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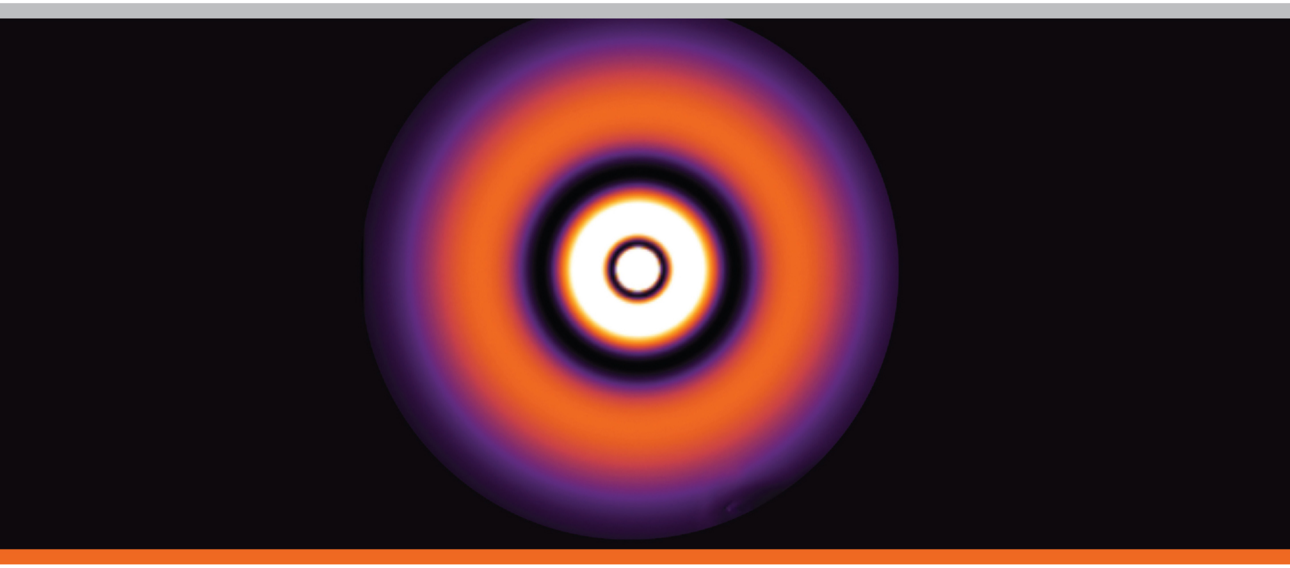
INTRODUCTION TO Quantum Mechanics



Nikhil Ranjan Roy

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Dedicated to the
Lighthouse of My Life
MY PARENTS

Foreword

As a teacher and researcher, nothing is more gratifying than to get your point of view successfully across to your students. You get immense satisfaction when students score well in your subject. And that is the experience of Professor Nikhil Ranjan Roy, formerly with Ranchi University! The book *Introduction to Quantum Mechanics* coming out of his forty years of teaching experience is highly lucid and a pleasure to read. Prof Roy has always been ‘to the point’, which is also one feels while going through this book of his. Learning quantum mechanics is not like learning a foreign language. There is no one-to-one translation of classical mechanics into it. This is a new concept all together and Prof Roy has introduced it with full passion and gravity that it deserves to arouse the interest of the reader in it. The book shows the necessity of using quantum mechanics while dealing with atomic and sub-atomic particles.

The book is meant for the beginners, especially for the undergraduate students of science and engineering. The contents of the book have been organized to cover the curricula of BSc (Hons) Physics of most Indian universities and those of engineering colleges. The contents have been arranged to emphasize the chronological evolution of the concepts, the laws and the basic mathematical theory of quantum mechanics—the most outstanding development of modern science. It is a complete book, including solved examples at the end of each chapter.

The book should be a delight to the teachers of quantum mechanics as well, as they need not jump from book to book while teaching the subject and can directly refer a single book to serve the purpose of the students.

I am sure the book will prove to be stimulating and useful not only for the students for whom it is meant but also for those who are intending to do their post-graduation and beyond.

Professor B K Mathur
Department of Physics
Indian Institute of Technology, Kharagpur

Preface

Before I introduce the book to the readers I would like to share some experience of my own student life. After my postgraduation, when I began my researches in quantum mechanics with Prof H G Venkatesh at BIT, Mesra, Ranchi I had to face many difficulties, some of which were of serious nature—in regard to my very understanding of the basics of the subject. It took me quite sometime to overcome this problem.

Thereafter, when I had the opportunity to teach the subject at both graduate and postgraduate levels, which I did for a number of years, I found that a more or less similar situation prevailed and this continues even now. A kind of barrier is encountered by a majority of students when they begin studying this subject. As a result, instead of trying to go deep into the subject for understanding its marvels and its wide scope, students take it very casually and prepare themselves for merely answering a few questions in the examination. However, it is an admitted fact that a psychological barrier was also faced by anyone who started getting involved in the subject of quantum mechanics during its formative years, particularly because it was difficult to break away from the so well established and accepted ideas, concepts and laws of classical physics based on everyday experience.

The situation has, however, changed during the last century and quantum mechanics has grown to such heights as to be one of the most magnificent edifices of human thought. It has revealed many hidden secrets of nature on the one hand and on the other has enabled men to progress many steps towards the understanding of matter and radiation—the two entities of which the Universe is composed.

I have been feeling strongly for quite sometime that our students need to tunnel through the barrier they face in order to understand this wonderful subject to its entire width and depth.

The present book, I believe, will serve as an introductory volume specially written for our undergraduate students at honours level and those of engineering colleges with no previous exposure to the subject. In preparing it the curricula of different Indian universities and engineering colleges have been kept in mind. Attempt has been made to present the contents of the book in a style of classroom teaching. The main emphasis has been on the evolution of the subject, the underlying ideas, the concepts, the laws and the mathematical apparatus for the formulation of the subject in a systematic and comprehensible manner. Each chapter is followed by a number of solved examples and problems which are so chosen that they may serve as guidelines to the solutions for more complex problems and for the application of the basic principles of quantum mechanics to some extent.

I presume the book will serve as a reasonably comprehensive introduction to the subject. Suggestions for the improvement of the book will be highly appreciated.

Prof N R Roy

Acknowledgements

Above all, I bow my head with hands folded before the Almighty for everything I have been blessed with.

I am grateful to Late Professor H G Venkatesh for his illuminating discussions on the subject throughout my researches at BIT, Mesra, Ranchi and for his constant inspiration for me to continue my studies in this fascinating field.

I express my deep sense of gratitude to my wife Manjushree, my son Shomik, daughter-in-law Purbasha, brothers Akhil and Sushil, their wives and children for constant encouragement and inspiration to me for authoring books after my retirement from the university services. Lastly, I express my sincere thanks to the publisher, Vikas Publishing House Pvt Ltd, for their co-operation and meticulous processing of the manuscript.

Nikhil Ranjan Roy

Scientists of Eminence in Quantum Mechanics

Name of the scientist	*Life span*	*Place of birth*	*Year of receiving the Nobel prize*
Joseph John Thomson	1856-1940	Manchester, England	1906s
Max Karl Ernst Ludwig Planck	1858-1947	Kiel, Germany	1919
Robert Andrews Millikan	1868-1953	Morrison, Illinois	1923
Ernest Rutherford	1871-1937	Nelson, New Zealand	1908
Albert Einstein	1879-1955	Ulm, Germany	1921
Max Born	1882-1970	Breslau, Germany	1954
Niels Henrick David Bohr	1885-1962	Copenhagen, Denmark	1922
Erwin Schrödinger	1887-1961	Vienna, Austria	1933
Louis Victor de-Broglie	1892-1987	Dieppe, France	1929
Wolfgang Pauli	1900-1958	Vienna, Austria	1945
Werner Karl Heisenberg	1901-1976	Wurzburg, Germany	1932
Enrico Fermi	1901-1954	Rome, Italy	1938
Eugene Paul Wigner	1902-1995	Budapest, Hungary	1963
Paul Adrien Maurice Dirac	1902-1984	Bristol, England	1933
Hideki Yukawa	1907-1981	Tokyo, Japan	1949

Contents

1

Origin and Growth of Quantum Physics

1.1 LAWS AND CONCEPTS OF CLASSICAL PHYSICS

The laws of nature which were discovered in the study of physical phenomena in the *macroscopic or the observable world* are the *laws of classical physics*.

One of the first and the most pioneering discoveries was due to Newton which came to be known as *Newtonian Mechanics*, the crux of which lies in the *three laws of motion*. These laws and the subsequent *law of universal gravitation*, also given by Newton, can describe precisely the motion of objects that we see around us.

New formulations of Newtonian mechanics which came to be known as *classical or analytical mechanics* were developed for the analysis of complex mechanical problems. Some brilliant mathematical works due to Euler, Lagrange, Hamilton, Poisson, Jacobi and many others developed this mechanics to the extent that it reached close to perfection.

Many *universal principles* in physics are enunciated. The *laws of thermodynamics* were formulated from the observations in nature. These laws were basically concerned with *transformation of energy*. The principle of *conservation of energy* was firmly established in such transformations. Carnot, Clausius, Kelvin, Planck, Rayleigh, Jeans, Stefan, Wien are some of the names associated with this field.

Significant progress in the studies in the apparently disconnected fields of electricity and magnetism took place through the pioneering works of Faraday, Ampere, Maxwell and others. These studies finally led to Maxwell's electromagnetic theory. Importantly, light was seen to be the manifestation of electromagnetic theory. Nineteenth century was an era of rapid growth in physics and towards the end of the century there existed laws of motion, laws of gravitation, laws of thermodynamics, universal principle of conservation of energy, laws of electricity and magnetism culminated into Maxwell's electromagnetic theory. The above laws of classical physics proved to be very close to perfection for the understanding and analysis of the phenomena in the observable world.

Concepts of Classical Physics

Like any other physical theory, the contents of classical physics are a number of concepts which evolved on the basis of prolonged human experience and which have stood the test of time. The basic concepts in classical physics are

(i) Continuous variation of physical quantities

(ii) The principle of classical determinism, and
(iii) The analytical method of studying objects and phenomena.

The above concepts have the following consequences:

(a) The state of a moving object at every instant of time is completely determined from a knowledge of its coordinates and velocities which are continuous functions of time thereby leading to the *concept of motion of objects along trajectories*.

(b) It is possible to predict precisely the state of an object at any instant of time from a knowledge of the state and the forces acting on the object at any previous instant of time. This, in other words, means that classical physics assumes an *unambiguous link between present and future in the same way as between past and present*.

(c) Matter is considered to be made up of different parts which, though interacting with one another, may be investigated individually. A special consequence of the principle of analysis is the motion of the mutual independence of the object of observation and the observer. Thus classical physics considers the object of investigation and the investigator to be completely isolated from each other so that *physical phenomena can be studied without interfering with their progress.*

The above notions of classical physics are based on everyday, commonplace experience and are readily acceptable to our common sense, i.e., they are considered as quite natural. The principle of analysis is not only natural but is the only effective method of studying matter. The principle of determinism reflects what is called *causality of phenomena in nature*.

Towards the end of the 19th century, it was generally believed that the description of the laws of nature in terms of the laws of classical physics and the basic concepts in classical physics was in a state of completion and a final description of physical phenomena was at hand.

However, this state of affairs turned to be a mere illusion at the turn of the 20th century. There occurred a crisis in physics.

1.2 ORIGIN OF QUANTUM PHYSICS

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.

1.3 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°C?

Why sodium vapour emits yellow light?

Why copper conducts electricity but sulphur does not?

Why uranium atom disintegrates spontaneously releasing energy? etc.

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.

1.4 OLD QUANTUM THEORY

Historically, a relatively complete quantum theory was first developed by Bohr, Sommerfeld and others; now called the old quantum theory. Although it has now been replaced by a much more satisfactory modern theory, it still represents a good means of arriving at the concepts of the quantum theory with a view to their understanding.

In the following we discuss how the old quantum theory originated. We start with a discussion on inadequacy of classical physics in explaining phenomena at atomic and sub-atomic levels followed by discussions on emergence of new concepts such as quantization of physical quantities, particle nature of radiation, and wave nature of matter.

1.5 INADEQUACY OF CLASSICAL PHYSICS

In the following, a few, phenomena among many observed, in the microscopic world have been presented which cannot be explained on the basis of the laws of classical physics.

1.5.1 Black Body Radiation

The radiation emitted by a body as a result of its temperature is called *thermal radiation*. All bodies emit such radiation to their surroundings and absorb such radiation which fall on them from the surroundings. At high temperatures, most bodies become self luminous by their emitted light, although the major part of the thermal radiation lies in the infrared region of the electromagnetic spectrum. When the temperature of a body is raised slowly, two principal effects are observed (i) the rate of emission of thermal radiation increases and (ii) the frequency of that part of the spectrum that radiated most intensely increases so that the colour of the hot body changes from red to yellow to white.

The amount of thermal radiation emitted per second per unit surface area and the spectrum of the radiation emitted by a body at a given temperature are found to depend upon (i) the nature of the material or the composition of the body and (ii) the nature of the surface of the body.

However, there exists one class of bodies called black bodies which emit thermal radiation with the same spectrum at a given temperature regardless of their individual compositions and surfaces. Such bodies absorb completely all thermal radiation incident on them. An object coated with a diffused layer of black pigment such as lamp black or bismuth black is nearly a black body. A *hollow enclosure* or *cavity* of any shape or size insulated from the surroundings and having inner walls maintained at a temperature, say, T is filled with thermal radiation characteristic of a black body at that temperature.

Lummer and Pringsheim, Paschen, Rubens and Kurlbaum conducted detailed experimental studies on black body radiation over a wide frequency/wavelength range during 1899–1900. The general nature of the observed spectra of radiation at different temperatures are as shown in the Fig. 1.1. In the figure E_λ represents the energy density of radiation at the wavelength λ. Using classical concepts, Rayleigh and Jeans calculated the energy density of cavity radiation (or black body radiation) as a function of frequency and obtained the formula (Rayleigh–Jeans law)

$$(E_\nu)_T \, d\nu = \frac{8\pi\nu^2}{C^3} \, kT \, d\nu \qquad \ldots(1)$$

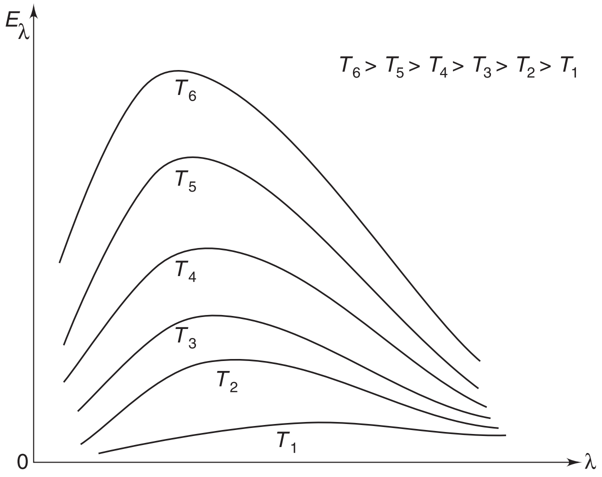


Fig. 1.1

The formula was found to agree well with experiments for low frequencies but led to absurd results for higher frequencies at any given temperature. The total energy emitted at any given temperature according to the above formula is

$$E = \int_0^\infty E_\nu d\nu = \int_0^\infty \frac{8\pi\nu^2}{C^3} kT \, d\nu \qquad \ldots(2)$$

which yields infinite values of E at all temperatures other than $T = 0$, which is totally an erroneous result. (This situation was known as ultraviolet catastrophe.) Wien in the year 1896, studying black body radiation using the concepts of thermodynamics, derived a formula for energy density of radiation as a function of frequency and temperature which accounted for the experimental results obtained for high radiation frequencies quite accurately but not for low frequencies.

We thus find that classical theories failed to explain the black body spectrum over the entire range of frequency of the emitted radiation.

1.5.2 Specific Heat of Solids

According to classical law of equipartition of energy, the average kinetic energy per degree of freedom of a gas molecule at the temperature T is $\frac{1}{2}kT$. For a monatomic gas there are three degrees of freedom of translational motion so that the total average kinetic energy of a molecule is $\frac{3}{2}kT$.

A solid may be supposed to consist of atoms each of which is bound to its respective neighbours but it resonates and vibrates freely when the solid is heated. Clearly, the mean kinetic energy of vibration of 1 mole of a solid at the temperature T is

$$\text{Mean kinetic energy} = N_O\frac{3}{2}kT = \frac{3}{2}RT \qquad \text{...(3)}$$

where N_O is the Avogadro's number and $N_Ok = R$ is the universal gas constant.

If we consider vibration of the atoms in the solid to be simple harmonic, then for each atom the average potential energy is equal to the average kinetic energy so that the mean potential energy for 1 mole of the solid at the temperature T is

$$\text{Mean potential energy} = \frac{3}{2}RT \qquad \text{...(4)}$$

Thus, the total energy of 1 mole of a solid at the temperature T becomes

$$E = \text{Kinetic energy} + \text{Potential energy} = 3\ RT \qquad \text{...(5)}$$

By definition, we then get the molar specific heat of a solid at constant volume as

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3\ R \approx 6\ \text{calories/g-mole} \qquad \text{...(6)}$$

The classical laws thus predict:

Specific heat of all solids is the same and is a constant, independent of temperature.

Physicists in the 19th century faced a violation of the above classical law referred to as Dulong-Petit's law. At high temperatures the law was found to hold only approximately. Also, it completely fails for light elements even at low temperatures where we

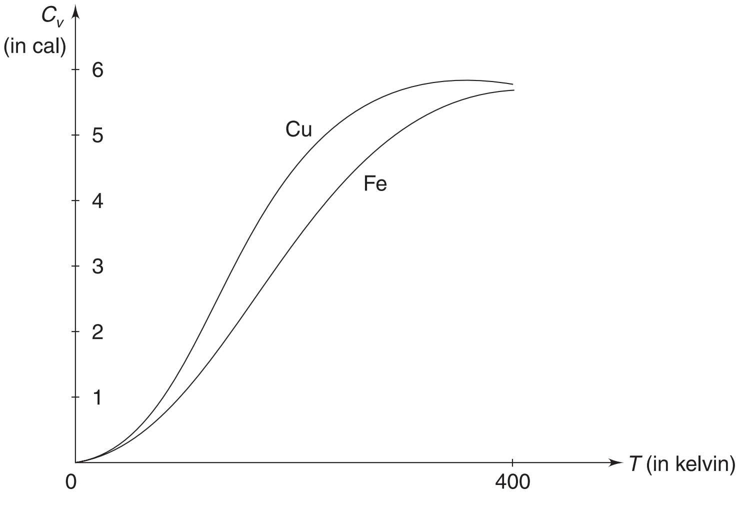


Fig. 1.2

observe marked variation of specific heat with temperature as shown in the Fig. 1.2. We thus find that the temperature dependence of specific heat of solids could not be explained within the framework of classical theory.

1.5.3 Stability of Atoms and Emission of Line Spectra by Atoms

In 1908 Geiger and Marsden under the guidance of Rutherford began studies on the scattering of α-particles passing through thin foils of different metals. They discovered that most of the α-particles pass through the foil without being scattered while some α-particles, roughly one in ten thousand, get strongly deflected by angles greater than 90°. In 1911, Rutherford came to the conclusion that the strong deflection of an α-particle occurs not as a result of many collisions, but in a single act of collision with an atom and, consequently there must be a small positively charged region (nucleus) at the centre of the atom, containing almost the entire mass of the atom and the negatively charged electrons are distributed around the nucleus.

Since the electrons experience electrostatic forces of attraction towards the nucleus, an atom can be stable, according to classical mechanics, only if the electrons revolve round the nucleus, the force of attraction providing the necessary centripetal force for rotation. This was a decisive step towards the creation of the planetary model of the atom which Rutherford formulated in 1913.

The revolving electrons are, however, accelerated and hence should radiate energy in the form of electromagnetic waves according to classical electromagnetic theory. As a consequence, the energy of the revolving electrons should continuously decrease and they should spiral down into the nucleus. This is contradictory to the observed fact of non-existence of electrons in the nucleus of an atom. The stable condition of an atom as observed experimentally is thus not explained by the laws of classical physics.

It is an experimental fact that when a salt of alkali metal or alkaline earth metal is heated to incandescence and the emitted light is examined using a spectrometer we observe the presence of a series of wavelengths forming what we call a line spectrum. The spectrum observed is a characteristic of the salt. Similarly, when a gas (in its atomic state) is discharged, it emits electromagnetic radiation of characteristic wavelengths, i.e., a line spectrum.

According to classical picture of atom outlined above, the excited atoms should, however, emit a continuous spectrum of wavelengths when the revolving electrons in the atoms spiral down to their respective nuclei.

We thus find that the laws of classical physics do not subscribe to the emission of line spectrum.

1.5.4 Photoelectric Effect

None of the experimental results on photoelectric effect could be explained on the basis of classical theory of electromagnetic radiation (light), namely, the wave theory. This will be considered in details in a section to follow.

1.5.5 Compton Effect

The experimental results on Compton Effect (the Compton shift) could not find explanation according to the classical wave theory of electromagnetic radiation. The effect will be discussed in details in a section to follow.

1.5.6 Remarks

Towards the end of the 19th century and the beginning of the 20th century physicists were faced with a situation which was rightly realized as the *crisis* in physics. Concepts, theories and the laws of classical physics were proving completely inadequate to provide explanation of the physical problems in the domain of small dimensions such as atoms, molecules, nuclei, electron and other subatomic particles.

1.6 DISCRETENESS OF ENERGY: A NEW IDEA

1.6.1 Planck's Quantum Hypothesis: Explanation of Black Body Radiation Spectrum

Max Planck in the year 1900 was able to obtain a formula for the energy density of radiation emitted by a black body at a given temperature as a function of the frequency of the emitted radiation by radically modifying the classical view and which was found to be in complete agreement with the experimentally obtained black body spectrum. The classical theory of black body radiation is based on the law of equipartition of energy. Planck asserted that for cavity radiation at least, the average energy of the stationary waves in the cavity should depend on the frequency of the waves besides the temperature and not independent of frequency as follows from the classical law of equipartition of energy. Considering the problem purely mathematically, Planck found that the desired dependence of average energy on frequency could be obtained if energy be considered as a discrete variable rather than a continuous variable as in classical physics.

Planck considered these discrete allowed energy values as

$$\in = 0, \Delta\in, 2\Delta\in, 3\Delta\in \qquad ...(7)$$

where $\Delta\in$ represents the uniform gap between the successive allowed values of energy.

The average energy was found to be

and

$$\left.\begin{aligned} \overline{\in} &= 0 \quad \text{if } \Delta\in \text{ is chosen to be large} \\ \overline{\in} &= kT \quad \text{if } \Delta\in \text{ is chosen to be small.} \end{aligned}\right\} \qquad ...(8)$$

Thus large differences in adjacent energies correspond to the high frequency behaviour of cavity radiation while small differences to the low frequency behaviour. Planck hence assumed that

$$\Delta\in \propto \nu$$

or

$$\Delta\in = h\nu \qquad ...(9)$$

where h is the proportionality constant. The formula for the average energy $\overline{\in}$ as obtained by Planck was

$$\overline{\in} = \frac{h\nu}{e^{h\nu/kT} - 1} \qquad ...(10)$$

in place of the classical formula $\overline{\in} \sim kT$.

With the above formula for $\overline{\in}$, Planck obtained the energy density of the radiation emitted by a black body at temperature 'T' at the frequency 'ν' as

$$(E\nu)_T \, d\nu = \frac{8\pi\nu^2}{C^3} \frac{h\nu}{e^{h\nu/kT} - 1} \qquad ...(11)$$

Planck found that the best agreement between the above formula and experimental data took place when the value of h was taken to be same as the modern value

$$h = 6.63 \times 10^{-34} \text{ Js}$$
$$= 4.14 \times 10^{-15} \text{ eV.s}$$

Ever since this fundamental constant has been called the *planck's constant*.

The experimental results shown in the Fig. 1.1 are in complete agreement with Planck's formula at all temperatures within the limits of experimental uncertainties.

Physical Explanation of Planck's Assumption

The electromagnetic waves within the cavity originate from radiation given off by electrons of the atoms which oscillate on the walls of the cavity due to thermal agitation. Classically, these atomic oscillators radiate their energies continually as the motion of the electrons gradually subside and the electrons fall to their respective nuclei.

Planck, on the other hand, conjectured that an oscillator emits energy in the form of radiation in *spurts* so that instead of decreasing continuously, its energy decreases discretely. For this reason, the allowed energy values of an atomic oscillator must be discrete and during exchange of energy with cavity radiation, the oscillator emits or absorbs radiant energy only in discrete amounts. Since the discrete energies that an oscillator can emit or absorb are directly proportional to its frequency, oscillators of low frequency can emit or absorb energy in small packets whereas those of high frequency absorb or emit only large energy packets. If the cavity wall is at a low temperature, there exists sufficient thermal energy to excite oscillators of low frequency but not those with high frequency. The high frequency oscillators need large energy to begin radiating and only a few of them are activated compared to low frequency oscillators. Hence the walls radiate more in the long wavelength or high frequency region and hardly at all in the ultraviolet region. As the temperature is raised, sufficient thermal energy becomes available to activate large number of high frequency oscillators and the emitted radiation shifts its character towards higher frequencies, i.e., towards the ultraviolet region.

From the above we find that *Planck's assumption of discreteness of energy* leads to the experimentially observed black-body spectrum.

It is instructive to note the following

(i) Under the condition $\frac{h\nu}{kT} << 1$, Planck's formula reduces to the classical formula of Rayleigh–Jean.

(ii) Under the short wavelength or high frequency limit $\frac{h\nu}{kT} >> 1$, Planck's formula takes the form as obtained by Wien as a fit to experiment in the high frequency end of the black-body spectrum.

1.6.2 Einstein's Explanation of Variation of Specific Heat of Solids with Temperature

The idea of discreteness of energy introduced by Planck in 1900 was extended by Einstein in 1907 to explain the variation of specific heat of solids with temperature. Einstein in his theory of specific heat of solids made the following assumptions:

(a) When a solid is heated, its atoms are set into simple harmonic vibrations about their respective positions of equilibrium with frequency characteristic of the solid.

(b) The energy of the vibrating atoms is a discrete variable.

(c) The average energy of vibration of an atom per degree of freedom is $\frac{h\nu}{e^{h\nu/kT}-1}$ as was used by Planck and not equal to kT according to the classical law of equipartition of energy.

(d) Each vibrating atom of a solid has three degrees of freedom.

With the above assumptions, Einstein obtained atomic heat at constant volume at the temperature T by

$$C_v = 3k\,\frac{e^{h\nu/kT}}{\left[e^{h\nu/kT}-1\right]^2}\left(\frac{h\nu}{kT}\right)^2 \qquad ...(12)$$

The above formula is found to predict almost correctly the variation of specific heat of a solid with temperature excepting in the case of certain light elements such as aluminium, copper, etc., for which C_v is found to decrease with decrease in temperature much more rapidly than predicted by Einstein's formula.

Debye modified Einstein's theory by considering

(a) mutual forces acting between the atoms

(b) elastic vibrations of transverse as well as longitudinal types in different modes

(c) the existence of an upper limit of vibration frequency characteristic of the solid.

It is found that the formula for atomic heat obtained by Debye explains quite successfully the variation of heat capacity of solids with temperature which classical theories could not do.

1.6.3 Bohr's Explanation of Stability of Atoms and Emission of Line Spectra

Neils Bohr in 1913 gave the theory of planetary model of the hydrogen atom based on the concepts of quantization of energy of atomic radiations introduced by Planck. Bohr could resolve to some extent the difficulties encountered by classical physics in explaining the stability of atoms and emission of line spectra.

Bohr's theory makes the following assumptions. These are known as Bohr's postulates.

(a) Electrons in an atom move round the nucleus in circular orbits, the necessary centripetal force for rotation being provided by the electrostatic forces of attraction on them offered by the positively charged nucleus.

(b) The orbits in which the electrons move define the *stationary states* of the atom in the sense that so long as the electrons continue to move in the orbits they do not lose energy by emitting electromagnetic radiation. This postulate is against classical electromagnetic theory.

(c) The stationary orbits in which electrons can move do not have radii varying continuously from zero to higher values but have only certain discrete values. These discrete values are such that the *angular mementa* of rotating electrons in the orbits are integral multiples of $\frac{h}{2\pi}$. It is this postulate by which Bohr introduced the idea of discreteness of angular momentum and hence of discreteness of energy of atoms. Resolutely departing from accepted concepts, Bohr ruled out any direct link between the frequencies of radiation emitted by an atom with the frequencies of rotation of electrons in stationary orbits and instead postulated that

(d) Energy is emitted or absorbed by an atom only when an electron makes discontinuous transition from an orbit of higher energy to an orbit of lower energy or from an orbit of lower energy to an orbit of higher energy.

Stability of an atom follows from the postulate '*b*'. It may, however, be noted that Bohr did not give any logical or other explanation for the existence of stationary orbits.

Bohr calculated the energy of the electron in a hydrogen atom rotating in the n^{th} circular orbit to be

$$E_n = -\frac{2\pi^2 me^4}{n^2h^2} \qquad ...(13)$$

In the above, '*m*' is the mass of the electron, and *e* is its charge.

Since orbits have discrete values of energy given by Eq. (13), the energy absorbed or radiated, according to postulate '*d*', is always discrete and not continuous. The frequency of electromagnetic radiation emitted or absorbed is obtained from Bohr's frequency rule.

$$\nu_{nm} = \frac{E_n - E_m}{h} \qquad ...(14)$$

where E_n and E_m are respectively the energies of the electron in the n^{th} and m^{th} allowed orbits ($n > m$) between which the transition of the electron's motion takes place.

Using Eq. (13) in Eq. (14) we obtain

$$\nu_{nm} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \qquad ...(15)$$

The experimentally observed spectral lines of hydrogen are found to fit the formula given by Eq. (15).

1.6.4 Experimental Evidence of Quantization of Internal Energy of Atoms: Franck and Hertz Experiment

James Franck and Gustav Hertz conducted experiments in 1914 which gave direct experimental evidence for the fact that an atom may change its energy only discretely. These were the famous experiments on the measurement of the electron energy spent on exciting mercury atoms.

A sectional diagram of the apparatus used by Franck and Hertz shown in the Fig. 1.3 consisted of a quartz chamber filled with mercury vapours. Within the chamber are mounted a filament (cathode), which could be heated by passing an electric current through it, a plate anode and an accelerating grid near the plate. The filament is in the form of a wire while the plate and the grid are cylindrical, surrounding the filament.

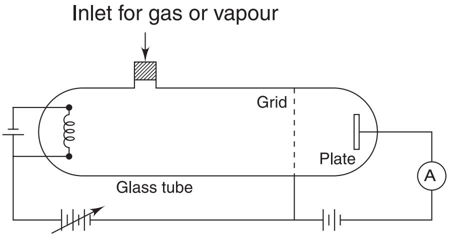


Fig. 1.3

The current through the filament and hence the temperature of the filament is so adjusted that thermoelectrons are emitted from its surface with very little kinetic energy. The grid voltage (V) is set to accelerate the electrons emitted from the filament towards the plate.

A small retarding potential is set up between the plate and the grid so that the electrons that pass through the openings in the grid with very small kinetic energy are not able to reach the plate.

The experiment consists in gradually increasing the accelerating voltage 'V' starting from a very small value and measuring the electron beam current passing through the plate circuit by means of the ammeter 'A'.

The results obtained are shown in the Fig. 1.4. We find that when the accelerating voltage V increases from zero value, the current increases and when V reaches the value 4.9 volt, the current suddenly drops. This observation can be interpreted as the loss of major fraction of the kinetic energy of majority of the electrons due to inelastic collisions with the mercury atoms in the chamber once they reach the kinetic energy 4.9 eV in front of the grid. They are thus left with very little kinetic energy and the retarding potential between the grid and the plate prevents them from reaching the plate and hence the plate current drops. The mercury atoms absorb the energy 4.9 eV and are said to get into an excited state.

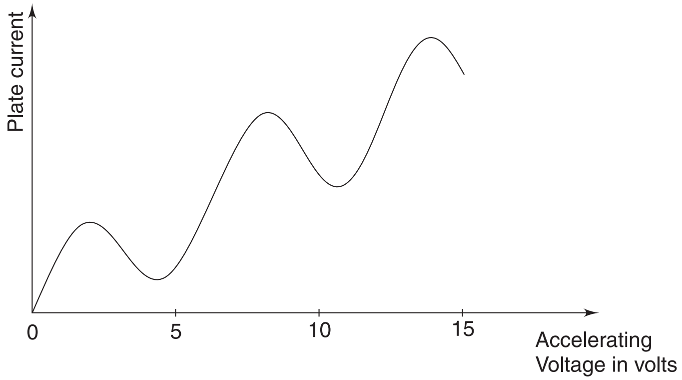


Fig. 1.4

As *V* increases beyond 4.9 volt, the electrons near the grid gain kinetic energy and become able to overcome the retarding potential and reach the plate. The current thus rises again when *V* becomes large enough so that the electrons have enough kinetic energy to be able to make two separate inelastic collisions with mercury atoms during their passage from cathode to anode, the current drops again. As the voltage is increased, as expected, a series of current drops are observed at equal intervals of 4.9 volt as shown in the Fig. 1.4.

The above results indicate that the first excited state of mercury atom is 4.9 eV above its lowest energy state or ground state. The results further tell that mercury atoms are not able to absorb energy from electrons having less energy than 4.9 eV.

The mercury atoms which get excited after the absorption of energy are expected to give up this energy as they make transition to the lowest energy state. In later experiments Hertz observed and analysed the spectrum emitted by the mercury vapour in the chamber. It was observed that when accelerating voltage *V* was less than 4.9 volt, the spectrum was not emitted at all.

However, as the accelerating voltage reached 4.9 volt, a single spectral line was observed. Even if the voltage was increased somewhat beyond 4.9 volt the same line was emitted having wavelength 2536 Å. The wavelength of the emitted line is seen to fit Bohr's frequency rule

$$\left[\lambda = \frac{c}{v} = \frac{3 \times 10^{8}(\text{ms}^{-1}) \times 6.63 \times 10^{-34}\ \text{Js}}{4.9 \times 1.6 \times 10^{-19}\ \text{J}} = 2536 \times 10^{-10}\ \text{m}\right]$$

Using different grid arrangements than the one used in the first experiment, Hertz found other spectral lines in the spectrum emitted by the mercury vapour. These lines corresponded to energies 6.67 eV, 8.84 eV and 10.4 eV above the ground state energy of mercury atom.

We thus find that mercury atoms absorb only and exactly energies 4.9 eV, 6.67 eV, 8.84 eV and 10.4 eV, i.e., the mercury atoms can exist only in states with a set of discrete values of energy.

Experiments of Franck and Hertz thus provided striking evidence of quantization of internal energies of atoms.

1.6.5 Conclusion

From Planck's analysis of black body radiation, Einstein's explanation of temperature dependence of specific heat of solids, Bohr's planetary model of hydrogen atom explaining stability and emission of spectral lines from hydrogen atom and from the results of Franck and Hertz experiment we are faced with a conclusion that contradicts the firmly established concepts of classical physics when they are applied to microscopic systems. In such systems energy cannot be changed in a continuous way by an arbitrary amount; instead, energy of such systems can take only certain discrete values.

1.7 WILSON–SOMMERFELD QUANTIZATION RULE

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 $q_1 \ldots q_s$ and generalized momenta $p_1, p_2 \ldots, p_s$ then phase integrals of the system are defined as

$$J_i = \oint p_i dq_i, \quad i = 1, 2, \ldots, s \qquad \ldots(16)$$

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.,

$$J_i = \oint p_i dq_i = n_i\, h; \quad n_i = 0, 1, 2, \ldots \qquad \ldots(17)$$

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 Eq. (17) reduces to

$$\oint mvr\, d\phi = nh$$

or
$$mvr\,2\pi = nh$$

so that
$$mvr = \frac{nh}{2\pi} \qquad ...(18)$$

We may note that Eq. (18) 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.

1.7.1 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

$$x = a \sin \omega_0 t \qquad ...(19)$$

where a is amplitude and ω_0 is the natural frequency related to the force constant according to

$$\omega_0 = \sqrt{\frac{k}{m}} \qquad ...(20)$$

The potential energy of the oscillator is given by

$$V = \frac{1}{2} kx^2 = \frac{1}{2} m\omega_0^2 a^2 \sin^2(\omega_0 t) \qquad ...(21)$$

The kinetic energy of the oscillator is

$$T = \frac{1}{2} mv^2 = \frac{1}{2} m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2} ma^2\omega_0^2 \cos^2(\omega_0 t) \qquad ...(22)$$

Thus, the total energy of the oscillator becomes

$$E = T + V = \frac{1}{2} m\, \omega_0^2 a^2 \qquad ...(23)$$

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

$$ma^2\omega_0^2 \times \frac{\pi}{\omega_0} = nh \qquad ...(24)$$

Using Eq. (24) in Eq. (23), the energy of the oscillator is

$$E = \frac{1}{2}\frac{nh\omega_0}{\pi} = n\hbar\omega_{0,} \quad n = 0,\ 1,\ 2 \qquad ...(25)$$

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.

1.7.2 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,

$$\oint p_x dx = \int_0^{2a} p_x dx = p_x 2a = n_x h \qquad ...(26)$$

$$\oint p_y dy = \int_0^{2b} p_y dy = p_y 2b = n_y h \qquad ...(27)$$

$$\oint p_z dz = \int_0^{2c} p_z dz = p_z 2a = n_z h \qquad ...(28)$$

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 Eqs. (26), (27) and (28) 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

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \qquad ...(29)$$

In the above equations, n_x, n_y and n_z are zero or integers. Equation (29) shows that the energy of the particle within the box is quantized.

1.7.3 The 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 θ 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

$$E = T = \frac{1}{2} I\dot{\theta}^2 = \frac{1}{2} I\omega^2 \qquad \text{...(30)}$$

The phase integral of the rotator can be written in terms of the total angular momentum p_θ and the angular coordinate θ as

$$J = \oint p_\theta d_\theta \qquad \text{...(31)}$$

According to Wilson–Sommerfeld quantization rule we have

$$J = nh, \quad n = 0, 1, 2, \ldots \qquad \text{...(32)}$$

Using Eq. (31) in Eq. (32) 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

$$p_\theta = I\omega = \frac{nh}{2\pi} \qquad \text{...(33)}$$

The above equation gives

$$\omega = \frac{nh}{2\pi I} = \frac{n\hbar}{I} \qquad \text{...(34)}$$

Substituting the value of ω in Eq. (30) we obtain

$$E = \frac{1}{2} I \frac{n^2\hbar^2}{I^2}$$

or
$$E = \frac{1}{2}\frac{n^2\hbar^2}{I} \qquad ...(35)$$

We find that the energy of the rigid rotator is discrete and not continuous.

1.7.4 Stern–Gerlach Experiment

In 1921, Stern and Gerlach performed an atomic beam experiment which directly revealed the essential features of the vector atom model. The results of the experiment gave direct evidence of quantization of the directions of magnetic moment vector of an atom placed in an external magnetic field with respect to the direction of the applied field (space quantization). Besides, the results gave evidence of existence of intrinsic angular momentum or spin of electrun.

Principle of the Experiment

An atom can be regarded as an elementary magnet, its magnetization arising due to the orbital motion and spin of its electrons. If the atomic magnet is placed in a non-uniform magnetic field of proper description then it experiences a net translatory force as well as a torque which tends to set its axis along the direction of the field.

If such a collection of atomic magnets is projected along a direction normal to a non-homogeneous magnetic field then the atomic beam moves along a curved path.

Experimental Arrangement

The substance under investigation (in the original experiment it was silver) is heated in an electric oven O. The substance evaporates and atomic rays are emitted in all directions. Slits S_1 and S_2 collimate the emitted rays into a very narrow beam. The beam is allowed to pass through a non-homogeneous magnetic field produced by specially designed pole-pieces (knife edge type pole pieces) which make the field very intense and strongly non-uniform. The field is much stronger near the edge than elsewhere so that the gradient of the field is very large near the knife edge. After passing through the magnetic field, the atomic beam is made to strike a plate P where the atoms condense showing their paths.

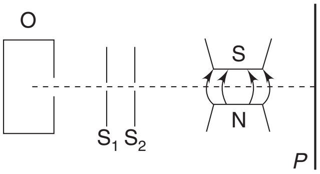


Fig. 1.5

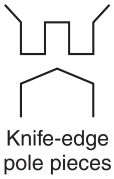


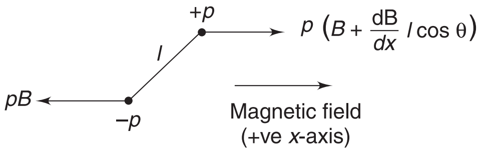
Fig. 1.6

The entire arrangement is enclosed in a chamber. Before the experiment is performed, each part of the apparatus is carefully aligned. The chamber is completely evacuated to prevent collision of the atoms in the beam with the atoms/molecules of the gas that may be present in the chamber otherwise.

Displacement of the atomic rays is measured by measuring the repulsion at various points between the pole pieces of a thin bismuth wire mounted parallel to the edge of the knife edge pole-pieces. The traces of the atomic rays on the plate are then developed.

Calculations

Let an atomic magnet be of length l and pole strength p. Let $\frac{dB}{dx}$ be the gradient of the magnetic field along the positive x-direction (direction of the magnetic field). Let the atomic magnet lie in the non-uniform magnetic field with its axis making an angle θ with the direction of the field, as shown in the figure below



The net force that acts on the atomic magnet along the positive x-axis is

$$F_x = p \frac{dB}{dx} l \cos \theta$$

If M be the mass of the atom, its acceleration along the positive x-axis is

$$f_x = \frac{p \frac{dB}{dx} l \cos \theta}{M}$$

If t be the time taken by the atom to travel through a distance d in a direction normal to the field, we get the displacement of the atom along the direction of the field as

$$D_x = \frac{1}{2} f_x t^2$$

$$= \frac{1}{2} f_x \left(\frac{d}{\nu}\right)^2$$

where ν is velocity of the atom at the temperature T of the oven and is given by

$$\nu = \sqrt{\frac{3\,\mathrm{kT}}{M}}.$$

Substituting for f_x we obtain

$$D_x = \frac{1}{2} \frac{p \frac{dB}{dx} l \cos \theta}{M} \left(\frac{d}{\nu}\right)^2$$

or $$D_x = \frac{1}{2} \frac{\mu}{M} \frac{dB}{dx} \left(\frac{d}{\nu}\right)^2$$

where $\mu = pl \cos \theta$ = component of the magnetic moment of the atom in the field direction.

Results

The traces of deposits on the plates in the case of beam of silver atoms are as shown in the figures below.

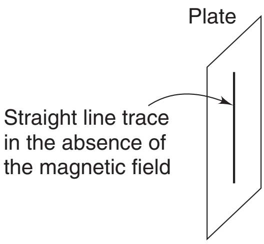


Fig. 1.7

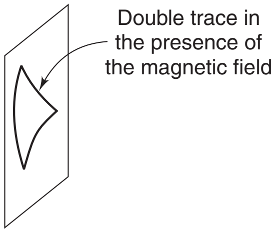


Fig. 1.8

A straight line trace is obtained in the absence of the magnetic field. A double trace with some irregularities is observed when the magnetic field is switched on. The irregularities arise due to irregularity of the magnetic field near the knife edge of the poles of the magnet.

The double trace is seen as converging. This occurs because the gradient of the field decreases along the transverse direction.

From a knowledge of d, ν, $\frac{dB}{dx}$ and the measured value of D_x, the value of the magnetic moment μ can be estimated.

In the case of silver atom, the magnetic moment was found to be equal to one Bohr magneton, i.e., equal to $\frac{e\hbar}{2m_e c}$.

The results of experiments performed with different substances were as given below:

(a) In the case of Cu, Au, H, Li, Na, K double traces were obtained. The separation D_x calculated corresponded to the value of μ equal to $+1$ and -1.

(b) In the case of Zn, Cd, Hg, the value of D_x was found to be equal to zero which corresponded to $\mu = 0$.

(c) In the case of Ni, three distinct traces were obtained, one at its original position and the other two traces corresponded to $\mu > 1$.

(d) In case of cobalt, the separation corresponded to $\mu = 6$.

(e) In case of iron, the separation obtained corresponded to $\mu > 6$.

The consequences of the results were that they established the existence of spin of electron and space quantization of angular momentum. They can be understood from the following:

The double trace in the case of Ag indicates the values of magnetic moment μ as equal to $+1$ and -1.

If we consider the ground state of Ag atom, then neglecting the spin we get the total angular momentum to be $J = L + S = 0 + 0 = 0$. This suggests that there should not be any splitting ($D_x = 0$) so that $\mu = m_J\, g = 0$.

If on the other hand we assign electron spin and give it the value $\frac{1}{2}$ then $\mu = m_J g$ ($g = 1$ for orbital motion and $g = 2$ for spin motion) should have two values $+1$ and -1. Clearly, the results confirm the existence of electron spin.

Classically, the atomic magnets can have their axes oriented in all possible directions with equal probability. If this be the correct picture, we should have obtained diffused trace instead of two distinctly visible traces. If we consider spin angular momentum to be quantized in space then all orientations of spin angular momentum are not possible. If we consider the atom to have one outermost electron in its ground state as in silver atom then we have orbital angular momentum $L = 0$, spin angular momentum equal to S(say) so that the total angular momentum of the atom becomes $J = L + S = S$. The number of possible orientations of $\vec{J}$ is then $2J + 1 = 2S + 1 = 2 \times \frac{1}{2} + 1 = 2$. Thus, a double trace should be obtained. Thus, experimentally observed double trace conforms to space quantization of angular momentum.

1.7.5 Limitations of Old Quantum Theory

The quantum theory developed by Max Planck, Einstein and Bohr and which used Bohr's quantum condition and Wilson–Sommerfeld quantization rule for periodic systems, provided explanation of black-body radiation spectrum, variation of specific heat of solids with temperature, and broad features of the spectrum of the hydrogen atom. It also provided quantitative understanding of the problems of a particle in a box, harmonic oscillator, rigid rotator etc. One remarkable achievement of the old quantum theory has been the realization of quantization of the magnitude and direction of angular momentum.

The theory, however, has several limitations. Some of these are–

(i) The quantization rule is not applicable to non-periodic systems

(ii) The theory cannot explain the relative intensities of the spectral lines of hydrogen atom

(iii) Results contrary to experiments are observed when the theory is applied to hydrogen molecule, helium atom, etc.

(iv) The postulate of stationary orbits by Bohr was empirical having no theoretical background

(v) The theory does not yield the concept of half odd integer quantum numbers and as such does not provide explanation of Zeeman Effect and hyperfine structure of spectral lines.

Shortcomings of the old quantum theory could not be resolved by modifications and extensions of the concepts and the mathematical theory used.

Subsequently, an entirely new conceptual structure, for dynamics in particular and physics in general, was evolved due to the brilliant work of Schrödinger, Heisenberg, Born, Jordan, Dirac and many others which has come to be known as quantum mechanics.

1.8 PARTICLE NATURE OF ELECTROMAGNETIC RADIATION

The idea of duality was first applied to electromagnetic radiation by Einstein.

Photoelectric effect, Compton effect, bremsstrahlung, pair-production and pair-annihilation are processes in which electromagnetic radiation interacts with matter. The first three processes involve absorption of radiation while the last two involve emission of radiation.

The experimental results of the above processes could not be explained using electromagnetic radiation as wave; instead, each of the processes gave evidence of radiation behaving as particle.

In the following two sections we discuss in detail the photoelectric effect and the Compton effect.

1.8.1 Photoelectric Effect

The phenomenon of ejection of electrons from some metal surfaces due to incidence of light on them is called *photoelectric effect*.

The effect was realized from Hertz's discovery that an electric discharge in a gas occurred more readily when ultraviolet radiation was allowed to be incident on one of the electrodes mounted in the discharge tube.

An experimental arrangement to study photoelectric effect is shown schematically in the Fig. 1.9. In the figure, B is an evacuated glass bulb, P is a metal plate mounted near one end of B, while C is a metallic cylinder mounted so as to enclose the plate.

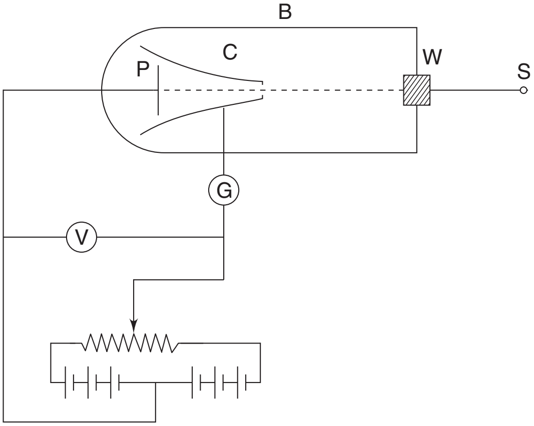


Fig. 1.9

By means of a potential divider arrangement, the cylinder can be kept at any desired positive or negative potential with respect to the plate. G is a sensitive galvanometer to measure any current (photoelectric current) that may pass through the circuit connected to the cylinder. The potential difference that may be applied between the cylinder and the plate is measured by the voltmeter V. Monochromatic light from a source S may be allowed to be incident on the plate P through a quartz window W fitted on the glass bulb and a narrow hole in the cylinder.

The experiment consists in allowing light of a *given frequency* to be incident on the plate and measuring the photoelectric current for different potential differences between the plate and the cylinder (for both the cylinder positive as well as negative with respect to the plate). The experiment is repeated for different intensities of the incident light.

Results of such experiments are shown in the Fig. 1.10.

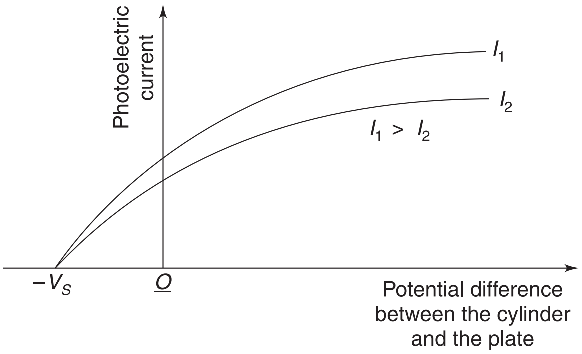


Fig. 1.10

We observe the following:

(i) The photoelectric current assumes different saturation (constant) values for different intensities at large positive potential of the cylinder with respect to the plate.

(ii) The photoelectric current has definite values even for zero potential difference between the cylinder and the plate at different intensities of the incident light.

(iii) The photoelectric current becomes zero at a given reverse potential difference V_s between the cylinder and the plate. V_s, called the *stopping potential*, is independent of the intensity of the incident light.

The above observations suggest the following:

(i) The photoelectrons emitted from the metal plate possess kinetic energy so that some of them having relatively high kinetic energy reach the cylinder giving rise to current even when the cylinder is at zero potential with respect to the plate being unable to attract electrons.

(ii) The photoelectric current becoming zero at $V = -V_s$ means that even those photoelectrons which are emitted with maximum kinetic energy (K_{max}) are just not able to overcome the strong repulsive force. We may hence write

$$K_{\text{max}} = eV_s,$$

e = charge of electron. Besides, V_s independent of intensity of the incident light means that maximum kinetic energy of the emitted photoelectrons is *independent of the intensity of the incident light*.

Another type of experiment on photoelectric effect consists in determining the stopping potential V_s for a given metal plate by allowing light of any intensity but of different frequencies to be incident on the plate. Results of such an experiment are shown in the Fig. 1.11.

The results show the following:

(i) Stopping potential, though independent of intensity of incident light, depends upon its frequency.

(ii) At a particular frequency ν_0, characteristic of the metal surface, the stopping potential V_s becomes zero. Clearly, at the frequency ν_0 we have

$$K_{\max} = 0$$

The above result means that ν_0 is that minimum frequency of the incident light at or below which the photoelectric effect does not occur. For this reason ν_0 is called the *cut-off frequency* or *threshold frequency* of the metal surface under consideration.

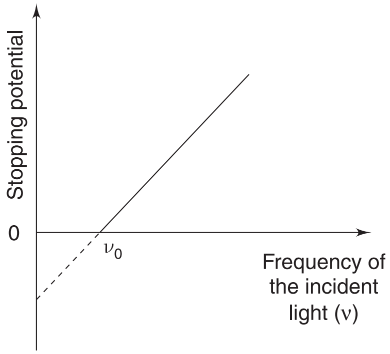


Fig. 1.11

The above results of photoelectric effect are not at all consistent with the classical wave theory of light. The wave theory of light should give:

(i) the stopping potential V_s and hence $K_{\max}$ to be dependent on the light intensity. This is because, with increase in the intensity of light of any frequency, the amplitude of the oscillating electric field increases so that the maximum force on an electron of an atom of the metal surface increases thereby increasing the maximum kinetic energy.

(ii) photoelectric effect to occur for any frequency of the incident light, as long as the light is intense enough to provide the energy needed to eject an electron from the atom, i.e., to provide energy to an electron in excess of its binding energy in the atom.

(iii) a definite time lag between the incidence of light on the metal surface and the ejection of photoelectrons particularly at small intensity of light. During this time, the electron should absorb energy from the incident light continuously till the energy it acquires is more than its binding energy in the atom.

Einstein's Explanation of Observed Results on Photoelectric Effect

Einstein extended Planck's concepts of quantization of energy of atomic oscillators and proposed that radiant energy (light energy), instead of being distributed in space like a wave, existed in concentrated bundles of particles which were later named *photons* and the energy of each photon in light of frequency ν being $h\nu$ while the momentum of the photon being $\frac{h\nu}{c}$.

In effect, Einstein proposed a granular or corpuscular structure to radiation where energy is distributed in space in a discontinuous way.

The photon hypothesis of Einstein explains all the observed results of photoelectric effect. This can be seen as below. When the light of frequency ν is incident on a metal surface then a photon having energy $h\nu$ transfers all its energy to an electron of an atom on the surface. The electron in turn, is ejected as a photoelectron having energy K given by

$$K = h\nu - \in \qquad \text{...(37)}$$

where $\in$ is the binding energy of that electron in the atom. $\in$ is different for different electrons in an atom and hence the emitted photoelectron possess different kinetic energies. In the case of electrons in the atoms having minimum binding energy, the corresponding photoelectrons emerge with maximum kinetic energy which is given by

$$K_{\max} = h\nu - \in_{\min}$$

$\in_{\min}$ is called the work function of the metal under consideration and is usually denoted by the symbol ϕ. Thus, we get

$$K_{\max} = h\nu - \phi \qquad \text{...(38)}$$

Increase of intensity of the incident light of a given frequency ν does not change the energy of a photon and instead only the number of photons crossing a unit area in unit time increases so that the number of electron–photon interactions increases and as a result the number of photoelectrons emitted per second, and hence the photoelectric current, increases. Further, increasing intensity in no way causes change in the energy distribution of the electrons of the atoms of the metal surface and hence the kinetic energy given by Eq. (37) and maximum kinetic energy given by Eq. (38) do not change with change in the intensity of the incident light. ϕ for a given metal is a constant. Clearly, for a particular frequency, say ν_0, we get

$$h\nu_0 = \phi$$

or

$$\nu_0 = \frac{\phi}{h} \qquad \text{...(39)}$$

For this frequency of the incident light we get from Eq. (39)

$$K_{\max} = 0$$

Clearly, at such a frequency of the incident light irrespective of the intensity, the energy $h\nu_0$ of a photon is just enough to free an electron from the binding of the atom but no extra energy to appear as kinetic energy.

At frequency less than ν_0, the individual photons, no matter how intense is the incident light, do not have enough energy individually to eject photoelectrons. $\nu_0 = \frac{\phi}{h}$ is thus the *cut-off* or *threshold frequency*.

Using Eq. (39) in Eq. (38) we get

$$eV_s = h\nu_0 - \phi$$

or $$V_s = \frac{h}{e}\,\nu_0 - \frac{\phi}{e} \qquad ...(40)$$

The above equation is referred to as *Einstein's photoelectric equation*. The equation predicts a linear relationship between stopping potential V_s and frequency ν as is observed experimentally.

According to Einstein, photoelectric effect is a result of particle-particle interaction (interaction between photon and bound electron in an atom). In such an interaction the exchange of momentum and energy take place instantly so that there is no time lag between the incidence of light and ejection of photoelectrons.

1.8.2 Compton Effect

In the year 1923, Arthur Compton performed experiments in which a beam of monochromatic X-rays was allowed to be incident on a graphite target. The experimental arrangement used is schematically shown in the Fig. 1.12.

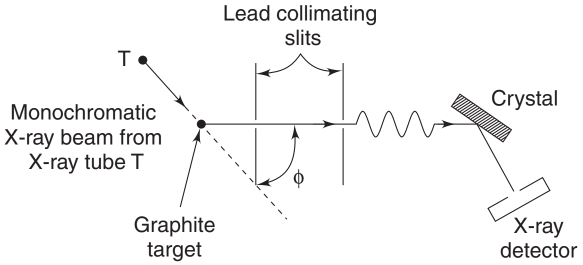


Fig. 1.12

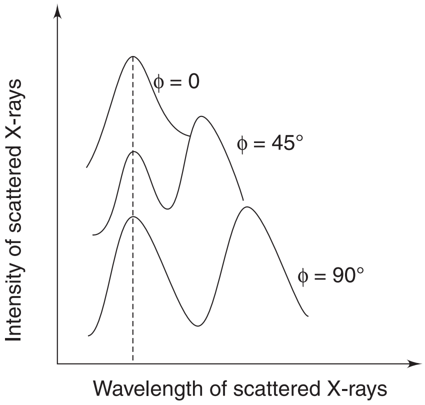


Fig. 1.13

Compton measured the intensity of the scattered X-rays as a function of their wavelengths for different angles of scattering. The experimental results are shown in the Fig. 1.13.

The following results were observed:

(i) the scattered X-rays at all angles (ϕ) of scattering, expecting $\phi = 0$, to have intensity peaks at two wavelengths, one being the same as the incident wavelength, the other being larger by an amount $\Delta\lambda$, called the Compton shift.

(ii) the Compton shift $\Delta\lambda$ to increase with the increase in the angle of scattering.

The above results do not find explanation on the basis of classical wave theory of electromagnetic radiation. According to the wave picture of radiation, the free electrons in the scattering block (graphite block) are set into forced oscillations, by the oscillating electric field vector of the incident radiation, at a frequency equal to the frequency of the radiation. These oscillating electrons in turn radiate electromagnetic waves of frequency equal to the frequency of oscillation, i.e., equal to the frequency of the incident X-ray beam. Clearly, the scattered wave, irrespective of the angle of scattering should have the wavelength equal to the wavelength of the incident X-ray beam. Thus, classical wave picture of radiation cannot account for the observed Compton shift.

Compton's Explanation of the Observed Results

Following Einstein's corpuscular picture of radiation, Compton assumed the incident X-ray beam of frequency ν to be a collection of photons, each photon having energy $h\nu$ and momentum $\frac{h\nu}{c}$. Photons of the incident beam collide with free electrons of the graphite scatterer. The recoil photons from the scatterer constitute the scattered radiation. Since the incident photons in their collision with electrons transfer some of their energy to the electrons, the scattered photons must have lower energy and consequently lower frequency and hence higher wavelength. These photons of the incident beam which escape any transfer of their energy to electrons in case of collision with the tightly bound electrons constitute the scattered radiation of the same wavelength as the incident radiation. The origin of Compton shift is thus explained qualitatively.

Considering a single photon–electron collision, Compton obtained, using the principle of conservation of linear momentum, the shift in the wavelength to be related to the scattering angle ϕ as

$$\Delta\lambda = \frac{h}{m_0 c}(1 - \cos\phi) \qquad \text{...(41)}$$

where m_0 is the rest mass of the electron. The above equation correctly predicts the experimentally observed values of $\Delta\lambda$ at different angles of scattering.

Conclusion

Experimental results of photoelectric effect and Compton effect confirm the corpuscular nature of electromagnetic radiation as advocated by Einstein. It is possible for us to remark that radiation in its propagation, as in the phenomena of reflection, refraction, interference, diffraction and polarization, exhibits wave characteristics, while the same radiation has corpuscular character in interaction with matter.

We may note the following:

(i) the factor $\frac{h}{m_0 c}$ in the expression for Compton shift is called the *Compton wavelength*.

(ii) the value of Compton shift varies between zero for $\phi = 0$ corresponding to grazing collision and $\frac{2h}{m_0 c}$ for $\phi = 180°$ corresponding to head-on collision.

1.9 WAVE NATURE OF MICROPARTICLES (MATTER WAVE): 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 argreed 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 ν and wavelength λ 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

$$E = h\nu \quad \text{and} \quad p = \frac{h\nu}{c} = \frac{h}{\lambda} \qquad ...(42)$$

The second relation is known as de-Broglie's equation.

The wavelength λ 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 (42) 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.

1.9.1 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 he observed.

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

1.9.2 Davisson and Germer's Experiment

The experimental arrangement used by Davisson and Germer is schematically shown in the Fig. 1.14.

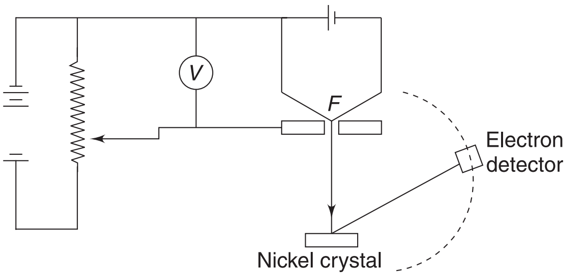


Fig. 1.14

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 ϕ and for different values of the accelerating potential were determined. The results obtained are shown in the Fig. 1.15 and Fig. 1.16. A peak in the intensity was observed at $\phi = 50°$ 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 of X-ray diffraction from crystals. Bragg reflection obeying Bragg's equation is illustrated in the Fig. 1.17. Bragg's equation is given by:

$$2d \sin \theta = m\lambda; \quad m = 1, 2, 3 \qquad ...(43)$$

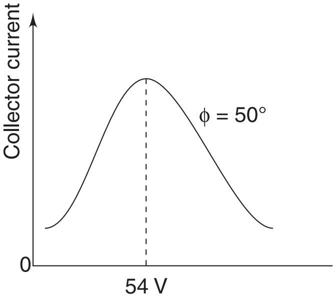


Fig. 1.15

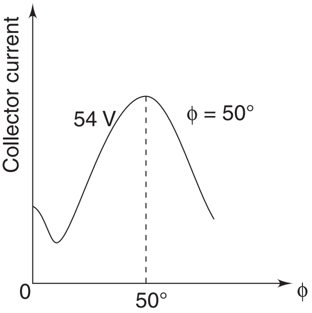


Fig. 1.16

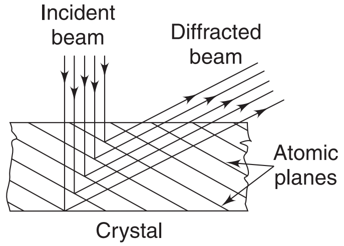


Fig. 1.17

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

$$2 \times (0.91 \text{ Å}) \sin 65° = \lambda$$

or

$$\lambda = 1.65 \text{ Å} \qquad \text{...(44)}$$

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

$$\lambda = \frac{h}{\sqrt{2mE}} \qquad \text{...(45)}$$

Substituting h, m and E we obtain

$$\lambda = 1.65 \text{ Å}. \qquad \text{...(46)}$$

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 ϕ. However, no such peaks are observed experimentally.

1.9.3 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. The scattered (diffracted) electrons were recorded on a photographic film placed perpendicular to the incident beam.

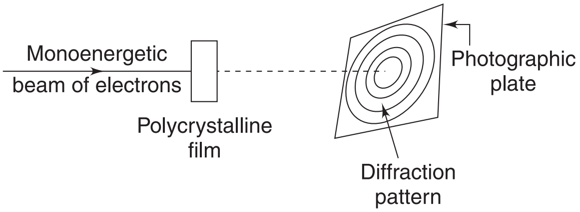


Fig. 1.18

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.

1.9.4 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 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.

1.9.5 Wave–Particle Duality

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.

1.9.6 Principle of Complementarity

The principle of complementarity, put forth by Neils Bohr forms the logical foundation of the entire system of quantum mechanical ideas (the ideas not known to classical physics).

According to Bohr, the term "complementarity" is used in order to stress that in the contrasting phenomena we have to do with equally essential aspects of the well defined knowledge about the object.

The wave and particle models of an entity (radiation or matter) are complementary to each other in the sense that if a measurement proves the wave character of the entity then it is impossible to prove the particle character in the same measurement and conversely.

1.10 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 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

$$\Delta p_x \, \Delta x \geq \frac{\hbar}{2} \qquad \text{...(47)}$$

In the above, Δp_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 Δx. There are exactly similar relations for the other two components.

$$\Delta p_y \, \Delta y \geq \frac{\hbar}{2} \qquad \text{...(48)}$$

$$\Delta p_z \, \Delta z \geq \frac{\hbar}{2} \qquad \text{...(49)}$$

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

$$\Delta E \, \Delta t \geq \frac{\hbar}{2} \qquad \text{...(50)}$$

The above relation means that an energy determination that has an uncertainty ΔE 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 Δt, 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 Eq. (47), (48), (49) and the time energy uncertainty relation given by the Eq. (50) 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.

1.10.1 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 ν is

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

If 2θ 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 2θ as illustrated is the Fig. 1.19.

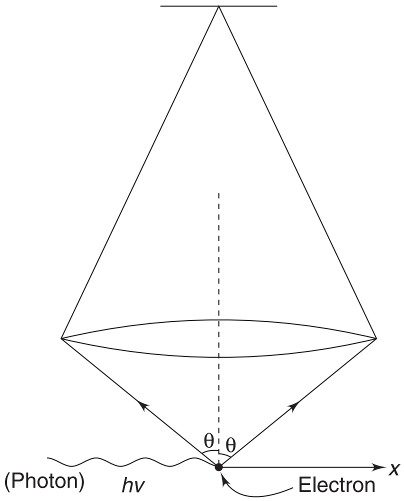


Fig. 1.19

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 Δp_x given by

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

or
$$\Delta p_x = \frac{2h}{\lambda} \sin\theta \qquad \text{...(51)}$$

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 Δp_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

$$\Delta x = \frac{\lambda}{\sin\theta} \qquad \text{...(52)}$$

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

$$\Delta p_x \, \Delta x = 2\,\frac{h}{\lambda} \sin\theta \times \frac{\lambda}{\sin\theta} = 2h > \frac{\hbar}{2} \qquad ...(53)$$

If we use light of short wavelength, say gamma rays, to reduce Δx, we simultaneously increase the Compton recoil and hence increase the Δp_x and conversely. Similarly, if we use a lens of small aperture to reduce θ, Δp_x is reduced but Δx increases and conversely. Thus it is not possible to simultaneously make Δp_x and Δx 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

$$E = \frac{p_x^{\,2}}{2m} \qquad ...(54)$$

If p_x is uncertain by Δp_x, then the uncertainty in the energy is

$$\Delta E = 2\,\frac{p_x}{2m}\,\Delta p_x = \nu_x \, \Delta p_x \qquad ...(55)$$

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

$$\Delta x = \nu_x \, \Delta t \qquad ...(56)$$

From the above, we have

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

or

$$\Delta p_x \, \Delta x = \Delta E \, \Delta t \qquad ...(57)$$

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

$$\Delta E \, \Delta t \geq \frac{\hbar}{2} \qquad ...(58)$$

1.10.2 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.

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 $p = \dfrac{h}{\lambda}$ 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.

1.11 SOLVED EXAMPLES

Example 1 Electrons emerging from a heated filament are accelerated by a potential V and collimated into a beam of diameter d. State the condition under which the beam may be treated (i) classically, (ii) quantum mechanically.

Solution: If E be the kinetic energy of an electron in the beam then we have according to question

$$E = eV \qquad \text{...(i)}$$

The momentum p of the electron is related to the kinetic energy as

$$p = \sqrt{2mE}$$

Using Eq. (i) in the above we obtain

$$p = \sqrt{2meV} \qquad \text{...(ii)}$$

The de-Broglie wavelength of the electrons in the beam is thus

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} \qquad \text{...(iii)}$$

If V be so *large* that $\lambda << d$, then the electrons are well located within the beam, a result which is in conformity with the concepts of classical physics. The beam of electrons should be treated classically under the above condition.

If V be so *small* that $\lambda >> d$ then the electrons are located outside the beam as well, a result which contradicts the concepts of classical physics. Under this condition the beam should be treated quantum mechanically.

Example 2 Experiments have shown that electrons of an atom cannot exist within the nucleus of the atom. Explain (using uncertainty relation).

Explanation: Consider an atom whose nucleus has a radius R. For an electron of the atom to exist inside the nucleus, the uncertainty in its position would be at least of the order $2R$. If we denote the position uncertainty by Δr then we have

$$\Delta r = 2R \qquad \text{...(i)}$$

If Δp represents the uncertainty in the measured value of the momentum of the electron we have according to Heisenberg's uncertainty principle

$$\Delta p \, \Delta r \approx \hbar$$

or

$$\Delta p = \frac{\hbar}{\Delta r} \qquad \text{...(ii)}$$

Considering the radius of the nucleus to be of the order of 10^{-14} m we get from eq. (ii)

$$\Delta p = \frac{\hbar}{2 \times 10^{-14}\,(\text{m})} = \frac{1.055 \times 10^{-34}\ (\text{Js})}{2 \times 10^{-14}\ (\text{m})}$$

$$= 5.28 \times 10^{-21}\ \text{Ns} \qquad \text{...(iii)}$$

Clearly, if the electron exists within the nucleus, the momentum of the electron cannot be less than the uncertainty, i.e., momentum of the electron must at least be

$$p = 5.28 \times 10^{-21}\ \text{Ns} \qquad \text{...(iv)}$$

The above momentum corresponds to a kinetic energy

$$E = \frac{p^2}{2m} = \frac{(5.28 \times 10^{-21})^2}{2 \times 9.1 \times 10^{-31}\ \text{J}}$$

$$E \approx 95.7\ \text{MeV} \qquad \text{...(v)}$$

β-decay phenomena, however, have shown that the electrons emitted from nuclei have energy of the order of a few MeV. Thus, we can conclude that electrons cannot exist within the nucleus of an atom.

Example 3 The position of an electron has been measured in an experiment with an accuracy of 0.04 m. With what minimum percentage accuracy can its momentum be measured if its speed is 10^3 m/s?

Solution: We have according to Heisenberg's uncertainty Principle

$$\Delta p \, \Delta x \approx h$$

which gives

$$\Delta p = h/\Delta x = \frac{6.63 \times 10^{-34}\ \text{Js}}{0.04\ \text{m}} = 1.66 \times 10^{-32}\ \text{Ns}$$

Momentum of the electron is

$$p = m\text{v} = 9.11 \times 10^{-31}\ (\text{ks}) \times 10^3\ (\text{ms}^{-1})$$

$$= 9.11 \times 10^{-28}\ \text{Ns}$$

Thus the percentage accuracy in the measurement of the momentum is

$$\frac{\Delta p}{p} \times 100 = \frac{1.66 \times 10^{-32}}{9.11 \times 10^{-28}} \times 100$$

$$= 0.18 \times 10^{-2}$$

$$= 0.0018\%$$

Example 4 An atom undergoes transition from an excited state to the ground state showing the emission of a spectral line of wavelength 6000 Å. If the width of the line is 0.012 Å, find the lifetime of the excited state.

Solution: Let ΔE be the uncertainty in the energy of the excited state (i.e., the spread in the energy of the excited state) and τ be the lifetime of the state then we have)

$$\Delta E \tau \approx h \qquad \text{...(i)}$$

The central energy of the excited state above the ground state is

$$E = h\nu = h\frac{c}{\lambda} \qquad \text{...(ii)}$$

The above gives

$$\Delta E = \frac{-hc}{\lambda^2} \Delta\lambda.$$

or

$$|\Delta\lambda| = \frac{\lambda^2 \Delta E}{hc} = \frac{\lambda^2}{hc}\frac{h}{\tau} = \frac{\lambda^2}{c\tau} \qquad \text{...(iii)}$$

The above gives

$$\tau = \frac{\lambda^2}{c|\Delta\lambda|} = \frac{(6000 \times 10^{-10})^2 \text{ (m}^2)}{3 \times 10^8 \text{ (ms}^{-1}) \times 0.012 \times 10^{-10} \text{ (m)}}$$

or

$$\tau = 10^{-9} \text{ s.}$$

Example 5 Explain with examples that the position and momentum uncertainties are important for microscopic systems but negligible for macroscopic systems.

Explanation: Consider a neutron (mass = 1.65×10^{-27} kg) moving at a speed of 5×10^6 m/s.

Uncertainty in the momentum cannot be greater than the momentum of the neutron given by

$$p = m_n v_n = 1.65 \times 10^{-27} \times 5 \times 10^6 \text{ Ns.}$$

The maximum uncertainty in the momentum of the neutron is thus

$$\Delta p = p = 1.65 \times 10^{-27} \times 5 \times 10^{6} \text{ Ns}$$

The minimum uncertainty in the position of the neutron is thus

$$(\Delta x)_{\min} = \frac{\hbar}{2\Delta p} = \frac{h}{4\pi\Delta p} = \frac{6.63 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 8.25 \times 10^{-21} \text{ Ns}} = 6.4 \times 10^{-15} \text{m}$$

We find Δx to be of the order of the size of a nucleus and is hence measurable.

Let us now consider a body (mass 50 kg) moving at a speed 2 m/s.

Making calculation as given above we get the uncertainty in the position of the body to be given by

$$(\Delta x)_{\min} = \frac{\hbar}{2\Delta p} = \frac{6.63 \times 10^{-34} \text{ J.s}}{4 \times 3.14 \times 50 \times 2 \text{ Ns}}$$

or

$$(\Delta x)_{\min} = 5 \times 10^{-37} \text{ m}$$

The position uncertainty of the body is thus beyond the scope of any measurement and can be neglected.

Example 6 A 60 kW broadcasting antenna is emitting electromagnetic waves at a frequency of 4 MHz. Explain whether or not will you treat the emitted radiation quantum mechanically?

Solution: The energy emitted by the antenna per second is

$$E = 60 \times 1000 = 60{,}000 \text{ J.}$$

If n be the number of photons being emitted per second, we get

$$E = nh\nu.$$

Thus, we have

$$n = \frac{E}{h\nu}$$

Substituting the values of E, h and ν, we get

$$\frac{n = 60{,}000 \text{ (J)}}{6.63 \times 10^{-34} \text{ (Js)} \times 4 \times 10^{6} \text{ (s}^{-1}\text{)}} = 2.2 \times 10^{31}$$

Since n is exceedingly large, the quantum nature of the emitted radiation is not meaningful.

2

Mathematical Preliminaries

2.1 INTRODUCTION

One of the main features of an atomic-subatomic system is that it can exist in states with discrete values of energy. The idea of discreteness or quantization of atomic state was first advanced by Bohr. According to him, the quantized atomic states are stationary states in the sense that the system in these states can neither emit nor absorb energy. Bohr further postulated that energy is emitted or absorbed in the form of electromagnetic radiation only in discontinuous transition between stationary states, the frequency of the radiation being given by

$$\nu = \frac{E_m - E_n}{h} \qquad (E_m > E_n).$$

The above postulates of Bohr, although in contradiction with the laws of classical mechanics and electrodynamics, were fully confirmed by experiments. This necessitated replacement of classical theory, at least for atomic systems, by a theory that would be logically consistent on the one hand and conform to Bohr's principles on the other. Existence of states characterized by definite energy values for a system is found to be analogous to the problem of mathematical physics, namely, the linear operator problem and the associated eigenvalue problem. Quantum mechanics has substantiated this idea of quantization of energy and of other physical quantities of systems in atomic and subatomic domain ever since Erwin Schrödinger in 1926 established quantization as an eigenvalue problem.

A linear operator is associated with every physical quantity and the theory of linear operator forms the basic mathematical apparatus of quantum mechanics. In the sections to follow we discuss some of the features of this mathematical apparatus which quantum mechanics employs.

2.2 THE OPERATOR CONCEPT

Consider a function of n independent variables, $q_1, q_2, ..., q_n$, such as

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

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

Addition operator $q_i + \psi = \phi_i$

Multiplication operator $q_i\psi = \Gamma_i$

Differential operator $\frac{\partial}{\partial q_i} \psi = \Lambda_i$

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

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

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

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

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

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

2.3 EQUALITY OF TWO OPERATORS

Let us write

$$\hat{A}\psi = \hat{B}\psi \qquad ...(3)$$

The above equation states that the result of operation on the function ψ with $\hat{A}$ is the same as the result obtained by operation on ψ with $\hat{B}$. The statement

$$\hat{A} = \hat{B} \qquad ...(4)$$

which seems to follow from Eq. (3) should be interpreted as operation with $\hat{A}$ on some specified function or a set of specified functions is equivalent to operation on the same function or the same set of function with $\hat{B}$. The above can be understood from the following examples:

If we consider a function $\psi = x^2$, then we get

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

and

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

Thus, for $\psi = x^2$, we find $\quad \frac{d}{dx} \equiv \frac{2}{x}$

If, however, we take $\psi = x^3$

then $$\frac{d}{dx}\psi = \frac{d}{dx}(x^3) = 3x^2$$

while $$\frac{2}{x}\psi = \frac{2}{x}x^3 = 2x^2$$

Clearly of $\psi = x^3$ we find $\frac{d}{dx} \neq \frac{2}{x}$

2.4 GENERAL OPERATORS

It is possible to define more general operators in terms of combination of simpler ones. However, it becomes important to outline certain limitation on the use of such combination operators.

(a) Product of Two Operators

Let $\hat{A}$ and $\hat{B}$ be two operators defined in the same domain of definition. It is possible to define two new operators

$$\hat{C} = \hat{A}\hat{B}$$

and

$$\hat{D} = \hat{B}\hat{A}$$

In general, it may be stated that

$$\hat{C}\psi \neq \hat{D}\psi$$

i.e.,

$$\hat{A}\hat{B}\psi \neq \hat{B}\hat{A}\psi$$

or

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi \neq 0 \qquad ...(5)$$

The above statement can be seen from the following example:

Let ψ be any function of x, $\hat{A}$ represent multiplication by x, while $\hat{B}$ represent differentiation with respect to x. We then have

$$\hat{A}\hat{B}\psi = x\frac{d\psi}{dx} \qquad ...(6)$$

and

$$\hat{B}\hat{A}\psi = \frac{d}{dx}(x\psi) = x\frac{d\psi}{dx} + \psi \qquad ...(7)$$

Thus

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi = x\frac{d\psi}{dx} - x\frac{d\psi}{dx} - \psi$$

or

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi = -\psi \qquad ...(8)$$

Equation (8) can be expressed by writing

$$(\hat{A}\hat{B} - \hat{B}\hat{A}) = -\hat{U} \qquad ...(9)$$

where $\hat{U}$ is the unit operator defined by

$$\hat{U}\psi = \psi \qquad ...(10)$$

(b) Commutator of Two Operators

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

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \qquad ...(11)$$

From the definition given by Eq. (11) it follows that

$$[\hat{B}, \hat{A}] = \hat{B}\hat{A} - \hat{A}\hat{B} \qquad ...(12)$$

Equations (11) and (12) give

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \qquad ...(13)$$

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

$$\hat{A}\hat{B} = \hat{B}\hat{A} \qquad ...(14)$$

or

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0 \qquad ...(15)$$

And hence the commutator

$$[\hat{A}, \hat{B}] = 0 \qquad ...(16)$$

If the operators $\hat{A}$ and $\hat{B}$ are such that Eq. (14) or Eq. (15) or Eq. (16) does not hold, then they are said to be non-commutative.

(c) Anti-commutator of Two Operators

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

$$[\hat{A}, \hat{B}]_+ \equiv \{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} \qquad ...(17)$$

The operators are said to anticommute, if

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

or

$$\hat{A}\hat{B} + \hat{B}\hat{A} = 0 \qquad ...(18)$$

(d) Inverse of an Operator

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

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

$$\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = 1 \qquad ...(19)$$

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

$$[\hat{A}, \hat{A}^{-1}] = \hat{A}\hat{A}^{-1} - \hat{A}^{-1}\hat{A} = 1 - 1 = 0 \qquad ...(20)$$

2.5 LINEAR OPERATOR

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

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

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

$$\hat{A}(\psi_1 + \psi_2) = \hat{A}\psi_1 + \hat{A}\psi_2 \qquad ...(21)$$

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

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

$$\hat{A}(c\psi_2) = c\hat{A}\psi_2 \qquad ...(22)$$

where c is a number.

The properties of linear operator expressed by the Eqs. (21) and (22) will be useful in later developments of quantum mechanics.

2.5.1 Eigenfunctions and Eigenvalues of a Linear Operator

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

$$\hat{A}\psi = \phi \qquad ...(23)$$

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

$$\begin{aligned} \hat{A}\psi_1 &= a_1\psi_1 \\ \hat{A}\psi_2 &= a_2\psi_2 \\ \vdots \quad &\quad \vdots \\ \hat{A}\psi_n &= a_n\psi_n \end{aligned} \qquad ...(24)$$

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

2.5.2 Eigenvalue Equation

The equation

$$\hat{A}\psi_i = a_i\psi_i \qquad (i = 1, 2, ..., n) \qquad ...(25)$$

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

2.5.3 Discrete and Continuous Spectra of Eigenvalues of Operators

Consider the differential equation

$$i\,\frac{d\psi(x)}{dx} = \lambda\psi(x) \qquad ...(26)$$

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

Equation (26) is a special case of the general operator equation

$$\hat{A}\psi(x) = a\psi(x) \qquad ...(27)$$

where $\hat{A}$ is an operator and a is a real number. The general solutions of Eq. (26) are

$$\psi(x) = \psi_\lambda(x) = c_\lambda e^{-i\lambda x} \qquad ...(28)$$

with c_λ as an arbitrary constant. There exists a function $\psi_\lambda(x)$ for each value of λ and each satisfies Eq. (26).

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 Eq. (27), one obtains a set of such characteristic functions ψ_i for any operator such that

$$\hat{A}\psi_i = a_i\psi_i \qquad ...(29)$$

We thus find that, in general, an operator possesses a set of eigenfunctions, each of which is characterized by a number a_i through Eq. (29). 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 Eq. (26) $\hat{A} \equiv i\dfrac{d}{dx}$

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

$$\psi_\lambda = c_\lambda e^{-i\lambda x} \qquad \text{...(30)}$$

Equation (30) defines one eigenfunction for each value of λ which may vary continuously from a minimum to a maximum value. The spectrum of λ is evidently continuous.

Example of an operator with discrete spectrum of eigenvalues:

Let us consider the second-order differential equation

$$\frac{d^2\psi(x)}{dx^2} + \lambda\psi(x) = \alpha(x) \qquad \text{...(31)}$$

subject to conditions

$$\begin{aligned} \alpha(x) &= 0 \quad \text{for } 0 < x < a \\ &= \infty \quad \text{for } x \le 0 \text{ and } x \ge a \end{aligned} \qquad \text{...(32)}$$

In Eq. (31), $\psi(x)$ is some arbitrary function of the variable x and λ is a constant real number.

In view of the condition $\alpha(x) = \infty$ for $x \le 0$ and $x \ge a$, we obtain the solution of equation (31) in these two regions to be

$$\psi(x) = 0$$

Clearly,

and

$$\left.\begin{aligned} \psi(x) &= 0 \quad \text{at } x = 0 \\ \psi(x) &= 0 \quad \text{at } x = a \end{aligned}\right\} \qquad \text{...(33)}$$

In the region $0 \le x \le a$, Eq. (31) becomes

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

or

$$-\frac{d^2\psi(x)}{dx^2} = \lambda\psi(x) \qquad \text{...(34)}$$

The above equation can be identified as the eigenvalue equation

$$\hat{A}\psi(x) = \lambda\psi(x) \qquad ...(35)$$

where $\hat{A}$ is the differential operator

$$\hat{A} \equiv -\frac{d^2}{dx^2} \qquad ...(36)$$

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

The most general solution of Eq. (34) is

$$\psi(x) = A \sin \sqrt{\lambda}x + B \cos \sqrt{\lambda}x \qquad ...(37)$$

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

Boundary condition given by Eq. (33) requires

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

The above when used in Eq. (37) yields

$$B = 0$$

So that the solution given by Eq. (37) becomes

$$\psi(x) = A \sin \sqrt{\lambda}x \qquad ...(38)$$

We also have the boundary condition

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

which when used in Eq. (38) gives

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

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

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

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

$\therefore$ $$\lambda = \frac{n^2\pi^2}{a^2} \qquad ...(39)$$

The possible values of λ from Eq. (39) are given as

$$0, \frac{\pi^2}{a^2}, \frac{4\pi^2}{a^2}, \frac{9\pi^2}{a^2}, \text{ etc.} \qquad ...(40)$$

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

$$\psi(x) = A \sin \sqrt{\lambda}x = A \sin\left(\frac{n\pi}{a}x\right) \qquad ...(41)$$

2.6 HERMITIAN OPERATOR

2.6.1 Defintion

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

$$\hat{A}\psi = \phi \qquad ...(42)$$

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 ψ^*(complex conjugate of the function ψ), we get the function ϕ^* (complex conjugate of the function ϕ), i.e., we get

$$\hat{A}^*\psi^* = \phi^* \qquad ...(43)$$

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

$$\int_V u^*\hat{A}v d\tau = \int_V (\hat{A}u)^* v dt = \int_V \hat{A}^* u^* v d\tau \qquad ...(44)$$

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

$$\int_v v(\hat{A}u)d\tau = \int_v u(\tilde{\hat{A}}v)\,d\tau \qquad ...(45)$$

The transposed operator $\tilde{\hat{A}}^*$ for the operator $\hat{A}^*$ is, according to Eq. (45), given by

$$\int v(\hat{A}^*u)d\tau = \int u(\tilde{\hat{A}}^* v)\,d\tau \qquad ...(46)$$

It is usual to denote $\tilde{\hat{A}}^*$ 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

$$\hat{A} = \hat{A}^\dagger \qquad ...(47)$$

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

2.6.2 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 ψ_n be an eigenfunction of $\hat{A}$ belonging to the eigenvalue a_n. We then have the eigenvalue equation

$$\hat{A}\psi_n = a_n\psi_n \qquad \text{...(48)}$$

Taking complex conjugate of Eq. (48), we get

$$\hat{A}^*\psi_n^* = a_n^*\psi_n^* \qquad \text{...(49)}$$

Multiplying Eq. (48) by ψ_n^* from the left and integrating over the entire domain of definition we obtain

$$\int \psi_n^*\,\hat{A}\,\psi_n d\tau = \int \psi_n^* a_n \psi_n d\tau = a_n \int \psi_n^* \psi_n\, d\tau \qquad \text{...(50)}$$

Since $\hat{A}$ is Hermitian we may write Eq. (50) as

$$\int \hat{A}^*\psi_n^*\psi_n d\tau = a_n \int \psi_n^*\psi_n d\tau \qquad \text{...(51)}$$

Multiplying Eq. (49) by ψ_n from the right and integrating over the entire domain of definition we obtain

$$\int \hat{A}^*\psi_n^*\psi_n d\tau = \int a_n^*\psi_n^*\psi_n d\tau = a_n^* \int \psi_n^*\psi_n d\tau \qquad \text{...(52)}$$

The L.H.S of Eqs. (51) and (52) 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

$$a_n = a_n^* \qquad \text{...(53)}$$

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

$$\int u^* v d\tau = 0 \qquad ...(54)$$

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

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

$$\hat{A}\psi_n = a_n\psi_n \qquad ...(55)$$

$$\hat{A}\psi_m = a_m\psi_m \qquad ...(56)$$

Multiplying Eq. (55) by ψ_m^* from the left and integrating over the entire domain of definition, we get

$$\int \psi_m^* \hat{A}\psi_n d\tau = \int \psi_m^* a_n \psi_n d\tau = a_n \int \psi_m^* \psi_n d\tau \qquad ...(57)$$

Taking complex conjugate of Eq. (56), we obtain

$$\hat{A}^* \psi_m^* = a_m^* \psi_m^* = a_m \psi_m^* \qquad \text{[since } a_m \text{ is real]} \qquad ...(58)$$

Multiplying Eq. (58) by ψ_m from the right and integrating over the entire domain of definition, we obtain

$$\int \hat{A}^* \psi_m^* \hat{A}_n d\tau = a_m \int \psi_m^* \psi_n d\tau \qquad ...(59)$$

Since $\hat{A}$ is Hermitian, Eq. (59) can be rewritten as

$$\int \psi_m^* \hat{A} \psi_n d\tau = a_m \int \psi_m^* \psi_n d\psi \qquad ...(60)$$

From Eqs. (57) and (60), we get

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

or

$$(a_n - a_m) \int \psi_m^* \psi_n d\tau = 0 \qquad ...(61)$$

Since a_n and a_m are two different eigenvalues

$$(a_n - a_m) \neq 0$$

and hence Eq. (61) yields

$$\int \psi_m^* \psi_n d\tau = 0 \qquad ...(62)$$

In view of Eq. (54), we thus find that eigenfunctions of the Hermitian operator $\hat{A}$ belonging to different eigenvalues are orthogonal to each other.

2.7 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 ψ_n be one such eigenfunction of both $\hat{A}$ and $\hat{B}$ belonging to eigenvalues a_n and b_n respectively. We then have

$$\hat{A}\psi_n = a_n\psi_n \qquad ...(63)$$

and

$$\hat{B}\psi_n = b_n\psi_n \qquad ...(64)$$

Operating Eq. (63) 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 Eq. (64) the above becomes

$$\hat{B}\hat{A}\psi_n = a_n b_n \psi_n \qquad ...(65)$$

Operating Eq. (64) 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 Eq. (63) in the above we get

$$\hat{A}\hat{B}\,\psi_n = b_n a_n \psi_n \qquad ...(66)$$

Combining Eqs. (65) and (66) we obtain

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

and hence we have

$$\hat{A}\hat{B} - \hat{B}\,\hat{A} = 0 \qquad ...(67)$$

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

$$\hat{A}\hat{B} = \hat{B}\hat{A} \qquad ...(68)$$

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

$$\hat{A}\psi_i = a_i\psi_i \qquad ...(69)$$

Operating Eq. (69) 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 Eq. (68) the above can be written as

$$\hat{A}(\hat{B}\psi_i) = a_i\ (\hat{B}\psi_i) \qquad \text{...(70)}$$

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 ψ_i only by a multiplicative constant, say b_i, i.e.,

$$\hat{B}\psi_i = b_i\psi_i \qquad \text{...(71)}$$

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

2.8 SOME IMPORTANT THEOREMS AND EXAMPLES

(1) 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 ψ and ϕ in the domain in which $\hat{A}$ and $\hat{B}$ are defined. Using the definition of transposed operator we can write

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

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

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

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

$$= \int(\phi\tilde{\hat{B}}\tilde{\hat{A}}\psi d\tau \qquad \text{...(72)}$$

We also have

$$\int\psi(\hat{A}\,\hat{B})\phi d\tau = \int\phi(\widetilde{\hat{A}\hat{B}})\psi d\tau \qquad \text{...(73)}$$

Comparing Eqs. (72) and (73) we get

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

The above gives

$$\widetilde{\hat{A}\hat{B}} = \tilde{\hat{B}}\tilde{\hat{A}} \qquad \text{...(74)}$$

Taking complex conjugate of Eq. (74), we obtain

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

or
$$(\hat{A}\hat{B})^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger} \qquad \text{...(75)}$$

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

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

and Eq. (75) thus becomes

$$(\hat{A}\hat{B})^{\dagger} = \hat{B}\hat{A} \qquad \text{...(76)}$$

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

$$(\hat{A}\hat{B})^{\dagger} = \hat{A}\hat{B} \qquad \text{...(77)}$$

In view of Eq. (76) and (77) we find that the product $\hat{A}\hat{B}$ is Hermitian if

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

or
$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

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

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

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

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

$$\hat{B}^{\dagger} = \hat{B} \qquad \text{...(78)}$$

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

$$\tilde{\hat{C}} = i(\widetilde{\hat{A}\hat{B}} - \widetilde{\hat{B}\hat{A}}) = i\,\widetilde{\hat{A}\hat{B}} - i\,\widetilde{\hat{B}\hat{A}}$$

$$= i\,\tilde{\hat{B}}\tilde{\hat{A}} - i\tilde{\hat{A}}\tilde{\hat{B}} \qquad \text{...(79)}$$

Taking complex conjugate of Eq. (79), we get

$$(\tilde{\hat{C}})^{*} = -i(\tilde{\hat{B}})^{*}\,(\tilde{\hat{A}})^{*} + i(\tilde{\hat{A}})^{*}\,(\tilde{\hat{B}}\,i)^{*}$$

$$= -i\hat{B}^{\dagger}\hat{A}^{\dagger} + i\hat{A}^{\dagger}\,\hat{B}^{\dagger}$$

or
$$\hat{C}^{\dagger} = -i\hat{B}^{\dagger}\hat{A}^{\dagger} + i\hat{A}^{\dagger}\,\hat{B}^{\dagger} \qquad \text{...(80)}$$

Using Eq. (78) in Eq. (80), we get

$$\hat{C}^{\dagger} = -i\hat{B}\hat{A} + i\hat{A}\hat{B} = i(\hat{A}\hat{B} - \hat{B}\hat{A}) \qquad \text{...(81)}$$

In view of Eqs. (79) and (81), we find

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

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

Examples

(1) From two non-commuting Hermitian operators $\hat{A}$ and $\hat{B}$ construct a Hermitian operator.

OR

If $\hat{A}$ and $\hat{B}$ are two non-commuting Hermitian operators, then prove that $\frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A})$ is Hermitian.

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

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

$$\hat{B}^{\dagger} = \hat{B} \qquad \text{...(82)}$$

Let us consider the operator $\hat{C}$ as

$$\hat{C} = \frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A}) \qquad \text{...(83)}$$

Taking transpose of Eq. (83) we get

$$\tilde{\hat{C}} = \frac{1}{2}(\widetilde{\hat{A}\hat{B}} + \widetilde{\hat{B}\hat{A}}) = \frac{1}{2}(\tilde{\hat{B}}\tilde{\hat{A}} + \tilde{\hat{A}}\tilde{\hat{B}}) \qquad \text{...(84)}$$

Taking complex conjugate of Eq. (84) we get

$$(\tilde{\hat{C}})^{*} = \frac{1}{2}(\tilde{\hat{B}})^{*}(\tilde{\hat{A}})^{*} + \frac{1}{2}(\tilde{\hat{A}})^{*}(\tilde{\hat{B}})^{*}$$

or

$$\hat{C}^{\dagger} = \frac{1}{2}\hat{B}^{\dagger}\hat{A}^{\dagger} + \frac{1}{2}\hat{A}^{\dagger}\hat{B}^{\dagger} \qquad \text{...(85)}$$

Use of Eq. (82) in the above gives us

$$\hat{C}^{\dagger} = \frac{1}{2}\hat{B}\hat{A} + \frac{1}{2}\hat{A}\hat{B} = \frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A}) \qquad \text{...(86)}$$

In view of Eqs. (83) and (86) we find that

$$\hat{C} = \frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A}) \text{ is Hermitian.}$$

(2) 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 ψ_n be an eigenfunction of $\hat{f}$ belonging to the eigenvalue f_n. We then have the eigenvalue equation

$$\hat{f}\psi_n = f_n\psi_n \qquad ...(87)$$

Operating Eq. (87) 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

$$\hat{f}^2\psi_n = f_n^2\psi_n \qquad \text{[using Eq. (87)]} \qquad ...(88)$$

Operating Eq. (88) 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

$$\hat{f}^3\psi_n = f_n^3\psi_n \qquad \text{[using Eq. (87)]} \qquad ...(89)$$

Generalizing the above procedure we obtain

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

(3) The operator $\hat{p}_x = -i\hbar\,\frac{\partial}{\partial x}$ (operator corresponding to the *x*-component of linear momentum) is Hermitian.

Let the system, whose *x*-component of linear momentum p_x is being considered, be in a state described by the wavefunction $\psi(x)$. We may note that $\psi(x)$ vanishes at infinity. We have

$$\int_{-\infty}^{+\infty} \psi^*(x)\hat{p}_x\psi(x)dx = \int_{-\infty}^{+\infty} \psi^*(x)\left[-i\hbar\frac{\partial\psi(x)}{\partial x}\right]dx$$

$$= -i\hbar\int \psi^*(x)\frac{\partial\psi(x)}{\partial x}\,dx$$

Integrating the right hand side of the above by parts we obtain

$$\int_{-\infty}^{+\infty} \psi^*(x)\hat{p}_x\psi(x)dx = -i\hbar\left[\{\psi^*(x)\psi(x)\}_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\psi(x)\frac{\partial\psi^*(x)}{\partial x}\,dx\right]$$

$$= i\hbar\int_{-\infty}^{+\infty}\psi(x)\frac{\partial\psi^*(x)}{\partial x}\,dx \qquad \text{[since } \psi(x) = 0 \text{ at } x = \pm\infty]$$

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

$$= \int_{-\infty}^{+\infty}\psi(x)\,\hat{p}_x^*\psi^*(x)dx$$

Thus we find that

$$\int_{-\infty}^{+\infty} \psi(x)\, \hat{p}_x \psi(x) dx = \int_{-\infty}^{+\infty} \psi(x)\, \hat{p}_x^* \psi(x) dx$$

Clearly,

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \text{ is Hermitian}$$

2.9 SOLVED EXAMPLES

Example 1 Prove that the commutator of two Hermitian operators is antihermitian.

Proof Let $\hat{A}$ and $\hat{B}$ be two hermitian operators. Clearly

$$\hat{A}^\dagger = \hat{A}, \quad \hat{B}^\dagger = \hat{B} \qquad ...(i)$$

We have $$[\hat{A}, \hat{B}]^\dagger = (\hat{A}\hat{B} - \hat{B}\hat{A})^\dagger = \hat{B}^\dagger\hat{A}^\dagger - \hat{A}^\dagger\hat{B}^\dagger$$

Using Eq. (i) in the above we get

$$[\hat{A}, \hat{B}]^\dagger = \hat{B}\hat{A} - \hat{A}\hat{B} = -(\hat{A}\hat{B} - \hat{B}\hat{A}) = -[\hat{A}, \hat{B}]$$

Thus $[\hat{A}, \hat{B}]$ is antihermitian.

Example 2 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

$$\hat{A}^{-1}\hat{A} = 1 \qquad ...(i)$$

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

$$\hat{A}\psi = a\psi \qquad ...(ii)$$

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

$$\hat{A}^{-1}\hat{A}\psi = a\,\hat{A}^{-1}\psi \qquad ...(iii)$$

Using Eq. (i) we get

$$\hat{A}^{-1}\hat{A}\psi = \psi \qquad ...(iv)$$

In view of Eqs. (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 $\hat{A}$.

Example 3 Show that the differential operator $i\frac{d}{dx}$ is a Hermitian operator.

Solution: Consider a function of x, namely $\psi(x)$ which vanishes at infinity. We get

$$\int_{-\infty}^{+\infty} \psi^*(x)\left(i\frac{d}{dx}\right)\psi(x)dx = i\int_{-\infty}^{+\infty} \psi^*(x)\frac{d\psi(x)}{dx}dx$$

Integrating by parts we obtain

$$\int_{-\infty}^{+\infty} \psi^*(x)\left(i\frac{d}{dx}\right)\psi(x)dx = i\left[\{\psi^*(x)\,\psi(x)\}_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\psi(x)\frac{d\psi^*(x)}{dx}dx\right]$$

Due to the boundary conditions on $\psi(x)$, the first term on the right hand side of the above equation vanishes. Hence, we get

$$\int_{-\infty}^{+\infty} \psi^*(x)\left(i\frac{d}{dx}\right)\psi(x)dx = \int_{-\infty}^{+\infty}\psi(x)\left(-i\frac{d}{dx}\right)\psi^*(x)dx$$

$$\int_{-\infty}^{+\infty} \psi^*(x)\left(i\frac{d}{dx}\right)\psi(x)dx = \int_{-\infty}^{+\infty}\psi(x)\left(-i\frac{d}{dx}\right)^*\psi^*(x)dx$$

$$= \int_{-\infty}^{+\infty}\left(i\frac{d}{dx}\right)^*\psi^*(x)\,\psi(x)dx$$

Clearly, the operator $i\frac{d}{dx}$ is Hermitian.

Example 4 The commutator of two operators $\hat{A}$ and $\hat{B}$ is $[\hat{A}, \hat{B}] = \alpha\hat{B}$, where α is a number. Show that $e^{\hat{A}}\hat{B}e^{-\hat{A}} = e^{\alpha}\hat{B}$

Solution: We have the general identity for any two operators $\hat{A}$ and $\hat{B}$ defined in the same domain of definition

$$e^{\hat{A}}\hat{B}\,e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!}[\hat{A},[\hat{A}, \hat{B}]] + \frac{1}{3!}[\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] + \ldots \quad \text{...(i)}$$

We have $$[\hat{A}, \hat{B}] = \alpha\hat{B} \quad \text{...(ii)}$$

Now

$$[\hat{A},\ [\hat{A},\ \hat{B}] = [\hat{A},\ \alpha\ \hat{B}] = \alpha[\hat{A},\ \hat{B}] = \alpha^2\ \hat{B} \qquad \text{...(iii)}$$

$$[A,\ [A,\ [\hat{A},\ \hat{B}]]] = [\hat{A},\ \alpha^2\ \hat{B}] = \alpha^2\ [\hat{A},\ \hat{B}] = \alpha^3\ \hat{B} \qquad \text{...(iv)}$$

Using the results given by Eqs. (ii), (iii) and (iv) in Eq. (i) we get

$$e^{-\hat{A}}\hat{B}\,e^{-\hat{A}} = \hat{B} + \alpha\hat{B} + \frac{\alpha^2\hat{B}}{2!} + \frac{\alpha^3\hat{B}}{3!} + \ldots$$

$$= \left[1 + \alpha + \frac{\alpha^2}{2!} + \frac{\alpha^3}{3!} + \ldots\right]^{\hat{B}}$$

or

$$e^{-\hat{A}}\hat{B}\ e^{-\hat{A}} = e^{\alpha}\hat{B}.$$

Example 5 $\hat{A}$ and $\hat{B}$ are two commuting Hermitian operators. Is the operator $(\hat{A}\hat{B} + \hat{B}\hat{A})$ also Hermitian?

Solution: Since the operators $\hat{A}$ and $\hat{B}$ are Hermitian and they commute with each other, the product operators $\hat{A}\hat{B}$ as well as $\hat{B}\hat{A}$ are Hermitian (see Section 2.8).

Let ψ_m and ψ_n be two functions defined in the domain of definition of $\hat{A}$ and $\hat{B}$. Since $\hat{A}\hat{B}$ is Hermitian, we have

$$\int\psi_m^*\hat{A}\hat{B}\ \psi_n d\tau = \int(\hat{A}\hat{B})^*\ \psi_m^*\psi_n d\tau \qquad \text{...(i)}$$

Similarly, since $\hat{B}\hat{A}$ is Hermitian we get

$$\int\psi_m^*\hat{B}\hat{A}\psi_n d\tau = \int(\hat{B}\hat{A})^*\ \psi_m^*\psi_n d\tau \qquad \text{...(ii)}$$

Now

$$\int\psi_m\ (\hat{A}\hat{B} + \hat{B}\hat{A})\psi_n d\tau = \int\psi_m^*\hat{A}\hat{B}\psi_n d\tau + \int\psi_m^*\hat{B}\hat{A}\psi_n d\tau$$

$$= \int(\hat{A}\hat{B})^*\psi_m^*\psi_n d\tau + \int(\hat{B}\hat{A})^*\psi_m^*\psi_n d\tau$$

$$= \int(\hat{A}\hat{B} + \hat{B}\hat{A})^*\psi_m^*\psi_n d\tau$$

Clearly, the operator $(\hat{A}\hat{B} + \hat{B}\hat{A})$ is Hermitian.

Example 6 In Example 5, is the operator $(\hat{A}\hat{B} - \hat{B}\hat{A})$ Hermitian?

Solution:

We have $$\int\psi_m^*\ (\hat{A}\hat{B} - \hat{B}\hat{A})\psi_n d\tau = \int\psi_m^*\hat{A}\hat{B}\psi_n d\tau - \int\psi_m^*\hat{B}\hat{A}\psi_n d\tau$$

Using Eqs. (i) and (ii) of Example 5, the above becomes

$$\int \psi_m^*(\hat{A}\hat{B} - \hat{B}\hat{A})\psi_n d\tau = \int (\hat{A}\hat{B})^* \psi_m^* \psi_n d\tau - \int (\hat{B}\hat{A})^* \psi_m^* \psi_n d\tau$$

$$= \int (\hat{A}\hat{B} - \hat{B}\hat{A})^* \psi_m^* \psi_n d\tau$$

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

3

Postulational Foundation of Quantum Theory

3.1 INTRODUCTION

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. 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 has been defined and discussed in Chapter 2.

(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.

3.2 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 ψ, called the **wave function**. In general, ψ is a complex-valued function of generalized coordinates q_1, q_2, ..., q_s and time 't'. The function ψ 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 below are given classical representations and corresponding quantum mechanical operators for the observables of a single particle.

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

☛ **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

$$\hat{A}\psi_n = a_n\psi_n \qquad \text{...(i)}$$

where $\{\psi_n\}$ forms a *complete set* of functions called eigenfuctions 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 ψ, the expected mean or expectation value, of a series of measurement of an observable, say A, is

$$\langle A \rangle = \frac{\int \psi^* \hat{A}\psi d\tau}{\int \psi^* \psi d\tau} \qquad \text{...(ii)}$$

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 ψ to be normalized, i.e.,

$$\int \psi^* \psi d\tau = 1 \qquad \text{...(iii)}$$

With normalized wave function, Eq. (ii) gives

$$\langle A \rangle = \int \psi^* \hat{A}\psi d\tau \qquad \text{...(iv)}$$

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

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

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.

3.3 CONSEQUENCES OF THE POSTULATES

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).

3.3.1 Eigenstates

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

$$\langle A \rangle = \int \phi^* \hat{A}\phi d\tau \qquad \text{...(1)}$$

Let us now suppose that the state function ϕ is an eigenfunction of $\hat{A}$, say ψ_n, belonging to eigenvalue a_n. Equation (1) can then be written as

$$\langle A \rangle = \int \psi_n^* \hat{A} \psi_n d\tau \qquad ...(2)$$

But we have the eigenvalue equation

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

and hence

$$\langle A \rangle = a_n \int \psi_n^* \psi_n d\tau = a_n \qquad ...(3)$$

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.

3.3.2 Superposition States

Consider the system in a state described by the state function ϕ in which the observable A dose 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 ϕ, and the observable to be measured be the linear momentum $\vec{p}$. Let the momentum operator $\hat{\vec{p}}$ have a complete set of momentum eigenfunctions say $\{\psi_n\}$. We can then express ϕ as the linear superposition

$$\phi = \sum a_n \psi_n \qquad ...(4)$$

The expectation value of the momentum of the system in state ϕ is, by definition,

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

or

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

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

$$\langle p\rangle = \sum_n |a_n|^2 p_m \qquad \text{...(5)}$$

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 ω_n. The mean value of the momentum can then be expressed mathematically as

$$\langle p\rangle = \sum_n \omega_n p_n \qquad \text{...(6)}$$

In view of Eqs. (5) and (6) it is reasonable to assume that $|a_n|^2$ of Eq. (5) are exactly the ω_n of Eq. (6). Since ϕ is normalized, we have

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

Using Eq. (4) the above gives

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

whence we get

$$\sum |a_n|^2 = 1 \qquad \text{...(7)}$$

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

If an observable A of a system on measurement exhibits a range of values a_n together with a given frequency distribution ω_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 ϕ represents a superposition state relative to one operator, it is, in general, an eigenstate of some other operator.

3.4 COMPATIBLE MEASUREMENTS: SIMULTANEOUS EIGENSTATES

Consider a system in an eigenstate described by the state function ϕ of the observable A corresponding to the sharp value a_n. Let another observable B of the system on measurement yield the sharp value b_m. The above results mean

$$\langle A\rangle = \int \phi^* \hat{A} \phi d\tau = a_n \qquad \text{...(8)}$$

and

$$\langle B \rangle = \int \phi^* \hat{B} \phi d\tau = b_n \quad ...(9)$$

We may expand ϕ in terms of either the set of eigenfunctions $\{\psi_n\}$ of $\hat{A}$, or $\{\lambda_m\}$ of $\hat{B}$. We then obtain

$$\langle A \rangle = \sum_k |c_k|^2 a_k = a_n \quad ...(10)$$

and

$$|c_k|^2 = \delta_{kn} \quad ...(11)$$

Similarly, we get

$$\langle B \rangle = \sum_l |d_l|^2 b_l = b_m \quad ...(12)$$

and

$$|d_l|^2 = \delta_{ln} \quad ...(13)$$

Thus $$\phi = \psi_n = \lambda_m \quad ...(14)$$

and ϕ is simultaneously an eigenstate of both the observables A and B.

Let us consider a state of a system described by the wave function ϕ which is simultaneously an eigenstate of two operators $\hat{A}$ and $\hat{B}$.

Consider the two equations

$$\hat{A}\psi_n = a_n\psi_n \quad ...(15)$$

and

$$\hat{B}\lambda_m = b_m\lambda_m \quad ...(16)$$

Let us assume $\psi_n = \lambda_m = \phi_{nm}$, then

$$\hat{A}\phi_{nm} = a_n\phi_{nm} \quad ...(17)$$

$$\hat{B}\phi_{nm} = b_m\phi_{nm} \quad ...(18)$$

From Eq. (17) we obtain

$$\hat{B}\hat{A}\phi_{nm} = \hat{B}a_n\phi_{nm} = a_n\hat{B}\phi_{nm} = a_nb_m\phi_{nm} \quad ...(19)$$

From Eq. (18) we similarly obtain

$$\hat{A}\hat{B}\phi_{nm} = \hat{A}b_m\phi_{nm} = b_m\hat{A}\phi_{nm} = b_ma_n\phi_{nm} \quad ...(20)$$

Equations (19) and (20) yield

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\phi_{nm} = 0 \quad ...(21)$$

Equation (21) shows that if a system be in a state which is an eigenstate of $\hat{A}$ belonging to an eigenvalue a_n and simultaneously is an eigenstate of $\hat{B}$ belonging to some eigenvalue b_n, then the operators $\hat{A}$ and $\hat{B}$ necessarily commute with each other. Conversely, if two operators corresponding to two observables of a system commute then the eigenstates of $\hat{A}$ are simultaneously the eigenstates of $\hat{B}$.

The above considerations establish the criterion for the probability of performing compatible measurements. If a certain preparation method provides the system in a state such that the observable A exhibits a sharp value, say a_n, it may happen that a series of measurement of the observable B yield a series of results, say $b_1, b_2, \dots b_i, \dots$ with appropriate frequencies $|C_{n\lambda}|^2$. However, if $\hat{A}$ and $\hat{B}$ commute, it is possible to vary the preparation method in order to prepare the system in a state such that A still exhibits the sharp value a_n and for which B also exhibits sharp value, say, b_m. Thus, if $\hat{A}$ and $\hat{B}$ commute, the scatter in the measurements of the observable B with system in any state is independent of the scatter in the measurement of the observable A, **and measurement of *A* is said to be compatible with that of *B*.**

On the other hand, if $\hat{A}$ and $\hat{B}$ do not commute, the above result is no longer true. A state in which the observable A exhibits a sharp value is one for which the scatter in the measured value of B is so great that no definite knowledge of B can be obtained. If one attempts to prepare the system in states for which the scatter in the measured value of B is finite, the states detained are necessarily such that a non-zero scatter in the measured value of A also results. Thus, if $\hat{A}$ and $\hat{B}$ do not commute, it is impossible to prepare the system in states for which $\hat{A}$ and $\hat{B}$ together exhibit sharp values. The measurements of A and B are then said to be **incompatible**. In the next section incompatible measurement is discussed in greater detail.

3.5 GENERAL UNCERTAINTY RELATION: INCOMPATIBLE MEASUREMENT

For any quantum mechanical system, it is possible to prepare states such that two observables simultaneously exhibit sharp values. This important result will be derived in the section to follow as a special case of a general uncertainty relation which relates the scatter in the results of measurement of two observables to the commutation properties of the operators corresponding to the observables.

At the outset, however, it becomes necessary to establish some precise quantitative definition for the scatter (spread or uncertainty) of measured values of an observable.

3.5.1 Definition of Uncertainty in Measured Value of an Observable

Consider a system prepared in an arbitrary state described by the wave function ϕ. The results of measurements of an observable, say f, can be represented by means of a table giving the results f_n and their relative frequencies of occurrence ω_n with

$$\sum \omega_n = 1 \qquad \text{...(22)}$$

The mean or the expectation value of observable $\langle f \rangle$ is then given by

$$\langle f \rangle = \sum_n \omega_n f_n \qquad \text{...(23)}$$

Let us then consider the set of numbers $(f_n - \langle f \rangle)$. These numbers are called *deviation* of the measured values from the average value. Some of these numbers are found to be positive, some negative and some zero. The average of these numbers is, however, zero provided the number of measurements made is very large. However, the number $(f_n - \langle f \rangle)^2$ representing the squares of deviation in individual measurement are all positive and as such their average, i.e., the number $\langle (f_n - \langle f \rangle)^2 \rangle$ is not zero.

If $\langle f \rangle$ is approximately equal to say f_k, then the larger the difference $|f_n - f_k|$, the greater becomes the magnitude of $(f_n - \langle f \rangle)^2$. If ω_n now represents a fairly sharp distribution, i.e., if $\omega_n \cong 1$ for $n = k$ and $\omega_n \cong 0$ for $n \neq k$ there will be few terms in the sum

$$(\delta f)^2 \equiv \sum_n \omega_n (f_n - \langle f \rangle)^2 \qquad \text{...(24)}$$

which are sensibly different from zero. Further each of the non-zero terms will be small since $(f_n - \langle f \rangle)^2$ is small for the contributing terms in the above sum. Thus $(\delta f)^2$ is small for a sharply peaked function. Similarly, if the distribution of ω_n over n is broad, or diffuse, there will be many terms ω_n which are nearly equal and of the order ω_k, where

$$\langle f \rangle \cong f_k \qquad \text{...(25)}$$

for the distribution. In this case, many terms will contribute to $(\delta f)^2$, all with approximately equal weight ω_n. For $n \cong k$, the factors $(f_n - \langle f \rangle)^2$ will be small and the terms $\{\omega_n (f_n - \langle f \rangle)^2\}$ contribute little to the sum $(\delta f)^2$. However, for n much different from $k\,(f_n - \langle f \rangle)^2$ can become large. The magnitude of $(\delta f)^2$ then becomes correspondingly large. Thus $(\delta f)^2$ is small for a sharp distribution and large for broad or diffuse distribution. In particular, if the state ϕ considered is an eigenstate of f belonging to the eigenvalue f_k, $\langle f \rangle$ is identically equal to f_k with $\omega_n = \delta_{nk}$. Then

$$(\delta f)^2 \equiv \sum_n \delta_{nk} (f_n - f_k)^2 \qquad \text{...(26)}$$

and $(\delta f)^2$ vanishes identically. For the above reasons the number $(\delta f)^2$ introduced above is defined as the statistical dispersion of the series of measurements. Its square root

$$\Delta f = \sqrt{(\delta f)^2} \qquad \text{...(27)}$$

is hence called the standard deviation of the series of measurements. The Δf defined above is taken as the measure of scatter in the results of a measurement of the observable f and will be considered to define **the uncertainty in the observable for the system in the given state under consideration.**

3.5.2 Derivation of the Uncertainty Relation

Let us consider two physical quantities f and g of a quantum system. Let $\hat{f}$ and $\hat{g}$ be the corresponding operators.

Let the system be prepared in a state described by the wave function ϕ.

By definition, the uncertainties in the measured values of f and g are

$$\Delta f = [\langle(f - \langle f\rangle)^2\rangle]^{\frac{1}{2}} \qquad ...(28)$$

$$\Delta g = [\langle(g - \langle g\rangle)^2\rangle]^{\frac{1}{2}} \qquad ...(29)$$

Equation (28) gives

$$(\Delta f)^2 = \langle(f - \langle f\rangle)^2\rangle$$

or $$(\Delta f)^2 = \int \phi^* (\hat{f} - \langle f\rangle \hat{I})^2 \phi d\tau,$$

$\hat{I}$ is a unit operator

or $$(\Delta f)^2 = \int \phi^* (\hat{f} - \langle f\rangle \hat{I})(\hat{f} - \langle f\rangle \hat{I})\phi d\tau \qquad ...(30)$$

Assuming the quantity f to be real, $\hat{f}$ is Hermitian. The unit operator $\hat{I}$ is always Hermitian. Hence, Eq. (30) may be rewritten as

$$(\Delta f)^2 = \int (\hat{f} - \langle f\rangle \hat{I})^* \phi^* (\hat{f} - \langle f\rangle \hat{I})\phi d\tau$$

or $$(\Delta f)^2 = \int \left|(\hat{f} - \langle f\rangle \hat{I})\phi\right|^2 d\tau \qquad ...(31)$$

Similarly, considering the quantity g to be real, we get

$$(\Delta g)^2 = \int \left|(\hat{g} - \langle g\rangle \hat{I})\phi\right|^2 d\tau \qquad ...(32)$$

From Eqs. (31) and (32) we obtain

$$(\Delta f)^2 (\Delta g)^2 = \int \left|(\hat{f} - \langle f\rangle \hat{I})\phi\right|^2 d\tau \int \left|(\hat{g} - \langle g\rangle \hat{I})\phi\right|^2 d\tau \qquad ...(33)$$

Let us now abbreviate

$$(\hat{f} - \langle f\rangle)\phi \text{ as } u \quad \text{and} \quad (\hat{g} - \langle g\rangle)\phi \text{ as } v \qquad ...(34)$$

Equation (33) then can be written as

$$(\Delta f)^2 (\Delta g)^2 = \left\{\int u^* u d\tau\right\} \left\{\int v^* v d\tau\right\} \qquad ...(35)$$

Now, consider that if η is a real number

$$\int (\eta u^* - iv^*)(\eta u + iv) d\tau > 0 \qquad ...(36)$$

in general, whence we obtain

$$\eta^2 \int u^* u d\tau + i\eta \int (u^* v - uv^*) d\tau + \int v^* v dt > 0 \qquad ...(37)$$

The above equation is a quardratic form in the real variable η of the type

$$f(\eta) = a\eta^2 + b\eta + c > 0 \qquad ...(38)$$

If η be complex, there exist no real roots of the Eq. (38).

However, there may be real roots if

$$b^2 < 4ac$$

We then obtain from Eq. (37)

$$\left\{\int u^* u d\tau\right\}\left\{\int v^* v d\tau\right\} \geq \frac{1}{4}\left|\int (u^* v - uv^*) d\tau\right|^2 \qquad ...(39)$$

Using the definitions of u and v given by Eq. (34), we obtain from Eq. (39)

$$(\Delta f)^2\,(\Delta g)^2 \geq \frac{1}{4}\left|\int (\hat{f}\hat{g} - \hat{g}\hat{f})\phi d\tau\right|^2 \qquad ...(40)$$

For any two arbitrary and in general complex functions u and v defined in the same domain, the following inequality called **Schwartz inequality** holds

$$\left\{\int |u|^2\, d\tau\right\}\left\{\int |v|^2\, d\tau\right\} \geq \left|\int u^* v d\tau\right|^2 \qquad ...(41)$$

In the above, the integration is carried over the entire domain of definition.

Abbreviating as

$$(\hat{f} - \langle f \rangle \hat{I})\phi = u \quad \text{and} \quad (\hat{g} - \langle g \rangle \hat{I})\phi = v \qquad ...(42)$$

and using the inequality given by Eq. (41), we obtain from Eq. (33)

$$(\Delta f)^2\,(\Delta g)^2 \geq \left|\int (\hat{f} - \langle f \rangle \hat{I})\phi^* (\hat{g} - \langle g \rangle \hat{I})\phi d\tau\right|^2 \qquad ...(43)$$

Since $\hat{f}$ and $\hat{I}$ are Hermitian operators, we may rewrite Eq. (43) as

$$(\Delta f)^2\,(\Delta g)^2 \geq \left|\int \phi^* (\hat{f} - \langle f \rangle \hat{I})\,(\hat{g} - \langle g \rangle \hat{I})\phi d\tau\right|^2 \qquad ...(44)$$

For convenience, let us define Hermitian operators $\hat{\alpha}$ and $\hat{\beta}$ as

$$(\hat{f} - \langle f \rangle \hat{I}) = \hat{\alpha} \qquad ...(45)$$

$$(\hat{g} - \langle g \rangle \hat{I}) = \hat{\beta} \qquad ...(46)$$

Using Eqs. (45) and (46) in Eq. (44), we obtain

$$(\Delta f)^2\ (\Delta g)^2 \geq \left| \int \phi^* \hat{\alpha}\hat{\beta}\phi d\tau \right|^2$$

or $$(\Delta f)^2\ (\Delta g)^2 \geq \left| \int \phi^* \frac{1}{2}(\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})\phi d\tau + \int \phi^* \frac{1}{2}(\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \right|^2$$

or $$(\Delta f)^2\ (\Delta g)^2 \geq \left[\int \phi^* \frac{1}{2}(\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})\phi d\tau + \int \phi^* \frac{1}{2}(\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \right]$$

$$\times \left[\int \phi^* \frac{1}{2}(\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})\phi d\tau + \int \phi^* \frac{1}{2}(\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \right]$$

$$\geq \frac{1}{4}\left| \int \phi^* (\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})\phi d\tau \right|^2 + \frac{1}{2}\left| \int \phi^* (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \right|^2 \qquad ...(47)$$

$$+ \frac{1}{4}\left[\{ \int \phi^* (\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})\phi d\tau \}^* \{ \int \phi^* (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \} \right]$$

$$+ \frac{1}{4}\left[\{ \int \phi^* (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \}^* \{ \int \phi^* (\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha})\phi d\tau \} \right]$$

Using the Hermiticity properties of $\hat{\alpha}$ and $\hat{\beta}$, we get

$$\left[\int \phi^* \hat{\alpha}\hat{\beta}\phi d\tau \right]^* = \left[\int \hat{\alpha}^* \phi^* \hat{\beta}\phi d\tau \right]^* = \left[\int \hat{\alpha}\phi \hat{\beta}^* \phi^* d\tau \right] = \int \phi^* \hat{\beta}\hat{\alpha}\phi d\tau \qquad ...(48)$$

Similarly, we have

$$\left[\int \phi^* \hat{\beta}\hat{\alpha}\phi d\tau \right]^* = \left[\int \hat{\beta}\phi^* \hat{\alpha}\phi d\tau \right]^* = \left[\int \hat{\beta}\phi^* \hat{\alpha}^* \phi^* \right] = \int \phi^* \hat{\alpha}\hat{\beta}\phi d\tau \qquad ...(49)$$

Using Eqs. (48) and (49) in Eq. (47) we obtain

$$(\Delta f)^2\ (\Delta g) \geq \frac{1}{4}\left| \int \phi^* (\hat{\alpha}\hat{\beta} + \hat{\alpha}\hat{\beta})\phi d\tau \right|^2 + \frac{1}{4}\left| \int \phi^* (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \right|^2 \qquad ...(50)$$

Whithout any loss of generality it is possible to consider $\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha} = 0$, whence Eq. (50) gives

$$(\Delta f)^2\ (\Delta g)^2 \geq \frac{1}{4}\left| \int \phi^* (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\phi d\tau \right|^2 \qquad ...(51)$$

From Eqs. (45) and (46), we get

$$\begin{aligned} \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha} &= (\hat{f} - \langle f \rangle \hat{I})\ (\hat{g} - \langle g \rangle \hat{I}) - (\hat{g} - \langle g \rangle \hat{I})\ (\hat{f} - \langle f \rangle \hat{I}) \\ &= \hat{f}\hat{g} - \hat{g}\hat{f} \qquad ...(52) \end{aligned}$$

Equation (52) used in Eq. (51) gives

$$(\Delta f)^2\,(\Delta g)^2 \geq \frac{1}{4}\left|\int \phi^*(\hat{f}\hat{g} - \hat{g}\hat{f})\phi d\tau\right|^2$$

or $$(\Delta f)\,(\Delta g) \geq \frac{1}{2}\left\{\left|\int \phi^*(\hat{f}\hat{g} - \hat{g}\hat{f})\phi d\tau\right|^2\right\}^{\frac{1}{2}}$$

or $$(\Delta f)\,(\Delta g) \geq \frac{1}{2}\left\langle(\hat{f}\hat{g} - \hat{g}\hat{f})\right\rangle \qquad ...(53)$$

Equation (53) is the general uncertainty relation between two physical quantities under simultaneous measurement.

3.5.3 Discussions

(i) Equation (53) tells us that if the quantities f and g be such that the corresponding operators commute with each other, then

$$(\Delta f)\,(\Delta g) \geq 0$$

which ensures both $\Delta f = 0$ and $\Delta g = 0$ to be together possible. In other words, the two quantities can be measured simultaneously with unlimited accuracy, i.e., the measurement is compatible.

(ii) Equation (53) further tells us that if $\hat{f}$ and $\hat{g}$ do not commute then the product of the uncertainties in a simultaneous measurement of f and g is greater than or equal to half the expectation value of the operator corresponding to their commutator $[\hat{f}, \hat{g}]$.

We thus observe that the measurements of two observables in a given state of a quantum system, whose operators do not commute, are incompatible.

(iii) Whether or not the equality or inequality holds in Eq. (53) depends on the state of the system in which measurements are made. The minimum value of $(\Delta f)\,(\Delta g)$ occurs evidently in such states for which equality holds in Eq. (53). The wave function describing such states is referred to as the minimum uncertainty wave packet.

Heisenberg's uncertainty relations can be seen to follow from the general uncertainty relation obtained above.

Position–Momentum Uncertainty Relation

Let us replace the quantity f by the coordinate x and the quantity g by the x-component of linear momentum p_x of a particle. The operators corresponding to x and p_x are

$$\hat{x} = x$$

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

Let $\psi(x)$ be an arbitrary function of x. We then get

$$(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi(x) = -xi\hbar \frac{\partial\psi(x)}{\partial x} + xi\hbar \frac{\partial\psi(x)}{\partial x} + i\hbar\psi(x)$$

or
$$(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi(x) = i\hbar\psi(x)$$

The above gives

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

Clearly,
$$\langle(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\rangle = \hbar$$

Hence, we obtain according to Eq. (53)

$$\Delta x\Delta p_x \geq \frac{\hbar}{2}$$

Time–Energy Uncertainty Relation

Let us replace f by energy E and replace g by time t. The operators corresponding to E and t are

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

and

$$\hat{t} = t$$

Consider any arbitrary function ϕ of variable t. We then get

$$\begin{aligned}(\hat{E}\hat{t} - \hat{t}\hat{E})\phi &= i\hbar \frac{\partial}{\partial t}(t\phi) - i\hbar t \frac{\partial\phi}{\partial t} \\ &= i\hbar t \frac{\partial}{\partial t} + i\hbar\phi - i\hbar t \frac{\partial\phi}{\partial t} \\ &= i\hbar\phi\end{aligned}$$

We thus have
$$(\hat{E}\hat{t} - \hat{t}\hat{E}) = i\hbar$$

Clearly,
$$\langle(\hat{E}\hat{t} - \hat{t}\hat{E})\rangle = \langle i\hbar\rangle = \hbar$$

Hence, according to the general uncertainty relation (Eq. 53), we get

$$\Delta E\Delta t \geq \frac{\hbar}{2}$$

4

Wave Mechanics of Schrödinger

4.1 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 form 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.

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 (ν), a wavelength (λ) and the phase velocity (v_p) related according to

$$v_p = \nu\lambda \ (= \omega/k) \qquad ...(1)$$

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

$$E = E_0 \sin(\omega t - kx)$$

$$B = B_0 \sin(\omega t - kx) \qquad ...(2)$$

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

$$\psi(x, t) = Ae^{i(kx - \omega t)} \qquad ...(3)$$

where A is the constant amplitude,

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p_x}{h} = \frac{p_x}{\hbar} \qquad ...(4)$$

and

$$\omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar} \qquad ...(5)$$

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

$$\omega = \frac{mc^2}{\hbar} \qquad ...(6)$$

The velocity u of the de-Broglie wave is thus

$$u = \nu\lambda = \frac{\omega}{2\pi}\frac{h}{mv} = \frac{mc^2}{\hbar} \times \frac{\hbar}{mv} = \frac{c^2}{v} \qquad ...(7)$$

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.*

4.2 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 Fig. 4.1.

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.

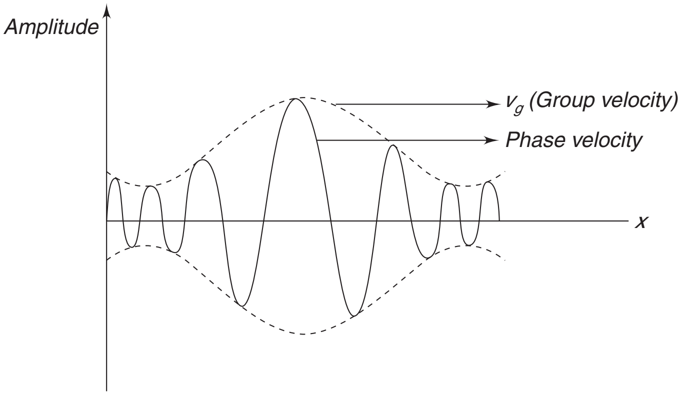


Fig. 4.1

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

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k)\, e^{i[kx - \omega t]}\, dk \qquad \text{...(8)}$$

where $\phi(k)$ is the amplitude and the frequency ω is a function of k

$$\omega = \omega(k) \qquad \text{...(9)}$$

4.2.1 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 Δk given by

$$\left(k_0 - \frac{\Delta k}{2}\right) < k < \left(k_0 + \frac{\Delta k}{2}\right), \Delta k << k_0 \qquad \text{...(10)}$$

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

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

or

$$\omega(k) = \omega_0 + (k - k_0)\, \frac{d\omega}{dk} \qquad \text{...(11)}$$

where we have written

$$\omega(k_0) = \omega_0 \qquad \text{...(12)}$$

and

$$\left(\frac{d\omega}{dk}\right)_{k=k_0} = \frac{d\omega}{dk} \qquad \text{...(13)}$$

We then obtain

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

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k)\, e^{ikx - ik_0x + ik_0x - i\omega_0 t - i(k-k_0)\frac{d\omega}{dk}t}\, dk$$

$$= \frac{1}{\sqrt{2\pi}} \int_{k_0 - \frac{\Delta k}{2}}^{k_0 + \frac{\Delta k}{2}} \phi(k)\, e^{i(k_0x - \omega_0 t)}\, e^{i(k-k_0)x - i(k-k_0)\frac{d\omega}{dk}t}\, dk$$

or $$\psi(x, t) = e^{i(k_0 x - \omega_0 t)} F(x, t) \qquad ...(14)$$

where $$F(x, t) = \frac{1}{\sqrt{2\pi}} \int \phi(k)\, e^{i(k-k_0)\left[x - \frac{d\omega}{dk} t\right]} dk \qquad ...(15)$$

$\psi(x, t)$ given by eq. (14) which represents the wave packet is a plane wave having propagation constant k_0, angular frequency ω_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

$$v_g = \frac{d\omega}{dk} \qquad ...(16)$$

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.

4.2.2 Equality of Group Velocity and Particle Velocity

The group velocity is given by

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

or $$v_g = \frac{d\omega}{dp} \frac{dp}{dk} \qquad ...(17)$$

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

$$\omega = \frac{E}{\hbar} \quad \text{and} \quad \frac{dp}{dk} = \hbar \qquad ...(18)$$

so that v_g becomes

$$v_g = \frac{d}{dp}\left(\frac{E}{\hbar}\right)\hbar = \frac{dE}{dp} \qquad ...(19)$$

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

$$E = \frac{p^2}{2m} \qquad ...(20)$$

so that $$\frac{dE}{dp} = \frac{p}{m} = v \qquad ...(21)$$

We find form Eqs. (19) and (21)

$$v_g = v \qquad \text{...(22)}$$

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

$$E^2 = m_0^2 c^4 + c^2 p^2 \qquad \text{...(23)}$$

On differentiation with respect to p, the above gives

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

or

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

or

$$\frac{dE}{dp} = v \qquad \text{...(24)}$$

In view of Eqs. (19) and (24) we find that the wave packets corresponding to both relativistic as well as non-relativistic particles have group velocity equal to particle velocity.

4.3 THEORY OF SCHRÖDINGER EQUATION

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 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.

Inspite 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.

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

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

$$\lambda = \frac{h}{p_x} \qquad \text{...(25)}$$

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

$$k = \frac{2\pi}{\lambda} \qquad \text{...(26)}$$

From the above two equations, we get

$$p_x = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k \qquad \text{...(27)}$$

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

$$E = \hbar\omega \qquad \text{...(28)}$$

Further, we have

$$E = \frac{px^2}{2m} \qquad \text{...(29)}$$

so that Eqs. (27), (28) and (29) yield

$$\omega = \frac{E}{\hbar} = \frac{p_x^2}{\hbar 2m} = \frac{\hbar^2 k^2}{\hbar 2m} = \frac{\hbar k^2}{2m} \qquad \text{...(30)}$$

The wave function $\psi(x, t)$ which describes the free particle localized in the region of the x-axis [refer to Eq. (8)] is given by

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k)\, e^{i(kx-\omega t)}\, dk \qquad \text{...(31)}$$

Using ω given by Eq. (30), the above becomes

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m}t\right]}\, dk \qquad \text{...(32)}$$

Differentiating Eq. (32) with respect to time t, we get

$$\frac{\partial\psi(x, t)}{\partial t} = \frac{-i\hbar}{2m}\int k^2 A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m}t\right]}\, dk \qquad \text{...(33)}$$

Further, differentiation of Eq. (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

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = -\int_{-\alpha}^{+\alpha} k^2 A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk \qquad \text{...(34)}$$

Multiplying Eq. (33) by $i\hbar$ we obtain

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{\hbar^2}{2m} \int_{-\alpha}^{+\alpha} k^2 A(k)\, e^{i\left[kx - \frac{\hbar k^2}{2m} t\right]} dk \qquad \text{...(35)}$$

In view of Eqs. (34) and (35) we obtain

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial t^2} \qquad \text{...(36)}$$

Equation (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 (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 eq. (8), whence we get

$$\psi(\vec{r}, t) = \iiint A(k)\, e^{i\left[\vec{k}\cdot\vec{r} - \frac{\hbar k^2}{2m} t\right]} dk_x\, dk_y\, dk_z$$

$$= \iiint A(k)\, e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x\, dk_y\, dk_z \qquad \text{...(37)}$$

Differentiating Eq. (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

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = \frac{\hbar^2}{2m} \iiint k^2 A(k)\, e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2)t\right]} dk_x\, dk_y\, dk_z \qquad \text{...(38)}$$

Differentiating Eq. (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

$$\frac{\partial^2\psi(\vec{r},t)}{\partial x^2} = -\iiint k_x^2\, A(k)\, e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2+k_y^2+k_z^2)t\right]} dk_x\, dk_y\, dk_z \qquad \text{...(39)}$$

We similarly obtain

$$\frac{\partial^2\psi(\vec{r},t)}{\partial y^2} = -\iiint k_y^2\, A(k)\, e^{i\left[k_x x + k_y y k_z z - \frac{\hbar}{2m}(k_x^2+k_y^2+k_z^2)t\right]} dk_x\, dk_y\, dk_z \qquad \text{...(40)}$$

and

$$\frac{\partial^2\psi(\vec{r},t)}{\partial z^2} = -\iiint k_z^2\, A(k)\, e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2+k_y^2+k_z^2)t\right]} dk_x\, dk_y\, dk_z \qquad \text{...(41)}$$

Adding Eqs. (39), (40) and (41), we get

$$\nabla^2\psi(r,\, t) = -\iiint k^2\, A(k)\, e^{i\left[k_x x + k_y y + k_z z - \frac{\hbar}{2m}(k_x^2+k_y^2+k_z^2)t\right]} dk_x\, dk_y\, dk_z \qquad \text{...(42)}$$

Equations (38) and (42) give

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) \qquad \text{...(43)}$$

Equation (43) is the three-dimensional time-dependent Schrödinger equation for a free particle described by the wavefunction $\psi(\vec{r},\, t)$. Equations (36) and (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*.

4.5 OPERATORS CORRESPONDING TO ENERGY AND LINEAR MOMENTUM

It is possible to write the one-dimensional Schrödinger equation for a free particle given by Eq. (36) as

$$\left(i\hbar\frac{\partial}{\partial t}\right)\psi(x,t) = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t) \qquad \text{...(44)}$$

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

$$E = \frac{1}{2m}p_x^2 = \frac{1}{2m}(p_x)(p_x) \qquad \text{...(45)}$$

Comparison of Eqs. (44) and (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

$$(E)_{op} = \hat{E} \rightarrow i\hbar\frac{\partial}{\partial t} \qquad \text{...(46)}$$

and

$$(p_x)_{op} = \hat{p}_x \rightarrow -i\hbar\frac{\partial}{\partial x} \qquad \text{...(47)}$$

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

$$\left.\begin{aligned} \hat{p}_x &\rightarrow -i\hbar\frac{\partial}{\partial x} \\ \hat{p}_y &\rightarrow -i\hbar\frac{\partial}{\partial y} \\ \hat{p}_z &\rightarrow -i\hbar\frac{\partial}{\partial z} \end{aligned}\right\} \qquad \text{...(48)}$$

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.

$$\hat{\vec{p}} \rightarrow -i\hbar\vec{\nabla} \qquad \text{...(49)}$$

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

4.6 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

$$E = \frac{p^2}{2m} + V(\vec{r}, t) \qquad \text{...(50)}$$

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

$$\hat{\vec{r}} = \vec{r} \qquad \text{...(51)}$$

and

$$\hat{t} = t \qquad \text{...(52)}$$

Replacing E, p, r and t by their respective operators given by Eqs. (46), (49), (50) and (51) in Eq. (50) we obtain

$$i\hbar \frac{\partial}{\partial t} \to -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \qquad ...(53)$$

Allowing the operator Eq. (53) to operate on the wave function $\psi(\vec{r}, t)$ describing the state of the particle, we get

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t)\right] \psi(\vec{r}, t) \qquad ...(54)$$

Equation (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 Hamiltonion of the particle. It is usual to denote this operator as $\hat{H}$ so that the Schrödinger Eq. (54) can be written in its usual form as

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \hat{H}\, \psi(\vec{r}, t) \qquad ...(55)$$

4.7 TIME-INDEPENDENT SCHRÖDINGER EQUATION

Consider a particle of mans 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 in the wave velocity of the de-Broglie wave. The above equation can also be written as

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

or

$$\nabla^2 \psi(\vec{r}, t) = \frac{1}{u^2} \frac{\partial^2 \psi(\vec{r}, t)}{\partial t^2} \qquad ...(56)$$

The solution of Eq. (56) in its most general form is given by

$$\psi(\vec{r}, t) = \psi(\vec{r})\, e^{-i\omega t} \qquad ...(57)$$

where

$$\omega = 2\pi\nu \qquad ...(58)$$

ν 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 Eq. (57) an differentiation with respect to time t

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

Differentiating the above equation with respect to time t we get

$$\frac{\partial^2\psi(\vec{r},t)}{\partial t^2} = -\omega^2\,\psi(\vec{r})\,e^{-i\omega t} \qquad \text{...(59)}$$

Using Eq. (59) in Eq. (56) we get

$$\nabla^2\psi(\vec{r},t) = -\frac{\omega^2}{u^2}\,\psi(\vec{r},t) \qquad \text{...(60)}$$

We have

$$\omega = 2\pi\nu = 2\pi\,\frac{u}{\lambda} \qquad \text{...(61)}$$

where λ is the wavelength of the de-Broglie wave. Equation (61) gives

$$\frac{\omega}{u} = \frac{2\pi}{\lambda} \qquad \text{...(62)}$$

Use of Eq. (62) in Eq. (60) gives

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

or

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

or

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

or

$$\nabla^2\psi(\vec{r}) + \frac{4\pi^2}{\lambda^2}\,\psi(\vec{r}) = 0 \qquad \text{...(63)}$$

It v the velocity of the particle, we have

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

Substituting the above in Eq. (63) we obtain

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

or

$$\nabla^2\psi(r) + \frac{m^2v^2}{\hbar^2}\,\psi(\vec{r}) = 0 \qquad \text{...(64)}$$

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

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

so that

$$m^2v^2 = 2m\,(E - V) \qquad \text{...(65)}$$

Substituting Eq. (65) in Eq. (64) we obtain

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}(E - V)\,\psi(\vec{r}) = 0 \qquad \text{...(66)}$$

Equation (66) 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.

For a freely moving particle in space, $V = 0$, so that Eq. (66) reduces to

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}E\,\psi(\vec{r}) = 0 \qquad \text{...(67)}$$

For one-dimensional motion localized in the region along the x-axis, Eq. (66) gives

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\,\psi(x) = 0 \qquad \text{...(68)}$$

4.8 PHYSICAL INTERPRETATION OF WAVE FUNCTION

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

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

$$= |\psi(\vec{r}, t)|^2\, d^3(\vec{r}) \qquad \text{...(69)}$$

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 is a complex valued function of position and time which satisfies the linear Schrödinger equation [Eq. (36) in one dimension and Eq. (43) 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 θ is an arbitrary real constant. The probability distribution defined by ψ and ψ' 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 ψ and ψ' 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.

4.9 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.,

$$P = 1$$

or

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

or

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

or

$$\int |\psi(\vec{r}, t)|^2\, d^3(\vec{r}) = 1 \qquad \text{....(70)}$$

The wave functions which satisfy Eq. (70) are called normalized wavefunctions. Equation (70) is usually referred to as the normalization integral.

Normalization of wavefunction can be understood from the following:

The Schrödinger equation given by Eq. (43) is linear and homogeneous in the wavefunction $\psi(\vec{r}, t)$ and its derivatives. Hence, if the solution of Eq. (43) 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

$$\int |\psi'(\vec{r},t)|^2\, d^3(\vec{r}) = N^2 \qquad ...(71)$$

The number N^2 is called the norm of the wavefunction $\psi'(\vec{r}, t)$.

Let us define

$$\psi(\vec{r}, t) = \frac{1}{N}\, \psi'(\vec{r}, t) \qquad ...(72)$$

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.

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 Eq. (71), the above gives

$$\int |\psi(\vec{r},t)|^2\, d^3(\vec{r}) = 1 \qquad ...(73)$$

The wave function $\psi(\vec{r}, t)$ satisfies Eq. (70) and is hence a normalized wavefunction. Comparing Eq. (73) with Eq. (71) 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 Eq. (72), 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 Eq. (71)

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

or

$$\psi'(\vec{r}, t) \to 0 \quad \text{as} \quad r \to \pm\infty \qquad ...(74)$$

Equation (74) is the boundary condition that must be satisfied by normalizable wavefunctions.

4.10 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

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t) \qquad ...(75)$$

Taking complex conjugate of Eq. (75) we get

$$-i\hbar \frac{\partial \psi^*(\vec{r},t)}{\partial t} = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi^*(\vec{r},t) \qquad ...(76)$$

Multiplying Eq. (75) by $\psi^*(\vec{r}, t)$ from the left, and Eq. (76) by $\psi(\vec{r}, t)$ from the left and subtracting we obtain

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

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

or $$\frac{\partial}{\partial t}[\psi^*\psi]=\frac{i\hbar}{2m}[\psi^*\nabla^2\psi-\psi\nabla^2\psi^*] \qquad ...(77)$$

Writing the Laplacian operator ∇^2 in terms of derivatives we get according to Eq. (77),

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

or $$\frac{\partial}{\partial t}[\psi^*\psi]=-\frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\psi\frac{\partial\psi^*}{\partial x}-\psi^*\frac{\partial\psi}{\partial x}\right]-\frac{i\hbar}{2m}\frac{\partial}{\partial y}\left[\psi\frac{\partial\psi^*}{\partial y}-\psi^*\frac{\partial\psi}{\partial y}\right]$$
$$-\frac{i\hbar}{2m}\frac{\partial}{\partial z}\left[\psi\frac{\partial\psi^*}{\partial z}-\psi^*\frac{\partial\psi}{\partial z}\right] \qquad ...(78)$$

Let us define

$$J_x=\frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial x}-\psi^*\frac{\partial\psi}{\partial x}\right] \qquad ...(79)$$

$$J_y=\frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial y}-\psi^*\frac{\partial\psi}{\partial y}\right] \qquad ...(80)$$

$$J_z=\frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial z}-\psi^*\frac{\partial\psi}{\partial z}\right] \qquad ...(81)$$

Then using Eqs. (79), (80) and (81) in Eq. (78) we obtain

$$\frac{\partial}{\partial t}[\psi^*\psi]+\left[\frac{\partial J_x}{\partial x}+\frac{\partial J_y}{\partial y}+\frac{\partial J_z}{\partial z}\right]=0 \qquad ...(82)$$

Equation (82) can alternatively be expressed as

$$\frac{\partial}{\partial t}[\rho(\vec{r},t)]+\vec{\nabla}\cdot\vec{J}(\vec{r},t)=0 \qquad ...(83)$$

where
$$\vec{J}(\vec{r},t)=\frac{i\hbar}{2m}[\psi\vec{\nabla}\psi^{*}-\psi^{*}\vec{\nabla}\psi] \qquad ...(84)$$

$$\rho(\vec{r},\,t)=\psi^{*}\psi \qquad ...(85)$$

We have the well known equation of continuity in fluid dynamics

$$\frac{\partial\rho}{\partial t}+\vec{\nabla}\cdot\vec{J}=0 \qquad ...(86)$$

where

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

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

Comparing Eq. (83) with Eq. (86) 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

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

4.11 NORMALIZATION INTEGRAL, A CONSTANT OF MOTION

Integrating Eq. (77) over the entire volume of space we get

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

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

or
$$\frac{\partial}{\partial t}\int\psi^{*}\psi\, d^3(\vec{r})=\frac{i\hbar}{2m}\{\psi^{*}\vec{\nabla}\psi-\psi\vec{\nabla}\psi^{*}\}_{-\infty}^{+\infty} \qquad ...(87)$$

In most of the physical problems, the wave packet representing a particle is localized so that we get, (as seen earlier, Eq. (74))

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

Using the above result in Eq. (87) 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.

4.12 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

$$\langle\vec{r}\rangle = \int \vec{r}\psi^*\psi\, d^3(\vec{r}) = \int \psi^*\vec{r}\psi\, d^3(\vec{r}) \qquad ...(88)$$

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

$$\langle\vec{r}\rangle = \frac{\int \psi^*\vec{r}\psi\, d^3(\vec{r})}{\int \psi^*\psi\, d^3(\vec{r})} \qquad ...(89)$$

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

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

or

$$\langle f(\vec{r})\rangle = \int \psi^*(\vec{r}, t)\, f(\vec{r})\, \psi(\vec{r}, t)\, d^3(\vec{r}) \qquad ...(90)$$

4.12.1 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

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

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

$$\left\langle i\hbar \frac{\partial}{\partial t} \right\rangle = \left\langle \frac{-\hbar^2}{2m} \nabla^2 \right\rangle + \langle V(\vec{r},t) \rangle \qquad ...(91)$$

In view of Eq. (46) and Eq. (49), Eq. (91) gives

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle\,. \qquad ...(92)$$

Classically, the total energy is

$$E = \text{Kinetic energy} + \text{Potential energy}\ \frac{p^2}{2m} + V \qquad ...(93)$$

Equation (92) tells that the expectation value of the total energy is the sum of the expectation values of the kinetic energy and the potential energy.

4.12.2 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 $\hat{A}$ in the domain of definition of the wave function then the expectation values of A is

$$\langle A \rangle = \int \psi^*(\vec{r},t) \hat{A} \psi\,(\vec{r},t)\, d^3(\vec{r}) \qquad ...(94)$$

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

4.13 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

$$\frac{d}{dt}\langle x\rangle = \frac{l}{m}\langle p_x\rangle \qquad \text{...(95)}$$

$$\frac{d}{dt}\langle p_x\rangle = \left\langle -\frac{dV(x)}{dx}\right\rangle \qquad \text{...(96)}$$

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

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \hat{H}\psi(x,t) \qquad \text{...(97)}$$

4.13.1 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,

$$\langle x\rangle = \int_{-\infty}^{+\infty}\psi^*(x,t)\,x\psi(x,t)dx \qquad \text{...(98)}$$

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

$$\frac{d\langle x\rangle}{dt} = \frac{\partial}{\partial t}\int_{-\infty}^{+\infty}\psi^*(x,t)\,x\psi(x,t)dx \qquad \text{...(99)}$$

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

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x,t) \qquad \text{...(100)}$$

The above gives

$$\frac{\partial\psi(x,t)}{\partial t} = \frac{-i}{\hbar}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x,t) \qquad \text{...(101)}$$

Taking complex conjugate of Eq. (101), we get

$$\frac{\partial\psi^*(x,t)}{\partial t} = \frac{-i}{\hbar}\left[\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x,t) \qquad \text{...(102)}$$

Equation (99) gives

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

Using Eqs. (101) and (102) in the above, we get

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

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

Simplifying, we get

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\left[x\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2} - x\psi(x,t)\frac{\partial^2\psi^*(x,t)}{\partial x^2}\right]dx \qquad ...(103)$$

Let

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

Integrating by parts, we get

$$I = \left\{x\psi(x,t)\frac{\partial\psi^*(x,t)}{\partial x}\right\}_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\frac{\partial\psi^*(x,t)}{\partial x^{-\infty}}\frac{\partial}{\partial x}[x\psi(x,t)]dx \qquad ...(104)$$

For a localized wave packet we have the boundary conditions

$$\left.\begin{array}{ll}\psi(x,t)\to 0 & \text{as}\quad x\to\pm\infty\\ \dfrac{\partial\psi(x,t)}{\partial x}\ \text{and}\ \dfrac{\partial\psi^*(x,t)}{\partial x}\to 0 & \text{as}\ \ x\to\pm\infty\end{array}\right\} \qquad ...(105)$$

Use of conditions given by Eqs. (105) in Eq. (104), we obtain

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

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 Eqs. (105), the above becomes

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

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

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

or

$$I = \int_{-\infty}^{+\infty} \psi^*(x,t) \left[2\frac{\partial \psi(x,t)}{\partial x} + x\frac{\partial^2 \psi(x,t)}{\partial x^2}\right]dx \qquad ...(106)$$

Using Eq. (106) in Eq. (103) 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

$$\langle p_x\rangle = m\frac{d\langle x\rangle}{dt} \qquad ...(107)$$

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

$$\langle x\rangle = x \text{ and } \langle p_x\rangle = p_x \qquad ...(108)$$

so that Eq. (104) reduces to the classical definition

$$p_x = m\frac{dx}{dt} \qquad ...(109)$$

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

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

or

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

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

Substituting for $\frac{\partial\psi^*(x,t)}{\partial t}$ and $\frac{\partial\psi(x,t)}{\partial t}$ from Eqs. (102) and (101) in the above we obtain

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

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

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

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

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

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

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

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

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

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

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

Using the condition given by Eqs. (105) in the above we find the first term in the above equation to vanish to yield

$$\frac{d\langle p_x\rangle}{dt} = \left\langle\frac{-\partial V(x)}{\partial x}\right\rangle \qquad ...(110)$$

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

$$F_x = \frac{-\partial V}{\partial x} \qquad ...(111)$$

The above two equations give

$$\frac{d\langle p_x\rangle}{dt} = \langle F_x\rangle \qquad ...(112)$$

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 Eq. (112) in that case takes the form

$$F_x = \frac{dp_x}{dt} \qquad ...(113)$$

which is Newton's second law of motion

4.14 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 probality 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.

4.15 STATIONARY STATES

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

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

$$= \hat{H}\psi(\vec{r}, t) \qquad \text{...(114)}$$

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

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r},t)] \qquad \text{...(115)}$$

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 eq. (115), one in the separated form:

$$\psi(\vec{r},\, t) = \psi(\vec{r})T\,(t) \qquad \text{...(116)}$$

Substituting Eq. (116) in Eq. (115) we get

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

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

$$\frac{1}{T(t)}i\hbar\frac{dT(t)}{dt} = \frac{1}{\psi(\vec{r})}\left[\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})\right] \qquad \text{...(117)}$$

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) $\dfrac{i\hbar}{T(t)}\dfrac{dT(t)}{dt} = E$ or $i\hbar\dfrac{dT(t)}{dt} = ET(t)$ ...(118)

(b) $\dfrac{1}{\psi(\vec{r})}\left[\dfrac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r})\right] = E$ or $\left[\dfrac{-\hbar^2}{2m}\nabla^2\; V(\vec{r})\right]\psi(\vec{r}) = E\psi(r)$ ...(119)

Solution of Eq. (118) is given by

$$T(t) = e^{\frac{-i}{\hbar}Et} \qquad \text{...(120)}$$

Using Eq. (120) in Eq. (116) we may write the solution of the Schrödinger Eq. (115) as

$$\psi(\vec{r},\, t) = \psi(\vec{r})\,e^{\frac{-i}{\hbar}Et} \qquad \text{...(121)}$$

Equation (119) can be written as

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \qquad ...(122)$$

where
$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}) = \frac{\hat{p}^2}{2m} + V(\vec{r}) \qquad ...(123)$$

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 (122) is the energy eigenvalue equation and the constant is thus identified as the energy eigenvalue. In general, Eq. (122) has a complete set of solutions $\psi_n(\vec{r})$ such that

$$\hat{H}\psi_n(\vec{r}) = E_n\psi_n(\vec{r}) \qquad ...(124)$$

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

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{\frac{-i}{\hbar}E_n t} \qquad ...(125)$$

Equation (125) 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

$$\begin{aligned} P_n(\vec{r}, t) &= |\psi_n(\vec{r}, t)|^2 \\ &= \psi_n^*(\vec{r})e^{\frac{i}{\hbar}E_n t}\, \psi_n^*(\vec{r})e^{\frac{-i}{\hbar}E_n t} \\ &= |\psi_n(\vec{r})|^2 \end{aligned} \qquad ...(126)$$

We find that $P_n(\vec{r}, t)$ = constant in time. ...(127)

The states described by wavefunction such as $\psi_n(\vec{r}, t)$ given by eq.(125) for which the probability density is constant in time are called stationary or steady states of the system.

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

$$\begin{aligned} \langle A \rangle &= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}, t)\, \hat{A}\psi_n(\vec{r}, t) d^3(\vec{r}) \\ &= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r}, t)\, e^{\frac{iEn}{\hbar}t}\, \hat{A}\psi_n(\vec{r})\, e^{\frac{-iEn}{\hbar}t}\, d^3(\vec{r}) \\ &= \int_{-\infty}^{+\infty} \psi_n^*(\vec{r})\, \hat{A}\psi_n(r)\, d^3(\vec{r}) = \text{constant in time} \end{aligned} \qquad ...(128)$$

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

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

$$\frac{\partial P(\vec{r},t)}{\partial t} + \vec{\nabla}.\vec{J}(\vec{r},t) = 0 \qquad \text{...(129)}$$

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 Eq. (129), satisfies

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

or

$$\text{div } \vec{J}(\vec{r}, t) = 0 \qquad \text{...(130)}$$

4.15.1 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.

4.15. 2 Superposition States

As we have seen, the particular solutions of Eq. (115) are of the form

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{\frac{-iE_n}{\hbar}t} \qquad \text{...(131)}$$

The general solutions of Eq. (115) are of the form

$$\psi_n(\vec{r}, t) = \sum_n a_n\ \psi_n(\vec{r},t) = \sum a_n \psi_n(\vec{r}) e^{\frac{-iE_n}{\hbar}t} \qquad \text{...(132)}$$

where a_n are constants and, in particular, do not depend on time. The state of the system described by the wavefunction $\psi(\vec{r}, t)$ [eq. (132)] is called a superposition state.

The probability density corresponding to the superposition state is given by

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

$$= \sum_m \sum_n a_m^* a_n \psi^*_{\hat{m}}(\vec{r}) \psi_n(\vec{r}) e^{\frac{i(E_m - E_n)}{\hbar}t} \qquad \text{...(133)}$$

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

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

$$= \sum_m \sum_n a_m^* a_n\, e^{\frac{i(E_m - E_n)t}{\hbar}} \int \psi_m^*(\vec{r})\hat{A}\psi_n(\vec{r}) d^3(\vec{r}) \qquad \text{...(134)}$$

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

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

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

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

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

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

Hence, we obtain

$$\langle A \rangle = \sum |a_m|^2 A_m \qquad \text{...(135)}$$

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 $\hat{H}$, $(\hat{A})$ is time-dependent in general as indicated by Eq. (134).

4.16 SOLVED EXAMPLES

Example 1 The wavefunction of a particle is given by

$$\psi(x) = Ne^{-\alpha x^2}$$

Normalize the wavefunction if N and α are constants in the region $-\infty \leq x \leq +\infty$.

Solution: The wavefunction is normalized if

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

Using $\psi(x) = Ne^{-\alpha x^2}$ in the above we get

$$N^2 \int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx = 1$$

Using the standard integral

$$\int_{-\infty}^{+\infty} e^{-bu2} du = \sqrt{\frac{\pi}{b}}, \quad b = \text{a constant}$$

the above gives

$$N^2\sqrt{\frac{\pi}{2\alpha}} = 1$$

or
$$N^2 = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}}$$

or
$$N = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}}$$

The normalized wavefunction is thus

$$\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2}$$

Example 2 Based on the properties of wavefunction, explain whether $\psi = e^x$ is an acceptable quantum mechanical wavefunction or not.

Explanation: Probability interpretation of wavefunction ψ makes it necessary that ψ should satisfy some general conditions. The conditions must ensure that $|\psi|^2 d\tau$ have the properties of a probability. This requires (i) ψ should be finite at each point in space, (ii) ψ should be single valued at all points in space, (iii) ψ should be quadratically integrable, (iv) ψ and its partial derivatives with respect to positions be continuous throughout.

The given wavefunction is

$$\psi(x) = e^x$$

We find that as $x \to \pm \infty$, $\psi(x) \to \pm \infty$.

Furtte the total probability is

$$P = \int_{-\infty}^{+\infty} \psi^*(x)\psi(x)dx = \int_{-\infty}^{+\infty} e^{2x}dx$$

$$= \left\{\frac{e^{2x}}{2}\right\}_{-\infty}^{+\infty}$$

or
$$P = \infty$$

Thus the given function is neither finite for all value of x, nor it is quadratieally integrable. Hence the function e^x, does not repnsent an acceptable wavefunction.

Example 3 Is Schrödinger equation valid for relativistic particle? Explain your answer.

Explanation: Consider a free particle of mass m having momentum p and kinetic energy E moving along the x-axis. For non-relativistic particle ($v << c$) we have

$$p = mv \quad \text{and} \quad E = \frac{1}{2}mv^2$$

So that the energy-momentum relation is $E = \dfrac{p^2}{2m}$. The Hamiltonian of the particle is $H = \dfrac{p^2}{2m}$.

The Schrödinger equation obtained from the above Hamiltonian is

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial t^2} \qquad \text{...(i)}$$

$\psi(x, t)$ being the wavefunction that describes the state of the particle.

If the particle travels at a speed close to that of light i.e., if the particle is a relativistic particle, the Hamiltonian is no longer given by $\dfrac{p^2}{2m}$. Hence the Schrödinger equation given by Eq. (i) is not applicable to relativistic particles.

We may try to obtain wave equation for a relativistic particle by considering the Hamiltonian which is represented by the energy E to be given by

$$H \equiv E = [c^2p^2 + m^2c^4]^{1/2} \qquad \text{...(ii)}$$

Using the operator corresponding to E and p namely

$$E \to i\hbar\frac{\partial}{\partial t}, \qquad p \to -i\hbar\vec{\nabla}$$

We obtain the wave equation

$$i\hbar\frac{\partial\psi}{\partial t} = [-\hbar^2c^2\nabla^2 + m^2c^4]\psi \qquad \text{...(iii)}$$

In the above the meaning of the operator $[-\hbar^2c^2\nabla^2 + m^2c^4]^{1/2}$ is not clear. Further, in relativity theory, space and time play quite symmetric roles but in the above equation space and time differential appear in very different ways.

Example 4 For a one-dimensional bound particle described by the wavefunction $\psi(x, t)$, show that

(a) $\dfrac{d}{dt}\displaystyle\int_{-\infty}^{+\infty} \psi^*(x,t)\psi(x,t)dx = 0$

(b) If the particle is in a stationary state at a given time, then it will remain in the stationary state at all times.

Solution: (a) $\psi(x, t)$ satisfies the Schrödinger equation

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}+V(x)\psi(x,t) \qquad \text{...(i)}$$

Taking complex conjugate of Eq. (i), we get

$$-i\hbar\frac{\partial\psi^*(x,t)}{\partial t}=\frac{-\hbar^2}{2m}\frac{\partial^2\psi^*(x,t)}{\partial x^2}+V(x)\psi(x,t) \qquad \text{...(ii)}$$

Multiplying Eq. (i) by $\psi^*(x, t)$ from the left, Eq. (ii) by $\psi(x, t)$ from the right and subtracting we obtain

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

Integrating the above for the entire region we get

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

$$=\frac{i\hbar}{2m}\left\{\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\psi(x,t)\frac{\partial\psi^*(x,t)}{\partial x}\right\}_{-\infty}^{+\infty} \qquad \text{...(iii)}$$

Since $\psi(x, t)$ describes a bound state of the particle we have

$$\psi(x, t) = 0 \quad \text{as } x \to \pm\infty.$$

Using the above boundary condition in Eq. (iii), we get

$$\frac{d}{dt}\int_{-\infty}^{+\infty}\psi^*(x,t)\psi(x,t)dx = 0$$

(*l*) Let the particle be in a stationary state with energy E at $t = t_0$. We then have

$$\hat{H}\psi(x, t_0) = E\psi(x, t_0) \qquad \text{...(iv)}$$

In the above the Hamiltonian $\hat{H}$ does not depend on time explicitly.

If $\psi(x, t)$ is the wavefunction at the time t, we have the Schrödinger equation

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

or

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

Integrating over time between the limits $t = t_0$ to $t = t$, (since $\hat{H}$ is not an explicit function of time), we get

$$\{\ln \psi(x,t)\}_{t_0}^{t} = \frac{-i}{\hbar}\hat{H}(t-t_0)$$

or
$$\ln \frac{\psi(x,t)}{\psi(x,t_0)} = \frac{-i}{\hbar}\hat{H}(t-t_0)$$

or
$$\psi(x,t) = e^{\frac{-i}{\hbar}\hat{H}(t-t_0)}\psi(x,t_0) \qquad \text{...(v)}$$

Multiplying both sides by $\hat{H}$ and from the left and using commutability between $\hat{H}$ and $e^{\frac{-i}{\hbar}\hat{H}(t-t_0)}$, the above gives

$$\hat{H}\psi(x,t) = e^{\frac{-i}{\hbar}\hat{H}(t-t_0)}\hat{H}\psi(x,t_0)$$

Using Eq. (iv) the above gives

$$\hat{H}\psi(x,t) = E\, e^{\frac{-i}{\hbar}\hat{H}(t-t_0)}\psi(x,t_0)$$

or

$$\hat{H}\psi(x,t) = E\,\psi(x,t) \qquad \text{...(vi)}$$

In view of Eqs. (iv) and (v), we can say that the wavefunction $\psi(x, t)$ repersents a stationary state.

Example 5 Using Schrödinger equation, find the potential $V(x)$ and energy E for which the wavefunction $\psi(x) = A\left(\frac{x}{x_0}\right)^n e^{-x/x_0}$ is an eigenfunction (Assume that as $x \to \infty$, $V(x) \to 0$).

Solution: If the wavefunction $\psi(x)$ is an eingnfunction of the Hamiltonian operator $\hat{H}$ belonging to the energy eigenvalue E we have

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

or
$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad \text{...(i)}$$

We have
$$\psi(x) = A\left(\frac{x}{x_0}\right)^n e^{\frac{-x}{x_0}} \qquad \text{...(ii)}$$

We get on differentiating with respect to x

$$\frac{d\psi(x)}{dx} = An\left(\frac{x}{x_0}\right)^{n-1}\frac{i}{x_0}e^{\frac{-x}{x_0}} - \frac{i}{x_0}A\left(\frac{x}{x_0}\right)^{n}e^{\frac{-x}{x_0}}$$

Differentiating the above with respect to x and simplifying we get

$$\frac{d^2\psi(x)}{dx^2} = \left[\frac{n(n-1)}{x^2} - 2\frac{n}{x_0 x} + \frac{i}{x_0^2}\right]\psi(x) \qquad \text{...(iii)}$$

Substituting Eq. (iii) in Eq. (ii) we obtain

$$\frac{-\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - 2\frac{n}{x_0 x} + \frac{1}{x_0^2}\right]\psi(x) = [E - V(x)]\psi(x)$$

The above gives

$$E - V(x) = \frac{-\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - 2\frac{n}{x_0 x} + \frac{1}{x_0^2}\right] \qquad \text{...(iv)}$$

Since $V(x) \to 0$ as $x \to \infty$ (assumption given) the above gives

$$E = \frac{-\hbar^2}{2mx_0^2} \qquad \text{...(v)}$$

Using Eq. (v) in Eq. (iv) we get

$$V(x) = \frac{\hbar^2}{2mx_0^2} + \frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x}\right]$$

or

$$V(x) = \frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2} - \frac{1}{x_0^2}\right]$$

or

$$V(x) = \frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x}\right] \qquad \text{...(vi)}$$

Example 6 The wavefunction for a particle in a one-dimensional potential $V(x)$ is given by

$$\psi(x, t) = \alpha x\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}} \quad \text{for } x > 0$$

$$= 0 \qquad \text{for } x < 0$$

where α, β and γ are positive constants.

(a) Is the particle bound? Explain your answer.

(b) Find $V(x)$ for $x > 0$

Solution: (a) We have

$$\psi(x,\, t) = \alpha x\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}}$$

Clearly $\underset{x \to \infty}{\mathrm{Lt}}\ \psi(x,\, t) = 0$ (the factor) $e^{-\beta x} \to 0$)

and $\underset{x \to -\infty}{\mathrm{Lt}}\ \psi(x,\, t) = 0$

Thus, $\underset{x \to \pm\infty}{\mathrm{Lt}}\ \psi(x,\, t) = 0$ ...(i)

Clearly, the particle is in a bound state.

(b) For $x > 0$, the Schrödinger equation is

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

(m = mass of the particle)

or

$$i\hbar \frac{\partial}{\partial t}\left[\alpha x\, e^{-\beta x}\, \frac{i\gamma t}{e^{\hbar}}\right] = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[\alpha x\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}}\right] + V(x)\left[\alpha x\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}}\right]$$

or

$$i\hbar\, \alpha x\, e^{-\beta x}\left(\frac{i\gamma}{\hbar}\right) e^{\frac{i\gamma t}{t}} = \frac{-\hbar^2}{2m}\alpha\, e^{\frac{i\gamma t}{\hbar}}\left[\beta^2 x e^{-\beta x} - 2\beta\, e^{-\beta x}\right] + V(x)\, \alpha x\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}}$$

or

$$-\gamma \alpha x\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}} = \frac{-\hbar^2}{2m}\alpha\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}}\left[\beta^2 x - 2\beta\right] + V(x)\, x\alpha\, e^{-\beta x}\, e^{\frac{i\gamma t}{\hbar}}$$

Dividing throughout by $\alpha\, e^{-\beta x} e^{\frac{i\gamma t}{\hbar}}$ we obtain

$$-\gamma x = -\frac{\hbar^2}{2m}\left[\beta^2 x - 2\beta\right] + V(x)x$$

From the above the potential function $V(x)$ for $x > 0$ is given by

$$V(x) = -\gamma + \frac{\hbar^2}{2m}\left[\beta^2 - \frac{2\beta}{x}\right] \qquad \text{...(ii)}$$

Example 7 The wavefunction of a particle is

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L} \quad \text{for } 0 < x < L$$

and $\psi(x) = 0$ for $x < 0$ and $x > L$.

Find the probability of finding the particle in the region $0 < x < \frac{L}{2}$

Solution: Probability of finding the particle in the region $0 < x < \frac{L}{2}$ is given by

$$P = \int_0^{L/2} \psi^*(x)\psi(x)dx$$

Since $$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L}, \text{ we get}$$

$$P = \frac{2}{L}\int_0^{L/2} \sin^2\frac{\pi x}{L}\,dx = \frac{2}{L}\int_0^{L/2} \frac{1-\cos\frac{2\pi X}{L}}{2}\,dx$$

$$= \frac{1}{L}\left[\int_0^{L/2} dx - \int_0^{L/2} \cos\frac{2\pi}{L}x\,dx\right]$$

$$= \frac{1}{L}\left[\frac{L}{2} - \left\{\frac{\sin\frac{2\pi}{L}x}{2\pi/L}\right\}_0^{L/2}\right]$$

or $$P = \frac{1}{2}.$$

Example 8 Wavefunction of a particle is given by

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L} \quad \text{for } 0 < x < L$$

and $$\psi(x) = 0$$

Show that while the expectation value of momentum p_x is zero, that of p_x^2 is not zero in the region $0 < x < L$.

Solution: The expectation value of the momentum p_x in the region $0 < x < L$ is given by

$$\langle p_x \rangle = \int_0^L \psi^*(x)\,\hat{p}_x\psi(x)dx$$

$$= \frac{2}{L}\int_0^L \sin\frac{\pi x}{L}\left(-i\hbar\frac{\partial}{\partial x}\right)\sin\frac{\pi x}{L}\,dx$$

$$= -i\hbar\frac{2}{L}\times\frac{\pi}{L}\int_0^L \sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\,dx$$

$$= \frac{-i\hbar 2\pi}{L^2}\int_0^L \frac{\sin\frac{2\pi x}{L}}{2}\,dx$$

$$= -\frac{i\hbar\pi}{L^2}\left\{-\frac{\cos\frac{2\pi x}{L}}{2\pi / L}\right\}_0^L$$

or

$$\langle p_x\rangle = \frac{i\hbar\pi}{L^2}\times\frac{L}{2\pi}[\cos 2\pi - \cos 0]$$

or

$$\langle p_x\rangle = 0$$

We have

$$\langle p_x^2\rangle = \int_0^L \psi^*(x)\,\hat{p}_x^2\,\psi(x)dx$$

$$= \frac{2}{L}\int_0^L \sin\frac{\pi x}{L}(-\hbar^2)\frac{\partial^2}{\partial x^2}\left(\sin\frac{\pi x}{L}\right)dx$$

$$= +\frac{2\hbar^2}{L}\left(\frac{\pi}{L}\right)^2\int_0^L \sin^2\frac{\pi x}{L}\,dx$$

$$= \frac{2\hbar^2\pi^2}{L^3}\int_0^L \frac{1-\cos\frac{2\pi x}{L}}{2}\,dx$$

$$= \frac{\hbar^2\pi^2}{L^3}\left[\int_0^L dx - \int_0^L \cos\frac{2\pi x}{L}\,dx\right]$$

$$= \frac{\hbar^2\pi^2}{L^3}\left[L - \left\{\frac{\sin\frac{2\pi x}{L}}{\frac{2\pi}{L}}\right\}_0^L\right]$$

or

$$\langle p_x^2\rangle = \frac{\hbar^2\pi^2}{L^3}\times L = \frac{\hbar^2\pi^2}{L^2}$$

Example 9 If the normalized wavefunction for a particle moving along the x-axis be

$$\psi(x) = A\, e^{-x^2/2a^2}\, e^{ikx}$$

find $\langle x \rangle$ and $\langle p_x \rangle$.

Solution:

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

$$= A^* A \int_{-\infty}^{+\infty} e^{\frac{-x^2}{2a^2}}\, e^{-ikx}\, x\, e^{\frac{-x^2}{2a^2}}\, e^{-ikx}\, dx$$

$$= |A|^2 \int_{-\infty}^{+\infty} e^{-x^2/a^2}\, x\, dx$$

Clearly,
$$\langle x \rangle = 0 \qquad \left(\because \int_{-\infty}^{+\infty} e^{\frac{-x^2}{a^2}}\, x\, dx = 0 \right)$$

Since the wavefunction is normalized we have

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

Using the given wavefunction in the above, we get

$$A^* A \int_{-\infty}^{+\infty} e^{\frac{-x^2}{2a^2}}\, e^{-ikx}\, e^{\frac{-x^2}{2a^2}}\, e^{ikx}\, dx = 1$$

or
$$|A|^2 \int_{-\infty}^{+\infty} e^{\frac{-x^2}{2a^2}}\, dx = 1 \qquad \text{...(i)}$$

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

$$= A^* A \int_{-\infty}^{+\infty} e^{\frac{-x^2}{2a^2}}\, e^{-ikx} (-i\hbar) \frac{\partial}{\partial x} \left[e^{\frac{-x^2}{2a^2}}\, e^{ikx} \right] dx$$

$$= -i\hbar\,|A|^2 \int_{-\infty}^{+\infty} e^{\frac{-x^2}{2a^2}}\, e^{-ikx} \left[e^{\frac{-x^2}{2a^2}}\, ik\, e^{ikx} - e^{\frac{-x^2}{2a^2}} \times \left(\frac{-1}{2a^2}\right) 2x\, e^{ikx} \right] dx$$

$$= -i\hbar\,|A|^2 \left[\int_{-\infty}^{+\infty} ik\, e^{\frac{-x^2}{a^2}}\, dx + \frac{1}{a^2} \int_{-\infty}^{+\infty} e^{\frac{-x^2}{2a^2}}\, x\, dx \right]$$

or

$$\langle p_x \rangle = \hbar k\,|A|^2 \int_{-\infty}^{+\infty} e^{\frac{-x^2}{a^2}}\, dx - i\hbar\,|A|^2 \times \frac{1}{a^2} \int_{-\infty}^{+\infty} e^{\frac{-x^2}{a^2}}\, x\, dx$$

In view of Eq. (i) and the standard integral we get $\langle p_x \rangle = \hbar k$.

5

One-dimensional Problems

5.1 INTRODUCTION

The formalism of quantum mechanics, in particular, the theory due to Schrödinger, has been extensively applied in the study of physical problems in atomic, molecular and nuclear physics. The main purpose of such application has been to compare the results according to Schrödinger's theory with those obtained experimentally.

In spite of drastic assumptions involved, Schrödinger's theory has been found to be immensely successful in understanding a large number of phenomena in the microscopic domain both qualitatively and quantitatively to a large extent.

In the following sections, we have considered application of the time-independent Schrödinger equation to some problems in which motions take place in one-dimension. The problems considered allow us to compare the classical results with the quantum mechanical results. Besides, the results illustrate some effects in the microscopic domain which may be called the *quantum effects* which are disallowed according to classical physics.

5.2 GENERAL CHARACTERISTICS OF ONE-DIMENSIONAL MOTION

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

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x) = 0 \qquad \ldots(1)$$

The solutions of the above equation give the energy eigenfunctions $\psi_n(x)$ belonging to different energy eigenvalues E_n for the particle.

Equation (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 problem of linear harmonic oscillator will be discussed in a separate chapter to follow.

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 eignfunction $\psi_n(x)$ 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 $n = 1$.

5.3 FREE PARTICLE

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

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

or

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

or

$$\frac{d^2\psi(x)}{dx^2} + k^2\,\psi(x) = 0 \qquad ...(2)$$

where

$$k^2 = \frac{2m}{\hbar^2}E \qquad ...(3)$$

The most general solution of Eq. (2) is a combination of two linearly independent plane wave solutions e^{ikx} and e^{-ikx}

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx} \qquad ...(4)$$

where A and B are arbitrary constants. The complete wavefunction is given by

$$\psi_k\,(x,\ t) = Ae^{\,i(kx - \omega t)} + Be^{\,-i(kx + \omega t)} \qquad ...(5)$$

where

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

The first term in Eq. (4) $\psi_+(x, t) = Ae^{i(kx-\omega t)}$ 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 partical 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 $\dfrac{\hbar^2 k^2}{2m}$. 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 $\Delta x \to \infty$ and the uncertainty in the time $\Delta t \to \infty$. 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

$$v_{\text{wave}} = \frac{\omega}{k} = \frac{E}{\hbar k} = \frac{\hbar^2 k^2 / 2m}{\hbar k} = \frac{\hbar k}{2m} \qquad \text{...(7)}$$

The speed of the particle according to classical mechanics is given by

$$v_{\text{particle}} = \frac{p}{m} = \frac{\hbar k}{m} \qquad \text{...(8)}$$

We thus observe

$$v_{\text{particle}} = 2v_{\text{wave}} \qquad \text{...(9)}$$

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

$$\int_{-\infty}^{+\infty} \psi_+^*(x,t)\,\psi_+(x,t)\,dx = |A|^2 \int_{-\infty}^{+\infty} dx = \infty \qquad \text{...(10)}$$

and
$$\int_{-\infty}^{+\infty} \psi_-^*(x,t)\,\psi_-(x,t)\,dx = |B|^2 \int_{-\infty}^{+\infty} dx = \infty \qquad \ldots(11)$$

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 partical cannot be represented by single (monochromatic) plane wave. Physically acceptable representation of a free particle is a wave packet as has been discussed earlier in Chapter 4. We may further conclude that solutions of the Schrödinger equation which are physically acceptable cannot be plane waves.

5.4 THE POTENTIAL STEP

Consider a particle of mass m moving in a one-dimensional potential specified in the Fig. 5.1. Mathematically, the potential function $V(x)$ is of the form

$$V(x) = 0 \qquad x < 0 \qquad \text{(Region I)}$$
$$= V_0 \qquad x > 0 \qquad \text{(Region II)}$$

The particle moving freely in region I encounters the potential V_0 at $x = 0$.

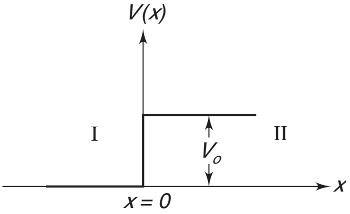


Fig. 5.1 The potential step

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
$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x) = 0 \qquad \ldots(12)$$

In the above, E is the total energy of the particle.

In the region I, if $\psi_1(x)$ is the wavefunction, Eq. (12) takes the form

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2m}{\hbar^2} E\,\psi_1(x) = 0$$

or
$$\frac{d^2\psi_1(x)}{dx^2} + k^2\,\psi_1(x) = 0$$

where
$$k^2 = \frac{2m}{\hbar^2} E \qquad \text{...(14)}$$

If $\psi_2(x)$ be the wavefunction of the particle in region II, Eq. (12) gives

$$\frac{d^2\psi_2(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V_o]\,\psi_2(x) = 0$$

or
$$\frac{d^2\psi_2(x)}{dx^2} + \alpha^2\psi_2(x) = 0 \qquad \text{...(15)}$$

where
$$\alpha^2 = \frac{2m}{\hbar^2}[E - V_o] \qquad \text{...(16)}$$

Most general solutions of Eqs. (13) and (15) can be written as

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \qquad \text{...(17)}$$

$$\psi_2(x) = Ce^{i\alpha x} + De^{-i\alpha x} \qquad \text{...(18)}$$

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 Eq. (17), $\psi_{1+}(x) = Ae^{ikx}$ 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 Eq. (18) $\psi_{2+}(x) = Ce^{i\alpha x}$ 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 throughtout 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 Eq.(18) reduces to

$$\psi_2(x) = C\,e^{i\alpha x} \qquad \text{...(19)}$$

We have the following boundary conditions in view of single valuedness and continuity of wavefunction at a potential boundary:

(i)
$$\psi_1(x) = \psi_2(x) \quad \text{at } x = 0 \qquad \text{...(20)}$$

Using the above we obtain from Eqs. (17) and (19)

$$A + B = C \qquad ...(21)$$

(ii) $$\frac{d\psi_1(x)}{dx} = \frac{d\psi_2(x)}{dx} \quad \text{at } x = 0 \qquad ...(22)$$

From Eq. (17) we have

$$\frac{d\psi_1(x)}{dx} = ikAe^{ikx} - ikBe^{-ikx} \qquad ...(23)$$

From Eq. (19) we have

$$\frac{d\psi_2(x)}{dx} = i\alpha Ce^{i\alpha x} \qquad ...(24)$$

Using Eqs. (23) and (24) we get using Eq. (22)

$$k\,(A - B) = \alpha C \qquad ...(25)$$

Solving Eqs. (21) and (25) we obtain

$$C = \frac{2k}{k+\alpha} A \qquad ...(26)$$

$$B = \frac{k-\alpha}{k+\alpha} A \qquad ...(27)$$

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

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \qquad ...(28)$$

We get on differentiating Eq. (28) with respect to x

$$\frac{d\psi_1(x)}{dx} = ik\,[Ae^{ikx} - Be^{-ikx}] \qquad ...(29)$$

Taking complex conjugate, Eq. (28) becomes

$$\psi_1^*(x) = A^* e^{-ikx} + B^* e^{ikx} \qquad ...(30)$$

Taking complex conjugate, Eq. (29) we get

$$\frac{d\psi_1^*(x)}{dx} = -ik[A^* e^{-ikx} - B^* e^{ikx}] \qquad ...(31)$$

The general expression for probability current density is given by

$$J = \frac{-i\hbar}{2m}[\psi^*\nabla\psi - \psi\,\nabla\psi^*] \qquad ...(32)$$

Since we are considering one-dimensional motion we get from Eq. (32) the probability current density in region I to be

$$J_1 = \frac{-i\hbar}{2m}\left[\psi_1^*(x)\frac{d\psi_1(x)}{dx} - \psi(x)\frac{d\psi_1^*}{dx}\right]$$

Substituting from Eqs. (28), (29), (30), and (31) in the above we obtain

$$J_1 = \frac{\hbar k}{m}(|A|^2 - |B|^2) \qquad \text{...(33)}$$

The first term on the right hand side of Eq. (33) gives the probability current density of the incident wave/beam

$$(J_1)_{\text{incident}} = \frac{\hbar k}{m}|A|^2 \qquad \text{...(34)}$$

while the second term gives the probability current density of the reflected wave/beam

$$(J_1)_{\text{reflected}} = \frac{\hbar k}{m}|B|^2 \qquad \text{...(35)}$$

Let us now consider region II in which the wavefunction is given by

$$\psi_2(x) = Ce^{i\alpha x} \qquad \text{...(36)}$$

The above gives

$$\frac{d\psi_2(x)}{dx} = i\alpha\, Ce^{idx} \qquad \text{...(37)}$$

Taking complex conjugate of Eq. (36) we get

$$\psi_2^*(x) = C^*\ e^{-i\alpha x} \qquad \text{...(38)}$$

and taking complex conjugate of Eq. (37) we get

$$\frac{d\psi_2^*(x)}{dx} = -i\alpha\, C^*\ e^{-i\alpha x} \qquad \text{...(39)}$$

The probability current density in region II by definition is given by

$$J_2 = \frac{-i\hbar}{2m}\left[\psi_2^*(x)\frac{d\psi_2}{dx} - \psi_2\frac{d\psi_2^*}{dx}\right] \qquad \text{...(40)}$$

Substituting from Eqs. (36), (37), (38) and (39) in Eq. (40) we obtain

$$J_2 = \frac{\hbar\alpha}{m}|C|^2 \qquad \text{...(41)}$$

Since in region II, there exists only the transmitted wave we get the probability current density of the transmitted wave/beam

$$(J_2)_{\text{transmitted}} = \frac{\hbar\alpha}{m}|C|^2 \qquad \text{...(42)}$$

The *reflectance* or the *reflection coefficient* is, by definition, given by

$$R = \frac{\text{Probability current density for reflected beam}}{\text{Probability current density for incident beam}}$$

$$= \frac{(J_1)_{\text{reflected}}}{(J_1)_{\text{incident}}}$$

Using Eqs. (34) and (35) we obtain

$$R = \frac{\frac{\hbar k}{m}|B|^2}{\frac{\hbar k}{m}|A|^2} = \frac{|B|^2}{|A|^2}$$

Using Eq. (27) in the above we obtain

$$R = \left(\frac{k-\alpha}{k+\alpha}\right)^2 \qquad \text{...(43)}$$

Similarly, the transmittance or transmission coefficient is

$$T = \frac{(J_2)_{\text{transmitted}}}{(J_1)_{\text{incident}}}$$

Using Eqs. (34) and (42), 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 Eq. (26) in the above we get

$$T = \frac{\alpha}{k}\left(\frac{2k}{k+\alpha}\right)^2$$

or

$$T = \frac{4k\alpha}{(k+\alpha)^2} \qquad \text{...(44)}$$

We note the following:

1. We have $k = \sqrt{\frac{2m}{\hbar^2}E}$, a real positive quantity

   $\alpha = \sqrt{\frac{2m}{\hbar}(E - V_0)}$, a real positive quantity under the condition $E > V_0$

   Equation (43) 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 $E >> V_0$, that is for $\alpha \to k$ from below, the ratio of the reflected flux to the incident flux, that is, $|R|^2$ approaches zero. This agrees with intution 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, α given by $\alpha = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$ becomes imaginary. We may write

$$\alpha = \sqrt{-\frac{2m}{\hbar^2}(V_0 - E)} = i\sqrt{\frac{2m}{\hbar^2}(V_0 - E)} = i\beta \qquad \text{...(45)}$$

hence

$$\beta = \sqrt{\frac{2m}{\hbar}(V_0 - E)} \text{ is real positive} \qquad \text{...(46)}$$

The solution of the Schrödinger equation in region II is now given by

$$\psi_2(x) = C\,e^{ii\beta x} = C\,e^{-\beta x} \qquad \text{...(47)}$$

We find that $\psi_2(x)$ does not blow up at $x = +\infty$

The reflection coefficient given by Eq. (43), in this case becomes

$$R = \left(\frac{k - i\beta}{k + i\beta}\right)\left(\frac{k - i\beta}{k + i\beta}\right)^* = \left(\frac{k - i\beta}{k + i\beta}\right)\left(\frac{k + i\beta}{k - i\beta}\right) \qquad \text{...(48)}$$

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 Eq. (44) 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.*

5.5 INFINITE SQUARE-WELL POTENTIAL

5.5.1 Asymmetric Square Well

Consider a particle of mass m moving in a one-dimensional infinitely deep asymmetric potential well as shown in the Fig. 5.2, the potential function $V(x)$ being of the form

$$\begin{aligned} V(x) &= +\infty \quad \text{for} \quad x < 0 && \text{[Region I]} \\ &= 0 \quad \text{for} \quad 0 \le x \le a && \text{[Region II]} \\ &= +\infty \quad \text{for} \quad x > a && \text{[Region III]} \end{aligned}$$

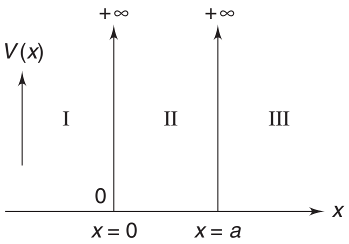


Fig. 5.2

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.

$$\psi(x = 0) = 0 = \psi(x = a) \qquad \text{...(49)}$$

If $\psi(x)$ represents the wavefunction for the particle inside the well ($0 \le x \le a$), we have the Schrödinger equation

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

or

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad \text{...(50)}$$

where

$$k = \sqrt{\frac{2m}{\hbar^2} E} \qquad \text{...(51)}$$

The general solutions of Eq. (50) are

$$\psi(x) = C\,e^{ikx} + De^{-ikx}$$

or

$$\psi(x) = A \sin kx + B \cos kx \qquad \text{...(52)}$$

where A and B are constants.

Using the boundary condition given by Eq. (49), namely $\psi(0) = 0$ in Eq. (52) we get

$$B = 0$$

so that the solution becomes

$$\psi(x) = A \sin kx \qquad \text{...(53)}$$

Further, applying the other boundary condition namely $\psi(a) = 0$, we get from Eq. (53)

$$A \sin ka = 0$$

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

$$ka = n\pi; \quad n = \text{a positive integer}$$

$$= 1, 2, 3, \ldots \qquad \ldots (54)$$

We may note that n cannot be 0 because that would make $k = 0$ so that wavefunction would vanish everywhere.

From Eq. (54) we thus get

$$k = \frac{n\pi}{a} \qquad \ldots(55)$$

Using Eq. (55) in Eq. (53) we get the energy eigenfunctions of the particle to be given by

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right) \quad ; n = 1, 2, \ldots \qquad \ldots(56)$$

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
$$A = \sqrt{\frac{2}{a}} \qquad \ldots(57)$$

The energy eigenfunctions are thus

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right); \quad n = 1, 2, \ldots \qquad \ldots(58)$$

Using Eq. (51) in Eq. (55) we get the energy eigenvalues of the particle to be given by

$$\sqrt{\frac{2m}{\hbar^2} E_n} = \frac{n\pi}{a}$$

or
$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2, \quad n = 1, 2, \ldots \qquad \text{...(59)}$$

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 Eq. (59) we get

$$E_{n+1} - E_n = \frac{\hbar^2\pi^2}{2ma^2}(2n+1) \qquad \text{...(60)}$$

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

$$\underset{n\to\infty}{\text{Lt}}\left(\frac{E_{n+1} - E_n}{E_n}\right) = \underset{n\to\infty}{\text{Lt}}\left(\frac{2}{n} + \frac{1}{n^2}\right) = 0 \qquad \text{...(61)}$$

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

$$E_1 = \frac{\hbar^2\pi^2}{2ma^2} \qquad \text{...(62)}$$

and the ground state wavefunction is given by

$$\psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right) \qquad \text{...(63)}$$

Energy given by Eq. (62) 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 Fig. 5.3. We observe from the plots that the eigenfunction $\psi_n(x)$ has $(n - 1)$ nodes as mentioned in Section 5.2.

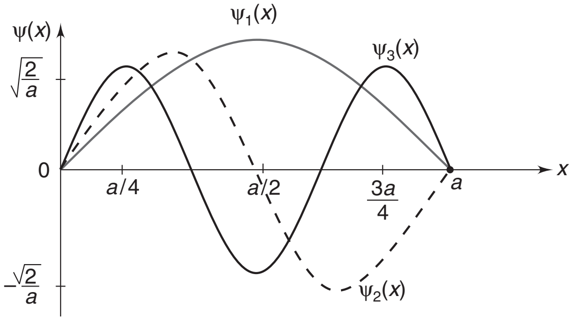


Fig. 5.3

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 $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$.

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 Δp 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.

5.5.2 Symmetric Square-Well Potential of Infinite Depth

A symmetric infinite square well potential is defined as

$$\begin{aligned} V(x) &= +\infty \quad \text{for} \quad x < -a \\ &= 0 \quad \text{for} \quad -a \le x \le a \\ &= +\infty \quad \text{for} \quad x > a \end{aligned}$$

and is represented in the Fig. 5.4

Consider the motion of a particle of mass m in the one-dimensional potential described above.

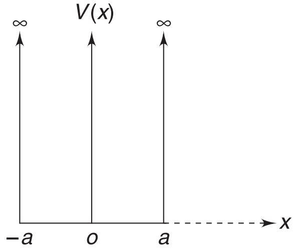


Fig. 5.4

If $\psi(x)$ is the wavefunction describing the state of the particle in the region $-a \le x \le a$ then it satisfies the time-independent Schrödinger equation

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

or

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad ...(64)$$

where

$$k = \sqrt{\frac{2m}{\hbar^2} E} \qquad ...(65)$$

The most general solution of Eq. (64) is given by

$$\psi(x) = A \sin(kx) + B \cos(kx) \qquad ...(66)$$

where A and B are constants.

Since $V(x) = \infty$ for $x < -a$ and $x > a$, the wavefunctions in these two regions vanish giving

$$\psi(-a) = 0 \quad \text{and} \quad \psi(+a) = 0 \qquad ...(67)$$

Using the conditions given by Eq. (67) in Eq. (66) we get

$$A \sin ka + B \cos ka = 0 \qquad ...(68)$$

and

$$-A \sin ka + B \cos ka = 0 \qquad ...(69)$$

For the above two equations to hold simultaneously we must have

$$A \sin ka = 0 \qquad ...(70)$$

and

$$B \cos ka = 0 \qquad ...(71)$$

In view of Eqns. (70) and (71) we may have $A = 0$ and $B = 0$ but these are physically unacceptable because $\psi(x)$ given by Eq. (66) would then vanish.

Since $B \neq 0$, we have from Eq. (71),

$$\cos ka = 0 = \cos \frac{n\pi}{2}, \quad n = 1, 3, 5, \ldots$$

or

$$ka = \frac{n\pi}{2} \quad \text{or} \quad k = \frac{n\pi}{2a} \qquad \ldots(72)$$

Using Eq. (65) in the above we obtain the energy eigenvalues

$$E_n = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} = \frac{\pi^2\hbar^2}{8ma^2}n^2, \quad n = 1, 3, 5, \ldots \qquad \ldots(73)$$

The energy eigenfunctions corresponding to the above energy eigenvalues are

$$\psi_n(x) = B \cos kx = B\cos\left(\frac{n\pi}{2a}x\right), \quad n = 1, 3, 5 \qquad \ldots(74)$$

The condition given by Eq. (70) gives

$$\sin ka = 0 = \sin n\pi \qquad \text{(since } A \neq 0\text{)}$$

or

$$ka = n\pi \quad \text{or} \quad k = \frac{n\pi}{a}; \quad n = 2, 4, 6 \qquad \ldots(75)$$

Using the above value of k in Eq. (65) we get the energy eigenvalues

$$E_n = \frac{\hbar^2}{2m}k^2 = \frac{\pi^2\hbar^2 n^2}{8ma^2}, \quad n = 2, 4, 6, \ldots \qquad \ldots(76)$$

The corresponding energy eigenfunctions are

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{2a}\right), \quad n = 2, 4, 6, \ldots \qquad \ldots(77)$$

The normalization conditions of the wavefunctions

$$\int_{-a}^{+a} \psi_n^*(x)\, \psi_n(x)\, dx = 1$$

lead to

$$A = \frac{1}{\sqrt{a}}, \; B = \frac{1}{\sqrt{a}} \qquad \ldots(78)$$

We can thus write the set of energy eigenfunctions for the particle in the symmetric infinite square well potential as

$$\psi_n(x) = \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi}{2a}x\right), \quad n = 2, 4, \ldots \qquad \ldots(79)$$

$$\psi_n(x) = \frac{1}{\sqrt{a}}\cos\left(\frac{n\pi}{2a}x\right), \quad n = 1, 3, 5, \ldots \qquad \ldots(80)$$

and the discrete set of energy eigenvalues as

$$E_n = \frac{\pi^2\hbar^2}{8ma^2}n^2, \quad n = 1, 2, 3, \ldots \qquad \ldots(81)$$

Discussion

The wavefunctions corresponding to $n = 1, 3, 5, \ldots$ i.e., corresponding to odd quantum numbers are symmetric, $\psi(-x) = \psi(x)$

The wavefunctions corresponding to $n = 2, 4, 6, \ldots$ 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

$$\psi_1(x) = \frac{1}{\sqrt{a}}\cos\frac{\pi x}{2a}$$

5.5.3 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

$$\begin{aligned} V(z) &= V_0 \quad \text{for} \quad x < -a & \text{(Region I)} \\ &= 0 \quad \text{for} \quad -a \le x \le a & \text{(Region II)} \\ &= V_0 \quad \text{for} \quad x > a & \text{(Region III)} \end{aligned}$$

The potential function is shown in the Fig. 5.5

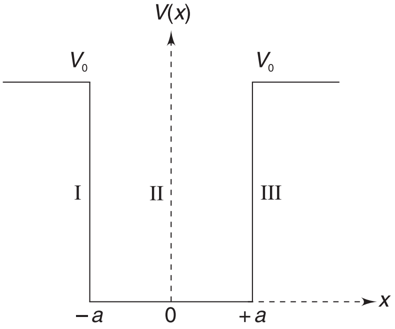


Fig. 5.5

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
$$\frac{d^2\psi(x)}{dx^2}+\frac{2m}{\hbar^2}(E-V_0)\,\psi(x)\ =0 \qquad ...(82)$$

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

$$\frac{d^2\psi(x)}{dx^2}+k^2\psi(x)=0 \qquad ...(83)$$

where
$$k=\sqrt{\frac{2m}{\hbar^2}E} \qquad ...(84)$$

Let us consider the cases where: $E < V_0$, and $E > V_0$

Case $E < V_0$: We may write Eq. (82) in the form

$$\frac{d^2\psi(x)}{dx^2}-\alpha^2\psi(x)=0 \qquad ...(85)$$

where
$$\alpha=\sqrt{\frac{2m}{\hbar^2}(V_0-E)}\quad \text{is real positive} \qquad ...(86)$$

The most general solution of Eq. (85) is

$$\psi(x) = Ae^{+\alpha x} + Be^{-\alpha x},\quad A \text{ and } B \text{ are constants} \qquad ...(87)$$

Specific solution in region I $\psi_1(x) = A\,e^{\alpha x}$ ...(88)

Specific solution in region III $\psi_3(x) = B\,e^{-\alpha x}$ ...(89)

Solution of Eq. (83) gives the wavefunction in region II

$$\psi_2(x) = C\sin(kx) + D\cos(kx) \qquad ...(90)$$

$\psi_2(x)$ is either symmetric or antisymmetric about $x = 0$. The first term in Eq. (90) 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

$$(\psi_2(x))_{\text{symmetric}} = D\cos(kx) \qquad ...(91)$$

At $x = \pm a$, we have, using the single valuedness of wavefunction

$$Ae^{-\alpha a} = D\cos ka \qquad ...(92)$$

$$Be^{-\alpha a} = D\cos ka \qquad ...(93)$$

Similarly, using the continuity of wavefunction at $x = \pm a$ gives

$$\alpha A\, e^{-\alpha a} = +D\, k\sin(ka) \qquad ...(94)$$

$$+\alpha B\, e^{-\alpha a} = D\, k\sin(ka) \qquad ...(95)$$

The above equations give

$$A = B \qquad ...(96)$$

and

$$k\tan ka = \alpha \qquad ...(97)$$

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

$$(\psi_2(x))_{\text{antisymmetric}} = C\sin(kx) \qquad ...(98)$$

Using the single valuedness and continuity of wavefunction at the boundaries at $x = \pm a$ we get

$$A\, e^{-\alpha a} = -C\sin(ka) \qquad ...(99)$$

$$B\, e^{-\alpha a} = C\sin(ka) \qquad ...(100)$$

$$\alpha A\, e^{-\alpha a} = -C\, k\cos(ka) \qquad ...(101)$$

$$-\alpha Be^{-\alpha a} = C\, k\cos(ka) \qquad ...(102)$$

From the above four equations, we obtain

$$A = -B \qquad ...(103)$$

and

$$k\cot ka = -\alpha \qquad ...(104)$$

The energy eigenvalues for the particle can be obtained by solving Eqs. (97) and (104) graphically as explained in the following:

Let us put

$$ka = x \qquad ...(105)$$

$$\alpha a = y \qquad ...(106)$$

From the above we get

$$x^2 + y^2 = (k^2 + \alpha^2)\, a^2$$

Substituting for k and α from Eqs. (84) and (86), the above becomes

$$x^2 + y^2 = \left[\frac{2m}{\hbar^2} E + \frac{2m}{\hbar^2}(V_0 - E)\right] a^2$$

or
$$x^2 + y^2 = \frac{2ma^2}{\hbar^2} V_0 \qquad ...(107)$$

Substituting Eqs. (105) and (106) in Eqs. (97) and (104), respectively, we obtain

$$x \tan x = y \qquad ...(108)$$

$$-x \cot x = y \qquad ...(109)$$

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 (Fig. 5.6)

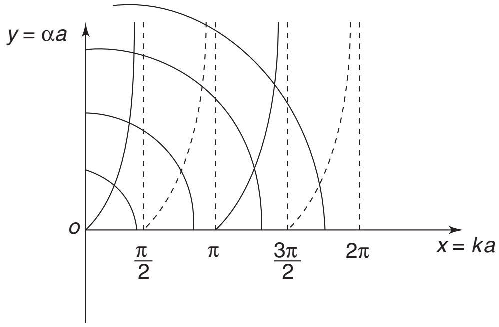


Fig. 5.6

In the figure

Full line curves → $x \tan x$ against x plots

Dashed curves → $-x \cot x$ against x plots

Circular sections → 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 $x_1, x_2, ..., x_n, ...$ then we get

$$x_n^2 = k^2 a^2 = \frac{2mE_n}{\hbar^2} a^2$$

or
$$E_n = \frac{\hbar^2}{2ma^2} x_n^2, \quad n = 1, 3, 5, \ldots$$

Similarly, if the intersections of $-x \cot x$ against x curves and the circles occur at values of x equal to $x_{1'}, x_{2'}, \ldots x_{n'} \ldots$, then we get

$$x_{n'}^2 = k^2a^2 = \frac{2mE_{n'}}{\hbar^2} a^2$$

or
$$E_{n'} = \frac{\hbar^2}{2ma^2} x_{n'}^2; \quad n' = 2, 4, 6, \ldots$$

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_0a^2. From the figure we find the following

(i) Only one energy level of symmetric type, if $0 < V_0a^2 < \frac{\pi^2\hbar^2}{8m}$

(ii) Two energy levels of which one is of symmetric type and the other of antisymmetric type, if $\frac{\pi^2\hbar^2}{8m} < V_0a^2 < \frac{4\pi^2\hbar^2}{8m}$

(iii) Three energy levels of which two are of symmetric type and one of antisymmetric type, if $\frac{4\pi^2\hbar^2}{8m} < V_0a^2 < \frac{9\pi^2\hbar^2}{8m}$ and so on.

Some of the energy eigenfunctions corresponding to bound states are shown in the Fig. 5.7.

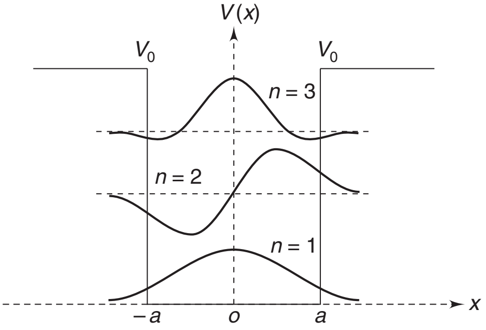


Fig. 5.7

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 Schordinger 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.

5.6 POTENTIAL BARRIER PROBLEM

A one-dimensional potential barrier of height V_0 and width a is defined by potential function $V(x)$ given by

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad x < 0 \\ &= V_0 \quad \text{for} \quad 0 < x < a \\ &= 0 \quad \text{for} \quad x > a \end{aligned}$$

The above potential function is shown in the Fig. 5.8.

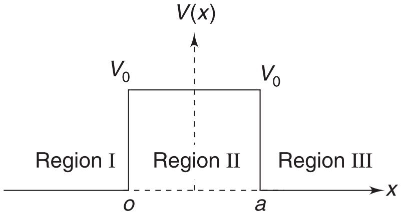


Fig. 5.8

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

$$\frac{d^2\psi_1(x)}{dx^2}\,k^2\psi_1(x) = 0, \quad k = \sqrt{\frac{2m}{\hbar^2}E} \qquad ...(111)$$

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

$$\sqrt{\frac{2m}{\hbar^2}(V_0 - E)} = \alpha \text{ (a positive quantity)} \qquad ...(112)$$

The above equation becomes

$$\frac{d^2\psi_2(x)}{dx^2} - \alpha^2\psi_2(x) = 0 \qquad ...(113)$$

In the region III ($x \geq, a$), we have the equation

$$\frac{d^2\psi_3(x)}{dx^2} + k^2\psi_3(x) = 0 \qquad ...(114)$$

The general solutions of Eqs. (111), (113) and (114) are given respectively by

$$\psi_1(x) = A_1\, e^{ikx} + B_1\, e^{-ikx} \qquad ...(115)$$

$$\psi_2(x) = A_2\, e^{\alpha x} + B_2\, e^{-\alpha x} \qquad ...(116)$$

$$\psi_3(x) = A_3\, e^{ikx} + B_3\, e^{-ikx} \qquad ...(117)$$

In the above A_1, A_2, A_3, B_1, B_2, B_3 are constants.

The first term in Eq. (115) which represents a plane wave travelling along the positive x-axis in region I can be considered as the wave *incident* an 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 Eq. (116) 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 Eq. (117) 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 Eq. (117) is identically zero.

Considering the amplitude of the incident wave as unity we may write the solutions in the three regions as

$$\psi_1(x) = e^{ikx} + B_1\, e^{-ikx} \qquad ...(118)$$

$$\psi_2(x) = A_2\, e^{\alpha x} + B_2\, e^{-\alpha x} \qquad ...(119)$$

$$\psi_3(x) = A_3\, e^{ikx} \qquad ...(120)$$

Single valuedness and continuity of the wavefunctions at the boundaries at $x = 0$ and at $x = a$ give the following boundary conditions:

and

$$\left.\begin{aligned} &\psi_1(0) = \psi_2(0) \\ &\frac{\partial\psi_1(x)}{\partial x} = \frac{\partial\psi_2(x)}{\partial x} \text{ at } x = 0 \\ &\psi_2(a) = \psi_3(a) \\ &\frac{\partial\psi_2(x)}{\partial x} = \frac{\partial\psi_3(x)}{\partial x} \text{ at } x = -a \end{aligned}\right\} \qquad \text{...(121)}$$

Using these boundary conditions we obtain

$$I + B_1 = A_2 + B_2 \qquad \text{...(122)}$$

$$ik(I - B_1) = \alpha(A_2 - B_2) \qquad \text{...(123)}$$

$$A_2\, e^{\alpha a} + B_2\, e^{-\alpha a} = A_3\, e^{ika} \qquad \text{...(124)}$$

$$\alpha[A_2\, e^{\alpha a} - B_2\, e^{-\alpha a}] = ik\, A_3\, e^{ika} \qquad \text{...(125)}$$

Solving the simultaneous equations (122 to 125) we obtain

$$A_3 = \frac{2ik\,\alpha\, e^{-ika}}{(\alpha^2 - k^2)\sin h\,(\alpha a) - 2i\alpha k \cos h(\alpha a)} \qquad \text{...(126)}$$

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

$$T = \frac{4k^2\alpha^2}{(\alpha^2 - k^2)^2 \sin h^2(\alpha a) + 4\alpha^2 k^2 \cos h^2(\alpha a)} \qquad \text{...(127)}$$

Since both k as well as α are real quantities, the transmission coefficient has a finite value.

When $E \to 0$, $k \to 0$ and hence $T \to 0$.

As the energy E of the incident particle increases, remaining less than V_0, both k as well as α increase and the transmission coefficient increases.

Under the condition $E \to V_0$, $\alpha \to 0$, we obtain from Eq. (127)

$$T = \frac{4k^2\alpha^2}{k^4\alpha^2 a^2 + 4\alpha^2 k^2} = \frac{1}{1 + \left(\frac{ka}{2}\right)^2} \qquad \text{...(128)}$$

Under the condition of the barrier height V_0 large and the barrier width a also large we get αa large, so that

$$\sin h\ (\alpha a) = \frac{1}{2} e^{\alpha a}$$

$$\cos h\ (\alpha a) = \frac{1}{2} e^{\alpha a}$$

The transmission coefficient given by Eq. (127) 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 α in the above we obtain for such a barrier

$$T = \frac{16E(V_0 - E)}{V_0^2} e^{-2\left[\frac{2m}{\hbar^2}(V_0 - E)\right]^{1/2} a} \qquad ...(129)$$

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 one exihibited by the particle. This *tunneling* of a particle through a barrier is frequently encountered. We note that when αa is large, the ratio of the transmitted flux to incident flux is

$$T \approx \left(\frac{2k\alpha}{\alpha^2 + k^2}\right)^2 e^{-4\alpha a} \qquad ...(130)$$

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, α-particle emission from a heavy nucleus.

5.6.1 Alpha-Particle Emission

It is observed that some radioactive nuclei disintegrate by the emission of alpha (α) particle which is the nucleus of a helium atom having charge of $+2e$ and a mass 4 units.

An α-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 α-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 α-particle). The variation of the potential energy of the α-particle with distance from the centre of the nucleus is qualitatively as shown in the Fig. 5.9.

If r_0 be the radius of the nucleus and Ze be the change of the residual nucleus then the coulomb potential energy of the α-particle just beyond the surface of the nucleus becomes $\frac{1}{4\pi \in_0}\frac{2Ze^2}{r_1}$. For the α-emitting nuclides this energy is several times larger than the energy of the α-particles. The question thus arises how the α-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.

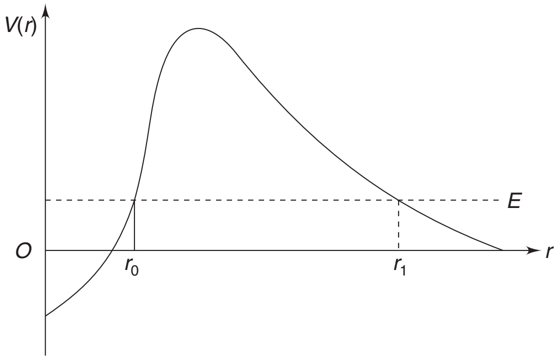


Fig. 5.9

Let E be the energy of the α-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

$$E = \frac{1}{4\pi \in_0}\frac{2Ze^2}{r_1} \qquad \text{...(131)}$$

or

$$r_1 = \frac{1}{4\pi \in_0}\frac{2Ze^2}{E} \qquad \text{...(132)}$$

We may, for some qualitative understanding of the phenomenon of α-emission, consider the potential $V(r)$ in the region $r_0 \le r \le r_1$ as a one-dimensional square potential barrier and use the result of the last section to write the transmission coefficient from the barrier as

$$T = \frac{16E(V_0 - E)}{V_0^2}\, e^{-\left[\sqrt{\frac{8m}{\hbar^2}(V_0 - E)}\right](r_1 - r_0)} \qquad \text{...(133)}$$

where

$$V_0 = \frac{1}{4\pi \in_0}\frac{2Ze^2}{r_0} = \frac{1}{4\pi \in_0}\frac{2Ze^2}{r_1} \qquad \text{...(134)}$$

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

$$T = e^{\frac{-2}{\hbar}\int_{r_0}^{r_1}\sqrt{2m\left[\frac{1}{4\pi\epsilon_0}\frac{2ze^2}{r}-E\right]}\,dr} \qquad \text{...(135)}$$

The speed of an α-particle in a heavy nucleus has been estimated to be of the order of 10^7 ms^{-1}. Considering the nucleus's radius to be 10^{-14} m we find that the time taken by the α-particle to move once across the nucleus to be 10^{-21}. Clearly the α-particle strikes the coulomb barrier at the surface of the nucleus 10^{21} times per second. The probability that the α-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 τ of the α-decaying nucleus, i.e.

$$\tau = \frac{1}{P} = \frac{1}{T \times 10^{21}} \qquad \text{...(136)}$$

If λ 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

$$\log \lambda = A + BE, \quad A \text{ and } B \text{ constants} \qquad \text{...(137)}$$

which is the well-known Geiger-Nuttal law.

5.7 SOLVED EXAMPLES

Example 1 Calculate the zero point energy in an infinite potential well for

(a) a 10 g ball confined to a 10 m long line

(b) an electron confined to an atom (atomic size 10^{-10} m)

(c) an oxygen atom confined to a 2×10^{-10} m lattice.

Solution: (a) The zero point energy is given by

$$E_0 = \frac{\hbar^2\pi^2}{2ma^2} \approx \frac{10 \times 10^{-68}}{2 \times 10 \times 10^{-3} \times 100}\,\text{J}$$

$$= 5 \times 10^{-69}\,\text{J} = \frac{5 \times 10^{-69}}{1.6 \times 10^{-19}} \simeq 3.1 \times 10^{-50}\,\text{eV}$$

E_0 is too small to be measured.

(b) The zero point energy for the electron is

$$E_0 = \frac{10\times10^{-68}}{2\times9\times10^{-31}\times10^{-20}} = 5\times10^{-18}\ \text{J}$$

$$= \frac{5\times10^{-18}}{1.6\times10^{-19}} \approx 31\,\text{eV}$$

E_0 is measurable (binding energy of electron in the ground state of hydrogen atom is 13.6 eV)

(c) Mass of the oxygen atom is

$$m \sim 16 \times 1.6 \times 10^{-27}\ \text{kg}$$

The zero point is

$$E_0 = \frac{\hbar^2\pi^2}{2ma^2} = \frac{10\times10^{-68}}{2\times16\times1.6\times10^{-27}\times4\times10^{-20}}$$

$$\approx 5 \times 10^{-23}\ \text{J} = \frac{5\times10^{-23}}{1.6\times10^{-19}} = 3.1\times10^{-4}\ \text{eV}$$

E_0 is measurable.

Example 2 A particle of mass *m* moves in a potential $V(x)$ given by

$$\begin{aligned} V(x) &= \infty \quad \text{for} \quad x < 0 \\ &= 0 \quad \text{for} \quad 0 \le x \le a \\ &= V_0 \quad \text{for} \quad x > a \end{aligned}$$

Show that the bound state energies ($E < V_0$) are given by the equation

$$\tan\left[\frac{\sqrt{2mE}}{\hbar}a\right] = -\left[\frac{E}{V_0 - E}\right]^{1/2}$$

Solution: The Schrödinger equation in the region $0 \le x \le a$ is given by

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2m}{\hbar^2}E\,\psi_1(x) = 0$$

or
$$\frac{d^2\psi_1(x)}{dx^2} + k^2\,\psi_1(x) = 0 \qquad \text{...(i)}$$

where
$$k = \sqrt{\frac{2m}{\hbar^2}E} \qquad \text{...(ii)}$$

Considering $E < V_0$, the Schrödinger equation in the region $x > a$ is

$$\frac{d^2\psi_2(x)}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\,\psi_2(x) = 0$$

or

$$\frac{d^2\psi_2(x)}{dx^2} - \alpha\,\psi_2(x) = 0 \qquad \text{...(iii)}$$

where

$$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} \qquad \text{...(iv)}$$

We have the boundary conditions

$$\psi_1(0) = 0, \quad \psi_2(\infty) = 0 \qquad \text{...(v)}$$

In view of the above boundary conditions we get the solutions of Eqs. (i) and (iii) as

$$\psi_1(x) = A \sin kx = A \sin \sqrt{\frac{2mE}{\hbar^2}}\,x \qquad \text{...(vi)}$$

$$\psi_2(x) = B\,e^{-\alpha x} = B\,e^{-\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\,x} \qquad \text{...(vii)}$$

We also have the boundary conditions

$$\psi_1(a) = \psi_2(a)$$

and

$$\left(\frac{d\psi_1}{dx}\right)_{x=a} = \left(\frac{d\psi_2}{dx}\right)_{x=a}$$

Using the above conditions we obtain from Eqs. (vi) and (vii)

$$A \sin\left(\sqrt{\frac{2mE}{\hbar^2}}\,a\right) = B\,e^{-\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\,a}$$

and

$$\sqrt{\frac{2mE}{\hbar^2}}\,A \cos\left(\sqrt{\frac{2mE}{\hbar^2}}\,a\right) = -\sqrt{\frac{2mE}{\hbar^2}(V_0 - E)}\;B\,e^{-\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\,a}$$

Dividing we obtain from the two equations

$$\frac{\tan\left(\sqrt{\frac{2mE}{\hbar^2}}\,a\right)}{\sqrt{\frac{2mE}{\hbar^2}}} = \frac{-1}{\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}}$$

or
$$\tan\left(\sqrt{\frac{2mE}{\hbar^2}}\,a\right) = -\sqrt{\frac{2mE}{\hbar^2}\times\frac{\hbar^2}{2m(V_0 - E)}} = -\left[\frac{E}{V_0 - E}\right]^{1/2}$$

Example 3 A one-dimensional wavefunction for a particle of mass *m* is

$$\psi(x) = A\left(\frac{x}{x_0}\right)^n e^{-\frac{x}{x_0}}$$

where A, n and x_0 are constants. Using Schrödinger equation, find the potential function $V(x)$ and energy E such that above wavefunction is an energy eigenfunction (Take $V(x) \to 0$ as $x \to \infty$).

Solution

$$\psi(x) = A\left(\frac{x}{x_0}\right)^n e^{-\frac{x}{x_0}} \qquad \text{...(i)}$$

Differentiating Eq. (i) with respect to x we get

$$\frac{d\psi(x)}{dx} = A\frac{n}{x_0}\left(\frac{x}{x_0}\right)^{n-1} e^{-\frac{x}{x_0}} - A\left(\frac{x}{x_0}\right)^n \frac{1}{x_0} e^{\frac{-x}{x_0}}$$

Differentiating the above equation with respect to x we get

$$\frac{d^2\psi(x)}{dx^2} = A\frac{n(n-1)}{x_0^2}\left(\frac{x}{x_0}\right)^{n-2} e^{-\frac{x}{x_0}} - A\frac{n}{x_0^2}\left(\frac{x}{x_0}\right)^{n-1} e^{\frac{-x}{x_0}}$$

$$-A\frac{n}{x_0^2}\left(\frac{x}{x_0}\right)^{n-1} e^{-\frac{x}{x_0}} + A\frac{1}{x_0^2}\left(\frac{x}{x_0}\right)^n e^{\frac{-x}{x_0}}$$

$$= A\left(\frac{x}{x_0}\right)^n e^{-\frac{x}{x_0}}\left[\frac{n(n-1)}{x_0^2}\frac{x_0^2}{x^2} - \frac{2n}{x_0^2}\frac{x_0}{x} + \frac{1}{x_0^2}\right]$$

or
$$\frac{d^2\psi(x)}{dx^2} = \left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right]\psi(x) \qquad \text{...(ii)}$$

We have the Schrödinger equation

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2}[E - V(x)]\,\psi(x) \qquad \text{...(iii)}$$

Substituting Eqs. (i) and (ii) in Eq. (iii) we obtain

$$\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right]\psi(x) = -\frac{2m}{\hbar^2}[E - V(x)]\,\psi(x)$$

or $$E - V(x) = \frac{-\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right] \qquad \text{...(iv)}$$

Using the given condition, namely $V(x) \to 0$ as $x \to \infty$, in the above equation we get

$$E = \frac{-\hbar^2}{2m} \times \frac{1}{x_0^2} = \frac{-\hbar^2}{2mx_0^2} \qquad \text{...(v)}$$

Substituting Eq. (v) in Eq. (iv) we obtain

$$V(x) = E + \frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 + x} + \frac{1}{x_0^2}\right]$$

or $$V(x) = \frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x}\right] \qquad \text{...(vi)}$$

Example 4 A particle of mass m moves inside an infinite square well of width a. The energy eigenfunctions and energy eigenvalues are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2$$

Calculate the expectation values (a) $\langle x\rangle_n$, (b) $\langle p\rangle_n$, (c) $\langle x^2\rangle_n$ and (d) $\langle p^2\rangle_n$ and compare them with their classical values.

Solution:

(a) $$\langle x\rangle_n = \int_0^a \psi_n^*(x)\, x\psi_n(x)\, dx = \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi}{a}x\right)dx$$

$$= \frac{2}{a}\int_0^a x\left[\frac{1-\cos\left(\frac{2n\pi}{a}x\right)}{2}\right]dx$$

$$= \frac{1}{a}\left[\int_0^a x\,dx - \int_0^a x\cos\left(\frac{2n\pi}{a}x\right)dx\right]$$

The second integral is zero and hence we get

$$\langle x\rangle_n = \frac{a}{2}$$

(b) $\langle p\rangle_n = \int_0^a \psi_n^*(x)\,\hat{p}\,\psi_n(x)\,dx = -i\hbar\int_0^a \psi_n^*(x)\frac{d\psi_n(x)}{dx}dx$. $\psi_n(x)$ is a real function and so is $\frac{d\psi_n(x)}{dx}$ and as such the integral $\int_0^a \psi_n^*(x)\frac{d\psi_n(x)}{dx}dx$ is also real. Hence, we get $\langle p\rangle_n$ to be imaginary. But the expectation value of the momentum must be real. Hence we find

$$\langle p\rangle_n = 0$$

(c)

$$\langle x^2\rangle_n = \int_0^a \psi_n^*(x)\,x^2\,\psi_n(x)\,dx$$

$$= \frac{2}{a}\int_0^a x^2\sin^2\left(\frac{n\pi}{a}x\right)dx = \frac{1}{a}\int_0^a x^2\left[1-\cos\left(\frac{2n\pi}{a}x\right)\right]dx$$

$$= \frac{1}{a}\int_0^a x^2 dx - \frac{1}{a}\int_0^a x^2\cos\left(\frac{2n\pi}{a}x\right)dx$$

Integrating the second integral by parts we get

$$\langle x^2\rangle_n = \frac{a^2}{3} - \frac{1}{a}\left[\left\{\frac{x^2\sin\left(\frac{2n\pi}{a}\right)x}{\frac{2n\pi}{a}}\right\}_o^a - \frac{a}{2n\pi}\int_o^a \sin\left(\frac{2n\pi}{a}\right)x\,2dx\right]$$

or

$$\langle x^2\rangle_n = \frac{a^2}{3} - \frac{a^2}{2\pi^2 n^2}$$

(d)

$$\langle p^2\rangle_n = \int_0^a \psi_n^*(x)(-\hbar^2)\frac{d^2\psi_n(x)}{dx^2}dx$$

$$= +\hbar^2\int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\sqrt{\frac{2}{a}}\frac{n^2\pi^2}{a^2}\sin\left(\frac{n\pi}{a}x\right)dx$$

$$= \hbar^2 \frac{2}{a} \frac{n^2\pi^2}{a^2} \int_0^a \sin^2\left(\frac{n\pi}{a} x\right) dx$$

$$= \frac{\pi^2\hbar^2}{a^2} n^2 \int_0^a |\psi_n(x)|^2 \, dx$$

or
$$\langle p^2 \rangle_n = \frac{\pi^2\hbar^2}{a^2} n^2$$

We may also express the above result as

$$\langle p^2 \rangle_n = 2mE_{n.}$$

Classical average values are

$$x_{av} = \frac{a}{2}$$

$$p_{av} = 0$$

$$x_{av}^2 = \frac{a^2}{3}$$

$$p_{av}^2 = 2mE$$

We observe that in the limit of large quantum number (n large)

$$\langle x^2 \rangle_n = \frac{a^2}{3} = x_{av}^2$$

Example 5 A particle of mass m moves inside an infinite square well of width a. The energy eigenfunctions and energy eigenvalues are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

$$E_n = \frac{\pi^2\hbar^2}{2ma^2} n^2$$

Calculate (a) the uncertainty product $\Delta x_n \, \Delta p_n$ and (b) estimate the zero point energy.

Solution: As shown in the previous example (example 4) we have

$$\langle x \rangle_n = \frac{a}{2}, \langle x^2 \rangle_n = \frac{a^2}{3} - \frac{a^2}{2\pi^2 n^2}$$

$$\langle p \rangle_n = 0 \;\; \langle p^2 \rangle_n = \frac{\pi^2\hbar^2}{a^2} n^2$$

We get, by definition, the uncertainty in the measured value of x_n

$$\Delta x_n = \sqrt{\langle x^2 \rangle_n - (\langle x \rangle_n)^2} = \sqrt{\frac{a^2}{3} - \frac{a^2}{2\pi^2 n^2} - \frac{a^2}{4}}$$

$$= a\sqrt{\frac{1}{12} - \frac{1}{2\pi^2 n^2}}$$

Similarly, the uncertainty in the measured value of p_n is

$$\Delta p_n = \sqrt{\langle p^2 \rangle_n - (\langle p^2 \rangle_n)^2} = \sqrt{\frac{\pi^2 \hbar^2}{a^2} n^2 - 0} = \frac{\pi\hbar}{a} n$$

We thus get

$$\Delta x_n \, \Delta p_n = \frac{\pi\hbar}{a} n \, a\sqrt{\frac{1}{12} - \frac{1}{2\pi^2 n^2}}$$

$$= \pi\hbar \, n\sqrt{\frac{1}{12} - \frac{1}{2\pi^2 n^2}}$$

(b) We have obtained

$$\Delta p_n = \frac{\pi\hbar}{a} n$$

For the ground state ($n = 1$) we get

$$(\Delta p)_{\text{ground state}} = \frac{\pi\hbar}{a}$$

Clearly, in the ground state the particle possesses kinetic energy which is the minimum kinetic energy, also called the zero point energy. We get,

$$\text{Zero point energy} = \frac{[(\Delta p)_{\text{ground state}}]^2}{2m}$$

$$= \frac{\pi^2 \hbar^2}{2ma^2}$$

6

Linear Harmonic Oscillator Problems

Quantum mechanical treatment of a linear harmonic oscillator is of considerable importance. Many physical systems in the microscopic domain can be approximated as linear harmonic oscillator and hence quantum mechanical behaviour of a linear harmonic oscillator becomes a necessity for a thorough understanding of such systems. As for example, we can understand vibrations of diatomic and polyatomic molecules and hence vibrational spectra of molecules, vibrations in solids, electronic specific heats of solids, detailed theory of emission/absorption of radiation, etc., on the basis of the results of quantum mechanical treatment of a linear harmonic oscillator.

6.1 LINEAR HARMONIC OSCILLATOR IN CLASSICAL MECHANICS

Consider a particle of mass m undergoing simple harmonic oscillation along the x-axis with a frequency ν_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

$$x = x_0 \sin \omega_0 t \qquad \text{...(1)}$$

The force constant k (restoring force acting on the particle per unit displacement) is related to the frequency ω_0 as

$$k = m\omega_0^2 \qquad \text{...(2)}$$

The kinetic energy of the oscillator is

$$T = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}m\, x_0^2\, \omega_0^2 \cos^2 \omega_0 t$$

$$= \frac{1}{2}m\,\omega_0^2\, x_0^2\,(1-\sin^2 \omega_0 t)$$

or

$$T = \frac{1}{2}m\,\omega_0^2\,(x_0^2 - x^2) \qquad \text{...(3)}$$

The potential energy of the oscillator is

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\,\omega_0^2\, x^2 \qquad \text{...(4)}$$

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 Eq. (3) and (4) we obtain

$$E = \frac{1}{2} m \omega_0^2 x_0^2 \qquad \text{...(5)}$$

We find for an oscillator of given frequency and given amplitude the total energy to be a constant.

6.2 TIME-INDEPENDENT SCHRÖDINGER EQUATION FOR AN OSCILLATOR

In the following we treat the oscillator described in the preceding section using the quantum mechanical concepts.

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

$$\frac{d^2\psi(x)}{dx^2} + \frac{2\mathrm{m}}{\hbar^2}[E - V(x)]\,\psi(x) = 0 \qquad \text{...(6)}$$

Using the expression for $V(x)$ given by Eq. (4), Eq. (6) becomes

$$\frac{d^2\psi(x)}{dx^2} + \frac{2\mathrm{m}}{\hbar^2}\left[E - \frac{1}{2} m \omega_0^2 x^2\right]\psi(x) = 0 \qquad \text{...(7)}$$

For the convenience of solving Eq. (7), we define a new variable y and a new parameter λ as

$$y = \left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}} x \qquad \text{...(8)}$$

and

$$\lambda = \frac{2E}{\hbar\omega_0} \qquad \text{...(9)}$$

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,

$$\frac{d\psi(x)}{dx} = \frac{d\psi(y)}{dy}\frac{dy}{dx} = \left(\frac{m\omega_0}{\hbar}\right)^{1/2} \frac{d\psi(y)}{dy} \qquad \text{[using Eq. (8)]}$$

and

$$\frac{d^2\psi(x)}{dx^2} = \frac{d}{dx}\frac{d\psi(x)}{dx} = \frac{d}{dx}\left[\left(\frac{m\omega_0}{\hbar}\right)^{1/2}\frac{d\psi(y)}{dy}\right]$$

$$= \left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}}\frac{d}{dx}\left(\frac{d\psi(y)}{dy}\right)\frac{dy}{dx}$$

or $$\frac{d^2\psi(x)}{dx^2} = \frac{m\omega_0}{\hbar}\frac{d^2\psi(y)}{dy^2} \qquad \text{...(10)}$$

Using Eqs. (8), (9) and (10) in Eq. (7) we get

$$\frac{m\omega_0}{\hbar}\frac{d^2\psi(y)}{dy^2} + \left[\frac{2m}{\hbar^2}E - \frac{2m}{\hbar^2}\times\frac{1}{2}m\,\omega_0^2\,\frac{\hbar}{m\omega_0}y^2\right]\psi(y) = 0$$

or $$\frac{d^2\psi(y)}{dy^2} + \left[\frac{2E}{\hbar\omega_0} - y^2\right]\psi(y) = 0$$

or $$\frac{d^2\psi(y)}{dy^2} + [\lambda - y^2]\,\psi(y) = 0 \qquad \text{...(11)}$$

Equation (11) is the time independent Schrödinger equation for the oscillator.

The solution of Eq. (11) yields $\psi(y)$ and hence the wave function $\psi(x)$ for the oscillator.

6.3 SOLUTION OF THE WAVE EQUATION

6.3.1 Asymptotic Solution

Asymptotic solution of the wave equation is the solution of Eq. (11) in the limit $y \to \infty$ or $x \to \infty$. In this limit

$$\lambda - y^2 \to -y^2$$

so that Eq. (11) reduces to

$$\frac{d^2\psi(y)}{dy^2} - y^2\,\psi(y) = 0$$

or $$\frac{d^2\psi(y)}{dy^2} = y^2\,\psi(y) \qquad \text{...(12)}$$

The general solution of Eq. (12) may be taken as

$$\psi(y) = e^{\frac{+y^2}{2}} \text{ and } \psi(y) = e^{\frac{-y^2}{2}}$$

i.e., as

$$\psi(y) = e^{\pm\frac{y^2}{2}} \qquad ...(13)$$

The above can be easily seen. We get from eq. (13):

$$\frac{d\psi(y)}{dy} = \pm\, y\, e^{\pm\frac{y^2}{2}}, \quad \frac{d^2\psi(y)}{dy^2} = (y^2+1)\, e^{\pm\frac{y^2}{2}} = y^2\, e^{\pm\frac{y^2}{2}} = y^2\psi(y)$$

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 $|x| \to \infty$. We thus have the asymptotic solution for the oscillator

$$\psi(y) = e^{-\frac{y^2}{2}} \qquad ...(14)$$

In terms of the variable x, the asymptotic solution can be expressed as

$$\psi(x) = e^{-\frac{m\omega_0}{2\hbar}x^2} \qquad ...(15)$$

6.3.2 Exact Solution: Recursion Formula

In view of the asymptotic solution given by Eq. (14), we may express the exact solution of the wave equation for the oscillator given by Eq. (11) as

$$\psi(y) = e^{-\frac{y^2}{2}}\, H(y) \qquad ...(16)$$

where $H(y)$ is a function of y such that the product $e^{-\frac{y^2}{2}}\, H(y)$ tends to zero as $|y| \to \infty$ or $|\infty| \to \infty$ as is required by the asymptotic solutions given by Eq. (14) or Eq. (15).

From Eq. (16) we obtain

$$\frac{d\psi(y)}{dy} = e^{\frac{-y^2}{2}}\frac{dH(y)}{dy} - y\, e^{\frac{-y^2}{2}}\, H(y)$$

$$= \left[\frac{dH(y)}{dy} - y\, H(y)\right] e^{\frac{-y^2}{2}}$$

and

$$\frac{d^2\psi(y)}{dy^2} = \frac{d^2H(y)}{dy^2}\, e^{\frac{-y^2}{2}} - y\, e^{\frac{-y^2}{2}}\frac{dH(y)}{dy} + y^2 H(y)\, e^{\frac{-y^2}{2}} - y\, e^{\frac{-y^2}{2}}\frac{dH(y)}{dy} - H(y)\, e^{\frac{-y^2}{2}}$$

or

$$\frac{d^2\psi(y)}{dy^2} = \left[\frac{d^2H(y)}{dy^2} - 2y\frac{dH(y)}{dy} + (y^2-1)\, H(y)\right] e^{\frac{-y^2}{2}} \qquad ...(17)$$

Substituting Eqs. (16) and (17) in Eq. (11) we get

$$\left[\frac{d^2H(y)}{dy^2} - 2y\frac{dH(y)}{dy} + (y^2 - 1)\,H(y)\right]e^{\frac{-y^2}{2}} + (\lambda - y^2)\,H(y)\,e^{\frac{-y^2}{2}} = 0$$

or $$\frac{d^2H(y)}{dy^2} - 2y\frac{dH(y)}{dy} + (\lambda - 1)\,H(y) = 0 \qquad ...(18)$$

We find that the function $H(y)$ in the exact solution of the Schrödinger equation for the oscillator given by Eq. (16) satisfies the *Hermite differential equation*.

Power series solution

We now assume a power series solution of Eq. (18) of the type

$$H(y) = \sum_{r=0}^{\infty} a_r\, y^{s+r} \qquad ...(19)$$

where r takes integral values including zero. Equation (19) gives

$$\frac{dH(y)}{dy} = \sum_{r=0}^{\infty} a_r (s+r)\, y^{s+r-1} \qquad ...(20)$$

and

$$\frac{d^2H(y)}{dy^2} = \sum_{r=0}^{\infty} a_r (s+r)(s+r-1)\, y^{s+r-2} \qquad ...(21)$$

Substituting Eqs. (19), (20) and (21) in Eq. (18) we obtain

$$\sum_{r=0}^{\infty} a_r (s+r)(s+r-1)\, y^{s+r-2} - 2\sum_{r=0}^{\infty} a_r (s+r)\, y^{s+r} + (\lambda - 1)\sum_{r=0}^{\infty} a_r\, y^{s+r} = 0$$

Dividing throughout by y^{s-2}, the above becomes

$$\sum_{r=0}^{\infty} a_r (s+r)(s+r-1)\, y^{r} - \sum_{r=0}^{\infty} a_r (2s+2r-\lambda+1)\, y^{r+2} = 0$$

or $$a_0\, s(s-1)\, y^0 + a_1\, s(s+1)\, y^1 + \sum_{r=2}^{\infty} [a_r\,(s+r)\,(s+r-1) - a_{r-2}\,(2s+2r-3-\lambda)]\, y^r = 0 \qquad ...(22)$$

For Eq. (22) 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

$$a_0\, s(s-1) = 0 \qquad ...(23)$$

$$a_1\, s(s+1) = 0 \qquad ...(24)$$

$$a_r(s + r)\,(s + r - 1) - a_{r-2}\,(2s + 2r - 3 - \lambda) = 0 \qquad ...(25)$$

Equation (25) gives

$$a_r = \frac{2s + 2r - 3 - \lambda}{(s + r)\,(s + r - 1)}\,a_{r-2}; \quad (r \geq 2) \qquad ...(26)$$

Equation (26) is called the *recurrence relation.*

As $a_0 \neq 0$, we have according to Eq. (23)

$$s = 0 \quad \text{or} \quad s = 1 \qquad ...(27)$$

According to Eq. (24) we may have

$$a_1 = 0 \quad \text{or} \quad s = 0 \quad \text{or} \quad s = -1 \qquad ...(28)$$

Since $s \neq -1$ we get either $a_1 = 0$ or $s = 0$ or both.

The recurrence relation given by Eq. (26) allows us to calculate all the even coefficients in terms of a_0 and all odd coefficients in terms of a_1. Equation (19) will have only odd coefficients if $a_0 = 0$ and only even coefficients if $a_1 = 0$. We thus have two independent solutions of Eq. (19). A linear combination of these two solutions gives the most general solution of Eq. (19).

Considering the root $s = 0$, Eq. (26) gives

$$a_r = \frac{2r - 3 - \lambda}{r(r - 1)}\,a_{r-2}\ (r \geq 2) \qquad ...(29)$$

The above equation yields the even coefficients as

$$\left.\begin{aligned} a_2 &= \frac{1-\lambda}{2\times 1}\,a_0 = \frac{1-\lambda}{21}\,a_0 \\ a_4 &= \frac{5-\lambda}{4\times 3}\,a_2 = \frac{(5-\lambda)\,(1-\lambda)}{4!}\,a_0 \end{aligned}\right\}\text{etc.} \qquad ...(30)$$

and the odd coefficients as

$$\left.\begin{aligned} a_3 &= \frac{3-\lambda}{3\times 2}\,a_1 = \frac{3-\lambda}{3!}\,a_1 \\ a_5 &= \frac{7-\lambda}{5\times 4}\,a_3 = \frac{(7-\lambda)\,(3-\lambda)}{5\times 4\times 3!}\,a_1 = \frac{(7-\lambda)\,(3-\lambda)}{5!}\,a_1 \end{aligned}\right\}\text{etc.} \qquad ...(31)$$

With $s = 0$, the solution given by Eq. (19) becomes

$$H(y) = \sum_{r=0}^{\infty} a_r\, y^r$$

The above can be written conveniently as

$$H(y) = (a_0 + a_2y^2 + a_4y^4 + ...) + (a_1y + a_3y^3 + a_5y^5 + ...)$$

Using the results given by Eqs. (30) and (31), the above gives

$$H(y) = a_0\left[1+\frac{1-\lambda}{2!}y^2+\frac{(5-\lambda)(1-\lambda)}{4!}y^4+...\right]+a_1\left[y+\frac{3-\lambda}{3!}y^3+\frac{(7-\lambda)(3-\lambda)}{5!}y^5+...\right] \quad ...(32)$$

An inspection of Eq. (32) shows the following:

(1) for $\lambda = 1, 5, 9$, etc., the first series in eq. (32) 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

$$\lambda = (2n + 1), \quad n = 0, 1, 2, ... \quad ...(33)$$

one of the solutions is a polynomial.

6.4 ENERGY EIGENVALUES OF THE OSCILLATOR

Equation (29) 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

$$\frac{a_r}{a_{r-2}} \rightarrow \frac{2}{r} \quad ...(34)$$

From the above we obtain

$$\underset{r\to\infty}{\text{Lt}}\frac{a_r}{a_{r-2}} = 0 \quad ...(35)$$

Thus under the condition given by Eq. (33), both the infinite series in Eq. (32) converage for all values of y.

We have the Taylor series expansion of e^{y^2} as

$$e^{y^2} = 1+y^2+\frac{y^4}{2!}+\frac{y^6}{3!}+...$$

$$= \sum_{r=0,2,4...}\frac{1}{(r/2)!}y^r$$

Writing

$$b_r = \frac{1}{(r/2)!}... \quad ...(36)$$

we get

$$e^{y^2} = \sum_{r=0,24,...} b_r y^r \quad ...(37)$$

The ratio of the coefficients of the successive terms in Eq. (37) is

$$\frac{b_r}{b_{r-2}} = \frac{\dfrac{1}{(r/2)!}}{\dfrac{1}{\left(\dfrac{r}{2}-1\right)!}} = \frac{\left(\dfrac{r}{2}-1\right)!}{\left(\dfrac{r}{2}\right)!} = \frac{2}{r} \qquad ...(38)$$

In view of Eqs. (34) and (38) we may write

$$\frac{a_r}{a_{r-2}} = \frac{b_r}{b_{r-2}} \text{ (for large } r) \qquad ...(39)$$

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 Eq. (32) while it will behave like $y\, e^{y^2/2}$ if $H(y)$ is given by the second (or odd) series in Eq. (32). This is not physically acceptable. This unrealistic situation is resolved if the infinite series in Eq. (19) terminates after a certain number of terms so that $\psi(y) \to 0$ as $y \to \pm\infty$ 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 λ 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

$$\lambda = 2n + 1, \quad n = 0, 1, 2, ... \qquad ...(40)$$

Using λ given by Eq. (9) in Eq. (40) we get

$$\frac{2E}{\hbar\omega_0} = 2n + 1$$

or

$$E = \frac{2n+1}{2}\hbar\omega_0 = \left(n + \frac{1}{2}\right)\hbar\omega_0 \qquad ...(41)$$

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 $\hbar\omega_0$.

6.5 ENERGY EIGENFUNCTIONS OF THE OSCILLATOR

As seen in the last section, for the wave function of the oscillator to satisfy the boundary conditions ($\psi(y) \to 0$ as $y \to \pm\infty$), the parameter λ should take the value $(2n + 1)$ where n is a positive integer including zero.

When $\lambda = (2n + 1)$, $H(y)$ in Eq. (18) can be conveniently replaced by $H_n(y)$ to get

$$\frac{d^2H_n(y)}{dy^2} - 2y\frac{dH_n(y)}{dy} + (2n + 1 - 1)\, H_n(y) = 0$$

or
$$\frac{d^2 H_n(y)}{dy^2} - 2y\frac{dH_n(y)}{dy} + 2n\, H_n(y) = 0 \qquad ...(42)$$

The solution of Eq. (42) is the well known Hermite polynomial of degree n given by

$$H_n(y) = (-1)^n\, e^{y^2} \frac{d^n}{dy^n}\,(e^{-y^2}) \qquad ...(43)$$

We may note the following recurrence relation that holds between $H_{n-1}(y)$, $H_n(y)$ and $H_{n+1}(y)$

$$H_{n+1}(y) = 2y\, H_n(y) - 2n\, H_{n-1}(y) \qquad ...(44)$$

Hermite polynomials of different degrees may be obtained from Eq. (43)

$$\begin{aligned} n &= 0, \quad H_0(y) = 1 \\ n &= 1, \quad H_1(y) = 2y \\ n &= 2, \quad H_2(y) = 4y^2 - 2 \\ n &= 3, \quad H_3(y) = 8y^3 - 12y \quad \text{etc.} \end{aligned} \qquad ...(45)$$

We may obtain the Hermite polynomials of higher degrees using Eqs. (45) and the Eq. (44).

The energy eigenfunctions of the oscillator given by Eq. (14) can now be expressed in the most general form as

$$\psi_n(y) = N_n\, H_n(y)\, e^{-y^2/2} \qquad ...(46)$$

or
$$\psi_n(x) = N_n\, e^{\frac{-m\omega_0}{2\hbar}x^2}\, H_n\left(\sqrt{\frac{m\omega_0}{\hbar}}\,x\right) \qquad ...(47)$$

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 Eq. (46) 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

$$N_n = \left[\left(\frac{m\omega_0}{\hbar\pi}\right)^{\frac{1}{2}} \frac{1}{2^n(n!)}\right]^{\frac{1}{2}} \qquad \text{...(48)}$$

Using N_n given by Eq. (48) in Eq. (47), we obtain the normalized energy eigenfunctions of the oscillator to be given as

$$\psi_n(x) = \left[\left(\frac{m\omega_0}{\hbar\pi}\right)^{1/2} \frac{1}{2^n(n!)}\right]^{1/2} e^{\frac{-m\omega_0}{2\hbar}x^2} H_n\left(\sqrt{\frac{m\omega_0}{\hbar}}\, x\right) \qquad \text{...(49)}$$

In the following table are given the energy eigenfunctions, representing the quantized states of the oscillator and the corresponding energy eigenvalues

State	*Energy eigenfunctions*	*Energy eigenvalue*
Ground state	$\psi_0(x) = \left(\frac{m\omega_0}{\hbar\pi}\right)^{\frac{1}{4}} e^{\frac{-m\omega_0}{2\hbar}x^2}$	$\frac{1}{2}\hbar\omega_0$
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	$\psi_2(x)$ $= \frac{1}{2^{3/2}}\left[\frac{m\omega_0}{\pi\hbar}\right]^{\frac{1}{4}}\left(\frac{4m\omega_0}{\hbar}x^2 - 2\right) e^{\frac{-m_0\omega_0}{2\hbar}x^2}$	$\frac{5}{2}\hbar\omega_0$, etc.

Some of the energy eigenfunctions $\psi_n(x)$, the corresponding energy eigenvalues E_n, the potential energy function $V(x)$ are shown in the Fig. 6.1.

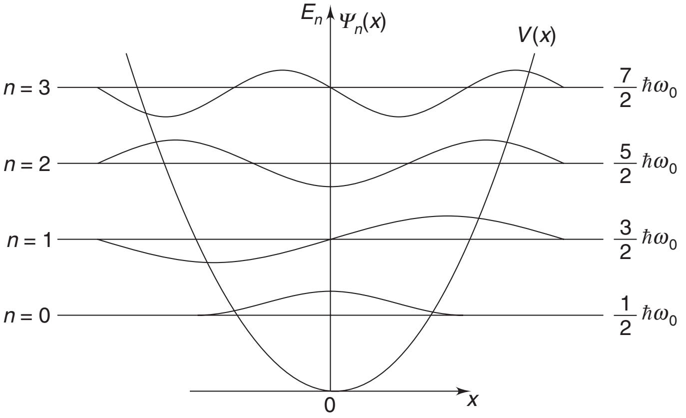


Fig. 6.1 Normalized wave functions $\psi_n(x)$ for $n = 0, 1, 2, 3$
Energy eigenvalues E_n for $n = 0, 1, 2, 3$
The potential energy function $V(x)$

The probability of finding the oscillating particle between x and $x + dx$ when the oscillator is in the n^{th} state described by the wavefunction $\psi_n(x)$ and according to the definition is given by

$$P_n(x)\, dx = \psi_n^*(x)\, \psi_n(x)\, dx = |\psi_n(x)|^2\, dx \qquad \text{...(50)}$$

Using Eq. (49) in Eq. (50) 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 Fig. 6.2.

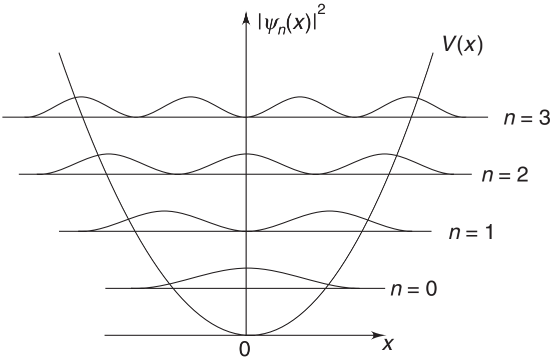


Fig. 6.2 Probability density $|\psi_n(x)^2|$ for n = 0, 1, 2, 3. Potential energy function $v(x)$

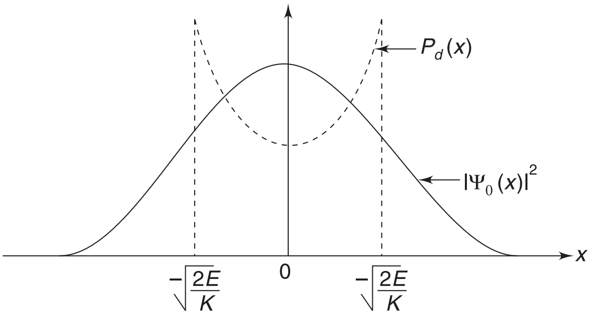


Fig. 6.3

6.6 DISCUSSIONS

From the wave mechanical treatment of linear harmonic oscillator presented in the preceeding 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

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0, \quad n = 0, 1, 2, ... \qquad ...(51)$$

In the lowest or the ground state, which corresponds to $n = 0$, the oscillator has the finite energy

$$E_0 = \frac{1}{2}\hbar\omega_0 \qquad ...(52)$$

which is called the *zero-point energy*.

According to old quantum theory, the energy values of the oscillator are given by

$$E_n = n\hbar\omega_0, \quad n = 0, 1, 2, ... \qquad ...(53)$$

A comparison of the result given by Eq. (53) with that given by Eq. (51) 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.

(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 form Fig. 6.1.

(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 form the above, the velocity of the oscillator at the position $\pm x$ to be

$$v = \left[\frac{2E - kx^2}{m}\right]^{1/2} \qquad ...(54)$$

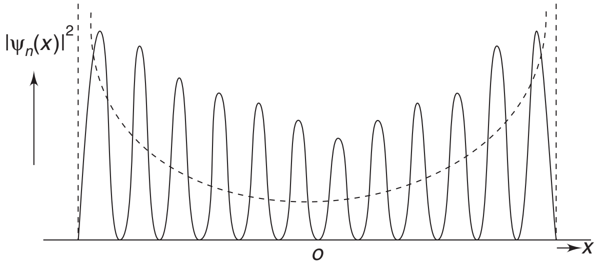


Fig. 6.4 Solid curve represents the variation of $|\psi_{10}(x)|^2$ with *x*. Dotted curve represents the probability density of a classical oscillator of the same total energy.

Classically, the probability of finding the oscillator at the position ±*x* is inversely proportional to the velocity, i.e.

$$P_{cl}(x) \propto \sqrt{\frac{m}{2E - kx^2}} \qquad \text{...(55)}$$

We find the probability to be the minimum at the mean position ($x = 0$) and maximum at the two extreme positions $\left(x_0 = \pm\sqrt{\dfrac{2E}{k}}\right)$. This is shown by the dotted curve in Fig. 6.3.

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 Fig. 6.3. Figure 6.2 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 Fig. 6.4 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 $|\psi_n(x)|^2$.

6.7 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 $\hat{x} \equiv x$ and $\hat{p} = -i\hbar\dfrac{d}{dx}$, 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

$$[\hat{x},\ \hat{p}] = i\hbar \qquad \text{...(56)}$$

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

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\,x^2 \qquad \text{...(57)}$$

Let us introduce two operators $\hat{a}$ and $\hat{a}^\dagger$ according to

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\,x + i\sqrt{\frac{1}{2m\hbar\omega_0}}\,\hat{p} \qquad \text{...(58)}$$

and

$$\hat{a}^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}}\,x - i\sqrt{\frac{1}{2m\hbar\omega_0}}\,\hat{p} \qquad \text{...(59)}$$

In the above $\hat{a}^\dagger$ is the Hermitian adjoint of $\hat{a}$ and ω_0 is the natural angular frequency of the oscillator. From Eqs. (58) and (59) we obtain

$$\hat{a}\hat{a}^\dagger = \left(\sqrt{\frac{m\omega_0}{2\hbar}}\,x + i\sqrt{\frac{1}{2m\hbar\omega_0}}\,\hat{p}\right)\left(\sqrt{\frac{m\omega_0}{2\hbar}}\,x - i\sqrt{\frac{1}{2m\hbar\omega_0}}\,\hat{p}\right)$$

$$= \frac{m\omega_0}{2\hbar}x^2 + \frac{1}{2m\hbar\omega_0}\hat{p}^2 + \frac{i}{2\hbar}(\hat{p}x - x\hat{p})$$

Using Eq. (56) 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

$$\hat{a}\hat{a}^\dagger = \frac{\hat{H}}{\hbar\omega_0} + \frac{1}{2} \qquad \text{[using Eq. (57)]} \qquad \text{...(60)}$$

Similarly, we obtain

$$\hat{a}^\dagger \hat{a} = \frac{\hat{H}}{\hbar\omega_0} - \frac{1}{2} \qquad \text{...(61)}$$

Adding Eqs. (60) and (61) we obtain

$$2\frac{\hat{H}}{\hbar\omega_0} = \hat{a}\hat{a}^\dagger + \hat{a}^\dagger \hat{a}$$

or

$$\hat{H} = \frac{1}{2}\hbar\omega_0(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}) \qquad \text{...(62)}$$

Subtracting Eq. (61) from Eq. (60) 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

$$[\hat{a}, \hat{a}^\dagger] = 1 \qquad \text{...(63)}$$

We may also express the Hamiltonian operator $\hat{H}$ as

$$\hat{H} = \hbar\omega_0\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) \qquad \text{...(64)}$$

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 eignvalues $\hat{H}$ and that of $\hat{a}^\dagger \hat{a}$ bear the same relationship.

Eigenvalues of $\hat{a}^\dagger \hat{a}$

We have

$$[\hat{a}^\dagger \hat{a}, a] = \hat{a}^\dagger \hat{a}\hat{a} - \hat{a}\hat{a}^\dagger \hat{a} = (\hat{a}^\dagger \hat{a} - \hat{a}\hat{a}^\dagger)\ \hat{a} = -(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a})\ \hat{a}$$

Using the result given by Eq. (63) in the above we obtain

$$[\hat{a}^\dagger \hat{a}, \hat{a}] = -\hat{a} \qquad \text{...(65)}$$

Also we have

$$[\hat{a}^\dagger \hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger \hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a}^\dagger \hat{a} = \hat{a}^\dagger\ (\hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a}) = \hat{a}^\dagger \qquad \text{...(66)}$$

Let ψ be an eigenfunction of the operator $\hat{a}^\dagger \hat{a}$ belonging to eigenvalue λ, i.e.

$$\hat{a}^\dagger \hat{a}\psi = \lambda\psi \qquad \text{...(67)}$$

We now have

$$
\begin{aligned}
(\hat{a}^\dagger \hat{a})\ (\hat{a}\psi) &= (\hat{a}\hat{a}^\dagger - 1)\ (\hat{a}\psi) && \text{[using Eq. (63)]} \\
&= \hat{a}\hat{a}^\dagger \hat{a}\psi - \hat{a}\psi \\
&= \hat{a}\lambda\psi - \hat{a}\psi && \text{[using Eq. (67)]}
\end{aligned}
$$

or

$$(\hat{a}^\dagger \hat{a})\ (\hat{a}\psi) = (\lambda - 1)\ \hat{a}\psi \qquad \text{...(68)}$$

Similarly, we get

$$(\hat{a}^\dagger \hat{a})\,(\hat{a}^\dagger\psi) = (\lambda + 1)\;\hat{a}^\dagger\psi \qquad \text{...(69)}$$

Equations (68) and (69) 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 ψ 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 $(\lambda - 1)$, $(\lambda - 2)$, ... must terminate before the negative value is reached and also the sequence $\hat{a}\psi$, $\hat{a}^2\psi$, ... must terminate.

Denoting the limiting eigenfunction (the last of the eigenfunctions) in the sequence as ψ_0 we obtain

$$\hat{a}\psi_0 = 0 \qquad \text{...(70)}$$

The above gives

$$\hat{a}^\dagger \hat{a}\psi_0 = 0 = 0 \times \psi_0 \qquad \text{...(71)}$$

indicating that ψ_0 is an eigenfunction of the operator $\hat{a}^\dagger \hat{a}$ belonging to the eigenvalue 0.

In view of Eq. (69) we then obtain

$$\begin{aligned} \hat{a}^+ \hat{a}\;(\hat{a}^\dagger\psi_0) &= 1 \times (\hat{a}^\dagger\psi_0) \\ \hat{a}^\dagger \hat{a}\;[(\hat{a}^\dagger)^2\,\psi_0] &= 2 \times (\hat{a}^\dagger)^2\,\psi_0 \\ \hat{a}^\dagger \hat{a}\;[(\hat{a}^\dagger)^3\,\psi_0] &= 3(\hat{a}^\dagger)^3\,\psi_0, \quad \text{etc.} \end{aligned} \qquad \text{...(72)}$$

or generalizing, we get

$$\hat{a}^\dagger \hat{a}\;[(\hat{a}^\dagger)^n\,\psi_0] = n(\hat{a}^\dagger)^n\,\psi_0 \qquad \text{...(73)}$$

We observe that the eigenvalue spectrum of the operator $\hat{a}^\dagger \hat{a}$ consists of a set of positive integers n. Equation (73) when applied to Eq. (64) gives

$$\hat{H}\,[(\hat{a}^\dagger)^n\,\psi_0] = \hbar\omega_0\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\left[(\hat{a}^\dagger)^n\psi_0\right] = \hbar\omega_0\left(n + \frac{1}{2}\right)(\hat{a}^\dagger)^n\psi_0$$

Thus the energy eigenvalues of the oscillator are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0, \quad n = 0, 1, 2, \ldots \qquad \text{...(75)}$$

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 $-i\hbar \dfrac{d}{dx}$ in Eqs. (58) and (59) 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 Eq. (70) 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

$$\psi_0 = N_0\ e^{\frac{-m\omega_0 x^2}{2\hbar}}, \quad N_0 = \text{a constant} \qquad ...(76)$$

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

$$\psi_1 = \hat{a}^{\dagger}\psi_0 = \frac{1}{(2m\hbar\omega_0)^{1/2}}\left(m\omega_0 x - \hbar \frac{d}{dn}\right)N_0\ e^{\frac{-m\omega_0 x^2}{2\hbar}}$$

or $$\psi_1 = \frac{N_0}{(2m\hbar\omega_0)^{1/2}}\left(m\omega_0 x - \hbar \frac{d}{dx}\right)e^{\frac{-m\omega_0 x^2}{2\hbar}}$$

$$= N_1\left(m\omega_0 x - \hbar \frac{d}{dx}\right)e^{\frac{-m\omega_0 x^2}{2\hbar}} \qquad ...(77)$$

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

$$\psi_n = N_n\left(m\omega_0 x - \hbar\frac{d}{dx}\right)^n e^{\frac{-m\omega_0 x^2}{2\hbar}} \qquad \text{...(78)}$$

ψ_n given by Eq. (78) is the same as the eigenfunction for the oscillator obtained using the previous method.

6.8 SOLVED EXAMPLES

Example 1 Find the probability density at the position *x* of a linear harmonic oscillator of mass *m* and natural angular frequency ω_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

$$\frac{dP(x)}{dx} = 0$$

or

$$\left(\frac{m\omega_0}{\hbar\pi}\right)^{1/2} e^{\frac{-m\omega_0}{\hbar}x^2}\, x\left(\frac{-m\omega_0}{\hbar}\right)2x = 0$$

The above gives $x = 0$. Thus the probability density is the maximum at the mean position ($x = 0$). The maximum probability density is clearly

$$P_{\max} = P(0) = \left(\frac{m\omega_0}{\hbar\pi}\right)^{1/2}$$

Example 2 A linear harmonic oscillator is described at some instant of time by the wavefunction $\psi = a\psi_0 + b\psi_1$, where ψ_0 and ψ_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

$$a^2 + b^2 = 1 \qquad \text{...(i)}$$

since $\int \psi_0^2 \, dx = 1; \int \psi_1^2 \, dx = 1$ and $\int \psi_0 \psi_1 \, dx = 0$ (ψ_0 and ψ_1 being orthogonal)

Now

$$\langle x \rangle = \int (a\psi_0 + b\psi_1) \, x(a\psi_0 + b\psi_1) \, dx$$

$$= \int x(a\psi_0 + b\psi_1)^2 \, dx$$

or

$$\langle x \rangle = 2ab \int \psi_0 \, x \, \psi_1 \, dx \qquad \text{...(ii)}$$

Since a and b are not zero, in general, we get $\langle x \rangle \neq 0$.

(b) We may write the result given by Eq. (ii), in view of Eq. (i) as

$$\langle x \rangle = [1 - (a^2 + b^2 - 2ab)] \int \psi_0 \, x \, \psi_1 \, dx$$

or

$$\langle x \rangle = [1 - (a - b)^2] \int \psi_0 x \psi_1 \, dx \qquad \text{...(iii)}$$

From the above we find for $\langle x \rangle$ to be the maximum

$$a - b = 0$$

or

$$a = b = \frac{1}{\sqrt{2}} \quad \text{(using eq. (i))}$$

(c) From eq. (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 eV undergoes harmonic oscillation of angular frequency ω_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

$$E = \langle T\rangle + \langle V\rangle = 2\langle V\rangle = 2 \times \frac{1}{2}\, m_0\, \omega_0^2 \,\langle x^2\rangle \qquad \text{...(i)}$$

Since the particle is confined in the ground state we have

$$E = \frac{1}{2}\hbar\omega_0 \qquad \text{...(ii)}$$

From (i) and (ii) we have

$$\frac{1}{2}\hbar\omega_0 = m_0\omega_0^2 \,\langle x^2\rangle$$

or

$$\omega_0 = \frac{\hbar}{2m_0\langle x^2\rangle} \qquad \text{...(iii)}$$

We know that for the harmonic oscillator $\langle x\rangle = 0$. We have according to the problem

$$\sqrt{\langle (x-\langle x\rangle)^2\rangle} = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = \sqrt{\langle x^2\rangle} = 10^{-10}\ m \qquad \text{...(iv)}$$

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

$$\Delta E = \hbar\omega_0 = \hbar\frac{\hbar}{2m_0\langle x^2\rangle} = \frac{\hbar^2}{2m_0\langle x^2\rangle}$$

$$= \frac{(6.58\times 10^{-16})^2 \times c^2}{2m_0\, 10^{-20}\times c^2}$$

$$= \frac{(6.58\times 10^{-16})^2 \times (3\times 10^8)^2}{2\times 0.51\times 10^{-20}}$$

$= 3.8$ eV.

Example 4 A particle of mass m undergoes simple harmonic motion along the x-axis with an angular frequency ω. Considering the uncertainty relation $\Delta x\, \Delta p = \frac{\hbar}{2}$, where

$$(\Delta x)^2 = \langle (x - \langle x\rangle)^2\rangle \text{ and } (\Delta p)^2 = \langle (p - \langle p\rangle)^2\rangle,$$

find the minimum energy of the oscillator.

Solution: We know that for the linear harmonic oscillator

$$\langle x\rangle = 0 \text{ and } \langle p\rangle = 0 \qquad \text{...(i)}$$

We hence get

$$(\Delta x)^2 = \langle x^2\rangle \text{ and } (\Delta p)^2 = \langle p^2\rangle \qquad \text{...(ii)}$$

The Hamiltonian of the oscillator is given by

$$H = \text{kinetic energy } (T) + \text{potential energy } (V)$$

Clearly

$$\langle H \rangle = \langle T \rangle + \langle V \rangle$$

$$= \left\langle \frac{p^2}{2m} \right\rangle + \left\langle \frac{1}{2} m\omega^2 x^2 \right\rangle$$

$$= \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} m\omega^2 \langle x^2 \rangle \qquad \text{...(iii)}$$

Since both terms on the right hand side of Eq. (iii) are real and positive, we get

$$\langle H \rangle = \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} m\omega^2 \langle x^2 \rangle \geq 2\sqrt{\frac{1}{2m} \langle p^2 \rangle \times \frac{1}{2} m\omega^2 \langle x^2 \rangle}$$

or $$\langle H \rangle \geq 2\sqrt{\frac{1}{4} \omega^2 \langle p^2 \rangle \langle x^2 \rangle} = \omega\sqrt{(\Delta x)^2 \, (\Delta p)^2} \qquad \text{(using eq. (iii))}$$

or $$\langle H \rangle \geq \omega \, \Delta x \, \Delta p$$

or $$\langle H \rangle \geq \frac{\hbar\omega}{2}$$

Clearly, the minimum energy is given by

$$\langle H \rangle_{\text{min}} = \frac{1}{2} \hbar\omega$$

Example 5 A particle of mass m is undergoing harmonic oscillation of angular frequency ω. 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 ψ satisfies the Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V] \, \psi = 0 \qquad \text{...(i)}$$

In the above, E is the energy eigenvalue in the state under consideration, V is the potential energy given by

$$V = \frac{1}{2} m\omega^2 x^2 \qquad \text{...(ii)}$$

We have

$$\psi = x\, e^{\frac{-m\omega}{2\hbar}x^2}$$

Clearly,

$$\frac{d\psi}{dx} = e^{\frac{-m\omega}{2\hbar}x^2} - x\frac{m\omega}{2\hbar}2x\, e^{\frac{-m\omega}{2\hbar}x^2}$$

$$= e^{\frac{-m\omega}{2\hbar}x^2}\left[1 - \frac{m\omega}{\hbar}x^2\right]$$

Further, we get

$$\frac{d^2\psi}{dx^2} = e^{\frac{-m\omega}{2\hbar}x^2}\left[-\frac{m\omega}{\hbar}2x\right] - \left[1 - \frac{m\omega}{\hbar}x^2\right]\times\frac{m\omega}{2\hbar}2x\, e^{\frac{-m\omega}{2\hbar}x^2}$$

or
$$\frac{d^2\psi}{dx^2} = e^{\frac{-m\omega}{2\hbar}x^2}\left[\frac{-m\omega}{\hbar}2x \frac{-m\omega}{\hbar}x \frac{+m^2\omega^2}{\hbar^2}x^3\right]$$

or
$$\frac{d^2\psi}{dx^2} = \frac{m\omega x}{\hbar}e^{\frac{-m\omega}{2\hbar}x^2}\left[\frac{m\omega}{\hbar^2}x^2 - 3\right] \qquad \text{...(iii)}$$

Substituting Eqs. (ii) and (iii) in Eq. (i) we get

$$\frac{m\omega}{\hbar}x\, e^{\frac{-m\omega}{2\hbar}x^2}\left[\frac{m\omega}{\hbar^2}x^2 - 3\right] + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}m\omega^2x^2\right]x\, e^{\frac{-m\omega}{2\hbar}x^2} = 0$$

or
$$\frac{2m}{\hbar^2}x\, e^{\frac{-m\omega}{2\hbar}x^2}\left[E - \frac{1}{2}m\omega^2x^2 + \frac{m\omega^2x^2}{2} - \frac{3}{2}\hbar\omega\right] = 0$$

The above gives

$$E - \frac{3}{2}\hbar\omega = 0$$

or
$$E = \frac{3}{2}\hbar\omega.$$

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 ω.

If a be the amplitude of oscillation, the total energy of the particle when we treat the oscillator classically is

$$E = \frac{1}{2}m\omega^2a^2 \qquad \text{...(i)}$$

According to the problem, the oscillator is in its ground state and hence its energy is

$$E = \frac{1}{2}\hbar\omega \qquad \text{...(ii)}$$

Thus, we have

$$\frac{1}{2}m\omega^2 a^2 = \frac{1}{2}\hbar\omega$$

or

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

or

$$a = \sqrt{\frac{\hbar}{m\omega}} \qquad \text{...(iii)}$$

The wavefunction describing the ground state of the oscillator is given by

$$\psi_0 = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} e^{\frac{-\alpha^2 x^2}{2}} \qquad \text{...(iv)}$$

where

$$\alpha = \sqrt{\frac{m\omega}{\hbar}} = \frac{1}{a} \qquad \text{...(v)}$$

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
$$p = \frac{2}{\sqrt{\pi}}\left[\int_0^1 dy - \int_0^1 y^2\,dy + \int_0^1 \frac{y^4}{2!}\,dy - \int_0^1 \frac{y^6}{3!}\,dy + \ldots\right]$$

or
$$p = \frac{2}{\sqrt{\pi}}\left[1 - \frac{1}{3} + \frac{1}{10} - \frac{1}{42} + \ldots\right]$$

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 $(1 - 0.84) \simeq 0.16$ 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 ω. If at any time t, x be the displacement and p the linear momentum, the Hamiltonian of the oscillator is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}kx^2 \qquad \text{...(i)}$$

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.,

$$\langle x \rangle = 0 \quad \text{and} \quad \langle p \rangle = 0 \qquad \text{...(ii)}$$

According to Ehrenfest's theorem, Eq. (ii) also holds for the quantum mechanical oscillator. If Δx and Δp 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 Eq. (ii), the above become

$$\left.\begin{aligned}(\Delta x)^2 &= \langle x^2 \rangle \\ (\Delta p)^2 &= \langle p^2 \rangle\end{aligned}\right\} \qquad \text{...(iii)}$$

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 Eq. (iii) we get

$$\langle E \rangle = \frac{1}{2m}(\Delta p)^2 + \frac{1}{2}k(\Delta x)^2 \qquad \text{...(iv)}$$

We have the uncertainty relation

$$\Delta p\ \Delta x \geq \frac{\hbar}{2}$$

or

$$(\Delta p)^2\ (\Delta x)^2 \geq \frac{\hbar^2}{4} \qquad \text{...(v)}$$

Using Eq. (5), Eq. (4) can be written as

$$\langle E\rangle \geq \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}k(\Delta x)^2 \qquad \text{...(vi)}$$

For $\langle E\rangle$ to be the minimum we must have

$$\frac{d\langle E\rangle}{d(\Delta x)^2} = 0$$

or

$$\frac{-\hbar^2}{8m(\Delta x)^4_{\min}} + \frac{1}{2}k = 0$$

or

$$(\Delta x)^4_{\min} = \frac{\hbar^2}{4mk} = \frac{\hbar^2}{4m\,m\omega^2}$$

or

$$(\Delta x)^2_{\min} = \frac{\hbar}{2m\omega} \qquad \text{...(vii)}$$

Clearly

$$\langle E\rangle_{\min} = \frac{\hbar^2}{8m(\Delta x)^2_{\min}} + \frac{1}{2}m\omega^2(\Delta x)^2_{\min}$$

$$= \frac{\hbar^2 2m\omega}{8m\hbar} + \frac{1}{2}m\omega^2\,\frac{\hbar}{2m\omega}$$

or

$$\langle E\rangle_{\min} = \frac{1}{2}\hbar\omega \qquad \text{...(viii)}$$

Example 8 A particle of mass m undergoes simple harmonic motion along the x-axis with an angular frequency ω. 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

(a) the normalization constant A
(b) an expression for $\psi(x, t)$.
(c) expectation value of the energy at $t = 0$ and
(d) 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
$$|A|^2 \sum_{n,m} \int \left(\frac{1}{\sqrt{2}}\right)^{n+m} \psi_n^*(x)\, \psi_m(x)\, dx = 1 \qquad \text{...(i)}$$

The orthonormality property of eigenfunctions gives

$$\int \psi_n^*(x)\, \psi_m(x)\, dx = \delta_{nm}$$

Using the above in Eq. (i) we get

$$|A|^2 \sum_n \left(\frac{1}{\sqrt{2}}\right)^{2n} = 1$$

or
$$|A|^2 \sum_n \left(\frac{1}{2}\right)^{\frac{2n}{2}} = 1$$

or
$$|A|^2\, 2 = 1$$

or
$$|A| = \frac{1}{\sqrt{2}} \qquad \text{...(ii)}$$

(b) $\psi(x, t)$ and $\psi(x, 0)$ are related according to

$$\psi(x, t) = \psi(x, 0)\, e^{\frac{-i\hat{H}t}{\hbar}}$$

$$= \sum_n \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}}\right)^n \psi_n(x)\, e^{\frac{-i\hbar\omega\left(n + \frac{1}{2}\right)t}{\hbar}}$$

or $$\psi(x, t) = \sum_n \left(\frac{1}{\sqrt{2}}\right)^{n+1} e^{-i\omega\left(n+\frac{1}{2}\right)t} \psi_n(x) \qquad \text{...(iii)}$$

(c) By definition, the expectation value of energy at $t = 0$ is given by

$$\langle E \rangle = \int \psi^*(x, 0)\, \hat{H}\, \psi(x, 0)\, dx$$

$$= \sum_{n,m} \left(\frac{1}{2}\right)^{\frac{n+m}{2}+1} \int \psi_n^*(x)\, \psi_m(x)\, dx$$

$$= \sum_{n,m} \left(\frac{1}{2}\right)^{\frac{n+m}{2}+1} \left(n+\frac{1}{2}\right) \hbar\omega\, \delta_{nm}$$

$$= \sum_{n=0}^{\infty} \left(\frac{1}{2}\right)^{n+1} \left(n+\frac{1}{2}\right) \hbar\omega$$

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

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

$$= 1 \times \hbar\omega + \frac{1}{2} \hbar\omega$$

or $$\langle E \rangle = \frac{3}{2} \hbar\omega$$

(d) The probability density is given by

$$|\psi(x, t)|^2 = \psi^*(x, t)\, \psi(x, t)$$

$$= \sum_{n,m} \left(\frac{1}{2}\right)^{\frac{n+m}{2}+1} e^{-i\omega t(n-m)}\, \psi_n^*(x)\, \psi_m(x)$$

The time factor, namely $e^{-i\omega(n-m)t}$ is a function of time with period $\dfrac{2\pi}{(n-m)\,\omega}$.

Example 9 The Hamiltonian operator for a harmonic oscillator of angular frequency ω in terms of raising and lowering operators $\hat{a}^+$ and $\hat{a}$ is given by

$$\hat{H} = \hbar\omega\left(\hat{a}^+\hat{a} + \frac{1}{2}\right)\cdot$$

where $$\hat{a} = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}} x + i\left(\frac{1}{2m\hbar\omega}\right)^{1/2} \hat{p}$$

$$\hat{a}^{\dagger} = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}} x - i\left(\frac{1}{2m\hbar\omega}\right)^{1/2} \hat{p}$$

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 ψ in energy.

Solution: If we take $m = 1$, $\omega = 1$ and $\hbar = 1$ we get

$$\left.\begin{aligned} \hat{a} &= \frac{1}{\sqrt{2}}(x + i\hat{p}) \\ \hat{a}^{\dagger} &= \frac{1}{\sqrt{2}}(x - i\hat{p}) \end{aligned}\right\} \qquad \text{...(i)}$$

Let ψ_n be an energy eigenfunction of the oscillator belonging to the energy eigenvalue

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \ldots \qquad \text{...(ii)}$$

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

$$\hat{a}\hat{a}^{\dagger}\, \psi_n = \hat{a}(\sqrt{n+1})\, \psi_{n+1} = (n+1)\, \psi_n \qquad \text{...(iii)}$$

Using Eqs. (i) we have

$$\hat{a}\hat{a}^{\dagger}\, \psi = \frac{1}{2}(x + i\hat{p})(x - i\hat{p})\,\psi$$

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 ψ 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

$$\hat{a}\hat{a}^{\dagger}\, \psi = 4(2x^3 - 3x)\, e^{\frac{-x^2}{2}} = (3 + 1)\, \psi \qquad \text{...(iv)}$$

Comparing Eq. (iv) with Eq. (iii) we get

$$n = 3$$

Hence, the eigenfunctions closest in energy to ψ 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

$$\psi_0(x) = \left[\frac{\alpha}{\sqrt{\pi}}\right]^{1/2} e^{\frac{-\alpha^2x^2}{2}}$$

and
$$\psi_1(x) = 2\left[\frac{\alpha}{2\sqrt{\pi}}\right]^{1/2} \alpha x\, e^{\frac{-\alpha^2x^2}{2}}$$

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

$$\hat{H}\,\psi_0(x) = \frac{1}{2}\hbar\omega\,\psi_0(x) \qquad \text{...(i)}$$

$$\hat{H}\,\psi_1(x) = \frac{3}{2}\hbar\omega\,\psi_1(x) \qquad \text{...(ii)}$$

We also have the following orthonormal properties of $\psi_0(x)$ and $\psi_1(x)$

$$\int_{-\infty}^{+\infty} \psi_0^*(x)\,\psi_0(x)\,dx = \int_{-\infty}^{+\infty} |\psi_0(x)|^2\,dx = \int_{-\infty}^{+\infty} \psi_0^2(x)\,dx = 1 \qquad \text{...(iii)}$$

$$\int_{-\infty}^{+\infty} \psi_1^*(x)\,\psi_1(x)\,dx = \int_{-\infty}^{+\infty} |\psi_1(x)|^2\,dx = \int_{-\infty}^{+\infty} \psi_1^2(x)\,dx = 1 \qquad \text{...(iv)}$$

$$\int \psi_0^*(x)\, \psi_1(x)\, dx = \int_{-\infty}^{+\infty} \psi_0(x)\, \psi_1(x)\, dx = 0 \qquad \text{...(v)}$$

The expectation value of energy in the state described by the wavefunction $\psi(x)$ is given by

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

$$= \int_{-\infty}^{+\infty} \left[\frac{1}{\sqrt{2}} \{\psi_0(x) + \psi_1(x)\}^* \hat{H} \frac{1}{\sqrt{2}} \{\psi_0(x) + \psi_1(x)\} \right] dx$$

$$= \frac{1}{2} \left[\int_{-\infty}^{+\infty} \{\psi_0(x) + \psi_1(x)\}\, \hat{H}\, \{\psi_0(x) + \psi_1(x)\}\, dx \right]$$

or

$$\langle E \rangle = \frac{1}{2} \left[\int_{-\infty}^{+\infty} \psi_0(x)\, \hat{H}\, \psi_0(x)\, dx + \int_{-\infty}^{+\infty} \psi_1(x)\, \hat{H}\, \psi_1(x)\, dx \right.$$
$$\left. + \int_{-\infty}^{+\infty} \psi_0(x)\, \hat{H}\, \psi_1(x)\, dx + \int_{-\infty}^{+\infty} \psi_1(x)\, \hat{H}\, \psi_0(x)\, dx \right]$$

Using Eqs. (i) and (ii) the above becomes

$$\langle E \rangle = \frac{1}{2} \left[\int_{-\infty}^{+\infty} \frac{1}{2} \hbar\omega\, \psi_0^2(x)\, dx + \int_{-\infty}^{+\infty} \frac{3}{2} \hbar\omega\, \psi_1^2(x)\, dx \right.$$
$$\left. + \int_{-\infty}^{+\infty} \frac{3}{2} \hbar\omega\, \psi_0(x)\, \psi_1(x)\, dx + \int_{-\infty}^{+\infty} \frac{1}{2} \hbar\omega_0\, \psi_1(x)\, \psi_0(x)\, dx \right]$$

Using Eqs. (iii), (iv) and (v) the above gives

$$\langle E \rangle = \frac{1}{2} \left[\frac{1}{2} \hbar\omega + \frac{3}{2} \hbar\omega \right] = \hbar\omega$$

7

Three-dimensional Problems: Spherically Symmetric Potentials

7.1 SCHRÖDINGER EQUATION FOR MOTION UNDER SPHERICALLY SYMMETRIC POTENTIAL

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

$$\vec{F}(r) = \frac{-dV}{dr} \qquad \text{...(1)}$$

It is evident that the potential function depends only on the distance r and can be expressed as

$$V = V(r) \qquad \text{...(2)}$$

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 change etc.

The wavefunction ψ which is a function of the coordinates of the particle in space and which describes the state of the particle satisfies the Schrödinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0 \qquad \text{...(3)}$$

For motion under spherically symmetric potential, it is advantageous to express the Schrödinger equation in terms of spherical polar coordinates r, θ, ϕ instead of Cartesian coordinates x, y, z because the potential is independent of the angular coordinates θ and ϕ.

The operator ∇^2 in spherical polar coordinates is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad \text{...(4)}$$

which when used in Eq. (3) gives the Schrödinger equation in spherical polar coordinates

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

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}+\frac{2m}{\hbar^2}[E-V(r)]\psi(r,\theta,\phi)=0 \qquad ...(5)$$

The above equation can be separated into three independent equations corresponding to the three independent variables r, θ and ϕ using the well known method of separation of variables. The method consists in writing

$$\psi(r,\theta,\phi)=R(r)\,\Theta(\theta)\,\Phi(\phi) \qquad ...(6)$$

where $R(r)$, $\Theta(\theta)$ and $\Phi(\phi)$ are respectively functions of only r, only θ and only ϕ.

Substituting Eq. (6) in Eq. (5) we obtain

$$\Theta\Phi\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+R\Phi\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\frac{d\Theta}{d\theta}\right)+R\Theta\frac{1}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{2m}{\hbar^2}[E-V(r)]\,R\Theta\Phi=0$$

Multiplying throughout by $\dfrac{r^2\sin^2\theta}{R\Theta\Phi}$, the above equation gives

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+\frac{2m}{\hbar^2}[E-V(r)]r^2\sin^2\theta=0$$

or

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2m}{\hbar^2}[E-V(r)]r^2\sin^2\theta=\frac{-1}{\Phi}\frac{d^2\Phi}{d\phi^2} \qquad ...(7)$$

Since the left hand side of the above equation is a function of r and θ while the right hand side is a function of only ϕ, we must have each side equal to some constant. For convenience let the constant be put equal to m^2. We then get

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=m^2 \text{ or } \frac{d^2\Phi}{d\phi^2}+m^2\Phi=0 \qquad ...(8)$$

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

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[E-V(r)]r^2=\frac{-1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+m^2/\sin^2\theta=0 \qquad \text{...(9)}$$

In the above equation the left hand side is a function of only r while the right hand side is a function of θ only. Hence each side of the equation must be equal to a constant. Considering the constant to be λ, we get

(i)
$$-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\frac{d\Theta}{d\theta}\right)+m^2\sin^2\theta=\lambda$$

or
$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\theta=0 \qquad \text{...(10)}$$

and
$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[E-V(r)]r^2=\lambda$$

Multiplying by $\frac{R}{r^2}$, the above gives

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[E-V(r)]R=\frac{\lambda R}{r^2}$$

or
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[E-V(r)]R=\frac{\lambda}{r^2}R=0 \qquad \text{...(11)}$$

Equation (11) is usually referred to as the radial wave equation. We have thus been able to separate the three-dimensional Schrödinger equation given by Eq. (5) into three independent, one-dimensional equations involving the independent coordinate r, θ and ϕ given by Eqs. (8), (10) and (11), respectively.

It is important to note that the equation involving the angular co-ordinates namely θ and ϕ 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 Eq. (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.

7.2 SOLUTION OF THE SCHRÖDINGER EQUATION

Solutions of the eqs. (8), (10) and (11) respectively give the functions $R(r)$, $\Theta(\theta)$, $\Phi(\phi)$. We can then obtain the solution of the Schrödinger equation given by Eq. (5) in terms of $R(r)$, $\Theta(\theta)$ and $\Phi(\phi)$ as

$$\psi(r,\theta,\phi)=R(r)\,\Theta(\theta)\,\Phi(\phi)$$

7.2.1 Solution of the Φ-equation

The function $\Phi(\phi)$ satisfies Eq. (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

$$\Phi(\phi) = Ae^{\pm im\phi} \qquad ...(12)$$

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.,

$$m = 0, 1, 2, \qquad ...(13)$$

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 Eq. (12) in the above we obtain

$$|A|^2 \int_0^{2\Pi} d\phi = 1$$

or

$$|A|^2 = \frac{1}{2\pi} \quad \text{or} \quad A = \frac{1}{\sqrt{2\pi}} \qquad ...(14)$$

The normalized solution of the Φ-equation is thus

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, ... \qquad ...(15)$$

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 $$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \cos m\phi \qquad ...(16)$$

Imaginary from $$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \sin m\phi \qquad ...(17)$$

7.2.2 Solution of the Θ-equation

We have the Θ-equation given by Eq. (10)

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

Let us introduce a new variable ξ as

$$\xi = \cos\theta \qquad ...(18)$$

We then get

$$\frac{d\Theta}{d\theta} = \frac{d\Theta}{d\xi}\frac{d\xi}{d\theta} = -\sin\theta\frac{d\Theta}{d\xi} \qquad ...(19)$$

Further

$$\sin\theta = \sqrt{1-\cos^2\theta} = \sqrt{1-\xi^2} \qquad ...(20)$$

Using Eq. (20) in Eq. (19) we get

$$\frac{d}{d\theta} = -\sqrt{1-\xi^2}\frac{d}{d\xi} \qquad ...(21)$$

Using Eqs. (19), (20) and (21), the Θ equation becomes

$$\frac{d}{d\xi}\left[(1-\xi^2)\frac{d\Theta(\xi)}{d\xi}\right] + \left[\lambda - \frac{m^2}{1-\xi^2}\right]\Theta(\xi) = 0 \qquad ...(22)$$

Equation (22) is the well known *associated Legendre equation.* Since ξ = cos θ, the above equation is physically meaningful only for values of ξ lying between –1 and +1. Physically acceptable solutions of Eq. (22) give

$$\lambda = l(l+1); \quad l = 0, 1, 2,... \qquad ...(23)$$

$$m = 0, \pm 1, \pm 2,... \pm l \qquad ...(24)$$

When $m = 0$, Eq. (22) reduces to the well known Legendre differential equation whose solution is the Legendre polynomial

$$P_l(\xi) = P_l(\cos\theta) \qquad ...(25)$$

For $m \neq 0$, the solutions are *associated Legendre polynomials*

$$P_l^{|m|}(\xi) = P_l^{|m|}(\cos\theta) \qquad ...(26)$$

The normalized solutions of eq. (22) are given by

$$\Theta_l^m(\theta) = (-1)^m \sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta),\ m > 0 \qquad ...(27)$$

$$\Theta_l^m(\theta) = \sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta),\ m \le 0 \qquad ...(28)$$

Normalized Angular Part of the Wavefunction

The normalized angular part of the wavefunction is the product of $\Theta(\theta)$ given by Eq. (27) and $\Phi(\phi)$ given by Eq. (15)

$$\underset{angular}{\psi(\theta, \phi)} = \frac{1}{\sqrt{2\pi}}(-1)^m \sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta), e^{im\phi} \qquad ...(29)$$

where

$$l = 0, 1, 2, ...; \quad m = 0, \pm 1, \pm 2, ..., \pm l \qquad ...(30)$$

The angular part of the wavefunction is called *spherical harmonic* and written as $Y_{lm}(\theta, \phi)$. We get

$$Y_{lm}(\theta, \phi) = \in \sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta), e^{im\phi} \qquad ...(31)$$

We observe that the angular part of the wavefunction neither depends upon the total energy E nor upon the potential function $V(r)$.

7.2.3 Solution of the Radial Wave Equation

The radial wave equation is given by Eq. (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

$$u(r) = rR(r) \qquad ...(32)$$

The above gives,

$$\frac{dR}{dr} = \frac{-u}{r^2} + \frac{1}{r}\frac{du}{dr} \qquad ...(33)$$

Using Eqs. (32) and (33) and $\lambda = l(l+1)$ in the radial wave equation and simplifying we obtain

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right]u = 0 \qquad \text{...(34)}$$

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 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 Eq. (34) as

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}[E - V_{eff}]u = 0 \qquad \text{...(35)}$$

where V_{eff} which may be called the effective potential under which the particle moves is given as

$$V_{\text{eff}} = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \qquad \text{...(36)}$$

Equation (35) has the form of one-dimensional Schrödinger equation and can be solved from a knowledge of the spherically symmetric potential $V(r)$.

7.3 GENERAL 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

$$F_x = -k_x x, \quad F_y = -k_y y, \quad F_z = -k_z z \qquad \text{...(37)}$$

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 ν_x, ν_y, ν_z be respectively the components of the natural frequency ν_0 of the oscillator along the x, y and z axes then we have

$$\left.\begin{aligned} k_x &= m\omega_x^2 = m(2\pi\nu_x)^2 = 4\pi^2\, m\nu_x^2 \\ k_y &= m\omega_y^2 = m(2\pi\nu_y)^2 = 4\pi^2\, m\nu_y^2 \\ k_z &= m\omega_z^2 = m(2\pi\nu_z)^2 = 4\pi^2\, m\nu_z^2 \end{aligned}\right\} \qquad \text{...(38)}$$

$$k = m\omega_0^2 = m(2\pi\nu_0)^2 = 4\pi^2\, m\nu_0^2 \qquad ...(39)$$

The potential energy function of the oscillator is spherically symmetric and is given by

$$V = V(r) = \frac{1}{2}kr^2 = \frac{1}{2}m\omega_0^2 r^2 \qquad ...(40)$$

Alternatively, we may write the potential energy function as

$$V(x, y, z) = \frac{1}{2}m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) \qquad ...(41)$$

The Schrödinger equation for the oscillator given by

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

can be expressed in Cartesian coordinates as

$$\frac{\partial^2\psi(x, y, z)}{\partial x^2} + \frac{\partial^2\psi(x, y, z)}{\partial y^2} + \frac{\partial^2\psi(x, y, z)}{\partial z^2} + \frac{2m}{\hbar^2}[E - m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)]\psi(x, y, z) = 0 \qquad ...(42)$$

Solution of the Schrödinger Equation

Equation (42) can be solved using the method of separation of variables as in Section 7.1. 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

$$\psi(x, y, z) = X(x)\, Y(y)\, Z(z) \qquad ...(43)$$

Using Eq. (43) in Eq. (42) we get

$$YZ\frac{d^2X}{\partial x^2} + XZ\frac{d^2Y}{\partial y^2} + XY\frac{d^2Z}{\partial z^2} + \frac{2m}{\hbar^2}[E - m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)]XYZ = 0$$

Dividing by XYZ and rearranging the terms the above becomes

$$\left[\frac{1}{x}\frac{d^2X}{dx^2} - \frac{2m^2}{\hbar^2}\omega_x^2 x^2\right] + \left[\frac{1}{y}\frac{d^2Y}{dy^2} - \frac{2m^2}{\hbar^2}\omega_y^2 y^2\right] + \left[\frac{1}{z}\frac{d^2Z}{dz^2} - \frac{2m^2}{\hbar^2}\omega_z^2 z^2\right] = -\frac{2mE}{\hbar^2} \qquad ...(44)$$

We find

(i) the sum of the three terms on the left hand side of Eq. (44) 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 Eq. (44) 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 Eq. (44) to be equal to a separate constant, we put

$$\frac{1}{X}\frac{d^2X}{dx^2}-\frac{2m^2}{\hbar^2}\omega_x^2x^2=\frac{-2m}{\hbar^2}E_x,\quad E_x = \text{a constant}$$

or

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{2m^2}{\hbar^2}\left[E_x-m\omega_x^2x^2\right]=0$$

or

$$\frac{d^2X}{dx^2}+\frac{2m^2}{\hbar^2}\left[E_x-m\omega_x^2x^2\right]X=0 \qquad \text{...(45)}$$

Similarly, writing the second term and the third term on the left hand side of Eq. (44) equal to $\frac{-2m}{\hbar^2}E_y$ and $\frac{-2m}{\hbar^2}E_z$ respectively, we obtain

$$\frac{d^2Y}{dy^2}+\frac{2m}{\hbar^2}[E_y-m\omega_y^2y^2]Y=0 \qquad \text{...(46)}$$

$$\frac{d^2Z}{dz^2}+\frac{2m}{\hbar^2}[E_z-m\omega_y^2y^2]Z=0 \qquad \text{...(47)}$$

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

$$E_x+E_y+E_z=E \qquad \text{...(48)}$$

Equations (45), (46) and (47) are mathematically identical with the time-independent Schrödinger equation for linear harmonic oscillator given by Eq. (11) in Section 6.2.

As in Sections 6.2, 6.3, 6.4 and 6.5 we get the results (A) and (B) as below:

(A)

$$\left.\begin{aligned} E_x &= \left(n_x+\frac{1}{2}\right)\hbar\omega_x \\ E_y &= \left(n_y+\frac{1}{2}\right)\hbar\omega_y \\ E_z &= \left(n_z+\frac{1}{2}\right)\hbar\omega_z \end{aligned}\right\} \qquad \text{...(49)}$$

where n_x, n_y, n_z are positive integers including zero.

In view of the results given by Eqs. (48) and (49) we get the energy eigenvalues of the three-dimensional harmonic oscillator to be

$$E_{n_xn_yn_z}=E_x+E_y+E_z=\left[\left(n_x+\frac{1}{2}\right)\omega_x+\left(n_y+\frac{1}{2}\right)\omega_y+\left(n_z+\frac{1}{2}\right)\omega_z\right]\hbar \qquad \text{...(50)}$$

(B) The normalized solutions of Eqs. (45), (46) and (47) to be given respectively by

$$X_{n_x}(x) = N_{n_x}\, H_{n_x}(\xi) e^{-\frac{\xi^2}{2}}$$

or

$$X_{n_x}(x) = \left[\frac{\gamma_k}{2^{n_x} n_x! \sqrt{\pi}}\right]^{1/2} H_{n_x}(\xi) e^{-\frac{\xi^2}{2}} \qquad ...(51)$$

where

$$\gamma_x = \sqrt{\frac{m\omega_x}{\hbar}} \quad \text{and} \quad \xi = \gamma_x x \qquad ...(52)$$

$$Y_{n_y}(y) = \left[\frac{\gamma_y}{2^{n_y} n_y! \sqrt{\pi}}\right]^{1/2} H_{n_y}(\eta) e^{-\eta^2 2} \qquad ...(53)$$

where

$$\gamma_y = \sqrt{\frac{m\omega_y}{\hbar}} \quad \text{and} \quad \eta = \gamma_y y \qquad ...(54)$$

and

$$Z_{n_z}(z) = \left[\frac{\gamma_3}{2^{n_z} n_z! \sqrt{\pi}}\right]^{1/2} H_{n_z}(\zeta) e^{-\zeta^2/2} \qquad ...(55)$$

$$\gamma_z = \sqrt{\frac{m\omega_z}{\hbar}} \quad \text{and} \quad \zeta = \gamma_z z \qquad ...(56)$$

Substituting Eqs. (51), (53) and (55) in Eq. (43) we get the normalized eigenfunctions of the three-dimensional oscillator to be given by

$$\psi_{n_x n_y n_z}(x, y, z) = \left[\frac{\gamma_x \gamma_y \gamma_z}{2^n n_x! n_y! n_z! \pi^{3/2}}\right]^{1/2} H_{n_x}(\xi) H_{n_y}(\eta) H_{n_z}(\zeta) \times e^{-\frac{1}{2}(\xi^2 + \eta^2 + \zeta^2)} \qquad ...(57)$$

In the above,

$$n = n_1 + n_2 + n_3 \qquad ...(58)$$

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 ω_x, ω_y, and ω_z then are also equal. Let us assume

$$\omega_x = \omega_y = \omega_z = \omega_0 \qquad ...(59)$$

Equation (50) 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

$$E_n = \left(n + \frac{3}{2} \right) \hbar\, \omega_0; \quad n = n_x + n_y + n_z = 0, 1, 2,... \qquad ...(60)$$

In view of eq. (59) we find

$$\gamma_x = \gamma_y = \gamma_z \sqrt{\frac{m\omega_0}{\hbar}} \qquad ...(61)$$

$$\xi = \sqrt{\frac{m\omega_0}{\hbar}}\, x; \quad \eta = \sqrt{\frac{m\omega_0}{\hbar}}\, y; \quad \zeta = \sqrt{\frac{m\omega_0}{\hbar}}\, z \qquad ...(62)$$

Substituting Eqs. (61) and (62) in Eq. (57) we get the eignfunctions of the oscillator to be given by

$$\psi_{n_x n_y n_z}(x, y, z) = \left[\frac{\left(\dfrac{m\omega_0}{\hbar} \right)^3}{2^{(n_x + n_y + n_z)}\, n_x!\, n_y!\, n_z!\, \pi^{3/2}} \right]^{1/2} H_{n_x}(\xi) H_{n_y}(\eta) H_{n_z}(\zeta) \times e^{-\frac{1}{2} \frac{m\omega_0}{\hbar} (x^2 + y^2 + z^2)} \qquad ...(63)$$

The *ground state of the oscillator* corresponds to

$$n_x = n_y = n_z = 0 \qquad ...(64)$$

From Eq. (60) 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 Eq. (63) to be

$$\psi_{000}(x, y, z) = \left(\frac{m\omega_0}{\hbar \pi^{1/2}} \right)^{3/2} e^{-\frac{1}{2} \frac{m\omega_0}{\hbar}} (x^2 + y^2 + x^2) \qquad ...(65)$$

The first excited state corresponds to

$$n = 1$$

so that we may have

$$\left. \begin{array}{lll} n_x = 1, & n_y = 0, & n_z = 0 \\ n_x = 0, & n_y = 1, & n_z = 0 \\ n_x = 0, & n_y = 0, & n_z = 1 \end{array} \right\} \qquad ...(66)$$

Equation (60) gives the energy eigenvalues corresponding to this state to be

$$E_1 = \frac{5}{2}\hbar\omega_0 \qquad ...(67)$$

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

$$\left.\begin{array}{l} n_x = 2, n_y = 0, n_z = 0 \\ n_x = 0, n_y = 2, n_z = 0 \\ n_x = 0, n_y = 0, n_z = 2 \\ n_x = 1, n_y = 1, n_z = 0 \\ n_x = 1, n_y = 0, n_z = 1 \\ n_x = 0, n_y = 1, n_z = 1 \end{array}\right\} \qquad ...(68)$$

The energy eigenvalue for this state from eq. (60) is given by

$$E_2 = \frac{7}{2}\hbar\omega_0 \qquad ...(69)$$

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

$$\text{degree of degeneracy} = \frac{1}{2}(n + 1)(n + 2) \qquad ...(70)$$

7.4 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.

7.4.1 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_o. Let the system of particles rotate with an angular velocity 'ω' about the axis *XY* passing though the centre of mass *O* and normal to the line joining the particles as shown in the Fig. 7.1.

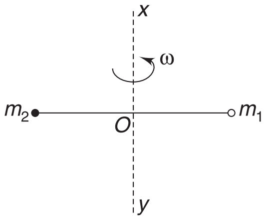


Fig. 7.1

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, θ, ϕ) 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

$$\left.\begin{aligned} x_1 &= r_1 \sin\theta \cos\phi \\ y_1 &= r_1 \sin\theta \sin\phi \\ z_1 &= r_1 \cos\theta \end{aligned}\right\} \quad ...(71)$$

and

$$\left.\begin{aligned} x_2 &= r_2 \sin(\theta+\pi)\cos(\phi+\pi) = r_2 \sin\theta\cos\phi \\ y_2 &= r_2 \sin(\theta+\pi)\sin(\phi+\pi) = r_2 \sin\theta\sin\phi \\ z_2 &= r_2 \cos(\theta+\pi) = -r_2 \cos\theta \end{aligned}\right\} \qquad \text{...(72)}$$

The kinetic energy of the particle of mass m_1 is

$$T_1 = \frac{1}{2} m_1 (\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) \qquad \text{...(73)}$$

Obtaining the time derivatives $\dot{x}_1$, $\dot{y}_1$ and $\dot{z}_1$ from Eq. (71), substituting them in Eq. (73) and simplifying we obtain

$$T_1 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2) \qquad \text{...(74)}$$

Similarly, the kinetic energy of the particle of mass m_2 is found to be

$$T_2 = \frac{1}{2} m_2 (\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) = \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) \qquad \text{...(75)}$$

The total kinetic energy of the rotator is thus

$$T = T_1 + T_2 = \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2\right)(\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2) \qquad \text{...(76)}$$

Since for the rigid rotator the distance r_0 between the two particles is fixed (r_0 = 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

$$E = T = \frac{1}{2} (m_1 r_1^2 \; m_2 r_2^2)(\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2)$$

$$E = \frac{1}{2} I (\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2) \qquad \text{...(77)}$$

where

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \text{...(78)}$$

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 Eq. (77) 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

$$\vec{r} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \qquad \text{...(79)}$$

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 Eq. (79)

$$O = \frac{m_1 r_1 - m_2 r_2}{m_1 + m_2}$$

The above gives

$$m_1 r_1 = m_2 r_2 \qquad \text{...(80)}$$

We may write Eq. (80) as

$$m_1 r_1 = m_2 (r_0 - r_1)$$

or

$$r_1 = \frac{m_2}{m_1 + m_2} r_0 \qquad \text{...(81)}$$

Similarly, we obtain

$$r_2 = \frac{m_1}{m_1 + m_2} r_0 \qquad \text{...(82)}$$

Substituting Eqs. (81) and (82) in Eq. (78) 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

$$I = \mu r_0^2 \qquad \text{...(83)}$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ in the reduced mass of the two particles.

Using Eq. (83) in Eq. (77) we get the total energy of the rotator as

$$E = \frac{1}{2} \mu r_0^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \qquad \text{...(84)}$$

If for convenience, we set the distance between the particles equal to unity, i.e., $r_0 = 1$, we get

$$\mu r_0^2 = \mu = I_0 (\text{say}) \qquad \text{...(85)}$$

We can then write the total energy of the rotator as

$$E = \frac{1}{2} I_0(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \qquad \text{...(86)}$$

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

$$\nabla^2 \psi(x, y, z) + \frac{2m}{\hbar^2}[E - V]\psi(r, \theta, \phi) = 0 \qquad \text{...(87)}$$

In spherical polar coordinates the above becomes

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

$$+ \frac{1}{r^2 \sin^2 \theta}\frac{\partial \psi(r, \theta, \phi)}{\partial \phi^2} + \frac{2m}{\hbar^2}[E - V]\psi(r, \theta, \phi) = 0 \qquad \text{...(88)}$$

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

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial \phi^2}\right) = 0 \qquad \text{...(89)}$$

Equation (88) then becomes

$$\frac{1}{\sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \phi}\right) + \frac{1}{\sin^2 \theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2I_0}{\hbar^2}[E - V]\psi = 0 \qquad \text{...(90)}$$

Further for the rigid rotator $V = 0$, so that Eq. (90) reduces to

$$\frac{1}{\sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{\sin^2 \theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2I_0}{\hbar^2}E\psi = 0 \qquad \text{...(91)}$$

In the above, ψ is a function of only θ and ϕ since r = constant i.e., $\psi = \psi(\theta, \phi)$

7.4.2 Solution of the Wave Equation: Energy Eigenvalues and Energy Eigenfunctions for the Rotator

The wave equation given by Eq. (91) can be solved using the method of separation of variables. We do this by writing

$$\psi(\theta, \phi) = \Theta(\theta)\, \Phi(\phi) \qquad \text{...(92)}$$

where Θ and Φ are respectively functions of θ alone and ϕ alone.

Using Eq. (92) in Eq. (91) we obtain

$$\Phi \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \Theta \frac{1}{\sin^2\theta} \frac{d^2\Phi}{d\phi^2} + \frac{2I_0E}{\hbar^2} \Theta\Phi = 0$$

Dividing the above throughout by $\dfrac{\Theta\Phi}{\sin^2\theta}$, we get

$$\frac{1}{\Theta}\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{2I_0E}{\hbar^2}\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \qquad \text{...(93)}$$

The left hand side of Eq. (93) depends only on θ while the right hand side depends only on θ. Hence for the Eq. (93) to be valid, each side of it must separately be equal to a constant. For convenience we set

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2 \ (m = \text{constant})$$

or

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \qquad \text{...(94)}$$

Let us call it Φ equation.

We also have

$$\frac{1}{\Theta}\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{2I_0E}{\hbar^2}\sin^2\theta = m^2$$

Dividing the above by $\dfrac{\sin^2\theta}{\Theta}$ we obtain

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{2I_0E}{\hbar^2}\Theta = \frac{m^2}{\sin^2\theta}\Theta$$

or

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left(\frac{2I_0E}{\hbar^2} - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad \text{...(95)}$$

Let us call it Θ equation.

Solution of the Φ Equation

The most general solution of Eq. (94) is given by

$$\Phi = Ae^{\pm im\phi} \qquad \text{...(96)}$$

where A is an arbitrary constant, and can be evaluated using the requirement of the normalization of Φ

$$\int_0^{2\pi} \Phi^* \Phi \, d\phi = 1$$

Using Eq. (96) 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

$$A = \frac{1}{\sqrt{2\pi}} \qquad \text{...(97)}$$

For Φ to be a factor in the total wavefunction of the rotator, the single valuedness of Φ demands

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

Using Eq. (96) 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.,

$$m = 0, \pm 1, \pm 2, \ldots \qquad \text{...(98)}$$

Using the results given in Eqs. (97) and (98), we obtain from Eq. (96)

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad \text{...(99)}$$

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
$$L = E \qquad (\because V = 0 \text{ and } E = T)$$

Using the expression for the total energy E given by Eq. (77) we get

$$L = \frac{1}{2} I\,(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

We observe that ϕ does not appear explicitly in the Lagrangian function and hance ϕ is a cyclic or ignorable coordinate.

Solution of the Θ Equation

Putting
$$\lambda = \frac{2I_0E}{\hbar^2} \qquad \text{...(100)}$$

the Θ equation which is given by Eq. (95) becomes

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad \text{...(101)}$$

Let us introduce a new variable ξ as

$$\xi = \cos\theta \qquad \text{...(102)}$$

Now

$$\frac{d\Theta}{d\theta} = \frac{d\Theta}{d\xi}\frac{d\xi}{d\theta} = -\sin\theta\frac{d\Theta}{d\xi} \qquad \text{(using eq.102)}$$

or

$$\frac{d}{d\theta} = -\sin\theta\frac{d}{d\xi} \qquad \text{...(103)}$$

Using Eqs. (102) and (103) in Eq. (101) we get

$$-\frac{d}{d\xi}\left[-(1-\xi)^2\frac{d\Theta}{d\xi}\right] + \left[\lambda - \frac{m^2}{1-\xi^2}\right]\Theta = 0$$

or

$$(1-\xi^2)\frac{d^2\Theta}{d\xi^2} - 2\xi\frac{d\Theta}{d\xi} + \left[\lambda - \frac{m^2}{1-\xi^2}\right]\Theta = 0 \qquad \text{...(104)}$$

For mathematical convenience let us substitute

$$\Theta = (1-\xi^2)^{\frac{m}{2}}X(\xi) \qquad \text{...(105)}$$

where $X(\xi)$ is a function of only ξ.

Substituting for $\frac{d\Theta}{d\xi}$ and $\frac{d^2\Theta}{d\xi^2}$ as obtained from Eq. (105) in Eq. (104) and simplifying we obtain

$$(1-\xi^2)\frac{d^2X}{d\xi^2} - 2\,(m+1)\,\xi\,\frac{dX}{d\xi} + [\lambda - m(m+1)]X = 0 \qquad \text{...(106)}$$

Equation (106) can be solved using power series method. For this we express the function X as a power series in ξ as

$$X = \sum_{n=0}^{\infty} a_n \xi^n, \quad n = 0, 1, 2, ... \qquad \text{...(107)}$$

The above gives

$$\frac{dX}{d\xi} = \sum_{n=0}^{\infty} n\,a_n \xi^{n-1} \qquad \text{...(108)}$$

and

$$\frac{d^2X}{d\xi^2} = \sum_{n=2}^{\infty} n\,(n-1)\xi^{n-2} \qquad \text{...(109)}$$

Substitution of Eqs. (107), (108) and (109) in Eq. (106) yields

$$\sum_{n=2}^{\infty} n(n-1)\,a_n\xi^{n-2} - \sum_{n=2}^{\infty} n\,(n-1)a_n\xi^n - 2(m+1)\sum_{n=1}^{\infty} n\,a_n\xi^n + [\lambda - m(m+1)]\sum_{n=0}^{\infty} a_n\xi^n = 0 \qquad \text{...(110)}$$

For Eq. (110) to be valid for all possible values of ξ, the coefficients of the individual powers of ξ must separately vanish.

Thus we obtain, in general, for the coefficient of ξ^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

$$\frac{a_{n+2}}{a_n} = \frac{n(n-1) + 2n\,(m+1) + m(m+1) - \lambda}{(n+1)\,(n+2)} \qquad \text{...(111)}$$

Equation (110) 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 Eq. (111) gives

$$n(n - 1) + 2n\,(m + 1) + m(m + 1) - \lambda = 0$$

or
$$\lambda = (n + m)\,(n + m + 1) \qquad \text{...(112)}$$

In Eq. (112) $m = 0, 1, 2, \ldots$ and $n = 0, 1, 2, \ldots$, Hence we may write

$$n + m = l \text{ is an integer including } 0 \qquad \text{...(113)}$$

We can thus write Eq. (112) as

$$\lambda = l(l + 1) \qquad \text{...(114)}$$

Using the above values of λ, Eq. (104) becomes

$$(1-\xi^2)\frac{d^2\Theta}{d\xi^2} - 2\xi\frac{d\Theta}{d\xi} + \left[l(l+1) - \frac{m^2}{1-\xi^2}\right]\Theta = 0 \qquad \text{...(115)}$$

It is well known that the associated Legendre function $p_l^{|m|}(\xi)$ of degree l and order $|m|$ where $l = 0, 1, 2, \ldots$ and $m = 0, 1, 2, \ldots, l$ is defined in terms of Legendre polynomial $P_l(\xi)$ as

$$P_l^{|m|}(\xi) = (1-\xi^2)^{\frac{|m|}{2}}\frac{d^{|m|}}{d\xi^{|m|}}P_l(\xi) \qquad \text{...(116)}$$

$P_l(\xi)$ satisfies the Legendre differential equation

$$\frac{d}{d\xi}\left[(1-\xi^2)\frac{dP_l(\xi)}{d\xi}\right] + l(l+1)\,P_l(\xi) = 0 \qquad \text{...(117)}$$

Differentiating Eq. (117) $|m|$ times with respect to ξ and using Eq. (116) we obtain

$$(1-\xi^2)\frac{d^2P_l^{|m|}}{d\xi^2} - 2\xi\frac{d\,P_l^{|m|}(\xi)}{d\xi} + \left\{l(l+1) - \frac{m^2}{1-\xi^2}\right\}P_l^{|m|}(\xi) = 0 \qquad \text{...(118)}$$

Comparing Eqs. (115) and (118) we identify

$$\Theta(\theta) = P_l^{|m|}(\xi) = P_l^{|m|}(\cos\theta) \qquad \text{...(119)}$$

Thus we can express the general solution of the Θ equation as

$$\Theta(\theta) = B\,P_l^{|m|}\,(\cos\theta) \qquad \text{...(120)}$$

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 Eq. (120) 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

$$B = \sqrt{\frac{2l+l(l-|m|)!}{2(l+|m|)!}} \qquad \text{...(121)}$$

Thus the general solution of the Θ equation given by Eq. (120) becomes

$$\Theta(\theta) = \sqrt{\frac{2l+l(l-|m|)!}{2(l+|m|)!}} \, P_l^{|m|}(\cos\theta) \qquad \text{...(122)}$$

In view of Eq. (99) and Eq. (122) we can now write the wavefunction ψ for the rigid rotator with free axis as

$$\psi_{l,|m|} = \Theta(\theta)\Phi(\theta) = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{2l+l(l-|m|)!}{2(l+|m|)!}} \, P_l^{|m|}(\cos\theta) e^{im\phi} \qquad \text{...(123)}$$

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

$$E_l = \frac{\hbar^2}{2I_0}[l(l+1)] \qquad \text{...(124)}$$

7.4.3 Rigid Rotator with Fixed Axis

For a rigid rotator with fixed axis, θ becomes 90° so that the Schrödinger equation for the rotator given by Eq. (91) becomes

$$\frac{\partial^2\psi}{\partial\phi^2} + \frac{2I_0}{\hbar^2} E\psi = 0 \qquad ...(125)$$

Writing $\frac{2I_0}{\hbar^2} E = m^2$ as before, Eq. (125) becomes

$$\frac{\partial^2\psi}{\partial\phi^2} + m^2\psi = 0 \qquad ...(126)$$

The general solution of Eq. (126) is given by

$$\psi(\phi) = Ae^{\pm im\phi} \qquad ...(127)$$

As has been shown earlier, the requirement of normalization of $\psi(\phi)$ gives

$$A = \frac{1}{\sqrt{2\pi}} \qquad ...(128)$$

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

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2,... \qquad ...(129)$$

and the corresponding energy eigenvalues are

$$E_m = \frac{\hbar^2}{2I_0} m^2 \qquad ...(130)$$

Note: The total wave function describing the state of a rigid rotator with free axis as obtained above is

$$\psi = \Theta_{l,\pm m}(\theta)\ \Phi_{\pm m}(\phi) = Y_{1,\pm m}(\theta, \phi)$$

The functions $Y_{e,\pm m}(\theta, \phi)$ 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

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

$$\hat{L}_z\ Y_{l,\pm m}(\theta\ \phi) = \pm m\ \hbar\ Y_{l,\pm m}.$$

We find that the quantum mechanical problems of rigid rotator and angular momentum are directly related.

7.5 HYDROGEN ATOM AND HYDROGEN-LIKE 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 (e.g. 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

$$V(r) = \frac{-1}{4\pi \in_0} \frac{Ze^2}{r} = -k \frac{Ze^2}{r} \qquad \left[k = \frac{1}{4\pi \in_0} \right] \qquad \text{...(131)}$$

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

$$\nabla^2 \psi(\vec{r}) + \frac{2m}{\hbar^2}[E - V(r)]\psi(\vec{r}) = 0 \qquad \text{...(132)}$$

where

$$m = \frac{m_e(Zm_p)}{m_e + (Zm_p)} \text{ is the reduced mass.}$$

Equation (132) expressed in spherical polar coordinate (r, θ, ϕ) is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0 \quad \text{...(133)}$$

In the above,

$$\psi = \psi(r, \theta, \phi).$$

Using the method of separation of variables we may write

$$\psi = \psi(r, \theta, \phi) = R(r)\,\Theta\,(\theta)\,\Phi\,(\phi) \qquad \text{...(134)}$$

and as shown in Section 7.2 we obtain the following three equations

(i) Φ equation:
$$\frac{d^2\Phi}{d\phi^2}\, m^2\Phi = 0 \qquad \text{...(135)}$$

(ii) Θ equation:
$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad \text{...(136)}$$

(iii) R (radial) equation:
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2}[E - v(r)]R - \frac{\lambda}{r^2}R = 0 \qquad \text{...(137)}$$

In the above, $\lambda = l(l + 1)$ ...(138)

Solution of the Φ equation was obtained in Section 7.2.1 and is given by

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots \qquad \ldots(139)$$

Solution of the Θ equation was obtained in Section 7.2.2 and is given by

$$\Theta_{lm}(\theta) = (-1)^m \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta); \quad m > 0 \qquad \ldots(140)$$

$$\Theta_{lm}(\theta) = \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta); \quad m \le 0 \qquad \ldots(141)$$

In the above,

$$l = 0, 1, 2, \ldots \qquad \ldots(142)$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm l \qquad \ldots(143)$$

The normalized angular part of the wavefunction is given by

$$\underset{lm}{\psi}(\theta, \phi) = \underset{lm}{\Theta}(\theta)\, \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} (-1)^m \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta)\, e^{im\phi} \qquad \ldots(144)$$

7.5.1 Solution of the Radial Equation

Substituting for $V(r)$ given by Eq. (131) and λ given by Eq. (138) the radial wave equation (137) becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left[E - \frac{l(l+1)\hbar^2}{2mr^2} + k\frac{Ze^2}{r}\right] R = 0 \qquad \ldots(145)$$

For solving Eq. (145) let us introduce a dimensionless variable ρ as

$$\rho = \gamma r \qquad \ldots(146)$$

The parameter γ is chosen as

$$\gamma = \sqrt{\frac{-8mE}{\hbar^2}} \qquad \ldots(147)$$

Further let us introduce a constant λ as

$$\lambda = \frac{kZe^2}{\hbar}\sqrt{\frac{m}{-2E}} \qquad \ldots(148)$$

We may note that E is negative for bound states of the atom under consideration and hence both ρ and λ are real.

In terms of ρ and λ, Eq. (145) becomes

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]R = 0 \qquad \text{...(149)}$$

Let us first find the *asymptotic solution* of Eq. (149). It is the solution in the limit ρ (and hence *r*) → ∞. In this limit Eq. (149) reduces to

$$\frac{d^2R}{d\rho^2}-\frac{1}{4}R=0 \qquad \text{...(150)}$$

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 $\rho \to \infty$ $R \to \infty$. 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 Eq. (149) as

$$R(\rho) = F(\rho)e^{-\rho/2} \qquad \text{...(151)}$$

where $F(\rho)$ is some function of ρ.

Using Eq. (151) in Eq. (149) we obtain

$$\rho^2\frac{d^2R(\rho)}{d\rho^2}+\rho(2-\rho)\frac{dF(\rho)}{d\rho}+[\rho\lambda-\rho-l(l+1)]F(\rho)=0 \qquad \text{...(152)}$$

We find that when $\rho = 0$

$$l(l+1)\,F(0) = 0$$

or

$$F(0) = 0,\ l \neq 0 \qquad \text{...(153)}$$

Clearly, a power series solution for $F(\rho)$ must not contain a constant term. Hence, we may write the power series solution as

$$F(\rho) = \sum_{k=0}^{\infty} C_k\,\rho^{s+k} \qquad \text{...(154)}$$

The above gives

$$\frac{dF(\rho)}{d\rho} = \sum C_k\,(s+k)\rho^{s+k-1} \qquad ...(155)$$

$$\frac{d^2F(\rho)}{d\rho^2} = \sum C_k\,(s+k)\,(s+k-1)\rho^{s+k-2} \qquad ...(156)$$

Substituting Eqs. (154), (155), (156) in Eq. (152) we obtain

$$\sum_k C_k\,(\lambda-1-s+k)\,\rho^{s+k-1} + \sum_k C_k(s^2+2sk+k^2+s+k-l^2-l)\rho^{s+k} = 0 \qquad ...(157)$$

For the above equation to be valid for all value of ρ, the coefficient of each power of ρ must separately vanish. Equating the coefficient of ρ^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

$$s = l \quad \text{or} \quad s = -(l+1) \qquad ...(158)$$

If $s = -(l+1)$, the first term in $F(\rho)$ given by Eq. (154) becomes $C_0\rho^{-(l+1)k} = \dfrac{C_0}{\rho^{(l+1)k}}$ which tends to infinity as ρ and hence r tends to zero. We hence get $s = l$. Equating the coefficient of $\rho^{S+k+1} = \rho^{l+k+1}$ in Eq. (157) to zero we obtain the recurrence relation

$$C_{k+1} = \frac{l+k+1-\lambda}{(k+1)\,(k+2l+2)}\,C_k \qquad ...(159)$$

Using the above relation we can find the coefficients C_1, C_2, C_3, etc., in terms of the coefficient C_0.

For large values of k, Eq. (159) gives

$$C_{k+1} = \frac{k}{k^2}\,C_k$$

or

$$\frac{C_k+1}{C_k} = \frac{1}{k} \qquad ...(160)$$

We have

$$e^\rho = \sum_{k=0}^{\infty} \frac{1}{k!}\rho^k = \sum_{k=0}^{\infty} b_k\rho^k \qquad ...(161)$$

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
$$\frac{b_k + 1}{b_k} = \frac{1}{k} \qquad ...(162)$$

$F(\rho)$ given by Eq. (154) can be written as
$$F(\rho) = \rho^s \sum_{k=0}^{\infty} C_k \rho^k = \rho^l \sum_{k=0}^{\infty} C_k \rho^k \qquad ...(163)$$

Using Eq. (161) we obtain
$$\rho^l e^{\rho} = \rho^l \sum b_k \rho^k \qquad ...(164)$$

In view of the results given by Eqs. (160), (162), (163) and (164) we get
$$F(\rho) = \rho^l e^{\rho}$$

So that
$$R(\rho) = \rho^l e^{\rho} e^{-\rho/2} = \rho^l e^{\rho/2} \qquad ...(165)$$

$R(\rho)$ given by eq. (165) is not acceptable because $R(\rho) \to \infty$ as ρ and hence $r \to \infty$. Thus the series governed by the recursion relation given by Eq. (159) does not lead to an acceptable radial wavefunction unless the series breaks off after a finite number of terms.

7.5.2 Energy Eigenvalues

Let us assume the series to break off after the k^{th} term so that C_{k+1} becomes zero. The recursion formula given by Eq. (159) then gives
$$l + k + 1 + \lambda = 0$$

or
$$\lambda = l + k + 1 = n \text{ (say)} \qquad ...(166)$$

In Eq. (166), 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 Eq. (148) we get

$$\lambda^2 = \frac{k^2 Z^2 e^4}{\hbar^2} \frac{m}{(-2E)}$$

Using Eq. (166) in the above equation we obtain the energy eigenvalues for a hydrogen-like atom to be

$$E_n = \frac{-k^2 m Z^2 e^4}{2\hbar^2 n^2} - \frac{me^4 Z^2}{32\,\pi^2 \in_0^2 \hbar^2 n^2} \qquad \text{...(167)}$$

The energy eigenvalues for a hydrogen atom are obtained by putting $Z = 1$ in Eq. (167). We get

$$E_n = \frac{-me^4}{32\,\pi^2 \in_0^2 \hbar^2 n^2} \qquad \text{...(168)}$$

Substituting the values of m, e, $\in_o$ and $\hbar$ we obtain the energy eigenvalues of hydrogen atom to be

$$E_1 = -13.6 \text{ eV}, \quad E_2 = -3.4 \text{ eV}, \quad E_3 = -1.51 \text{ eV, etc.}$$

The above values are the same as obtained by Bohr on the basis of old quantum theory.

7.5.3 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

$$F(\rho) = \rho^l L(\rho) \qquad \text{...(169)}$$

We then get

$$\frac{dF(\rho)}{d\rho} = \rho^l \frac{dL(\rho)}{d\rho} + l\rho^{l-1} L(\rho) \qquad \text{...(170)}$$

$$\frac{d^2F(\rho)}{d\rho^2} = \rho^l \frac{d^2L(\rho)}{d\rho^2} + l\rho^{l-1}\frac{dL(\rho)}{d\rho} + l\rho^{l-1}\frac{dL(\rho)}{d\rho} + l(l-1)\rho^{l-2}L(\rho)$$

$$= \rho^l \frac{d^2L(\rho)}{d\rho^2} + 2l\rho^{l-1}\frac{dL(\rho)}{d\rho} + l(l-1)\rho^{l-2}L(\rho) \qquad \text{...(171)}$$

Substituting Eqs. (169), (170) and (171) in Eq. (152) and simplifying we get

$$\rho \frac{d^2L(\rho)}{d\rho^2} + (2l + 2 - \rho)\frac{dL(\rho)}{d\rho} + (n - l - 1)\, L(\rho) = 0 \qquad \text{...(172)}$$

If $L_q^p(\rho)$ be the associated Laguerre polynomial of the order p and degree $(q - p)$ then it satisfies the differential equation

$$\rho \frac{d^2 L_q^p(\rho)}{d\rho^2} + (p + 1 - \rho) \frac{dL_q^p(\rho)}{d\rho} + (q - p)\, L_q^p(\rho) = 0 \qquad \text{...(173)}$$

If we consider $q = n + l$ and $p = 2l + l$ then Eq. (172) becomes identical with Eq. (173) 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

$$R_{nl}(r) = N_{nl}\, \rho^l L_{n+l}^{2l+1}(\rho) e^{-\rho/2} \qquad \text{...(174)}$$

The normalization constant N_{nl} can be obtained from the normalized integral

$$\int_0^\infty R_{nl}^2(r) r^2 dr = 1 \qquad \text{...(175)}$$

Using $R_{nl}(r)$ given by Eq. (174) and the orthogonal properties of associated Laguerre polynomials we obtain

$$N_{nl} = \pm \left[\left(\frac{2Zmke^2}{n\hbar^2} \right)^3 \frac{(n - l - 1)!}{2n[(n + l)!]^3} \right]^{1/2} \qquad \text{...(176)}$$

Using the result given by Eq. (176) in Eq. (174) we obtain

$$R_{nl}(r) = -\left[\left(\frac{2Z}{na_{\mathrm{H}}} \right)^3 \frac{(n - l - 1)!}{2n[(n + l)!]^3} \right]^{1/2} e^{-\rho/2}\, \rho^l L_{n+l}^{2l+1}(\rho) \qquad \text{...(177)}$$

where

$$a_{\mathrm{H}} = \frac{4\pi \epsilon_0\, \hbar^2}{me^2} \qquad \text{...(178)}$$

Since the reduced mass m is almost the same as the electron mass m_e (for both hydrogen and hydrogen-like atoms), we get

$$a_{\mathrm{H}} = \frac{4\pi \epsilon_0\, \hbar^2}{m_e e^2} = a_0 \text{ (a constant)} \qquad \text{...(178)}$$

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 Eq. (178), the radial wavefunction becomes

$$R_{ne}(r) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right] e^{-\rho/2}\, \rho^l L_{n+l}^{2l+1}(\rho) \qquad \text{...(179)}$$

The negative sign for N has been used to make R_{10} positive.

ρ and r are related according to $\rho = \gamma r = \sqrt{\dfrac{-8mE}{\hbar^2}}\, r$

Substituting for E given by Eq. (167) we get

$$\rho = \frac{2Z}{na_0}\, r \qquad \text{...(180)}$$

Equation (180) used in Eq. (177) gives the radial wavefunction for hydrogen-like atom as

$$R_{nl}(r) = -\sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{\frac{-Z}{na_0}r} \left(\frac{2Zr}{na_0}\right)^l L_{n+1}^{2l+1}\left(\frac{2Zr}{na_0}\right) \qquad \text{...(181)}$$

Putting $Z = 1$ in the above, the radial wavefunction for hydrogen atom is found to be

$$R_{nl}(r) = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{\frac{-r}{na_0}} \left(\frac{2r}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) \qquad \text{...(182)}$$

7.5.4 Complete Wavefunction

The complete wavefunction is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, \Theta_{lm}(\theta)\, \Phi_m(\phi)$$

where $\quad \Theta_{lm}(\theta) = \sqrt{\dfrac{(2l+1)\,(l-|m|)!}{2(l+|m|)!}}\; P_l^m\,(\cos\theta)$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

and $\quad R_{nl}(r) = \sqrt{\left(\dfrac{2Z}{na_0}\right)^3 \dfrac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{\frac{-Zr}{na_0}} \left(\dfrac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\dfrac{2Zr}{na_0}\right)$

In the above

$$
\begin{aligned}
n &= 1, 2, 3,... \\
l &= 0, 1, 2,...\ (n-1) \\
m &= 0, \pm 1, \pm 2,...\ \pm l.
\end{aligned}
$$

The explicit forms of the complete wavefunctions ψ_{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* ψ_{nlm}
1	0	0	1*s*	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{\frac{-Z}{a_0}r}$
2	0	0	2*s*	$\psi_{200} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{\frac{-Z}{2a_0}r}$
2	1	0	2*p*	$\psi_{210} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{5/2} r\, e^{\frac{-Z}{2a_0}r} \cos\theta$
2	1	+1	2*p*	$\psi_{211} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\, e^{\frac{-Z}{2a_0}r} \sin\theta\, e^{i\phi}$
2	1	–1	2*p*	$\psi_{21-1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\, e^{\frac{-Zr}{2a_0}} r \sin\theta\, e^{-i\phi}$

Putting $Z = 1$ in the above, we obtain the wavefunctions for the hydrogen atom.

7.5.5 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 (167) and (168). 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

$$D = \sum_{l=0}^{n-1} (2l+1) = n^2 \qquad ...(183)$$

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.

7.5.6 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, θ, ϕ) is then given by

$$P_{nlm}\, d\tau = |\psi_{nlm}|^2\, d\tau = |\psi_{nlm}|^2\, r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= |R_{nl}(r)|^2\, |Y_{lm}(\theta, \phi)|^2\, r^2 dr \sin\theta\, d\theta\, d\phi$$

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

$$P_{nl}(r)dr = |R_{nl}(r)|^2\, r^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

or

$$P_{nl}(r)\, dr = 4\pi\, |R_{nl}(r)|^2\, r^2 dr \qquad \text{...(184)}$$

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 Eq. (184) given by

$$P_{10}(r) = \frac{4\pi}{(\pi a_0^3)}\, e^{\frac{-2r}{a_0}}\, r^2 = \frac{4}{a_0^3}\, e^{\frac{-2r}{a_0}}\, r^2 \qquad \text{...(185)}$$

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

$$2r - \frac{2r^2}{a_0} = 0$$

or

$$1 - \frac{r}{a_0} = 0 \quad \text{or} \quad \frac{r}{a_0} = 1$$

or

$$r = a_0 \qquad ...(186)$$

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 (185) 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.

7.5.7 Properties of the Radial Wave Function of Hydrogen Atom

The radial wavefunctions of the hydrogen atom have the properties shown in the Fig. 7.2. 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}.

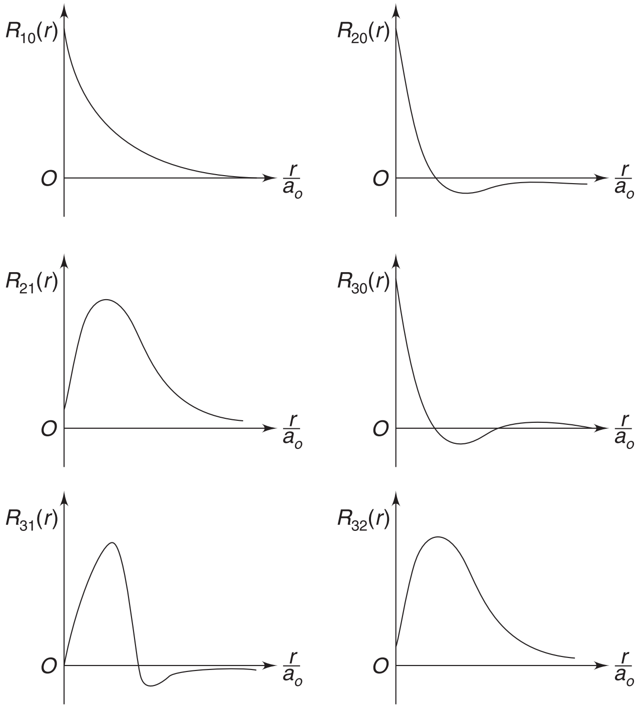


Fig. 7.2

(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 $n - l - 1$.

7.6 SOLVED EXAMPLES

Example 1 A rigid rotator which rotates freely in the x–y plane has a moment of inertia I about the axis of rotation. ϕ 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

$$\hat{H} = \frac{-\hbar^2}{2I} \frac{d^2}{d\phi^2} \qquad \text{...(i)}$$

If ψ 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

$$\frac{d^2\psi}{d\phi^2} + m^2\psi = 0 \qquad \text{...(ii)}$$

where

$$m^2 = \frac{2I}{\hbar^2} E \qquad \text{...(iii)}$$

The general solution of Eq. (ii) is

$$\psi(\phi) = Ae^{im\phi} \qquad \text{...(iv)}$$

where A is an arbitrary constant.

Single valuedness of $\psi(\phi)$ requires

$$\psi(\phi) = \psi(\phi + 2\pi) \qquad \text{...(v)}$$

Using Eq. (iv) in Eq. (v) we get

$$m = 0, \pm 1, \pm 2, \ldots \qquad \text{...(vi)}$$

Thus, we may write the solution given by Eq. (iv) as

$$\psi(\phi) = Ae^{im\phi}, \; m = 0, \pm 1, \pm 2, \ldots \qquad \text{...(vii)}$$

Normalization of $\psi(\phi)$ gives

$$\int_0^{2\pi} \psi^*(\phi)\psi(\phi)d\phi = 1$$

or

$$|A|^2 = \frac{1}{2\pi} \quad \text{or} \quad A = \frac{1}{\sqrt{2\pi}} \qquad \text{...(viii)}$$

We thus get energy eigenvalues, using Eq. (iii), as

$$E_m = \frac{\hbar^2}{2I} m^2, \quad m = 0, \pm 1, \pm 2, \ldots \qquad \text{...(ix)}$$

and the energy eigenfunctions, using Eq. (viii) in Eq. (vii), as

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots \qquad \text{...(x)}$$

(b) We have

$$\psi(0) = A \sin^2 \phi$$

We may express the above as

$$\psi(0) = \frac{A}{2}[1 - \cos 2\phi] = \frac{A}{2} - \frac{A}{4}(e^{i2\phi} + e^{-i2\phi}) \qquad \text{...(xi)}$$

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

$$\psi(t) = \frac{A}{2} - \frac{A}{4} e^{i2\phi} e^{-iE_2 t} - \frac{A}{4} e^{-i2\phi} e^{-iE_2 t}$$

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

$$\psi(t) = \frac{A}{2} - \frac{A}{4} e^{2i\left(\phi - \frac{\hbar^2}{I} t\right)} - \frac{A}{4} e^{-2i\left(\phi - \frac{\hbar^2}{I} t\right)} \qquad \text{...(xii)}$$

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

$$E_l = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2,... \qquad ...(i)$$

where I = the moment of inertia of the molecule

$$= \mu a^2 = \frac{mm}{m+m} a^2 = \frac{m}{2} a^2 \qquad ...(ii)$$

In the above m is the mass of each atom and a is the bond length.

We have from Eq. (i)

the energy corresponding to $l = 1$ as $E_1 = \frac{\hbar^2}{I}$

the energy corresponding to $l = 2$ as $E_2 = \frac{3\hbar^2}{I}$

We get

$$E_2 - E_1 = \frac{2\hbar^2}{I}$$

which gives

$$I = \frac{2\hbar^2}{E_2 - E_1} \qquad ...(iii)$$

From Eq. (ii) we have the bond length given by

$$a = \sqrt{\frac{2I}{m}}$$

Using Eq. (iii) in the above we get

$$a = \sqrt{\frac{2 \times 2\hbar^2}{(E_2 - E_1)m}} = 2\hbar\sqrt{\frac{1}{m(E_2 - E_1)}} \qquad ...(iv)$$

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

(i) an infinite potential well along the x-axis
(ii) an infinite potential well along the y-axis
(iii) a harmonic oscillator potential along the z-axis.

The energy due to the potential well along the x-axis $= \dfrac{\pi^2\hbar^2}{2ma^2} n_x^2$

The energy due to the potential well along the y-axis $= \dfrac{\pi^2\hbar^2}{2ma^2} n_y^2$

The energy due to the harmonic oscillator potential $= \left(n_z + \dfrac{1}{2}\right)\hbar\omega$

(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 is terms of Hermite polynomial as

$$Z_{n_z}(z) = \frac{1}{[\sqrt{\pi}\, 2^{n_z}\, n_z! z_0]^{1/2}} e^{\frac{-z^2}{2z_0 2}} H_{n_z}\left(\frac{z}{z_0}\right)$$

$$z_0 = \sqrt{\frac{\pi\hbar}{n\omega}}$$

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

$$\langle r\rangle = \int \psi_{100}^* \, r\, \psi_{100}\, d\tau = \int_0^\infty |\psi_{100}|^2\, r\, r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= 4\pi \int_0^{2\pi} \frac{1}{\pi a_0^3} e^{\frac{-2r}{a_0}} r^3 \, dr$$

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

$$\langle r^2 \rangle = 4\pi \int_0^{\infty} \frac{1}{\pi a_0^3} e^{\frac{-2r}{a_0}} r^4 \, dr$$

$$= \frac{4}{a_0^3} \left(\frac{a_0}{2} \right)^5 4!$$

or

$$\langle r^2 \rangle = 3 a_0^2$$

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

$$\langle V(r) \rangle = \int |\psi_{100}|^2 \left(-\frac{1}{4\pi \epsilon_0} \frac{e^2}{r} \right) d\tau$$

$$= \int_0^{\infty} |\psi_{100}|^2 \left(-\frac{1}{4\pi \epsilon_0} \frac{e^2}{r} \right) r^2 dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$$= -\frac{e^2}{4\pi \epsilon_0} 4\pi \times \frac{1}{\pi a_0^3} \int_0^{\infty} e^{\frac{-2r}{a_0}} r \, dr$$

$$= -\frac{e^2}{\pi \in_0 a_0^3} \times \frac{1}{\left(\frac{2}{a_0}\right)^2} = -\frac{e^2}{\pi \in_0 a_0^3} \times \frac{a_0^2}{4}$$

or
$$\langle V(r) \rangle = -\frac{1}{4\pi \in_0} \frac{e^2}{a_0}$$

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

$$R_{10}(r) = 2\left(\frac{2}{a_0}\right)^{3/2} e^{-\frac{2}{a_0}r}$$

$$= \frac{4\sqrt{2}}{a_0^{3/2}} e^{-\frac{2}{a_0}r}$$

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

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \frac{1}{r} P(r)\, dr = \int_0^\infty \frac{1}{r} \frac{32}{a_0^3} r^3 e^{\frac{-4r}{a_0}} dr$$

$$= \frac{32}{a_0^3} \int_0^\infty e^{\frac{-4r}{a_0}} r\, dr$$

$$= \frac{32}{a_0^3} \times \frac{a_0^2}{16}$$

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

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[E-V(r)]\,R-\frac{l(l+1)}{r^2}R\ =0 \qquad \text{...(i)}$$

where $R = R\ (r)$ is the radial wavefunction for the atom.

We can write Eq. (i) as

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}[E-V(r)]\,R-l(l+1)\,R=0 \qquad \text{...(ii)}$$

Let us introduce a function of r, namely $u(r)$ as

$$u(r) = r\,R(r) \qquad \text{...(iii)}$$

The above gives

$$R(r) = \frac{u(r)}{r} \qquad \text{...(iv)}$$

Using Eq. (iv) in Eq. (ii) 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

$$r\frac{d^2u(r)}{dr^2}+\frac{du(r)}{dr}-\frac{du(r)}{dr}+\frac{2m}{\hbar^2}[E-V(r)]\,ru(r)-\frac{l(l+1)}{r}u(r)\ =0$$

Dividing throughout by r, we get

$$\frac{d^2u(r)}{dr^2}+\frac{2m}{\hbar^2}[E-V(r)]\,u(r)-\frac{l(l+1)}{r^2}u(r)=0$$

or

$$\frac{d^2u(r)}{dr^2}+\frac{2m}{\hbar^2}\left[E-V(r)-\frac{l(l+1)\hbar^2}{2mr^2}\right]u(r)=0$$

or
$$\frac{d^2u(r)}{dr^2} + \frac{2m}{\hbar^2}[E - V_{\text{effective}}]\,u(r) = 0 \qquad \text{...(v)}$$

where
$$V_{\text{effective}} = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \qquad \text{...(vi)}$$

Equation (v) 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 eq. (vi).

The first term in eq. (vi) 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 $\sqrt{l(l+1)}\,\hbar$.

The plot of $V_{\text{effective}}$ against r is as shown in the Fig. 7.3.

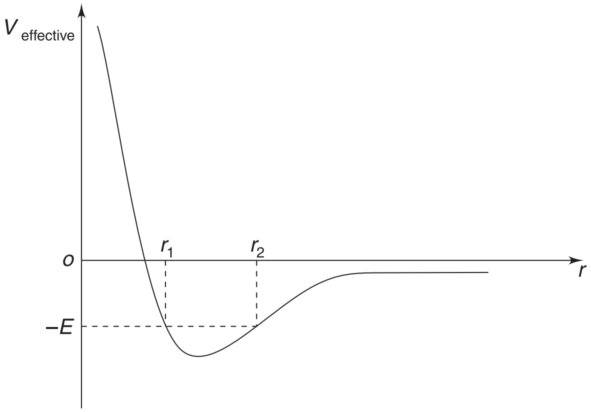


Fig. 7.3

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 is Example 4

$$\langle r \rangle = \frac{3}{2} a_0$$

and

$$\langle r^2 \rangle = 3\, a_0^2$$

We hence obtain

$$\Delta r = \sqrt{3a_0^2 - \frac{a}{4} a_0^2} = \sqrt{\frac{3}{4}}\, a_0.$$

8

Angular Momentum in Quantum Mechanics

One of the important properties of a physical system is the angular momentum which is found to play an important role in the problems of collision and scattering. In quantum systems, particularly in bound state problems, angular momentum concept is used with advantage. In the studies of atomic, molecular and nuclear spectroscopy, a thorough understanding of angular momentum is found to be essential. Besides, angular momentum is found to bear intimate relation with rotation of a system. Such relations find important uses in problems which, for mathematical convenience, require to be described in rotating coordinate frame.

8.1 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 Fig. 8.1. 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 $\overrightarrow{OP}$ 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.

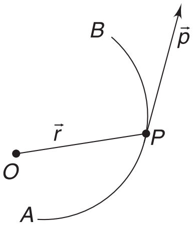


Fig. 8.1

Classically, the angular momentum (which is a vector quantity) of the particle about the point O when it is at P is defined as

$$\vec{L} = \vec{r} \times \vec{p} \qquad \ldots(1)$$

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

$$\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z \qquad \ldots(2)$$

Further, if p_x, p_y and p_z be respectively the components of $\vec{p}$ along X, Y and Z axes then

$$\vec{p} = \hat{i}p_x + \hat{j}p_y + \hat{k}p_z \qquad \text{...(3)}$$

If $L_{x,}$ L_y and L_z be respectively the X, Y and Z components of $\vec{L}$, then using equations (2) and (3) in Eq. (1), we get

$$\hat{i}L_x + \hat{j}L_y + \hat{k}L_z = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

Evaluating the r.h.s of the above equation and comparing the coefficients of $\hat{i}$, $\hat{j}$ and $\hat{k}$ on both sides we obtain

$$L_x = yp_z - zp_y \qquad \text{...(4)}$$

$$L_y = zp_x - xp_z \qquad \text{...(5)}$$

$$L_z = xp_y - yp_x \qquad \text{...(6)}$$

8.2 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

$$x \rightarrow \hat{x} = x$$

$$y \rightarrow \hat{y} = y$$

$$z \rightarrow \hat{z} = z$$

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

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

$$p_z \rightarrow \hat{p}_z = -i\hbar\frac{\partial}{\partial z} \qquad \text{...(7)}$$

Substituting the above in Eqs. (1), (4), (5) and (6) we obtain the quantum mechanical operators corresponding to the quantities $\vec{L}$, L_x, L_y, L_z as

$$\vec{\hat{L}} = -i\hbar\vec{r} \times \vec{\nabla} \qquad \text{...(8)}$$

$$\hat{L}_x = -t\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \qquad \text{...(9)}$$

$$\hat{L}_y = -t\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad \text{...(10)}$$

$$\hat{L}_z = -t\hbar\left(x\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right) \qquad \ldots(11)$$

8.3 COMMUTATION RELATION BETWEEN ANGULAR MOMENTUM OPERATORS

Consider an arbitrary function ψ defined in the domain of definition of the angular momentum operators. We then have,

$$\left[\hat{L}_x, \hat{L}_y\right]\psi = \hat{L}_x\hat{L}_y\psi - \hat{L}_y\hat{L}_x\psi$$

Using Eqs. (9) and (10) in the above we get

$$[\hat{L}_x, \hat{L}_y]\,\psi = -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\psi + \hbar^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\psi$$

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

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

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

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

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

$$= -\hbar^2 y\frac{\partial\psi}{\partial x} + \hbar^2 x\frac{\partial\psi}{\partial y}$$

$$= \hbar^2\left(x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}\right)$$

$$[\hat{L}_x, \hat{L}_y]\,\psi = i\hbar \times (-i\hbar)\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]\psi = i\hbar\hat{L}_z\psi$$

The above thus gives

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \qquad \ldots(12)$$

Proceeding as above we obtain

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x \qquad \ldots(13)$$

and

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y \qquad \ldots(14)$$

The commutation relations given by Eqs. (12), (13) and (14) can be written collectively as

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\hat{L}_k \qquad \ldots(15)$$

i, j and k being respectively x, y and z taken in a cyclic manner.

We observe that the components of angular momentum operators do not commute with each other and as a consequence, the operators do not possess simultaneous eigenfunctions. Clearly, any pair of the three components of angular momentum cannot be simultaneously measured with unlimited accuracy, a result which follows from the general uncertainty relation.

The commutation relation given by Eqs. (12), (13) and (14) can be written in a compact form as

$$\hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}} \qquad \ldots(16)$$

Note: In the usual sense the vector product of a vector with itself is zero. Hence we have to consider $\hat{\vec{L}}$ as a vector operator and not as a vector in the usual sense. The left hand side has to be considered as a determinant and has to be expanded before the term-by-term comparison with the right hand side.

8.4 SQUARE ANGULAR MOMENTUM OPERATOR ($\hat{L}^2$) AND COMMUTATION RELATIONS

(i) $\hat{L}^2$ and $\hat{L}_x$

(ii) $\hat{L}^2$ and $\hat{L}_y$

(iii) $\hat{L}^2$ and $\hat{L}_z$

Since angular momentum $\vec{L}$ is an observable L^2 is also an observable given by

$$L^2 = \vec{L} \cdot \vec{L} = L_x^2 + L_y^2 + L_z^2 \qquad \text{...(17)}$$

The operator corresponding to the quantity L^2 is a scalar operator (unlike the operator corresponding to $\vec{L}$ which is a vector operator) and can be expressed as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \qquad \text{...(18)}$$

We have using Eq. (18)

(i) $$\left[\hat{L}^2, \hat{L}_x\right] = \left[\left(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\right), \hat{L}_x\right]$$

$$= \left[\hat{L}_x^2, \hat{L}_x\right] + \left[\hat{L}_y^2, \hat{L}_x\right] + \left[\hat{L}_z^2, \hat{L}_x\right]$$

$$= \left[\hat{L}_x, \hat{L}_x\right]\hat{L}_x + \hat{L}_x\left[\hat{L}_x, \hat{L}_x\right] + \left[\hat{L}_y, \hat{L}_x\right]\hat{L}_y + \hat{L}_y\left[\hat{L}_y, \hat{L}_x\right] + \left[\hat{L}_z, \hat{L}_x\right]\hat{L}_z + \hat{L}_z\left[\hat{L}_z, \hat{L}_x\right]$$

$$= 0 + 0 - i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_z\hat{L}_y$$

or $$\left[\hat{L}^2, \hat{L}_x\right] = 0 \qquad \text{[using Eq. (15)]} \quad \text{...(19)}$$

(ii) $$\left[\hat{L}^2, \hat{L}_y\right] = \left[(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2), \hat{L}_y\right]$$

$$= \left[\hat{L}_x^2, \hat{L}_y\right] + \left[\hat{L}_y^2, \hat{L}_y\right] + \left[\hat{L}_z^2, \hat{L}_y\right]$$

$$= \left[\hat{L}_x, \hat{L}_y\right]\hat{L}_x + \hat{L}_x\left[\hat{L}_x, \hat{L}_y\right] + \left[\hat{L}_y, \hat{L}_y\right]\hat{L}_y + \hat{L}_y\left[\hat{L}_y, \hat{L}_y\right] + \left[\hat{L}_z, \hat{L}_y\right]\hat{L}_z + \hat{L}_z\left[\hat{L}_z, \hat{L}_y\right]$$

$$= -i\hbar\hat{L}_z\hat{L}_x + i\hbar\hat{L}_x\hat{L}_z + 0 + 0 - i\hbar\hat{L}_x\hat{L}_z - i\hbar\hat{L}_z\hat{L}_x$$

or $$\left[\hat{L}^2, \hat{L}_y\right] = 0 \qquad \text{...(20)}$$

(iii) $$\left[\hat{L}^2, \hat{L}_z\right] = \left[(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2), \hat{L}_z\right]$$

$$= \left[\hat{L}_x^2, \hat{L}_z\right] + \left[\hat{L}_y^2, \hat{L}_z\right] + \left[\hat{L}_z^2, \hat{L}_z\right]$$

$$= \left[\hat{L}_x, \hat{L}_z\right]\hat{L}_x + \hat{L}_x\left[\hat{L}_x, \hat{L}_z\right] + \left[\hat{L}_y, \hat{L}_z\right]\hat{L}_y + \hat{L}_y\left[\hat{L}_y, \hat{L}_z\right] + \left[\hat{L}_z, \hat{L}_z\right]\hat{L}_z + \hat{L}_z\left[\hat{L}_z, \hat{L}_z\right]$$

$$= -i\hbar\hat{L}_y\hat{L}_x - i\hbar\hat{L}_x\hat{L}_y + i\hbar\hat{L}_x\hat{L}_y + i\hbar\hat{L}_y\hat{L}_x + 0 + 0$$

or $$\left[\hat{L}^2\ \hat{L}_z\right] = 0 \qquad \text{...(21)}$$

8.5 CONCLUSION

Results expressed by Eqs. (19), (20) and (21) show that $\hat{L}^2$ commutes with all the three component operators $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$. As a consequence, the square of angular momentum can be measured simultaneously with any of the three components with unlimited accuracy. However, as the component operators among themselves are non-commuting, it is not possible to measure L^2 and all the three componets L_x, L_y and L_z simulataneously. Thus we cannot have a representation in which all the four operators (namely, $\hat{L}^2$, $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$) have simultaneous eigenfunctions. It is usual to consider the eigenvalue problem in such a way that $\hat{L}^2$ and one of the components usually $\hat{L}_z$ have simultaneous eigenfunctions. The selection of $\hat{L}_z$ is however, completely arbitrary.

8.6 EXPRESSION FOR ANGULAR MOMENTUM OPERATORS IN SPHERICAL POLAR COORDINATES

Transformation equations between the cartesian coordinates x, y, z and the spherical polar coordinates r, θ, ϕ of a point in space are

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned} \qquad \text{...(22)}$$

The reverse transformation relations are

$$\begin{aligned} r^2 &= x^2 + y^2 + z^2 \\ \tan\phi &= \frac{y}{x} \\ \tan\theta &= \frac{\sqrt{x^2 + y^2}}{z} \end{aligned} \qquad \text{...(23)}$$

We have from Eq. (11)

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

In units of $\hbar$ the above becomes

$$\hat{L}_z = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad \text{...(24)}$$

We may write Eq. (24) as

$$\hat{L}_z = -i\left[x\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial y} + \frac{\partial}{\partial \phi}\frac{\partial \phi}{\partial y}\right) - y\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \phi}\frac{\partial \phi}{\partial x}\right)\right] \qquad ...(25)$$

We have

$$r^2 = x^2 + y^2 + z^2 \qquad ...(26)$$

Differentiating Eq. (26) with respect to x we get

$$2r\frac{\partial r}{\partial x} = 2x \quad \text{or} \quad \frac{\partial r}{\partial x} = \frac{x}{r} \qquad ...(27)$$

Similarly, we get on differentiating Eq. (26) with respect to y and z

$$\frac{\partial r}{\partial y} = \frac{y}{r} \qquad ...(28)$$

$$\frac{\partial r}{\partial z} = \frac{z}{r} \qquad ...(29)$$

Further, we have

$$\tan\phi = \frac{y}{x} \qquad ...(30)$$

Differentiating the above with respect to x we get

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

or

$$\frac{\partial \phi}{\partial x} = -\frac{y}{x^2\sec^2\phi} \qquad ...(31)$$

Similarly, differentiating Eq. (30) with respect to y we get

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

or

$$\frac{\partial \phi}{\partial y} = \frac{1}{x\sec^2\phi} \qquad ...(32)$$

The last of Eq. (23) gives

$$\tan^2\theta = \frac{x^2 + y^2}{z^2} \qquad ...(33)$$

Differentiating Eq. (33) with respect to x we obtain

$$2\tan\theta\sec^2\theta\,\frac{\partial \theta}{\partial x} = \frac{2x}{z^2}$$

or
$$\frac{\partial\theta}{\partial x} = \frac{x}{z^2 \tan\theta \sec^2\theta} \quad \ldots(34)$$

Similarly, we get
$$\frac{\partial\theta}{\partial y} = \frac{y}{z^2 \tan\theta \sec^2\theta} \quad \ldots(35)$$

Substituting Eqs. (27), (28), (31), (32), (34) and (35) in Eq. (25), we get

$$\hat{L}_z = -i\left[\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial y}\right)x + \left(\frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y}\right)x + \left(\frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial y}\right)x - \left(\frac{\partial}{\partial r}\frac{\partial r}{\partial y}\right)y - \left(\frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y}\right)y + \left(\frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial y}\right)y\right]$$

$$= -i\left[\frac{\partial}{\partial r}\left\{\frac{\partial r}{\partial y}x - \frac{\partial r}{\partial x}y\right\} + \frac{\partial}{\partial\theta}\left\{\frac{\partial\theta}{\partial y}x - \frac{\partial\theta}{\partial x}y\right\} + \frac{\partial}{\partial\phi}\left\{\frac{\partial\phi}{\partial y}x - \frac{\partial\phi}{\partial x}y\right\}\right]$$

$$= -i\left[\frac{\partial}{\partial r}\left(\frac{y}{r}x - \frac{x}{r}y\right) + \frac{\partial}{\partial\theta}\left(\frac{y}{z^2\tan\theta\sec^2\theta}x - \frac{x}{z^2\tan\theta\sec^2\theta}y\right)\right.$$
$$\left. + \frac{\partial}{\partial\phi}\left(\frac{x}{x\sec^2\phi} + \frac{y^2}{x^2\sec^2\phi}\right)\right]$$

or
$$\hat{L}_z = -i\frac{\partial}{\partial\phi}[\cos^2\phi + \tan^2\phi\cos^2\phi]$$

or
$$\hat{L}_z = -i\frac{\partial}{\partial\phi} \quad \ldots(36)$$

Proceeding as above we can show that

$$\hat{L}^2 = -\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] \quad \ldots(37)$$

We may note that the expressions for $\hat{L}_z$ and $\hat{L}^2$ were derived using $\hbar = 1$. To be exact, the expressions for $\hat{L}_z$ and $\hat{L}^2$ are

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \quad \ldots(36a)$$

and

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] \quad \ldots(37a)$$

8.7 EIGENVALUES AND EIGENFUNCTIONS OF $\hat{L}_z$

Angular momentum $\vec{L}$ is a vector quantity. Hence, the eigenvalues of angular momentum operator $\hat{\vec{L}}$ are defined along specific directions. It is customary to define (and hence to measure) angular momentum along the *Z*-direction. We are thus interested in determining the eigenvalues and also the eigenfunctions of $\hat{L}_z$.

Let $\psi(r, \theta, \phi)$ be an eigenfunction of $\hat{L}_z$ belonging to an eigenvalue L_z. We then have the eigenvalue equation given by

$$\hat{L}_z \psi(r, \theta, \phi) = L_z \psi\,(r, \theta, \phi) \qquad \ldots(38)$$

The operator $\hat{L}_z$ (in spherical polar coordinates) is given by Eq. (36)

$$\hat{L}_z = -i\,\frac{\partial}{\partial\phi}$$

so that Eq. (38) takes the form

$$-i\,\frac{\partial\psi(r, \theta, \phi)}{\partial\phi} = L_z\psi(r, \theta, \phi)$$

or

$$\frac{\partial\psi(r, \theta, \phi)}{\psi(r, \theta, \phi)} = iL_z\partial\phi$$

Integrating the above we obtain

$$\ln \psi(r, \theta, \phi) = iL_z\phi + \text{constant} \qquad \ldots(39)$$

The constant in the above equation is independent of ϕ and hence it can be taken as a function of r and θ. Considering the constant as 1n $f(r, \theta)$, Eq. (39) yields

$$\psi(r, \theta\ \phi) = f(r, \theta)\ e^{it_z\phi} \qquad \ldots(40)$$

For $\psi(r, \theta, \phi)$, given by Eq. (40), to be an acceptable eigenfunction it must be single valued. This condition requires

$$\psi(r, \theta, \phi) = \psi(r, \theta, \phi + 2\pi) \qquad \ldots(41)$$

Using Eq. (41) in Eq. (40) we obtain

$$f(r, \theta)\ e^{iL_z\phi} = f(r, \theta)\ e^{iL_z(\phi + 2\pi)} \qquad \ldots(42)$$

The above gives

$$e^{iL_z 2\pi} = 1 = e^{i2\pi m} \qquad \ldots(42)$$

where $$m = 0, \pm 1, \pm 2, \ldots\ldots\ldots \qquad \ldots(43)$$

Equation (42) thus gives $$L_z = m \qquad \ldots(44)$$

We find that the eigenvalues $\hat{L}_z$ are 0, +ve, as well as –ve integers. The possible values of L_z are thus

$$L_z = 0, \pm 1, \pm 2, \ldots\ldots \qquad \ldots(45)$$

Eigenfunction $\psi(r, \theta, \phi)$ of $\hat{L}_z$ given by Eq. (40) can be rewritten as

$$\psi(r, \theta, \phi) = f(r, \theta)\, e^{im\phi}$$

or

$$\psi(r, \theta, \phi) = f(r, \theta)\, \Phi_m(\phi) \qquad \ldots(46)$$

where we have written

$$\Phi_m(\phi) = e^{irh\phi} \qquad \ldots(47)$$

Since the acceptable wavefunction must be normalized, we have

$$\int_0^{2\pi} \psi^*(r, \theta, \phi)\, \psi(r, \theta, \phi)\, d\phi = 1$$

or

$$\int f^*(r, \theta)\, e^{-im\phi} f(r, \theta)\, e^{im\phi}\, d\phi = 1$$

or

$$\int_0^{2\pi} |f(r, \theta)|^2\, d\phi = 1$$

or

$$|f(r, \theta)|^2\, 2\pi = 1$$

or

$$|f(r, \theta)|^2 = \frac{1}{2\pi}$$

The above gives

$$f(r, \theta) = |f(r, \theta)| = \frac{1}{\sqrt{2\pi}} \qquad \ldots(48)$$

The eigenfunctions of $\hat{L}_z$ are thus

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

Since the RHS does not contain r and θ, we may write the eigenfunctions of $\hat{L}_z$ as $\psi(\phi)$

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi} \qquad \ldots.(49)$$

8.8 EIGENVALUES AND EIGENFUNCTIONS OF $\hat{L}^2$

Denoting by $Y(\theta, \phi)$ the eigenfunction of $\hat{L}^2$ belonging to eigenvalues $\lambda\hbar^2$ we may write the eigenvalue equation for $\hat{L}^2$ as

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

Using the expression for $\hat{L}^2$, given by Eq. (37a), the above becomes

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

or

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

The solution of the above equation gives

$$\lambda = l(l+1), \quad l = 0, 1, 2 \qquad \text{...(50)}$$

$$Y(\theta, \phi) = Y_{im}(\theta, \phi) = \varepsilon\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_1^{|m|}(\cos\theta)\, e^{im\phi} \qquad \text{....(51)}$$

where $\varepsilon = (-1)^m$ for $m > 0$ and $\varepsilon = 1$ for $m \leq 0$. $P_l^{|m|}(\cos\theta)$ are the associated Legendre polynomials.

We thus find the eigenvalues of $\hat{L}^2$ to be $l(l+1)\,\hbar^2$.

We may note that the spherical harmonic functions $Y_{lm}(\theta, \phi)$ are also the eigenfunctions of $\hat{L}_z$ belonging to eigenvalue $m\hbar$. Thus we may write the eigenvalue equation for $\hat{L}_z$ as

$$\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$$

8.9 ANGULAR MOMENTUM AND ROTATION

Consider a point P in space having Cartesian coordinates x, y, z with respect to the coordinate system (X, Y, Z). Let the coordinate frame be **rotated** about the **Z-axis** by a small angle $\Delta\theta$ anti-clockwise. The positions of the new axes X', Y', Z' are then as indicated in the Fig. 8.2

The coordinates of the point P with respect to the rotated coordinate system are

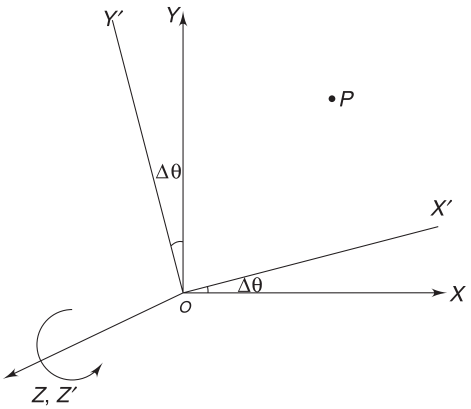


Fig. 8.2

$$
\begin{aligned}
x' &= x \cos(\Delta\theta) + y \sin(\Delta\theta) \\
y' &= -x \sin(\Delta\theta) + y \cos(\Delta\theta) \qquad \ldots(52) \\
z' &= z
\end{aligned}
$$

Considering $\Delta\theta$ to be infinitesimally small, we get

$$\cos(\Delta\theta) = 1, \quad \sin \Delta\theta = \Delta\theta$$

and hence Eq. (52) gives

$$
\begin{aligned}
x' &= x + y\Delta\theta \\
y' &= -x\Delta\theta + y \qquad \ldots(53) \\
z' &= z
\end{aligned}
$$

Let us now consider an arbitrary function $\psi(x, y, z)$. Let us denote the operator corresponding to the above rotation by $\hat{R}_z(\Delta\theta)$. The effect of the rotation yields a new function $\psi(x', y', z')$ and we may express this effect as

$$\hat{R}_z(\Delta\theta)\, \psi(x, y, z) = \psi(x', y', z')$$

or

$$\hat{R}_z(\Delta\theta)\, \psi(x, y, z) = \psi(x + y\Delta\theta, -x\Delta\theta + y, z)$$

Making a Taylor expansion of the right hand side of the above equation and retaining only the first term (which is justified because $\Delta\theta$ is small) we obtain

$$\hat{R}_z\,(\Delta\theta)\, \psi(x, y, z) = \psi(x, y, z) + y\Delta\theta \frac{\partial\psi(x, y, z)}{\partial x} - x\Delta\theta \frac{\partial\psi(x, y, z)}{\partial y} \qquad \ldots(54)$$

We have the operator corresponding to the Z-component of angular momentum given by Eq. (11)

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad \ldots(55)$$

Using Eq. (55) we may write Eq. (54) as

$$\hat{R}_z(\Delta\theta)\ \psi(x, y, z) = \psi(x, y, z) + \frac{\Delta\theta}{i\hbar}\hat{L}_z\psi(x, y, z)$$

or

$$\hat{R}_z(\Delta\theta)\ \psi(x, y, z) = \left[1 + \frac{\Delta\theta}{i\hbar}\hat{L}_z\right]\psi(x, y, z) \qquad \ldots(56)$$

Since the above relation should hold for all arbitrary functions $\psi(x, y, z)$ we obtain

$$\hat{R}_z(\Delta\theta) = 1 + \frac{\Delta\theta}{i\hbar}\hat{L}_z \qquad \ldots(57)$$

Considering rotations by an infinitesimal angle $\Delta\theta$ about the X-axis, and Y-axis, we obtain the operators affecting the rotations as

$$\hat{R}_x(\Delta\theta) = 1 + \frac{\Delta\theta}{i\hbar}\hat{L}_x \qquad \ldots(58)$$

and

$$\hat{R}_y(\Delta\theta) = 1 + \frac{\Delta\theta}{i\hbar}\hat{L}_y \qquad \ldots(59)$$

In view of Eqs. (57), (58) and (59) we can interpret the angular momentum operators $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ as generators for infinitesimal rotations about X, Y and Z axes, respectively.

Let $\hat{R}_z(\theta)$ represent the rotational operator corresponding to a rotation by a **finite** angle θ about the Z-axis. If we increase the rotation angle from θ to $\theta+\Delta\theta$, we may write the operator corresponding to rotation by the angle $\theta+\Delta\theta$ as

$$\hat{R}_z(\theta + \Delta\theta) = \hat{R}_z(\Delta\theta)\ \hat{R}_z(\theta) = \left[1 + \frac{\Delta\theta}{i\hbar}\hat{L}_z\right]\hat{R}_z(\theta) \qquad \ldots(60)$$

We have

$$\frac{d\hat{R}_z(\theta)}{d\theta} = \underset{\Delta\theta\to 0}{Lt}\ \frac{\hat{R}_z(\theta+\Delta\theta) - \hat{R}_z(\theta)}{\Delta\theta} = \frac{1}{i\hbar}\hat{L}_z\ \hat{R}_z(\theta) = -\frac{i}{\hbar}\hat{L}_z\hat{R}_z(\theta) \qquad \ldots(61)$$

Integrating Eq. (61) between the limits $\theta = 0$ to $\theta = \theta$ we obtain

$$\int_0^\theta \frac{d\hat{R}_z(\theta)}{\hat{R}_z(0)} = \int_0^\theta -\frac{i}{\hbar}\hat{L}_z d\theta$$

or

$$\{1\text{n}\hat{R}_z(\theta)\}_0^\theta = -\frac{i}{\hbar}\theta\hat{L}_z$$

or $$1\text{n}\frac{\hat{R}_z(\theta)}{\hat{R}_z(0)} = -\frac{i}{\hbar}\theta\hat{L}_z$$

or $$\hat{R}_z(\theta) = \hat{R}_z(0)\, e^{-\frac{i}{\hbar}\theta\hat{L}_z}$$

or $$\hat{R}_z(\theta) = e^{-\frac{i}{\hbar}\theta\hat{L}_z} \qquad \text{...(62)}$$

In the above we have taken $\hat{R}_z(0)$ as a unit operator.

The above procedure can be used to obtain the most general operator corresponding to a rotation by an angle say α about an axis specified by a unit vector $\hat{n}$. The result is

$$\hat{R}_{\hat{n}}(0, \alpha) = e^{-i\alpha\vec{\hat{L}}\cdot\hat{n}}$$

An operator $\hat{O}$ which depends on the variables r, θ and ϕ satisfying the condition

$$[\hat{O}, \hat{R}_{\hat{n}}(0, \alpha)] = 0$$

is said to be a rotationally invariant operator. The condition for rotational invariance of the operator $\hat{O}$ is satisfied if the following commutation relations hold

$$[\hat{O}, \hat{L}_x] = 0;$$
$$[\hat{O}, \hat{L}_y] = 0;$$
$$[\hat{O}, \hat{L}_z] = 0$$

8.10 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 $\hat{L}_x \pm i\hat{L}_y$.

The operator $$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \qquad \text{...(63)}$$

is called the step-up operator.

The operator $$\hat{L}_- = \hat{L}_x - i\hat{L}_y \qquad \text{...(64)}$$

is called the step-down operator.

We find $$\hat{L}_z\hat{L}_+ = \hat{L}_z(\hat{L}_x + i\hat{L}_y) = \hat{L}_z\hat{L}_x + i\hat{L}_z\hat{L}_y \qquad \text{...(65)}$$

Using the commutation relations given by Eqs. (13) and (14), Eq. (65) becomes

$$\begin{aligned}\hat{L}_z\hat{L}_+ &= \hat{L}_x\hat{L}_z + i\hat{L}_y + i(\hat{L}_y\hat{L}_z - i\hat{L}_x)\\ &= (\hat{L}_x + i\hat{L}_y)\,\hat{L}_z + (\hat{L}_x + i\hat{L}_y)\\ &= \hat{L}_+\hat{L}_z + \hat{L}_+\end{aligned}$$

or

$$\hat{L}_z\hat{L}_+ = \hat{L}_+\,(\hat{L}_z + 1) \qquad \text{...(66)}$$

Similarly, we obtain

$$\hat{L}_z\hat{L}_- = \hat{L}_-\,(\hat{L}_z + 1) \qquad \text{...(67)}$$

Let Y_{im} be a simultaneous eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ belonging to eigenvalue m of $\hat{L}_z$. We obtain

$$\begin{aligned}\hat{L}_z\hat{L}_+Y_{lm} &= \hat{L}_+(\hat{L}_z + 1)\,Y_{lm} \qquad \text{[using eq. (66)]}\\ &= \hat{L}_+\hat{L}_zY_{lm} + \hat{L}_+Y_{lm}\\ &= \hat{L}_+mY_{lm} + \hat{L}_+Y_{lm}\end{aligned}$$

or

$$\hat{L}_z(\hat{L}_+Y_{lm}) = (m + 1)\,(\hat{L}_+Y_{lm}) \qquad \text{...(68)}$$

Similarly, we get

$$\hat{L}_z(\hat{L}_-Y_{lm}) = (m - 1)\,(\hat{L}_-Y_{lm}) \qquad \text{...(69)}$$

Equation (68) 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 Eq. (69) 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.

8.11 SOLVED EXAMPLES

Example 1 Evaluate the following commutators

(i) $[\hat{x}, \hat{L}_x]$ (ii) $[\hat{x}, \hat{L}_y]$ (iii) $[\hat{x}, \hat{L}_z]$ (iv) $[\hat{p}_x, \hat{L}_x]$ (v) $[\hat{p}_y, \hat{L}_y]$ (vi) $[\hat{p}_z, \hat{L}_z]$

Solution: (i) We have

$$\begin{aligned}[\hat{x}, \hat{L}_x]\,\psi &= x\hat{L}_x\psi - \hat{L}_xx\psi\\ &= -i\hbar\, x\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\psi + i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)x\psi\\ &= -i\hbar xy\,\frac{\partial\psi}{\partial z} + i\hbar xz\,\frac{\partial\psi}{\partial y} + i\hbar yx\,\frac{\partial\psi}{\partial z} - i\hbar zx\,\frac{\partial\psi}{\partial y}\end{aligned}$$

Clearly $[\hat{x}, \hat{L}_x] = 0$

(ii) $[\hat{x}, \hat{L}_y]\ \psi = x\ \hat{L}_y\psi - \hat{L}_y x\psi$

$$= -i\hbar\ x\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\psi + i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)x\psi$$

$$= -i\hbar xz\frac{\partial\psi}{\partial x} + i\hbar x^2\frac{\partial\psi}{\partial z} + i\hbar z\psi + i\hbar zx\frac{\partial\psi}{\partial x} - i\hbar x^2\frac{\partial\psi}{\partial z}$$

$$= i\hbar z\psi$$

Clearly,

$$[\hat{x}, \hat{L}_y] = i\hbar z = i\hbar\hat{z}.$$

(iii) $[\hat{x}, \hat{L}_z]\ \psi = x\hat{L}_z\psi - \hat{L}_z x\psi$

$$= -i\hbar x\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi + i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)x\psi$$

$$= -i\hbar x^2\frac{\partial\psi}{\partial y} + i\hbar xy\frac{\partial\psi}{\partial x} + i\hbar x^2\frac{\partial\psi}{\partial y} - i\hbar y\psi - i\hbar yx\frac{\partial\psi}{\partial x}$$

$$= -i\hbar y\psi$$

Clearly,

$$[\hat{x}, \hat{L}_z] = i\hbar y = -i\hbar\hat{y}$$

(iv) $[\hat{p}_x, \hat{L}_x]\ \psi = \hat{p}_x\hat{L}_x\psi - \hat{L}_x\hat{p}_x\psi$

$$= -i\hbar\frac{\partial}{\partial x}(-i\hbar)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\psi + i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\times -i\hbar\frac{\partial}{\partial x}\Psi$$

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

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

$$= 0$$

Thus

$$[\hat{p}_x, \hat{L}_x] = 0$$

(v) $$[\hat{p}_{x,}\ \hat{L}_y]\,\psi = -i\hbar\frac{\partial}{\partial x}(-i\hbar)\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\psi + i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\times(-i\hbar)\frac{\partial\psi}{\partial x}$$

$$= -\hbar^2\frac{\partial}{\partial x}\left(z\frac{\partial\psi}{\partial x}-x\frac{\partial\psi}{\partial z}\right)+\hbar^2\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\frac{\partial\psi}{\partial x}$$

$$= -\hbar^2 z\frac{\partial^2\psi}{\partial x^2}+\hbar^2\frac{\partial\psi}{\partial z}+\hbar^2 x\frac{\partial^2\psi}{\partial x\partial z}+\hbar^2 z\frac{\partial^2\psi}{\partial x^2}-\hbar^2 x\frac{\partial^2\psi}{\partial z\partial x^2}$$

$$= \hbar^2\frac{\partial\psi}{\partial z} = i\hbar\left(-i\hbar\frac{\partial}{\partial z}\right)\psi = i\hbar\,\hat{p}_z\psi$$

Thus

$$[\hat{p}_x,\ \hat{L}_y] = i\hbar\,\hat{p}_z$$

(vi) $$[\hat{p}_x,\ \hat{L}_z]\,\psi = \hat{p}_x\hat{L}_z\psi - \hat{L}_z\hat{p}_x\psi$$

$$= -i\hbar\frac{\partial}{\partial x}(-i\hbar)\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\psi + i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\times(-i\hbar)\frac{\partial}{\partial x}\psi.$$

$$= -\hbar^2\frac{\partial}{\partial x}\left(x\frac{\partial\psi}{\partial y}-y\frac{\partial\psi}{\partial x}\right)+\hbar^2\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\frac{\partial\psi}{\partial x}$$

$$= -\hbar^2\frac{\partial\psi}{\partial y}-\hbar^2 x\frac{\partial^2\psi}{\partial x\partial y}+\hbar^2 y\frac{\partial^2\psi}{\partial x^2}+\hbar^2 x\frac{\partial^2\psi}{\partial y\partial x}-\hbar^2 y\frac{\partial^2\psi}{\partial x^2}$$

$$= -\hbar^2\frac{\partial\psi}{\partial y} = -i\hbar\left(-i\hbar\frac{\partial}{\partial y}\right)\psi$$

Thus $$[\hat{p}_x,\ \hat{L}_z] = -i\hbar\,\hat{p}_{y.}$$

Example 2 Find the cammutator $[\hat{L}_z, \cos\phi]$, ϕ being the azimuthal angle.

Solution: In spherical polar coordinates (r, θ, ϕ), $\hat{L}_z$ is given by

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}.$$

Consider a function $\psi = \psi(r, \theta, \phi)$. We get

$$[\hat{L}_z, \cos\phi]\,\psi = \hat{L}_z\cos\phi\,\psi - \cos\phi\,L_z\,\psi$$

$$= -i\hbar\frac{\partial}{\partial\phi}(\cos\phi\,\psi) + i\hbar\cos\phi\frac{\partial}{\partial\phi}(\psi)$$

$$= i\hbar \sin\phi\, \psi - i\hbar \cos\phi \frac{\partial\psi}{\partial\phi} + i\hbar \cos\phi \frac{\partial\psi}{\partial\phi}$$

$$= i\hbar \sin\phi\,\psi$$

Thus

$$[\hat{L}_z, \cos\phi] = i\hbar \sin\phi.$$

Example 3 Evaluate the commutator $[\hat{L}_z, \sin 2\phi]$.

Solution: We have

$$[\hat{L}_z, \sin 2\phi]\,\psi = \hat{L}_z \sin 2\phi\, \psi - \sin 2\phi\, \hat{L}_z\, \psi$$

$$= -i\hbar \frac{\partial}{\partial\phi}(\sin 2\phi\, \psi) + i\hbar \sin 2\phi \frac{\partial\psi}{\partial\phi}$$

$$= -i\hbar \cos 2\phi\, \psi - i\hbar \sin 2\phi \frac{\partial\psi}{\partial\phi} + i\hbar \sin 2\phi \frac{\partial\psi}{\partial\phi}$$

or $$[\hat{L}_z, \sin 2\phi]\,\psi = -i\hbar \cos 2\phi\, \psi$$

Thus $$[\hat{L}_z, \sin 2\phi] = -i\hbar \cos 2\phi = i\hbar\,(\sin^2\phi - \cos^2\phi)$$

Example 4 In the common eigenfunction ψ, $\hat{L}^2$ and $\hat{L}_z$ have eigenvalues given respectively by $l(l+1)\,\hbar^2$ and $m\hbar$. Calculate the expectation values of (a)L_x and (b) L_x^2 in the state described by the eigenfunction ψ.

Solution:

(a) Given, $\hat{L}^2\psi = l(l+1)\,\hbar^2\psi$ ...(i)

$\hat{L}_z\psi = m\hbar\psi$ ...(ii)

Since $\hat{L}_z$ is Hermitian, we get

$$\hat{L}_z^{*}\psi^{*} = m\hbar\psi^{*} \qquad \text{...(iii)}$$

We have by definition

$$\langle L_x\rangle = \int \psi^{*}\hat{L}_x\, \psi\, d\tau \qquad \text{...(iv)}$$

Using the commutation relation

$$[\hat{L}_y, \hat{L}_z] = i\hbar\, \hat{L}_x \qquad \text{...(v)}$$

we may write the above as

$$\langle L_x\rangle = \int \psi^{*} \frac{1}{i\hbar} [\hat{L}_y, \hat{L}_z]\, \psi\, d\tau$$

$$= \frac{1}{i\hbar}\int \psi^* \hat{L}_y \hat{L}_z \psi\, d\tau - \frac{1}{i\hbar}\int \psi^* \hat{L}_z \hat{L}_y \psi\, d\tau \qquad \text{...(vi)}$$

Since $\hat{L}_z$ is Hermitian, we get

$$\int \psi^* \hat{L}_z \hat{L}_y \psi\, d\tau = \int \hat{L}_z \psi^* \hat{L}_y \psi\, d\tau \qquad \text{...(vii)}$$

$$= m\hbar \int \psi^* \hat{L}_y \psi d\tau$$

Using Eqs. (ii) and (vii) in Eq. (vi) we obtain

$$\langle L_x \rangle = \frac{m\hbar}{i\hbar}\int \psi^* \hat{L}_y \psi\, d\tau - \frac{m\hbar}{i\hbar}\int \psi^* \hat{L}_y \psi\, d\tau = 0 \qquad \text{...(viii)}$$

(b) Since the choice of X and Y axes does not have any restriction we may write

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \frac{1}{2}\langle L_x^2 + L_y^2 \rangle = \frac{1}{2}\langle L^2 - L_z^2 \rangle \qquad \text{...(ix)}$$

By definition, we have

$$\langle L_x^2 \rangle = \int \psi^* \hat{L}_x^2 \psi\, d\tau = \frac{1}{2}\int \psi^* (\hat{L}^2 - \hat{L}_z^2) \psi\, d\tau$$

$$= \frac{1}{2}\left[\int \psi^* \hat{L}^2 \psi\, d\tau - \int \psi^* \hat{L}_z^2 \psi\, dt\right].$$

Using the result given by Eqs. (i) and (ii) in the above we obtain

$$\langle L_x^2 \rangle = \frac{1}{2}\left[l(l+1)\hbar^2 \int \psi^* \psi\, d\tau - m^2\hbar^2 \int \psi^* \psi\, d\tau\right]$$

Since the eigenfunction ψ is normalized we obtain

$$\langle L_x^2 \rangle = \frac{1}{2}\hbar^2\, [l(l+1) - m^2]\,.$$

Example 5 If $\hat{J}$, $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$ and $\hat{J}^2$ respectively represent the operators corresponding to the total angular momentum $\vec{J}$, the three Cartesian components of $\vec{J}$ and the square angular momentum J^2, then find

(a) $\langle J_x \rangle$, (b) $\langle J_y \rangle$, (c) $\langle J_x^2 \rangle$, (d) $\langle J_x^2 \rangle$, (e) $\Delta J_x \Delta J_y$

where $\Delta J_x = \sqrt{\langle J_x^2 \rangle - \langle J_x \rangle^2}$ and $\Delta Jy = \sqrt{\langle J_y^2 \rangle - \langle J_y \rangle^2}$

Solution: We know that $\hat{J}^2$ and $\hat{J}_z$ commute with each other so that they have a common set of eigenfunctions. Let ψ be one such common eigenfunction. The eigenvalue equations are given by

$$\hat{J}^2\psi = J(J+1)\,\hbar^2\psi \qquad \text{...(i)}$$

and
$$\hat{J}_z\,\psi = m\hbar\psi \qquad \text{...(ii)}$$

Since $\hat{J}_z$ is Hermitian according to Eq. (ii) we have

$$\hat{\vec{J}}_z^{\,*}\psi^* = m\hbar\,\psi^* \qquad \text{...(iii)}$$

(a) By definition, we get

$$\langle J_x\rangle = \int \psi^*\,\hat{J}_x\,\psi\,d\tau$$

Using the commutation relation

$$[\hat{J}_y, \hat{J}_z] = i\hbar\,J_x$$

we may write the above equation as

$$\begin{aligned}
\langle J_x\rangle &= \frac{1}{i\hbar}\int \psi^*\,[\hat{J}_y, \hat{J}_z]\,\psi\,d\tau \\
&= \frac{1}{i\hbar}\int \psi^*\,\hat{J}_y\,\hat{J}_z\,\psi\,d\tau - \frac{1}{i\hbar}\int \psi^*\,\hat{J}_z\,J_y\,\psi\,d\tau \\
&= \frac{1}{i\hbar}\int \psi^*\,\hat{J}_y\,\hat{J}_z\,\psi\,d\tau - \frac{1}{i\hbar}\int \hat{J}_z^*\psi^*\,\hat{J}_y\,\psi\,d\tau \\
&= \frac{m\hbar}{i\hbar}\int \psi^*\hat{J}_y\,\psi\,d\tau - \frac{m\hbar}{i\hbar}\int \psi^*\,\hat{J}_y\,\psi\,d\tau
\end{aligned}$$

(using Eqs. (ii) and (iii))

Clearly

$$\langle J_x\rangle = 0 \qquad \text{...(iv)}$$

(b) By an exactly similar procedure we get

$$\langle J_y\rangle = 0 \qquad \text{...(v)}$$

(c) Since the choice of *x* and *y* axes is completely arbitrary we must have

$$\langle J_x^2\rangle = \langle J_y^2\rangle = \frac{1}{2}\langle J_x^2 + J_y^2\rangle = \frac{1}{2}\langle J^2 - J_z^2\rangle$$

(Since $J_x^2 + J_y^2 + J_z^2 = J^2$)

Thus
$$\begin{aligned}
\langle J_x^2\rangle &= \frac{1}{2}\langle J^2\rangle - \frac{1}{2}\langle J_z^2\rangle \\
&= \frac{1}{2}\int \psi^*\hat{J}^2\,\psi\,d\tau - \frac{1}{2}\int \psi^*J_z^2\,\psi\,d\tau
\end{aligned}$$

Using the eigenvalue equations (i) and (ii) in the above equation we obtain

$$\langle J_x^2 \rangle = \frac{1}{2}\, j(J+1)\,\hbar^2 \int \psi^* \psi\, d\tau - \frac{m^2\hbar^2}{2} \int \psi^* \psi\, d\tau$$

or

$$\langle J_x^2 \rangle = \frac{1}{2}\,[J(J+1) - m^2]\,\hbar^2 \qquad \text{...(vi)}$$

(d)

$$\langle J_y^2 \rangle = \langle J_x^2 \rangle = \frac{1}{2}\,[J(J+1) - m^2]\,\hbar^2 \qquad \text{...(vii)}$$

(e)

$$\Delta J_x = \sqrt{\langle J_x^2 \rangle - \langle Jx \rangle^2}$$

Using the results given by equations (iv) and (vi) in the above we get

$$\Delta J_x = \sqrt{\frac{1}{2}[J(J+1) - m^2]\,\hbar^2 - 0}$$

or

$$\Delta J_x = \hbar \sqrt{\frac{J(J+1)}{2} - \frac{m^2}{2}} \qquad \text{...(viii)}$$

Similarly, using the results given by equations (v) and (vii) in

$$\Delta J_y = \sqrt{\langle J_y^2 \rangle - \langle J_y \rangle^2}$$

we obtain

$$\Delta J_y = \hbar \sqrt{\frac{j(J+1)}{2} - \frac{m^2}{2}}$$

Thus, we get

$$\Delta J_x\, \Delta J_y = \hbar^2 \left[\frac{j(J+1) - m^2}{2}\right]$$

9

Dirac's Formulation of Quantum Mechanics: Dirac's Bra Ket Notation

9.1 INTRODUCTION

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

$$i\hbar \frac{\partial \psi(q,t)}{\partial t} = \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + V(q) \right] \psi(q,t) \qquad \ldots(1)$$

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

$$\phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(q,t)\, e^{\frac{-ipq}{\hbar^2}}\, dq \qquad \ldots(2)$$

$\phi(p, t)$ 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.

9.2 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 ψ's are, in general, complex valued functions, the vector representing the state is not an ordinary vector in real space.

Following 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 ψ and is written as $|\psi\rangle$.

In the Fig. 9.1 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).

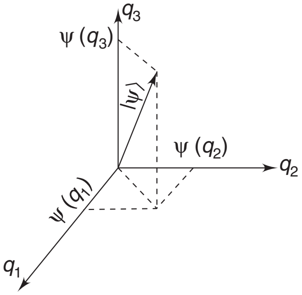


Fig. 9.1 Ket vector $|\psi\rangle$ and three of its coordinate representatives.

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., $|\psi\rangle = [\psi(q_1), \psi(q_2), \ldots]$. 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 $|\psi\rangle = [\phi(p_1), \phi(p_2), \ldots.]$. We may visualize $\phi(p_1)$, $\phi(p_2)$, etc., as the components of $|\psi\rangle$ on a rotated orthogonal set of axes $p_1, p_2\ldots.$ as shown in the Fig. 9.2. The relation between the new p-axes and the old q-axes is given by Fourier transform.

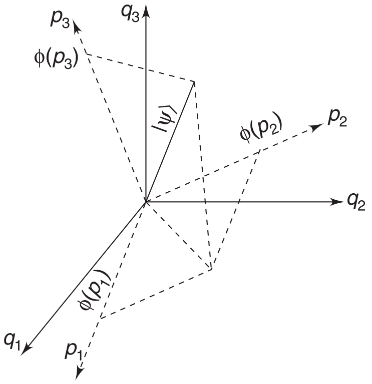


Fig. 9.2 Ket vector $|\psi\rangle$ and three of its momentum representatives.

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.

9.3 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

$$|\alpha\rangle = C_1\,|a\rangle + C_2\,|b\rangle \qquad \ldots(3)$$

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 Eq. (3) as

$$|\beta\rangle = \int_{q_1'}^{q_2'} C(q')\,|q'\rangle\,dq' \qquad \ldots(4)$$

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 Eqs. (3) and (4) 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

$$C_1|a\rangle + C_2|a\rangle = (C_1 + C_2)|a\rangle \qquad \ldots(5)$$

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 Eq. 5); 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.

9.4 SCALAR PRODUCT, BRA VECTOR

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

$$f(|a_1\rangle + |a_2\rangle) = f(|a_1\rangle) + f(|a_2\rangle) \qquad \ldots(6)$$

$$f(C|a\rangle) = C\,f\,|a\rangle \qquad \ldots(7)$$

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 Eqs. (6) and (7) as

$$\langle f|\,(|a_1\rangle + |a_2\rangle) = \langle f|a_1\rangle + \langle f\,a_2\rangle \qquad \ldots(8)$$

$$\langle f\,|(C\,|a\rangle) = C\,\langle f\,|a\rangle \qquad \ldots(9)$$

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*.

If, $$\langle b_1|a\rangle = \langle b_2|a\rangle \text{ for all } |a\rangle \qquad \ldots(10)$$

then $$\langle b_1| = \langle b_2| \qquad \ldots(11)$$

The sum of two bras $\langle b_1|$ and $\langle b_2|$ is defined by its scalar product with $|a\rangle$. Thus

$$(\langle b_1| + \langle b_2|)|a\rangle = \langle b_1|a\rangle + \langle b_2|a\rangle \qquad \ldots(12)$$

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

$$|\alpha\rangle = |a\rangle + |b\rangle \qquad \ldots(13)$$

The bra associated with $|\alpha\rangle$ is then

$$\langle\alpha| = \langle a| + \langle b| \qquad \ldots(14)$$

With the ket

$$|\beta\rangle = C\,|a\rangle, \quad C = \text{a complex number} \qquad \ldots(15)$$

is associated the bra

$$\langle\beta| = C^*\,\langle a|, \quad C^* = \text{complex conjugate of C} \qquad \ldots(16)$$

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.,

$$\langle\alpha| = (|\alpha\rangle)^\dagger, \quad |\alpha\rangle = (\langle\alpha|)^\dagger \qquad \ldots(17)$$

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.

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

$$\langle a|b\rangle = \langle b|a\rangle^* \qquad \ldots(18)$$

Replacing $|b\rangle$ by $|a\rangle$ in Eq. (18) we get

$$\langle a|a\rangle = \langle a|a\rangle^* \qquad \ldots(19)$$

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.,

$$\langle a|a\rangle \geq 0 \qquad \ldots(20)$$

Equality sign holds in the above if $|a\rangle = 0$.

The assumption given by equations (18) and (20) 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

$$\psi^*(q, t)\,\chi(q, t) = [\chi^*(q, t)\,\psi(q, t)]^* \qquad \ldots(21)$$

We also know that

$$\int |\psi(q, t)|^2\, dq \geq 0 \qquad \ldots(22)$$

Since bras and kets are intimately related to wave functions, relations similar to those given by eqs. (21) and (22) should hold also for them. Such relations are given by eqs. (18) and (20).

Orthogonality of Kets and Bras

In wave mechanics, the wave functions $\psi(q)$ and $\phi(q)$ are orthogonal, if

$$\int \psi^*(q)\,\phi(q)\,dq = 0 \qquad \ldots(23)$$

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

$$\langle a|b\rangle = 0 \qquad \ldots(24)$$

The orthogonality involved with ket/bra vector is different from the orthgonality 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 $\vec{A}.\vec{B} = 0$, $\vec{A}$ and $\vec{B}$ are at right angles to each other and they lie in the same vector space. In the orthogonality condition given by eq. (24), 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.

9.5 LINEAR OPERATORS IN THE SPACE OF KET AND BRA VECTORS

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

$$|b\rangle = \hat{\alpha}\,|a\rangle \qquad \text{...(25)}$$

$\hat{\alpha}$ 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

$$\hat{\alpha}\,(|a_1\rangle + |a_2\rangle) = \hat{\alpha}\,|a_1\rangle + \hat{\alpha}\,|a_2\rangle \qquad \text{...(26)}$$

and

$$\hat{\alpha}\,(C\,|\,a\rangle) = C\,\hat{\alpha}\,|a\rangle \qquad \text{...(27)}$$

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

$$\hat{\alpha}_1|a\rangle = \hat{\alpha}_2\,|a\rangle \quad \text{for all } |a\rangle \qquad \text{...(28)}$$

Null operator

A linear operator a is a *null operator* if

$$\hat{\alpha}\,|a\rangle = 0 \quad \text{for all } |a\rangle \qquad \text{...(29)}$$

Identity operator

A linear operator $\hat{\alpha}$ is said to be an *identity operator* if

$$\hat{\alpha}\,|a\rangle = |a\rangle \quad \text{for all } |a\rangle \qquad \text{...(30)}$$

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

$$(\hat{\alpha}_1 + \hat{\alpha}_2)\,|a\rangle = \hat{\alpha}_1\,|a\rangle + \hat{\alpha}_2\,|a\rangle \qquad \text{...(31)}$$

(ii) **Product** of two linear operators α_1 and $\hat{\alpha}_2$, i.e., $(\hat{\alpha}_1\,\hat{\alpha}_2)$ is defined according to

$$(\hat{\alpha}_1\,\hat{\alpha}_2)\,|a\rangle = \hat{\alpha}_1\,(\hat{\alpha}_2\,|a\rangle) \qquad \text{...(32)}$$

From eq. (32) it is possible to define powers of a linear operator.

We further find the following relations to hold

$$(\hat{\alpha}_1 + \hat{\alpha}_2)\,|a\rangle = (\hat{\alpha}_2 + \hat{\alpha}_1)\,|a\rangle \qquad \text{...(33)}$$

$$[(\hat{\alpha}_1 + \hat{\alpha}_2) + \hat{\alpha}_3]\,|a\rangle = [\hat{\alpha}_1 + (\hat{\alpha}_2 + \hat{\alpha}_3)]\,|a\rangle \qquad \text{...(34)}$$

$$[\hat{\alpha}_1\,(\hat{\alpha}_2 + \hat{\alpha}_3)]\,|a\rangle = \hat{\alpha}_1\,\hat{\alpha}_2\,|a\rangle + \hat{\alpha}_1\,\hat{\alpha}_3\,|a\rangle \qquad \text{...(35)}$$

(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

$$[\hat{\alpha}_1, \hat{\alpha}_2] = \hat{\alpha}_1\, \hat{\alpha}_2 - \hat{\alpha}_2\, \hat{\alpha}_1 \qquad \ldots(36)$$

The operator $\hat{\alpha}_1$ and $\hat{\alpha}_2$ are said to be *non-commutative* if

$$\hat{\alpha}_1\, \hat{\alpha}_2 \neq \hat{\alpha}_2\, \hat{\alpha}_1 \quad \text{i.e. } [\hat{\alpha}_1, \hat{\alpha}_2] \neq 0 \qquad \ldots(37)$$

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

$$\hat{\alpha}_1\, \hat{\alpha}_2 = \hat{\alpha}_2\, \hat{\alpha}_1 = \hat{I} \text{ (identity operator)} \qquad \ldots(38)$$

then $\hat{\alpha}_2$ is said to be the *inverse* of $\hat{\alpha}_1$ and vice-versa, provided the inverse exists and we write

$$\hat{\alpha}_2 = \hat{\alpha}_1^{-1}, \quad \hat{\alpha}_1 = \hat{\alpha}_2^{-1} \qquad \ldots(39)$$

The inverse of a product of operators $(\hat{\alpha}_1, \hat{\alpha}_2, \hat{\alpha}_3)$ is

$$(\hat{\alpha}_1\, \hat{\alpha}_2\, \hat{\alpha}_3)^{-1} = \hat{\alpha}_3^{-1}\, \hat{\alpha}_2^{-1}\, \hat{\alpha}_1^{-1} \qquad \ldots(40)$$

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

$$\langle d| = \langle c|\hat{\alpha} \qquad \ldots(41)$$

The operation is defined through the equation

$$\langle c|\,(\hat{\alpha}\,|a\rangle) = (\langle c|\,\hat{\alpha})\,|a\rangle. \qquad \ldots(42)$$

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

$$|a\rangle\ \langle b| = \hat{P} \qquad \ldots(43)$$

$\hat{P}$ 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

$$\langle c|\hat{P} = \langle ca\rangle\ \langle b. \qquad \ldots(44)$$

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 is Chapter 2, 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 Eq. (18) we take $\langle a| = \langle p|\ \hat{\alpha}^{\dagger}$ and $|a\rangle = \hat{\alpha}\,|p\rangle$, then we get

$$\langle p|\ \hat{\alpha}^{\dagger}\ |b\rangle = \langle b|\ \hat{\alpha}\ |p\rangle^{*} \qquad \ldots(45)$$

Equation (45) 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 Eq. (45) to obtain

$$\langle p|\ \hat{\alpha}^{\dagger\dagger}|b\rangle = \langle b|\hat{\alpha}^{\dagger}|p\rangle^{*} \qquad \ldots(46)$$

Let us now replace $|a\rangle$ in Eq. (18) by $|a\rangle = \hat{\alpha}^{\dagger}\ |p\rangle$

and $\langle a| = \langle p|\hat{\alpha}$. We then get

$$\langle p|\,\hat{\alpha}\,|b\rangle = \langle b|\,\hat{\alpha}^{\dagger}\,|p\rangle^{*} \qquad \ldots(47)$$

Comparing Eqs. (46) and (47) we obtain

$$\langle p|\,\hat{\alpha}^{\dagger}\,|b\rangle = \langle p|\,\hat{\alpha}\,|b\rangle. \qquad \ldots(48)$$

Since in Eq. (48) ket $|b\rangle$ and bra $\langle p|$ are arbitrary, we find that

$$\hat{\alpha}^{\dagger\dagger} = \hat{\alpha} \qquad \ldots(49)$$

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 Eq. (45) we find that if $\hat{\alpha}$ is hermitian, it must satisfy

$$\langle p|\,\hat{\alpha}^{\dagger}\,|b\rangle = \langle b|\,\hat{\alpha}\,|p\rangle^{*} \qquad \ldots(50)$$

for arbitrary $|b\rangle$ and $|p\rangle$.

9.6 EIGENVALUE PROBLEM FOR OPERATORS IN KET AND BRA SPACE

Let us consider a linear operator $\hat{\alpha}$. In general, $\hat{\alpha}$ operating as a ket gives another ket in the same space.

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

$$\hat{\alpha}\,|a\rangle = \alpha_a\,|a\rangle \qquad \ldots(51)$$

α_a being a number.

Equation (51) 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 α_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

$$\hat{\alpha}\,|\,\alpha_a\rangle = \alpha_a\,|\,\alpha_a\rangle \qquad \ldots(51a)$$

If $|\alpha_a\rangle$ is an eigenket of $\hat{\alpha}$, then by Eq. (52) any constant c times $|\alpha_a\rangle$ is also an eigenket of $\hat{\alpha}$ with the same eigenvalue α_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

$$\langle\beta_{a}|\hat{\beta} = \beta_a\,\langle\beta_{a}|. \qquad \ldots(51b)$$

In the above $\langle\beta_a|$ is an eigenbra of the linear operator $\hat{\beta}$ belonging to the eigenvalue β_a.

Theorems Valid for All Linear Hermitian Operators

In Chapter 4 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

$$\langle\alpha_k|\,\hat{\alpha}\,|\alpha_k\rangle = \alpha_k\,\langle\alpha_k\,|\alpha_k\rangle \qquad \ldots(52)$$

Taking complex conjugate of both sides we obtain

$$\langle\alpha_k|\,\hat{\alpha}\,|\alpha_k\rangle^* = \langle\alpha_k|\,\hat{\alpha}^\dagger\,|\alpha_k\rangle = \alpha_k^*\,\langle\alpha_k\,|\alpha_k\rangle \qquad \ldots(53)$$

But since $\hat{\alpha}^\dagger = \hat{\alpha}$ and $\langle\alpha_k \mid \alpha_k\rangle \neq 0$, comparing Eqs. (52) and (53) we get

$$\alpha_k = \alpha_k^* \qquad \ldots(54)$$

Clearly the eigenvalue α_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 α_j and $|\alpha_k\rangle$ be the eigenvector of $\hat{\alpha}$ belonging to eigenvalue α_k.

We then have according to our considerations

$$\left.\begin{aligned} &\hat{\alpha} = \hat{\alpha}^\dagger \\ &\alpha_j = \alpha_j^* \ ; \ \alpha_k = \alpha_k^* \end{aligned}\right\} \qquad \ldots(56)$$

Let $\langle\alpha_k|$ be the eigenbra associated with the eignket $|\alpha_k\rangle$.

We then have the eigenvalue equations

$$\hat{\alpha}\,|\alpha_j\rangle = \alpha_j\,|\alpha_j\rangle \qquad \ldots(56)$$

$$\langle\alpha_k|\,\hat{\alpha} = \alpha_k\,\langle\alpha_k| \qquad \ldots(57)$$

Forming scalar product of Eq. (56) with $\langle\alpha_k|$, we get

$$\langle\alpha_k|\,\hat{\alpha}\,|\,\alpha_j\rangle = \alpha_j\,\langle\alpha_k\,|\alpha_j\rangle \qquad \ldots(58)$$

Similarly, forming scalar product of Eq. (57) with $|\alpha_j\rangle$ we obtain

$$\langle\alpha_k|\hat{\alpha}|\alpha_j\rangle = \alpha_k \langle\alpha_k|\alpha_j\rangle \quad \text{...(59)}$$

Subtracting Eq. (59) from Eq. (58), we get

$$(\alpha_j - \alpha_k) \langle\alpha_k|\alpha_j\rangle = 0 \quad \text{...(60)}$$

Since α_j and α_k are two different eigenvalues, Eq. (60) gives

$$\langle\alpha_k|\alpha_j\rangle = 0 \quad \text{...(61)}$$

Clearly, the eigenvectors $|\alpha_j\rangle$ and $|\alpha_k\rangle$ are orthogonal to each other.

We may note from Eqs. (56) and (57) that the eigenvalues associated with eigenkets are the same as those associated with the corresponding bras.

9.7 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.

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 (Refer to Chapter 5).

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 α we obtain the value α_k. We assume that if we measure α and in each measurement we obtain the value α_k with certainty, that is, if we measure α for a large number of systems each prepared in an identical way and always get the value α_k, then we say that the system is in the state $|\alpha_k\rangle$.

Furthermore, when a single measurement of α 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 eignekets of the operator $\hat{\alpha}$ corresponding to the observable α form an orthonormal set

$$\langle l_1 | l_j\rangle = \delta_{ij} \quad \text{...(62)}$$

where δ_{ij} is the Kronecker delta

$$\left.\begin{aligned} \delta_{ij} &= 0 \quad \text{if} \quad i \neq j \\ &= 1 \quad \text{if} \quad i = j \end{aligned}\right\} \quad \text{...(63)}$$

It is postulated that any state of the system is linearly dependent on the eigenkets $|\alpha_k\rangle$. In after 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

$$|P\rangle = \sum_k a_k |\alpha_k\rangle \qquad \ldots(64)$$

If a measurement of α is made in the state described by $|P\rangle$ then $|a_k|^2$ gives the probability of obtaining the value α_k.

If the system is in a state described by the normalized ket

$$|P\rangle = a_1|\alpha_1\rangle + a_2 \,|\alpha_2 \qquad \ldots(65)$$

then a measurement of α gives either the value α_1 with probability $|a_1|^2$ or the value α_2 with probability $|a_2|^2$. Since $\langle P|P\rangle = 1$, we obtain

$$|a_1|^2 + |a_2|^2 = 1. \qquad \ldots(66)$$

We know that the eigenkets of $\hat{\alpha}$ form an orthonormal set so that

$$\langle\alpha_i\,|\alpha_j\rangle = \delta_{ij}$$

We have

$$\langle\alpha_i\,|P\rangle = \sum_k C_k \langle\alpha_i\,|\alpha_k\rangle = \sum_k C_k\,\delta_{ik} = C_i \qquad \ldots(67)$$

Thus,
$$|P\rangle = \Sigma\,|\alpha_k\rangle\, C_k = \left\{\sum_k |\alpha_k\rangle\,\langle\alpha_k\right\}|P\rangle$$

$(\because C_k = \langle\alpha_k|P\rangle$ from Eq. (67))

Since the above result holds for all arbitrary kets we must have

$$\sum_k |\alpha_k\rangle\,\langle\alpha_k| = 1. \qquad \ldots(68)$$

The above equation is referred to as the completeness condition of eigenkets of the operator corresponding to an observable of a quantum system.

9.8 ILLUSTRATIVE EXAMPLES

Example 1 Solution of eigenvalue problems.

The solution of a particular simple eigenvalue problem (in many cases, the solution is complicated) is presented with the purpose of illustrating the method.

Consider a linear hermitian operator $\hat{\sigma}_z$.

Let us assume $\hat{\sigma}_z$ to satisfy the auxiliary condition

$$\sigma_z^2 = \hat{I} \qquad \ldots(69)$$

where $\hat{I}$ is an identity operator.

Our problem is to solve the eigenvalue problem

$$\hat{\sigma}_z\,|S\rangle = S|S\rangle \qquad \ldots(70)$$

According to theorem 1 (refer to Section 9.6), the eigenvalue S is real while from theorem 2, if $|S_1\rangle$ and $|S_2\rangle$ be two eigenkets of $\hat{\sigma}_z$ belonging to different eigenvalues S_1 and S_2 then

$$\langle S_1|S_2\rangle = 0 \qquad \ldots(71)$$

Multiplying both sides of Eq. (70) by $\hat{\sigma}_z$ from the left and using Eq. (69) we obtain

$$\hat{\sigma}_z^2\,|S\rangle = \hat{I}\,|S\rangle = |S\rangle \qquad \ldots(72)$$

Also, from (70) we get

$$\hat{\sigma}_z^2\,|S\rangle = \hat{\sigma}_z\,\hat{\sigma}_z\,|S\rangle = S\,\hat{\sigma}_z\,|S\rangle = S^2\,|S\rangle \qquad \ldots(73)$$

Equations (72) and (73) give

$$S^2\,|S\rangle = |S\rangle$$

or

$$(S^2 - 1)\,|S\rangle = 0 \qquad \ldots(74)$$

Forming scalar product of Eq. (74) with bra $\langle S|$ we get

$$(S^2 - 1)\,\langle S|S\rangle = 0 \qquad \ldots(75)$$

Since $\langle S|S\rangle$ is positive and not equal to zero we obtain from Eq. (75)

$$S^2 - 1 = 0$$

The above yields

$$S = +1 \text{ and } S = -1 \qquad \ldots(76)$$

According to our assumption there can be no degeneracy (two eigenvalues are same) and hence there are only two eigenvalues given by Eq. (76) and we may write Eq. (70) as

$$\hat{\sigma}_z|+1\rangle = +1\,|+1\rangle \text{ and } \hat{\sigma}_z\,|-1\rangle = -1|-1\rangle \qquad \ldots(77)$$

According to the theorem 2 (Section 9.6) we have

$$\langle +1|\,-1\rangle = 0 = \langle -1|+1\rangle \qquad \ldots(78)$$

Equations (78) are the orthogonality relations obeyed by eigenkets belonging to different eigenvalues.

We know that an eigenket multiplied by a constant gives an eigeket that belongs to the same eigenvalue. This allows us to choose the constant such that the norm of the eigenkets be unity and to write

$$\langle +1 | +1 \rangle = 1 = \langle -1 | -1 \rangle \qquad \ldots(79)$$

Equations (79) are the normalization conditions of the eigenkets of $\hat{\sigma}_z$.

It is important to see that normalization does not specify the eigenkets uniquely. If we multiply $|+1\rangle$ and $|-1\rangle$ by $e^{i\alpha}$(α real) then the corresponding bras will be multiplied by $e^{-1\alpha}$ so that we once again get

$$\langle +1 | +1 \rangle = 1 + \langle -1 | -1 \rangle$$

Thus eigenkets and eigenbras are known only within a phase factor.

The phase factor, however, does not have any physical significance and hence it is usual to choose $\alpha = 0$.

Example 2 If $|a\rangle$ and $|b\rangle$ are two arbitrary ket vectors and $\{|k\rangle\}$ forms a complete set of kets then prove that

$$\langle a | b \rangle = \sum_k \langle a | k \rangle \langle k | b \rangle$$

Solution: Since $\{|k\rangle\}$ forms a complete set, we may expand $|a\rangle$ and $|b\rangle$ in terms of $\{|k\rangle\}$ as

$$|a\rangle = \sum_k \alpha_k |k\rangle \qquad \ldots(\text{i})$$

$$|b\rangle = \sum_j \beta_j |j\rangle \qquad \ldots(\text{ii})$$

Taking scalar product of Eq. (i) with $\langle k|$ we get

$$\langle k | a \rangle = \langle k (\Sigma\, a_k | k \rangle) = \alpha_k \qquad \ldots(\text{iii})$$

Similarly, taking scalar product of Eq. (ii) with $\langle j|$

$$\langle j | b \rangle = \langle j (\sum_j \beta_j |j\rangle)\, \beta_j \qquad \ldots(\text{iv})$$

We have,

$$\langle a | = \sum_k \langle k | \alpha_k^* = \sum_k \langle a | k \rangle \langle k | \qquad \ldots(\text{v})$$

(using Eq. (iii))

Now, we get

$$\langle a | b \rangle = \sum_{k,j} \langle a | k \rangle \langle k | j \rangle \langle j | b \rangle$$

$$= \sum_{k,j} \langle a | k \rangle\, \delta_{kj}\, j | b \rangle$$

$$\langle a | b \rangle = \sum_k \langle a | k \rangle \langle k | b \rangle$$

Example 3 Show that

$$\overline{|a\rangle\ \langle b|} = |b\rangle\ \langle a|$$

where bar (—) denotes complex conjugate.

Solution:

$$|a\rangle\ \langle b| = c \text{ (say).} \quad (c \text{ being a complex number}) \qquad \ldots\text{(i)}$$

Let the ket $|\alpha\rangle$ be equal to c multiplied by a ket $|\beta\rangle$

i.e.

$$|\alpha\rangle = c|\beta\rangle$$

Using Eq. (i) in Eq. (ii) we get

$$|\alpha\rangle = [\langle b\ |\beta\rangle]\ |a\rangle$$

The bra associated with $|\alpha\rangle$ is then,

$$\langle\alpha| = \overline{\langle b|\beta\rangle}\ \langle a| = \langle\beta|b\rangle\ \langle a| \qquad \ldots\text{(iii)}$$

We, however, have

$$\langle\alpha| = \langle\beta|\ \bar{c} \qquad \ldots\text{(iv)}$$

From Eqs. (iii) and (iv) we obtain

$$\bar{c} = |b\rangle\ \langle a|. \qquad \ldots\text{(v)}$$

From Eq. (i) we get

$$\bar{c} = \overline{|a\rangle\ \langle b|} \qquad \ldots\text{(vi)}$$

Equating the right hand sides of Eqs. (v) and (vi) we get

$$\overline{|a\rangle\ \langle b|} = |b\rangle\ \langle a|.$$

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