.2 Einstein's A & B Coefficients
- 13.3 Semi-Classical and Quantum Theory of Radiation
- 13.4 Answers to Check Your Progress Questions
- 13.5 Summary
- 13.6 Key Words
- 13.7 Self Assessment Questions and Exercises
- 13.8 Further Readings

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### 13.0 INTRODUCTION

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The theory of the interaction of light with atomic matter reveals enormous in the historical development of quantum mechanics. This circumstance is simply a consequence of the fact that the light emitted or absorbed by atomic matter provides clues into its nature. The synthesis of the quantum theory that resulted from spectroscopic and other optical investigations and is still developing.

Einstein coefficients are mathematical quantities which are a measure of the probability of absorption or emission of light by an atom or molecule. The Einstein  $A$  coefficient is related to the rate of spontaneous emission of light, and the Einstein  $B$  coefficients are related to the absorption and stimulated emission of light. The semi-classical radiation theory states that the electromagnetic radiation is treated as a classically prescribed field while the atomic matter with which it interacts is described according to the directives of quantum mechanics. Quantum theory has, of course, been developed and applied with remarkable success in many areas of physics, but it is important to remember that it was originally a theory of the interaction of light with atoms and molecules. In this historical sense, semi-classical radiation theory strikes at the very roots of quantum mechanics.

In this unit, you will study about the Einstein's  $A$  and  $B$  coefficients, semi-classical and quantum theory of radiation in detail.

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### 13.1 OBJECTIVES

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After going through this unit, you will be able to:

- Explain the Einstein's  $A$  and  $B$  coefficients
- Understand semi-classical and quantum theory of radiation

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### 13.2 EINSTEIN'S A & B COEFFICIENTS

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Let us consider  $E(\nu)$  as the energy density at equilibrium, where  $\nu$  is the frequency of photon.

If  $N_1$  and  $N_2$  are the number of atoms in the lower energy state (ground state) and higher energy state (excited state) respectively, then we can write,

$$N_1 P_{12} = N_1 B_{12} E(\nu) \quad \dots(13.1)$$

where  $P_{12}$  is the probability of absorption proportional to energy density  $E(\nu)$  and  $B_{12}$  is the Einstein's coefficient of absorption.

Therefore, we can express the energy state of  $N_2$  as follows:

$$N_2 P_{21} = N_2 [A_{21} + B_{21} E(\nu)] \quad \dots(13.2)$$

Where  $P_{21}$  is the probability (stimulated) proportional to energy density  $E(\nu)$  with addition to  $A_{21}$ ,  $A_{21}$  is the Einstein's coefficient of spontaneous and  $B_{21}$  is the Einstein's coefficient of stimulated emission.

When thermal equilibrium exists, we can say that the total absorption probability is equal to the total emission probability.

So, from Equations (13.4) and (13.5), we have

$$N_1 B_{12} E(\nu) = N_2 [A_{21} + B_{21} E(\nu)]$$

or

$$E(\nu) = \frac{A_{21} / B_{21}}{\left(\frac{N_1}{N_2}\right) \left(\frac{B_{12}}{B_{21}}\right) - 1} \quad \dots(13.3)$$

According to Einstein's assumption, coefficient of stimulated absorption and coefficient of stimulated emission are equal, i.e.,  $B_{12} = B_{21} = B$  (say) and if we consider  $A_{21} = A$  (say), then the Equation (13.3) reduces to,

$$E(\nu) = \frac{A/B}{\frac{N_1}{N_2} - 1} \quad \dots(13.4)$$

$A$  and  $B$  in the above equation are called Einstein's 'A' and 'B' coefficients. According to Planck's radiation law, we know that

$$E(\nu) = \frac{8\pi h\nu^3}{c^3 e^{h\nu/KT} - 1} \quad \dots(13.5)$$

By comparing equations (13.4) and (13.5), we can write,

$$\frac{N_1}{N_2} = e^{h\nu/KT}$$

And 
$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}$$

(Ratio of coefficients of spontaneous and stimulated emission, i.e., ratio of Einstein's 'A' and 'B' Coefficient)

Where  $h$  is the Planck's Constant.

$K$  is the Boltzman's Constant.

$c$  is the Velocity of Light.

$T$  is the Temperature in Kelvin.

## NOTES

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### 13.3 SEMI-CLASSICAL AND QUANTUM THEORY OF RADIATION

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Semi-classical physics, or simply semi-classical refers to a theory in which one part of a system is described quantum-mechanically whereas the other is treated classically. For example, external fields will be constant, or when changing will be classically described. In general, it incorporates a development in powers of Planck's constant, resulting in the classical physics of power 0, and the first nontrivial approximation to the power of (-1). Thus, there is a clear link between the quantum-mechanical system and the associated semi-classical and classical approximations, as it is similar in appearance to the transition from physical optics to geometric optics.

Four examples of a semi-classical approximations include:

- WKB approximation: electrons in classical external electromagnetic fields.
- Semi-classical gravity: quantum field theory within a classical curved gravitational background (see general relativity).
- Quantum chaos: quantization of classical chaotic systems.
- Quantum field theory: only Feynman diagrams with at most a single closed loop are considered, which corresponds to the powers of Planck's constant.

## NOTES

The semi-classical radiation theory consists of two elements: the classical Maxwell equations that is satisfied by the electric 'E' and the magnetic 'B' fields, and the ordinary quantum mechanics that is based on the Schrödinger equation of a single charged matter particle interacting with the electromagnetic field. The single particle Schrödinger quantum mechanics can be modified to take into account spin or be replaced by the nonrelativistic quantum mechanics of many particles.

The distribution of energy in the spectrum of radiations of a hot body cannot be explained by applying the classical concepts of physics. Max Planck gave an explanation to this observation by his '**Quantum Theory of Radiation**'. His theory states that,

1. The 'Radiant Energy' is always in the form of tiny bundles of light called '**quanta**', i.e., the energy is absorbed or emitted discontinuously.
2. Each **quantum** has some definite energy ' $E$ ', which depends upon the frequency of the radiations as,

$$E = h\gamma$$

Here,  $E$  is the energy of each quantum in Joules,  $\gamma$  is the frequency of the radiations in  $s^{-1}$ ,  $h$  is known as Planck's constant (a fundamental constant), whose value is,  $h = 6.626 \times 10^{-34}$  J-s.

Also,  $E = hcw$ , where  $w$  is known as wave number.  $w = (1/\lambda) m^{-1}$ .

From these equations, it is evident that  $\gamma = c/\lambda = cw$ .

The energy emitted or absorbed by a body is a multiple of a quantum, i.e., a body cannot absorb or emit energy in fractions of quantum. This concept is known as quantization of energy.

### Check Your Progress

1. Explain the Einstein's coefficient of absorption.
2. What are Einstein's A and B coefficients?
3. What is semi-classical physics?
4. Give examples of semi-classical approximations.
5. Define semi-classical radiation theory.

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## 13.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

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1. If  $N_1$  and  $N_2$  are the number of atoms in the lower energy state (ground state) and higher energy state (excited state) respectively, then we can write,

$$N_1 P_{12} = N_2 B_{12} E(\nu)$$

where  $P_{12}$  is the probability of absorption proportional to energy density  $E(\nu)$  and  $B_{12}$  is the Einstein's coefficient of absorption.

2. According to Einstein's assumption, coefficient of stimulated absorption and coefficient of stimulated emission are equal, i.e.,  $B_{12} = B_{21} = B$  (say) and if we consider  $A_{21} = A$  (say), then the Equation (13.3) reduces to,

$$E(\nu) = \frac{A/B}{\frac{N_1}{N_2} - 1}$$

$A$  and  $B$  in the above equation are called Einstein's 'A' and 'B' coefficients.

3. Semi-classical physics, or simply semi-classical refers to a theory in which one part of a system is described quantum-mechanically whereas the other is treated classically. For example, external fields will be constant, or when changing will be classically described. In general, it incorporates a development in powers of Planck's constant, resulting in the classical physics of power 0, and the first nontrivial approximation to the power of (-1).
4. Four examples of a semi-classical approximations include:
- WKB approximation: electrons in classical external electromagnetic fields.
  - Semi-classical gravity: quantum field theory within a classical curved gravitational background (see general relativity).
  - Quantum chaos: quantization of classical chaotic systems.
  - Quantum field theory: only Feynman diagrams with at most a single closed loop are considered, which corresponds to the powers of Planck's constant.
5. The semi-classical radiation theory consists of two elements: the classical Maxwell equations that is satisfied by the electric 'E' and the magnetic 'B' fields, and the ordinary quantum mechanics that is based on the Schrödinger equation of a single charged matter particle interacting with the electromagnetic field.

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### 13.5 SUMMARY

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- If  $N_1$  and  $N_2$  are the number of atoms in the lower energy state (ground state) and higher energy state (excited state) respectively, then we can write,

$$N_1 P_{12} = N_2 B_{12} E(\nu)$$

where  $P_{12}$  is the probability of absorption proportional to energy density  $E(\nu)$  and  $B_{12}$  is the Einstein's coefficient of absorption.

- When thermal equilibrium exists, we can say that the total absorption probability is equal to the total emission probability.
- According to Einstein's assumption, coefficient of stimulated absorption and coefficient of stimulated emission are equal, i.e.,  $B_{12} = B_{21} = B$  (say) and if we consider  $A_{21} = A$  (say), then the Equation reduces to,

$$E(\nu) = \frac{A/B}{\frac{N_1}{N_2} - 1}$$

$A$  and  $B$  in the above equation are called Einstein's 'A' and 'B' coefficients.

- According to Planck's radiation law, we know that

$$E(\nu) = \frac{8\pi h\nu^3}{c^3 e^{h\nu/KT} - 1}$$

- Semi-classical physics, or simply semi-classical refers to a theory in which one part of a system is described quantum-mechanically whereas the other is treated classically.
- In general, Semi-classical incorporates a development in powers of Planck's constant, resulting in the classical physics of power 0, and the first nontrivial approximation to the power of (-1).
- The semi-classical radiation theory consists of two elements: the classical Maxwell equations that is satisfied by the electric 'E' and the magnetic 'B' fields, and the ordinary quantum mechanics that is based on the Schrödinger equation of a single charged matter particle interacting with the electromagnetic field.
- The single particle Schrödinger quantum mechanics can be modified to take into account spin or be replaced by the nonrelativistic quantum mechanics of many particles.
- The distribution of energy in the spectrum of radiations of a hot body cannot be explained by applying the classical concepts of physics.
- The 'Radiant Energy' is always in the form of tiny bundles of light called 'quanta', i.e., the energy is absorbed or emitted discontinuously.

- Each quantum has some definite energy ‘ $E$ ’, which depends upon the frequency of the radiations as,

$$E = h\gamma$$

Here,  $E$  is the energy of each quantum in Joules,  $\gamma$  is the frequency of the radiations in  $s^{-1}$ ,  $h$  is known as Planck’s constant (a fundamental constant), whose value is,  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ .

- The energy emitted or absorbed by a body is a multiple of a quantum, i.e., a body cannot absorb or emit energy in fractions of quantum. This concept is known as quantization of energy.

## NOTES

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### 13.6 KEY WORDS

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- **Einstein’s assumption:** According to Einstein’s assumption, coefficient of stimulated absorption and coefficient of stimulated emission are equal, i.e.,  $B_{12} = B_{21} = B$ .
- **Semi-classical radiation theory:** It consists of two elements: the classical Maxwell equations that is satisfied by the electric ‘ $E$ ’ and the magnetic ‘ $B$ ’ fields, and the ordinary quantum mechanics that is based on the Schrödinger equation of a single charged matter particle interacting with the electromagnetic field.
- **Radiant energy:** It is always in the form of tiny bundles of light called ‘quanta’, i.e., the energy is absorbed or emitted discontinuously.

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### 13.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

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#### Short Answer Questions

1. Explain the Einstein’s  $A$  and  $B$  coefficients.
2. What is semi-classical theory of radiation?
3. What does quantum theory of radiation states?

#### Long Answer Questions

1. Briefly discuss the Einstein’s  $A$  and  $B$  coefficients giving relevant examples.
2. Explain the basic concept of semi-classical and quantum theory of radiation.
3. Explain the Max Planck explanation for semi-classical and quantum theory of radiation.

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**13.8 FURTHER READINGS**

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
- Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.
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# UNIT 14 THEORY OF SCATTERING

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## Structure

- 14.0 Introduction
- 14.1 Objectives
- 14.2 Theory Of Scattering
  - 14.2.1 Rayleigh Scattering
  - 14.2.2 Raman Scattering
- 14.3 Answers to Check Your Progress Questions
- 14.4 Summary
- 14.5 Key Words
- 14.6 Self Assessment Questions and Exercises
- 14.7 Further Readings

## NOTES

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### 14.0 INTRODUCTION

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In mathematics and physics, scattering theory is a framework for studying and understanding the scattering of waves and particles. Wave scattering corresponds to the collision and scattering of a wave with some material object, for instance sunlight scattered by rain drops to form a rainbow.

Rayleigh scattering, named after the nineteenth-century British physicist Lord Rayleigh (John William Strutt), is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process. The particles may be individual atoms or molecules. It can occur when light travels through transparent solids and liquids, and is most prominently seen in gases. Rayleigh scattering results from the electric polarizability of the particles. Rayleigh scattering of sunlight in Earth's atmosphere causes diffuse sky radiation, which is the reason for the blue color of the daytime and twilight sky, as well as the yellowish to reddish hue of the low Sun.

Raman scattering or the Raman effect is the inelastic scattering of a photon by molecules which are excited to higher energy levels. Since this effect was discovered in 1928 by C. V. Raman hence named so. The Raman effect forms the basis for Raman spectroscopy which is used by chemists and physicists to gain information about materials.

In this unit, you will study about the scattering theory basics, Rayleigh scattering, Raman scattering and selection rules.

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### 14.1 OBJECTIVES

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After going through this unit, you will be able to:

- Understand the basics of scattering theory

## NOTES

- Explain Rayleigh scattering
- Discuss the advantages and limitations of Rayleigh scattering
- Understand what Raman scattering is
- Define the selection rules, advantages and disadvantages of Raman scattering

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### 14.2 THEORY OF SCATTERING

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The ‘Scattering Theory’ is significantly used for studying and understanding the scattering of waves and particles in mathematics and physics. Typically the wave scattering corresponds to the collision and scattering of a wave with some material object, for example formation of rainbow is resultant of sunlight scattered by rain drops. Latest technology of ultrasonic testing is another example of scattering theory which is used in medical imaging, non-destructive testing of metals and quantum field theory.

Rayleigh scattering is one commonly known type of scattering which mainly consists of scattering from atmospheric gases, it occurs when the particles causing scattering are smaller in size than the radiation wavelengths in contact with them.

Mie scattering, and non-selective scattering are the two other types of wave scattering. Principally, the Mie scattering is considered to be elastic scattered light of particles that have a diameter similar to or larger than the wavelength of the incident light. The Mie signal is proportional to the square of the particle diameter, where as in case of non-selective scattering also known as Raman scattering, it occurs in all wavelengths of electromagnetic radiation equally in the atmosphere and is usually caused by particles which are much larger than the energy wavelengths.

#### Definitions of Scattering

1. Scattering, in physics, is defined as a change in the direction of motion of a particle because of a collision with another particle. As defined in physics, a collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.
2. Scattering occurs when light or other energy waves pass through an imperfect medium, such as air filled with particles of some sort, and are deflected from a straight path. The light is deflected off of its straight path and scatters in many directions.
3. Scattering is a general physical process where some forms of radiation, such as light, sound, or moving particles, are forced to deviate from a straight trajectory by one or more paths due to localized non-uniformities in the medium through which they pass.
4. As per the Encyclopaedia Britannica, the ‘Scattering, in physics, a change in the direction of motion of a particle because of a collision with another

particle. A collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.

The physicist Ernest Rutherford passed a stream of alpha particles through a thin sheet of gold foil. The alpha particles were emitted by a radioactive material and had enough energy to penetrate an atom; although most passed right through the gold foil, some were deflected in a way that indicated that the scattering was produced by a Coulomb force. Because the alpha particles are positively charged and the electrons in the atom are negatively charged, it followed that there must be a large positive charge inside the atom to create the Coulomb force by interacting with the alpha particles. In this way the nucleus of the atom was discovered.

### **Elastic and Inelastic Scattering**

The term ‘Elastic Scattering’ implies that the internal states of the scattering particles do not change, and hence they emerge unchanged from the scattering process. In inelastic scattering, by contrast, the particles’ internal state is changed, which may amount to exciting some of the electrons of a scattering atom, or the complete annihilation of a scattering particle and the creation of entirely new particles.

When two atoms are scattered off one another, one can understand them as being the bound state solutions of some differential equation. Thus, for example, the hydrogen atom corresponds to a solution to the Schrödinger equation with a negative inverse-power, i.e., attractive Coulombic, central potential. The scattering of two hydrogen atoms will disturb the state of each atom, resulting in one or both becoming excited, or even ionized, representing an inelastic scattering process.

#### **14.2.1 Rayleigh Scattering**

Rayleigh scattering is named after the nineteenth-century British physicist Lord Rayleigh (John William Strutt). It is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process. The particles may be individual atoms or molecules. It can occur when light travels through transparent solids and liquids, and is most prominently seen in gases. Rayleigh scattering results from the electric polarizability of the particles. The oscillating electric field of a light wave acts on the charges within a particle, causing them to move at the same frequency. The particle therefore becomes a small radiating dipole whose radiation we see as scattered light. This radiation is an integral part of the photon and no excitation or de-excitation occurs.

Rayleigh scattering of sunlight in Earth’s atmosphere causes diffuse sky radiation, which is the reason for the blue colour of the daytime and twilight sky, as well as the yellowish to reddish hue of the low Sun.

For wave frequencies that are below the resonance frequency of the scattering particle (normal dispersion regime), the amount of scattering is inversely proportional to the fourth power of the wavelength.

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Rayleigh scattering of molecular nitrogen and oxygen in the atmosphere includes elastic scattering as well as the inelastic contribution from rotational Raman scattering in air, since the changes in wavenumber of the scattered photon are typically smaller than  $50 \text{ cm}^{-1}$ . This can lead to changes in the rotational state of the molecules. Furthermore, the inelastic contribution has the same wavelengths dependency as the elastic part.

Scattering by particles similar to, or larger than, the wavelength of light is typically treated by the Mie scattering theory, the discrete dipole approximation and other computational techniques. Rayleigh scattering applies to particles that are small with respect to wavelengths of light, and that are optically ‘soft’ (i.e., with a refractive index close to 1).

In 1871, Lord Rayleigh published two papers on the colour and polarization of skylight to quantify Tyndall’s effect in water droplets in terms of the tiny particulates’ volumes and refractive indices. In 1881 with the help of James Clerk Maxwell’s 1865 proof of the electromagnetic nature of light, he exhibited that his equations followed from electromagnetism.

**Small Size Parameter Approximation**

The size of a scattering particle is often parameterized by the ratio,

$$x = \frac{2\pi r}{\lambda}$$

Where  $r$  is its characteristic length (radius) and  $\lambda$  is the wavelength of the light. The amplitude of light scattered from within any transparent dielectric is proportional to the inverse square of its wavelength and to the volume of material that is to the cube of its characteristic length. The wavelength dependence is characteristic of dipole scattering and the volume dependence will apply to any scattering mechanism. Objects with  $x \gg 1$  act as geometric shapes, scattering light according to their projected area. At the intermediate  $x \approx 1$  of Mie scattering, interference effects develop through phase variations over the object’s surface. Rayleigh scattering applies to the case when the scattering particle is very small, i.e.,  $x \ll 1$ , with a particle size  $< 1/10$  wavelength, and the whole surface re-radiates with the same phase. Because the particles are randomly positioned, the scattered light arrives at a particular point with a random collection of phases; it is incoherent and the resulting intensity is just the sum of the squares of the amplitudes from each particle and therefore proportional to the inverse fourth power of the wavelength and the sixth power of its size.

In detail, the intensity  $I$  of light scattered by any one of the small spheres of diameter  $d$  and refractive index  $n$  from a beam of unpolarized light of wavelength  $\lambda$  and intensity  $I_0$  is given by,

$$I = I_0 \frac{1 + \cos^2 \theta}{2R^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \left( \frac{d}{2} \right)^6$$

Where  $R$  is the distance to the particle and  $\theta$  is the scattering angle. Averaging this over all angles gives the Rayleigh scattering cross-section,

$$\sigma_s = \frac{2\pi^5}{3} \frac{d^6}{\lambda^4} \left( \frac{n^2 - 1}{n^2 + 2} \right)^2$$

The fraction of light scattered by a group of scattering particles is the number of particles per unit volume  $N$  times the cross-section. For example, the major constituent of the atmosphere, nitrogen, has a Rayleigh cross section of  $5.1 \times 10^{-31} \text{ m}^2$  at a wavelength of 532 nm (green light). This means that at atmospheric pressure, where there are about  $2 \times 10^{25}$  molecules per cubic meter, about a fraction  $10^{-5}$  of the light will be scattered for every meter of travel.

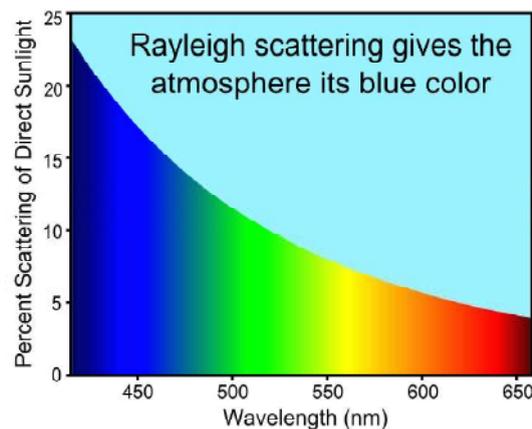
The strong wavelength dependence of the scattering ( $\sim \lambda^{-4}$ ) means that shorter (blue) wavelengths are scattered more strongly than longer (red) wavelengths.

### From Molecules

The above expression can also be written in terms of individual molecules by expressing the dependence on refractive index in terms of the molecular polarizability ' $\alpha$ ', proportional to the dipole moment induced by the electric field of the light. In this case, the Rayleigh scattering intensity for a single particle is given in CGS units by,

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 R^2} (1 + \cos^2 \theta).$$

The Rayleigh scattering gives the atmosphere its blue colour as shown in Figure (14.1).



**Fig. 14.1** Blue Light Scattered by the Atmosphere Relative to Red Light

The Rayleigh scattering is mostly seen occurring in nature, and therefore it is considered to be one of the most commonly observed optical phenomena. Foremost example for this phenomena is that the sky looks blue because of the intensity of light scattered by a molecule is inversely proportional to the fourth power of the

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wavelength of the incident light, which means that 10 times more blue light than red light gets scattered from a molecule. As such, sunlight incident on gas molecules in the air gets scattered as blue light in every direction, and the sky looks blue. Therefore, the Rayleigh scattering is the elastic scattering of light by particles which are much smaller than the wavelength of the light.

Figure (14.1) illustrates the greater proportion of blue light scattered by the atmosphere relative to red light. This phenomena occurs when radiation or beam of light interacts with molecules and particles in the atmosphere which happen to be smaller in diameter than the wavelength of the incoming radiation. Shorter wavelengths are more quickly and promptly scattered than the longer wavelengths. Light at shorter wavelengths (blue and violet) are scattered by small particles that include NO<sub>2</sub> and O<sub>2</sub>. Since blue light is at the short wavelength end of the visible spectrum, it is more strongly scattered in the atmosphere than longer wavelength red light. This results in the blue colour of the sky. Rayleigh scatter is also responsible for haze in the photographic images. In aerial photography special filters are used to filter out the scatter blue light to reduce haze. In digital images there are different techniques used to minimize the impacts of Rayleigh scatter.

**Effect of Fluctuations**

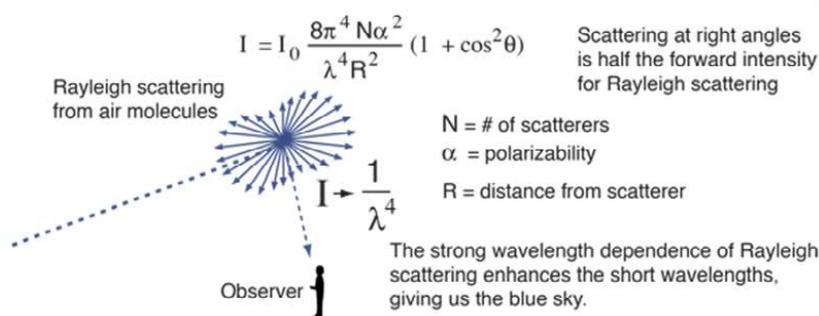
When the dielectric constant  $\epsilon$  of a certain region of volume  $V$  is different from the average dielectric constant of the medium  $\bar{\epsilon}$ , then any incident light will be scattered according to the following equation,

$$I = I_0 \frac{\pi^2 V^2 \sigma_\epsilon^2}{2\lambda^4 R^2} (1 + \cos^2 \theta)$$

Where  $\sigma_\epsilon^2$  represents the variance of the fluctuation in the dielectric constant  $\epsilon$ .

**Rayleigh Scattering Theory**

Rayleigh scattering theory refers to the scattering of light off of the molecules of the air, and can be extended to scattering from particles up to about a tenth of the wavelength of the light. It is Rayleigh scattering off the molecules of the air which gives us the blue sky. Lord Rayleigh calculated the scattered intensity from dipole scatterers much smaller than the wavelength to be:



**Fig. 14.2** Rayleigh Scattering Theory

Figure (14.2) illustrates Rayleigh scattering theory considering an air molecule. The Rayleigh scattering can be considered to be elastic scattering since the photon energies of the scattered photons is not changed. Scattering in which the scattered photons have either a higher or lower photon energy is called Raman scattering. Usually this kind of scattering involves exciting some vibrational mode of the molecules, giving a lower scattered photon energy, or scattering off an excited vibrational state of a molecule which adds its vibrational energy to the incident photon.

### Advantages of Rayleigh Scattering

- It is an easy technique.
- Arbitrary laser wavelength can be used, but shorter wavelengths leads to stronger signal (the  $\lambda^{-4}$ -dependence).
- Signal is proportional to number concentration  $\rightarrow N$  and/or  $1/T$ .
- Signal is proportional to laser pulse energy, i.e., no quenching or saturation effects.

### Limitations of Rayleigh Scattering

- The technique is not species selective, since all atoms/molecules/particles scatter at the same wavelength.
- For accurate thermometry, the Rayleigh cross-sections for individual species must be taken into account, since the mole fraction distribution must be known in every point.
- It is an incoherent technique.
- Stray light from particles, optics and surfaces can interfere with the Rayleigh signal.

### 14.2.2 Raman Scattering

Raman scattering or the Raman effect is the inelastic scattering of a photon by molecules which are excited to higher energy levels. The effect was discovered in 1928 by C. V. Raman and hence named as Raman scattering or the Raman effect.

When photons are scattered by a material, most of them are elastically scattered (Rayleigh scattering), such that the scattered photons have the same energy (frequency and wavelength) as the incident photons but different direction. However, a small fraction of the scattered photons (approximately 1 in 10 million) are scattered in-elastically, with the scattered photons having an energy different from, and usually lower than, those of the incident photons—these are Raman scattered photons. Because of conservation of energy, the material either gains or loses energy in the process. Typically this is vibrational energy and the incident photons are of visible light, although rotational energy (if gas samples are used) and electronic energy levels (if an X-ray source is used) may also be investigated.

## NOTES

## NOTES

The Raman effect forms the basis for Raman spectroscopy which is used by chemists and physicists to gain information about materials.

It is also possible to observe molecular vibrations by an inelastic scattering process. In the inelastic (Raman) scattering, an absorbed photon is re-emitted with lower energy; the difference in energy between the incident photons and scattered photons corresponds to the energy required to excite a molecule to a higher vibrational mode.

Typically, in Raman spectroscopy high intensity laser radiation with wavelengths in either the visible or near-infrared regions of the spectrum is passed through a sample. Photons from the laser beam produce an oscillating polarization in the molecules, exciting them to a virtual energy state. The oscillating polarization of the molecule can couple with other possible polarizations of the molecule, including vibrational and electronic excitations. If the polarization in the molecule does not couple to these other possible polarizations, then it will not change the vibrational state that the molecule started in and the scattered photon will have the same energy as the original photon. This type of scattering is known as Rayleigh scattering.

When the polarization in the molecules couples to a vibrational state that is higher in energy than the state they started in, then the original photon and the scattered photon differ in energy by the amount required to vibrationally excite the molecule. In perturbation theory, the Raman effect corresponds to the absorption and subsequent emission of a photon via an intermediate quantum state of a material. The intermediate state can be either a 'real', i.e., stationary state, or a virtual state.

### Stokes and Anti-Stokes

The Raman interaction leads to following two possible outcomes:

1. The material absorbs energy and the emitted photon has a lower energy than the incident photon. This outcome is labeled Stokes Raman scattering in honour of George Stokes who showed in 1852 that fluorescence is due to light emission at longer wavelength, now known to correspond to lower energy, than the absorbed incident light.
2. The material loses energy and the emitted photon has a higher energy than the absorbed photon. This outcome is labeled anti-Stokes Raman scattering.

The energy difference between the absorbed and emitted photon corresponds to the energy difference between two resonant states of the material and is independent of the absolute energy of the photon.

The spectrum of the scattered photons is termed the Raman spectrum. It shows the intensity of the scattered light as a function of its frequency difference  $\nu$  to the incident photons. The locations of corresponding Stokes and anti-Stokes peaks form a symmetric pattern around  $\Delta\nu = 0$ .

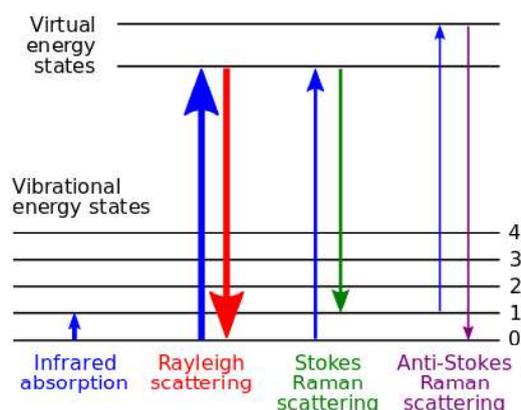
The frequency shifts are symmetric because they correspond to the energy difference between the same upper and lower resonant states. The intensities of

the pairs of features will typically differ, though. They depend on the populations of the initial states of the material, which in turn depend on the temperature. In thermodynamic equilibrium, the lower state will be more populated than the upper state. Therefore, the rate of transitions from the more populated lower state to the upper state, the ‘Stokes Transitions’ will be higher than in the opposite direction, the ‘Anti-Stokes Transitions’. Correspondingly, Stokes scattering peaks are stronger than anti-Stokes scattering peaks. Their ratio depends on the temperature, and can therefore be exploited to measure it.

## NOTES

### Raman Spectroscopy

Raman spectroscopy is named after Indian physicist Sir C. V. Raman. It is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. Figure 14.3 illustrates the Energy-level diagram showing the states involved in Raman spectra.



*Fig. 14.3 Energy-Level Diagram Showing the States Involved in Raman Spectra*

Raman spectroscopy relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

### Distinction from Fluorescence

The Raman effect differs from the process of fluorescence in that it is a scattering process. For fluorescence, the incident light is completely absorbed, transferring the system to an excited state. After a certain resonance lifetime, the system de-excites to lower energy states via emission of photons. The result of both processes is in essence the same.

**NOTES**

A photon with a frequency different from that of the incident photon is produced and the molecule is brought to a higher or lower energy level. But the major difference is that the Raman effect can take place for any frequency of incident light. In contrast to the fluorescence effect, the Raman effect is therefore not a resonant effect. In practice, this means that a fluorescence peak is anchored at a specific frequency, whereas a Raman peak maintains a constant separation from the excitation frequency.

**Selection Rules**

A Raman transition from one state to another is allowed only if the molecular polarizability of those states is different. For a vibration, this means that the derivative of the polarizability with respect to the normal coordinate associated to the vibration is non-zero:

$$\frac{\partial \alpha}{\partial Q} \neq 0.$$

In general, a normal mode is Raman active if it transforms with the same symmetry of the quadratic forms,  $(x^2, y^2, z^2, xy, xz, yz)$ , which can be verified from the character table of the molecule's symmetry group.

The specific selection rules state that the allowed rotational transitions are  $\Delta J = \pm 2$ , where 'J' is the rotational state.

The allowed vibrational transitions are  $\Delta \nu = \pm 1$ , where 'u' is the vibrational state.

**Advantages of Raman Effect**

- Organic and inorganic materials are suitable for Raman analysis. These can be solids, liquids, polymers or vapours.
- No sample preparation is required.
- It is not interfered by water.
- It is a non-destructive application.
- It is highly specific like a chemical fingerprint of a material.
- Raman spectra are acquired quickly within seconds.
- Samples can be analyzed through glass or a polymer packaging.
- Laser light and Raman scattered light can be transmitted by optical fibers over long distances for remote analysis.
- In Raman spectroscopy, the region from  $4000 \text{ cm}^{-1}$  to  $50 \text{ cm}^{-1}$  can be covered by a single recording.

- Raman spectra can be collected from a very small volume ( $< 1 \frac{1}{4}$  m in diameter).
- Inorganic materials are easily analysable with Raman spectroscopy.

#### Disadvantages of Raman Effect

- This cannot be used for metals or alloys.
- Raman effect is very weak. The detection needs a sensitive and highly optimized instrumentation.
- Fluorescence of impurities or of the sample itself can hide the Raman spectrum. Some compounds fluoresce when irradiated by the laser beam.
- Sample heating through the intense laser radiation can destroy the sample or cover the Raman spectrum.

#### NOTES

#### Check Your Progress

1. Explain the term scattering theory?
2. How scattering occurs?
3. What is Rayleigh scattering? Why it is named as Rayleigh scattering?
4. Define the size of a scattering particle.
5. What are the two possible outcomes of Raman interaction?
6. Explain Raman scattering or the Raman effect.
7. What is Raman spectrum?
8. What does specific selection rules states?

### 14.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The 'Scattering Theory' is significantly used for studying and understanding the scattering of waves and particles in mathematics and physics. Typically the wave scattering corresponds to the collision and scattering of a wave with some material object, for example formation of rainbow is resultant of sunlight scattered by rain drops. Latest technology of ultrasonic testing is another example of scattering theory which is used in medical imaging, non-destructive testing of metals and quantum field theory.
2. Scattering occurs when light or other energy waves pass through an imperfect medium, such as air filled with particles of some sort, and are deflected from a straight path. The light is deflected off of its straight path and scatters in many directions.

## NOTES

3. Rayleigh scattering is named after the nineteenth-century British physicist Lord Rayleigh (John William Strutt). It is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process.

4. The size of a scattering particle is often parameterized by the ratio,

$$x = \frac{2\pi r}{\lambda}$$

Where  $r$  is its characteristic length (radius) and  $\lambda$  is the wavelength of the light.

5. The Raman interaction leads to following two possible outcomes:

- The material absorbs energy and the emitted photon has a lower energy than the incident photon. This outcome is labeled Stokes Raman scattering in honour of George Stokes who showed in 1852 that fluorescence is due to light emission at longer wavelength, now known to correspond to lower energy, than the absorbed incident light.
- The material loses energy and the emitted photon has a higher energy than the absorbed photon. This outcome is labeled anti-Stokes Raman scattering.

6. Raman scattering or the Raman effect is the inelastic scattering of a photon by molecules which are excited to higher energy levels. The effect was discovered in 1928 by C. V. Raman and hence named as Raman scattering or the Raman effect. The Raman effect forms the basis for Raman spectroscopy which is used by chemists and physicists to gain information about materials.

7. The spectrum of the scattered photons is termed the Raman spectrum. It shows the intensity of the scattered light as a function of its frequency difference  $\Delta\nu$  to the incident photons. The locations of corresponding Stokes and anti-Stokes peaks form a symmetric pattern around  $\Delta\nu = 0$ .

8. The specific selection rules state that the allowed rotational transitions are

$\Delta J = \pm 2$ , where ' $J$ ' is the rotational state. The allowed vibrational transitions are  $\Delta\nu = \pm 1$ , where ' $\nu$ ' is the vibrational state.

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## 14.4 SUMMARY

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- The 'Scattering Theory' is significantly used for studying and understanding the scattering of waves and particles in mathematics and physics. Typically the wave scattering corresponds to the collision and scattering of a wave with some material object.

- Rayleigh scattering is one commonly known type of scattering which mainly consists of scattering from atmospheric gases, it occurs when the particles causing scattering are smaller in size than the radiation wavelengths in contact with them.
- Mie scattering, and non-selective scattering are the two other types of wave scattering. Principally, the Mie scattering is considered to be elastic scattered light of particles that have a diameter similar to or larger than the wavelength of the incident light.
- Scattering, in physics, is defined as a change in the direction of motion of a particle because of a collision with another particle. As defined in physics, a collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.
- Scattering occurs when light or other energy waves pass through an imperfect medium, such as air filled with particles of some sort, and are deflected from a straight path. The light is deflected off of its straight path and scatters in many directions.
- Scattering is a general physical process where some forms of radiation, such as light, sound, or moving particles, are forced to deviate from a straight trajectory by one or more paths due to localized non-uniformities in the medium through which they pass.
- As per the Encyclopaedia Britannica, the ‘Scattering, in physics, a change in the direction of motion of a particle because of a collision with another particle. A collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.
- The term ‘Elastic Scattering’ implies that the internal states of the scattering particles do not change, and hence they emerge unchanged from the scattering process.
- In inelastic scattering, by contrast, the particles’ internal state is changed, which may amount to exciting some of the electrons of a scattering atom, or the complete annihilation of a scattering particle and the creation of entirely new particles.
- Rayleigh scattering is named after the nineteenth-century British physicist Lord Rayleigh (John William Strutt). It is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process.
- Rayleigh scattering of sunlight in Earth’s atmosphere causes diffuse sky radiation, which is the reason for the blue colour of the daytime and twilight sky, as well as the yellowish to reddish hue of the low Sun.

## NOTES

## NOTES

- For wave frequencies that are below the resonance frequency of the scattering particle (normal dispersion regime), the amount of scattering is inversely proportional to the fourth power of the wavelength.
- Rayleigh scattering applies to the case when the scattering particle is very small, i.e.,  $x \ll 1$ , with a particle size  $< 1/10$  wavelength, and the whole surface re-radiates with the same phase.
- The intensity  $I$  of light scattered by any one of the small spheres of diameter  $d$  and refractive index  $n$  from a beam of unpolarized light of wavelength  $\lambda$  and intensity  $I_0$  is given by,

$$I = I_0 \frac{1 + \cos^2 \theta}{2R^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \left( \frac{d}{2} \right)^6$$

Where  $R$  is the distance to the particle and  $\theta$  is the scattering angle.

- The strong wavelength dependence of the scattering ( $\sim \lambda^{-4}$ ) means that shorter (blue) wavelengths are scattered more strongly than longer (red) wavelengths.
- Shorter wavelengths are more quickly and promptly scattered than the longer wavelengths. Light at shorter wavelengths (blue and violet) are scattered by small particles that include  $\text{NO}_2$  and  $\text{O}_2$ .
- Since blue light is at the short wavelength end of the visible spectrum, it is more strongly scattered in the atmosphere than longer wavelength red light. This results in the blue colour of the sky.
- Raman scattering or the Raman effect is the inelastic scattering of a photon by molecules which are excited to higher energy levels. The effect was discovered in 1928 by C. V. Raman and hence named as Raman scattering or the Raman effect.
- The Raman effect forms the basis for Raman spectroscopy which is used by chemists and physicists to gain information about materials.
- The energy difference between the absorbed and emitted photon corresponds to the energy difference between two resonant states of the material and is independent of the absolute energy of the photon.
- The spectrum of the scattered photons is termed the Raman spectrum. It shows the intensity of the scattered light as a function of its frequency difference  $\Delta\nu$  to the incident photons. The locations of corresponding Stokes and anti-Stokes peaks form a symmetric pattern around  $\Delta\nu = 0$ .
- Raman spectroscopy is named after Indian physicist Sir C. V. Raman. It is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system.
- The Raman effect differs from the process of fluorescence in that it is a scattering process. For fluorescence, the incident light is completely absorbed, transferring the system to an excited state.

- A Raman transition from one state to another is allowed only if the molecular polarizability of those states is different. For a vibration, this means that the derivative of the polarizability with respect to the normal coordinate associated to the vibration is non-zero:

$$\frac{\partial \alpha}{\partial Q} \neq 0.$$

- In general, a normal mode is Raman active if it transforms with the same symmetry of the quadratic forms,  $(x^2, y^2, z^2, xy, xz, yz)$ , which can be verified from the character table of the molecule's symmetry group.
- The specific selection rules state that the allowed rotational transitions are, where ' $J$ ' is the rotational state.  
The allowed vibrational transitions are, where ' $\nu$ ' is the vibrational state.

## NOTES

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### 14.5 KEY WORDS

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- **Scattering theory:** This is significantly used for studying and understanding the scattering of waves and particles in mathematics and physics.
- **Elastic scattering:** It implies that the internal states of the scattering particles do not change, and hence they emerge unchanged from the scattering process.
- **Inelastic scattering:** In this the particles' internal state is changed, which may amount to exciting some of the electrons of a scattering atom, or the complete annihilation of a scattering particle and the creation of entirely new particles.
- **Rayleigh scattering:** It is named after the nineteenth-century British physicist Lord Rayleigh (John William Strutt). It is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process.
- **Raman scattering or the Raman effect:** It is the inelastic scattering of a photon by molecules which are excited to higher energy levels. The effect was discovered in 1928 by C. V. Raman and hence named as Raman scattering or the Raman effect.
- **Raman spectroscopy:** It is named after Indian physicist Sir C. V. Raman, a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system.

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## 14.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

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### NOTES

#### Short Answer Questions

1. What is scattering theory?
2. Define elastic scattering.
3. Who developed Rayleigh scattering?
4. What does Rayleigh scattering cross-section mean?
5. What is Raman scattering?
6. Explain the selection rules for Raman scattering.

#### Long Answer Questions

1. Discuss the significance of term scattering theory giving appropriate examples.
2. Briefly explain elastic and inelastic scattering.
3. Explain Rayleigh scattering theory and methods.
4. Discuss the small size parameter approximation for Rayleigh scattering theory.
5. Explain about the Rayleigh scattering cross-section.
6. Explain the advantages and limitations of Rayleigh scattering.
7. Discuss the Raman scattering method.
8. Explain the selection rules, advantages and disadvantages of Raman scattering.

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## 14.7 FURTHER READINGS

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- Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.
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