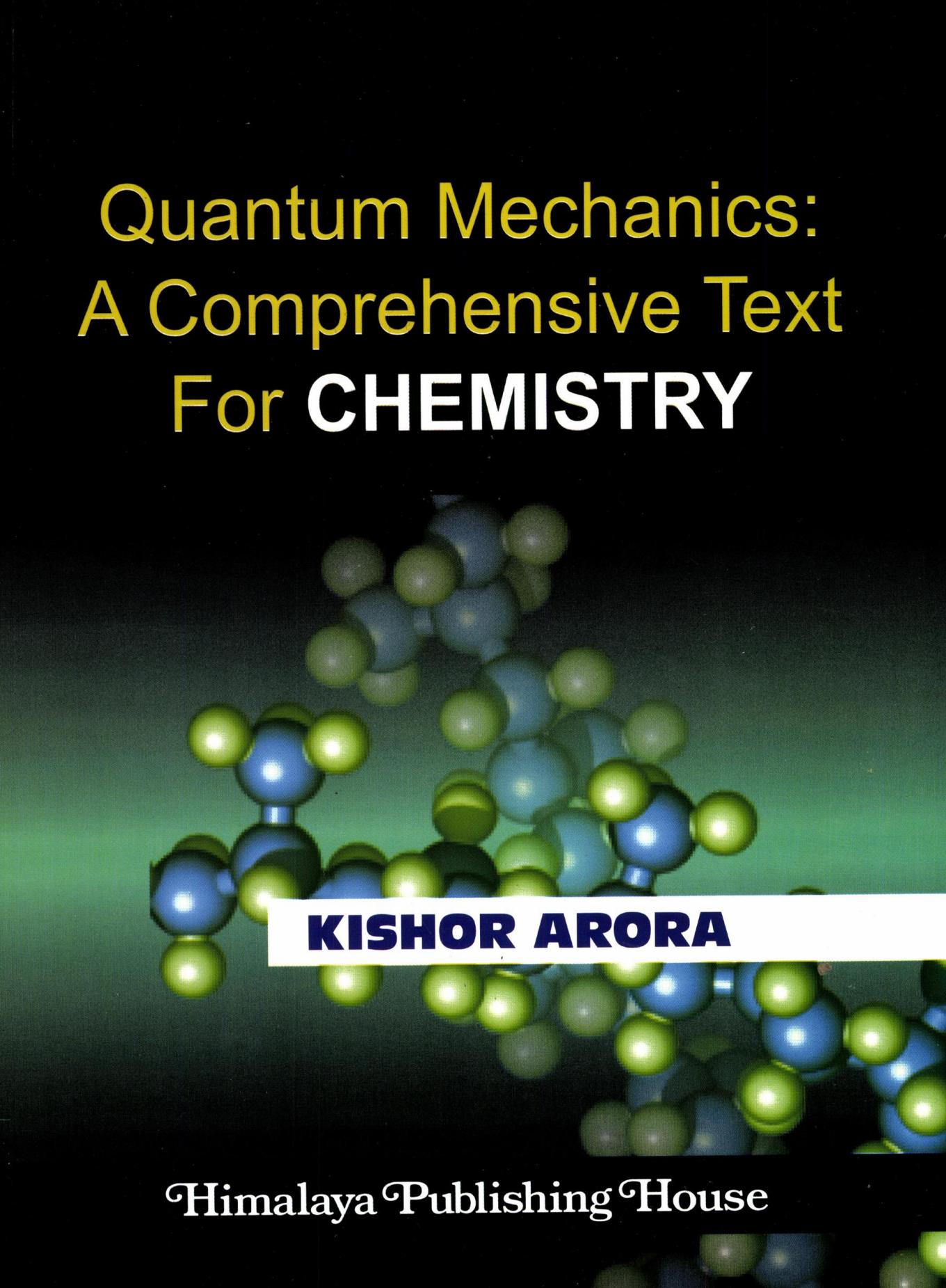


Quantum Mechanics: A Comprehensive Text For CHEMISTRY

The background of the book cover features a dense, abstract arrangement of glowing spheres in various sizes and colors, primarily green and blue, set against a dark, textured background.

KISHOR ARORA

Himalaya Publishing House

QUANTUM MECHANICS : A COMPREHENSIVE TEXT FOR CHEMISTRY

KISHOR ARORA

First Edition : 2010



Himalaya Publishing House

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ISBN : 978-81-84889-36-9

First Edition : 2010

Published by : Mrs. Meena Pandey for **Himalaya Publishing House Pvt. Ltd.**,
“Ramdoot”, Dr. Bhalerao Marg, Girgaon, Mumbai - 400 004.
Phone: .022-2386 01 70/2386 38 63, Fax: 022-2387 71 78
Email: himpub@vsnl.com Website: www.himpub.com

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Typeset by	: Elite-Art, New Delhi-110002, Mobile : 9911297688
Printed by	: A to Z Printers, New Delhi

Preface

Studies of matter and to get structural parameters and properties of it has been a question in front of mankind since past. Several experiments and observations were made in this regard. Several laws and theories were given for this purpose. These studies can be broadly divided into studies based on classical mechanics and those based on quantum mechanics. Classical mechanics which is based on Newton's law of motion, was not able to explain the behaviour and concept of black body radiation. Due to inadequacy of classical mechanics, quantum mechanics was originated. This mechanics is based on concept of quantization as explained by Max Planck. Need to study this mechanics is obvious if one has to get the first hand knowledge of structure and properties of material/matter.

This mechanics has been a part of curricula of physical sciences at undergraduate as well as postgraduate level. The present book includes 14 chapters starting from inadequacy of classical mechanics and covers basic and fundamental concepts of quantum mechanics including concept of quantization of translational, vibration, rotation and electronic energies, introduction to concepts of angular momenta, approximate methods and their applications, concepts related to electron spin, symmetry concepts and quantum mechanics and ultimately the book features the theories of chemical bonding and use of computer softwares in quantum mechanics. Author hopes that this book will cover the syllabi and serve the purpose of students' pursuing their studies in chemistry at undergraduate and postgraduate level in different universities. Suggestions for further improvement are invited.

—Author

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Acknowledgements

On the occasion of publication of this book I wish to acknowledge with deep sense of gratitude and indebtedness to all my teachers who framed me and shaped me as a faculty of chemistry. I would like to mention a few names Prof. N.K. Ray, recipient of Dr. Shanti Swaroop Bhatnagar award who taught me the subject during post graduate level. I am highly thankful to Dr. R.K. Agarwal Editor-in-Chief, Asian J. chem. who has been an ideal for me since childhood and who guided me for my research degree. I bow my head and stand beholden to all my teachers.

I am also thankful to Dr. Archana Bhardwaj (Principal), Dr. Prabha Mehta (Head) and all my colleagues of my college. I am also thankful to my research colleagues and I would like mention the name of Dr. D. Kumar here who has been always supporting in nature to me in the subject. My thanks are also due to C-DAC and team of Pune University *viz.*, Prof. S.R. Gadre, Prof. S.P. Gejji for supporting me with Quantum Chemical Packages/Softwares. I sincerely acknowledge their contribution. I am also thankful to my research students who have supported me to carryout research in the field.

Last but not the least I sincerely acknowledge the continuous support and efforts of my parents Late Shri S.P. Arora and Smt. Swadesh Arora who have been always encouraging me with full enthusiasm to come out with the best. I am also highly thankful to my family *viz.*, Mrs. Reena Arora (wife), Ms. Yashaswina Arora (Daughter) and Master Chittin Arora (Son) for their continuous understanding. My thanks are also due to Dhamija family *viz.*, Shri S.P. Dhamija (Father-in-law), Mrs. Sheela Dhamija (Mother-in-law) Mr. Deepak Dhamija (Brother-in-law), Mrs. Simmi Dhamija (Sister-in-law) and Master Vibhor Dhamija for their cooperation.

I would like to extend my gratitude to the readers of this book and their suggestions for improvement are invited.

Author

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SECTION-1

- 1. Classical Mechanics and Origin of Quantum Mechanics**
 - 2. Fundamental Concepts of Quantum Mechanics**
-

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CHAPTER-1

Classical Mechanics and Origin of Quantum Mechanics

SYNOPSIS

Section	Topics
1.1	Newtonian Mechanics
1.2	Wave Concepts and Electromagnetic Theory of Radiation
1.3	Inadequacy of Classical Mechanics
1.4	Planck's Quantum Theory
1.5	Photo Electric Effect
1.6	Heat Capacity of Solids
1.7	Atomic Spectra and Bohr's Hypothesis
1.8	Debroglie's Hypothesis
1.9	Compton Effect
1.10	Hiesenberg's Uncertainty Principle

Classical mechanics provides a satisfactory description of various mechanical phenomena, however, in the late nineteenth century it became apparent, as two important contributions of this mechanics viz. Newtonian Mechanics and Maxwell's theory for electromagnetic radiation were unable to explain some experimental facts regarding microscopic particles. Contributions of Max Planck, Einstein and Niel Bohr combined the classical concepts with quantum hypothesis. Theories given by them may be considered as old quantum theories. Though contribution of Max Planck to explain the concept of Black Body radiation is the foundation stone of concept quantization of energy but new concepts of quantum mechanics were developed later on. The present chapter deals with some old concepts of classical mechanics with its inadequacy and need and origin of quantum mechanics.

1.1 NEWTONIAN MECHANICS

In classical mechanics, matter is regarded as being made up of particles, each having a certain fixed mass. The motion of these particles is governed by Newton's Laws of Motion :-

- i. "A body at rest will remain at rest and in motion will continue in motion unless and until some external force is acted upon it". (Newton's Ist Law) (Law of Inertia)
- ii. "A particle/object of mass m, if shows a displacement x in time t, then force F_x acting on the particle along the direction $-x$ can be written as :

$$F_x = m \frac{d^2 x}{dt^2} \quad \dots (1.1)$$

(Newton's II law)

- iii. "To every action there is an equal and opposite reaction." (Newton's III Law)

These laws of motion along with Newton's law of gravity provide a satisfactory explanation of the motion of electrically neutral bodies of large dimensions (macroscopic objects)

The basic concepts of the classical mechanics lies in the following points :

- (1) The state of any object at any instant of time is completely determined by describing its co-ordinates and velocities which are the function of time.
- (2) If the state of the object and the force applied on it are known at some instant of time using equation 1.1, state of the object can be predicted at any other time instant.
- (3) Matter may be considered as made up of different particles, each of which can be studied individually.
- (4) In the measuring process, it is assumed that the object of observation and measuring instrument or observer are mutually independent from each other.

In brief – "motion of an object can be viewed as in sharply defined paths of motion of projectiles or any other material body". This is the basic idea of classical mechanics.

1.2 WAVE CONCEPTS AND ELECTROMAGNETIC THEORY OF RADIATION

In order to understand the nature of matter, it is the basic requirement to have first hand knowledge of light/radiation as almost all the experiments in the study of matter are based on matter-radiation interaction. Some notable contributions in this regard are given as under :

Newton's Corpuscular Theory : According to this theory, radiation/light beam is made up of tiny particles called corpuscles. This theory is supportive of particle like nature of light. Some phenomena related to radiation like interference, diffraction, polarisation, etc can not be explained on the basis of this corpuscular theory.

Later on, **Huygen** suggested that light travels in a medium in the form of waves, and each secondary wavelet is formed over the primary wavelet. Phenomena like reflection, refraction, interference, diffraction and polarisation, etc can be successfully explained on the basis of wave nature of light. But, light can travel even in vacuum. The question regarding the material medium that carries the vibration in a light wave was answered by **Maxwell**.

At the end of the nineteenth century, Maxwell proposed that light travels in the medium in the form of waves.

Light waves are transverse in nature. According to this theory, light waves are electromagnetic in nature. That is why this theory is known as **Maxwell theory of electromagnetic radiation**. Electromagnetic radiation is being considered as being produced by the oscillating motion of electric charge. This oscillation results in a periodically changing electric field surrounding the charge and this also produces an oscillating magnetic field. These oscillating electric and magnetic field disturbances propagate through medium as radiation. The range of wavelengths or frequencies of these electromagnetic radiation is called as electromagnetic spectrum. This spectrum is given in table 1.1.

Some characteristics of electromagnetic radiations are given below :

1. These radiations can propagate through space without the support of any medium and travel in a medium with uniform velocity $2.99979 \times 10^8 \text{ ms}^{-1}$.
2. These radiations are produced by the oscillations of electric charges and magnetic fields. The electric and magnetic fields are at right angles to each other and to the direction of propagation.

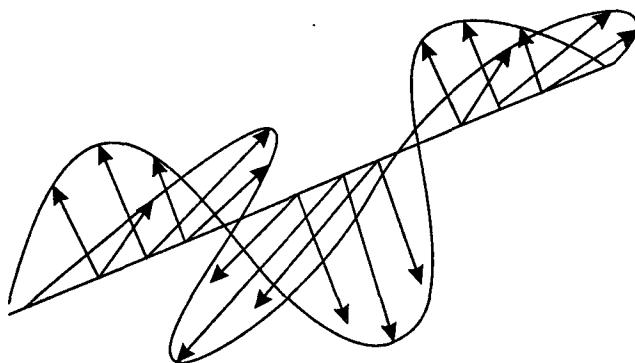


Fig 1.1. An electromagnetic wave

3. The electromagnetic radiations are characterised by their frequency ν or wavelength λ and these quantities are related to each other by the equation :
 $c = \nu\lambda$ where c is the velocity of light or radiation.

According to Maxwell's theory, the energy carried by an electromagnetic wave is proportional to the square of the amplitude of the wave, which in turn is proportional to the intensity (energy per unit volume) of the radiation. Further, the exchange of energy between matter and radiation is assumed to take place continuously.

TABLE 1.1
Range of wavelength and frequency of electromagnetic radiation

Type of radiation	Cosmic rays	γ -rays	X-rays	UV radiation	Visible	Infrared	micro-wave	Radio frequency
Wavelength λ (in m)	10^{-14} —	10^{-13} —	10^{-10} —	10^{-8} —	10^{-7} —	10^{-6} —	10^{-3} —	10^{-1} – 10^4
Frequency v (in Hz)	10^{22} —	10^{21} —	10^{18} —	10^{16} —	10^{15} —	10^{14} —	10^{11} —	10^9 – 10^4

1.3 INADEQUACY OF CLASSICAL MECHANICS

Black body radiation :

The first definite failure of classical theory was found in the study of the nature of distribution of energy in the spectrum of radiation from a black body. When a black body is heated, it emits electromagnetic radiations and when its temperature is lowered energy is absorbed by it. In case of heat radiation, when the radiant energy absorbed by the body is equal to the heat emitted, the system will be in thermal equilibrium. If a body absorbs all the radiation that falls upon it, it is known as a black body and radiation emitted by such a body is known as black body radiation. Actually no object is a perfect black body.

Kirchoff formulated two laws concerning the properties of a black body.

1. A black body, not only absorbs all the radiation falling on it but also acts as a perfect radiator when heated.
2. The radiation given out by a black body is dependent on its temperature and is independent of the nature of the internal material.

The radiant energy associated with a black body at different wavelengths can be shown as in fig. 1.2. This figure may be termed as spectral distribution for black body.

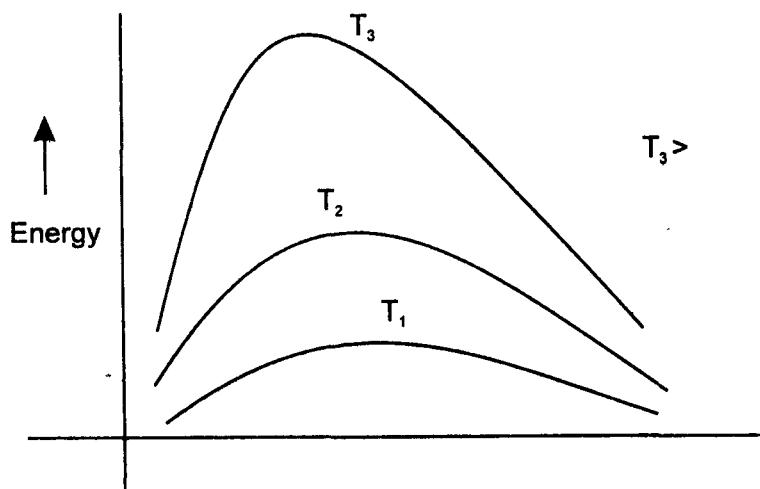


Fig. 1.2 Spectral distribution of a black body

According to classical mechanics the following laws were given to explain the behaviour of a black body :

Wein's Law : Wein established a relation between wavelength λ corresponding to the maximum of the spectral distribution and the temperature of a black body. This law is known as Wein's displacement law and is given by :

$$\lambda_{\max} T = \text{Constt.} \quad \dots (1.2)$$

Where constt. = 2.88 mmk

$$\Rightarrow \lambda_{\max} = \frac{\text{Constt}}{T} \quad \dots (1.3)$$

or
$$\lambda_{\max} \propto \frac{1}{T} \quad \dots (1.4)$$

which implies that in the spectral distribution of a black body its maximum wavelength i.e. λ_{\max} is inversely related to the temperature of the black body.

Stefan – Boltzmann's Law : According to this law for a black body electromagnetic energy per unit volume i.e. energy density can be related to the temperature of a black body as per the following relation :

$$\epsilon = aT^4 \quad \dots (1.5)$$

Where ϵ = energy density and 'a' is a constant. This expression is also written in terms of emittance R and is given by:

$$R = \sigma T^4 \quad \dots (1.6)$$

$$\sigma = \frac{ac}{4} = 5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$$

The quantity R (emittance) is defined as the power emitted by the region of surface divided by the area of the surface. The quantity σ is known as Stefan Boltzmann's constant. Equation 1.6 is Stefan Boltzmann's law.

For theoretical interpretation to explain the spectral distribution of a black body, the following laws were proposed :

(i) Wein Distribution Law : Wein derived an expression for spectral distribution of a black body on the basis of its thermodynamic considerations, according to which the amount of energy ($E_\lambda d\lambda$) emitted by a black body at a temperature T within the wavelength range λ to $\lambda + d\lambda$ is given by

$$E_\lambda d\lambda = A \lambda^{-5} e^{-B/\lambda T} d\lambda \quad \dots (1.7)$$

Where A & B are constants. This relation is known as Weins' Distribution Law.

At $\lambda = 0$ $E_\lambda d\lambda = 0$ and .

At $\lambda = \infty$ again $E_\lambda d\lambda = 0$

Therefore, it may be concluded that no energy is emitted by a wave at infinite or zero wavelength

which is against the actual behaviour of a black body. Equation 1.7 was found to be satisfactory in lower wavelength range but it fails to explain the experimental curves for a black body at higher wavelength range.

(ii) Rayleigh – Jean Distribution Law : Rayleigh – Jean applied the principle of equipartition of energy to black body radiation. This law considered a black body to be made up of a number of oscillators with one possible frequency for each oscillator. According to it, an oscillator in equilibrium with the source at a temperature T, possesses a mean kinetic energy kT where k is Boltzmann's constant. The number of oscillators per unit volume (dN) in the frequency range ν and $\nu+dv$ is calculated on the basis of classical view point as

$$dN = \frac{8\pi\nu^2}{c^3} dv$$

Where c is the velocity of light. Therefore, the energy density $E_\nu dv$ is simply the product of the number of oscillators per unit volume and the mean energy kT of the oscillator.

$$E_\nu dv = \frac{8\pi\nu^2}{c^3} kT dv \quad \dots (1.8)$$

On increasing ν , the energy density gradually increases without going through the maximum and ultimately becomes infinite at $\nu = \infty$. This situation leads to ultraviolet catastrophe. This theory is also not in agreement with the experimental facts over the complete range of the wavelength. The Rayleigh-Jean formula agrees fairly well with the experimental results in lower wavelength region.

Neither, Wein Distribution Law nor Rayleigh-Jean distribution law are consistent with the experimental results in the larger wavelength range. Therefore, this may be concluded that black body radiation concept cannot be explained satisfactorily using classical mechanics.

1.4 PLANCK'S QUANTUM THEORY

In order to explain the spectral distribution of a black body over a wide range of wavelength, Max Planck gave this theory in 1900. This theory was proposed by him keeping in mind Wein's equation and Rayleigh-Jean's equation and this revolutionary theory discarded the classical concepts that an oscillator emits or takes up energy continuously.

According to the theory of Max Planck :

- (1) An oscillator absorbs or emits radiation / energy in a discrete manner in the form of energy packets called quanta (singular quantum), which may be considered as behaving like a stream of particles, possessing mass, energy and momentum. The energy of a quantum of radiation is directly proportional to its vibrating frequency

$$\epsilon \propto \nu$$

or

$$\epsilon = h\nu \quad \dots (1.9)$$

- (2) The oscillator has a definite amount of energy in discrete levels called energy levels. The energy E_n of the n^{th} level will be an integral multiple of a quantum i.e.

$$E_n = n \hbar v$$

Where n is any integer having value 0, 1, 2, 3,

Spectral distribution of a black body radiation can be explained on the basis of the theory of Max Planck as following :

Let us consider that a black body consists of N simple harmonic oscillators, each having fundamental frequency v . If these oscillators can take up energy only in the multiples of $\hbar v$ the allowed energies will be $0, \hbar v, 2\hbar v, 3\hbar v, \dots$. Let N_0, N_1, N_2, \dots be the number of oscillators with corresponding energies E_0, E_1, E_2, \dots . The number N_i having energy E_i above the lowest energy level E_0 can be determined using the Boltzmann's distribution law as :

$$N_i = N_0 \exp(-E_i/kT) \quad \dots (1.10)$$

$$N_1 = N_0 \exp(-E_1/kT) = N_0 \exp(-\hbar v/kT)$$

$$N_2 = N_0 \exp(-E_2/kT) = N_0 \exp(-2\hbar v/kT)$$

----- and so on

Where k is the Boltzmann's constant

The total number of oscillators (N) in all energy states is given by

$$\begin{aligned} N &= N_0 + N_1 + N_2 + \dots \\ &= N_0 + N_0 \exp(-\hbar v/kT) + N_0 \exp(-2\hbar v/kT) + \dots \\ &= N_0 + [1 + N_0 \exp(-\hbar v/kT) + N_0 \exp(-2\hbar v/kT) + \dots] \\ &= N_0 \sum_{i=0}^{\infty} \exp\left(-i \frac{\hbar v}{kT}\right) \end{aligned} \quad \dots (1.11)$$

The total energy of all the oscillators is given by

$$\begin{aligned} E &= E_0 N_0 + E_1 N_1 + E_2 N_2 + \dots \\ &= 0 N_0 + \hbar v N_0 \exp(-\hbar v/kT) + 2\hbar v N_0 \exp(-2\hbar v/kT) + \dots \\ &= N_0 \hbar v [\exp(-\hbar v/kT) + 2 \exp(-2\hbar v/kT) + \dots] \\ &= N_0 \hbar v \sum_{i=0}^{\infty} i \exp\left(-i \frac{\hbar v}{kT}\right) \end{aligned} \quad \dots (1.12)$$

The average energy (\bar{E}) of an oscillator with fundamental frequency v is given by

$$\bar{E} = \frac{E}{N} = \frac{N_0 \hbar v \sum_{i=0}^{\infty} i \exp(-i \hbar v/kT)}{N_0 \sum_{i=0}^{\infty} \exp(-i \hbar v/kT)} \quad \dots (1.13)$$

Substitute $\exp(-\hbar v / kT) = x$

$$\Rightarrow \bar{E} = \frac{h\nu \sum_{i=0}^{\infty} ix^i}{\sum_{i=0}^{\infty} x^i}$$

Where denominator will be

$$\begin{aligned} & \sum_{i=0}^{\infty} x^i (1+x+x^2+x^3+\dots) \\ &= \frac{1}{(1-x)^2} \text{ for } x < 1 \end{aligned}$$

And numerator

$$\begin{aligned} & \sum_{i=0}^{\infty} i x^i (0+x+x^2+3x^3+\dots) \\ &= x (1+2x+3x^2+\dots) \\ &= \frac{1}{(1-x)^2} \text{ for } x < 1 \end{aligned}$$

Therefore \bar{E} will be

$$\bar{E} = \frac{h\nu x (1-x)}{(1-x)^2} = \frac{h\nu x}{(1-x)}$$

$$\Rightarrow \bar{E} = \frac{h\nu \exp(1-h\nu/kT)}{1-\exp(-h\nu/kT)}$$

Multiplying by $\exp(h\nu/kT)$

$$\bar{E} = \frac{h\nu}{(\exp h\nu/kT - 1)} \quad \dots (1.14)$$

The number of oscillators per unit volume within the frequency range ν & $\nu + d\nu$ is given by

$$dN = \frac{8\pi\nu^2}{C^3} d\nu$$

Therefore, energy density ($E_v dv$) in the region v & $v + dv$ is simply the product of the number of oscillators per unit volume and average energy of the oscillators.

$$= E_v dv = \frac{8\pi v^2}{C^3} dv \frac{hv}{[\exp(hv/kT) - 1]} \\ = \frac{8\pi hv^3}{C^3} \frac{1}{[\exp(hv/kT) - 1]} \quad \dots (1.15)$$

This equation is known as Planck's distribution equation. This equation can also be expressed in terms of wavelength as

$$E_\lambda d_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{[\exp(hv/\lambda kT) - 1]} d\lambda \quad \dots (1.16)$$

This equation was found to be in agreement with experimental results for a black body.

When $hc \gg \lambda kT$ (i.e. T or λ is small)

$\exp(hc/\lambda kT) \gg 1$. So, one can be neglected in denominator.

$$= E_\lambda d_\lambda = \frac{8\pi hc}{\lambda^5} \exp(-hc/\lambda kT) d\lambda$$

$$= A \lambda^{-5} \exp(B/\lambda T) d\lambda \quad (1.7)$$

Which is Wein's equation

When $h c \ll kT$ (i.e. T or λ is large)

$$\exp(hc/\lambda kT) = 1 + \left(\frac{hc}{\lambda kT}\right) + \frac{1}{2!} \left(\frac{hc}{\lambda kT}\right)^2 + \dots \quad \dots (1.17)$$

$$= 1 + \frac{hc}{\lambda kT} \quad (\text{Neglecting the terms with higher powers})$$

$$= E_\lambda d_\lambda =$$

Or

$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda \quad \dots (1.18)$$

or

$$E_\lambda d\lambda = \frac{8\pi v^2}{C^3} kT dv \quad \dots (1.18)$$

Which is Rayleigh – Jean equation

Example 1.1

Consider the Sun as a black body radiator. If maxima in the spectral distribution of Sun's emitted energy appears at 480 nm. Calculate the temperature of the outer core of the sun.

Solution

According to Wein's law

$$\lambda_{\max} T = 2.88 \text{ mm K}$$

$$T = \frac{(\text{constt}) 2.88 \text{ mmk}}{480 \text{ nm}} \left(\text{or } \frac{\text{constt}}{\lambda_{\max}} \right)$$

$$T = \frac{2.88 \times 10^{-3} \text{ mk}}{480 \times 10^{-9} \text{ m}} = 600 \text{ k} - \text{Ans.}$$

1.5 PHOTO-ELECTRIC EFFECT

An experiment were performed with alkali metal surface and showed that when a beam of visible or UV light falls on a clean alkali metal surface, electrons are ejected out from the surface. This effect is known as photo-electric emission or photo-electric effect. This may be observed in different states if appropriate frequency is used. The typical experimental setup for this purpose is shown in fig. 1.3. In a photo cell which is a vacuum tube containing two electrodes light falls on the metal surface and because of photo-electric emission photo – electrons are ejected out from this metal cathode which are then captured at the pointed anode. (Fig. 1.3) Flow of electric current is registered by the Galvanometer or electrometer G. This current is known as total photo-electric current.

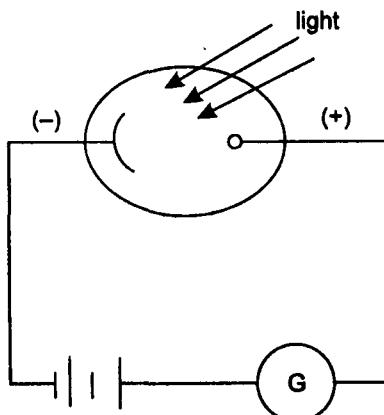


Fig. 1.3. Schematic Circuit diagram for the study of photo-electric effect

On the application of monochromatic radiations of same frequency but varying intensities on the metal surface, a series of current potential curves may be obtained (Fig. 1.4). When V is positive, the current I may reach to a maximum limiting value which is known as saturation current. When V is made increasingly negative, the current begins to decrease until at a sharply defined value V, it

becomes zero. The limiting retarding potential, at which all electrons are stopped and at which current becomes zero is called as stopping potential, 'V' for a particular metal surface and at a given frequency.

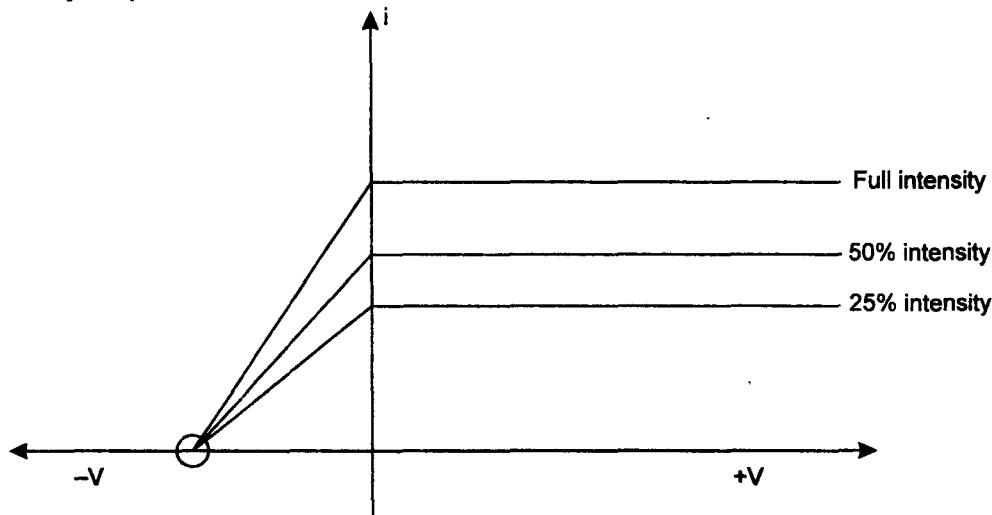


Fig. 1.4. Photo-electric current I V & v graph

As voltage V_0 is required to stop electrons with maximum speed V_m , this potential is a measure of the maximum kinetic energy of the electron. The stopping potential is just equal to the maximum kinetic energy of electrons.

$$\frac{1}{2}mv^2 = eV_0 \quad \dots(1.19)$$

The stopping potential is independent of the light intensity and the total electric current is proportional to the intensity. The stopping potential is a constant quantity for a given frequency, it varies with frequency. (Fig. 1.5) The stopping potential V_0 becomes zero below a definite frequency indicating that no electrons are emitted. This limiting frequency below which no electrons are emitted is called the threshold frequency V_0 .

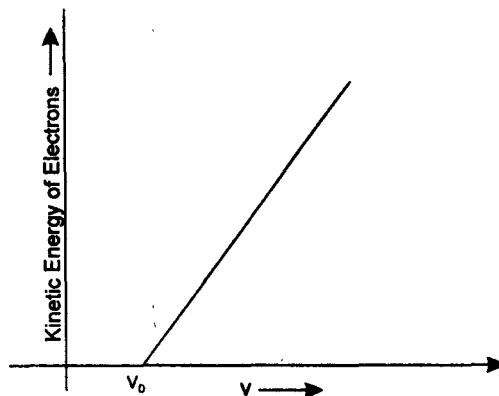


Fig. 1.5. Variation of kinetic energy with frequency of incident light.

It was shown by Einstein that this observation of the phenomenon of photo-electric effect could be understood in terms of Planck's Quantum Theory. He pointed out that the emission or absorption of energy takes place in quanta or photons of energy $h\nu$. When a photon of energy $h\nu$ (frequency ν_0), strikes with the metal surface it transfers its energy to the electron on the metal surface, a portion of which is being utilised in emission of photoelectron and the rest of which has been transferred to photoelectrons which is being utilised by this electron as its kinetic energy. So, total energy of photon may be considered as the sum of work function and the kinetic energy of the photoelectron.

$$h\nu = \text{work function} + \text{kinetic energy}$$

or

$$h\nu = h\nu_0 + \frac{1}{2} mv^2 \quad \dots (1.20)$$

where ν_0 is the threshold frequency or minimum frequency required to initiate the photo-electric effect with its corresponding energy $h\nu_0$ and $\frac{1}{2} mv^2$ is the kinetic energy of the photo-electron emitted with velocity v . The equation 1.20 is known as Einstein's equation for photo-electric emission.

$$\text{K.E. or } \frac{1}{2} mv^2 = h(v - v_0) \quad \dots (1.21)$$

1.6 HEAT CAPACITY OF SOLIDS

According to the classical theory, an ideal solid may be regarded as consisting of a space lattice of independent atoms. These atoms are not at rest but they vibrate about their equilibrium positions. They do not interact with each other but their vibration continues even at absolute zero. As temperature is raised, the amplitude of vibration increases and hence, the potential and kinetic energies.

Dulong & Petit gave a law to explain heat capacities of solids, which states that all solids have the same heat capacities per gram atom or the atoms of all elements have the same heat capacity or atomic heat capacities of most of the solid elements measured at atmospheric pressure and at ordinary temperature. This value is a constant about 6.4 cal deg^{-1} .

This law fails to explain the variation of heat capacities with temperatures and when it is applied to light elements such as Beryllium, Boron, Carbon and Silicon, etc. at ordinary temperature, the values of heat capacities have been found to be different from the constant value as proposed by the Dulong Petit law. In view of the variation of heat capacity of solids with temperature it might be thought that the Dulong Petit law is not universally correct and that the atomic heat capacity of $\sim 6.0 \text{ cal deg}^{-1}$ has only a theoretical significance.

Classical Theory of Heat Capacity

Classical theory of heat capacity explains well the concept of heat capacity of solids by taking into account the law of equipartition of energy. According to this theory, in solids each atom should have each mode of vibration which should contribute kT energy for atom or molecule where k is Boltzmann's constant. Therefore, total energy content E per gram atom or per mole of the ideal solid would be

$$E = N_A \times 3 kT \quad \dots (1.22)$$

$$\text{As } k = R/N_A$$

$$E = N_A \cdot 3 \times \frac{R}{N_A} \times T$$

$$E = 3 RT$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V = \left[\frac{\partial (3RT)}{\partial T} \right]_V = 3R$$

$= 3 \times 1.998 \sim 5.96 \text{ cal deg}^{-1} \text{ of atom}^{-1}$

...(1.23)

This shows the theoretical value of the heat capacity of an ideal solid should be $5.96 \text{ cal deg}^{-1}$ for each gram atom or per mole present. This theoretical conclusion is in agreement with Dulong Petit's law according to which heat capacity of solids at constant value is 6.4 cal deg^{-1} .

Quantum Theory for Heat Capacity

Both Dulong and Petit law and Classical Theory of Heat capacity of solids were not able to explain the variation of heat capacity of solids with temperature. An important step in the improvement of classical theory was taken by A. Einstein who applied quantum theory in place of classical equipartition principle to solve the problem of heat capacity of solids. He obtained an expression for atomic heat capacity of a solid at constant volume as given below :

$$C_v = 3R \frac{[e^{hc\omega/kT}]}{[e^{hc\omega/kT} - 1]^2} \left(\frac{hc\omega}{kT} \right)^2$$
...(1.24)

Where 'w' is the oscillating frequency of the atomic oscillators in wave number units in the lattice of the solid. From equation (1.24) one can predict that:-

- (i) At high temperature, the factor $(hc\omega/kT)^2$ is small in comparison to unity. Hence $C_v = 3R$. This is in agreement with the classical theory.
- (ii) At very low temperature heat capacity approaches to zero. Therefore, at very low temperature all the atoms in solids are in lowest vibration level, hence there would be no vibrational contribution to the heat capacity.
- (iii) On increasing temperature vibration energy increases, hence the heat capacity becomes applicable.

Thus, Einstein equation explains the variation of heat capacities of solids with change in temperature.

1.7 ATOMIC SPECTRA AND BOHR'S HYPOTHESIS

This theory was given by Niel Bohr to explain the electronic energy of an electron in H-atom and in turn to explain the origin of atomic spectral lines in its atomic spectra. The theory was based on the following postulates:

- (i) Electron in H-atom revolves round the nucleus in certain stationary orbit of radius r ,
- (ii) Coloumbic force of attraction between nucleus and negatively charged electron is balanced by the centripetal force of the moving electron.

- (iii) Angular momentum of moving electron in stationary orbit is quantized and is given by the following formula

$$mv r = n \hbar \quad \text{or}$$

$$mv r = \frac{n\hbar}{2\pi} \quad \left[= \frac{\hbar}{2\pi} \right] \quad \dots (1.25)$$

- (iv) Spectral lines may appear in the atomic spectra of H-atom because of motion of electrons from higher orbit to lower orbit and energy gap between the orbits involved in a spectral transition i.e. ΔE is directly proportional to the frequency of that particular spectral line

$$\text{i.e.} \quad \Delta E = E_{n_2} - E_{n_1} = h\nu \quad \dots (1.26)$$

On the basis of these postulates, Niel Bohr gave his theory to derive the formula for electronic energy of an electron in a circular stationary orbit. This theory is valid for single electron system such as H-atom, Be^+ ion, Li^{2+} - ion, etc. The concept of Rutherford to explain the nuclear model was in an explicit manner but one of the conclusions of this concept, that electrons revolve round the nucleus in its own path, formed the foundation stone of Bohr's Theory. In order to understand Bohr's Theory, let us consider the single electron system (Fig. 1.6).

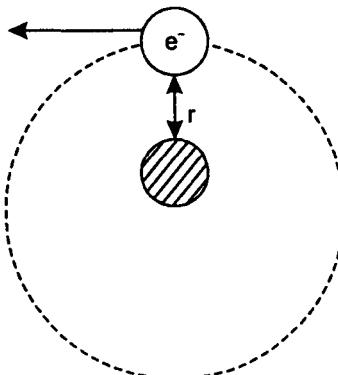


Fig. 1.6 Proposed Model for H-atom

According to postulate (ii)

Coloumbic force of Attraction between = Centripetal force of Moving of moving electron Nucleus and electron

$$\text{Or} \quad \frac{(Ze)e}{(4\pi\epsilon_0)r^2} = \frac{mv^2}{r} \quad \dots (1.27)$$

Where m is the mass of electron and v is its velocity

$$\text{Or} \quad \frac{(Ze)e}{(4\pi\epsilon_0)r^2} = \frac{mv^2}{r} \\ = \frac{Ze^2}{(4\pi\epsilon_0)r^2} = mv^2r \quad \dots (1.28)$$

$$= \frac{Ze^2}{(4\pi\epsilon_0)} = (mv)r \quad \dots(1.29)$$

Since according to postulate (iii)

$$mv = nh$$

or

$$mv = \frac{nh}{2\pi}$$

$$= \frac{Ze^2}{(4\pi\epsilon_0)} = \left(\frac{nh}{2\pi}\right)v \quad \dots(1.30)$$

Or

$$v = \frac{2\pi Ze^2}{(4\pi\epsilon_0)nh} \quad \dots(1.31)$$

Substituting the value of v in equation (1.28)

$$= \frac{Ze^2}{(4\pi\epsilon_0)} = m \left(\frac{2\pi Ze^2}{(4\pi\epsilon_0)nh} \right) r \quad \dots(1.32)$$

$$\Rightarrow r = \frac{(4\pi\epsilon_0)n^2 e^2}{4\pi^2 m e^2 Z} \quad \dots(1.33)$$

For H – atom $Z = 1$ and if $n = 1$, the radius of the first Bohr orbit (a_0) becomes

$$R = a_0 = \frac{(4\pi\epsilon_0)h^2}{4\pi^2 m e^2} \quad \dots(1.34)$$

Substituting the values of constant quantities

$$a_0 = 5.292 \times 10^{-11} \text{ m} = 0.0529 \text{ nm}$$

this quantity is known as Bohr's radius

Energy for a moving electron in H-atom is given by the sum total of its Kinetic energy and its potential energy

\Rightarrow

$$E = KE + PE.$$

Or

$$E = T + V$$

as

$$T (\text{or K.E.}) = \frac{1}{2} m v^2$$

and since

$$mv^2 = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

$$= T (\text{or K.E.}) = \frac{1}{(4\pi\epsilon_0)} \frac{1}{2} \frac{Ze^2}{r} \quad \dots(1.35)$$

P.E. for the moving electron (or V) is given by

$$V \text{ (or P.E.)} = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

Therefore

$$E_n = \frac{-Ze^2}{(4\pi\epsilon_0)r} + \frac{1}{2} \cdot \frac{1}{(4\pi\epsilon_0)} \cdot \frac{Ze^2}{r}$$

$$E_n = \frac{-Ze^2}{(4\pi\epsilon_0)2r}$$

Substituting the value for r in the above equation

$$E_n = \frac{-2\pi^2 Z^2 e^4 m}{(4\pi\epsilon_0)^2 n^2 h^2} \quad \dots (1.36)$$

For H-atom ($Z = 1$)

$$E_n = \frac{-2\pi^2 m e^4}{(4\pi\epsilon_0)^2 n^2 h^2} \quad \dots (1.37)$$

$$E_n = \frac{-(\text{const tan t})}{n^2} \quad \dots (1.38)$$

The above energy equation (1.36) is valid for certain discrete energy levels and n is the principal quantum number here.

Origin of atomic spectral lines may be explained on the basis of energy equation derived by Niel Bohr as per following :

According to equation (1.36) E_n (or energy) of electron in n^{th} orbit is given by

$$E_n = \frac{-2\pi^2 m e^4 z^2}{(4\pi\epsilon_0)^2 n^2 h^2} \quad \dots (1.36)$$

And since

$$\Delta E = E_{n_2} - E_{n_1} = h\nu$$

$$E_{n_2} = \frac{-2\pi^2 m e^4 z^2}{(4\pi\epsilon_0)^2 n_2^2 h^2} \quad \dots (1.37)$$

$$E_{n_1} = \frac{-2\pi^2 m e^4 z^2}{(4\pi\epsilon_0)^2 n_1^2 h^2} \quad \dots (1.38)$$

$$\Delta E = \frac{-2\pi^2 m e^4 z^2}{(4\pi\epsilon_0)^2 h^2} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \dots (1.39)$$

$$= \Delta E = \frac{-2\pi^2 me^4 z^2}{(4\pi \epsilon_0)^2 h^2} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \dots (1.40)$$

$$= \bar{v} = \frac{-2\pi^2 me^4 z^2}{(4\pi \epsilon_0)^2 h^3} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \dots (1.41)$$

Or in wave number units

$$= \bar{v} = \frac{-2\pi^2 me^4 z^2}{(4\pi \epsilon_0)^2 Ch^3} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \dots (1.42)$$

For H-atom ($Z = 1$) on substituting the values of constants in the above equation

$$\bar{v} = R_H \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \dots (1.43)$$

Rydberg's formula

Where R_H = Rydberg's constant for H-atom

And R_H is equal to 109678 cm^{-1} or

$$1.09678 \times 10^7 \text{ m}^{-1}$$

On the basis of the above equation (1.43) and according to Bohr's Theory, origin of atomic spectral lines may be explained. As orbits are characterised by principal quantum numbers n

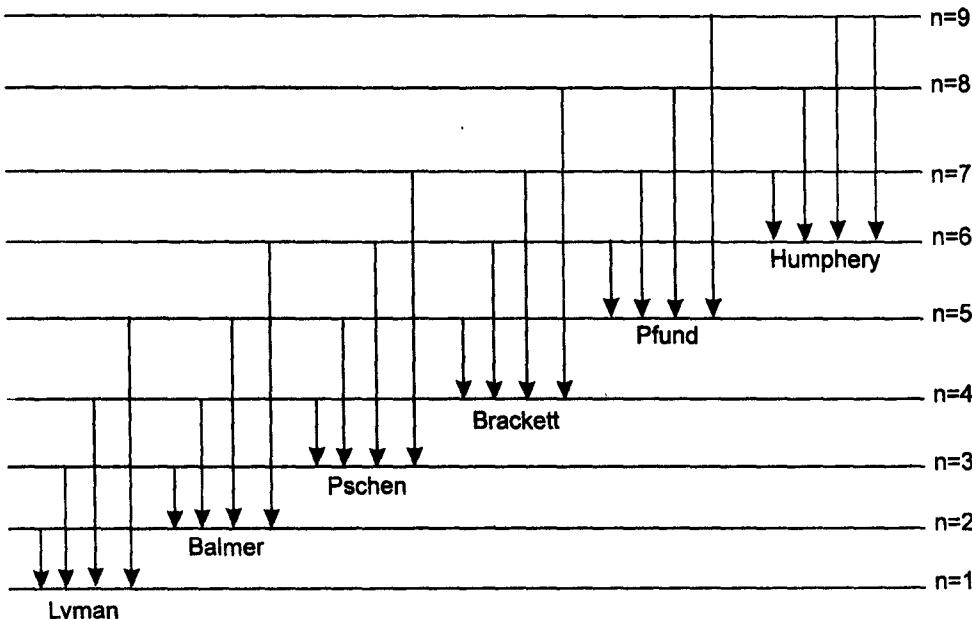


Fig. 1.7. Atomic spectral lines series in case of H – atom

$= 1, 2, 3 \dots$, atomic spectral lines appear because of jumping of electrons from outer orbit to an inner orbit as shown in Fig. 1.7. Following series of atomic spectral lines may be obtained in atomic spectra of H – atom.

Luman series : $n_1 = 1, n_2 = 2, 3, 4, 5 \dots$

Balmer series : $n_1 = 2, n_2 = 3, 4, 5, 6 \dots$

Paschen series : $n_1 = 3, n_2 = 4, 5, 6, 7 \dots$

Brackett series : $n_1 = 4, n_2 = 5, 6, 7, 8 \dots$

Pfund series : $n_1 = 5, n_2 = 6, 7, 8, 9 \dots$

Humphery series : $n_1 = 6, n_2 = 7, 8, 9, 10 \dots$

When energy is absorbed by an atom, the electron moves from ground state ($n=1$) to the higher energy states ($n > 1$). The amount of energy necessary to remove an electron from its lowest level to infinite distance, resulting in the formation of a free ion is called the ionization energy (I). This energy change for the H-atom is given by

$$\Delta E = \frac{-2\pi^2 e^4 m^2}{(4\pi \epsilon_0)^2 h^2} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \dots (1.44)$$

$$\frac{-2\pi^2 e^4 m^2}{(4\pi \epsilon_0)^2 h^2} \frac{1}{1^2} \quad \dots (1.44)$$

Substituting the appropriate values in terms of S.I. units, we get

$$I = |\Delta E| = 2.181 \times 10^{-18} \text{ J} = 13.61 \text{ eV}$$

(as $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$). The experimental value for H – atom is $21.75 \times 10^{-19} \text{ J}$. or 13.58 eV

Example 1.2 : A beam of electron is used to bombard gaseous hydrogen atoms. What is the minimum energy the electron must have if the number of Balmer series, corresponding to a transition from $n = 3$ to $n = 2$ state is to be emitted ?

$$= \Delta E = \frac{-2\pi^2 e^4 m}{(4\pi \epsilon_0)^2 h^2} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$$

as

$$m = 9.1 \times 10^{-31} \text{ kg} ; e = 1.602 \times 10^{-19} \text{ C} ;$$

$\pi = 3.1415$; $4\pi \epsilon_0 = 1.113 \times 10^{-10}$, $\text{C}^2 \text{J}^{-1} \text{m}^{-1}$ and $h = 6.626 \times 10^{-34} \text{ Js}$ and $n_1 = 2$ and $n_2 = 3$ on substituting the values of all the constants and n_1 & n_2

$$E = 2.98 \times 10^{-19} \text{ J}$$

Example 1.3 : Calculate the third ionization energy of Lithium

The third ionization energy of lithium means the removal of an electron from Li^{2+}

Since $Z = 3$ we have

$$\Delta E = \frac{-2\pi^2 e^4 m}{(4\pi \epsilon_0)^2 h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\Delta E = \frac{-2\pi^2 e^4 m}{(4\pi \epsilon_0)^2 h^2} (3)^2$$

On substituting values of $\pi = 3.1415$; $m = 9.1 \times 10^{-31}$ kg; $e = 1.6 \times 10^{-19}$ C; $h = 6.626 \times 10^{-34}$ Js and $4\pi \epsilon_0 = 1.113 \times 10^{-10}$ C²N⁻¹ m⁻²

$$I = |\Delta E| = 1.962 \times 10^{-17} \text{ J for lithium}$$

Shortcomings of Bohr's Theory :

Though Bohr's Theory had explained well the origin of atomic spectral lines and explained the spectral data for H-atom. But it did not give the explanation for their fine structures as observed with spectrometers of high resolution power or about splitting of spectral lines in presence of external magnetic or electric field. It had also not accounted for the spectra of other atoms or molecules and intensity variations in spectral lines. Arbitrary stationary orbits have given us theoretical basis and the stability of the orbits can't be understood easily, on the basis of Bohr's theory. Pictorial concept of electrons in orbit is not justified.

Another major shortcoming of the Bohr's theory is its proposal for angular momentum of electrons. According to this theory, angular momentum for moving electron is the integral multiple of \hbar (or $h/2\pi$) which is not true, as in certain cases electrons also possess the zero angular momentum.

WAVE ASPECT OF MATTER

1.8 DEBROGLIE'S HYPOTHESIS

Tiny particles, like photons exhibit dual behaviour while motion. This observation was given by De Broglie's. According to the hypothesis of De Broglie, micro particles like photon shows two types of behaviour viz particle like nature and wave like nature.

Phenomenon like interference, diffraction and Polarization which are shown by light photons are the evidences of wave like nature of the photon. Similarly, production of scintillations or spots when photons strike with ZnS or photographic plate is the evidence of particle like nature of photon.

As a photon in motion shows two types of behaviour, therefore, the two equations viz. Einstein's equation and Planck's equation must hold good for the same photon.

$$E = mc^2 \text{ (Equation favouring particle like nature)} \quad \dots(1.45)$$

$$\& \quad E = hv \text{ (Equation favouring wave like nature)} \quad \dots(1.46)$$

Where v is the frequency of the moving photons. From these two equations, we get

$$E = mc^2 = hv$$

$$\text{Or} \quad mc^2 = hv$$

$$c = v\lambda \quad \dots(1.47)$$

$$v = \frac{c}{\lambda}$$

$$mc^2 = \frac{hc}{\lambda}$$

$$\lambda = \frac{h}{mc} \text{ or } \lambda = \frac{h}{p} \quad \dots(1.48)$$

Where p is momentum of photon and c is the velocity of light, with m is mass of photon. Therefore, the wavelength of moving photon which exhibits wave like behaviour is also inversely related to its momentum. Later on, this observation was extended to micro particles like electron also, and c (velocity of photon) was replaced by v (velocity of electron).

$$\lambda = \frac{h}{mv} \quad \dots(1.49)$$

$$\text{Or} \quad \lambda = \frac{h}{p_e} \quad \dots(1.49)$$

Where p_e = momentum of electron and is equal to mv and m is mass of electron.

Experimentally Debroglie's wavelength λ can be determined as follows : When an electron is accelerated through a potential difference of V volts, its kinetic energy will be

$$\frac{1}{2} mv^2 = Ve \quad \dots(1.50)$$

$$mv = (2meV)^{\frac{1}{2}} \quad \dots(1.51)$$

Where m , e and v are the mass, charge and velocity of the electron respectively.

Therefore

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

$$\text{Or} \quad \lambda = \frac{h}{(2meV)^{\frac{1}{2}}} \quad \dots(1.52)$$

It is obvious $\frac{h}{mv}$ is negligible for relatively large objects (macro-particles), while for subatomic

particles (micro-particles), this quantity is not small enough to be considered as negligible. Therefore, one may conclude that wave character is predominant in micro particles and particle character is predominant in macro-particles.

The Debroglie concept does not imply that matter behaves like a particle at one time and like waves at other time. Rather the wave nature has to be an inherent property of each particle. Micro-particles are capable of exhibiting particle or wave like properties to some extent, depending upon

circumstances which was considered as two distinct concepts by classical mechanics.

Example 1.4 : Calculate the wavelength of a matter wave associated with a particle of weight 1 kg moving with a speed of 10m/sec.

As according to DeBroglie's equation

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

$h = 6.626 \times 10^{-34}$ Js; $m = 1\text{kg}$ and $v = 10\text{m/sec}$. On substituting these values.

$$\lambda = 6.626 \times 10^{-34} \text{ cm or } 6.626 \times 10^{-29} \text{ m}$$

Example 1.5 : An electron is accelerated by applying a potential difference of 1000V. What is the DeBroglie wavelength associated with it?

As

$$\lambda = \frac{h}{(2meV)^{\frac{1}{2}}}$$

$$I_{eV} = 1.6.2 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{6.026 \times 10^{-34} \text{ Js}}{(2 \times 9.101 \times 10^{-31} \text{ kg} \times 1.602 \times 10^{-19} \text{ J} \times 1000V)^{\frac{1}{2}}} \\ = \lambda = 38.7 \times 10^{-12} \text{ m}$$

1.9 COMPTON EFFECT

A.H. Compton discovered that if monochromatic x-rays with frequency ν are allowed to fall on some material of low atomic weight i.e. light elements such as C or Al, the scattered x-rays contain somewhat longer wavelength than the incident wavelength in addition to the incident rays. The phenomenon of scattering of radiation from the surface of scattering material accompanied by an increase in the wavelength of scattered radiation is called Compton Effect. The scattering of radiation took place almost in the same direction as that of the incident x-rays.

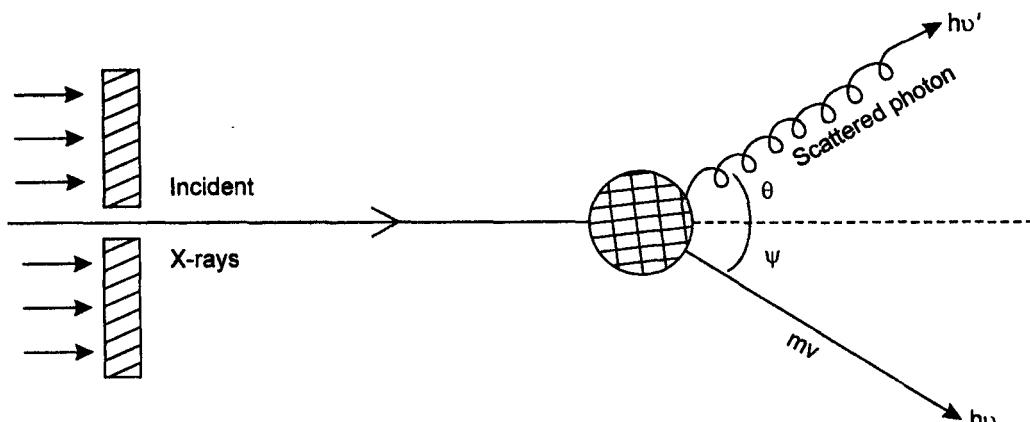


Fig. 1.8 Scattering of radiation from the surface of element

Since the scattered x-rays have larger wavelength than the incident, it is evident that scattered radiations shall have lower frequency ($\nu \propto \frac{1}{\lambda}$) and hence, they are of lower energy. Now since scattering is produced by the loosely bound electrons on the surface of the elements it appears that some interaction between the x-rays and electrons has taken place as a result of which wavelength of x-rays increases or energy of scattered x-rays decreases. If these scattered radiations are examined with the help of x-ray spectrometer, two sets of spectral lines are obtained, one of the original x-ray frequency and other of the lower frequency than that of the incident frequency. These lines are called Compton lines. Compton Effect can be shown as fig 1.8.

Assuming the x-rays to consist of particles each having energy $h\nu$ and momentum $h\nu/c$. Compton calculated the increase $\Delta\lambda$ in the wavelength by ordinary considerations of conservation of energy and of momentum with the help of the expression

$$\Delta\lambda = \frac{h}{mc} \sin^2 \frac{\theta}{2}$$

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{mc} (1 - \cos \theta)$$

Where λ' is the wavelength of the scattered photon which is larger than that of the incident wavelength λ , m is the mass of electron and θ is the angle between the incident and scattered x-rays. $\Delta\lambda$ is called shift in wavelength or Compton shift.

Dependence of Compton shift on the scattering angle θ : This is understood by the following three cases :

Case I

θ (or angle of scattering) is 0°

Therefore $\cos \theta = \cos 0 = 1$ or $\sin^2 \theta/2 = 0$

$$= \Delta\lambda = \frac{2h}{mc} \times 0 = 0$$

Hence, scattered wavelength will not change

Case II

θ ((or angle of scattering) is 90°)

In this case $\sin^2 \theta/2 = \sin^2 (45^\circ)$

$$= \left(\frac{1}{\sqrt{2}} \right)^2 = \frac{1}{2}$$

$$\Delta\lambda = \frac{2h}{mc} \times \frac{1}{2} = \frac{h}{mc}$$

$$= \frac{6.626 \times 10^{-27} \text{ erg sec}}{9.1 \times 10^{-28} \text{ g} \times 3 \times 10^{10} \text{ cm sec}^{-1}}$$

$$= 0.0242 \text{ Å}^\circ$$

This value of $\Delta\lambda$ is constant and is known as Compton wavelength.

$$\sin^2 \theta = \sin^2 90 = 1$$

$$= \Delta\lambda = \frac{2h}{mc} \times 1 = 0.0484 \text{ A}^\circ$$

1.10 HEISENBERG'S UNCERTAINTY PRINCIPLE

Classical mechanics does not impose any limitations on the accuracy with which any observable quantity may be measured. For example, according to classical theory, it is possible to measure the position as well as momentum of a particle to any desired accuracy. Heisenberg gave a principle based on his observations. He used matrix mechanics to formulate his principle. His principle states that it is impossible to determine simultaneously or with high accuracy the position as well as momentum of small moving particles like electrons. If the position is measured accurately, momentum (or velocity) becomes less precise, on the other hand if momentum (or velocity) is determined with high accuracy, its position will remain uncertain. Heisenberg showed that the uncertainty in position Δx and uncertainty in the determination of momentum (or velocity) are related to each other by the following relation.

$$\Delta x \cdot \Delta p \geq \hbar/2$$

$$\Delta x \cdot \Delta p \geq \hbar/4\pi$$

$$\Delta x, m\Delta v > \hbar/4\pi$$

Or

$$\Delta x \cdot \Delta v \geq \hbar/4\pi m$$

For numerical purposes product of Δx and Δp may be taken as equal to $\hbar/2$, where Δx is uncertainty in position and Δp is uncertainty in momentum. One another statement of the uncertainty principle can be expressed in terms of uncertainty in energy (ΔE) and uncertainty in relaxation time ($\Delta \tau$) as

$$\Delta E \cdot \Delta \tau \geq \hbar/2$$

or

$$\Delta E \cdot \tau \geq \hbar/4\pi$$

or

$$\hbar \Delta v \cdot \Delta t \geq \hbar/4\pi$$

or

$$\Delta v, \Delta \tau \geq 1/4\pi$$

This statement of the uncertainty principle has its use in spectroscopy as band width for any spectral transition can be explained on the basis of this statement of uncertainty principle.

Example 1.6 : Calculate the product of uncertainty in position and uncertainty in velocity for an electron whose mass is 9.1×10^{-31} kg.

1

$$\Delta x \cdot \Delta p \geq \left(\text{or } \frac{\hbar}{4\pi} \right)$$

8

$$x \cdot m\Delta v \geq \frac{\hbar}{2} \left(\text{or } \frac{\hbar}{4\pi} \right)$$

Or $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$

Since $m = 9.1 \times 10^{-31} \text{ kg}$ $h = 6.626 \times 10^{-34} \text{ Js}$ & $\pi = 3.1415$

$$\begin{aligned} &= \Delta x \cdot \Delta v = \frac{6.626 \cdot 10^{-34}}{4 \cdot 3.1415 \cdot 9.1 \cdot 10^{-31} \text{ kg}} \\ &= 5.78 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

PROBLEMS SET-1

1. Discuss Bohr's theory for H-atom (See Section 1.7)
2. Derive Rydberg's formula and explain the origin of atomic spectral lines (See Section 1.7).
3. Explain in detail Planck's Quantum Theory to explain concept of Black Body Radiation (See Section 1.4).
4. What is photo-electric effect? How can kinetic energy of photoelectrons be derived? (See Section 1.5).
5. State Dulong Petit law. (See Section 1.6)
6. Give Quantum theory for heat capacity of solids (See section 1.6)
7. How ionization energy can be calculated on the basis of expression of energy as derived by Niel Bohr. (See Section 1.7).
8. Derive DeBroglie's Equation and explain wave, particle duality for micro-particles. (See Section 1.8)
9. How can DeBroglie's wavelength be determined experimentally ? (See Section 1.8).
10. Write a short note on Compton Effect. (See Section 1.9)
11. Give statement for Heisenberg's Uncertainty Principle (See Section 1.10).
12. Calculate the Bohr's Radius (See Section 1.7) (Ans. 0.0529 nm)
13. Calculate the wavelength of matter waves associated with the particle of weight 100 g moving with the speed of 100m/sec

As $\lambda = \frac{h}{mv} = \frac{6.626 \cdot 10^{-34} \text{ Js}}{100 \cdot 100 \text{ m s}^{-1}}$
 $= 6.626 \times 10^{-35} \text{ m}$

14. An object of 500 g (0.5 kg) is moving with a speed of 60 m s^{-1} . Find out the wavelength of the wave associated with this object ($h = 6.626 \times 10^{-34} \text{ Js}$) [Ans. $2.0266 \times 10^{-35} \text{ m}$]
15. Calculate the value for Compton wavelength. (See Section 1.9) [Ans. 0.0242 \AA]
16. Calculate the Compton shift if angle of scattering is 180° (See Section 1.9) [Ans. 0.0484 \AA]
17. A beam of x-rays is scattered by loosely bound electrons at 45° to be direction of the beam. The wavelength of scattered x-rays is 0.242 \AA . What is the wavelength of the incident beam of x-rays [Given $h/mc = 0.0242 \text{ \AA}$] [Ans. $0.2129 \times 10^{-10} \text{ m}$ or 0.2129 \AA]
18. The uncertainty in position of an electron is 1 nm. Calculate its uncertainty in velocity. (Given mass of electron as $9.1 \times 10^{-31} \text{ kg}$) [Ans. $5.795 \times 10^5 \text{ ms}^{-1}$].
19. An object of mass 50 kg exhibits uncertainty in its speed of 0.001 km hr^{-1} . Find out uncertainty in its position. [Ans. $3.796 \times 10^{-35} \text{ m}$].

CHAPTER-2

Fundamental Concepts of Quantum Mechanics

SYNOPSIS	
Section	Topics
2.1	Introduction to Sinosidal equation
2.2	Schrodinger's Wave Equation
2.3	Postulates of Quantum Mechanics
2.4	Introduction to wave function
2.5	Operator's Concept
2.6	Concept of Eigen Value and Eigen Function
2.7	To show $\hat{H} \Psi = E\Psi$ is operator form of Schrodinger equation
2.8	How to write Hamiltonian operators for different atomic or molecular systems

Chapter – 1 of the present book deals with the fundamental concepts pertaining to the origin of quantum mechanics. This mechanics may be treated as mechanics of limited scope as only H-atom problem can be solved with the help of it accurately even then this may be treated as mechanics of wide scope as all other huge molecular systems can be solved on the approximation using quantum mechanics. In this chapter, fundamental concepts of Quantum Mechanics are dealt with. This chapter includes introduction to sinusoidal equation, derivation of Schrodinger equation, wave function and its physical significance, operator's concept, postulates of quantum mechanics etc.

2.1 INTRODUCTION TO SINOSIDAL EQUATION

As it has been shown in Section 1.8, that during motion, a micro-particle shows particle as well as wave like nature. Matter waves may be considered to understand the concepts of quantum mechanics.

Matter waves can be expressed on the basis of an equation called sinusoidal equation for wave. Sinusoidal equation may be expressed as follows:

$$y = A \sin(2\pi vt) \quad \dots (2.1)$$

Here y is the displacement during propagation of wave, A is amplitude of the wave, v is the vibration frequency and t is time. This equation can also be expressed as

$$\begin{aligned} y &= A \sin(2\pi t) \\ y &= A \sin(\omega t) \end{aligned} \quad \dots (2.2)$$

Where ω is angular velocity and $v = \omega/2\pi$ or $\omega = 2\pi v$

$$y = A \sin\left(\frac{2\pi vx}{c}\right) \quad \dots (2.3)$$

As $x = ct$; x = distance covered by particle in time t and c is its speed

Since $c = v\lambda$ or $\lambda = c/v$

$$\text{Therefore } y = A \sin \frac{2\pi x}{\lambda} \quad \dots (2.4)$$

The wave function Ψ for such a wave may be written as

$$\Psi = A \sin \frac{2\pi x}{\lambda} \quad \dots (2.5)$$

Where λ is the wavelength of the wave

2.2 SCHRODINGER'S WAVE EQUATION

Erwin Schrodinger (1925), had derived an equation, incorporating the previous observations such as wave particle duality, etc. and considering that micro-particles exhibit their motion as matter waves. This equation serves as a basis of quantum mechanics. This equation of quantum mechanics was derived by E. Schrodinger taking into consideration the basic equation of standing wave.

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{C^2} \left(\frac{\partial \Psi}{\partial t^2} \right) \quad \dots (2.6)$$

' Ψ ' the wave function here is the function of space and time and may be expressed as

$$\Psi = f(\text{space, time}) \text{ or } f(x, t) \quad \dots (2.7)$$

Or $\Psi = \Psi(x) f(t)$

$$\text{Or } \Psi = 2A \left(\sin \frac{2\pi x}{\lambda} \right) \cos(2\pi i v t)$$

$$\text{Or } \Psi = \Psi(x) \cos(2\pi i v t) \quad \dots (2.8)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{C^2} \frac{\partial^2 \Psi(x) \cos(2\pi i v t)}{\partial t^2}$$

$$\cos(2\pi v t) \frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{4\pi^2 v^2 i^2}{C^2} \Psi(x) \cos(2\pi v t)$$

$$\Rightarrow \frac{\partial^2 \Psi(x)}{\partial x^2} = -\frac{4\pi^2 v^2}{C^2} \Psi(x) \quad \dots (2.9)$$

Equation 2.6 is a time dependent equation and equation 2.9 is an time independent equation

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{4\pi^2 v^2}{C^2} \Psi(x) \quad \dots (2.9)$$

$$c = v\lambda$$

$$\Rightarrow \frac{v}{c} = \frac{1}{\lambda}$$

Or $\frac{v^2}{c^2} = \frac{1}{\lambda^2}$

$$\Rightarrow \frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{-4\pi^2 \Psi(x)}{\lambda^2} \quad \dots (2.10)$$

According to De Broglie's equation

$$\lambda = \frac{h}{mv} \text{ or } \frac{h}{p}$$

$$\Rightarrow \frac{1}{\lambda} = \frac{p}{h}$$

Or $\frac{1}{\lambda^2} = \frac{p^2}{h^2} \quad \dots (2.11)$

Substituting the value of $1/\lambda^2$ in equation 2.10

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{-4\pi^2 p^2}{h^2} \Psi(x)$$

Or

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{-4\pi^2 m^2 v^2 \Psi(x)}{h^2} \quad \dots (2.12)$$

As energy of electron may be considered as sum of its kinetic energy and potential energy

$$E = T + V$$

$$T (\text{or K.E.}) = E - V \quad \dots (2.13)$$

$$\text{Since } T (\text{or KE}) = \frac{1}{2} mv^2 \quad \dots (2.14)$$

Multiply numerator and denominator of equation 2.14 by 'm' mass of electron (or micro-particle)

$$T = m^2 v^2 / 2m$$

Or $m^2 v^2 = 2m T \quad \dots (2.15)$

Substitute the value of T from equation 2.13 in equation 2.15.

$$m^2 v^2 = 2m (E - V) \quad \dots (2.16)$$

Substituting the value of $m^2 v^2$ from equation 2.16 in equation 2.12

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{-4\pi^2 m(E - V)\Psi(x)}{h^2}$$

Or $\frac{\partial^2 \Psi(x)}{\partial x^2} = \frac{-8\pi^2 m(E - V)\Psi(x)}{h^2} \quad \dots (2.17)$

This is time independent Schrodinger equation for a single particle of mass 'm' moving in one direction only. Considering the motion of micro-particle in three dimension, this equation has been modified as

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{-8\pi^2 m(E - V)\Psi}{h^2}$$

Or $\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi + \frac{8\pi^2 m(E - V)\Psi}{h^2}$

Or $\nabla^2 \Psi + \frac{8\pi^2 m(E - V)\Psi}{h^2} = 0 \quad \dots (2.18)$

Here ∇^2 is Laplacian operator which is a differential operator and is defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Equation 2.18 is three-dimensional time independent Schrodinger wave equation for micro-particle which serves as the basis for quantum mechanics. Here in this equation Ψ is the function of three dimension space.

i.e. $\Psi = f(x, y, z)$
 or $\Psi = \Psi(x)\Psi(y)\Psi(z) \quad \dots (2.19)$

2.3 POSTULATES OF QUANTUM MECHANICS

Postulates of quantum mechanics are as under:

Postulate I : The state of a microsystem can be described in terms of a function of position coordinates and time, called wave function (Ψ)

$$\Psi = f(\text{space, time})$$

Or

$$\Psi = f(q, t)$$

... (2.20)

This postulate follows from the quantum mechanical concept of state based on experiments and expresses an act of faith in quantum mechanics by asserting that the ' Ψ ' wave function contains all the information that can be obtained about the system.

Postulate II : "To every observable" i.e. a quantity which can be measured experimentally (eg. Position, momentum, energy, etc.), there corresponds a quantum mechanical operator. The operators corresponding to the quantities are listed in table 2.1 below :

Table 2.1
Quantum Mechanical equivalents for physical quantities

<i>Physical Quantity</i>	<i>Quantum Mechanical (equivalent) operator</i>
Space x	x
y	y
z	z
Momentum $p_x = mv_x$	$\frac{\hbar}{2\pi i} \frac{\partial}{\partial x}$ (x- component)
$p_y = mv_2$	$\frac{\hbar}{2\pi i} \frac{\partial}{\partial y}$ (y- component)
$p_z = mv_2$	$\frac{\hbar}{2\pi i} \frac{\partial}{\partial z}$ (z- component)
Kinetic Energy	
$T = \frac{1}{2} mv^2$	$\frac{-\hbar^2}{8\pi^2 m} \nabla^2$
$= \frac{p^2}{2m}$	
Potential Energy V	V
Total Energy E	$\frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V$

Postulate III : The possible values of any physical quantity of a system (eg. energy, momentum, etc.) are given by the Eigen values 'a' in the operator form of equation

$$\hat{A}\Psi = a\Psi \quad \dots (2.21)$$

Where \hat{A} is the operator corresponding to the physical quantity and Ψ is the Eigen function. In other words, each single measurement of a physical quantity, \hat{A} (A operator) given an Eigen value 'a'.

Postulate IV : The expected, average (or expectation) value of a physical quantity $\langle A \rangle$ of a system, whose state function is Ψ is given by

$$\langle A \rangle = \frac{\int \Psi^* |\hat{A}| \Psi d\tau}{\int \Psi^* |\Psi| d\tau} \quad (2.22)$$

or
$$\langle A \rangle = \frac{\langle \Psi^* | \hat{A} | \Psi^* \rangle}{\langle \Psi | \Psi^* \rangle}$$

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

If Ψ is normalized

Postulate V : The wave function that represents the state of the system changes with time, according to the time dependent Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t}(x, y, z, t) = \hat{H} \Psi(x, y, z, t) \quad (2.23)$$

Where \hat{H} is the Hamiltonian operator of the system.

These postulates cannot be proved or derived. These postulates can be treated in the same light as the acceptance of Newton's Second law of motion.

2.4 INTRODUCTION TO WAVE FUNCTION

A wave function may be expressed as ' Ψ ' (shi). According to the postulate of quantum mechanics wave function ' Ψ ' describes the state of microsystem in terms of function of space and time

i.e. $\Psi = f(x, y, z, t)$
or $\Psi = f(\text{space, time})$... (2.24)

Physical significance of the wave function :

A function expressing state of micro system or wave i.e. wave function ' Ψ ' may be any mathematical function which has its significance in physical sciences. Actually, it is Ψ^2 (shi square) or squared value of Ψ which is in use to find out the probability of finding electron (or microparticle) in small volume element $d\tau$ as per the following probability integral

P.I. $= \int \Psi^2 d\tau$... (2.25)
Over
Whole
Space

Or P.I. $= \int_{-\infty}^{\infty} \Psi \Psi^* d\tau$... (2.26)

Where $d\tau$ is small volume element as $d\tau = dx dy dz$

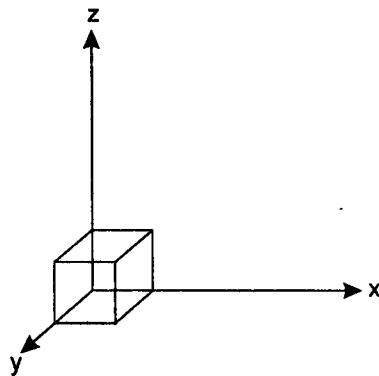


Fig. 2.1 Small volume element $d\tau = dx dy dz$

Mathematically any function, whether real or imaginary, is possible but imaginary functions are not at all acceptable or not at all significant physically. This can be shown as follows :

Let $\Psi = a$ (real function) ... (2.27)

This implies that $\Psi^2 = a^2$ (real function) ... (2.28)

Which means that if Ψ is a real function Ψ^2 (i.e. a^2) will also be a real function, but

If $\Psi = a + ib$ (containing imaginary part i.e. complex function) ... (2.29)

which $\Psi^2 = (a + ib)^2$

or $\Psi^2 = a^2 + i^2 b^2 + 2abi$

or $\Psi^2 = a^2 - b^2 + 2abi$... (2.30)

(Contains imaginary part i.e. complex function)

Which means that if Ψ is a complex function i.e. if Ψ contains imaginary part, its square i.e. Ψ^2 will also be a complex function i.e. containing imaginary part ($2abi$) as shown above. Such a function may be significant mathematically but it is not at all significant physically as probability from Ψ^2 (containing imaginary part) will also be complex (or contains imaginary part). Therefore, probability integral as shown in equation 2.25 & 2.26 will change as

$$PI = \int \Psi \Psi^* d\tau \quad \dots (2.31)$$

Over
Whole
Space

Or P.I. $\int_{-\infty}^{+\infty} \Psi \Psi^* d\tau$... (2.32)

Here Ψ^* is a complex conjugate of Ψ , probability from P.I. expressed in equation 2.31 or 2.32 will also come out to be real as $\Psi \Psi^*$ will be real, as shown below

If $\Psi = a + ib$ (say)

Then

$$\Psi^* = a - ib \text{ (its complex conjugate)} \quad \dots (2.33)$$

So,

$$\begin{aligned} \Psi \Psi^* &= (a + ib)(a - ib) \\ &= a^2 - (ib)^2 \\ &= a^2 - i^2 b^2 \quad (i^2 = -1) \\ \Psi \Psi^* &= a^2 + b^2 \text{ (real)} \end{aligned} \quad \dots (2.34)$$

Therefore, this may be concluded that instead of Ψ , Ψ^2 rather $\Psi \Psi^*$ has its physical significance.

Normalized and Orthogonal wave function :

As it has been shown above in the same section that Ψ^2 (or $\Psi \Psi^*$) are physically significant and are in use to evaluate probability from probability integrals as expressed in equations 2.25, 2.26 2.31 and 2.32.

According to the rule of mathematics probability may have value zero (minimum) to one (maximum).

If value of probability is one

$$\begin{aligned} \int_{\text{over whole space}} \Psi^2 d\tau &= 1 \quad \text{or} \quad \int_{\text{over whole space}} \Psi \Psi^* d\tau = 1 \\ \text{Or} \quad \int_{-\infty}^{+\infty} \Psi^2 d\tau &= 1 \quad \text{or} \quad \int_{-\infty}^{+\infty} \Psi \Psi^* d\tau = 1 \end{aligned} \quad \dots (2.35)$$

In this case function will be normalized function and the condition expressed in equation 2.35 is normalization condition.

If value of probability is zero.

$$\begin{aligned} \Rightarrow \quad \int_{\text{over whole space}} \Psi^2 d\tau &= 0 \quad \text{or} \quad \int_{\text{over whole space}} \Psi \Psi^* d\tau = 0 \\ \text{Or} \quad \int_{-\infty}^{+\infty} \Psi^2 d\tau &= 0 \quad \text{or} \quad \int_{-\infty}^{+\infty} \Psi \Psi^* d\tau = 0 \end{aligned} \quad \dots (2.36)$$

This is the condition of orthogonality and function Ψ is orthogonal to Ψ^* (i.e. its complex conjugate)

If wave function ' Ψ ' is a normalized wave function and it follows the condition as expressed in equation 2.35, normalization constant may be determined as follows :

$$\int_{-\infty}^{+\infty} \Psi \Psi^* d\tau = N \text{ (say)} \quad \dots (2.37)$$

Where N is any numerical value

$$\Rightarrow \int_{-\infty}^{+\infty} \Psi \Psi^* d\tau = 1.N$$

$$\text{Or } \frac{1}{N} \int_{-\infty}^{+\infty} \Psi \Psi^* d\tau = 1 \quad \dots(2.38)$$

(Condition for normalization)

$$\text{Or } \int \left(\frac{1}{\sqrt{N}} \Psi \right) \left(\frac{1}{\sqrt{N}} \Psi^* \right) d\tau = 1 \quad \dots(2.39)$$

In equation 2.39 $\left(\frac{1}{\sqrt{N}} \right) \Psi$ is normalized wave function with $\left(\frac{1}{\sqrt{N}} \right) \Psi^*$ as its conjugate part

and $\left(\frac{1}{\sqrt{N}} \right)$ is normalization constant .

Acceptable wave function :

A wave function will be acceptable if and only if it follows the following three conditions

- (i) It should be a single valued function
- (ii) It should be a finite function and
- (iii) It should be a continuous function

These conditions can be expressed by the following graphs (Fig. 2.2)

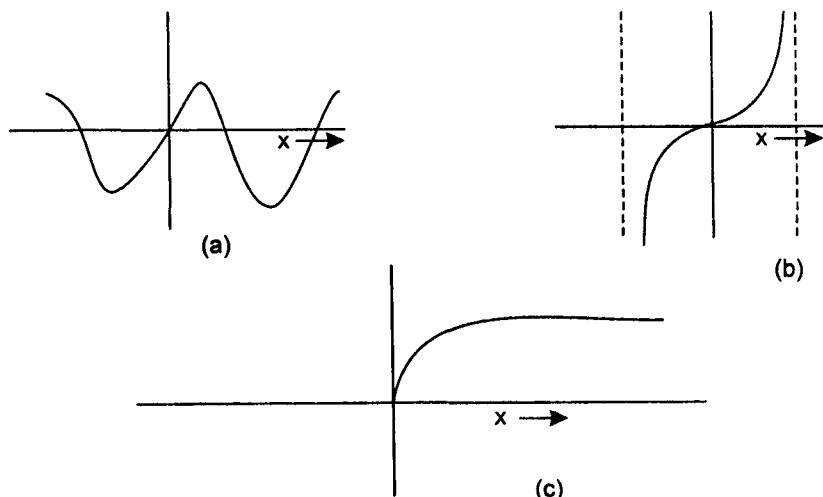


Fig. 2.2 (a) An acceptable function as it is single valued, finite and continuous function.

- (b) It is not at all acceptable function as it tends to infinite value at certain x.
 (c) it is also an acceptable function.

Example 2.1: Which of the following functions are acceptable wave functions and why ?

(i) $\sin x$

(ii) $\cos x$

(iii) $\tan x$

(iv) $\operatorname{cosec} x$ and

(v) $\cos x + \sin x$; for $x \leq x \leq \pi/2$

- (i) $\sin x$ will be acceptable wave function in the specified range as it follows all the three conditions and its graph will be

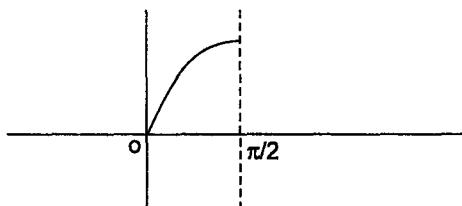


Fig. 2.3 $\sin x$ (within $0 \leq x \leq \pi/2$)

- (ii) $\cos x$ will also be an acceptable wave function in the specified range $0 \leq x \leq \pi/2$

- (iii) $\tan x$ will not be acceptable wave function at all as it tends to infinity at $x = \pi/2$ as it is clear from its graph

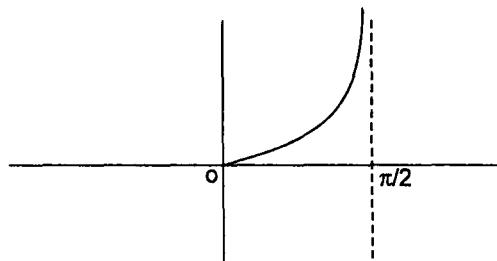


Fig. 2.4 $\tan x$ (within $0 \leq x \leq \pi/2$)

- (iv) $\operatorname{cosec} x$ will also not be an acceptable wave function as it also tends to infinity at $x = 0$

- (v) $\cos x + \sin x$ will be an acceptable wave function within specified range i.e. $0 \leq x \leq \pi/2$

Example 2.2: The value of P.I. using a wave function Ψ is 3 (say) find out its normalization constant

$$\text{As } \int_{\text{over whole space}} \Psi \Psi^* d\tau = N \quad (\text{equation 2.37})$$

$N = 3$ (given)

$$\Rightarrow \frac{1}{N} \int \Psi \Psi^* d\tau = 1$$

$$\text{Or} \quad \frac{1}{3} \int \Psi \Psi^* d\tau = 1$$

which implies that $\frac{1}{\sqrt{N}} = \frac{1}{\sqrt{3}}$ will be

The normalization constant and normalized wave function will be $\frac{1}{\sqrt{3}} \Psi$.

2.5 OPERATOR'S CONCEPT

An operator may be defined as a mathematical director which directs the mathematical operation to be carried out on the wave function. Table 2.2 shows some examples of operators.

TABLE 2.2
Some examples of operators used in mathematics

<i>Operator</i>	<i>Operation</i>
+	To add the functions
-	To subtract the function
$\frac{d}{dx} \left(\frac{d}{dy} \text{ or } \frac{d}{dz} \right)$	To differentiate the function w.r.t. x (or y or z)
* (or \times)	To multiply the function
/	To divide the function
$\int \dots dx$	To integrate the function

Like mathematics, operators have their significance in quantum mechanics also as operators may be used to find out physical quantity (or observable) in quantum mechanics. For every observable (or physical quantity) there exists a quantum mechanical equivalent operator as shown in table 2.1. An operator in quantum mechanics is designated by the (^) cap. Symbol or by subscript op as

$$\hat{A} \text{ or } A_{op} \text{ is A operator} \quad \dots(2.40)$$

Properties of operators

Although operators do not have their physical meaning, they can be added, subtracted or multiplied and have some other properties also.

Addition of operators

The addition yields new operator e.g. ∇^2 is addition of three differential operators viz. $\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2},$

$$\frac{\partial^2}{\partial z^2} \text{ and}$$

As

$$\nabla^2 \Psi = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi$$

$$= \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \quad \dots(2.41)$$

Subtraction of operation

Like addition, subtraction of operators can also be done and it would also yield a new operator

e.g. \hat{A} ; $\log_e \hat{B} = \frac{d}{dx}$ & $\Psi = x^2$

or

$$\left(\log_e - \frac{d}{dx} \right) x^2$$

$$\Rightarrow \log_e (x^2) - \frac{d}{dx} (x^2)$$

$$\Rightarrow 2 \log_e (x) - \frac{d}{dx} (x^2) \quad (x^2)$$

$$\Rightarrow 2 \log_e x - 2x = \hat{A} \Psi - \hat{B} \Psi \quad \dots(2.42)$$

Therefore, for addition and subtraction of operators, following mathematical statement may be written

$$(A \pm B) \Psi = A \Psi \pm B \Psi \quad \dots(2.43)$$

Multiplication of Operators

Similarly, for multiplication of operators, following algebraic property may be shown

$$\hat{A} \hat{B} \Psi = \hat{A} [\hat{B} \Psi]$$

As $\hat{B} \Psi = \phi$ (say)

$$\hat{A} [\hat{B} \Psi] = \hat{A} \phi$$

If $\hat{A} \phi = x$ (say)

$$= \hat{A} \cdot \hat{B} \Psi = \hat{A} [\hat{B} \Psi] = \hat{A} \phi = \chi \quad \dots(2.44)$$

Commutative Property of Operators

If two operators follow the following condition, they show the commutative property

$$\hat{A} \hat{B} \Psi = \hat{B} \hat{A} \Psi \quad \dots(2.45)$$

For any two operators \hat{A} & \hat{B} , the difference $\hat{A} \hat{B} - \hat{B} \hat{A}$, which is denoted by $[\hat{A}, \hat{B}]$ is called commutator operator. If $[\hat{A}, \hat{B}] = 0$ it is called as zero operator.

Linear Operator

An operator \hat{A} is said to be linear if its application on the sum of two functions gives the result which is equal to the sum of operations on two functions independently i.e. if it follows. The following conditions

$$\hat{A} [\Psi + \phi] = \hat{A}\Psi + \hat{A}\phi \quad \dots(2.46)$$

Hermitian Operator

An operator will be hermitian operator if it follows the following condition

$$\int_{\text{over whole space}} \Psi |\hat{A}| \Psi^* d\tau = \int_{\text{over whole space}} \Psi^* |\hat{A}| \Psi d\tau \quad \dots(2.47)$$

Example 2.4 Which of the following will be a linear operator ?

(i) $\int dx$ (ii) $\sqrt{\cdot}$

(i) $\int [\Psi + \phi] dx = \int \Psi dx + \int \phi dx$

and $\int c \Psi dx = c \int \Psi dx$. So it is a linear operator by definition.

(ii) $A_s = \sqrt{\Psi + \phi} \neq \sqrt{\Psi} + \sqrt{\phi}$

So it is not a linear operator

Example 2.5 Show that $\hat{p}_x = -i\hbar \frac{d}{dx}$ is Hermitian operator. To show this, let us consider f is any function and f^* is its conjugate. If \hat{p}_x is hermitian operator then

$$\int_{-\infty}^{\infty} f^* \hat{p}_x f dx = \int_{-\infty}^{\infty} f \hat{p}_x f^* dx$$

L.H.S. of the above equation is $= -i\hbar |f^* f|_{-\infty}^{\infty}$

and R.H.S. of the equation is $= -i\hbar |ff^*|_{-\infty}^{\infty}$

As L.H.S. = R.H. S. i.e. $-i\hbar |f^* f|_{-\infty}^{\infty} = -i\hbar |ff^*|_{-\infty}^{\infty}$

So, \hat{p}_x is a Hermitian operator

After properties of operators, now let us consider some important operators which have their importance in quantum mechanics.

Laplacian Operator : Laplacian operator is a linear differential operator which is designated by the symbol ∇^2 (del squared). This can be expressed as follows

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \dots(2.48)$$

Hamiltonian operator : Hamiltonian operator is an energy operator. It is designated by the symbol \hat{H} (or Hop). When Hamiltonian operator is operated on wave function Ψ , wave function Ψ has been obtained back with a constant value (or Eigen value) for energy as per following equation (or Eigen equation).

$$\hat{H} \Psi = E \Psi \quad \dots(2.49)$$

Equation 2.49 is operator's form of Schrodinger equation, it is shown later in Section 2.7.

2.6 Concept of Eigen value and Eigen function

If a function follows the following equation

$$\hat{A} \Psi = a \Psi \quad \dots(2.50)$$

It is said to be an Eigen function and equation 2.50 is an Eigen equation. In this equation, \hat{A} is \hat{A} Operator which is operated on Ψ to yield a constant value 'a', the Eigen value (or possible value for any physical quantity).

Example 2.6: Show that $\Psi = \sin 2x$ is an Eigen function for the operator $\frac{\partial^2}{\partial x^2}$
 $\frac{\partial^2}{\partial x^2}$ (operator) is operated on wave function $\Psi = \sin 2x$ as per follows

$$\frac{\partial^2}{\partial x^2} (\sin 2x) = -4 \sin 2x$$

This shows that $\Psi = \sin 2x$ is a Eigen function for the operator $\frac{\partial^2}{\partial x^2}$ with Eigen value -4.

2.7 TO SHOW THAT $\hat{H}\Psi = E\Psi$ IS OPERATOR FORM OF SCHRODINGER EQUATION:

H or H_{op} is the notation for Hamiltonian operator. Since Hamiltonian is an energy operator. So, this operator may be considered as combination of K.E. (Kinetic Energy) and PE (Potential energy)

$$\text{i.e.} \quad \hat{H} = \hat{T} + \hat{V} \quad \dots(2.51)$$

$$T = \frac{1}{2} m v^2 \quad \dots(2.52)$$

Multiply equation 2.52 by m , both numerator and denominator

$$\Rightarrow T = \frac{1}{2} \frac{m^2 v^2}{m} \quad \dots(2.53)$$

$$= T = \frac{p^2}{2m} \quad \dots(2.54)$$

$$\text{Since } p^2 = p_x^2 + p_y^2 + p_z^2 \quad \dots(2.55)$$

Where p_x , p_y & p_z are components of linear momenta along x, y, & z directions and taking their quantum mechanical equivalents (table 2.1)

$$p^2 = \left(\frac{h}{2\pi i} \right) \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots (2.56)$$

Or $p^2 = \frac{+h^2}{4\pi^2 i^2} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots (2.57)$

as since $i^2 = -1$

$$p^2 = \frac{-h^2}{4\pi^2} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots (2.58)$$

Substituting the value of p^2 from equation 2.58 to equation 2.54

$$T = \frac{\frac{-h^2}{4\pi^2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}{2m} \quad \dots (2.59)$$

Or $T = \frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad \dots (2.60)$

Therefore \hat{H} or H_{op} will be

$$\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \quad \dots (2.61)$$

Substituting it in equation $\hat{H}\Psi = E\Psi$

$$= \left[\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right] \Psi = E\Psi \quad \dots (2.62)$$

Or $\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = E\Psi - V\Psi$

Or $\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = (E - V)\Psi \quad \dots (2.63)$

Multiply equation 2.63 by

$$\Rightarrow \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = \frac{-8\pi^2 m}{h^2} (E - V)\Psi$$

Or $\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi + \frac{-8\pi^2 m}{h^2} (E - V)\Psi \quad \dots (2.64)$

Or $\nabla^2 \Psi + \frac{-8\pi^2 m}{h^2} (E - V)\Psi = 0$

Which is the required Schrodinger wave equation. This proves that $\hat{H}\Psi = E\Psi$ is operator form of Schrodinger wave equation as this equation, can also be derived from $\hat{H}\Psi = E\Psi$ equation.

2.8 HOW TO WRITE HAMILTONIAN OPERATORS FOR DIFFERENT ATOMIC OR MOLECULAR SYSTEMS:

Hamiltonian operator has been introduced in Section 2.5. It is an energy operator and it has also been shown in the previous section that Schrodinger wave equation can be deduced from \hat{H} (or Hop) i.e. from Hamiltonian operator. In this section, Hamiltonian operators of some simple systems have been given as it is necessary to have their first hand knowledge for further quantum chemical calculations.

H-atom : H-atom has only one electron and one nucleus. This can be shown by the following diagram



Fig. 2.5. H-atom, one electron system

Its Hamiltonian operator may be written

$$\text{as } \hat{H}_{\text{op}} = \hat{T} + \hat{V} \quad \dots (2.65)$$

$$\hat{H}_{\text{op}} = \left(-\frac{\hbar^2}{8\pi^2 m} \nabla_e^2 \right) + \frac{-e^2}{r_A} \quad \dots (2.66)$$

H₂ ion : This molecule ion can be shown as per following:

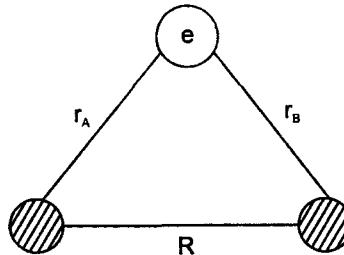


Fig. 2.6. H₂ – ion

Therefore, its Hamiltonian operator can be written as

$$\hat{H}_{\text{op}} = \left(-\frac{\hbar^2}{8\pi^2 m} \nabla_e^2 \right) + \left(\frac{-e^2}{r_A} + \frac{e^2}{R} \frac{-e^2}{r_B} \right) \quad \dots (2.67)$$

H₂ molecule : This molecule can be shown as per following diagram

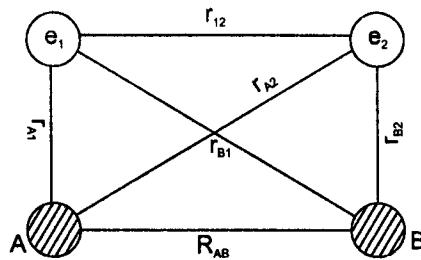


Fig. 2.7. H₂ Molecule

So, its Hamiltonian operator can be shown as

$$\hat{H}_{\text{op}} = \left[\left(\frac{-\hbar^2}{8\pi^2 m_1} \nabla_1^2 \right) + \left(\frac{-\hbar^2}{8\pi^2 m_2} \nabla_2^2 \right) + \left[\frac{-e^2}{r_{A_1}} - \frac{e^2}{r_{A_2}} - \frac{e^2}{r_{B_1}} - \frac{e^2}{r_{B_2}} + \frac{e^2}{r_{12}} + \frac{e^2}{R_{AB}} \right] \right] \dots (2.68)$$

He – atom : This molecule can be written as

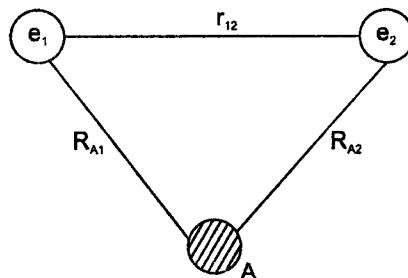


Fig. 2.8. He – atom

$$\hat{H}_{\text{op}} = \left[\left(\frac{-\hbar^2}{8\pi^2 m_1} \nabla_1^2 \right) + \left(\frac{-\hbar^2}{8\pi^2 m_2} \nabla_2^2 \right) + \left[\frac{-e^2}{R_{A_1}} - \frac{e^2}{R_{A_2}} + \frac{e^2}{r_{12}} \right] \right] \dots (2.69)$$

PROBLEMS SET-2

1. What do you understand by a sinusoidal equation? (See section 2.1)
2. Derive Schrodinger wave equation (See section 2.2)
3. Differentiate between time dependent and time independent Schrodinger wave equations? (See section 2.2)
4. Enlist the postulates of Quantum Mechanics (See section 2.3)
5. What do you understand by wave function? (See section 2.4)

6. Write a note on physical significance of wave function. (see section 2.4)
7. What do you understand by probability integral? (See section 2.4)
8. Differentiate between normalized and orthogonal wave functions. (See section 2.4)
9. Explain the criteria for an acceptable wave function ? (See section 2.4)
10. What do you understand by an operator (See Section 2.5)
11. Write a note on properties of operator. (See section 2.5)
12. Write notes on :

(a) Hermitian Operator	(b) Linear Operator
(c) Laplacian Operator and	(d) Hamiltonian operator (See section 2.5)
13. What do you understand by Eigen value and Eigen functions? (See section 2.6)
14. Prove that $\hat{H}\Psi = E\Psi$ is operator form of Schrodinger wave equation. (See section 2.7)
15. Write down Hamiltonian operators for

(a) H-atom	(b) H_2^+ -ion
(c) H_2 – molecule and	(d) He – atom (See section 2.8)
16. Prove that T (or K.E.) = $P^2/2m$ Quantum mechanically. (See section 2.5).
17. If $\Psi = x + 2bi$, prove that Ψ^2 or Ψ will not be significant in this case. (See section 2.4)
18. If $\int \Psi \Psi^* d\tau = 2$, find out normalization constant for Ψ . (See section 2.4) [Ans. $\frac{1}{\sqrt{2}}$]
19. Prove that $\Psi = \cos 2x$ is an Eigen function for the operator $\partial^2/\partial x^2$. Find out its Eigen value (See section 2.6) [Ans. -4]

SECTION-2

- 3. Quantization of Transation Energy**
 - 4. Quantization of Vibration Energy**
 - 5. Quantization of Rotation Energy**
 - 6. Hydrogen like Atoms**
-

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CHAPTER-3

Quantization of Translational Energy

SYNOPSIS

Section	Topics
3.1	Particle in a one dimensional box
3.2	Free electron model (An application of particle in a box problem)
3.3	Particle in three dimensional box
3.4	Particle in a cubic box
3.5	Particle in a Circular Ring
3.6	Tunnelling

In this chapter, concepts related to quantization of Translational energy are being discussed. Translational energy is least among all modes of energies attained by any particle viz. vibration, rotation and electronic energies etc. Quantization of Translational energy can be studied in terms of particles considering them in boxes of different dimensions.

3.1 PARTICLE IN ONE-DIMENSIONAL BOX

In order to study the concept of quantization of translational energy, Let us consider a particle in one-dimensional box. Let it be in continuous motion in the box. Its potential energy is zero inside the box ($V(x) = 0$) and it is infinite outside the box ($V(x) = \infty$). Let 'm' be the mass of the particle. Let 'x' be the dimension of the box.

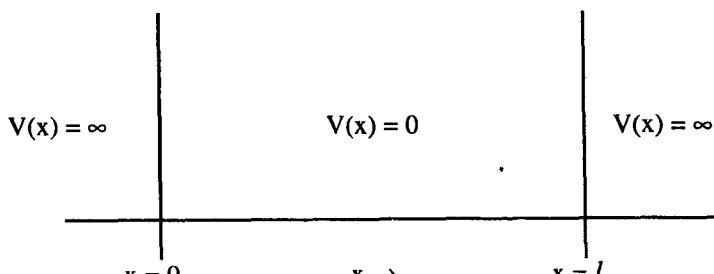


Fig. 3.1 Consideration of a particle in a one-dimensional box.

Let l be the length of the box. Above consideration (i.e. $V(x)$ (at $x = 0$ & $x = l$) = ∞) shows that the particle is deeply buried inside the box.

Schrodinger wave equation for the particle outside the box will be

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - \infty) \Psi(x) = 0 \quad \dots(3.1)$$

Or $\frac{\partial^2 \Psi(x)}{\partial x^2} + \infty \Psi(x) = 0 \quad \dots(3.1)$

Solution of above equation shows that the particle does not exist outside the box as outside the box $\Psi(x) = 0$. Therefore, this may be concluded that the particle is deeply buried inside the box. Schrodinger equation for the particle inside the box may be written as

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - 0) \Psi(x) = 0 \quad \dots(3.2)$$

Or $\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2} E \Psi = 0 \quad \dots(3.2)$

To solve this equation, let us suppose

$$\frac{8\pi^2 m E}{h^2} = \lambda^2 \quad \dots(3.3)$$

Therefore, equation 3.2 becomes

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \lambda^2 \Psi(x) = 0 \quad \dots(3.4)$$

Solution of this equation will be

$$\Psi(x) = A \sin(\lambda x) + B \cos(\lambda x) \quad \dots(3.5)$$

Where A & B are constants. To find out these unknown constants let us apply first boundary conditions i.e. at $x = 0$; $\Psi(x) = 0$

$$0 = A \sin(0) + B \cos(0) \quad \dots(3.6)$$

$$B = 0 \quad \dots(3.7)$$

On incorporating this constant, the equation for $\Psi(x)$ will become

$$\Psi(x) = A \sin(\lambda x) \quad \dots(3.8)$$

Now applying second boundary condition i.e. at $x = l$; $\Psi(x) = 0$

$$0 = A \sin(\lambda l) \quad \dots(3.9)$$

This equation holds good if and only if

$$\lambda l = n\pi \quad \dots(3.10)$$

$$\lambda = n\pi/l \quad \dots(3.11)$$

So $\Psi(x)$ will become

$$\Psi(x) = A \sin(n\pi x/l) \quad \dots(3.12)$$

From equation 3.3 and 3.11

$$\frac{8\pi^2 m E}{h^2} = \frac{n^2 \pi^2}{l^2} \quad \dots(3.13)$$

$$\text{or } E = \frac{n^2 h^2}{8ml^2} \quad \dots(3.14)$$

Above equation 3.14 shows that the translational energy E is quantized and depends upon the quantum number (n^2)

Applying normalization condition to $\Psi(x)$ as $\Psi(x)$ should be normalized in itself.

$$\int_{x=0}^{x=l} \Psi^2(x) dx = 1 \quad \dots(3.15)$$

$$\Rightarrow \int_{x=0}^{x=l} A^2 \sin^2 \left(\frac{n\pi x}{l} \right) dx = 1$$

Or $A^2 = \left(\frac{l}{2} \right) = 1$

$$\Rightarrow A^2 = \frac{2}{l} \Rightarrow A = \sqrt{\frac{2}{l}} \quad \dots(3.16)$$

So incorporating A , $\Psi(x)$ will become

$$\Psi(x) = \sqrt{\frac{2}{l}} \sin \left(\frac{n\pi x}{l} \right) \quad \dots(3.17)$$

To show the orthogonality of wave functions, let us apply the condition of orthogonality to wave functions

$$\int_{\text{over whole space}} \Psi_m^* \Psi_m d\tau = 0 \quad \dots(3.18)$$

Where m & n are different quantum numbers. For a particle in one-dimensional box

$$\Psi_m^* = \Psi_m = \sqrt{\frac{2}{l}} \sin \left(\frac{m\pi x}{l} \right) \quad \dots(3.19)$$

and $\Psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$ $\dots(3.20)$

Thus, from condition of orthogonality

$$\int_{x=0}^{x=1} \Psi_m^* \Psi_n d\tau = 0$$

Or this integral becomes

$$\frac{2}{l} \int_{x=0}^{x=1} \sin\left(\frac{m\pi x}{l}\right) \sin\left(\frac{n\pi x}{l}\right) dx \quad \dots(3.21)$$

From following trigonometric relation

$$(\sin \alpha)(\sin \beta) = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)$$

Equation 3.21 may be written as

$$\frac{1}{l} \int_{x=0}^{x=1} \left[\cos\left\{(m-n)\frac{\pi x}{l}\right\} - \cos\left\{(m+n)\frac{\pi x}{l}\right\} \right] dx$$

Or which is equal to

$$\frac{1}{l} \left[\frac{l}{(m+n)\pi} \sin\left\{(m-n)\frac{\pi x}{l}\right\} - \frac{1}{(m+n)\pi} \sin\left\{(m+n)\frac{\pi x}{l}\right\} \right]_0^1 \quad \dots(3.22)$$

Since m & n both are integers the above expressions is numerically equal to zero which shows that the different wave function that are generated from equation 3.17 for particle in a box problem will form orthogonal set of wave functions. As $\Psi(x)$'s are normalized in itself and orthogonal to each other, therefore, this can be concluded that $\Psi(x)$'s for particle in a box problem are orthonormal set of wave functions.

From equation 3.14 different energy levels may be obtained as

$$\text{Viz. } E_1 = \frac{h^2}{8ml^2}, E_2 = \frac{4h^2}{8ml^2} (\text{or } 4E_1), E_3 = \frac{9h^2}{8ml^2}$$

(or $9 E_1$) and so on. Graphs of $\Psi(x)$ and $\Psi^2(x)$ can be plotted as shown in figure 3.2

A few features of a particle in a box problem:

1. In case of particle in a box problem wave function $\Psi(x)$ is zero at walls, the length ' l ' of the box must be an integral multiple of half wave lengths i.e.

$$l = n (\lambda/2) \quad \dots(3.23)$$

This can be shown as follows

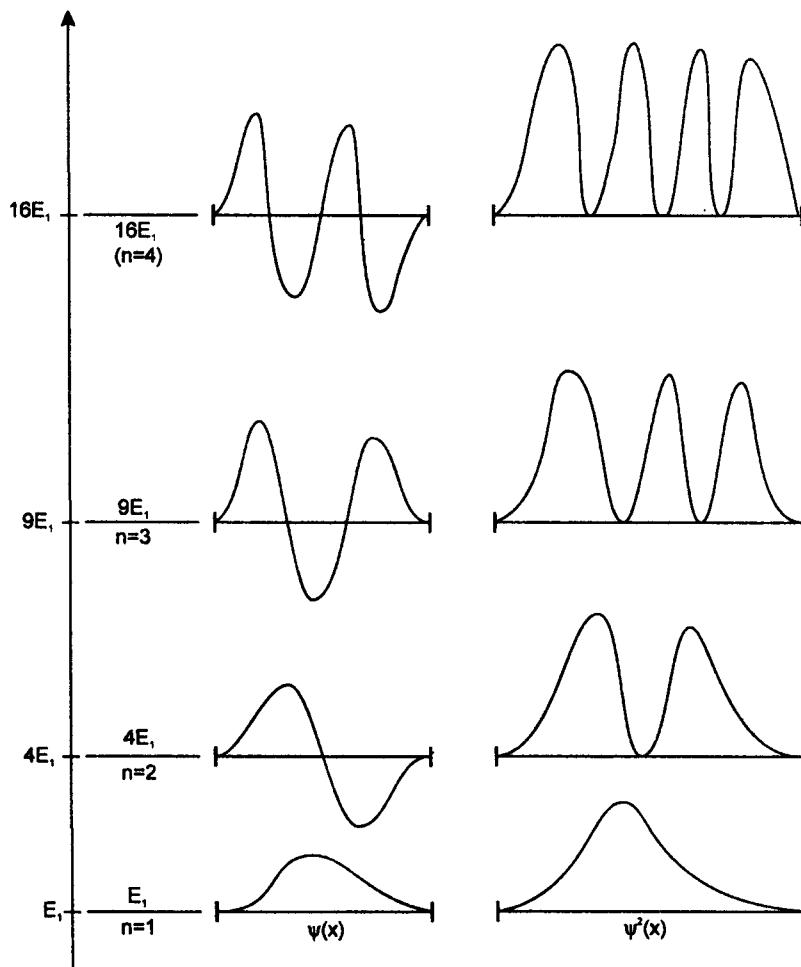


Fig. 3.2. The energies, wave function $\Psi(x)$ and probability densities $\Psi^2(x)$ of a particle in a box.

$$E = n^2 \quad \dots (3.14)$$

And $E = \frac{1}{2} mv^2 (= \text{K.E.}) \quad \dots (3.24)$

Or $E = p^2/2m \quad \dots (3.25)$

Using de broglie's equation

$$E = \frac{(h/\lambda)^2}{2m} = \frac{h^2}{2m\lambda^2} \quad \dots (3.26)$$

Equating energy of the particle inside the box by equation 3.14 and equation 3.26.

$$= \frac{n^2 h^2}{8ml^2} = \frac{h^2}{2m\lambda^2}$$

$$\Rightarrow \frac{1}{\lambda^2} = \frac{n^2}{4l^2}$$

or
$$l = n \left(\frac{\lambda}{2} \right) \quad \dots(3.27)$$

Therefore, function besides having zero value at boundaries, it also has zero value at some points within the box, as shown in fig. 3.2. These points where $\Psi(x) = 0$ (or rather the points where $\Psi(x)$ is zero) are known as nodes and can be expressed by the formula

$$\text{No. of nodes} = (n-1) \quad \dots(3.28)$$

2. The energy associated with wave function increases with increase in number of nodes of the wave function $\Psi(x)$
3. Wave functions may be categorised into two categories w.r.t. their symmetry

Symmetric wave functions (or even wave function)

$$\Psi(x) = \Psi(-x)$$

And antisymmetric wave functions (or odd wave functions)

$$\Psi(x) = -\Psi(-x)$$

From fig. 3.2 it is clear that Ψ_1, Ψ_3, Ψ_5 — are symmetric and Ψ_2, Ψ_4, Ψ_6 — are antisymmetric wave functions w.r.t. centre of the box.

4. The probability densities is not uniform at all the points in the box for particle while it varies with n and $\Psi(x)$.

3.2 FREE ELECTRON MODEL (AN APPLICATION OF PARTICLE IN A BOX PROBLEM)

The π - electrons in polyene may be considered as a system of particle in a one-dimensional box as free electron. So, this model may be considered as free electron model. In this case, the length (l) of the box may be considered as the end to end distance of molecule (in most of the cases this distance may be extended by half of C-C distance on either side of the molecule i.e. another 154 pm distance may be considered. So using m_e (i.e. mass of electron) and l the electronic energy levels in polyenes can be determined. The energy difference between the HOMO (highest occupied m.o.) (i.e. n) and LUMO (lowest unoccupied m.o.) (i.e. $n + l$) may be determined with transition energy for electron as

$$\Delta E = E_{n+1} - E_n$$

Or
$$\Delta E = \frac{(n+1)^2 h^2}{8ml^2} - \frac{n^2 h^2}{8ml^2}$$

Or
$$\Delta E = [(n+1)^2 - n^2] \frac{h^2}{8ml^2}$$

Or
$$\Delta E = (2n+1) \frac{h^2}{8ml^2} \quad \dots(3.29)$$

Example 3.1 : Evaluate expectation value $\langle x \rangle$ and $\langle p \rangle$ for a particle in one-dimensional box of length l .

For a particle in a one-dimensional box

$$\Psi(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

Since $\Psi(x)$ is the normalised wave functions so, we will have

$$\langle x \rangle = \int_0^l \Psi | \hat{x} | \Psi dx$$

$$\frac{2}{l} = \int_0^l x \sin^2\left(\frac{n\pi x}{l}\right) dx$$

$$= \frac{2}{l} \int_0^l x \left[\frac{1 - \cos\left(\frac{2n\pi x}{l}\right)}{2} \right] dx = \left(\frac{2}{l}\right) \left(\frac{l^2}{4}\right) = \frac{l}{2}$$

for

$$\langle p \rangle = \int_0^l \Psi(x) | \hat{p}_x | \Psi_x dx$$

$$= \int_0^l \Psi(x) \left| \frac{h}{2\pi i} \frac{d}{dx} \right| \Psi dx$$

$$= \frac{h}{2\pi i} \int_0^l \left(\frac{2}{l} \right) \sin\left(\frac{n\pi x}{l}\right) \left| \frac{d}{dx} \right| \sin\left(\frac{n\pi x}{l}\right) dx$$

$$= \frac{h}{2\pi i} \left(\frac{n\pi}{l} \right) \int_0^l \left(\frac{2}{l} \right) \sin\left(\frac{n\pi x}{l}\right) \cos\left(\frac{n\pi x}{l}\right) dx = 0$$

Example 3.2 : Evaluate the expectation value of Kinetic energy of a particle in a one-dimensional box.

As the kinetic energy of the particle is given by

$$T = \frac{1}{2} mv^2 = \frac{1}{2} \frac{p^2}{2m}$$

or $T = \frac{1}{2} \frac{m^2 \partial^2}{m}$

$$T_{op} \text{ or } \hat{T} = \frac{1}{2m} \left(\frac{h}{2\pi i} \frac{\partial}{\partial x} \right)^2 = \frac{-h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}$$

And since

$$\Psi(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

$$\langle T \rangle = \int_0^l \Psi(x) |T| \Psi(x) dx$$

Substituting the $\Psi(x)$ and T in above equation.

$$\begin{aligned} \langle T \rangle &= \int_0^l \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) \left| \frac{-h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} \right| \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) dx \\ &= \left(\frac{2}{l} \right) \left(\frac{-h^2}{8\pi^2 m} \right) \int_0^l \sin\left(\frac{n\pi x}{l}\right) \left| \frac{d^2}{dx^2} \right| \sin\left(\frac{n\pi x}{l}\right) dx \\ &= \left(\frac{2}{l} \right) \left(\frac{-h^2}{8\pi^2 m} \right) \left(-\left(\frac{n\pi}{l}\right)^2 \right) \int_0^l \sin^2\left(\frac{n\pi x}{l}\right) dx \\ &= \left(\frac{2}{l} \right) \left(\frac{-h^2}{8\pi^2 m} \right) \left(\frac{n\pi}{l} \right)^2 \int_0^l \frac{1}{2} \left[1 - \cos\left(\frac{2n\pi x}{l}\right) \right] dx \\ &= \left(\frac{2}{l} \right) \left(\frac{-h^2}{8\pi^2 m} \right) \left(\frac{n\pi}{l} \right)^2 \left(\frac{1}{2} \right) l = \frac{n^2 h^2}{8ml^2} \end{aligned}$$

Example 3.3 : For butadiene molecule, calculate the transition energy ΔE considering it as free electron model.

For butadiene molecule we will have

$$\begin{aligned} L &= 1 \text{ (Single bond length)} + 2 \text{ (double bond length)} + 154 \text{ pm} \\ &= (154 \text{ pm}) + 2 (135 \text{ pm}) + 154 \text{ pm} \\ &= 578 \text{ pm} = 5.78 \times 10^{-10} \text{ m} \\ n &= \text{No. of electrons}/2 = 4/2 \end{aligned}$$

$$\begin{aligned} \Delta E &= (2 \times 2 + 1) \frac{(6.626 \times 10^{-34}) \text{ Js}}{8(5.78 \times 10^{-10} \text{ m})^2 (9.11 \times 10^{-31} \text{ kg})} \\ &= 9.02 \times 10^{-19} \text{ J (or } 4.54 \times 10^4 \text{ cm}^{-1}) \end{aligned}$$

3.3 PARTICLE IN A THREE-DIMENSIONAL BOX

Let us consider a particle in three-dimensional box of lengths a, b, c in x, y, z dimensions, let m be the mass of particle.

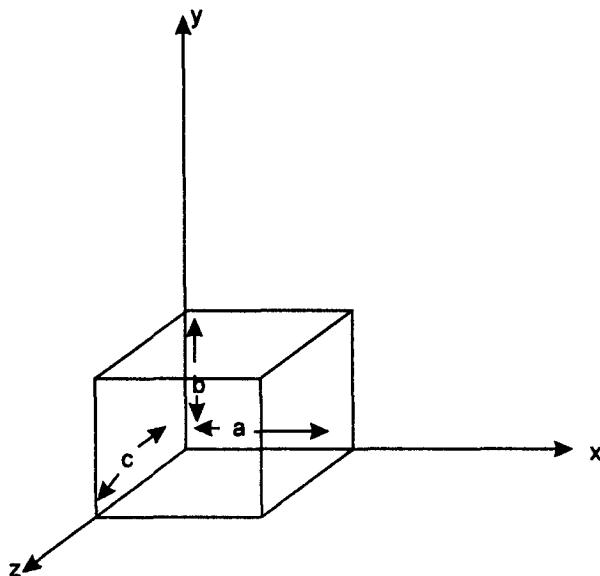


Fig. 3.3 : A particle in three dimensional box of dimensions a, b & c respectively.

Schrodinger equation for this particle may be written as

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi + \frac{8\pi^2 m E \Psi}{h^2} = 0 \quad \dots(3.30)$$

Here $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2$ is Laplacian operator

Wave function for this particle will be

$$\Psi = f(x, y, z) = \Psi(x) \Psi(y) \Psi(z) \quad \dots (3.31)$$

And Energy E for this particle will be

$$E = (E_x + E_y + E_z) \quad \dots (3.32)$$

Equation 3.30 can be resolved into three simpler equations (as similar to the particle in a one-dimensional box problem) as

$$\frac{\partial^2}{\partial x^2} \Psi(x) + \frac{8\pi^2 m}{h^2} E_x \Psi(x) = 0 \quad \dots(3.33)$$

$$\frac{\partial^2}{\partial y^2} \Psi(y) + \frac{8\pi^2 m}{h^2} E_y \Psi(y) = 0 \quad \dots(3.34)$$

$$\text{And } \frac{\partial^2}{\partial z^2} \Psi(z) + \frac{8\pi^2 m}{h^2} E_z \Psi(z) = 0 \quad \dots(3.35)$$

Similar to one-dimensional box problem, solutions for the equations 3.33, 3.34 and 3.35 are

$$\Psi(z) + \sqrt{\frac{2}{a}} \sin\left(\frac{n_y \pi z}{a}\right) \quad \dots(3.36)$$

$$\Psi(y) + \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \quad \dots(3.37)$$

$$\Psi(z) + \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad \dots(3.38)$$

With corresponding energies

$$E_x = n_x^2 h^2 / 8ma^2 \quad \dots(3.39)$$

$$E_y = n_y^2 h^2 / 8mb^2 \quad \dots(3.40)$$

$$E_z = n_z^2 h^2 / 8mc^2 \quad \dots(3.41)$$

The total wave function for the particle moving in three-dimensional box is

$$\Psi = \Psi(x) \Psi(y) \Psi(z)$$

$$\Psi = \sqrt{\frac{2}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \quad \dots(3.42)$$

Similarly, total energy for the particle in three dimensional box is

$$E = E_x + E_y + E_z$$

$$E = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \quad \dots(3.43)$$

3.4 PARTICLE IN A CUBIC BOX

In a cubic box $a = b = c$, the total energy becomes

$$E = \left(\frac{h^2}{8ma^2} \right) (n_x^2 + n_y^2 + n_z^2) \quad \dots(3.44)$$

It is apparent from this equation that in a cubic box energy depends upon the sum of squares of quantum numbers n_x, n_y and n_z if sides of the cube are equal. In this case, energy levels of different sets of quantum numbers may have same energy which leads to degeneracy of levels and the number of different states belonging to the same energy level is known as degree of degeneracy. Table 3.1 shows energy levels corresponding to different states with their degree of degeneracy

TABLE 3.1
Energy levels and degeneracy of various states

<i>Quantum Numbers(n_x, n_y, n_z) and States</i>	<i>Energy</i>	<i>Degree of Degeneracy</i>
(1, 1, 1)	$3h^2 / 8m a^2$	Non – degenerate
(211) (121) (112)	$6h^2/8ma^2$	Three – fold degenerate
(221) (212) (122)	$9h^2/8ma^2$	Three – fold degenerate
(311) (131) (113)	$11h^2/8 ma^2$	Three – fold degenerate
(222)	$12 h^2 / 8 ma^2$	Non – degenerate
(123) (132) (213)	$14 h^2/8ma^2$	Six – fold degenerate
(322) (232) (223)	$17 h^2/8a^2$	Three-fold degenerate

Example 3.4 : Find the lowest energy of an electron in a three-dimensional box of dimensions 0.1×10^{-15} , 1.5×10^{-15} and 2.0×10^{-15} m.

Total kinetic energy for a particle in three-dimensional box is given by

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

$a = 0.1 \times 10^{-15}$ b = 1.5×10^{-15} and c = 2.0×10^{-15} m respectively

$n_x = n_y = n_z = 1$ for lowest state

Therefore,

$$E = \left(\frac{6.626 \times 10^{-34} \text{ Js}}{8 \times 9.1 \times 10^{-31} \text{ kg}} \right) \left[\frac{1^2}{(0.1 \times 10^{-15})^2} + \frac{1^2}{(1.5 \times 10^{-15})^2} + \frac{1^2}{(2.0 \times 10^{-15})^2} \right]$$

$$= 6.06 \times 10^{-8} \text{ J}$$

Example 3.5 : Determine the degeneracy of energy level $12h^2 / 8ma^2$ in a cubic box.

Energy of a particle moving in a cubic box is given by

$$E = \frac{h^2}{8ma^2} \left[n_x^2 + n_y^2 + n_z^2 \right]$$

$a = b = c$ for cubic box

Given energy $E = 12h^2/8ma^2$

Therefore ,

$$\frac{h^2}{8ma^2} \left[n_x^2 + n_y^2 + n_z^2 \right] = 12h^2 / 8ma^2$$

$$n_x^2 + n_y^2 + n_z^2 = 12$$

The possible ways in which the sum of squares of n_x , n_y & n_z is

$$n_x = 2$$

$$n_y = 2 \text{ &}$$

$$n_z = 2$$

3.5 PARTICLE IN A CIRCULAR RING

Let a particle (say electron) be restricted to move along a circular track on which potential energy is constant. Schrodinger equation for this particle is

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{8\pi^2 m (E - V)\Psi}{h^2} = 0 \quad \dots(3.45)$$

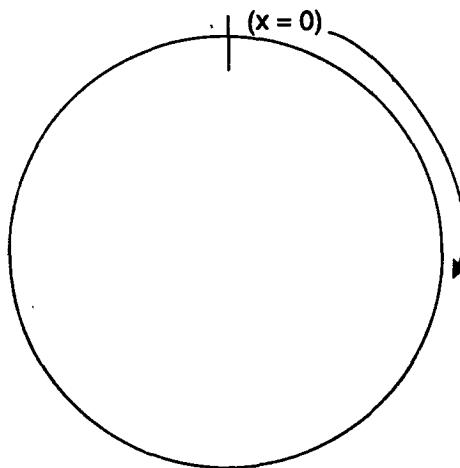


Fig. 3.4 A particle moving in a ring

As shown in fig 3.4, an arbitrary point on the ring is chosen as origin ($x = 0$) and the co-ordinate x varies around the circular track. Let C be the circumference of the ring. Since wave functions may be single valued, therefore.

$$\Psi(x) = \Psi(x+c) \quad \dots(3.46)$$

If potential energy $V = 0$; then

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E \Psi = 0 \quad \dots(3.47)$$

Assuming

$$\frac{8\pi^2 m}{h^2} E = \lambda^2 \quad \dots(3.47)$$

Solution of Schrodinger equation

$$\frac{\partial^2 \Psi}{\partial x^2} + \lambda^2 \Psi = 0 \quad \dots(3.47)$$

Will be

$$\Psi = A \sin \lambda x + B \cos \lambda x \quad \dots (3.50)$$

The boundary conditions are different from those of a particle in one-dimensional box. According to equation 3.46

$$\Psi(0) = \Psi(c) \quad \dots (3.51)$$

Therefore,

$$B = A \sin \lambda c + B \cos \lambda c \quad \dots (3.52)$$

In this case, Ψ and its differential $\partial\Psi/\partial x$ must be continuous. Therefore,

$$\left(\frac{\partial \Psi}{\partial x}\right)_{x=0} = \left(\frac{\partial \Psi}{\partial x}\right)_{x=c} \quad \dots (3.53)$$

Which leads to

$$A\lambda = A\lambda \cos \lambda c - B\lambda \sin \lambda c \quad \dots (3.54)$$

Multiplying equation 3.52 by $B\lambda$ and equation 3.54 by A and then adding them

$$\cos \lambda c = 1 \quad \dots (3.55)$$

$$\text{Or } \lambda c = 2n\pi = \lambda = \frac{2n\pi}{c} \quad \dots (3.56)$$

Where $n = 0, \pm 1, \pm 2, \pm 3, \dots$. The energy levels for such a particle are given by

$$E = \frac{n^2 h^2}{8m c^2} \quad \dots (3.57)$$

This result may be compared with a particle in a box. It differs in two aspects. In this case n can have values of zero, positive and negative integers so that each energy level is doubly degenerate (except $n = 0$). For state having $n = 0$ ($E = 0$) the wave function is

$$\Psi_0 = B = \text{constant}$$

Which shows that there is no variation of Ψ round the ring in the lowest state

The normalization of Ψ gives

$$\int_0^c \left[A \sin\left(\frac{2n\pi}{c}x\right) + B \cos\left(\frac{2n\pi}{c}x\right) \right]^2 dx \quad \dots (3.58)$$

$$\Rightarrow A^2 \int_0^c \sin^2\left(\frac{2n\pi}{c}x\right) dx + B^2 \int_0^c \cos^2\left(\frac{2n\pi}{c}x\right) dx + 2AB \int_0^c \sin\left(\frac{2n\pi}{c}x\right) \cos\left(\frac{2n\pi}{c}x\right) dx = 1 \quad \dots (3.59)$$

$$= (A^2 + B^2) c/2 = 1 \quad \dots (3.60)$$

$$= A^2 + B^2 = 2/c \quad \dots (3.61)$$

To satisfy equation 3.61 we can substitute

$$A = \sqrt{\frac{2}{c}} \cos \alpha \text{ & } B = \sqrt{\frac{2}{c}} \sin \alpha \quad \dots (3.62)$$

α may have any value

Therefore, normalized wave function for particle in a ring is

$$\Psi = \sqrt{\frac{2}{c}} \cos \alpha \sin \left(\frac{2n\pi}{c} \right) + \sqrt{\frac{2}{c}} \sin \alpha \cos \left(\frac{2n\pi}{c} \right) x \quad \dots (3.63)$$

3.6 TUNNELLING

Let us consider a particle in a one-dimensional box of length l with walls of finite height & width which shows that potential energy have finite values at the walls and upto a certain distance from walls (Fig. 3.5). The potential energy is thus defined as

$$V = 0 \text{ for } x < 0 \text{ and } x > l$$

$$V = V_0 \text{ for } 0 \leq x \leq l \quad \dots (3.64)$$

Let in region II, the total energy E is less than that of the potential energy barrier V_0 of finite width (say b). According to classical mechanics, this behaviour of a particle is not allowed because its kinetic energy (K.E.) is always greater than or equal to zero. Hence, total energy $E = \text{K.E.} + V_0$ implies that kinetic energy must be a negative quantity if E is to be less than V_0 . This behaviour of the particle can be justified in quantum mechanics.

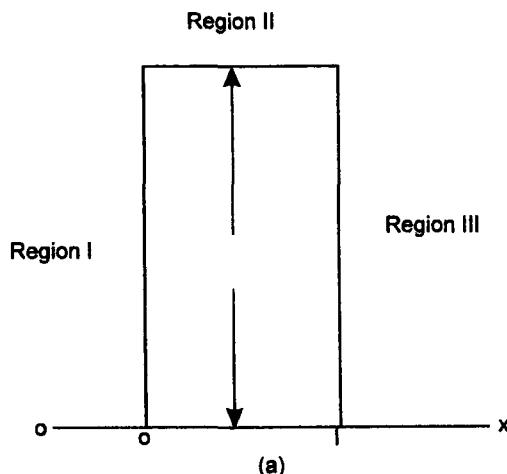
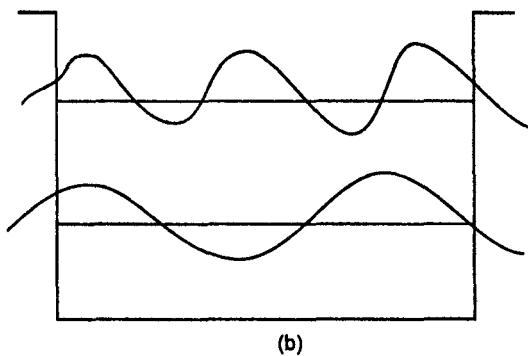


Fig. 3.5. (a) Particle in a box of finite heights & thickness



(b) The wave function of particle shows its existence even outside the box.

In region I & III as $V = 0$, the Schrodinger equation will be :

$$\frac{d^2\Psi(x)}{dx^2} + \frac{8\pi^2m}{r^2} E\Psi = 0 \quad \dots(3.65)$$

Whose solution will be

$$\Psi(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) \quad \dots(3.66)$$

In region II, Schrodinger equation can be written as

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V_0) \Psi = 0 \quad \dots(3.67)$$

The general solution of this equation in Exponential form is given by

$$\Psi(x) = A \exp\left[\left(\frac{2\pi ix}{h}\right)\sqrt{(E - V_0)2m}\right] + B \exp\left[\left(\frac{-2\pi ix}{h}\right)\sqrt{(E - V_0)2m}\right] \quad \dots(3.68)$$

For $\Psi(x)$ to be finite B must be zero

$$\Rightarrow B = 0 \quad \dots(3.69)$$

So, that $\Psi(x) = A \exp\left[\left(\frac{-2\pi ix}{h}\right)\sqrt{(E - V_0)2m}\right]$... (3.70)

As $E < V_0$, the quantity with square root is negative so that

$$\Psi(x) = A \exp\left[\left(\frac{-2\pi ix}{h}\right)\sqrt{-1}\sqrt{|(V_0 - E)|/2m}\right] \quad \dots(3.71)$$

Or $\Psi(x) = A \exp \left[\left(\frac{-2\pi x}{h} \right) \sqrt{|V_0 - E| / 2m} \right] \quad \dots(3.72)$

This solution describes the behaviour of wave function within the potential energy barrier. The probability of finding particle within this region is a positive quantity. With increase in distance (x) in region II along the positive direction of the barrier the probability Ψ^2 decreases exponentially. If barrier is not infinitely high ($V_0 \neq \infty$) and not with infinite width ($b \neq \infty$) there will be certain probability that the particle exists in region I & III also. In other words, particle can penetrate through the barriers. Such a penetration or leakage of particle is known as tunnelling or quantum mechanical tunnelling. This phenomenon is important for particles of low mass like electron, proton, etc. The emission of α -particles from radioactive nucleus is a process of tunnelling. In C_2H_6 molecule, Hydrogen can undergo tunnelling through the barriers from one staggered position to another. Tunnelling of electron is also important in the redox reactions.

PROBLEMS SET-3

- Derive wave function for particle in a one-dimensional box. (See section 3.1).
- Explain the concept of quantization of translational energy (See section 3.1)
- Derive an expression for energy of a particle in three-dimensional box. (See section 3.3)
- Show normalization of wave function of a particle in one dimensional box (See section 3.1)
- Derive energy expression for a particle in a box considering it as free electron model (See section 3.2).
- Explain the degeneracy of energy levels taking example of particle in a cubic box (See section 3.4).
- Derive expression for energy of a particle moving in a circular ring (See section 3.5).
- "Phenomenon of penetration of a particle through barriers is known as tunnelling." Justify this statement with derivation. (See section 3.6).
- Show that the length of the box is an integral multiple of $\lambda/2$ where λ is the wavelength associated with the particle wave (See section 3.1).
- Consider electron in a box of size of the nucleus (10^{-14} m). Calculate its ground state energy.
(Ans. 6.03×10^{-10} J).
- Determine the degree of degeneracy of the energy level $17h^2/8ml^2$ of a particle moving in a cubic box.
- What are the degrees of degeneracies of the first three energy levels for a particle in a three-dimensional box with $a = b = 2c$?
- Consider an electron in a one dimensional box of length 20A° . What is its energy in ground state?
[Hint : taking $n = 1$, $E_1 = h^2/8 ml^2$, $l = 20 \times 10^{-10}$ m; substituting value of h and $m_e = 9.1 \times 10^{-31}$ kg; E_1 can be calculated]
(Ans. 3.01×10^{-19} J).

CHAPTER-4

Quantization of Vibration Energy

SYNOPSIS

Section	Topics
4.1	Classical treatment for harmonic oscillator
4.2	Quantum mechanical treatment for harmonic oscillator

Apart from translation mode, a particle can have vibration mode also. In order to understand the vibration modes and quantization of vibration energy, a particle may be considered as a simple harmonic oscillator. In this chapter, concepts related to oscillations are discussed.

In harmonic motion the restoring force 'F' acting on the particle, is proportional to the amount of displacement 'x' from the equilibrium position

$$F \propto -x \quad \dots (4.1)$$

$$\text{Or} \quad F = -kx \quad \dots (4.2)$$

Where k is the force constant and is a measure of stiffness of a spring if we consider a spring as harmonic oscillator. A strong and inflexible spring will have larger value of k while a weaker spring will have lesser value of k . Negative sign in equation 4.2 indicates that the restoring force is always in the opposite direction to that of displacement in the oscillator. A simple harmonic oscillation in a spring can be shown as in fig. 4.1

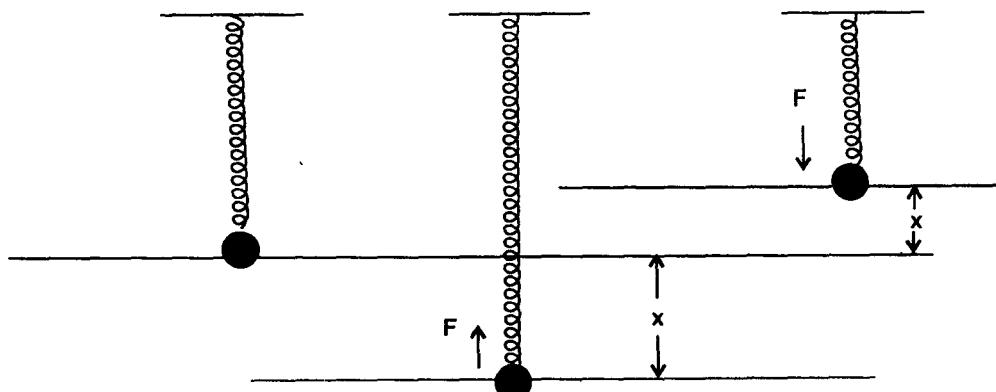


Fig.4.1 A harmonic oscillator showing oscillation.

Classical treatment for harmonic oscillator

On the basis of classical mechanics vibration motion as shown above can be described in terms of Newton's second law of motion according to which

$$F = ma = m \frac{d^2x}{dt^2} \quad \dots(4.3)$$

Equating equations 4.2 and 4.3

$$kx = m \frac{d^2x}{dt^2} \quad \dots(4.4)$$

$$= \frac{d^2x}{dt^2} = \frac{k}{m} x \quad \dots(4.5)$$

Above differential equation has solution

$$x = A \sin (2\pi\nu t)$$

$$\text{Or} \quad x = A \cos (2\pi\nu t) \quad \dots(4.6)$$

Here A is the maximum displacement or amplitude of vibration and ν is the frequency of vibration. Its value can be derived as follows :

Substituting value of x from 4.6 in equation 4.4. we get

$$m [-A (2\pi\nu)^2 \sin (2\pi\nu t)] = -k A \sin (2\pi\nu t) \quad \dots(4.7)$$

$$\text{Or} \quad m (2\pi\nu)^2 = k \quad \dots(4.8)$$

$$\text{Or} \quad (2\pi\nu) = \sqrt{k/m}$$

$$\text{Or} \quad \nu = 1/2 \pi \sqrt{k/m} \quad \dots(4.9)$$

This shows that the frequency of vibration of an oscillator (i.e. ν) depends upon the restoring force constant k and mass of the particle m.

The potential energy of the particle at any instant is evaluated as per follows :

$$\text{Since} \quad F = -dV/dx \quad \dots(4.10)$$

i.e. force can be expressed as differential of potential energy w.r.t. displacement x. Substituting value of F from equation 4.2

$$dV = kx dx \quad \dots(4.11)$$

on integrating this equation

$$V = \frac{kx^2}{2} + I \quad \dots(4.12)$$

Here I is the integration constant whose value can be evaluated on substituting the limits i.e. at $x = 0; V = 0$. This gives $I = 0$, therefore, expression for the potential energy becomes

$$V = \frac{kx^2}{2} \quad \dots(4.13)$$

The variation of potential energy with displacement x is shown in the figure 4.2. The momentum of the particle at any instant is given by

$$p = mv \quad \dots(4.14)$$

or $p = m \frac{dx}{dt} \quad \dots(4.15)$

Considering $x = A \sin(2\pi\nu t)$; momentum p of the particle, showing harmonic oscillation, is given by

$$p = m A ((2\pi\nu) \cos(2\pi\nu t)) \quad \dots(4.16)$$

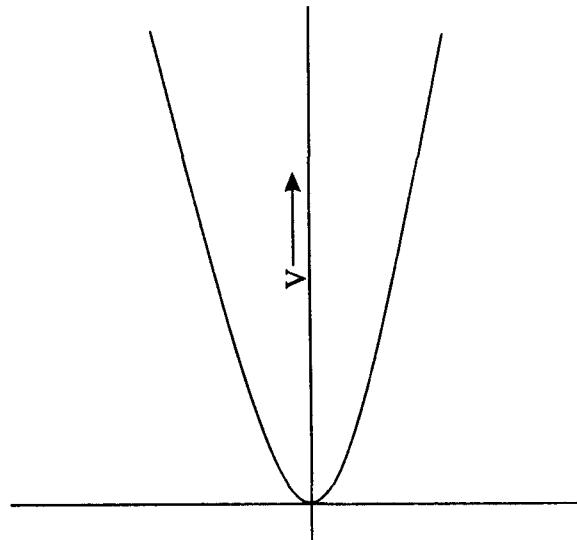


Fig. 4.2 : The parabolic variation of potential energy of the harmonic oscillator

Total energy of this particle at any instant is the sum of its kinetic and potential energy.

$$E = T + V \quad \dots(4.17)$$

Or $E = \frac{1}{2} mv^2 + V \quad \dots(4.18)$

Or multiplying T term both numerator and denominator by m

$$E = \frac{p^2}{2m} + V \quad \dots(4.19)$$

$$E = \frac{[mA(2\pi\nu)\cos(2\pi\nu t)]^2}{2m} + \frac{kx^2}{2} \quad \dots(4.20)$$

Or $E = \frac{[mA(2\pi\nu)\cos(2\pi\nu t)]^2}{2m} + \frac{k[A \sin(2\pi\nu t)]^2}{2} \quad \dots(4.21)$

Or $E = \frac{m^2 A^2 \left(\frac{k}{m}\right) \cos^2(2\pi\nu t)}{2m} + \frac{kA^2 \sin^2(2\pi\nu t)}{2} \quad \dots(4.22)$

$$[\nu \text{ as } = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \Rightarrow 2\pi\nu = \sqrt{\frac{k}{m}} \text{ or}$$

$$(2\pi\nu)^2 = \frac{k}{m} \quad \dots(4.23)$$

Or $E = \frac{1}{2} k A^2 \cos^2(2\pi\nu t) + \frac{1}{2} k A^2 \sin^2(2\pi\nu t)$

Or $E = \frac{1}{2} k A^2$...(4.23)

[as $\sin^2(2\pi\nu t) + \cos^2(2\pi\nu t) = 1$]

On the basis of classical treatment of the particle executing simple harmonic motion, following salient features may be noted for it :

- (i) The frequency (ν) of the particle depends only on (k), the force constant and (m) mass of the particle. It is independent of the maximum amplitude (A) of the vibration.
- (ii) The potential energy of the particle exhibiting simple harmonic motion is given by equation 4.13 i.e. it depends upon square of displacement during oscillation so its variation can be expressed as per figure 4.2
- (iii) Total energy of the particle (E) can be expressed by equation 4.23 and E depends on square of A i.e. amplitude of vibration, therefore, total energy E of particle may vary continuously as particle can possess any amount of maximum amplitude during oscillation.
- (iv) From energy considerations for the particle exhibiting harmonic oscillation i.e. on the basis of its total energy E and its potential energy V (ref. equation 4.13 and 4.23) this can be concluded that :

At $x = 0$ kinetic energy or velocity of the oscillator is maximum and

At $x = A$; kinetic energy is zero or velocity of the oscillator is zero.

because of above facts this may also be concluded that particle will spend maximum time at the extremes (i.e. at amplitude A) position and minimum time at the equilibrium position ($x = 0$) during the course of vibration.

4.2 QUANTUM MECHANICAL TREATMENT FOR HARMONIC OSCILLATOR :

As for one particle in one-dimensional system, kinetic energy operator T is written as

$$\hat{T} = \frac{p^2}{2m}$$

Or $\hat{T} = \frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}$...(4.24)

The potential energy operator may be written as (equation 4.13)

$$V = \frac{1}{2} kx^2$$

Considering both T and V hamiltanian for the system is

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{-\hbar^2}{8\pi^2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2\end{aligned}\quad \dots(4.25)$$

Therefore, Schrodinger equation for the system may be written as

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{-\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \Psi = 0 \quad \dots(4.26)$$

It is found that the well behaved solutions exist for the equation 4.26 only for the following Eigen values E

$$E_v = (v + \frac{1}{2}) \hbar \nu_0$$

$$\text{Or} \quad E_v = (v + \frac{1}{2}) \frac{\hbar}{2\pi} \sqrt{\frac{k}{m}} \quad \dots(4.27)$$

Where v is the vibrational quantum number which can have values v = 0, 1, 2, 3, Equation 4.27 may be rewritten as

$$E_v = (v + \frac{1}{2}) \hbar \omega \quad \dots(4.28)$$

$$\text{where} \quad \omega = \sqrt{\frac{k}{m}} \quad \dots(4.29)$$

The well-behaved solution for the Schrodinger equation 4.26 for the first few lowest states are given by

$$\begin{aligned}\Psi_0 &= \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\alpha x^2} \\ \Psi_1 &= \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{4}} 2\alpha^{\frac{1}{2}} x e^{-\alpha x^2} \\ \Psi_2 &= \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{2}} (4\alpha x^2 - 1) e^{-\alpha x^2}\end{aligned}$$

and so on $\dots(4.30)$

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

These wave functions are given using Hermite polynomials $H_v(y)$ where $y = \alpha x$. Figure 4.3 shows the plots of first few levels of harmonic oscillator with their relative energies. These are Ψ and Ψ^2 (probability densities) graph.

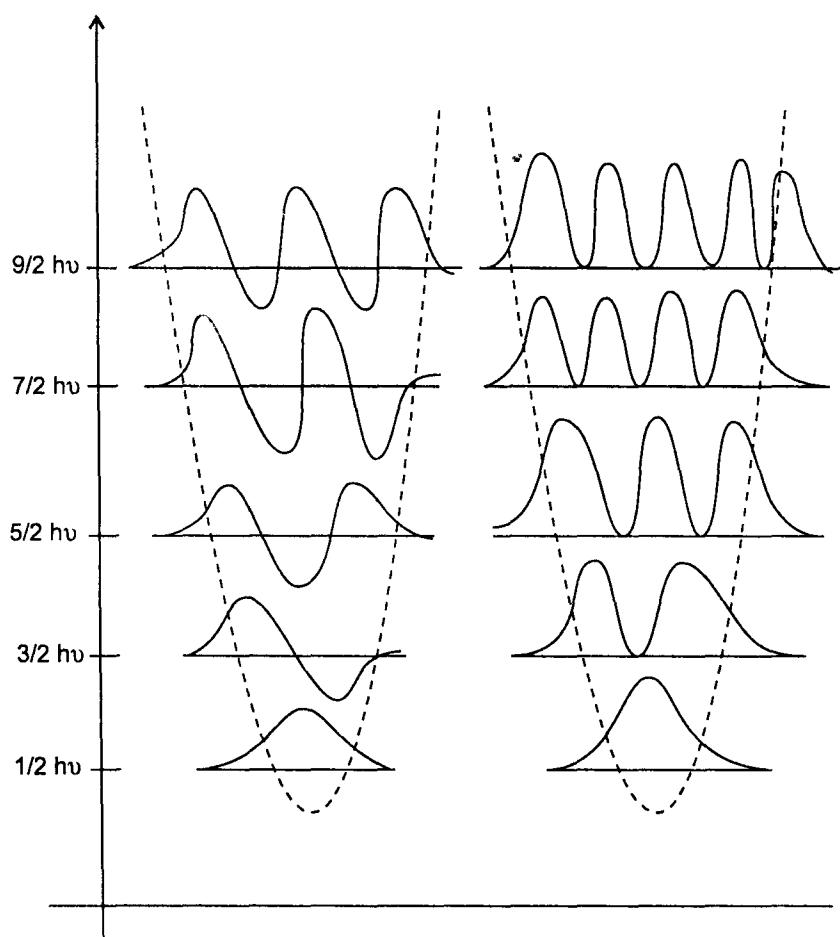


Fig. 4.3 : Ψ_x and Ψ_x^2 graphs for Harmonic oscillator

A few features of the solution of harmonic oscillator problem are given below :

- The Eigen values of the states are quantized and are given by

$$E = (v + \frac{1}{2}) \hbar \nu_0$$

- The lowest energy of the oscillator can be obtained by putting $v = 0$ in the above equation as

$$E_0 = (0 + \frac{1}{2}) \hbar \nu_0$$

Or $E_0 = \frac{1}{2} \hbar \nu$... (4.30)

This energy is known as zero point energy of the oscillator. This shows that particle can never be stand still. In contrast to it, classical mechanics predicts that the particle has zero potential energy at its equilibrium position i.e. at $x = 0$.

- The wave function falls exponentially to zero as $x \rightarrow \pm \infty$. Hence, Ψ and Ψ^2 are not zero even for a large value of x . So, there is some probability of finding the particle at some large value of x .

iv. Classical mechanics predicts that the oscillator has a finite amplitude. This amplitude may be calculated as per follows:-

From equation 4.23

$$E_v = \frac{1}{2} kA^2$$

And from equation 4.27

$$E_v = (v + \frac{1}{2}) \hbar v_0$$

Equating them & on solving for A

$$\begin{aligned} \frac{1}{2} kA^2 &= (v + \frac{1}{2}) \hbar v_0 \\ \Rightarrow A &= \left[\frac{(2v+1)\hbar v_0}{k} \right]^{\frac{1}{2}} \end{aligned} \quad \dots(4.31)$$

v. The difference between two successive levels of an oscillator is given by

$$\Delta E = E_{v+1} - E_v = (v + 1 + \frac{1}{2})\hbar v_0 - (v + \frac{1}{2})\hbar v_0$$

Or

$$\Delta E = \hbar v_0 \quad \dots(4.32)$$

Thus, this can be concluded that in an oscillator, successive energy levels are equally spaced and the separation is given by $\hbar v_0$.

vi. Like particle in a box, the wave function varies over the symmetric range from $-\infty$ to $+\infty$ and are alternately symmetric and anti-symmetric about the origin. Therefore, in each harmonic oscillator wave function is either even or odd function depending upon the value of v which may be either even or odd.

Example 4.1 : Evaluate expectation value of x and x^2 for the ground state of the harmonic oscillator.

The normalized ground state wave function for harmonic oscillator is

$$\begin{aligned} \Psi &= \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\alpha x^2} \\ &= \langle x \rangle = \int_{-\infty}^{\infty} \sqrt{\frac{2\alpha}{\pi}} e^{-\alpha x^2} x e^{-\alpha x^2} dx \\ &= \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{+\infty} x e^{-2\alpha x^2} dx \end{aligned}$$

= 0 (as this is odd function and integral over the whole space for odd function is zero).

$$\text{Similarly } \langle x^2 \rangle = \int_{-\infty}^{+\infty} \Psi |x^2| \Psi dx$$

$$= \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} dx$$

$$= \frac{1}{4\alpha}$$

Example 4.2 : Evaluate $\langle p \rangle$ for the harmonic oscillator

The normalized ground state wave function for the harmonic oscillator is

$$\Psi = \left(\frac{2\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2}$$

$$\Rightarrow \langle p_x \rangle = \int_{-\infty}^{\infty} \sqrt{\frac{2\alpha}{\pi}} e^{-\alpha x^2} \left| \frac{\hbar}{2\pi i} \frac{\partial}{\partial x} \right| e^{-\alpha x^2} dx$$

$$= \sqrt{\frac{2\alpha}{\pi}} \left(\frac{\hbar}{2\pi i} \right) \int_{-\infty}^{\infty} e^{-\alpha x^2} (-2\alpha x) e^{-\alpha x^2} dx$$

= 0 (as this is an odd function and integral of odd function over the whole space is zero).

Example 4.3 : Evaluate the expectation value of the kinetic energy $\langle T \rangle$ for the harmonic oscillator

As for harmonic oscillator ground state normalized wave function is

$$\Psi = \left(\frac{2\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2}$$

$$\Rightarrow \langle T \rangle = \int_{-\infty}^{+\infty} \Psi \hat{T} \Psi dx$$

$$= \int_{-\infty}^{+\infty} \sqrt{\frac{2\alpha}{\pi}} e^{-\alpha x^2} \left| \frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} \right| e^{-\alpha x^2} dx = \frac{\hbar\nu}{4}$$

Example 4.4 : Evaluate the expectation value of the potential energy $\langle V \rangle$ for the harmonic oscillator.

As for harmonic oscillator ground state normalized wave function is

$$\Psi = \left(\frac{2\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2}$$

$$\langle V \rangle = \int_{-\infty}^{+\infty} \Psi \hat{V} \Psi dx$$

$$\langle V \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2\alpha}{\pi}} e^{-\alpha x^2} \left| \frac{1}{2} kx^2 \right| e^{-\alpha x^2} dx$$

On solution it provides the value of $\langle V \rangle$ as

$$\langle V \rangle = \frac{\hbar\nu}{4}$$

Here in the case of harmonic oscillator the expectation values of kinetic energy and potential energy are same

i.e. $\langle T \rangle = \langle V \rangle = \frac{\hbar\nu}{4}$

This equality is a special case for the virial theorem, As according to this theorem if potential energy of the particle is in the form of equation $V = C x^n$ where C is any constant, the kinetic and potential energies are related to each other by

$$2 \langle T \rangle = n \langle V \rangle$$

For harmonic oscillator $V = \frac{1}{2} kx^2$

So, $n = 2$ here, therefore

$$\langle T \rangle = \langle V \rangle$$

PROBLEMS SET-4

- Find out frequency of an oscillator based on classical mechanics (See section 4.1)
 - Prove that $V = \frac{1}{2} kx^2$ for an oscillator based on classical mechanics (see section 4.1)
 - On the basis of classical mechanics, prove that E_{tot} for the oscillator is $\frac{1}{2} K A^2$ (See section 4.1)
 - Show that the energy levels in harmonic oscillator are equally spaced. (See section 4.2)
 - What do you understand by zero point energy? (See section 4.2)
 - Find out expression for amplitude for a harmonic oscillator (See section 4.2)
 - Plot Ψ and Ψ^2 for harmonic oscillator (See section 4.2)
 - Show that the force constant is $k = 4\pi^2 m v^2$ in case of harmonic oscillator
- [Hint : as $v = 1/2\pi \sqrt{k/m}$ rearrange this equation and find out k]
- Prove that harmonic oscillator is a special case of virial thereon (See section 4.2)
 - Frequency of a harmonic oscillator is 10^{10} Hz. Find out its zero point energy. (Ans 3.313×10^{-24} J)

CHAPTER-5

Quantization of Rotation Energy

SYNOPSIS	
<i>Section</i>	<i>Topics</i>
5.1	Classical treatment for rotational motion of particle
5.2	Quantum mechanical treatment for rigid rotator

Rotational motion is another type of basic motion which is of great interest in atomic and molecular problems. It sets up in atom/molecule whenever its motion is under the influence of central field of force. For example, motion of electron around the nucleus is also rotational motion.

For a single particle which is in such type of motion Schrodinger equation can be solved exactly. One such type of problem i.e. rotational motion of a particle in one plane (particle in a ring) has been included in Chapter – 3 (Section 3.5) therefore, rotational motion in three dimension is dealt here with.

5.1 CLASSICAL TREATMENT FOR ROTATIONAL MOTION OF PARTICLE

Let us consider a rigid rotator to explain rotation motion of a diatomic molecule in which two atoms A & B of masses m_1 and m_2 are separated by the distance r . Let C be the centre of mass of the system and r_1 and r_2 be the distances of A & B from c respectively. Let v_1 and v_2 be the velocities of A and B with which they are rotating around an axis passing through C. The kinetic energy of the rotator is given by the equation

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \quad \dots(5.1)$$

For two particles of rigid rotator

$$v_1 = r_1 \omega \quad \dots(5.2)$$

$$v_2 = r_2 \omega \quad \dots(5.3)$$

Where ω is the angular velocity of the particles

$$= T = \frac{1}{2} m_1(r_1\omega)^2 + \frac{1}{2} m_2(r_2\omega)^2 \quad \dots(5.4)$$

$$= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega$$

Or $T = \frac{1}{2} I\omega^2 \quad \dots(5.5)$

Where I is the moment of inertia for the diatomic molecular system & by definition

$$I = \sum m_i r_i^2 \quad \dots(5.6)$$

For balancing of the system, the equation is

$$m_1 r_1 = m_2 r_2 \quad \dots(5.7)$$

And as

$$r_1 = (r - r_2)$$

On substituting value of r_1 in equation 5.7

$$\begin{aligned} m_1(r-r_2) &= m_2 r_2 \\ &= m_1 r - m_1 r_2 = m_2 r_2 \\ &= m_1 r = (m_1 + m_2) r_2 \end{aligned}$$

$$\Rightarrow r_2 = \frac{m_1}{(m_1 + m_2)} r \quad \dots(5.9)$$

Similarly this can be shown that

$$r_1 = \frac{m_2}{(m_1 + m_2)} r \quad \dots(5.10)$$

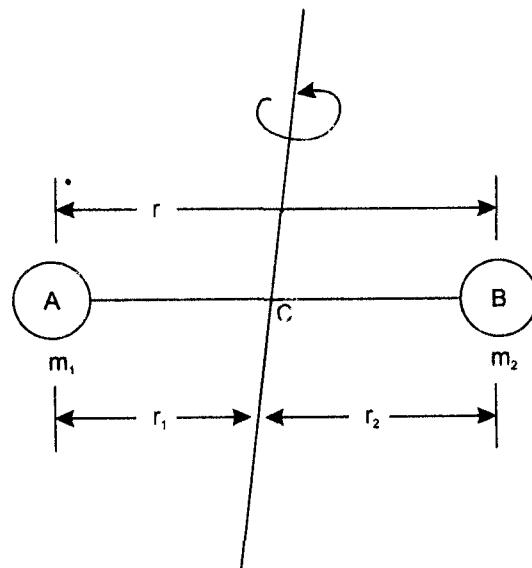


Fig. 5.1 Model of a rigid rotator.

Substituting r_1 & r_2 from equations 5.9 and 5.10 in equation 5.6

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(5.6)$$

$$\begin{aligned} I &= m_1 \left(\frac{m_2 r}{(m_1 + m_2)} \right)^2 + m_2 \left(\frac{m_1 r}{(m_1 + m_2)} \right)^2 \\ &= (m_1 m_2 / (m_1 + m_2)) r^2 \end{aligned}$$

Or

$$I = \mu r^2 \quad \dots(5.11)$$

Where μ is the reduced mass and by definition

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad \dots(5.12)$$

Angular momentum of such system is given by

$$L = I\omega \quad \dots(5.13)$$

$$= T = \frac{1}{2} I\omega^2 = \frac{1}{2} \frac{(I\omega)^2}{I} [\therefore L = I\omega]$$

Or

$$T = \frac{L^2}{2I} \quad \dots(5.14)$$

Classically, the kinetic energy of the rotator can have any value as ω can possess any value. This is not true in quantum mechanical framework. Energy of rotator quantized is shown in the next section.

Example 5.1 Show that for rotation motion $v = r\omega$

The angular velocity of a particle rotating around an axis is defined as the number of radians swept out by the particle in a second. For one complete revolution angle 2π radians is swept by the rotator. If v is the frequency of rotation (cycles/second)

$$\omega = 2\pi v \quad \dots(5.15)$$

Distance covered by the particle in one complete revolution is $2\pi r$ (i.e. equal to circumference of the rotation motion). Therefore, linear velocity of the particle is given by

$$v = (2\pi r) v \quad \dots(5.16)$$

From equations 5.15 and 5.16

$$\begin{aligned} v &= \frac{\omega}{2\pi} \text{ and } v = \frac{v}{2\pi r} \\ &= \frac{\omega}{2\pi} = \frac{v}{2\pi r} \quad \dots(5.17) \end{aligned}$$

$$= v = r\omega \quad \dots(5.18)$$

Example 5.2 Show that for rotation motion $L = I\omega$ considering a rigid body rotating about an axis.

Let ω be its angular velocity. Considering i^{th} particle going in a circular rotation with radius r_i with its plane perpendicular to AB. The linear velocity

$$v_i = r_i \omega \quad \dots(5.19)$$

v_i = linear velocity for the particle

$$\text{The angular momentum } L = |\vec{r} \times \vec{p}| \quad \dots(5.20)$$

$$\text{Or} \quad L = m_i v_i r_i [\text{where } \vec{p} = m_i \vec{v}_i] \quad \dots(5.21)$$

Substituting v_i from equation 5.19

$$L = m_i r_i^2 \omega$$

The angular momentum for the whole system will be

$$L = \sum m_i r_i^2 \omega \quad \dots(5.22)$$

$$\text{Or} \quad L = I\omega \quad \dots(5.23)$$

Hence proved

5.2 QUANTUM MECHANICAL TREATMENT FOR RIGID ROTATOR

The classical kinetic energy for the rigid rotator can be written as

$$\begin{aligned} T &= \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \\ &= \frac{m_1^2 v_1^2}{2m_1} + \frac{m_2^2 v_2^2}{2m_2} \\ &= T = \left(\frac{p_1^2}{2m_1} \right) + \left(\frac{p_2^2}{2m_2} \right) \end{aligned} \quad \dots(5.24)$$

Where p_1 & p_2 are linear momenta for the particles of rigid rotator. For freely rotating rotator, potential energy is zero, hence total energy is equal to the kinetic energy. So,

$$E = \left(\frac{p_1^2}{2m_1} \right) + \left(\frac{p_2^2}{2m_2} \right) \quad \dots(5.25)$$

$$\text{Or} \quad E = \frac{(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2)}{2m_1} + \frac{(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2)}{2m_2} \quad \dots(5.26)$$

Where p_x 's, p_y 's and p_z 's are the three components of the linear moments, of rotator along x, y & z axis. Replacing p 's with quantum mechanical operators

$$\hat{H}_{op} = \frac{-\hbar^2}{8\pi^2 m_1} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right] - \frac{\hbar^2}{8\pi^2 m_2} \left[\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right] \quad \dots(5.27)$$

It is convenient to express rotation in forms of internal co-ordinates

$$\begin{aligned} x &= x_2 - x_1 \\ y &= y_2 - y_1 \\ z &= z_2 - z_1 \end{aligned} \quad \dots(5.28)$$

$$\text{As } \frac{\partial^2}{\partial x_1^2} = \left(\frac{\partial}{\partial x_1} \right)^2 = \left[\frac{\partial x}{\partial x_1} \frac{\partial}{\partial x} \right]^2 = \left[(-1) \frac{\partial}{\partial x} \right]^2 = \frac{\partial^2}{\partial x^2} \quad \dots(5.29)$$

Similarly for $\frac{\partial^2}{\partial z^2}$ and $\frac{\partial^2}{\partial y^2}$

$$\hat{H}_{op} = \frac{-h^2}{8\pi^2 m_1} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] - \frac{h^2}{8\pi^2 m_2} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots(5.30)$$

$$\Rightarrow \hat{H}_{op} = \frac{-h^2}{8\pi^2} \left[\frac{1}{m_1^2} + \frac{1}{m_2^2} \right] \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots(5.31)$$

$$\text{Or } \hat{H}_{op} = \frac{-h^2}{8\pi^2 \mu} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots(5.32)$$

Therefore, the Schrodinger equation for the rigid rotator will be

$$\begin{aligned} \hat{H}_{op} &= \Psi = E\Psi \\ \Rightarrow \frac{-h^2}{8\pi^2 \mu} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \Psi &= E\Psi \end{aligned} \quad \dots(5.33)$$

Expressing x, y, z in terms of Polar coordinates i.e. r, θ & ϕ for which Ψ is function of r, θ & ϕ
i.e.

$$\Psi = f(r, \theta \text{ & } \phi)$$

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

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

$$z = r \cos \theta$$

... (5.34)

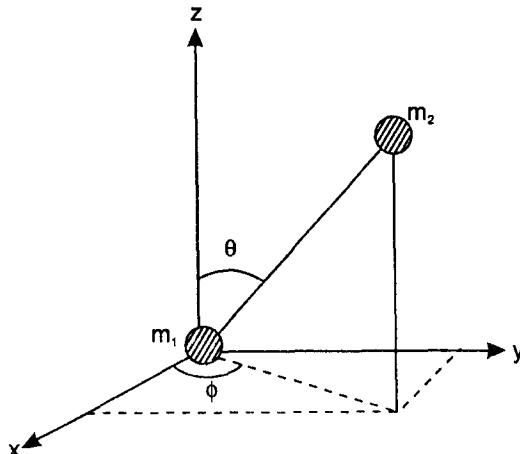


Fig. 5.2. Cartesian and spherical coordinates

The transformed expression is given by

$$\frac{-h^2}{8\pi^2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Psi = E\Psi \quad \dots(5.35)$$

As 'r' remains constant, so equation 5.35 may be written as

$$\frac{-h^2}{8\pi^2\mu r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \phi} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi^2} \right] Y(\theta, \phi) = EY(\theta, \phi) \quad \dots(5.36)$$

In the above equation (5.36) Ψ can be replaced by $Y(\theta, \phi)$ i.e. spherical harmonics and equation 5.36 can be rewritten as

$$\frac{-h^2}{4\pi^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \phi} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi^2} \right] Y(\theta, \phi) = (2EI) Y(\theta, \phi) \quad \dots(5.37)$$

As $2EI = L^2$...(5.38)

Operation of L.H.S. of equation (5.37) represents the operator of square of angular momentum. Hence, equation for angular momentum may be written as

$$\hat{L}_{op}^2 Y = L^2 Y \quad \dots (5.39)$$

Solution of above equation provides

$$L^2 = J(J+1) \left(\frac{h}{2\pi} \right)^2 \quad \dots(5.40)$$

Where J is the rotation quantum number. Therefore, energy for the rotator E is given by

$$E = \frac{L^2}{2\pi} = J(J+1) \frac{1}{2I} \left(\frac{h}{2\pi} \right)^2$$

Or $E = \frac{h^2}{8\pi^2 I} J(J+1)$...(5.41)

Substituting the value of L^2 equation (5.37) becomes

$$\frac{-h^2}{4\pi^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \phi} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi^2} \right] Y(\theta, \phi) = J(J+1) \left(\frac{h}{2\pi} \right)^2 Y(\theta, \phi) \quad \dots(5.42)$$

Or

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \phi} \right) + J(J+1) \sin^2 \theta Y + \frac{\partial^2 Y}{\partial \phi^2} = 0 \quad \dots(5.43)$$

Substituting Y as function of (θ & ϕ)

$$Y = \Theta(\theta) \Phi(\phi) \quad \dots(5.44)$$

$$\phi \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \phi} \right) + J(J+1) \sin^2 \theta \Theta + \Theta \frac{\partial^2 \phi}{\partial \phi^2} = 0 \quad \dots(5.45)$$

Dividing equation (5.45) by $\Theta \Phi$ and rearranging it

$$\frac{1}{\Theta} \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \phi} \right) + J(J+1) \sin^2 \theta = \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad \dots(5.46)$$

Both L.H.S. and R.H.S. of this equation may be taken as equal to m^2

$$\frac{1}{\Theta} \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \phi} \right) + J(J+1) \sin^2 \theta = m^2 \quad \dots(5.47)$$

$$\text{And } -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2 \quad \dots(5.48)$$

In this way equations (5.47) and (5.48) are two resolved equations for Schrodinger equation set up for a rigid rotator.

Solution of ϕ equation (5.48)

Since the ϕ equation is

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi$$

The acceptable solution of this equation is

$$\Phi_m = A \exp(im\phi) \quad \dots(5.49)$$

Applying boundary conditions

$$\begin{aligned} \Phi(\phi + 2\pi) &= \Phi(\phi) \\ &= A \exp\{im(\phi + 2\pi)\} = A \exp(im\phi) \end{aligned} \quad \dots(5.50)$$

$$\text{Or } \exp(im2\pi) = 1$$

As $\exp(im2\pi) = \cos(2\pi m) + i \sin(2\pi m)$ which is true if and only if

$$m = 0, \pm 1, \pm 2$$

'A' constant can be determined by applying normalization condition to function Φ

$$A * A \int_0^{2\pi} \exp(im\phi) \exp(im\phi) d\phi = 1 \quad \dots(5.51)$$

$$\text{Or } A^2 \int_0^{2\pi} \exp(-im\phi) \exp(im\phi) d\phi = 1$$

$$\text{or } A^2 (2\pi) = 1$$

$$A^2 = \frac{1}{2\pi}$$

Or $A = \frac{1}{2\pi}$... (5.52)

Incorporating the value of A

$$\Phi_m = \frac{1}{\sqrt{2\pi}} (\exp im \phi) \quad \dots (5.53)$$

Where $m = 0, \pm 1, \pm 2, \dots$

First few function are given in table 5.1

TABLE 5.1
First Few Functions

M	ϕ_m
0	$\frac{1}{\sqrt{2\pi}}$
+1	$\frac{1}{\sqrt{2\pi}} \exp(i\phi)$
-1	$\frac{1}{\sqrt{2\pi}} \exp(-i\phi)$
+2	$\frac{1}{\sqrt{2\pi}} \exp(2i\phi)$
-2	$\frac{1}{\sqrt{2\pi}} \exp(-2i\phi)$
+3	$\frac{1}{\sqrt{2\pi}} \exp(3i\phi)$
-3	$\frac{1}{\sqrt{2\pi}} \exp(-3i\phi)$

Solutions of equation 5.47

Equation 5.47 can be written as per following taking a new variable

$$\chi = \cos \theta \quad \dots (5.54)$$

Therefore $\frac{d}{d\theta} = \frac{d\chi}{d\theta} \frac{d}{dx} = (-\sin \theta) \frac{d}{dx}$... (5.55)

$$\sin^2 \theta = 1 - \chi^2 \quad \dots (5.56)$$

And the function $\Theta(\theta) = P(\chi)$

Equation 5.47 modifies to

$$\frac{1}{p} [-(1-\chi^2)] \frac{d}{dx} \left[-(1-\chi^2) \frac{dP}{d\chi} \right] + J(J+1)(1-\chi) = m^2 \quad \dots (5.57)$$

Dividing by $(1 - \chi^2)/\rho$ and on rearranging it

$$\frac{d}{dx} \left[-(1 - \chi^2) \frac{dP}{d\chi} \right] + \left[J(J+1) \frac{-m^2}{1 - \chi^2} \right] \rho = 0 \quad \dots(5.58)$$

Or

$$(1 - \chi^2) \frac{d^2\rho}{d\chi^2} - 2 \times \frac{d\rho}{d\chi} - \left[J(J+1) \frac{-m^2}{1 - \chi^2} \right] \rho = 0 \quad \dots(5.59)$$

Equation 5.59 is called as associated Legendre equation. Solution P of the associated Legendre polynomials are given by :

$$P = P_J^{l|m|} = (1 - \chi^2)^{l|m|/2} \frac{d^{|m|} P_J}{d \chi^{|m|}} \quad \dots(5.60)$$

$P_J^{l|m|}$ is associated Legendre polynomial of degree J and order m. P_J in equation 5.60 is Legendre polynomial and is given by

$$P_J = \frac{1}{2^J J!} \frac{d^J}{d\chi^J} (\chi^2 - 1)^J \quad \dots(5.61)$$

Solution of P of the function Θ also requires $|m| \leq J$ for finite function. The two quantum conditions therefore are

$$J = 0, 1, 2, 3,$$

$$\text{and } m = 0, \pm 1, \pm 2, \pm 3 \quad \dots(5.62)$$

Therefore, m can have $(2J + 1)$ values for a given value of J. After normalization θ is given by

$$\Theta_{J,m} = \left[\frac{(2J+1)(J-|m|)!}{2(J+|m|)!} \right]^{1/2} P_J^{|m|} \quad \dots(5.63)$$

Table 5.2 shows a few normalized

TABLE 5.2
First Few Functions

J	m	$\Theta_{J,m}$
0	0	$\sqrt{2}/2$
1	0	$(\sqrt{6}/2) \cos \theta$
1	± 1	$(\sqrt{3}/2) \sin \theta$
2	0	$(\sqrt{10}/4)(3 \cos^2 \theta - 1)$
2	± 1	$(\sqrt{15}/2) \sin \theta \cos \theta$
2	± 2	$(\sqrt{15}/4) \sin^2 \theta$

Physical significance of rotational quantum number J

From L² equation 5.40 we have

$$L^2 = J(J+1) \left(\frac{h}{2\pi} \right)^2$$

Or $L^2 = J(J+1)(\hbar)^2$... (5.64)

[Where $\hbar = h/2\pi$]

This implies that J quantum number is responsible for quantization of total angular momentum of the rotator. Similarly J is also responsible for quantization of E, the rotational energy as

$$E = J(J+1) \frac{h}{8\pi^2 I} \text{ or } \frac{L^2}{2I} \quad \dots(5.65)$$

Physical significance of quantum no m

When \hat{L}_z or L_z operator is operated on Φ part of the function z component of the angular momentum can be obtained

$$\begin{aligned} \hat{L}_z \Phi &= [\hat{L}_z] \left[\frac{1}{\sqrt{2\pi}} \exp(im\phi) \right] \\ &= \frac{mh}{2\pi} \left[\frac{1}{\sqrt{2\pi}} \exp(im\phi) \right] \end{aligned} \quad \dots(5.66)$$

Equation 5.66 implies that z component of the angular momentum has precise value as given by

$$L_z = m \frac{h}{2\pi} \text{ or } m\hbar \quad \dots(5.67)$$

Hence, m quantum number gives the quantization of angular momentum and can have values $0, \pm 1, \pm 2, \dots$

As $L_z = mh \text{ or } m\hbar/2\pi$

$$\Rightarrow L_z^2 = \left(\frac{mh}{2\pi} \right)^2 \quad \dots(5.68)$$

Since

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

$$\Rightarrow L^2 - L_z^2 = L_x^2 + L_y^2$$

Incorporating values of L^2 and L_z^2

$$[J(J+1) - m^2] \left(\frac{h}{2\pi} \right)^2 = L_x^2 + L_y^2 \quad \dots(5.69)$$

R.H.S. of above equation will be a positive quantity. Therefore, L.H.S. of equation 5.69 should also be positive quantity.

$$\Rightarrow J(J+1) - m^2 \geq 0 \quad \dots(5.70)$$

Or $|m| \leq J$

Therefore, m can have values $0, \pm 1, \pm 2, \dots, \pm J$ or m can have $(2J+1)$ values.

Example 5.3 : What is zero level energy for a rigid rotator ?

As for a rigid rotator

$$E_J = J(J+1) \left(\frac{\hbar}{2\pi}\right)^2 \frac{1}{2I}$$

$$\text{Or } E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

So, for zero level $J = 0$; Energy will be zero.

Example 5.4 : Show that spacing between the rotational levels increases with increase in rotational quantum number J .

As for a rigid rotator

$$E_J = J(J+1) \left(\frac{\hbar}{2\pi}\right)^2 \frac{1}{2I}$$

$$\text{Or } E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

$$J = 0 \quad E_0 = 0$$

$$J = 1 \quad E_1 = 2\hbar^2/8\pi^2 I$$

$$J = 2 \quad E_2 = 6\hbar^2/8\pi^2 I$$

$$J = 3 \quad E_3 = 12\hbar^2/8\pi^2 I \text{ and so on}$$

Above calculation of E_J for different J levels show that spacing between rotational levels increases with increase in rotational quantum number J .

PROBLEMS SET-5

1. Show that for a rigid rotator $T = \frac{1}{2} I\omega^2$ on the basis of classical mechanics (See Section 5.1)
2. Prove that $I = \mu r^2$ for a rigid rotator (See section 5.1)
3. Prove that for rotation motion $v = r\omega$ (See section 5.1 example 5.1)
4. Set up Schrodinger equation for a rigid rotator (See section 5.2)
5. Explain Cartesian and polar co-ordinates and write Schrodinger equation for a rigid rotator in terms of polar co-ordinates (See section 5.2).
6. What do you understand by spherical harmonics? (See Section 5.2)
7. Write a note on physical significance of J and m . (See section 5.2).
8. Discuss the solutions of Θ and Φ part of wave function or spherical harmonics for rigid rotator (See section 5.2).
9. Show that $E_0=0$ for $J=0$ i.e. energy of minimum or zero level for rigid rotator is zero. (See example 5.3).
10. Prove that spacing between rotational levels increases with increase in rotational quantum number J . (See example 5.4).

CHAPTER-6

Hydrogen like Atoms

SYNOPSIS	
Section	Topics
6.1	Schrodinger wave mechanical treatment for H-atom
6.2	Acceptable solutions for $\Phi(\phi)$ equation
6.3	Acceptable solution for $\Theta(\theta)$ equation
6.4	Acceptable solution for $R(r)$ equation
6.5	Energy of H-atom
6.6	Energy in atomic units (a.u.)
6.7	Quantum numbers and their significance
6.8	Total wave function for Hydrogen like atom
6.9	Radial probability distribution functions (RPDF)
6.10	Shapes of atomic orbitals
6.11	Energy levels and degeneracy of orbitals
6.12	Spectra of Hydrogen-like atom
6.13	Electron Spin

Hydrogen is the simplest of all chemical systems. It provides the model for the study of atomic structure in general. N. Bohr had also tried to explain the hydrogen atom and his mathematical framework was based on the basic assumption of quantization of orbital angular momentum of electron. This theory provides a basis for quantization of energies and to explain the experimental features of hydrogen – like atoms as H, He⁺, α_i^{2+} and $1Be^{3+}$ etc. This theory, however, failed to explain the relative line intensities in the hydrogen atom and it also failed to explain energies and spectra of complex atoms. In this chapter, quantum mechanics for Hydrogen like atoms is discussed.

6.1 SCHRODINGER WAVE MECHANICAL TREATMENT FOR H-ATOM

The time independent Schrodinger wave equation for H-atom system is

$$\hat{H} \Psi_{\text{tot}} = E_{\text{total}} \Psi_{\text{tot}} \quad \dots(6.1)$$

where

\hat{H} = Hamiltonian operator

E_{tot} = Total energy and

Ψ_{tot} = Total wave function for H-atom.

H-atom contains two particles viz. a nucleus and a electron. Therefore, Ψ_{tot} for this system is a function of six coordinates as

$$\Psi_{\text{tot}} = f(x_e, y_e, z_e, x_n, y_n, z_n)$$

Where x_e, y_e, Z_e are coordinates for electron and x_n, y_n & z_n are coordinates for nucleus. The Hamiltonian operator for this system may be written as

$$\begin{aligned} \hat{H}_{\text{op}} &= \hat{T}_{\text{op}} + \hat{V}_{\text{op}} \\ &= \left(\frac{-h^2}{8\pi m_e} \nabla_e^2 - \frac{h^2}{8\pi^2 m_n} \nabla_n^2 \right) - \frac{Ze^2}{r} \end{aligned} \quad \dots(6.2)$$

Where e' is electron charge in cgs- esu units

$$e' = \frac{e}{\sqrt{4\pi\epsilon_0}} \text{ in SI units.}$$

Incorporating equation 6.2, equation 6.1 becomes

$$\left[\frac{-h^2}{8\pi m_e} \left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{h^2}{8\pi m_n} \left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2} \right) - \frac{Ze^2}{r} \right] \Psi_{\text{tot}} = E_{\text{tot}} \Psi_{\text{tot}} \quad \dots(6.3)$$

Equation 6.3 can be resolved into two simple equations as

$$\frac{-h^2}{8\pi^2(m_e + m_n)} \left(\frac{\partial^2}{\partial x_m^2} + \frac{\partial^2}{\partial y_m^2} + \frac{\partial^2}{\partial z_m^2} \right) \Psi_m = E_{\text{trans}} \Psi_m \quad \dots(6.4)$$

and

$$\left[\frac{-h^2}{8\pi\mu_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{r} \right] \Psi_e = \Psi_e \quad \dots(6.5)$$

Equation 6.4 is associated to movement of centre of mass of H-atom system and E_{trans} is translational kinetic energy. Equation 6.5 corresponds to motion of electron w.r.t. to stationary nucleus and e is electronic energy here with μ_e is reduced mass. As this equation is the only equation which is concerned with motion of electron so, solution of this equation is discussed here only. This equation can be transformed into equation in terms of spherical polar co-ordinates i.e. r, θ & ϕ using relations.

$$\begin{aligned}x &= r \sin\theta \cos\phi \\y &= r \sin\theta \sin\phi \\z &= r \cos\theta\end{aligned}\quad \dots(6.6)$$

Result of this transformation is

$$\left[\frac{h^2}{8\pi^2\mu r^2} \left\{ \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right\} - \frac{Ze^{-2}}{r} \right] \Psi = E\Psi \quad \dots(6.7)$$

Here $\Psi = f(r, \theta, \phi)$

or Ψ can be expressed as

or $\Psi = R(r) (\Theta)(\theta) \Phi(\phi)$... (6.8)

Rearranging equation no. (6.7)

$$\begin{aligned}&\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \Psi \\&+ \frac{8\pi^2\mu}{h^2} \left(\frac{Ze^{-2}}{r} + E \right) \Psi = 0\end{aligned}\quad \dots(6.9)$$

Substituting Ψ from equation 6.8 in equation 6.9

$$\begin{aligned}&\frac{1}{r^2} \left[\Theta(\theta) \Phi(\phi) \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{R(r) \Phi(\phi)}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) \right] \\&+ \frac{R(r) \Theta(\theta)}{\sin^2\theta} \frac{d^2\Phi(\phi)}{d\phi^2} + \frac{8\pi^2\mu}{h^2} \left(\frac{ze^{-2}}{r} + E \right) R(r) \Theta(\theta) \Phi(\phi) = 0\end{aligned}\quad \dots(6.10)$$

Multiplying throughout by $r^2/R(r)\Theta(\theta)\Phi(\phi)$ we get

$$\begin{aligned}&\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{1}{\Theta\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) + \\&\frac{1}{\Phi(\phi)\sin^2\theta} \frac{d^2\Phi(\phi)}{d\phi^2} + \frac{8\pi^2\mu r^2}{h^2} \left(E + \frac{Ze^{-2}}{r} \right) = 0\end{aligned}\quad \dots(6.11)$$

Or

$$\begin{aligned}&\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{8\pi^2\mu r^2}{h^2} \left(E + \frac{Ze^{-2}}{r} \right) = \frac{1}{\Theta(\phi)\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) \\&- \frac{1}{\Phi(\phi)\sin^2\theta} \frac{d^2\Phi(\phi)}{d\phi^2}\end{aligned}\quad \dots(6.12)$$

Both the sides of equation 6.12 are equal to one constant $l(l+1)$ (say). Therefore, this equation can be separated into (i) Radial equation (involving radial part of function).

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{8\pi^2\mu r^2}{h^2} \left(E + \frac{Ze^{-2}}{r} \right) = l(l+1) \quad \dots(6.13)$$

and

(ii) The angular equation (involving angular part of the function).

$$\frac{1}{\Theta(\theta)\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) + \frac{1}{\Phi(\phi)\sin^2\theta} \frac{d^2\Phi(\phi)}{d\phi^2} = -l(l+1) \quad \dots(6.14)$$

Equation 6.14 can be further separated into two equations involving θ & ϕ parts of the wave function. For this purpose, multiply this equation by $\sin^2\theta$ and rearrange it.

$$\frac{\sin\theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) + l(l+1)\sin^2\theta = -\frac{1}{\Phi(\phi)} \frac{d^2\Phi(\phi)}{d\phi^2} \quad \dots(6.15)$$

Both the sides of equation 6.15 are equal to a constant m^2 say. Therefore, we get

$$\frac{\sin\theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) + l(l+1)\sin^2\theta = m^2 \quad \dots(6.16)$$

And

$$\frac{1}{\Phi(\phi)} \frac{d^2\Phi(\phi)}{d\phi^2} = -m^2 \quad \dots(6.17)$$

So, Schrodinger equation for H-atom can be resolved into three equations viz.

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{8\pi^2\mu r^2}{b^2} \left(E + \frac{Ze^{-2}}{r} \right) = l(l+1) \quad \dots(6.13)$$

$$\frac{\sin\theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) + l(l+1)\sin^2\theta = m^2 \quad \dots(6.16)$$

And

$$\frac{1}{\Phi(\phi)} \frac{d^2\Phi(\phi)}{d\phi^2} = -m^2 \quad \dots(6.17)$$

The acceptable solutions of these equations provide the information for $R(r)$ $\Theta(\theta)$ and $\Phi(\phi)$ parts of wave function and energy of electron can be obtained from $R(r)$ equation i.e. equation 6.13.

6.2 ACCEPTABLE SOLUTION FOR ϕ EQUATION

Equation 6.17 is equation involving ϕ i.e.

$$\frac{1}{\Phi(\phi)} \frac{d^2\Phi(\phi)}{d\phi^2} = -m^2 \quad \dots(6.17)$$

Its acceptable solution has already been discussed in chapter 5 in case of a rigid rotator. Its acceptable solution is

$$\phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad \dots(6.18)$$

where

$$m = 0, \pm 1, \pm 2, \dots$$

m is magnetic quantum number here and it represents the quantization of z-component of angular momentum

$$\text{as } (\hat{L}_z) \left[\frac{1}{\sqrt{2\pi}} \exp(im\phi) \right] = \frac{\hbar}{2\pi i} \frac{\partial}{\partial\phi} \left[\frac{1}{\sqrt{2\pi}} \exp(im\phi) \right] \quad \dots(6.19)$$

or it is equal to

$$= \frac{mh}{2\pi} \left[\frac{1}{\sqrt{2\pi}} \exp(im\phi) \right] \quad \dots(6.20)$$

Therefore, the permitted L_z values for moving electron i.e. values for z-components of angular momentum of electron are $m\hbar$ or $mh/2\pi$.

6.3 ACCEPTABLE SOLUTION FOR $\Theta(\theta)$ EQUATION

Equation involving $\Theta(\theta)$ part of the wave function is

$$\frac{\Theta \sin}{(\theta)} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta(\theta)}{d\theta} \right) + l(l+1) \sin^2\theta = m^2 \quad \dots(6.16)$$

The acceptable solution for this equation as per rigid rotator problem is

$$\Theta_{l,m} = \left[\frac{(2l+1)}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}} P_l^{|m|} \quad \dots(6.21)$$

$$\text{where } P_l^{|m|} = (1-\chi^2)^{\frac{|m|}{2}} \frac{d^{|m|} P_l}{d\chi^{|m|}} \quad \dots(6.22)$$

The associated Legendre polynomials

$$\text{and } P_l = \frac{1}{2^l l!} \frac{d^l}{d\chi^l} (x^2 - 1)^l \quad \dots(6.23)$$

The Legendre polynomials and

$$\chi = \cos\theta \quad \dots(6.24)$$

The above solutions are valid with the following condition

$$l = 0, 1, 2, 3, \dots \dots \dots \dots(6.25)$$

and $m = 0, \pm 1, \pm 2, \pm 3 \dots \dots \dots \dots(6.26)$

The quantum number l is known as azimuthal or subsidiary quantum number and it represents the quantization of total angular momentum of electron according to the following equation

$$\hat{L}_{op} \Theta_{l,m} = \sqrt{l(l+1)} \frac{\hbar}{2\pi} \Theta_{l,m} \quad \dots(6.27)$$

or

$$\hat{L}^{\Theta} \Theta_{l,m} = \sqrt{l(l+1)} \hbar \Theta_{l,m} \quad \dots(6.27)$$

6.4 ACCEPTABLE SOLUTION FOR R(r) EQUATION

Equation involving $R(r)$ part of the wave function is

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} \left(E + \frac{Ze^2}{r} \right) = l(l+1) \quad \dots(6.13)$$

Using suitable transformation it is possible to write this equation in most familiar form known as associated Laguerre Equation

$$\rho^2 \frac{d^2 L}{d\rho^2} + (j+1-\rho) \frac{dL}{d\rho} + (k-j) L = 0 \quad \dots(6.28)$$

where $R(r)$ function can be expressed as

$$R(r) = S(\rho) = e^{-\rho/2} F(\rho)$$

$$\text{or } e^{-\rho/2} \rho^j L(\rho) \quad \dots(6.29)$$

where terms ρ, j and k are given by

$$\rho = 2\alpha r \quad \dots(6.30)$$

$$j = 2l + 1 \quad \dots(6.31)$$

$$k = \lambda + l \quad \dots(6.32)$$

$$\text{and } \alpha^2 = -8\pi^2 \mu E / h^2 \quad \dots(6.33)$$

$$\text{and } \lambda = \frac{4\pi^2 \mu z e^2}{h^2 \alpha} \quad \dots(6.34)$$

Solution of equation 6.28 is

$$L = L_k^j = \frac{d^j}{dp^j} L_k \quad \dots(6.35)$$

where L_k is Laguerre polynomials of degree k

$$L_k = l^p \frac{d^k}{dp^k} (p^k e^{-p}) \quad \dots(6.36)$$

For acceptable solution

$$k = 1, 2, 3, \dots \infty \quad \dots(6.37)$$

This quantum restriction leads to the fact that λ which is equal to $k - l$ must also be an integer of l be written as n, therefore

$$k = n + l \quad \dots(6.38)$$

So the function R is given by

$$R(r) = p^l e^{-p/2} L_{n+l}^{2l+1} \quad \dots(6.39)$$

Normalization of above function leads to

$$\int_0^\infty R(r)^* R(r) r^2 dr = 1 \quad \dots(6.40)$$

we get $R = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{n-l-1}{2n[(n+1)!]^3} \right\}^{1/2} p^l e^{p/2} L_{n+l}^{2l+1} \quad \dots(6.41)$

where $p = (2\alpha r) = 2 \left(\frac{4\pi\mu Ze^2}{nh^2} \right) \text{ or } = \left(\frac{2Z}{na_0} \right) r \quad \dots(6.42)$

and $a_0 = \frac{\hbar^2}{4\pi^2 m e^2} \quad \dots(6.43)$

The constant n is referred to as principal quantum number. The associated Laguerre polynomical is not to vanish, we have

$$j \leq k \quad \dots(6.44)$$

Or $(2l+1) \leq (n+l) \quad \dots(6.45)$

[as $J = 2L + 1$

and $k = n+l] \quad \dots(6.46)$

or $l + 1 \leq n \quad \dots(6.46)$

or $l \leq n - 1 \quad \dots(6.47)$

The principal quantum number n may be any positive integer

$$n = 1, 2, 3, 4, \dots \quad \dots(6.48)$$

so allowed values for l are

$$l = 0, 1, 2, \dots, (n-1) \quad \dots(6.49)$$

6.5 ENERGY OF H-ATOM

As from operation (6.3)

$$\alpha^2 = \frac{-8\pi^2\mu E}{h^2} \quad \dots(6.33)$$

And from equation 6.34

$$\alpha = \frac{4\pi^2\mu z e^2}{\lambda h^2} \text{ or } \frac{4\pi^2\mu z e^2}{\eta h^2} \quad \dots(6.34)$$

Substituting value of α in equation 6.33

$$\begin{aligned} \left(\frac{4\pi^2\mu z e^2}{\eta h^2} \right)^2 &= \frac{-8\pi^2\mu E}{h^2} \\ \text{or } \frac{16\pi^4\mu^2 z^2 e^4}{\eta^2 h^4} &= \frac{-8\pi^2\mu E}{h^2} \\ \Rightarrow \frac{-2\pi^2 z^2 e^4 \mu}{\eta^2 h^2} & \end{aligned} \quad \dots(6.50)$$

This energy expression is identical with the energy expression as derived by Niels Bohr in Bohr's Theory.

6.6 ENERGY IN ATOMIC UNITS (Au)

Quantum chemical calculations can also be performed in atomic units (a.u) in which Eigen Values and Eigen functions are usually expressed. Table 6.1 shows the respective quantities in atomic units (a.u.).

The quantity of interest so far as quantum chemistry is concerned is energy can be deduced from the radial part of the equation whose rearranged form may be written as :

$$\left\{ \frac{-h^2}{8\pi^2 m} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] - \frac{Ze^2}{(4\pi\epsilon_0)r} \right\} R(r) = ER(r) \quad \dots(6.13)$$

It has been shown that energy from this equation is

$$E = -\frac{1}{\eta^2} \left(\frac{2\pi\mu z^2 e^4}{h^2} \right) \quad \dots(6.50)$$

TABLE 6.1 VALUES OF SOME QUANTITIES IN A.U.

<i>Quantity</i>	<i>Value in S.I Units</i>	<i>value in a.u.</i>
1. Mass of electron (m)	$9.11 \times 10^{-31} \text{ kg}$	1 a.u
2. Charge of Electron (e)	$1.602 \times 10^{-19} \text{ C}$	-1 a.u
3. Bohr radius $\left(a_0 = \frac{(4\pi\epsilon_0)h}{4\pi^2 me^2} \right)$	$0.529 \times 10^{-10} \text{ m}$	1 a.u
4. Angular momentum	$1.055 \times 10^{-34} \text{ Js}$	1.a.u
5. Energy of electron in first Bohr's orbit of H-atom	$-2.176 \times 10^{-19} \text{ J}$	$-\frac{1}{2} \text{ a.u}$
6. Permittivity constant ($4\pi\epsilon_0$)	$1.113 \times 10^{-10} \text{ Fm}^{-1}$	1.a.u

In atomic units

 $m = 1$ and $e = 1$ therefore this equation becomes

$$\left\{ -\frac{1}{2} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] - \frac{z}{r} \right\} R(r) = E R(r) \quad \dots (6.51)$$

and $E = \frac{-Z^2}{2\eta^2}$... (6.52)

In case of H-atom $Z = 1$ therefore

$$E = -\frac{1}{2} \text{ a.u.}$$

and $R = R_{(1,0)}^{(r)} = 2e^{-r} \text{ a.u}$

For any radial function $R_{n,l}(r)$ the eigen value can be obtained by solving equation (6.51) for example for H-atom in ground state the L.H.S. of this equation is

$$\begin{aligned} & \frac{-1}{2r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} (2e^{-r}) \right] - \frac{2e^{-r}}{r} \\ &= \frac{-1}{2r^2} \frac{d}{dr} [(-2r^2 e^{-r})] - \frac{2e^{-r}}{r} \end{aligned} \quad \dots (6.53)$$

$$= \frac{-1}{2r^2} [-4re^{-r} + 2r^2 e^{-r}] - \frac{2e^{-r}}{r} = -\frac{1}{2} (2e^{-r}) \quad \dots (6.54)$$

The R.H.S. of the equation 6.51 is

$$E (2e^{-r}) = E = -\frac{1}{2}$$

6.7 QUANTUM NUMBERS AND THEIR SIGNIFICANCE

As it is clear from the discussion given in the previous sections that Quantum numbers viz. n, l, m are the solutions of one or the other partial Schrodinger wave equation as set up for H-atom. ' n ' the principal quantum number is the solution of radial part or $R(r)$ part Equation as set up for H-atom (refer section 6.4). Similarly l and m i.e. azimuthal and magnetic quantum numbers are the solution of Scrodinger equation involving angular part of the function i.e. $Y(\theta, \phi)$ (refer section 6.2 and 6.3). Their values are interdependent on each other as shown previously in section 6.4. The principal quantum numbers n may be any positive number.

$$n = 1, 2, 3, 4, \dots \dots \dots \quad \dots(6.48)$$

and allowed values for l are

$$l = 0, 1, 2, 3, \dots \dots \dots (n-1) \quad \dots(6.49)$$

Similarly, value of m depends upon the value of l & m may have values

$$m = 0, \pm 1, \pm 2, \dots \dots \pm l \quad \dots(6.55)$$

They together form angular and radial part of the wave function as obtained for H-atom. m quantum number accounts for the quantization of z-component of angular momentum i.e. L_z value as L_z for moving electron is mh or $mh/2\pi$

l quantum number accounts for the total angular momentum L for moving electron as

$$\hat{L}^2 \Theta_{l,m} = L^2 \Theta_{l,m} \quad \dots(6.27)$$

and L^2 Eigen value is $\sqrt{l(l+1)} h$

n or principal quantum number is associated with energy level of the electron i.e. orbit of moving electron as

$$E \propto -\frac{1}{n^2}$$

or

$$E = -\frac{1}{n^2} \left(\frac{2\pi\mu e^4}{h^2} \right) \quad \dots(6.50)$$

In brief significance of quantum numbers can be summarised as

(a) **Principal quantum number (n)** has significance in deciding no. of orbit of electron and its corresponding energy level. ' n ' quantum number also provides the information of number of electron in n^{th} orbit as it is equal to $2n^2$.

(b) **Azumithal quantum number (l)** has significance in deciding the quantization of total angular momentum of moving electron and no. of electrons in orbital can also be given by the formula $2(2l+1)$, as no. of electron in different orbitals are given by

l	=	0	1	2	3....
orbital set	=	s	p	d	f.....
No. of electron	=	2	6	5	10....
		$2(2l+1)$			

(c) **Magnetic quantum number (m)** decides the magnetic orientation of moving electron in any orbital or it decides about ascertaining the value of z-component of angular momentum of moving electron as L_z value $m\hbar$ or $mh/2\pi$.

6.8 TOTAL WAVE FUNCTION FOR HYDROGEN LIKE ATOM

The complete wave function for H-like atom may be written as

$$\Psi_{n,l,m}(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad \dots (6.56)$$

$$\text{or} \quad = R(r) Y(\theta, \phi) \quad \dots (6.57)$$

Table 6.2 contains some normalized wave functions for H-like atom.

TABLE 6.2 : NORMALIZED WAVE FUNCTIONS FOR H-LIKE ATOM

<i>n</i>	<i>energy in (au)</i>	$\Psi_{n,l,m}$ (<i>in a.u.</i>)
1	$E_1 = \frac{-Z^2}{2}$	$\Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr}$
2	$E_2 = -\frac{Z^2}{8}$	$\Psi_{(2,0,0)} = \frac{1}{\sqrt{32\pi}} Z^{3/2} (2-Zr) e^{-Zr/2}$ $\Psi_{(2,1,0)} = \frac{1}{\sqrt{32\pi}} Z^{5/2} r e^{-Zr/2} \cos\theta$ $\Psi_{(2,1,1)} = \frac{1}{\sqrt{64\pi}} Z^{5/2} r e^{-Zr/2} \sin\theta e^{i\phi}$ $\Psi_{(2,1,-1)} = \frac{1}{\sqrt{64\pi}} Z^{5/2} r e^{-Zr/2} \sin\theta e^{-i\phi}$

6.9 RADIAL PROBABILITY DISTRIBUTION FUNCTIONS (RPDF)

Probability distribution graphs including only the radial part of wave function as solved for H-like atom considering atomic space as sphere are known as radial probability distribution functions (or RPDF). These functions may be expressed as follows

$$\int_{\text{over whole space}} 4\pi r^2 \Psi(r) dr..... \quad \dots (6.58)$$

Or

$$\int_{\text{over whole atomic space}} 4\pi r^2 R^2(r) dr \quad \dots (6.59)$$

Plots of radial probability distribution functions on the basis of above equations 6.58 or 6.59 are given in fig. 6.1 for various orbitals. These plots provide the information of probability of finding electron within the spherical atomic space of radius 'r'.

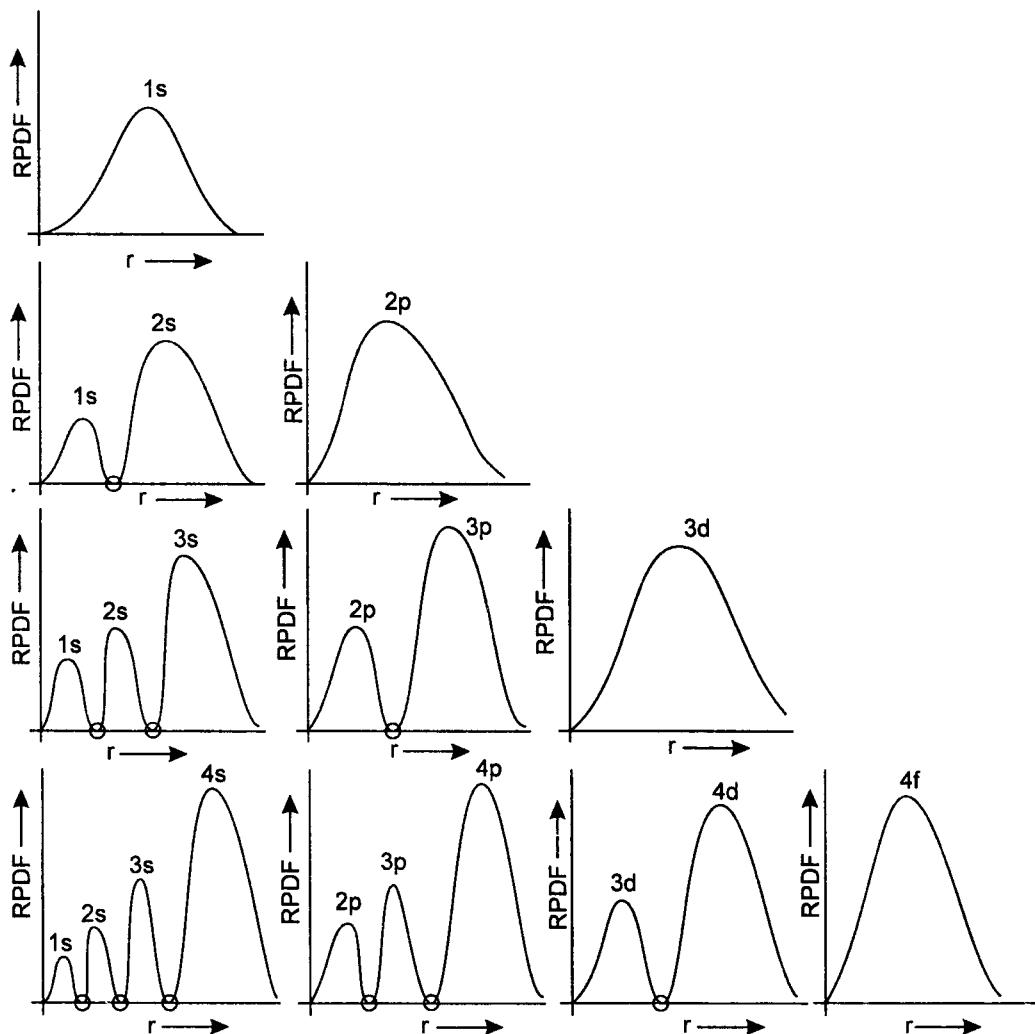


Fig. 6.1 : RPDF Plots for various orbital sets

'n' in the RPDF plots denote the points where the probability with radius becomes zero. These points are known as nodes. Presence of nodes in RPDF plots shows that in atomic space of radius 'r' these are regions where probability of finding electron becomes zero. Taking example of plots for 1s and 2s orbital set, presence of one node in RPDF plot clearly indicates that within the atomic space of radius 'r' after maximum electron density of 1s orbital there is a space where probability is zero, this region is node and after that 2s orbital has maximum probability for electron. In brief this

can be concluded that 1s is inner orbital and after nodal space there is 2s orbital as shown in figure 6.2.

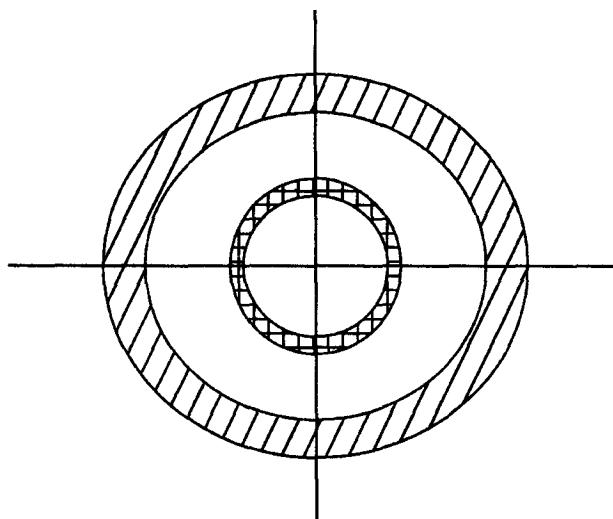


Fig. 6.2

6.10 SHAPES OF ATOMIC ORBITALS

In the last section RPDF have been explained. RPDF accounts for the probability of finding electron in spherical atomic space of radius r . In another method angular part of the wave function viz. spherical harmonics or $Y(\theta, \phi)$ are plotted. This process is similar to the process of drawing contour maps in Geography. For example in case of s-orbital $L = 0$ and symmetry of s orbital will be spherical. Graph of spherical harmonics i.e. $Y(\theta, \phi)$ within the radius r for s-orbital gives the spherical shaped plot. So, this may be concluded that shape of s-orbital is spherical. In case of p-orbital (where $L = 1$) wave function depends upon $r, \theta & \phi$. Quantum numbers $l & m$ are included in $\theta & \phi$ part of wave function. Shapes of orbital is basically governed by $Y(\theta, \phi)$. For example in case of $2p_z$ orbital wave function is

$$\Psi_{2p_z} = R_{2,1}(r) \cos \theta \quad \dots(6.60)$$

Above equation explains that at $\theta=\pi/2$ i.e. at x-y plane probability of finding electron is zero. Therefore, this can be concluded that orbital is distributed on z-axis above and below x-y plane. Function of $2p_z$ is independent of ϕ part. Therefore, this may be concluded that shape of $2p_z$ is dumbbell with +ve and -ve lobes. Similarly, this can be shown that in case of $2p_x$ and $2p_y$ orbitals y-z and x-z are the nodal planes. In case of atomic orbitals it is a significant fact that in their shapes Ψ is -ve also. This may be significant as Ψ is not at all important but it is Ψ^2 or $\Psi\Psi^*$ which is significant.

In case of d-orbitals (where $l=2$) the study of spherical harmonics shows that d-orbital set is a superimposition of two orbitals and it contains four electron density areas which are separated by two nodal planes. Shapes of s, p & d orbitals are given in fig. 6.3 as it is complicated to explain the shapes of f and g orbitals.

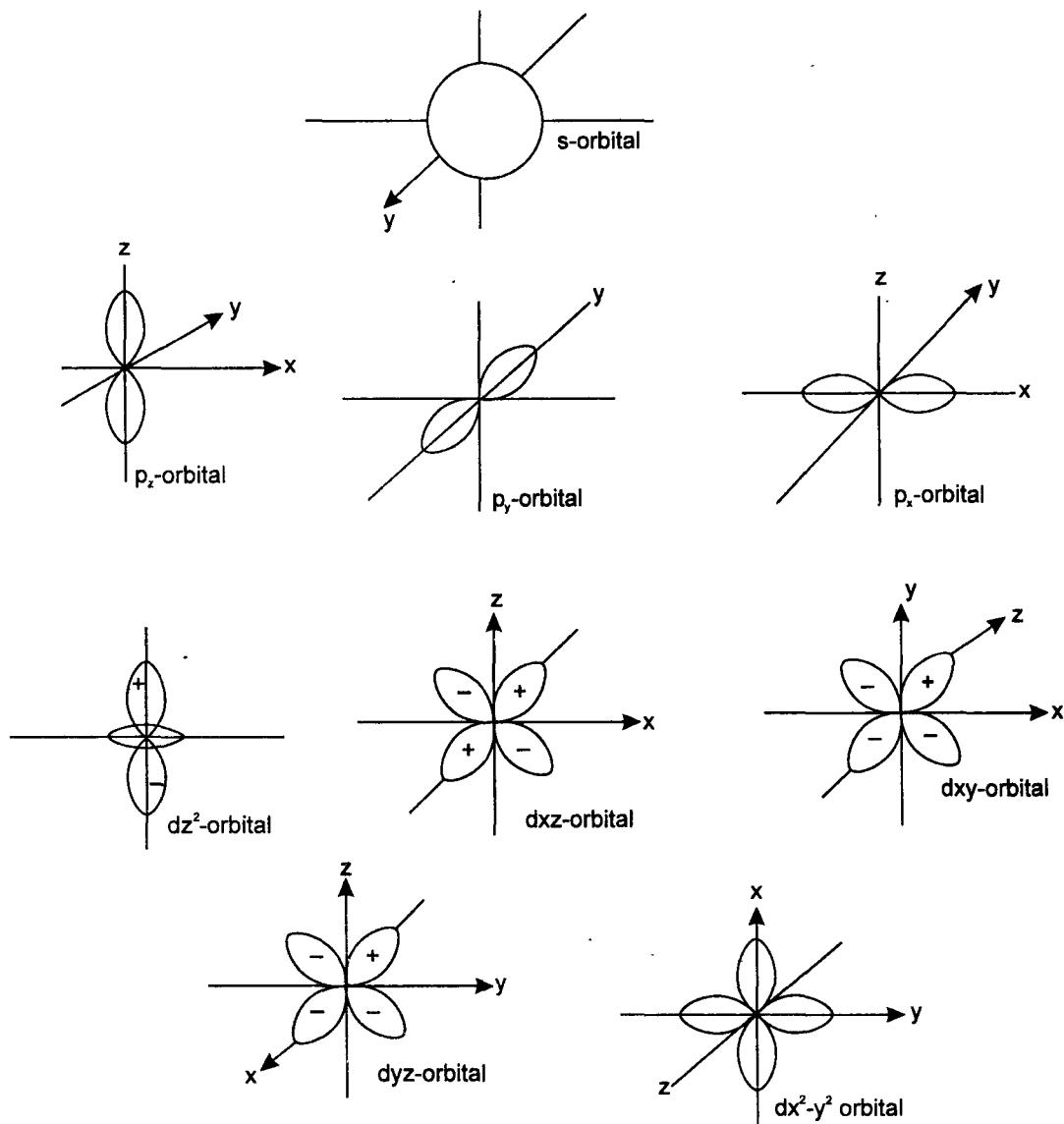


Fig. 6.3 shapes of different orbitals

6.11 ENERGY LEVELS AND DEGENERACY OF ORBITALS

As according to equation 6.50 it is clear that energy of hydrogenic wave functions depend only on the principal quantum number 'n'. The number of wave functions (orbitals) with different values of l and m but same value of n can be explained as follows :- For each value of n , the angular momentum, quantum number or azimuthal quantum number l can have values $0, 1, 2, \dots, n-1$ and for each value of l , m can have values $0, \pm 1, \pm 2, \pm 3, \dots, \pm l$ resulting $(2l+1)$ different sets of orbitals (or wave functions). Therefore, total number of orbitals for each value of n are given by

$$\sum (2l+1) = 1 + 3 + \dots + (2n-1) \quad \dots(6.61)$$

$$= \frac{n}{2} [2 + (n-1)2] = n^2 \quad \dots(6.61)$$

Therefore, no. of orbitals (or wave functions) having same value of energy is n^2 in case of hydrogenic wave functions. For $n = 1$ these are non-degenerate wave functions and for $n=2$ wave functions are with 2^2 -fold degeneracy and so on. The energy levels diagram with the relative degeneracy of orbitals is shown in figure 6.4

6.12 SPECTRA OF HYDROGEN LIKE ATOM

As energy of Hydrogen like atom can be expressed as

$$E_n = \frac{-1}{n^2} \left(\frac{2\pi^2 \mu z^2 e^4}{h^2} \right) \quad \dots(6.50)$$

or

$$E_n = \frac{-z^2 R_H hc}{n^2} \quad \dots(6.62)$$

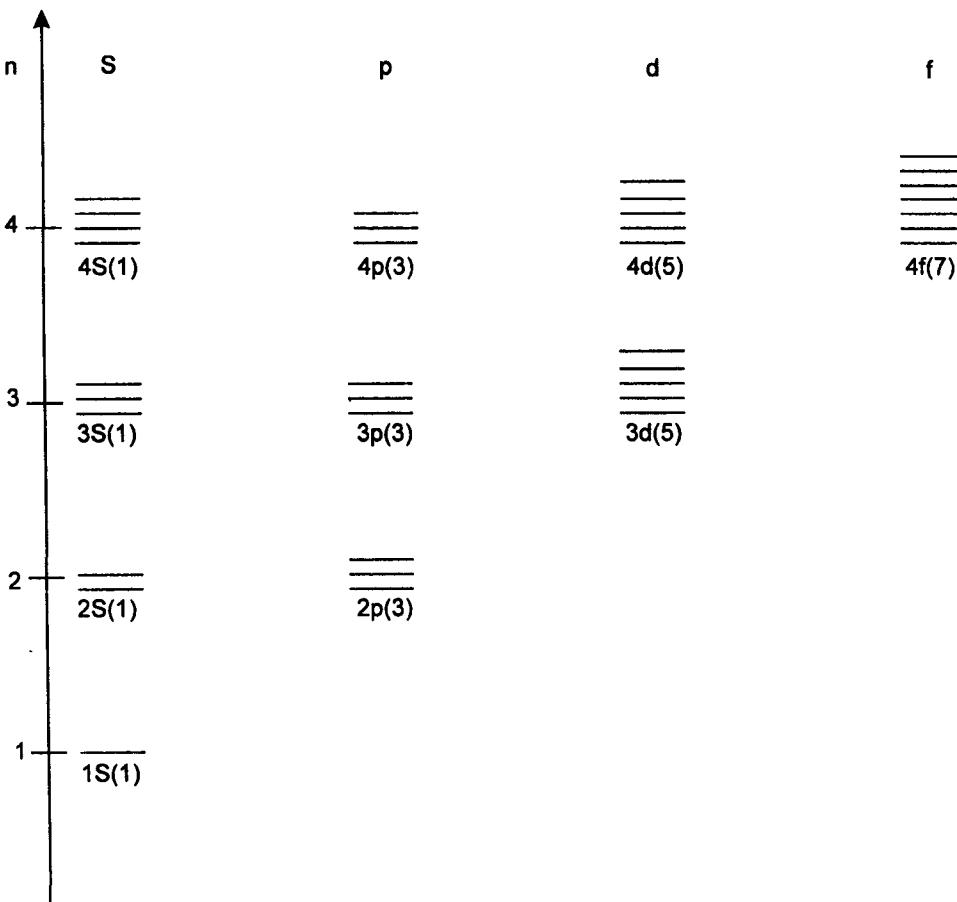


Fig. 6.4 Energy level diagram for atomic orbitals for H-atom

where R_H is hydberg's constant

$$R_H = \frac{hc^4}{8\epsilon_0^2 h^3 c}$$

In terms of wave number ν

$$\bar{\nu} = \frac{E_n}{hc} = \frac{-Z^2 R_H}{\eta^2} \quad \dots (6.63)$$

or $\Delta \nu$ (or energy in wave no units)

$$= Z^2 R_H \left[\frac{1}{\eta_1^2} - \frac{1}{\eta_2^2} \right] \quad \eta_2 > \eta_1 \quad \dots (6.64)$$

The fate of a transition can be decided on the basis of selection rules which can be framed on the basis of transition moment integral i.e.

$$\int \Psi_1, \hat{\mu} \Psi_2 d\tau \quad \dots (6.65)$$

where Ψ_1 , & Ψ_2 are wave functions of two different electronic states and if $\hat{\mu}$ is dipole moment operator. For allowed transition the integral given in equation 6.65, this should have value one or finite value but for forbidden transition this integral should have value zero. Therefore, the selection rules for Hydrogen like atom are

- (i) $\Delta n = (n_2 - n_1) =$ any integer means Δn can be any integer thus reproducing all the spectral lines of H-atom i.e. Lyman, Balmer, Paschen series, etc. This rule is in accordance to Bohr's postulate of transition between two energy levels.

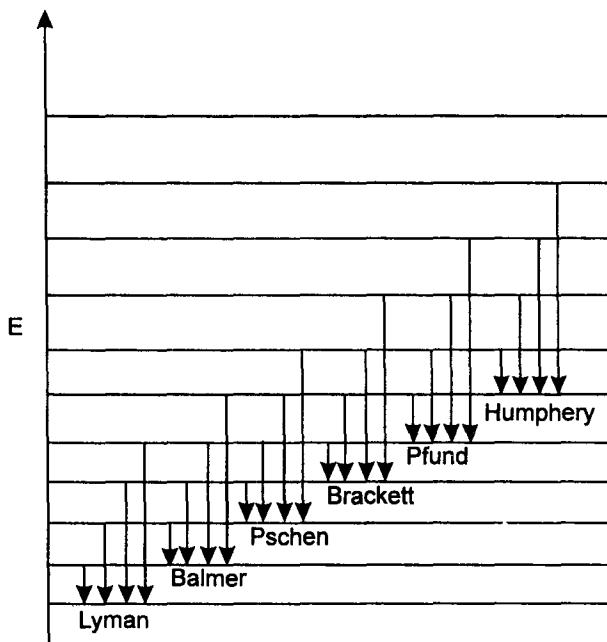


Fig. 6.5 : Spectral transitions for H – like atom

$$(ii) \Delta l = l_2 - l_1 = \pm 1$$

This means that the difference between angular momentum, quantum number or azimuthal quantum number of two states involved in transitions can never be greater or less than that of one. Therefore, $s \rightarrow p$, $p \rightarrow d$ and $d \rightarrow f$ for which $\Delta l = \pm 1$ are allowed transitions and $s \rightarrow s$, $p \rightarrow p$ and $d \rightarrow d$ or $s \rightarrow d$ or $s \rightarrow f$ transition for which $\Delta l = 0$ are forbidden transitions.

$$(iii) \Delta m = 0, \pm 1$$

This means that a spectral transition must be accompanied with change in magnetic quantum number as $\Delta m = 0$ or ± 1 . For hydrogen like atoms, these rules must be satisfied for any allowed transition. Transitions as $3d$ to $3p$ or $4f$ orbitals are allowed by selection rules only if $\Delta m = 0$ or ± 1 . The spectral transitions for H-like atom are shown in fig. 6.5

6.13 ELECTRON SPIN

In the study of atomic spectral lines in case of alkali metals, in presence of non-homogeneous magnetic field, it was found that these lines get sharply divided into doublets. This multiplicity does not appear if electron is assumed to have no properties other than mass and charge as it was observed and discussed for Hydrogen like atom. The explanation of the occurrence of doublet in this way was given by Unlenbeck and Ganschmidt who proposed this observation on the basis of electron spins around its own axis. As a result of which it will have a spin (or intrinsic) angular momentum of rotation about its own axis. This is discussed later in another chapter.

Example 6.1 : Calculate probability density for a $1s$ electron at nucleus.

Given $\Psi_{1s} = \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} e^{-Zr/a_0}$

At nucleus $r = 0$

$$\Rightarrow |\Psi_{1s}|^2 = \left[\left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} \right]^2 \\ = 2.15 \times 10^{-6} Z^3 \text{ nm}^{-3}$$

If $Z = 1$ as in case of H-atom

$$|\Psi_{1s}|^2 = 2.15 \times 10^{-6} \text{ nm}^{-3}$$

Example 6.2 : Making use of the Ψ_{1s} given in example 6.1. Prove that for H-atom in such a state the most probable distance from the proton to the electron is a_0 .

For s orbital

For $\text{RPDF} = r^2 R^2 = 4\pi r^2 \Psi^2$

And in case of H-atom $Z=1$

$$\Psi_{1s} = (\pi a_0^3)^{-1/2} e^{-r/a_0}$$

So, applying rule of maxima for most probable distance.

$$\frac{d}{dr} \left[4\pi r^2 (\pi a_0^3)^{-1} e^{-2r/a_0} \right] = 0$$

$$\Rightarrow \left(\frac{4\pi}{\pi a_0^3} \right) \left\{ 2r e^{-2r/a_0} - \frac{2}{a_0} r^2 e^{-2r/a_0} \right\} = 0$$

Or

$$\left(\frac{4\pi}{a_0^3} \right) e^{-2r/a_0} \left[2r - \frac{2r^2}{a_0} \right] = 0$$

In above equation since exponential function cannot be zero therefore, the term in [] square bracket will be zero

$$= 2r - \frac{2r^2}{a_0} = 0$$

$$= 2r = \frac{2r^2}{a_0}$$

Or

$r = a_0$ Hence proved

Example 6.3 : Predict that transition from 3d to 3p will be allowed or forbidden.

According to selection rule (i) $\Delta n =$ any integer for electronic states involved in a transition

For transition $3d \rightarrow 3p$, Δn is not an integer.

According to selection rule (ii) $\Delta l = \pm 1$ for electronic states involved in a transition and according to selection rule (iii) $\Delta m = 0, \pm 1$. Therefore, transition $3d \rightarrow 3p$ may be allowed if and only if $\Delta m = 0, \pm 1$ i.e. change in magnetic quantum number should be either zero or ± 1 .

PROBLEMS SET-6

- Set up and write Schrodinger wave equation for H-atom (see section 6.1).
- Write three simpler resolved equations for H-atom in terms of $R(r)$ $\Theta(\theta)$ & $\phi(\phi)$ (See section 6.1)
- Discuss the acceptable solution for $\phi(\phi)$ part equation (See section 6.2).
- Discuss acceptable solution for (θ) part of equation as set up for H-atom (see section 6.3).
- Give acceptable solution for $R(r)$ part of equation as set up for H-atom (See section 6.4).
- Derive the expression for energy for H-atom (See section 6.5).
- Derive the expression for energy for H-atom in atomic units (a.u)(see section 6.6).
- What are quantum numbers ? Give their significance (See section 6.7).
- Write about orbital angular momentum of electrons (See section 6.3).
- Write total wave function for H-like atom (See section 6.8).
- Write a note on Radial Probability Distribution function. What is the significance of RPDF ? (See section 6.9).
- How can shapes of different orbitals be explained (See section 6.10).
- Discuss the energy levels and degeneracy of atomic orbitals. (See section 6.11).
- Explain the spectra for H-like atom. (See section 6.12).
- What do you understand by electron spin? (See section 6.13).

SECTION-3

- 7. Introduction to Approximate Methods**
 - 8. Variation Theorem and its Application**
 - 9. Perturbation Method and its Application**
 - 10. Introduction to Angular Momentum**
 - 11. Electron Spin and Related Concepts**
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CHAPTER-7

Introduction to Approximate Methods

SYNOPSIS

<i>Section</i>	<i>Topics</i>
7.1	Variation Theorem
7.2	Perturbation method
7.3	Introduction to multi electron system

Exact solution for Schrodinger equation as set up for a one-electron system is possible. Even this solution is possible with lengthy mathematical calculations. This difficulty is because of presence of potential energy term in the hamiltonian for single electron system there is only one potential energy term viz. $-Ze^2/r$. In case of multielectron system, electron and nuclei interact with each other as a result of which many potential energy terms may be included in Hamiltonian operator or such systems. For simplicity in such cases one has to make use of approximate methods for calculations. The important and significant approximate methods are (i) variation theorem and (ii) perturbation method.

7.1 VARIATION THEOREM

This theorem says that with any trial function Ψ the expectation value of energy E will be greater than the true value E_0 which is the lowest energy Eigen value of the Hamiltonian operator of the system

$$E \geq E_0 \quad \dots (7.1)$$

Proof of the theorem

Let the trial function Ψ is a combination of set of normalized and orthogonal Eigen functions $\phi_1, \phi_2, \phi_3, \dots$ and for the same system energy values are E_1, E_2, E_3, \dots

$$\Psi = a_1 \phi_1 + a_2 \phi_2 + a_3 \phi_3 \dots \dots \dots \dots (7.2)$$

Schrodinger equation is

$$\hat{H} \phi_i = E \phi_i \quad \dots(7.3)$$

$$(i = 1, 2, 3 \dots)$$

Applying normalization condition

$$\int \Psi^2 d\tau$$

$$= \int [a_1 \phi_1 + a_2 \phi_2 + \dots]^2 d\tau = 1 \quad \dots(7.4)$$

$$\text{Or } [a_1^2 \int \phi_1^2 d\tau + a_2^2 \int \phi_2^2 d\tau + a_3^2 \int \phi_3^2 d\tau + \dots]$$

$$+ [a_1 a_2 \int \phi_1 \phi_2 d\tau + a_1 a_3 \int \phi_1 \phi_3 d\tau + \dots + a_2 a_3 \int \phi_2 \phi_3 d\tau + \dots] = 1 \quad \dots(7.5)$$

As ϕ 's are orthogonal to each other and normalized itself, so,

$$a_1^2 + a_2^2 + a_3^2 = 1 \quad \dots(7.6)$$

According to the postulate of quantum mechanics average energy of Eigen values of equation 7.3 is calculated according to the following formula

$$\bar{E} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \quad \dots(7.7)$$

Let us choose the trial function

$$\Psi = a_1 \phi_1 + a_2 \phi_2$$

$$\Rightarrow \bar{E} = \frac{\int (a_1 \phi_1 + a_2 \phi_2) \hat{H} (a_1 \phi_1 + a_2 \phi_2) d\tau}{\int (a_1 \phi_1 + a_2 \phi_2) (a_1 \phi_1 + a_2 \phi_2) d\tau} \quad \dots(7.8)$$

$$\Rightarrow \bar{E} = \frac{a_1^2 \int \phi_1 \hat{H} \phi_1 d\tau + a_2^2 \int \phi_2 \hat{H} \phi_2 d\tau + a_1 a_2 \int \phi_1 \hat{H} \phi_2 d\tau + a_2 a_1 \int \phi_2 \hat{H} \phi_1 d\tau}{a_1^2 \int \phi_1^2 d\tau + a_2^2 \int \phi_2^2 d\tau + 2 a_1 a_2 \int \phi_1 \phi_2 d\tau} \quad \dots(7.9)$$

As ϕ 's are orthonormal set of wave function

$$\Rightarrow \int \phi_1^2 d\tau = \int \phi_2^2 d\tau = 1 \quad \dots(7.10)$$

and

$$\int \phi_1 \phi_2 d\tau = \int \phi_2 \phi_1 d\tau = 0 \quad \dots(7.11)$$

$$\hat{H} \phi_1 = E \phi_1$$

$$\text{Similarly } \hat{H} \phi_2 = E_2 \phi_2 \quad \dots(7.12)$$

and

$$\Rightarrow \bar{E} = \frac{a_1^2 E + a_2^2 E}{a_1^2 + a_2^2} \quad \dots(7.13)$$

$$\Rightarrow \bar{E} = a_1^2 E + a_2^2 E_2 \quad \dots(7.14)$$

as from equation 7.6

$$a_1^2 + a_2^2 + \dots = 1$$

If E_0 is the lowest value of energy

$$\bar{E} - E_0 = (a_1 E_1 + a_2^2 E_2) - (a_1^2 + a_2^2) E_0 \quad \dots(7.15)$$

$$= a_1^2 (E_1 - E_0) + a_2^2 (E_2 - E_0) \quad \dots(7.16)$$

As E_0 is the lowest energy of the system

$E_1 > E_0$ and $E_2 > E_0$ while a_1^2 and a_2^2 are always positive, hence $E - E_0$ is always positive

or $E > E_0$ Hence proved

In order to apply the variation theorem, the following steps have to be applied in sequence

(i) Make a good guess of well behaved trial functions on the basis of the some physical and/or chemical consideration.

(ii) Calculate \bar{E} in each case

(iii) The value \bar{E} will always be greater than that of E_0 . Therefore, the lowest value among Eigen values so obtained is chosen as this is closest to the true or exact value E_0 . The trial function corresponding to the lowest energy value will be selected as best wave function

7.2 PERTURBATION METHOD

Perturbation method is applied if the system differs slightly from unperturbed state and if energy (E_0) and the wave function (Ψ_0) for the unperturbed state are known for example in case of a harmonic oscillator, hamiltonian may be written as

$$\hat{H} = \frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 \quad \dots(7.17)$$

If perturbed state of the oscillator is taken into account the hamiltonian will be

$$\hat{H} = \frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 + ax^3 + bx^4 \quad \dots(7.18)$$

where $ax^3 + bx^4$ are terms in the Hamiltonian due to perturbation

So, Hamiltonian may be expressed as

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad \dots(7.18)$$

Where \hat{H}' is the extra Hamiltonian terms due to perturbation.

The perturbation theory involves determination of the Eigen function (Ψ_n) Eigen values (E_n) corresponding to the perturbed Hamiltonian (H') in terms of those Ψ_0 & E_0 related to unperturbed Hamiltonian (H_0).

The perturbed Hamiltonian may be written as

$$\hat{H} = \hat{H}_0 + \lambda \hat{H} \quad \dots(7.19)$$

Where $\lambda \hat{H}$ is very small. It is always not possible to identify λ .

The Schrodinger equation may be written as

$$\hat{H}_0 \Psi_0 = E_0 \Psi_0 \text{ (unperturbed state)} \quad \dots(7.20)$$

and

$$\hat{H} \Psi_n = E_0 \Psi_0 \text{ (perturbed state)}$$

or

$$(\hat{H}_0 + \lambda \hat{H}') \Psi_n = E_n \Psi_n \text{ perturbed state} \quad \dots(7.21)$$

Ψ_n & E_n can be expanded in taylor series

$$\Psi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots \quad \dots(7.22)$$

And

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad \dots(7.23)$$

Where $\Psi_n^{(k)}$ and $E_n^{(k)}$ are the k^{th} order correction terms in Ψ_0 and E_0 respectively. In most of the problems in chemistry we go upto $\Psi_n^{(2)}$ and $E_n^{(2)}$ usually..

Therefore

$$\begin{aligned} &= (\hat{H}_0 + \lambda \hat{H}') (\Psi_0 + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots) \\ &= (E_0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (\Psi_0 + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots) \end{aligned} \quad \dots(7.24)$$

On rearranging the equation 7.24 we get

$$\begin{aligned} &(\hat{H}_0 \Psi - E_0 \Psi_0) + \lambda^{(1)} (\hat{H}^0 \Psi_n^{(1)} + \hat{H} \Psi_n^0 - E_n^0 \Psi_n^{(1)} - E_n^{(1)} \Psi_n^0) + \\ &\lambda^{(2)} (\hat{H}^0 \Psi_n^{(2)} + \hat{H} \Psi_n^{(1)} - E_n^{(0)} \Psi_n^{(2)} - E_n^{(1)} \Psi_n^{(1)} - E_n^{(2)} \Psi_n^0) = 0 \end{aligned} \quad \dots(7.25)$$

So, for $\lambda^0 : \hat{H}^0 \Psi_0 = E_0 \Psi_0$...(7.26)

And $\lambda^1 : (\hat{H}^0 - E_n^0) \Psi_n^{(1)} = -\hat{H}' \Psi_n^0 + E_n^{(1)} \Psi_n^0$...(7.27)

And $\lambda^2 : (\hat{H}^0 - E_n^0) \Psi_n^{(2)} = \hat{H}' \Psi_n^{(1)} + E_n^{(1)} \Psi_n^{(1)} + E_n^{(2)} \Psi_n^0$...(7.28)

And so on so forth

Equation 7.26 represents Schrodinger equation for unperturbed state and equation 7.27 and 7.28 are equations for first & second order perturbations respectively.

Usually first order corrections/perturbations are employed to get corrected values for wave function and energy. These correction terms are as under :

First order correction to energy :

As first order equation is

$$(\hat{H}^0 - E_n^0) \Psi_n^{(1)} = -\hat{H}' \Psi_n^0 + E_n^{(1)} \Psi_n^0 \quad \dots(7.27)$$

Multiplying this equation by Ψ and on integrating it

$$\int \Psi_n^{(0)*} \hat{H}' \Psi_n^{(0)} d\tau - E_n^{(1)} \int \Psi_n^{(0)*} \Psi_n^{(0)} d\tau + \\ \int \Psi_n^{(0)*} \hat{H}^0 \Psi_n^{(0)} d\tau - E_n^{(1)} \int \Psi_n^{(0)*} \Psi_n^{(0)} d\tau = 0 \quad \dots(7.29)$$

As \hat{H} is Hermitian operator

$$\int \Psi_n^{(0)*} \hat{H}^0 \Psi_n^{(1)} d\tau = \int \Psi_n^{*(1)} \hat{H}_n^0 \Psi_n^0 d\tau = \int \Psi_n^{*(1)} E_n^{(0)} \Psi_n^0 d\tau$$

Thus, equation 7.24 becomes

$$\int \Psi_n^{(0)*} \hat{H}' \Psi_n^{(1)} d\tau = - E_n^{(1)} \int \Psi_n^{(0)*} \Psi_n^{(0)} d\tau = 0$$

Or $E_n^{(1)} = \int \Psi_n^{(0)*} \hat{H}' \Psi_n^{(1)} d\tau \quad \dots(7.30)$

This is first order corrected energy.

Similarly, first order corrected wave function can also be obtained as

$$\Psi_n^{(1)} = \sum_{m \neq n} \left[\frac{\int \Psi_m^0 \hat{H}' \Psi_n^0 d\tau}{E_n^0 - E_m^0} \right] \Psi_m^0 \quad \dots(7.31)$$

Or $\sum_{m \neq n} \frac{H'_{mn}}{E_n^0 - E_m^0} \quad \dots(7.32)$

7.3 INTRODUCTION TO MULTI-ELECTRON SYSTEM :

As it is discussed earlier in the introduction part of this chapter, that exact solution for one electron system i.e. for Hydrogen atom is possible even by lengthy calculations but exact solutions for multi-electron systems even for two-electron system (i.e. He-atom) are not possible exactly. One has to apply approximation methods for obtaining near exact value. As introduction to approximate methods viz. variation principle and perturbation method are included in this chapter in sections 7.1 & 7.2. In this section, introduction to multi-electron system (i.e. two-electron system) is given.

Considering He-atom as independent electron system Hamiltonian may be written as

$$H(1,2) \text{ or simply } \hat{H} = \left[\frac{-\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) \right] + \left[\frac{-Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{R} \right] \quad \dots(7.33)$$

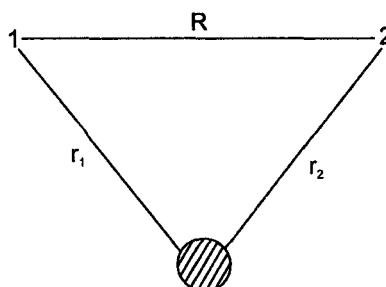


Fig. 7.1 He-atom

In terms of atomic unit Hamiltonian

$$\hat{H} = \frac{-1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{R} \quad \dots(7.34)$$

Schrodinger equation is

$$\hat{H} \Psi = E \Psi \quad \dots(7.35)$$

$$\text{Where } \Psi = \Psi(1,2) = \Psi(x_1, y_1, z_1, x_2, y_2, z_2) \quad \dots(7.36)$$

Considering it as two independent electrons system

$$\hat{H}^0 = \left[-\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} \right] + \left[-\frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} \right] \quad \dots(7.37)$$

(The term $1/R$ is not included in Hamiltonian)

$$\hat{H}^0 = \hat{H}(1) + \hat{H}(2) \quad \dots(7.38)$$

Ψ^0 (the zero order wave function) may be written as

$$\begin{aligned} &= \Psi(1,2) \\ &= \phi(1) \phi(2) \end{aligned} \quad \dots(7.39)$$

And zero order energy as

$$E^0 = E(1) + E(2) \quad \dots(7.40)$$

Here in these equations ϕ 's viz. $\phi(1)$ and (2) are obtital Eigen functions and $E(1)$ & $E(2)$ are orbital Eigen energies and Eigen equation is

$$\hat{H}(i) \phi(i) = E(i) \phi(i) \quad (i = 1, 2) \quad \dots(7.41)$$

$$\begin{aligned} \text{As } \hat{H}^0 \Psi &= [\hat{H}(1) + \hat{H}(2)] \phi(1) \phi(2) \\ &= \hat{H}(1) \phi(1) \phi(2) + \hat{H}(2) \phi(1) \phi(2) \\ &= E(1) \phi(1) \phi(2) + E(2) \phi(1) \phi(2) \\ &= [E_{(1)} + E_{(2)}] \phi(1) \phi(2) \\ \text{or } &= E \Psi \end{aligned} \quad \dots(7.42)$$

The wave function expressed here has its physical significance as $\Psi^2 = \phi(1)^2 \phi(2)^2$. It gives the probability that electron 1 is at point (x_1, y_1, z_1) and electron 2 at (x_2, y_2, z_2) . This implies that $\phi^2(1)$ is independent of $\phi(2)^2$ i.e. probabilities occur independently. Therefore, this model is independent electron model. In the present model zero order wavefunction of the atom is

$$\Psi^{(0)} = ls(1) ls(2) = \frac{Z^3}{\pi} e^{-Zr_1} e^{-Zr_2} \quad \dots(7.43)$$

The corresponding zero order energy is

$$E^0 = E_{ls(1)} + E_{ls(2)}$$

$$= 2 \left(-\frac{1}{2} Z^2 \right) = -Z^2 \text{ atomic units} \quad \dots(7.44)$$

or $E^0 = -4 \text{ a.u.} \quad \dots(7.45)$

As $Z = 2$ in case of He-atom

or $E^0 = -1.74 \times 10^{-17} \text{ J or } -108 \text{ eV} \quad \dots(7.46)$

Experimental value for energy for He-atom is $-1.25 \times 10^{-17} \text{ J or } -78.4 \text{ eV}$.

Therefore, in order to get more exact or near exact values for energy approximate methods can be employed which are included in the further chapters.

PROBLEMS SET-7

1. What is the need of approximate methods in quantum mechanics? (See section – introduction of chapter).
2. What is variation theorem? (See section 7.1)
3. What are the steps of application of variation theorem? (See section 7.1)
4. What is perturbation method? (See section 7.2)
5. What do you understand by first order and higher order perturbations? (See section 7.2)
6. Discuss the independent electron model for He-atom. (See section 7.3)

CHAPTER-8

Variation Theorem and Its Application

SYNOPSIS	
Section	Topics
8.1	L.C.A.O.-M.O. Theory for H_2^+ molecule ion
8.2	Application of variation theorem to He-atom

Approximate methods viz. variation principle and perturbation method have been introduced in chapter 7. Need of such methods in quantum mechanics has also been focused in the same chapter. In this chapter contents related to variation theorem and its application with its use in multi-electron system is being discussed.

As it is introduced in section 7.1, the linear variation theorem states that with any trial function Ψ the expectation value of energy E will be greater than the true value E_0 which is the lowest energy eigen-value of the Hamiltonian operator of the system.

$$E \geq E_0 \quad \dots (8.1)$$

Proof of this theorem has been introduced in section 7.1 and it is mentioned that according to one of the postulate of quantum mechanics average energy of Eigen values for the equation.

$$\hat{H}_i \Psi_i = E_i \Psi_i \quad \dots (8.2)$$

Can be calculated according to the following formula

$$\bar{E} = \frac{\int \psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \quad \dots (8.3)$$

Molecular orbital theory may be taken as one of the applications, of variation theorem. In the next section, molecular orbital theory or LCAO-MO concept is given.

8.1 L.C.A.O.-M.O. THEORY FOR H_2^+ MOLECULE ION

The H_2^+ molecule ion is the simplest molecule to be treated by LCAO-MO method. As H_2^+ molecule ion contains two hydrogen atoms A & B, the trial function may be written as

$$\Psi_{mo} = C_1 \Psi_A + C_2 \Psi_B \quad \dots(8.4)$$

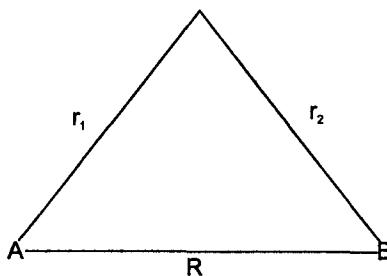


Fig. 8.1 H_2^+ molecule ion

The Schrodinger equation for the system is

$$\hat{H} \Psi_{mo} = E \Psi_{mo} \quad \dots(8.5)$$

Where \hat{H} may be written as

$$\hat{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \quad \dots(8.6)$$

As according to linear variation theorem energy can be calculated by the expression.

$$E = \frac{\langle \Psi_{mo} | \hat{H} | \Psi_{mo} \rangle}{\langle \Psi_{mo} | \Psi_{mo} \rangle} \quad \dots(8.7)$$

Substituting Ψ_{Mo} in equation 8.7

$$E = \frac{\langle C_1 \Psi_A + C_2 \Psi_B | \hat{H} | C_1 \Psi_A + C_2 \Psi_B \rangle}{\langle C_1 \Psi_A + C_2 \Psi_B | C_1 \Psi_A + C_2 \Psi_B \rangle} \quad \dots(8.8)$$

$$\text{Or } E = \frac{C_1^2 \langle \Psi_A | \hat{H} | \Psi_A \rangle + C_2^2 \langle \Psi_B | \hat{H} | \Psi_B \rangle + C_1 C_2 \langle \Psi_A | \hat{H} | \Psi_B \rangle + C_1 C_2 \langle \Psi_B | \hat{H} | \Psi_A \rangle}{C_1^2 \langle \Psi_A | \Psi_B \rangle + C_2^2 \langle \Psi_B | \Psi_A \rangle + 2 C_1 C_2 \langle \Psi_A | \Psi_B \rangle} \quad \dots(8.9)$$

As the \hat{H} is hermitian operator, therefore

$$\langle \Psi_A | \hat{H} | \Psi_B \rangle = \langle \Psi_B | \hat{H} | \Psi_A \rangle \quad \dots(8.10)$$

And if atomic orbitals are normalized

$$\langle \Psi_A | \Psi_A \rangle = \langle \Psi_B | \Psi_B \rangle = 1 \quad \dots(8.11)$$

From equation 8.10 & 8.11 equation 8.9 becomes

$$E = \frac{C_1^2 \langle \Psi_A | \hat{H} | \Psi_A \rangle + C_2^2 \langle \Psi_B | \hat{H} | \Psi_B \rangle + 2 C_1 C_2 \langle \Psi_A | \hat{H} | \Psi_B \rangle}{C_1^2 + C_2^2 + 2 C_1 C_2 \langle \Psi_A | \Psi_B \rangle} \quad \dots(8.12)$$

As in the above equation

$$\langle \Psi_A | \hat{H} | \Psi_A \rangle = \alpha_A$$

$$\langle \Psi_B | \hat{H} | \Psi_B \rangle = \alpha_B$$

$$\langle \Psi_A | \hat{H} | \Psi_B \rangle = \beta_{AB}$$

And $\langle \Psi_A | \Psi_B \rangle = S_{AB}$

... (8.13)

From equation 8.13, equation 8.12 becomes

$$E = \frac{C_1^2 \alpha_A + C_2^2 \alpha_B + 2C_1 C_2 \beta_{AB}}{C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}} \quad \dots (8.14)$$

The integrals α_A & α_B are Coloumb integrals. The values of α_A & α_B are close to E_A & E_B where E_A & E_B represent the energy of an electron in Ψ_A and Ψ_B in isolated H-atoms. The integral β_{AB} is resonance integral whose value is the measure of exchange of an electron from one atom to another. It is also known as exchange integral and has a negative value always. The integral S_{AB} is known as overlap integral and is a measure of the extent of overlapping of two atomic orbitals. To optimize the coefficients C_1 & C_2

$$\frac{\partial E}{\partial C_1} = 0 \text{ and } \frac{\partial E}{\partial C_2} = 0 \quad \dots (8.15)$$

Equation 8.14 may be re-written as

$$E (C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}) = C_1^2 \alpha_A + C_2^2 \alpha_B + 2C_1 C_2 \beta_{AB} \quad \dots (8.16)$$

Differentiating it w.r.t. C_1

$$\begin{aligned} E (2C_1 + 2C_2 S_{AB}) + (C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}) \left(\frac{\partial E}{\partial C_1} \right) \\ = 2C_1 \alpha_A + 2C_2 \beta_{AB} \end{aligned} \quad \dots (8.17)$$

$$\text{Or } \left(\frac{\partial E}{\partial C_1} \right) = \frac{2C_1 \alpha_A + 2C_2 \beta_{AB} - 2E(C_1 + C_2 S_{AB})}{C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}} \quad \dots (8.18)$$

Putting $(\partial E / \partial C_1) = 0$

$$C_1 \alpha_A + C_2 \beta_{AB} - E (C_1 + C_2 S_{AB}) = 0 \quad \dots (8.19)$$

Similarly, from $(\partial E / \partial C_2) = 0$ we get

$$C_1 \beta_{AB} + C_2 \alpha_B - E (C_1 S_{AB} - C_2) = 0 \quad \dots (8.20)$$

Equations 8.19 and 8.20 may written as

$$C_1(\alpha_A - E) + C_2(\beta_{AB} - ES_{AB}) = 0 \quad \dots(8.21)$$

$$C_1(\beta_{AB} - ES_{AB}) + C_2(\alpha_B - E) = 0 \quad \dots(8.22)$$

These equations 8.21 & 8.22 can be expressed in the matrix form as

$$\begin{vmatrix} \alpha_A - E & \beta_{AB} - ES_{AB} \\ \beta_{AB} - ES_{AB} & \alpha_B - E \end{vmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \quad \dots(8.23)$$

For non zero solution the first determinant must be equal to zero i.e.

$$\begin{vmatrix} \alpha_A - E & \beta_{AB} - ES_{AB} \\ \beta_{AB} - ES_{AB} & \alpha_B - E \end{vmatrix} = 0 \quad \dots(8.24)$$

Equation 8.23 is known as secular equation and determinant in equation 8.24 is known as secular determinant. On expansion of this determinant

$$(\alpha_A - E)(\alpha_B - E) - (\beta_{AB} - ES_{AB})^2 = 0 \quad \dots(8.25)$$

As here we are dealing with H-atoms viz. H_A & H_B therefore

$$\alpha_A = \alpha_B = \alpha \quad \dots(8.26)$$

So equation 8.25 may be expressed as

$$(\alpha - E)^2 - (\beta_{AB} - ES_{AB})^2 = 0 \quad \dots(8.27)$$

$$\text{Or } \alpha - E = \pm (\beta_{AB} - ES_{AB}) \quad \dots(8.28)$$

Which implies that two values of energy may be obtained which are

$$E_1 = \frac{(\alpha + \beta_{AB})}{(1 + S_{AB})} \quad \dots(8.29)$$

$$\text{And } E_2 = \frac{(\alpha - \beta_{AB})}{(1 - S_{AB})} \quad \dots(8.30)$$

On substitution of those energies in equation 8.23 we get

$$C_1 = \pm C_2 \quad \dots(8.31)$$

Therefore, two wave functions for M.O.'s are

$$\Psi_1 = C_1(\Psi_A + \Psi_B); E_1 = \frac{\alpha + \beta_{AB}}{1 + S_{AB}} \quad \dots(8.32)$$

$$\text{And } \Psi_2 = C_2(\Psi_A - \Psi_B); E_2 = \alpha - \beta_{AB} \quad \dots(8.33)$$

Applying normalization condition to Ψ_A

$$\langle \Psi_A | \Psi_A \rangle = 1 \quad \dots(8.34)$$

$$\text{Or } C_1^2 \{ \langle \Psi_A | \Psi_A \rangle + \langle \Psi_B | \Psi_B \rangle + 2 \langle \Psi_A | \Psi_B \rangle \} = 1 \quad \dots(8.35)$$

$$\text{Or } C_1^2 \{ 1 + 1 + 2S_{AB} \} = 1 \quad \dots(8.36)$$

Or

$$C_1 = \frac{1}{\sqrt{2(1+S_{AB})}} \quad \dots(8.37)$$

Similarly C_2 will have the value

$$C_2 = \frac{1}{\sqrt{2(1-S_{AB})}} \quad \dots(8.38)$$

E_1 & E_2 energies for the M.O.'s can be compared simply by taking $S_{AB} = 0$

$$\Rightarrow E_1 = \alpha + \beta_{AB} \text{ and}$$

$$E_2 = \alpha - \beta_{AB} \quad \dots(8.39)$$

Both α & β_{AB} are negative, therefore

$$E_1 < E_2 \quad \dots(8.40)$$

Which shows that m.o. Ψ_1 will have lower energy than Ψ_2 . Their display on energy level diagram gives us the M.O. diagram for H_2^+ - ion.

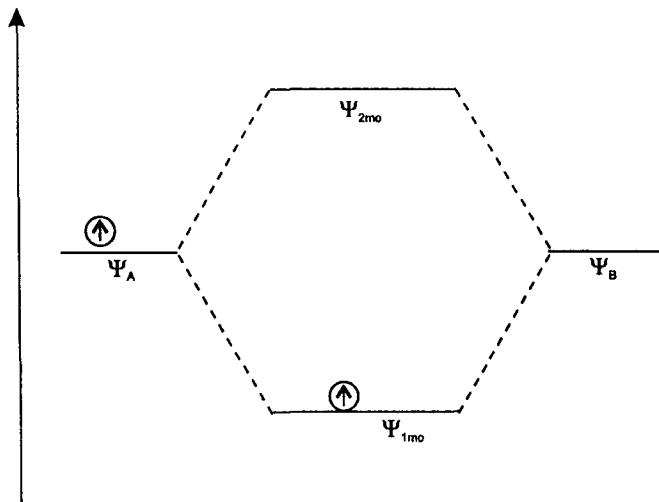


Fig. 8.2 M.O. Diagram for H_2^+ - ion

α_A integral : The integral α_A & α_B are represented by equation 8.40(a). α_A (or α_B) can be evaluated as follows :

$$\alpha_A = \langle \Psi_A | \hat{H} | \alpha_A \rangle \quad \dots(8.40(a))$$

From equation 8.6 substituting the Hamiltonian operator

$$\alpha_A = \langle \Psi_A | \left| \frac{-\hbar^2}{8\pi^2 m} \nabla^2 \frac{-e^2}{r_1} \frac{-e^2}{r_2} + \frac{e^2}{R} \right| \Psi_A \rangle \quad \dots(8.41)$$

Or

$$\alpha_A = \left\langle \Psi_A \left| \frac{-h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_1} \right| \Psi_A \right\rangle + \left\langle \Psi_A \left| \frac{-e^2}{r^2} \right| \Psi_A \right\rangle + \left\langle \Psi_A \left| \frac{-e^2}{R} \right| \Psi_A \right\rangle \quad \dots(8.42)$$

In the above equation, the first term is equal to the energy of 1s orbital of an isolated H-atom. As R is internuclear distance, so, third term is equal to e^2/R . Second term is coulomb integral J, so,

$$\alpha_A = E_H + J + \frac{e^2}{R} \quad \dots(8.43)$$

β_{AB} integral: As β_{AB} may be represented as

$$\beta_{AB} = \left\langle \Psi_A | \hat{H} | \Psi_B \right\rangle \quad \dots(8.44)$$

$$\beta_{AB} = \left\langle \Psi_A \left| \frac{-h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_1} + \frac{e^2}{R} - \frac{e^2}{r_2} \right| \Psi_B \right\rangle \quad \dots(8.45)$$

Or

$$\begin{aligned} \beta_{AB} &= \left\langle \Psi_A \left| \frac{-h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_2} \right. \right. \Psi_B \rangle + \\ &\quad \left. \left. \left\langle \Psi_A \left| \frac{-e^2}{r_1} \right. \right. + \Psi_B \right\rangle + \left\langle \Psi_A \left| \frac{-e^2}{R} \right. \right. \Psi_B \right\rangle \quad \dots(8.46) \end{aligned}$$

$$\text{Or} \quad \beta_{AB} = E_H S_{AB} + K + \frac{e^2}{R} S_{AB} \quad \dots(8.47)$$

Where K is actually known as exchange integral and it represents the exchange of electron between A & B atoms.

S_{AB} integral may be expressed as

$$S_{AB} = \left\langle \Psi_A | \Psi_B \right\rangle \quad \dots(8.48)$$

$$= \left(1 + R + \frac{R^2}{3} \right) \exp(-R) \quad \dots(8.49)$$

Energies E_1 & E_2 can be expressed as

$$E_1 = E_H + \frac{e^2}{R} + (J + K) \quad \dots(8.50)$$

$$\text{And} \quad E_2 = E_H + \frac{e^2}{R} + (J - K) \quad \dots(8.51)$$

M.O. expressed by E_1 whose energy is smaller than that of isolated A.O. is known as bonding M.O. and M.O. which is expressed by E_2 is antibonding M.O. If an electron is placed in bonding M.O., it will increase the stability of the molecule if and only if electron is placed in antibonding M.O. it will make the molecule ion less stable.

Wave functions for the M.O. is viz. Ψ_1 & Ψ_2 can be taken into account for the probability distribution as

$$\Psi_1^2 = (\Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B)/(2 + 2S_{AB}) \quad \dots (8.52)$$

$$\text{And } \Psi_2^2 = (\Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B)/(2 - 2S_{AB}) \quad \dots (8.53)$$

Graphical representation for Ψ_1 , Ψ_2 and Ψ_1^2 & Ψ_2^2 are shown in figure 8.3.

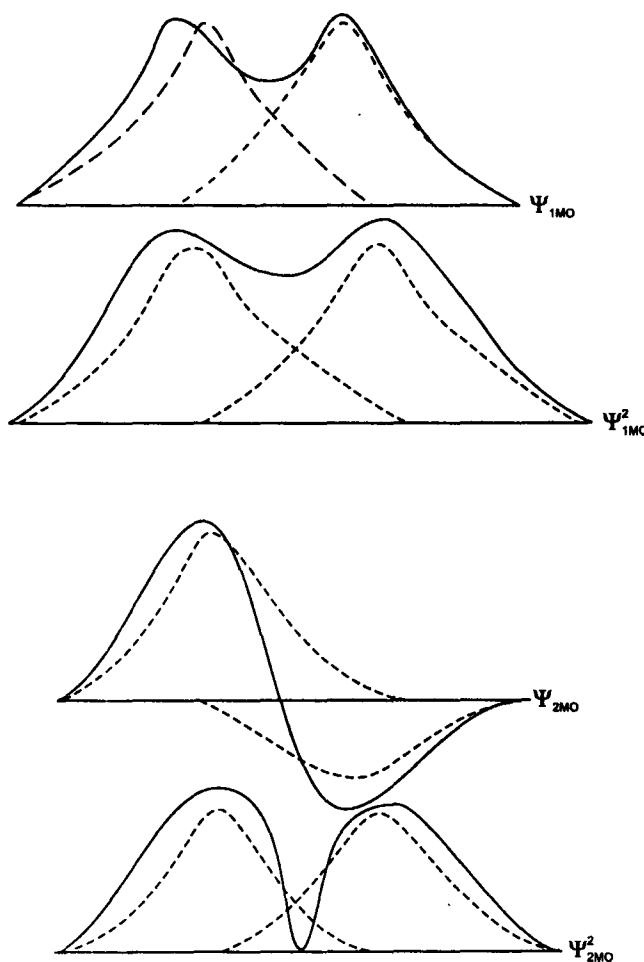


Fig. 8.3 Ψ_1 , Ψ_2 M.O.'s and Ψ_1^2 , Ψ_2^2 M.O.'s

8.2 APPLICATION OF VARIATION THEOREM TO HE-ATOM:-

This calculation is based on the fact that due to the presence of one electron, nuclear charge has been screened as a result of which Z_{eff} becomes less. Let us suppose this nuclear charge is Z' . The value of Z' can be evaluated by the principle of minimization.

$$\text{i.e. } \frac{dE_{1s}^2}{dz'} = 0 \quad \dots(8.54)$$

According to variation theorem

$$\bar{E}_{1s}^2 = \frac{\int \Psi |\hat{H}| \Psi d\tau}{\int \Psi^2 d\tau} \quad \dots(8.55)$$

If Ψ is normalized wave function

$$\int \Psi^2 d\tau = 1 \quad \dots(8.56)$$

Which implies that

$$E_{1s}^2 = \int \Psi |\hat{H}| \Psi d\tau \quad \dots(8.57)$$

Incorporating \hat{H} for He-atom (ref. to section 7.3)

$$E_{1s}^2 = \iint 1s(1) 1s(2) \left| \hat{H}(1) + \hat{H}(2) + \frac{1}{R} \right| 1s(1) 1s(2) d\tau_1 d\tau_2 \quad \dots(8.58)$$

$$\begin{aligned} = \bar{E}_{1s}^2 &= \iint 1s(1) 1s(2) \left| \hat{H}(1) \right| 1s(1) 1s(2) d\tau_1 d\tau_2 + \iint 1s(1) 1s(2) \left| \hat{H}(2) \right| 1s(1) 1s(2) d\tau_1 d\tau_2 + \\ &\quad + \int 1s(1) 1s(2) \left| \frac{1}{R} \right| 1s(1) 1s(2) d\tau_1 d\tau_2 \end{aligned} \quad \dots(8.59)$$

Where $\Psi_{\text{He}} = \Psi = 1s(1) 1s(2)$ involving 2 electrons in 1s orbitals and Hamiltonian may be written as

$$\hat{H} = \hat{H}(1) + \hat{H}(2) + \frac{1}{R} \text{ where } \hat{H}(1) \text{ and } \hat{H}(2) \text{ are hamiltonians for electron 1 \& 2 and } 1/R \text{ is the interaction term}$$

$$E_{1s}^2 = \iint 1s(1) 1s(2) E_{1s}^{\text{He}}(1) 1s(1) 1s(2) d\tau_1 d\tau_2 + \iint 1s(1) 1s(2) E_{1s}^{\text{He}}(2) 1s(1) 1s(2) d\tau_1 d\tau_2 + J \quad \dots(8.60)$$

Where J is coloumb integral

$$\text{Since, } E_{1s}^{\text{He}}(1) = E_{1s}^{\text{He}}(2) = E_{1s} \text{ (in general)}$$

$$\text{Therefore } \bar{E}_{1s}^2 = 2E_{1s} \iint [1s(1) 1s(2)]^2 d\tau_1 d\tau_2 + J \quad \dots(8.61)$$

$$\text{Or } E_{1s}^2 = 2E_{1s} + J \quad \dots(8.62)$$

As $1s(1)$ & $1s(2)$ are individually normalized functions

$$E_{1s} = \int 1s \left[-\frac{1}{2} \nabla^2 - \frac{Z}{R} \right] 1s d\tau \quad \dots(8.63)$$

$$\text{In case of He-atom} \quad E_{1s} = \frac{-z'^2}{2} - (2 - z') \int 1s \left(\frac{1}{2} \right) 1s dt \quad \dots(8.64)$$

Taking appropriate $1s$ function and $d\tau$ as $r^2 dr \sin\theta d\theta d\phi$

$$E_{1s} = -\frac{-z'^2}{2} - (2 - z') z' \quad \dots(8.65)$$

$$\bar{E}_{1s}^2 = 2E_{1s} + J \quad \dots(8.62)$$

$$= E_{1s}^2 = 2 \left(\frac{z'^2}{2} - (2 - z') z' \right) + J \quad \dots(8.66)$$

. On putting value of J finally, E_{1s}^2 becomes

$$\bar{E}_{1s}^2 = Z'^2 - \frac{27}{8} Z' \quad \dots(8.67)$$

On the basis of principle of minimization

$$\frac{dE_{1s}^2}{dz} = 0 \quad \dots(8.68)$$

$$= 2Z' - \frac{27}{8} = 0 \quad \dots(8.69)$$

$$= Z' = \frac{27}{16} \quad \dots(8.70)$$

Therefore, the value of

$$E_{1s}^2 = \left(\frac{27}{16} \right)^2 - \left(\frac{27}{8} \right) \left(\frac{27}{8} \right) = -2.84 \text{ atomic units.}$$

Or 77.48 ev or -1.24×10^{-17} J. This value of energy is almost near exact value energy of He-atom

PROBLEMS SET-8

- What is linear variation theorem? (See introduction of the chapter)
- Derive expression for energies for M.O.'s formed on the basis of LCAO-MO concept for H_2^+ ion (See section 8.1)
- What do you understand by
 - Coulomb Integral
 - Resonance integral and
 - Overlap integral (See section 8.1)
- How evaluation of α , β_{AB} and S_{AB} can be done ? (See section 8.1)
- Discuss the application of variation principle to He-atom (See section 8.2).

CHAPTER-9

Perturbation Method and Its Application

SYNOPSIS

<i>Section</i>	<i>Topics</i>
9.1	Particle in one dimensional box with perturbed potential energy
9.2	Application of perturbation method to He-atom

One approximate method viz. variation principle has been discussed in chapter 7 and its applications are given in chapter 8. Perturbation method is also another approximate method which is being used in quantum mechanics to get near exact values for energies, eigen values and wave function etc. This method has also been introduced in chapter 7. In this chapter contents related to applications of perturbation method with its use in multi-electron system are being introduced.

As it is given in section 7.2, the perturbation method is applied if the system differs slightly from unperturbed state and if energy (E_0) and the wave function (Ψ_0) for the unperturbed state are known. The perturbation theory involves the determination of the Eigen function (Ψ_n) and Eigen values (E_n) corresponding to the perturbed Hamiltonian (\hat{H}') in terms of (Ψ_0) and (E_0) related to unperturbed Hamiltonian (\hat{H}_0). It has also been introduced in the same chapter (section 7.2) that first order corrected energy is given by

$$E_n^{(1)} = \int \Psi_n^0 * \hat{H}' \Psi_n^0 d\tau \quad \dots(9.1)$$

And first order corrected wave function is given by

$$\Psi_n^{(1)} = \sum_{m \neq n} \left[\frac{\int \Psi_m^0 \hat{H}' \Psi_n^0 d\tau}{E_n^0 - E_m^0} \right] \Psi_m^0 \quad \dots(9.2)$$

Or

$$\sum_{m \neq n} \frac{H' mn}{E_n^0 - E_m^0} \Psi_m^0 \quad \dots (9.3)$$

In this chapter two applications of perturbation method viz. particle in one-dimensional box with difference in potential energy and application of perturbation method to He-atom are given.

9.1 PARTICLE IN ONE-DIMENSIONAL BOX WITH PERTURBED POTENTIAL ENERGY

In section 3.1, particle in one dimensional box problem has been discussed. While deriving the expression for translational energy potential energy of the particle moving in one-dimensional box was considered as zero. Let us consider that electrical potential has been applied to particle in one dimensional box. This potential depends upon x length. This potential can be shown by the formula

$$V(x) = \frac{ux}{L} \quad \dots (9.4)$$

At

$$x = 0$$

$$V(0) = 0 \text{ and at}$$

$$x = L \quad V(L) = u$$

Change in $V(x)$ in the box can be expressed as per figure 9.1

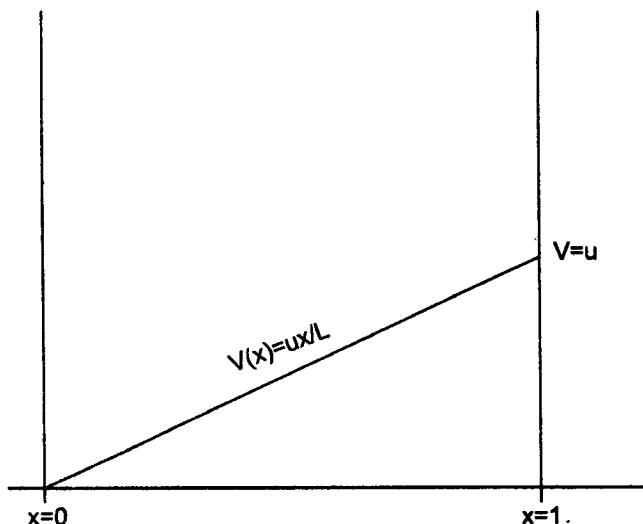


Fig. 9.1

Zero order energy for the particle is $n^2\hbar^2/8mL^2$. First order corrected energy after the perturbation can be evaluated as

$$E_n^{(1)} = \langle \Psi^0 | \hat{H}' | \Psi^0 \rangle \quad \dots (9.5)$$

Or $E_n^{(1)} = \int_0^L \left\{ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right| \frac{ux}{L} \left| \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx \right. \dots(9.6)$

As wave function for particle in one-dimensional box is given by

Or $\Psi = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

$$E_n^{(1)} = \frac{2}{L} \times \frac{u}{L} \int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx \dots(9.7)$$

Or $E_n^{(1)} = \frac{2}{L} \times \frac{u}{L} \times \frac{L^2}{4} = \frac{u}{2} \dots(9.8)$

[As the integral $\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx$ has value $L^2/4$]

Therefore, total energy including first order corrected energy for the particle in one-dimensional box is given by

$$E = E_n^{(0)} + E_n^{(1)} = \frac{n^2 L^2}{8mL^2} + \frac{u}{2} \dots(9.9)$$

Similarly, wave function after perturbation i.e. first order corrected wave function may be calculated as

$$\Psi_n^{(1)} = \frac{H'_{mn} \Psi_m}{E_1 - E_2} \dots(9.3)$$

Here in this case $\Psi_n^{(1)} = \Psi_1^{(1)}$ and which can be evaluated as

$$\Psi_1^{(1)} = \frac{H'_{2,1} \Psi_2}{E_1 - E_2} \dots(9.10)$$

Where $H_{2,1} = \int \Psi | \hat{H} | \Psi_1 d\tau \dots(9.11)$

$$= \frac{2}{L} \int_0^L \left(\sin \frac{2\pi x}{L} \left| \frac{ux}{L} \right| \sin \frac{\pi x}{L} \right) dx \dots(9.12)$$

$$E_1 - E_2 = \frac{h^2}{8mL^2} - \frac{4h^2}{8mL^2} \dots(9.13)$$

On substituting values from equations 9.12 and 9.13 in equation 9.10 & on solving it, the correction term will be

$$\Psi_1^{(1)} = \frac{32L^2u}{27\pi^4} \Psi \quad \dots (9.14)$$

Incorporating this first order corrected wave function total corrected wave function will be

$$\Psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) + \sqrt{\frac{2}{L}} \frac{32L^2u}{27\pi^4} \sin\left(\frac{2\pi x}{L}\right) \quad \dots (9.15)$$

9.2. APPLICATION OF PERTURBATION METHOD TO HE-ATOM

As mentioned in section 7.3, perturbed Hamiltonian for He-atom may be written as

$$\hat{H} = \hat{H}_0 + \frac{1}{R} \quad \dots (9.16)$$

Where \hat{H}_0 is the Hamiltonian for zeroth state i.e. it is the Hamiltonian for electron 1 and electron 2 in 1s orbital of He-atom.

$$\hat{H} = \hat{H}(1) + \hat{H}(2) + \frac{1}{R} \quad \dots (9.17)$$

Where $1/R$ term is perturbed Hamiltonian term

The first order corrected energy for He-atom may be calculated as

$$E^{(1)} = \int \Psi^0 \hat{H}' \Psi^0 d\tau \quad \dots (9.18)$$

$$= \iint \phi(1) \phi(2) \frac{1}{R} \phi(1) \phi(2) d\tau \quad \dots (9.19)$$

As $\phi(1)$ and $\phi(2)$ are normalized functions, Let us suppose $E^{(1)} = J$ where J is average columbic energy term for He-atom in ground state $J = \frac{5}{8} Z$

$$\therefore J = \frac{5}{8} Z \quad \dots (9.20)$$

Therefore, for He-atom total energy with first order corrected energy will be

$$\bar{E}_{1s}^2 = -Z^2 + \frac{5}{8} Z \quad \dots (9.21)$$

$$\text{i.e. } E_{1s}^2 = E^{(0)} + E^{(1)} \quad \dots (9.23)$$

On substitution of Z E_{1s}^2 for He-atom can be calculated as -2.75 au or -74.8 ev or $-1.196 \times 10^{-17} \text{ J}$. This value is nearly equal to the experimental value.

Example 9.1 : A hydrogen atom is placed in an electric field of strength E which is applied in the Z -direction. Calculate first order corrected energy for the ground state of the atom considering \hat{H}' the first order perturbed Hamiltonian as

$$H = F \cos \theta \text{ (in a.u.)}$$

$$\text{As } \Psi_{1s} \text{ for H-atom (in a.u.)} = \frac{1}{\sqrt{\pi}} \exp(-r) \text{ (as } \Psi_1^{(0)})$$

First order corrected energy corresponding to this wave function is given by

$$\begin{aligned} E_1^{(1)} &= \int \Psi_1^{(0)} \hat{H} \Psi_1 \delta r \\ &= E_1^{(1)} = \frac{F}{\pi} \iiint_0^{\pi} \exp(-r) r \cos \theta \exp(-r) r^2 \sin \theta d\theta d\phi \\ &= 0 \end{aligned}$$

$$\text{Therefore } E_1^{(1)} = 0$$

Hence, first order corrected energy has value equal to zero. Therefore, there is no first order effect in this case.

PROBLEMS SET-9

1. What do you understand by perturbation method? (See introduction of the chapter)
2. Give first order corrected wave function and energy. (See introduction of the chapter)
3. Explain application of perturbation method in one-dimensional box. (See section 9.1)
4. Explain application of perturbation method in He-atom (See section 9.2)
5. Calculate first order corrected wave function and first order corrected energy for a particle moving in a box, if its potential energy is $V_{(x)} = ux/L$ (See section 9.1)

CHAPTER-10

Introduction to Angular Momentum

SYNOPSIS	
<i>Section</i>	<i>Topics</i>
10.1	Introduction to angular momentum
10.2	Commutation of \hat{L}_x, \hat{L}_y and \hat{L}_z operators
10.3	Commutation of \hat{L}^2 and \hat{L}_z operators
10.4	Physical significance of commutation rules and quantum mechanical definition of angular momentum
10.5	Angular momentum operator in terms of polar coordinates
10.6	Concept of ladder operator
10.7	Eigen value and Eigen functions for angular momentum operator

Angular momentum, a physical property, has a lot of significance in quantum mechanics. This property was used by Bohr in his atomic theory (see postulates of Bohr's theory, section 1.7). While discussing the properties of a rigid rotator angular momentum has been introduced in context to quantum mechanics (See section 5.2). In this chapter, quantum mechanical concepts related to angular momentum starting from the introduction of angular momentum have been included.

10.1 INTRODUCTION TO ANGULAR MOMENTUM

According to Bohr's theory angular momentum is an important parameter for an electron moving in orbit. Actually angular momentum may have different components. In any orbit, an electron may have axial, angular momentum and total angular momentum. Apart from its spin, angular momentum may also be possible for a moving electron. These types of angular moments are being discussed in this section

If L_x, L_y & L_z are three components of angular momentum then

$$L^2 = L \cdot L = L_x^2 + L_y^2 + L_z^2$$

Where L^2 is the square of total angular momentum of moving electron. For a rigid rotator this can also be shown that for L^2 and L_z operators there exist some Eigen values. Here L^2 is the total angular momentum operator and L_z is z component of angular momentum. When these operators are operated on spherical harmonics, $Y(\theta, \phi)$ for a rigid rotator we get the following Eigen equations.

$$\hat{L}^2 Y = L^2 Y \quad \dots(10.1)$$

And

$$\hat{L}_z Y = m\hbar Y \quad \dots(10.2)$$

This has been proved earlier that the quantum number l may have values 0, 1, 2, 3 and 'm' may have values $0, \pm 1, \pm 2, \pm 3, \dots, \pm l$. Similar to L_z angular momentum may also have another component L_x & L_y . These L_x , L_y & L_z components of angular momentum can be defined as per the following equations.

$$L_x = y p_z - z p_y \quad \dots(10.3)$$

$$L_y = z p_x - x p_z \quad \dots(10.4)$$

and $L_z = x p_y - y p_x \quad \dots(10.5)$

On the basis of classical mechanics Let 'm' be the mass of a particle and Let this particle is moving around origin i.e. 'O', then angular momentum (\vec{L}). May be defined as $\vec{r} \times \vec{p}$

$$\text{i.e. } \vec{L} = \vec{r} \times \vec{p} \quad \dots(10.6)$$

where r is position and p is linear momentum vectors. Defining

$$\vec{r} = x \hat{i} + y \hat{j} + z \hat{k} \quad \dots(10.7)$$

and $\vec{p} = p_x \hat{i} + p_y \hat{j} + p_z \hat{k} \quad \dots(10.8)$

This implies that $\vec{L} = \vec{r} \times \vec{p}$ may be defined as per the following determinant.

$$\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \quad \dots(10.9)$$

Or $\vec{L} = (y p_z - z p_y) \hat{i} + (z p_x - x p_z) \hat{j} + (x p_y - y p_x) \hat{k} \quad \dots(10.10)$

Since \vec{L} is a vector quantity. Therefore

$$\vec{L} = L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \quad \dots(10.11)$$

So, on comparison of equation 10.10 & 10.11 equation 10.3, 10.4 and 10.5 can be obtained.

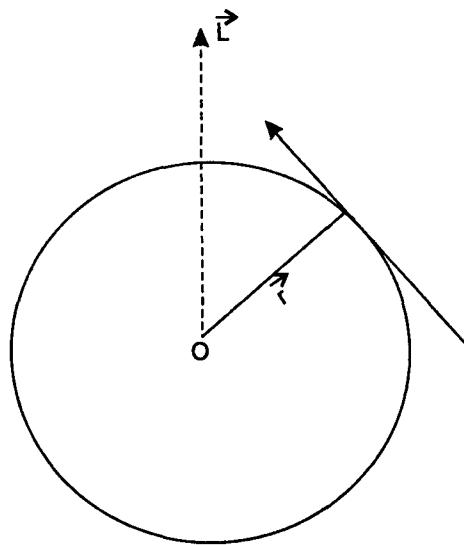


Fig. 10.1 : Showing Angular momentum and linear momentum vectors

On substituting the quantum mechanical values of p_x , p_y and p_z

$$p_x = \frac{\hbar}{i} \frac{d}{dx} \quad \dots (10.12)$$

$$p_y = \frac{\hbar}{i} \frac{d}{dy} \quad \dots (10.13)$$

$$p_z = -\frac{\hbar}{i} \frac{d}{dz} \quad \dots (10.14)$$

[where $\hbar = h/2\pi$]

Implies that

$$\vec{L}_x = \frac{\hbar}{i} \left[y \frac{d}{dz} - z \frac{d}{dy} \right] \quad \dots (10.15)$$

$$\vec{L}_y = \frac{\hbar}{i} \left[z \frac{d}{dx} - x \frac{d}{dz} \right] \text{ and} \quad \dots (10.16)$$

$$\vec{L}_z = \frac{\hbar}{i} \left[x \frac{d}{dy} - y \frac{d}{dx} \right] \quad \dots (10.17)$$

Equations for \vec{L}_x , \vec{L}_y and \vec{L}_z mentioned above are the operator form of angular momentum components L_x , L_y & L_z .

10.2 COMMULATION OF L_x, L_y, L_z OPERATORS

Commutation of angular momentum operators has significance. Here in this section commutation and its importance is being discussed. Let us consider first, the comutation of L_x & L_y operators

$$\text{i.e. } [\hat{L}_x \hat{L}_y] = [\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x] \quad \dots(10.18)$$

$$\hat{L}_x \hat{L}_y = \frac{\hbar}{i} \left[y \frac{d}{dz} - z \frac{d}{dy} \right] \frac{\hbar}{i} \left[z \frac{d}{dx} - x \frac{d}{dz} \right]$$

$$\text{Or } -\hbar^2 \left[y \frac{d}{dx} + yz \frac{d^2}{dxdz} - yx \frac{d^2}{dydx} - z^2 \frac{d^2}{dydx} + zx \frac{d^2}{dydz} \right] \quad \dots(10.19)$$

$$\text{Similarly } \hat{L}_y \hat{L}_x = -\hbar^2 \left[zy \frac{d^2}{dxdz} - z^2 \frac{d^2}{dxdy} - xy \frac{d^2}{dz^2} + x \frac{d}{dy} + xz \frac{d^2}{dxdy} \right] \quad \dots(10.20)$$

Therefore

$$\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = -\hbar^2 \left[y \frac{d}{dx} - x \frac{d}{dy} \right] \quad \dots(10.21)$$

$$= i^2 \hbar^2 \left[y \frac{d}{dx} - x \frac{d}{dy} \right] (\text{as } i^2 = -1) \quad \dots(10.22)$$

$$= i\hbar \left[-\frac{\hbar}{i} \left(y \frac{d}{dx} - x \frac{d}{dy} \right) \right] \quad \dots(10.23)$$

$$= i\hbar \hat{L}_z \quad \dots(10.24)$$

Likewise this can also be shown that

$$[\hat{L}_y \hat{L}_z] = i\hbar \hat{L}_x \quad \dots(10.24)$$

$$[\hat{L}_z \hat{L}_x] = i\hbar \hat{L}_y \quad \dots(10.26)$$

And similarly following relations can also be shown

$$[\hat{L}_y \hat{L}_x] = -i\hbar \hat{L}_z \quad \dots(10.27)$$

$$[\hat{L}_z \hat{L}_y] = -i\hbar \hat{L}_x \quad \dots(10.28)$$

$$[\hat{L}_x \hat{L}_z] = -i\hbar \hat{L}_y \quad \dots(10.29)$$

Above equations clearly denotes that components of angular momentum operator i.e. \hat{L}_x , \hat{L}_y & \hat{L}_z do not commute with each other. This fact has a significance that it is not possible to ascertain the values of two components of angular momentum simultaneously. Therefore, this may be concluded that at a time one component of angular momentum of a tiny particle like electron can be ascertained.

If commutation of \hat{L}^2 and \hat{L}_z operators is carried out this can be concluded that \hat{L}^2 and \hat{L}_z operators commute with each others. This clearly shows that L^2 and \hat{L}_z values i.e. square value of angular momentum and its one component i.e. z-component value for a tiny particle like electron can be ascertained.

10.3 COMMUTATION OF L^2 AND L_z OPERATORS

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad \dots(10.30)$$

Therefore

$$L = (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)^{1/2} \quad \dots(10.31)$$

The commutation of L^2 and L_z is as follows:

$$\begin{aligned} [\hat{L}^2, \hat{L}_z] &= [(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)\hat{L}_z] \\ &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)\hat{L}_z - (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \\ &= (\hat{L}_x^2\hat{L}_z) + (\hat{L}_y^2\hat{L}_z) + (\hat{L}_z^2\hat{L}_z) - (\hat{L}_z\hat{L}_x^2) - (\hat{L}_z\hat{L}_y^2) - (\hat{L}_z\hat{L}_z^2) \\ &= (\hat{L}_x^2\hat{L}_z - \hat{L}_z\hat{L}_x^2) + (\hat{L}_y^2\hat{L}_z - \hat{L}_z\hat{L}_y^2) + (\hat{L}_z^2\hat{L}_z - \hat{L}_z\hat{L}_z^2) \\ &= (\hat{L}_x^2\hat{L}_z) + (\hat{L}_y^2\hat{L}_z) + (\hat{L}_z^2\hat{L}_z) \end{aligned} \quad \dots(10.32)$$

First term of the equation 10.32 is

$$\begin{aligned} [\hat{L}_x^2\hat{L}_z] &= [\hat{L}_x\hat{L}_x\hat{L}_z] - [\hat{L}_z\hat{L}_x\hat{L}_x] \\ &= \hat{L}_x[\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x] + [\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x]\hat{L}_x \\ &= \hat{L}_x[\hat{L}_x\hat{L}_z] + [\hat{L}_x\hat{L}_z]\hat{L}_x \\ &= i\hbar[\hat{L}_x\hat{L}_y] - i\hbar[\hat{L}_y\hat{L}_x] \\ &= i\hbar[\hat{L}_x\hat{L}_y] + [\hat{L}_y\hat{L}_x] \end{aligned}$$

Therefore

$$[\hat{L}_x \hat{L}_y] = -[\hat{L}_y \hat{L}_x]$$

Or

$$[\hat{L}_x^2 \hat{L}_z] = 0$$

Similarly, this can also be shown that $[\hat{L}_y^2 \hat{L}_z]$ and $[\hat{L}_z^2 \hat{L}_x]$ are also zero.

In conclusion this can be stated that

$$[\hat{L}^2 \hat{L}_z] = 0 \quad \dots(10.33)$$

i.e. \hat{L}^2 can be commuted with \hat{L}_z operator. Likewise this can also be shown that $[\hat{L}^2 \hat{L}_x]$ and $[\hat{L}^2 \hat{L}_y]$ also commute with each other.

10.4 PHYSICAL SIGNIFICANCE OF COMMUTATION RULES AND QUANTUM MECHANICAL DEFINITION OF ANGULAR MOMENTUM

Commutation rules as shown in section 10.2 and 10.3 above shows that a particle in rotation motion may possess angular momentum L which can be denoted by a vector of definite length. Its z component L_z will be certain and other two components L_x & L_y are uncertain. These vectors may be present anywhere on cone formed around z -axis. On the basis of it, quantum chemical definition of the angular momentum is : Any vector \vec{J} may be angular momentum vector if and only if it follows the following conditions :

$$[J_x J_y] = i\hbar J_z \quad \dots(10.34)$$

$$[J_y J_z] = i\hbar J_x \quad \dots(10.35)$$

$$[J_z J_x] = i\hbar J_y \quad \dots(10.35)$$

and $[J^2, J_k] = 0 \ k = x, y \text{ or } z \quad \dots(10.37)$

and $J^2 = J_x^2 + J_y^2 + J_z^2 \quad \dots(10.38)$

This is shown in the fig. 10.2 as a cone



Fig. 10.2 cone around z – axis

10.5 ANGULAR MOMENTUM OPERATOR IN TERMS OF POLAR COORDINATES

x, y and z coordinates can be expressed in terms of r, θ , & ϕ as per following relations

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

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

$$z = r \cos \theta \quad \dots(10.39)$$

As

$$r^2 = x^2 + y^2 + z^2 \text{ and} \quad \dots(10.40)$$

$$\cos \theta = Z/(x^2 + y^2 + z^2)^{\frac{1}{2}} \quad \dots (10.41)$$

And

$$\tan \phi = y/x$$

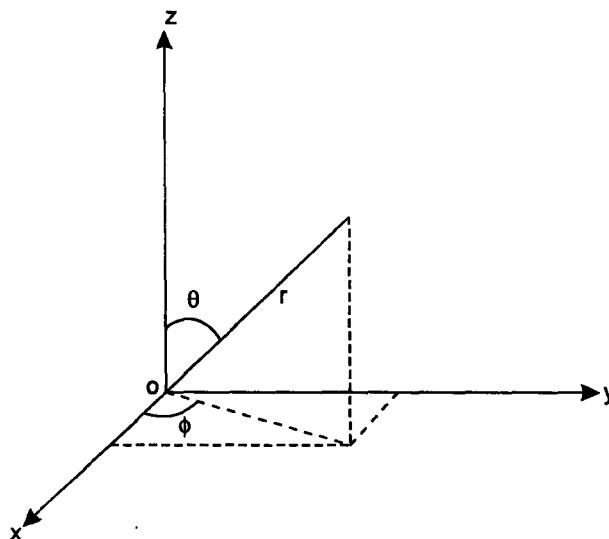


Fig. 10.3 : Showing r, θ & ϕ coordinates

Therefore, the differentials d/dx , d/dy & d/dz will be

$$\left. \begin{aligned} \frac{d}{dx} &= \frac{d}{dr} \frac{dr}{dx} + \frac{d}{d\theta} \frac{d\theta}{dx} + \frac{d}{d\phi} \frac{d\phi}{dx} \\ \frac{d}{dy} &= \frac{d}{dr} \frac{dr}{dy} + \frac{d}{d\theta} \frac{d\theta}{dy} + \frac{d}{d\phi} \frac{d\phi}{dy} \\ \frac{d}{dz} &= \frac{d}{dr} \frac{dr}{dz} + \frac{d}{d\theta} \frac{d\theta}{dz} + \frac{d}{d\phi} \frac{d\phi}{dz} \end{aligned} \right\} \quad \dots(10.42)$$

And

Which implies that

$$\left. \begin{aligned} \frac{d}{dx} &= \sin \theta \cos \phi + \theta + 0 \\ \frac{d}{dy} &= \sin \theta \sin \phi + \theta + 0 \\ \frac{d}{dz} &= \cos \theta + \theta + 0 \end{aligned} \right\} \quad \dots(10.43)$$

Similarly

$$\left. \begin{aligned} \frac{d\theta}{dx} &= \frac{\cos \theta \cos \phi}{r} \\ \frac{d\theta}{dy} &= -\frac{\cos \theta \sin \phi}{r} \\ \frac{d\theta}{dz} &= \frac{\sin \theta}{r} \end{aligned} \right\} \quad \dots(10.44)$$

And

$$\left. \begin{aligned} \frac{d\phi}{dx} &= \frac{-\sin \phi}{r \sin \theta} \\ \frac{d\phi}{dy} &= \frac{\cos \theta}{r \sin \theta} \\ \frac{d\phi}{dz} &= 0 \end{aligned} \right\} \quad \dots(10.45)$$

On the basis of above equation \hat{L}_x , \hat{L}_y & \hat{L}_z are

$$\hat{L}_x = -i\hbar \left(-\sin \phi \frac{d}{d\theta} - \cos \theta \cos \phi \frac{d}{d\phi} \right) \quad \dots(10.46)$$

$$\hat{L}_y = -i\hbar \left(\cos \phi \frac{d}{d\theta} - \cos \theta \sin \phi \frac{d}{d\phi} \right) \quad \dots(10.47)$$

$$\hat{L}_z = -i\hbar \left(\frac{d}{d\phi} \right) \quad \dots(10.48)$$

Similarly \hat{L}^2 can be expressed as

$$\hat{L}^2 = \left[-\hbar^2 \left(\frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta) \frac{d}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} \right] \quad \dots(10.49)$$

10.6 CONCEPT OF LADDER OPERATOR

Two new operators are being introduced in this section viz \hat{L}_+ & \hat{L}_- operators. These operators are also related to angular momentum. These operators can be defined as follows :

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \dots(10.50)$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y \quad \dots(10.51)$$

In order to check the commutation of \hat{L}^2 and \hat{L}_+

$$\begin{aligned} [\hat{L}^2, \hat{L}_+] &= [\hat{L}_x + i\hat{L}_y, \hat{L}^2] \\ &= [\hat{L}_x, \hat{L}^2] + i[\hat{L}_y, \hat{L}^2] \\ &= 0 + 0 = 0 \end{aligned} \quad \dots(10.52)$$

This shows that \hat{L}^2 and \hat{L}_+ commutation gives the result zero. Similarly, \hat{L}^2 and \hat{L}_- commutation will also give the result zero.

If $[\hat{L}_+, \hat{L}_z]$ commutation is checked

$$\begin{aligned} \text{i.e. } &[\hat{L}_+, \hat{L}_z]\Psi \\ &= [\hat{L}_x + i\hat{L}_y, \hat{L}_z]\Psi \\ &= ([\hat{L}_x, \hat{L}_z] + i[\hat{L}_y, \hat{L}_z])\Psi \\ &= (-i\hbar\hat{L}_y + i\hbar\hat{L}_x)\Psi \\ &= -\hbar(\hat{L}_x + i\hat{L}_y)\Psi \\ &= -\hbar(\hat{L}_x + i\hat{L}_y) = -\hbar\hat{L}_+\Psi \end{aligned} \quad \dots(10.53)$$

As $[\hat{L}_+, \hat{L}_z]\Psi$

$$= (\hat{L}_+ \hat{L}_z)\Psi - (\hat{L}_z \hat{L}_+)\Psi \quad \dots(10.54)$$

From equation 10.53 and 10.54

$$\Rightarrow \hat{L}_+ \hat{L}_z \Psi - \hat{L}_z \hat{L}_+ \Psi = \hbar \hat{L}_+ \Psi$$

$$\Rightarrow \hat{L}_z \hat{L}_+ \Psi = \hat{L}_+ \hat{L}_z \Psi + \hbar \hat{L}_+ \Psi$$

$$\text{Or} \quad \hat{L}_z \hat{L}_+ \Psi = \hat{L}_+ \hat{L}_z \Psi + \hbar \hat{L}_+ \Psi \quad \dots (10.55)$$

$$\Rightarrow \hat{L}_z (\hat{L}_+ \Psi) = \hat{L}_+ \hat{L}_z \Psi + \hbar \hat{L}_+ \Psi \quad \dots (10.56)$$

Operator defined in equation 10.56 is step-up operator. Similarly step down operator can also be shown as follows:

$$\hat{L}_z (\hat{L}_- \Psi) = \hat{L}_- \hat{L}_z \Psi + \hbar \hat{L}_- \Psi \quad \dots (10.57)$$

Collectively, these operators which are defined in equations 10.56 and 10.57 are known as Ladder operator.

10.7 EIGEN VALUES AND EIGEN FUNCTION FOR ANGULAR MOMENTUM OPERATOR

\hat{L}_z operator can be expressed in terms of polar coordinates as

$$\hat{L}_z = i\hbar \left(\frac{d}{d\phi} \right) \quad \dots (10.58)$$

As for the case of a rigid rotator ϕ_m can be expressed as

$$\phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad \dots (10.59)$$

Therefore, on operating \hat{L}_z operator on ϕ_m function value for z component of angular momentum i.e. L_z value can be obtained as

$$\hat{L}_z \phi_m = \frac{i\hbar}{2\pi} \frac{d}{d\phi} \left(\frac{1}{\sqrt{2\pi}} \exp(im\phi) \right) \quad \dots (10.60)$$

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

$$\text{Or} \quad = L_z \phi_m \quad \dots (10.61)$$

Therefore, it has been proved that ϕ_m is an Eigen function for L_z operator with eigen value L_z i.e. $m\hbar$ or $mh/2\pi$. The corresponding eigen equation may be written as

$$\hat{L}_z \Psi_m = L_z \Psi_m \quad \dots(10.62)$$

Similarly \hat{L}^2 operator in terms of polar co-ordinates may be expressed as

$$\hat{L}^2 = -\frac{\hbar^2}{2} \left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} \right] \quad \dots(10.63)$$

Taking example of spherical harmonics for 1s orbital i.e. for $l = 1$ and $m = 0$ orbital

$$\Psi_{(1,0)} = \left(\frac{3}{4\pi} \right)^{\frac{1}{2}} \cos \theta \quad \dots(10.64)$$

Leaving normalization factor

$$\hat{L}^2 \Psi_{(1,0)} = \frac{2\hbar^2}{4\pi^2} \Psi_{(1,0)} \quad \dots(10.65)$$

This equation shows that $\Psi_{(1,0)}$ is an eigen function for L^2 operator whose L^2 value i.e. the eigen value is $2\hbar^2/4\pi^2$. Therefore, equation 10.65 is an eigen equation. In comparison to it when \hat{L}_z operator is operated on $\Psi_{(1,0)}$ function, following equation has been obtained

$$\hat{L}_z \Psi_{(1,0)} = i\hbar \frac{d}{d\phi} (\cos \theta) = 0 \quad \dots(10.66)$$

Equation 10.66 shows that $\Psi_{(1,0)}$ is not an eigen function for L_z operator.

In general on the operation of \hat{L}_2 operator on $\Psi_{l,m}$ function

$$\hat{L}_2 \Psi_{(l,m)} = \frac{\beta \hbar^2}{4\pi^2} \Psi_{(l,m)} \quad \dots(10.67)$$

$$\text{Or} \quad \hat{L}_2 \Psi_{(l,m)} = l(l+1) \frac{\hbar^2}{4\pi^2} \Psi_{(l,m)} \quad \dots(10.68)$$

Which shows that the Eigen value for \hat{L}_2 operator i.e. L^2 value is $l(l+1)\hbar^2$ or the value of total angular momentum for electron is given by

$$\begin{aligned} \text{Since} \quad L^2 &= l(l+1) \hbar^2 \\ &= L = \sqrt{l(l+1)} \hbar \end{aligned}$$

$$\text{Or} \quad L = \sqrt{l(l+1)} \frac{\hbar}{2\pi} \quad \dots(10.69)$$

Equation 10.68 is an Eigen equation. In this way it is clear that on the operation of \hat{L}_z operator value of L_z and on the operation of \hat{L}^2 operator value of L^2 can be obtained. These are significant

results. Relation between L and m has been shown earlier in chapter 5, that for a definite value of l , m may have values $0, \pm 1, \pm 2, \pm 3, \dots, \pm l$ i.e. $(2l + 1)$ values for m are possible.

Concepts related to electronic spin, spin angular momentum and other related concepts are taken in chapter 11.

Example 10.1 Define ladder operators \hat{L}_+ and \hat{L}_- (See section 10.6)

Example 10.2 Prove that the commutation $[\hat{L}^2, \hat{L}_+]$ and $[\hat{L}^2, \hat{L}_-]$ are equal to zero (See section 10.6)

Example 10.3 : $\phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$. Find out the eigen value taking this function with L_z operator.

$$\text{As } \hat{L}_z \phi_m = L_z \phi_m$$

$$\text{Where } L_z \text{ value is } m\hbar \text{ or } \frac{mh}{2\pi}$$

[See section 10.7]

Example 10.4 Prove that total angular momentum of a moving particle (i.e. electron) is

$$\text{As } \hat{L}^2 \phi_{l,m} = l(l+1)\hbar^2/4\pi^2 \phi_{l,m}$$

Where l^2 value i.e. $l(l+1)\hbar^2/4\pi^2$ is the eigen value and is the square term of total angular momentum of electron. Therefore, L i.e. total angular momentum of electron is $\sqrt{l(l+1)}\hbar$ or $\sqrt{l(l+1)}\hbar/2\pi$.

[See section 10.7]

PROBLEMS SET-10

1. Define angular momentum and show its relation with linear momentum. (See section 10.1)
2. Show that in quantum mechanical terms the components of angular momentum are

$$\hat{L}_x = \left(\frac{\hbar}{i} \left(y \frac{d}{dz} - z \frac{d}{dy} \right) \right)$$

$$\hat{L}_y = \left(\frac{\hbar}{i} \left(z \frac{d}{dx} - x \frac{d}{dy} \right) \right)$$

$$\text{and } \hat{L}_z = \left(\frac{\hbar}{i} \left(x \frac{d}{dy} - y \frac{d}{dx} \right) \right)$$

(See section 10.1)

3. Find out the following commutations:

$$[\hat{L}_x \hat{L}_y]; [\hat{L}_y \hat{L}_z]; [\hat{L}_z \hat{L}_x];$$

$$[\hat{L}_y \hat{L}_x]; [\hat{L}_z \hat{L}_y] \text{ & } [\hat{L}_x \hat{L}_z]$$

(See section 10.2)

4. Define \hat{L}^2 operator (See section 10.3)
5. Find out the commutation $[\hat{L}^2 \hat{L}_z]$ (See section 10.3)
6. Explain the physical significance of angular momentum (See section 10.4)
7. Explain $\hat{L}_x \hat{L}_y \hat{L}_z$ and \hat{L}^2 operators in terms of polar coordinates (See section 10.5)
8. Express \hat{L}_+ and \hat{L}_- operators (See section 10.6)
9. What are step up and step down operators? (See section 10.6)
10. Find out eigen values for \hat{L}_z and \hat{L}^2 operators choosing appropriate eigen functions (See section 10.7).

CHAPTER-11

Electron Spin and Related Concepts

SYNOPSIS	
Section	Topics
11.1	Orbital and spinning motion of electron
11.2	Spin antisymmetry and Pauli's Exclusion Principle
11.3	Coupling of angular momentum vectors
11.4	Russell – Saundar's Coupling (L–S Coupling)
11.5	Relative Energies of terms and Hund's rule of Maximum Multiplicity
11.6	Spin Orbit coupling & Zeeman effect
11.7	Complex Zeeman effect (or Anomalous Zeeman effect)

In chapter 6 (Section 6.13), it has been introduced that Unlenbeck and Goldschmidt had introduced that electron possess some intrinsic angular momentum of rotation which may be expressed as momentum of electron due to its spinning motion around its own axis. In the previous chapter, concepts related to angular momentum of moving electron have been introduced. Therefore, in this chapter electron spin and its related topics are being introduced.

11.1 ORBITAL AND SPINNING MOTION OF ELECTRON

Subatomic particles like electrons while moving around the nucleus show two types of rotation motion

- (i) Motion of electron in its orbit around the nucleus which is known as orbital motion and
- (ii) Motion of electron around its own axis which is known as electron's spinning motion.

Angular momentum vectors related to these motions are \vec{L} and \vec{S} . Both of these show commutation in similar fashion. Commutation rules for \vec{L} are shown in previous chapter i.e. in

chapter 10. Similarly, \vec{S} can also show commutation. The Eigen values for these two operators are also similar. Similar to \vec{L}^2 and \vec{L}_z operator, \vec{S}^2 and \vec{S}_z operators are there for spin angular momentum. In order to characterise the Eigen function for both of them l , m_l and s , m_s quantum numbers are these.

As mentioned in chapter 10, for orbital angular momentum

$$\hat{L}^2 Y_{l,m} = l(l+1) \hbar Y_{l,m} \quad \dots(11.1)$$

Which implies that

$$L = \sqrt{l(l+1)} \hbar \quad \dots (11.2)$$

And

$$\hat{L}_z Y_{l,m_l} = m_e \hbar Y_{l,m_l} \quad \dots (11.3)$$

Which implies that

$$L_z (\text{value}) = m_e \hbar \text{ or } m_l h/2\pi \quad \dots (11.4)$$

Where Y_{l,m_l} is spherical harmonics and can be shown as

$$Y_{l,m_l} = P_l^m F(\theta) F_m(\phi) \quad \dots(11.5)$$

And

$$F_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad \dots(11.6)$$

Similar to \vec{L} for spinning motion of electron, on operating operators on the eigen function we get

$$\hat{S}^2 \phi_{s,ms} = s(s+1) \hbar^2 \phi_{s,ms} \quad \dots(11.7)$$

And

$$S_z \phi_{s,ms} = m_s \hbar \phi_{s,ms} \quad \dots (11.8)$$

On study of atomic spectra it is clear that for a single electron this quantum number is 's'. Its value for single electron is $\frac{1}{2}$. Therefore, the value of spin vector is $(\sqrt{3}/2)\hbar$ for a single electron. Its z component is $m_s \hbar$ where m may have values $\pm 1/2$. Therefore, for single electron two Eigen functions are

$$\phi_{1/2, 1/2} \text{ and } \phi_{1/2, -1/2} \quad \dots(11.9)$$

These can be denoted by the symbols α and β

So,

$$\left. \begin{aligned} \hat{S}^2 \alpha &= \frac{3}{4} \hbar^2 \alpha \\ \text{And } \hat{S}^2 \beta &= \frac{3}{4} \hbar^2 \beta \end{aligned} \right\} \quad \dots(11.10)$$

Similarly

$$\begin{aligned} \hat{S}_z\alpha &= \frac{\gamma}{2}\hbar^2\alpha \\ \text{and } \hat{S}_z\beta &= \frac{\gamma}{2}\hbar^2\beta \end{aligned} \quad \dots(11.11)$$

\hat{S}_x , \hat{S}_y and \hat{S}_z also don't commute with each other similar to \hat{L}_x , \hat{L}_y and \hat{L}_z operators. \hat{S}^2 and \hat{S}_z operators can commute with each other. This clearly shows that \vec{S} vector and its one component i.e. \hat{S}_z can be ascertained similar to L and L_z values.

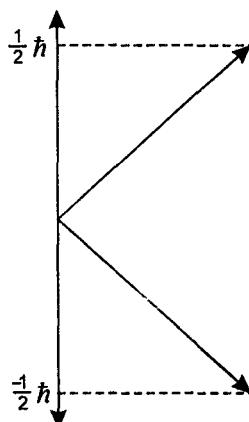


Fig. 11.1 showing S_z vectors for a single electron

11.2 SPIN ANTI-SYMMETRY AND PAULI'S EXCLUSION PRINCIPLE

For single electron system such as H-atom it is certain that electron has spinning motion which is designated by the symbol m_s and its value is either $+ \frac{1}{2}$ or $- \frac{1}{2}$. Discussion to specify the spin of two or multi-electron system can be explained as follows taking example of He-atom :

Taking into consideration two electrons in case of He-atom, wave function may be written as

$$\Psi = 1s(1) 1s(2) \quad \dots(11.12)$$

Where 1,2 are numbers given to two electrons in the He-atom. In excited state

$$\left. \begin{aligned} \Psi(1,2) &= 1s(1) \quad 1s(2) \\ \text{and } \Psi(2,1) &= 1s(2) \quad 1s(1) \end{aligned} \right\} \quad \dots(11.13)$$

These two functions are indistinguishable, therefore,

$$\begin{aligned} [\Psi(1,2)]^2 &= [\Psi(2,1)]^2 \\ \Psi(1,2) &= \pm \Psi(2,1) \end{aligned} \quad \dots(11.14)$$

Linear combination of Ψ^s may be written as

$$\Psi_+(\text{Sym}) = \frac{1}{\sqrt{2}} [1s(1) 1s(2) + 1s(2) 1s(1)]$$

$$\text{And } \Psi_-(\text{asym}) = \frac{1}{\sqrt{2}} [1s(1) 1s(2) - 1s(2) 1s(1)] \quad \dots(11.15)$$

Considering intrinsic (or spin) angular momentum for electron, from \hat{S} and \hat{S}_z operators this may be concluded that

$$\hat{S} = \sqrt{s(s+1)} \hbar \quad \dots(11.16)$$

On operation of S_z, m_s can be obtained as either $+ \frac{1}{2}$ or $- \frac{1}{2}$ for single electron and

$$\left. \begin{array}{l} \hat{S}_z \alpha = \frac{1}{2} \hbar \alpha(s) \\ \hat{S}_z \beta = -\frac{1}{2} \hbar \beta(s) \end{array} \right\} \quad \dots(11.17)$$

where $\alpha(s)$ and $\beta(s)$ are Eigen functions for electronic spin. These functions are usually orthonormal to each other which means that

$$\left. \begin{array}{l} \int \alpha^2 ds = \int \beta^2 ds = 1 \\ \int \alpha \beta ds = \int \beta \alpha ds = 0 \end{array} \right\} \quad \dots(11.18)$$

For He-atom i.e. for two electron system total four spin functions are possible which are given in table 11.1

Table 11.1

<i>Spin functions</i>	m_s	S_z
Symmetric $\alpha(1) \alpha(2)$	$+ \frac{1}{2} + \frac{1}{2} = 1$	$1 \hbar$
Anyisymmetric $\alpha(1) \beta(2)$	$+ \frac{1}{2} - \frac{1}{2} = 0$	0
Antisymmetric $\alpha(2) \beta(1)$	$- \frac{1}{2} + \frac{1}{2} = 0$	0
$\beta(1) \beta(2)$	$- \frac{1}{2} - \frac{1}{2} = -1$	$-1 \hbar$

Linear combinations for these functions are mentioned in table 11.2

Therefore, considering these spin functions orbital functions for He – atom i.e. for two electron system can be shown by equation 11.19.

Table 11.2

<i>Spin Functions</i>	<i>m_s</i>
$\alpha(1) \alpha(2)$	1
$\beta(1) \beta(2)$	-1
$\frac{1}{\sqrt{2}} (\alpha(1) \beta(2) + \alpha(2) \beta(1))$	0
$\frac{1}{\sqrt{2}} (\alpha(1) \beta(2) - \alpha(2) \beta(1))$	0

$$\left. \begin{array}{l} 1s(1)1s(2)[\alpha(1)\alpha(2)] \\ 1s(1)1s(2)[\beta(2)\beta(2)] \\ 1s(1)1s(2)\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\alpha(2)\beta(1))\right] \\ 1s(1)1s(2)\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\alpha(2)\beta(1))\right] \end{array} \right] \quad \dots(11.19)$$

Now the question arises that out of these functions which is the correct function for He-atom i.e. for $1s^2$ system? Answer of this question lies in one important principle known as Pauli's exclusion principle. This principle is also known as Pauli's spin antisymmetry wave function principle. According to this principle "for the systems where two or more electrons are there, total function including the spin function should be antisymmetric i.e. this function should be antisymmetric w.r.t. position of these two electrons". Therefore, on the basis of this principle the function.

$$1s(1)1s(2)\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\alpha(2)\beta(1))\right] \quad \dots(11.20)$$

will be valid function for the He-atom. This clearly indicates that in case of He – atom when two electrons are in same orbital (e.g. $1s^2$), their spin motion (m_s value) will be different i.e $\frac{1}{2}$ and $-\frac{1}{2}$, while in excited state following spin function combinations are possible.

$$\left. \begin{array}{l} \frac{1}{2}[1s(1)2s(2)+1s(2)2s(1)][\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\ \frac{1}{\sqrt{2}}[1s(1)2s(2)-1s(2)2s(1)][\alpha(1)\alpha(2)] \\ \frac{1}{\sqrt{2}}[1s(1)2s(2)-1s(2)2s(1)][\beta(1)\beta(2)] \\ \frac{1}{2}[1s(1)2s(2)-1s(2)2s(1)][\alpha(1)\beta(2)+\alpha(2)\beta(1)] \end{array} \right] \quad \dots(11.21)$$

11.3 COUPLING OF ANGULAR MOMENTUM VECTORS

Coupling of two angular momenta vectors is possible. For this coupling, following rules are to be followed :

- (1) Two angular momenta vectors \vec{L}_1 & \vec{L}_2 can couple to have one resultant \vec{L} vector whose magnitude will be $l(l+1)\ h$ where l is quantum number. For \vec{L} vector, allowed values for l can be ascertained on the basis of the following series.

$$l_1 + l_2, l_1 + l_2 - 1, \dots, (l_1 - l_2) \quad \dots (11.22)$$

- (2) Vector \vec{L} can lie anywhere on the cone formed around z-axis and L_z component will be fixed while L_x and L_y components of the vector are not certain.

- (3) \vec{L}_1 and \vec{L}_2 contributing to \vec{L} vector are also of fixed magnitude as $\sqrt{l_1(l_1+1)}\ h$ and $\sqrt{l_2(l_2+1)}\ h$,

- (4) L_z component of \vec{L} vector will have length $m_l h$ where m_l will have $2l+1$ values.

- (5) In this way two options are left :

- a. The values for l_1 & l_2 can be ascertained along with their z components m_{l_1} and m_{l_2} even if l and m_l are not certain. On the basis of this fact we can say that \vec{L}_1 and \vec{L}_2 have and \vec{L} will not have a well-defined cones. This is not the position of coupling.
- b. If l , l_1 and l_2 and m_l are ascertained but m_{l_1} & m_{l_2} are not certain. For example $m_l = l_1$ and $m_{l_2} = l_2$ then $m_{-l} = m_{l_1} + m_{l_2} = l_1 + l_2$, this implies that \vec{L} vector and its component L_z are well-defined with well-defined cones. In such a case individually \vec{L}_1 and \vec{L}_2 will also have well-defined cones, but their z components may not be certain. This is the case of coupling.

In order to understand these facts let us consider an example.

Example 11.1 Let two particles have $s = +\frac{1}{2}$ and $m_s = \pm \frac{1}{2}$. Explain their coupling.

Here

$$l_1 = s_1 = \frac{1}{2}; l_2 = s_2 = \frac{1}{2}$$

$$m_{l_1} = m_{s_1} = \pm \frac{1}{2} \text{ and } m_{l_2} = m_{s_2} = \pm \frac{1}{2}$$

\hat{S}^2 and \hat{S}_z will have Eigen functions

$$\alpha [s = \frac{1}{2}, m_s = \frac{1}{2}] \text{ and } \beta [s = \frac{1}{2}, m_s = -\frac{1}{2}]$$

On considering their coupling

$$\alpha_1 \alpha_2 [s_1 = \frac{1}{2}, m_{s_1} = \frac{1}{2}; s_2 = \frac{1}{2}, m_{s_2} = \frac{1}{2}]$$

$$\alpha_1 \beta_2 [s_1 = \frac{1}{2}, m_{s_1} = \frac{1}{2}; s_2 = \frac{1}{2}, m_{s_2} = -\frac{1}{2}]$$

$$\beta_1 \alpha_2 [s_1 = \frac{1}{2}, m_{s_1} = -\frac{1}{2}; s_2 = \frac{1}{2}, m_{s_2} = \frac{1}{2}]$$

And

$$\beta_1 \beta_2 [s_1 = \frac{1}{2}, m_{s_1} = -\frac{1}{2}; s_2 = \frac{1}{2}, m_{s_2} = -\frac{1}{2}]$$

In case of their coupling

$$S = \frac{1}{2} + \frac{1}{2} = 1 \text{ and } S = \frac{1}{2} - \frac{1}{2} = 0$$

With $S = 0$ value $m_s = 0$, this will be singlet state and

With $S = 1$ value $m_s = 1, 0$ and -1 , this will be triplet state

11.4 RUSSELL SAUNDER'S TERMS AND L.S. COUPLING

Electrons can show two types of motions viz. orbitals and spinning motion. Therefore, it may have two types of magnetic moments which can act as two magnets or two dipoles. The corresponding energy of which effects the energy levels of atoms. For example, in case of p-orbitals electrons ($l = 1, s = \frac{1}{2}$). Their orbital and spin motion can be in same direction ($\uparrow\uparrow$) or in opposite direction ($\downarrow\downarrow$) Fig. 11.2 shows such situation.

In first case total angular momentum J will have maximum ($j = 3/2$) and magnetic moments will be parallel. In second case these vectors will be antiparallel. In this way because of orbital-spin coupling two energy levels may be obtained in split manner viz $j = 3/2$ & $j = 1/2$. Difference between these two levels will be magnetic interaction energy which is known as spin orbital coupling constant.

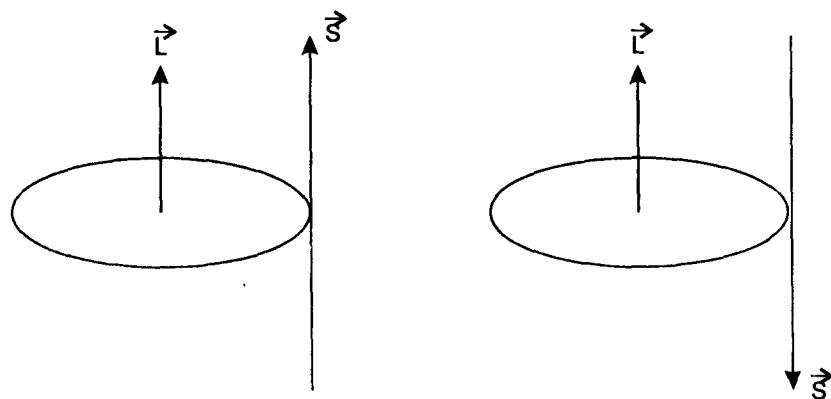


Fig. 11.2 Coupling of p-electrons

If couloumbic interaction between electrons is higher than that of spin – orbit interaction. It is taken as a less perturbation case. This may happen in case of light atoms. This type of coupling scheme is known as L-S coupling scheme or Russell Sannder's Coupling Scheme. On coupling of L & S, total angular momentum J may be obtained. From this scheme

$$\begin{aligned} L &= \sum l_i \text{ and} \\ S &= \sum S_i \end{aligned} \quad \dots (11.23)$$

And

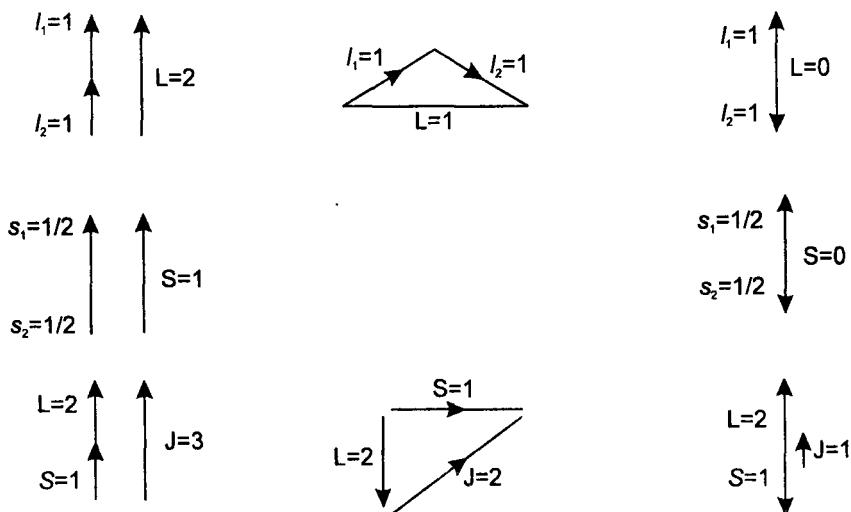
$$J = L + S, L + S - 1, \dots \dots \dots \quad \dots (11.24)$$

From this scheme j 's are not obtained with certainty separately. If spin orbit interaction is strong then for each electron (l) and (s) orbital momentum couples strongly and as a result j values

may be obtained. In second step j vectors of each electron may couple further but in a weak manner, this results in J angular momentum. This is known as $j-j$ coupling. In this scheme L and S are not significant. $L-S$ coupling scheme can be explained on the basis of the following examples :

Example 11.2 : Consider $2\ p\ 3\ p$ electronic configuration where $l_1 = 1; l_2 = 1; s_1 = s_2 = \frac{1}{2}$. Explain their $L-S$ coupling.

In this case l_1 and l_2 can couple to give $L = 2, 1, 0$. Similarly, S values will be $1, 0$ when $L & S$ will couple $J = 3, 2, 1$, values will be obtained as shown below :



In $L-S$ scheme energy levels are assigned symbols on the basis of L value as per follows

L	=	0	1	2	3	4
Symbol		S	P	D	F	G

Multiplicity for these levels may be ascertained on the basis of the following rules :

- (1) If $L \geq S$, then multiplicity will be $(2S+1)$ and which is known as spin multiplicity.
- (2) If $L \leq S$ then multiplicity will be $(2L + 1)$ which is known as term multiplicity.

On the basis of L and S value, complete term symbols may be assigned to energy levels which can be expressed as

$$(2S + 1) \cancel{\chi} L + S \dots |L-S| \quad \dots(11.25)$$

Where χ is the term symbol viz. S, P, D F, etc.

11.5 RELATIVE ENERGIES OF TERMS AND HUND'S RULE OF MAXIMUM MULTIPLICITY

After obtaining terms, the question arises to decide their energies. Hund had formulated rules for this purpose. For equivalent electrons those rules may be summarised as follows :

- (1) Term with maximum multiplicity will have less energy. Therefore, in $2p^2$ system order of energy for terms is ${}^3P \leq {}^1D$ or 1S . This rule means that in case of orbitals with same energy electrons should be first singly filled in them with parallel spin.
- (2) If two terms are such that their multiplicity is same, then the term with high L value will have less energy. Therefore, in $2p^2$ system ${}^1D \leq {}^1S$.
- (3) If orbitals are half filled then the terms with less J value will have less energy. Therefore, in $2p^2$ case in which orbitals are less than half filled, the order of energy will be

$${}^3P_0 < {}^3P_1 < {}^3P_2 \quad \dots(11.26)$$

Example 11.3 : Discuss the relative energies for terms in case of p^2 system.

In case of p^2 system L will have values 2, 1 and 0. Terms corresponding to these values are D, P and S. S values may be 1 and 0. Coupling L with S can be expressed as per the following energy level diagram with possible microstates and in increasing order of energies of the terms.

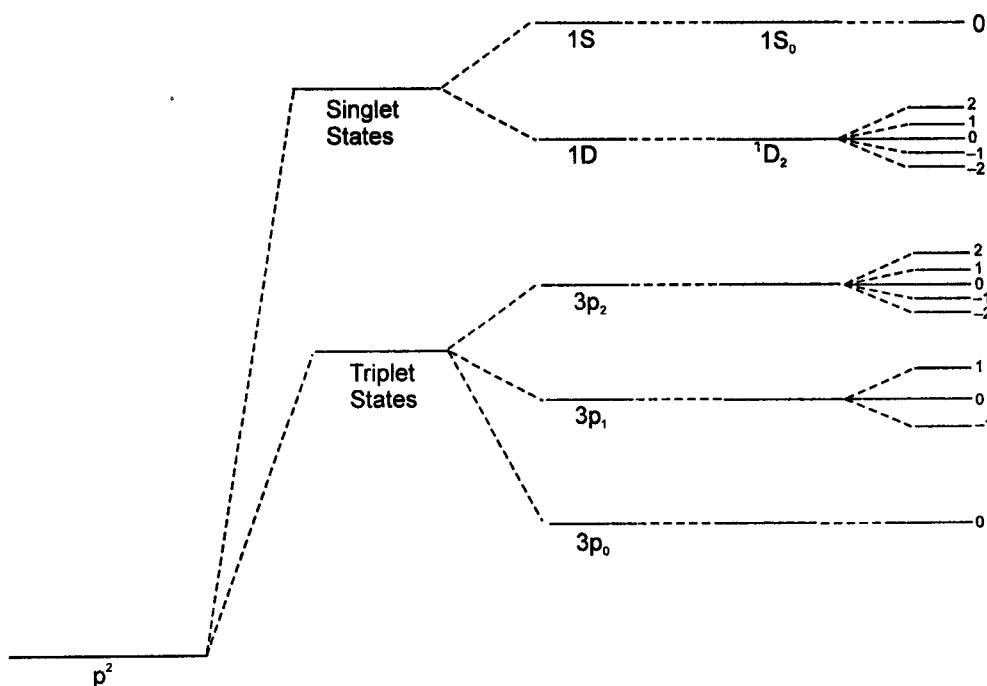


Fig. 11.3

Example 11.4 : Find out term for d^2 system and draw their energy level diagram.

In case of d^2 system, L values will be 4, 3, 2, 1, 0 and terms for this system will be G, F, P, D, & S. In this system, S will have the value 1 and 0 which shows that terms may be triplet or singlet terms. Taking into account only equivalent electrons, the valid terms will be 1S , 3P , 1D , 3F and 1G . Their energy level diagram with microstates is shown as per following figure 11.4.

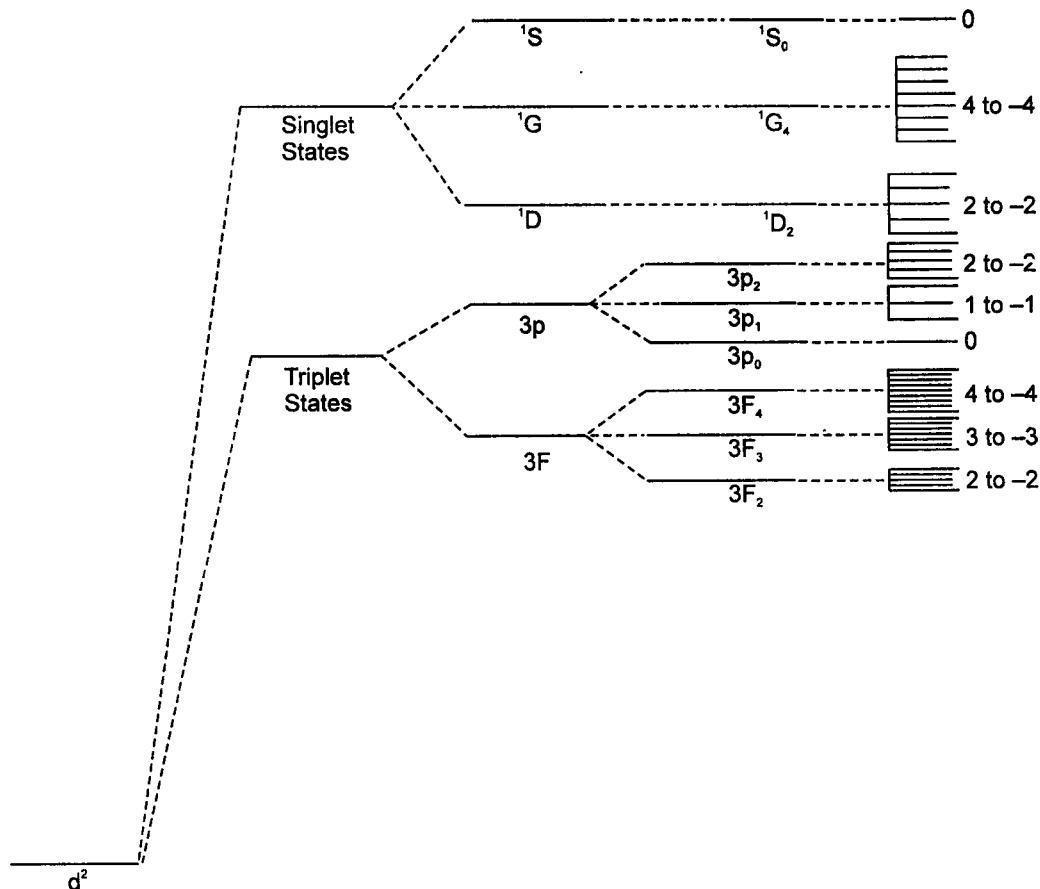


Fig. 11.4

11.6 SPIN ORBITAL COUPLING AND ZEEMAN EFFECT

On the basis of classical mechanics, according to Ampere's law (if we consider a moving electron in orbit as current flowing in a coil) in a coil where current is flowing with uniform rate magnetic field may be generated in this coil for which calculation of magnetic moment can be done as follows :

$$\left. \begin{array}{l} \text{Gauss's law} : \mu_m = \frac{iA}{C} \\ \text{SI} : \mu_m = iA \end{array} \right\} \dots(11.27)$$

Where

A = transverse area of coil

i = current flowing through it

and

c = Vel. Of light

considering electron in orbital motion as stated above

$$i = - \left(\frac{v}{2\pi r} \right) C \quad \dots(11.28)$$

Negative sign in equation 11.28 is because of negative charge of electron

$$\text{As } A = \pi r^2 \text{ (for orbital)} \quad \dots(11.29)$$

Therefore, for moving electron

$$\mu_m = - \left(\frac{ve}{2\pi r} \right) (\pi r^2) \frac{1}{c} = \frac{-vre}{2c}$$

and S.I. : $\mu_m = \frac{-vre}{2}$

$$\left. \begin{array}{l} \\ \end{array} \right\} \quad \dots(11.30)$$

Multiplying equation 11.30 by m_e i.e. mass of electron

$$\mu_m = - (m_e v_r) \left(\frac{e}{2m_e c} \right) = - L \left(\frac{e}{2m_e c} \right)$$

$$\text{S.I. : } \mu_m = - L \left(\frac{e}{2m_e} \right) \quad \dots(11.31)$$

$$\mu_m = - gL \quad \dots(11.32)$$

Where g is gyromagnetic ratio and is equal to $e/2m_e$ (S.I.). This type of system can be expressed as per the following figure 11.5.

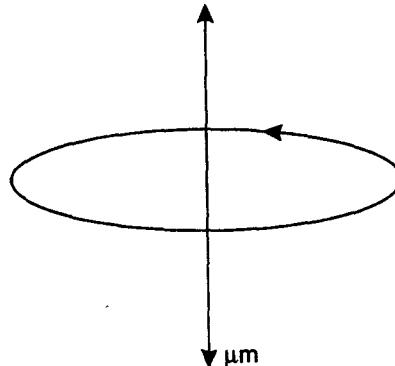


Fig.11.5

On the basis of quantum mechanics L for moving electron is

$$L = \sqrt{l(l+1)} \hbar \quad \dots(11.33)$$

$$\Rightarrow \mu_m = - \left(\frac{e\hbar}{4\pi mc} \right) \sqrt{l(l+1)} \quad \dots(11.34)$$

$$\text{S.I. : } \mu_m = - \left(\frac{e\hbar}{4\pi m} \right) \sqrt{l(l+1)} \quad \dots(11.35)$$

$$\Rightarrow \mu_m = \mu_s \sqrt{l(l+1)} \quad \dots(11.35)$$

Where μ_s = Bohr Magneton

As L_z component of angular momentum for moving electron is given by

$$L_z = m\hbar \quad \dots(11.36)$$

Therefore, if angle between z-axis and total angular momentum vector is ϕ

$$\Rightarrow \left(\sqrt{l(l+1)} \frac{\hbar}{2\pi} \cos \phi \right) = \frac{m\hbar}{2\pi} \quad \dots(11.37)$$

$$\begin{aligned} \text{Or } m &= \sqrt{l(l+1)} \cos \phi \\ &= \mu_m \cos \phi = \mu_z \end{aligned} \quad \dots(11.38)$$

If $l=1$, the angular momentum vector and magnetic moment vectors will have following allowed orientations as shown in figure 11.6

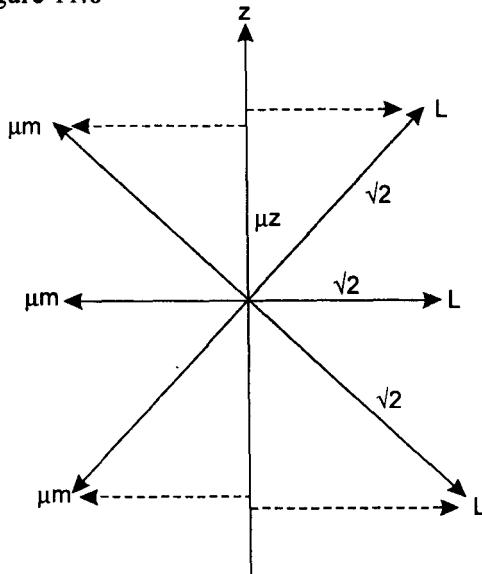


Fig. 11.6

In the presence of magnetic field these magnetic moment vectors show precession with magnetic field. Because of quantum restriction these vectors can't align with magnetic field. Let us suppose that in B magnetic field an electron possess the potential energy V . These two parameters can be correlated to each other as

$$V = -B\mu_z \quad \dots(11.39)$$

$$= -B(\mu_m \cos \phi) \quad \dots(11.40)$$

$$\text{Or } V = -B[-\mu_B \sqrt{l(l+1)}] \cos \phi \quad \dots(11.41)$$

$$\text{Or } V = B[\mu_B \sqrt{l(l+1)}] \cos \phi \quad \dots(11.42)$$

$$\text{Or } V = B\mu_B m \quad \dots(11.43)$$

$$\text{As } m = [\sqrt{l(l+1)}] \cos \phi$$

This implies that in a certain orbital energy of electrons will be

$$E = E_n + B\mu_B M \quad \dots(11.44)$$

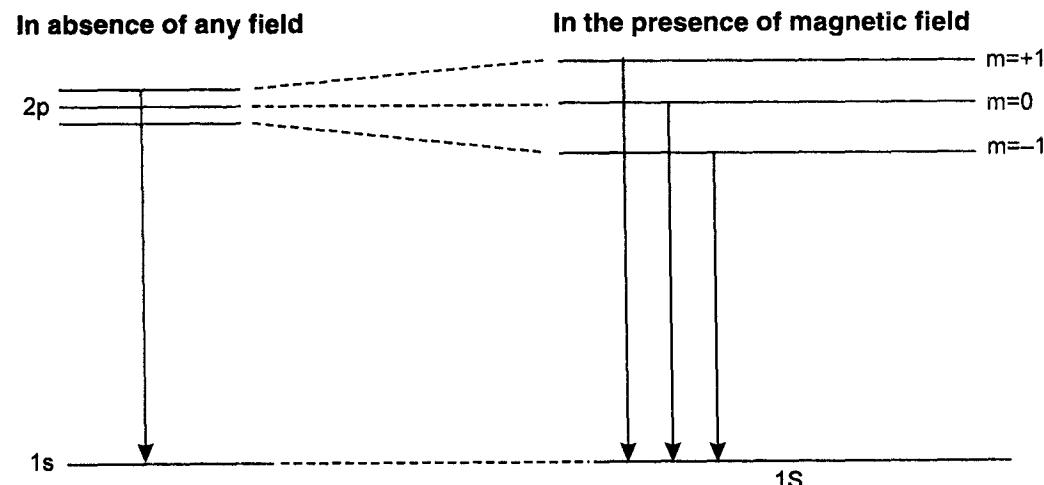
where E_n is the energy of electrons in the absence of any electric field.

In case of s-electrons $m = 0$ which implies that $E = E_n$. Therefore, this may be concluded that in the presence of external magnetic fields electrons remains unaffected

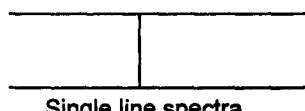
In case of p-electrons following energy levels may be obtained.

$$\left. \begin{array}{l} E(m=+1) = E_n + B\mu_B \\ E(m=0) = E_n \\ E(m=-1) = E_n - B\mu_B \end{array} \right\} \quad \dots(11.45)$$

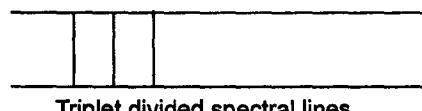
Therefore, in the presence of external magnetic field energy levels of p-orbitals may get split as a result of which in the presence of magnetic field spectral lines for the cases in which p-orbitals are involved may also get split. This effect is known as Zeeman effect. Fig. 11.7 shows such splitting.



The corresponding spectra will be



Single line spectra



Triplet divided spectral lines

Fig. 11.7

11.7 ANOMALONS ZEEMAN EFFECT

If atomic spectra is obtained with spectroscope of high resolution power, more complex spectra may be obtained. It is due to spin (or intrinsic) momentum of electrons. It has been proposed that for a moving electron the intrinsic momentum may also be effective which is known as spin angular momentum and for which

$$S = \sqrt{s(s+1)} \hbar$$

And $S_z = m_s \hbar$... (11.46)

And $S_z = S \cos \phi$ (similar to L) ... (11.47)

And $m_s = \sqrt{s(s+1)} \cos \phi$... (11.48)

For electron m_s will have $-s, -(s-1), \dots, (s-1)$ allowed values. For a single electron

$$S = \frac{1}{2} \text{ and}$$

$$S_z = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \frac{\hbar}{2\pi} \quad \dots (11.49)$$

Permitted values for m_s will be $\pm \frac{1}{2}$ therefore

$$S_z = \pm \frac{1}{2} \hbar \quad \dots (11.50)$$

The corresponding magnetic moment will be

$$\mu = -2gs \quad (\text{where } g \text{ is gyromagnetic ratio} = -e/2m_e : \text{SI}) \quad \dots (11.51)$$

This implies that

$$\mu = -2 \left(\frac{gh}{2\pi} \right) \sqrt{s(s+1)} \quad \dots (11.52)$$

or
$$\mu = -2 \left(\frac{eh}{4\pi m_e c} \right) \sqrt{s(s+1)} \quad \dots (11.53)$$

$$\text{S.I. : } \mu = -2 \left(\frac{e\hbar}{4\pi m_e} \right) \sqrt{s(s+1)} \quad \dots(11.53)$$

Therefore, taking spin only formula magnetic moment for electron will be

$$\mu = -2\mu_B \sqrt{s(s+1)} \quad \dots(11.54)$$

Therefore, potential energy for the electron will be

$$V = B\mu_z = -B(\mu \cos\phi) \quad \dots(11.55)$$

$$\text{Or } V = B [2\mu_B \sqrt{s(s+1)}] \cos\phi \quad \dots(11.56)$$

$$\text{Or } V = 2B\mu_B m_s \quad \dots(11.57)$$

$$\text{If } m_s = \frac{1}{2} = V = B\mu_B \quad \dots(11.58)$$

$$\text{And if } m_s = -\frac{1}{2} = V = -B\mu_B$$

Therefore, for electron total energy incorporating L & S angular momenta will be

$$E = E_n + B\mu_B m + 2B\mu_B m_s \quad \dots(11.59)$$

For s orbital $m = 0$

$$= E = E_n + 2B\mu_B m_s \quad \dots(11.60)$$

$$\text{If } m_s = +\frac{1}{2}$$

$$E = E_n + B\mu_B$$

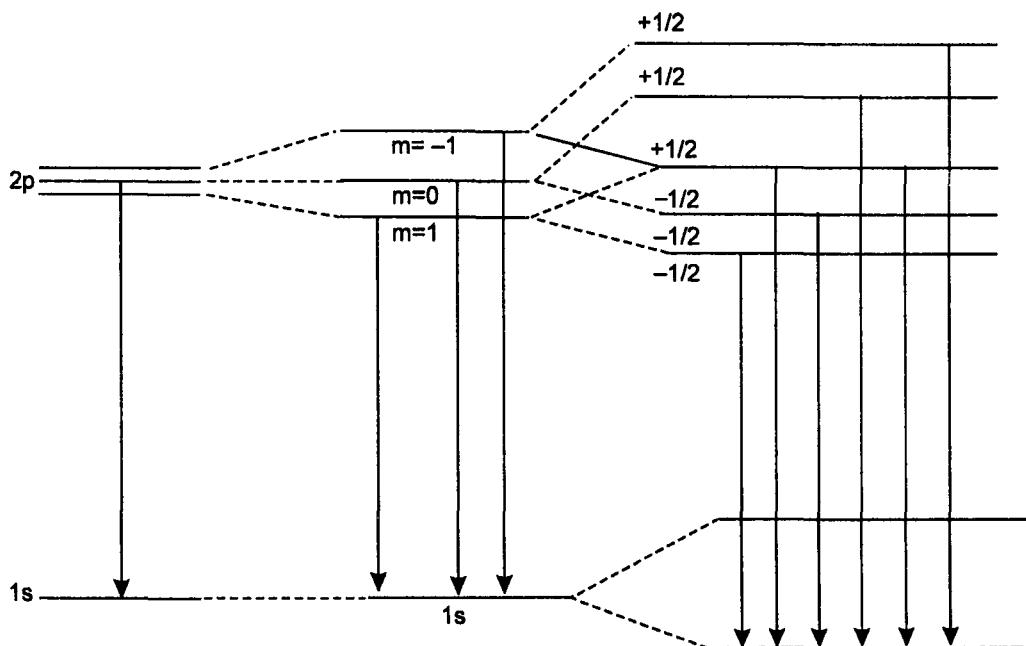
$$\text{And if } m_s = -\frac{1}{2}$$

$$E = E_n - B\mu_B \quad \dots(11.61)$$

Similarly for p-orbital

$m = 1$	$m_s = \frac{1}{2}$	$E = E_n + 2B\mu_B$	}
	$m_s = -\frac{1}{2}$	$E = E_n$	
$m = 0$	$m_s = \frac{1}{2}$	$E = E_n + B\mu_B$	}
	$m_s = -\frac{1}{2}$	$E = E_n - B\mu_B$	
$m = -1$	$m_s = \frac{1}{2}$	$E = E_n$	}
	$m_s = -\frac{1}{2}$	$E = E_n - 2B\mu_B$	

Considering energy levels mentioned in equation 11.61 and 11.62 following energy level diagram may be drawn on the basis of which this may be concluded that in presence of external magnetic field due to L & S coupling effect, Atomic spectral lines may split.



The corresponding spectra will be

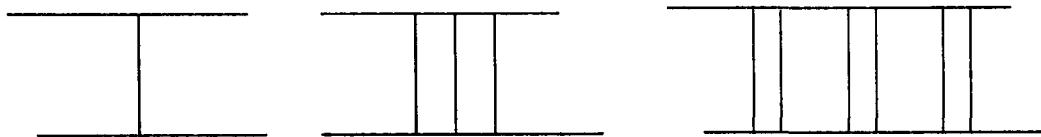


Fig. 11.8

PROBLEMS SET-10

1. Define intrinsic (spin) angular momentum of electron (See section 11.1)
2. Explain the operations of \hat{S}^2 and \hat{S}_z operators (See section 11.1)
3. Explain spin antisymmetry and Pauli's Exclusion Principle (See section 11.2)
4. Two subatomic particles have $s = + \frac{1}{2}$ and m_s values $\pm \frac{1}{2}$. Explain their coupling. (See section 11.3).
5. Explain the concept of coupling of angular moments vectors. (See section 11.3)
6. What do you understand by L – S coupling? (See section 11.4)
7. Explain the term symbols taking examples of p^2 and d^2 configuration. (See section 11.5)
8. What is Zeeman effect? (See section 11.6)
9. What do you understand by Anomalous Zeeman effect? (See section 11.1)
10. "Zeeman effect explains the splitting of atomic spectral lines" Explain. (See section 11.6 & 11.7).

SECTION-4

12. Concepts of Symmetry and Quantum Mechanics

13. Theories of Chemical Bonding

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CHAPTER-12

Concepts of Symmetry and Quantum Mechanics

SYNOPSIS	
<i>Section</i>	<i>Topics</i>
12.1	Symmetry elements and their related symmetry operations
12.2	Matrix representations for symmetry elements
12.3	Symmetry groups and point groups
12.4	Representation of a group
12.5	Character Table
12.6	Reducible and Irreducible Representations
12.7	Great Orthogonality Theorem
12.8	Reduction formula and its use
12.9	Projection operator and its use construction of SALC's (Symmetry adapted linear combinations).

Symmetry has a significant role in the determination of crystal structures and spectroscopic properties viz. Infrared and electronic spectroscopic properties of the molecules. Quantum mechanics provides a basis for solution of molecular structure. Therefore, consideration of symmetry of the molecule is basically its consideration in quantum mechanics. Therefore, it is required to have mathematics which provides a bridge between symmetry, properties of molecule and quantum mechanics and such mathematics is group theory. This chapter includes introduction to symmetry, properties of molecules viz. symmetry elements and related symmetry operations, their representations, point groups and their character tables, great orthogonality theorem, reduction formula with its applications, direct product representation and symmetry adapted linear combinations taking suitable example.

12.1 SYMMETRY ELEMENTS AND THEIR RELATED SYMMETRY OPERATIONS

Symmetry properties of the molecules may be defined w.r.t. some geometrical entities such as point, line or a plane. There are total five symmetry elements. These symmetry elements with their related operations are listed in table 12.1 and their discussion is being given thereafter.

Table 12.1
Symmetry Elements and their related operations

<i>Symmetry Element</i>	<i>Symbol</i>	<i>Symmetry operation related to this symmetry element</i>
(1)	(2)	(3)
Identity	E	—
Inversion centre	i	Inversion through this point (centre)
Axis of Symmetry	C _n	Rotation through this axis by an angle θ ($\theta = 360^\circ/n$) where n is the order of the axis.
Plane of symmetry	σ	Reflection through this plane
Improper axis of rotation	S _n	Rotation through this axis by an angle θ ($\theta=360^\circ/n$) (where n is the order of the axis) followed by reflection through a plane perpendicular to this axis.

Some of the example's showing symmetry elements and their related symmetry operations are given below :

Identity (E) : Identity means doing nothing to the molecule. Therefore, a well defined configuration of the molecule is its identity for example :

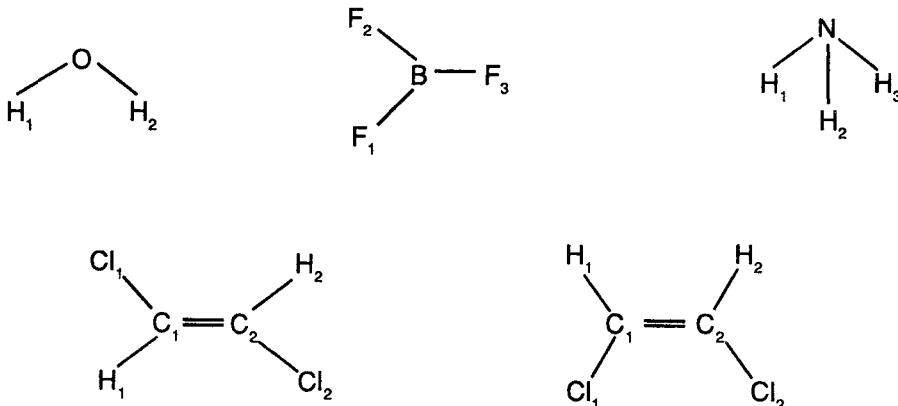
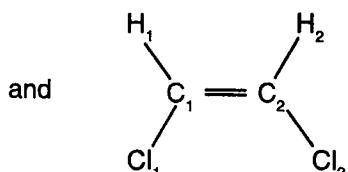
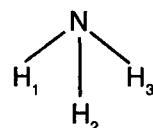
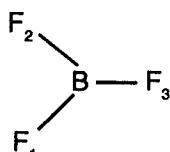
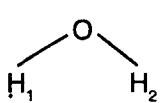


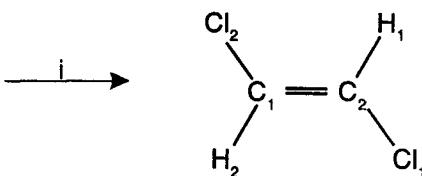
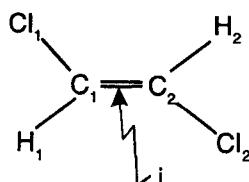
Fig.12.1

In above examples position of atoms have been fixed by numbers viz. 1, 2, 3 —— and no operation is being carried out on them. Therefore, these configurations may be treated as their identities.

Inversion Centre (i) : It is an imaginary centre which may be present inside the molecular body (on atom or in space) through which if inversion is carried out would yield a similar a equivalent structure. For example :



don't possess inversion centre, but trans $C_2H_2Cl_2$ possesses inversion centre.



Similarly CO_2 also possesses 'i'



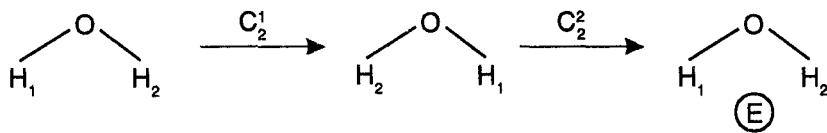
Fig. 12.2

For inversion centre following points may be noted:-

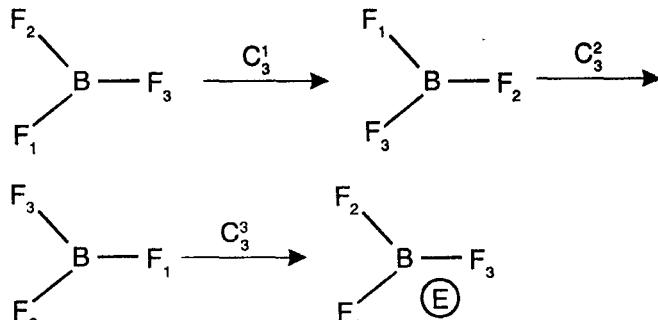
- i^n ($n = \text{odd}$) = i
- i^n ($n = \text{even}$) = E and
- $i^{-1} = i$

Proper Axis of rotation (C_n) : It is an imaginary line which passes through the molecular body through atom/s or through space on or along which if rotation in clockwise direction by an angle θ ($\theta = 360^\circ/n$) is carried out, it would yield a similar or equivalent structure.

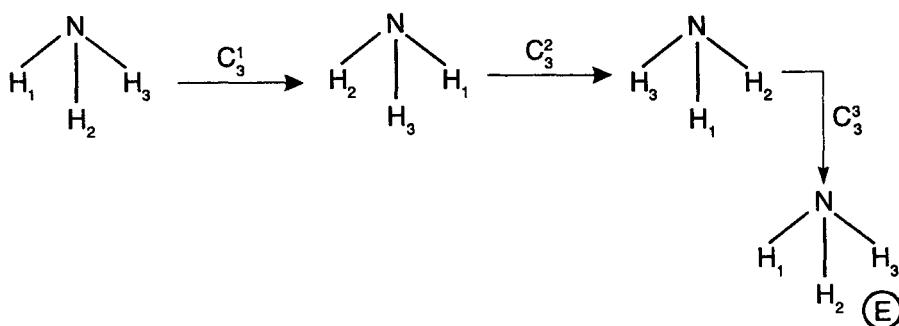
H_2O possesses C_2 axis



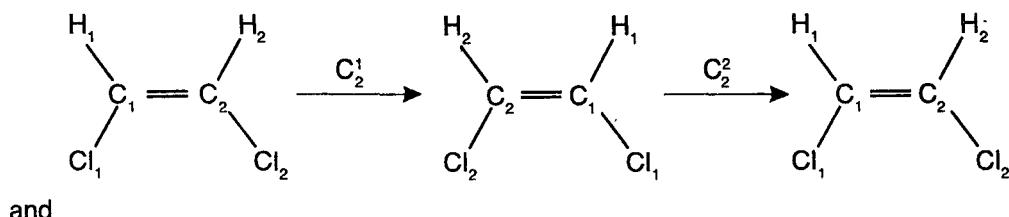
BF_3 possesses $C_3 \perp 3 C_2$. C_3 operations of BF_3 are shown below :



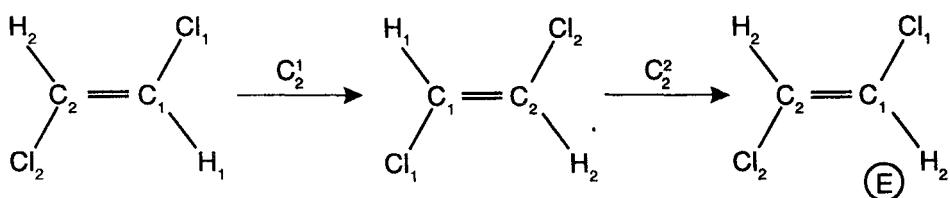
NH_3 possesses C_3 axis of rotation



$\text{C}_2\text{H}_2\text{Cl}_2$ (cis) and $\text{C}_2\text{H}_2\text{Cl}_2$ (trans) possess C_2 axis but their existence are different. In Cis- $\text{C}_2\text{H}_2\text{Cl}_2$, C_2 is parallel to the molecular plane but in trans- $\text{C}_2\text{H}_2\text{Cl}_2$, C_2 is perpendicular to the molecular plane.



and

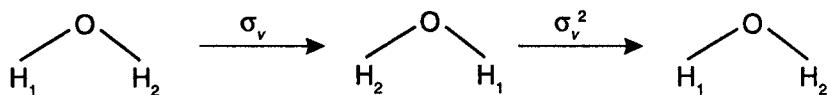


Following properties may be noted for proper axis of rotation (C_n axis):-

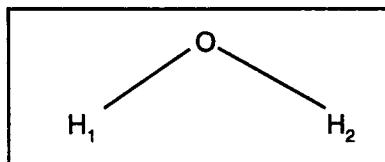
- (i) C_n^m may be any operation in C_n axis
- (ii) $C_n^n = E$ (or identity)
- (iii) If C_n^p is the inverse of C_n^m ; C_n^p may be computed as
Or inverse i.e. C_n^p is C_n^{n-m} for proper axis of rotation (viz C_n^m).

Plane of Symmetry (σ) : It is defined as an imaginary plane which passes through molecular body containing atoms or through space, through which if reflections are carried out would yield the similar or equivalent structure.

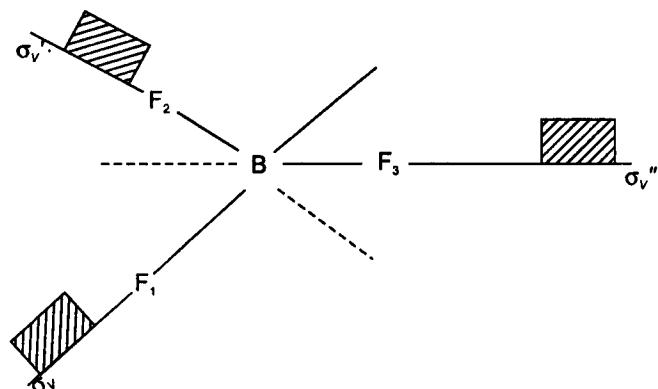
H_2O contains vertical planes



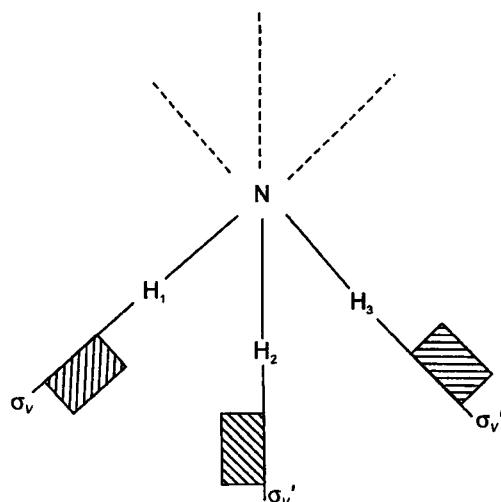
Another plane is molecular plane



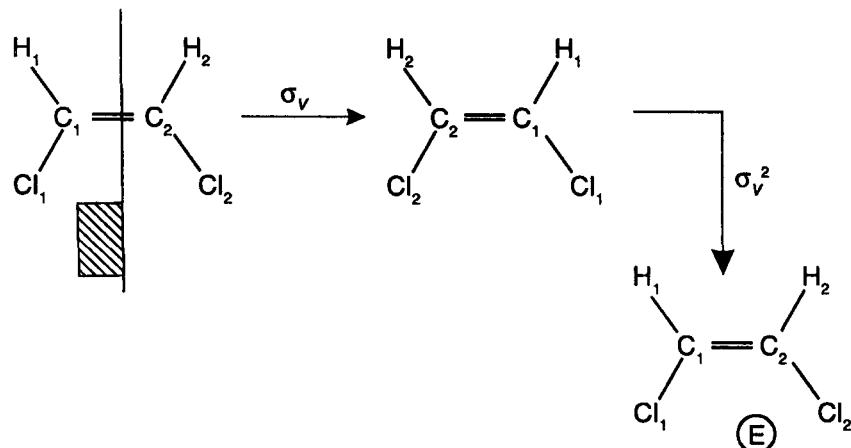
BF_3 contains $3\sigma_v$'s and one σ_h (i.e. molecular plane itself). Position of $3\sigma_v$'s are shown below :



NH_3 contains $3\sigma_v$'s and their existence can be made clear according to the following figure

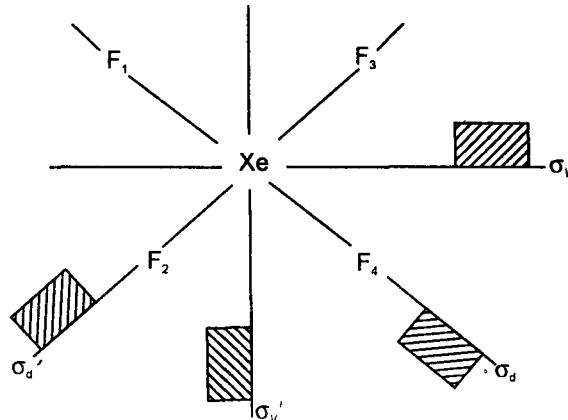


In case of Cis – C₂H₂Cl₂ two σ_v's are there out of which existence of one is shown in the following figure and other in the plane of molecular plane.

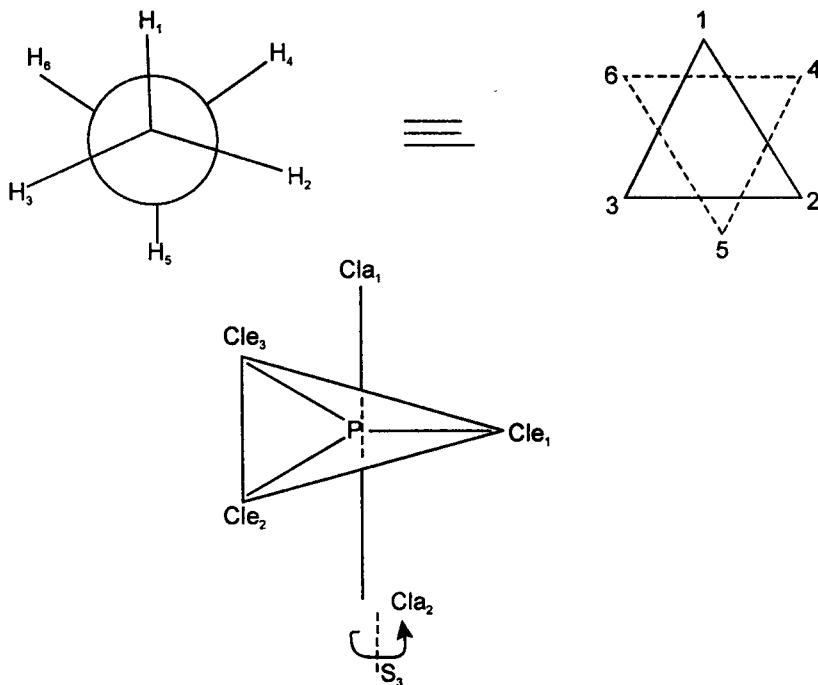


In case of trans – C₂H₂Cl₂ one σ_h is these which exists in the molecule as molecular plane.

XeF₄, AB₄ type square planer molecule contains one σ_h (the molecular plane) 2σ_v's and 2σ_d's whose existence can be made clear according to the following figure.



Improper Axis of Symmetry (S_n) : It is defined as an imaginary line which passes through the molecular body through atom or through space on or along which if rotation by an angle θ ($\theta = 360^\circ/n$) in clockwise direction is carried out followed by reflection through the plane perpendicular to this axis would yield the similar or equivalent structure. S_6 axis is present in staggered ethane which passes through central C–C axis. S_3 axis is present in PCl_5 molecule



If order of S_n is odd (i.e. $n = \text{odd}$) it requires $2n$ operations to reach upto identity as shown below (Taking example of S_3 axis).

$$S_3^1 = C_3^1 \cdot \sigma^1 = S_3^1$$

$$S_3^2 = C_3^2 \cdot \sigma^2 = C_3^2 \cdot E = C_3^2$$

$$S_3^3 = C_3^3 \cdot \sigma^3 = E \cdot \sigma = \sigma$$

$$S_3^4 = C_3^4 \cdot \sigma^4 = C_3^1 \cdot E = C_3^1$$

$$S_3^5 = C_3^5 \cdot \sigma^5 = C_3^2 \cdot \sigma = S_3^2$$

$$S_3^6 = C_3^6 \cdot \sigma^6 = E \cdot E = E$$

Similarly, it requires n operations to reach identity, if $n = \text{even}$ in case of S_n axis. This is shown below (taking example of S_6 axis)

$$S_6^1 = C_6^1 \cdot \sigma^1 = S_6^1$$

$$S_6^2 = C_6^2 \cdot \sigma^2 = E = C_6^2$$

$$S_6^3 = C_6^3 \cdot \sigma^3 = C_6^3 \cdot \sigma = C_6^3$$

$$S_6^4 = C_6^4 \cdot \sigma^6 = C_6^4 \cdot E = C_6^4$$

$$S_6^5 = C_6^5 \cdot \sigma^5 = C_6^5 \cdot \sigma = S_6^5$$

$$S_6^6 = C_6^6 \cdot \sigma^6 = E \cdot E = E$$

12.2 MATRIX REPRESENTATIONS FOR SYMMETRY ELEMENTS

Various symmetry elements can be expressed in the form of matrices w.r.t., x, y, z coordinates or p_x, p_y or p_z (where p's are the p-orbitals set) reference frame of axis. These symmetry elements and their matrix representations are given below :

Identity : Symbol is E, its matrix w.r.t. x, y & z axis of system is given by

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

Reflections : Considering x, y, z reference frame of axis i.e. considering σ_{xy}, σ_{yz} and σ_{xz} , matrices for plane of symmetry may be written as

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

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

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

Inversion centre (i) : Considering x, y, z reference frame of axis matrix representation for inversion centre is given by

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

Proper axis of rotation (C_n): For rotation axis or proper axis of rotation i.e.. for C_n axis with an assumption that z-axis may be considered as proper axis of rotation the matrix w.r.t. x, y, z coordinate is

$$C_n = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Where θ is the angle of rotation

Improper Axis of rotation (S_n) : Considering definition of improper axis of rotation, it is combination operation for C_n and σ_h . If z axis is considered as proper axis of rotation then σ_{xy} will be treated as σ_h . So, S_n may be the combination operation of C_n , σ_{xy} . Therefore, its matrix may be deduced as

$$\Rightarrow S_n = C_n \sigma_{xy}$$

$$S_n = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Or matrix for S_n is

$$S_n = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Example 12.1 : Find out matrices for C_2 & C_3 axis

$$\Rightarrow \text{Matrix for } C_2 = \begin{pmatrix} \cos 180^\circ & \sin 180^\circ & 0 \\ -\sin 180^\circ & \cos 180^\circ & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

($\theta = 180^\circ$ in case of C_2 axis)

$$\Rightarrow \text{Matrix of } C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Similarly for C_3 axis $\theta = 120^\circ$

$$\Rightarrow C_3 \text{ matrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

12.3 GROUPS AND POINT GROUPS

A group is a collection of elements which are inter-related to each other according to some rules. These rules are as follows :

- (i) The product of any two elements in a group and the square of element must be element of the same group

If E, A, B, C are elements of a group, then

$$AB = C \text{ or } BC = A \text{ or } A^2 B \text{ or } C$$

- (ii) A group must have an element that can commute with all other elements. In all the cases identity (or E) is such an element.
- (iii) In a group, associative law should hold good for elements. If E, A, B, C, is a group then $A(BC) = (AB)C$
- (iv) Every element should have a reciprocal (i.e. $(\text{element})^{-1}$) which should be the member of same group.

Order of a group : Total number of elements in a group is called as its order. It is designated by 'h'. If a group has elements E, A, B, C, then its order is 4, In case of molecules if symmetry is taken into consideration no. of possible symmetry operations is the order of the molecular point group.

Sub group : Smaller group that may be formed within the larger group. A subgroup must follow the necessary conditions for formation of a group. Let us consider that the order of a subgroup is 'k', then 'k' must be divisor of the order of larger group or h/k must be an integer.

Classes : Another way of expressing a smaller group from a large group is 'class'. It is defined as the complete set of those elements in a group which are conjugate to each other.

Point Groups : Combination or collection of all the possible symmetry elements (or related operations) in case of a molecule which meet at a point in it, is known as point group. Short hand representations are used to express the point groups which are in accordance to c- σ -i system. This system is known as Schonflies system to express a point group. This system may be used by spectroscopists. Another system which can be used to express point groups is Herman Manguin system which is used by crystallographists. In figure 12.1 flow chart to assign point groups to molecules in c- σ -i system is given.

Example 12.2 : Systematically analyze the molecules H_2O , NH_3 , CO_2 , BF_3 , C_2H_2 , Cl_2 (trans) $\text{C}_2\text{H}_2\text{Cl}_2$ (cis) for point groups.

H_2O : It is not a linear molecule or a molecule of high symmetry. It is the molecule with axial symmetry. Principal axis of symmetry in this molecule is C_2 . It also contains 2 σ_v 's. Therefore, its point group is C_2V

NH_3 : It is not a linear molecule. It is not a molecule with high symmetry. It is the molecule with axial symmetry. Principal axis in this case is C_3 . It also contains 3 σ_v 's. Therefore, its point group is C_3v

CO_2 : It is a linear AB_2 type molecule with 'i' or inversion centre. It has C_{∞} axis and perpendicular $\infty \text{ C}_2$. Therefore its point group is $\text{D}_{\infty}\text{h}$

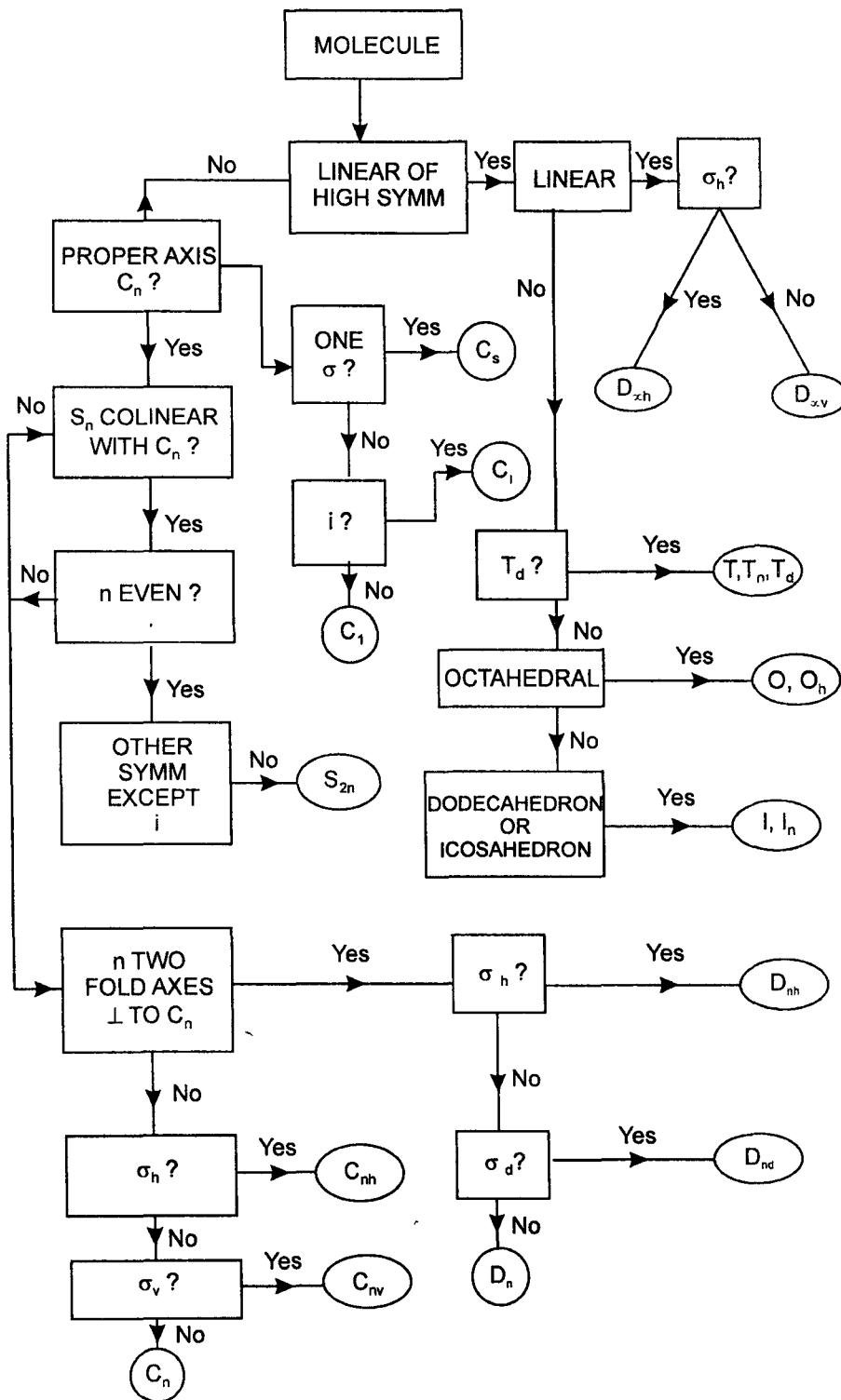


Fig. 12.3

BF₃ : It is not a linear molecule or a molecule with high symmetry. It is the molecule with axial symmetry and it possess C₃ axis as principal axis with perpendicular 3 C₂ axes. Apart from it, it also contains 3 σ_v's and σ_h. Therefore, its point group is D_{3h}

Trans-C₂H₂Cl₂ :— It is not a linear molecule or a molecule with high symmetry. It is the molecule with axial symmetry and it possess C₂ axis which is perpendicular to the plane of molecule. Apart from it also contains inversion centre 'i' and a plane σ_h. Therefore, its point group is C_{2h}

Cis-C₂H₂Cl₂ : It is not a linear molecule or with high symmetry. It is the molecule with axial symmetry and it possess C₂ axis which is present parallel passes through midpoint of C = C. It also contains 2 σ'v. Therefore, its point group is C_{2v}

12.4 REPRESENTATION OF A GROUP

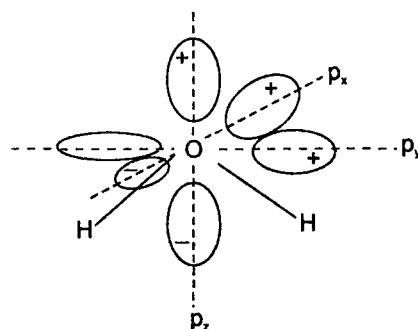
Representation of a point group can be done on some basis. These basis are :

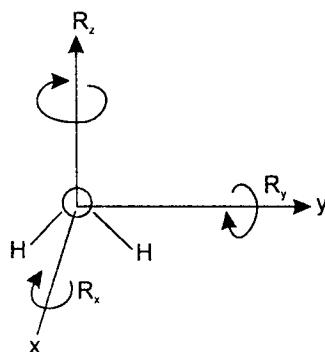
- (i) Cartesian coordinates x, y, z or basis vectors of specific length or position vectors, etc.
- (ii) Rotational vectors can also be taken as basis of representation.
- (iii) Mathematical functions or functions space as p_x, p_y or p_z or d-orbitals set also from the basis of representation.

Effect of any symmetry operation can be considered and represented using these set of basis. The representation will vary if the basis of representation is changed.

Let us try to have representation for C_{2v} point group on the basis of p-orbital set (i.e. p_x, p_y or p_z) considering + 1 for no change and -1 on any change during operation. The effect of these symmetry elements can be summarized as

E(p _x) = (+1) p _x	C ₂ (p _x) = (-1) p _x
E(p _y) = (+1) p _y	C ₂ (p _y) = (-1) p _y
E(p _z) = (+1) p _z	C ₂ (p _z) = (+1) p _z
σ _{xz} (p _x) = (+1) p _x	σ _{yz} (p _x) = (-1) p _x
σ _{xz} (p _y) = (-1) p _x	σ _{yz} (p _y) = (+1) p _y
σ _{xz} (p _z) = (+1) p _z	σ _{yz} (p _z) = (+1) p _z





Similarly considering rotational vectors as basis

$$E(R_x) = (+1) R_x$$

$$C_2(R_x) = (-1) R_x$$

$$\sigma_{xz}(R_x) = (-1) R_x$$

$$\sigma_{yz}(R_x) = (+1) R_x$$

$$E(R_y) = (+1) R_y$$

$$C_2(R_y) = (-1) R_y$$

$$\sigma_{xz}(R_y) = (+1) R_y$$

$$\sigma_{yz}(R_y) = (-1) R_y$$

$$E(R_z) = (+1) (R_z)$$

$$C_2(R_z) = (+1) (R_z)$$

$$\sigma_{xz}(R_z) = (-1) (R_z)$$

$$\sigma_{yz}(R_z) = (-1) (R_z)$$

On tabulating all these following table may be generated

C_2v	E	C_2	σ_{xz}	σ_{yz}	
	1	1	1	1	p_z
	1	1	-1	-1	R_z
	1	-1	1	-1	p_x, R_y
	1	-1	-1	1	$p_y R_x$

Considering d-orbitals as function space complete table is as follows :

C_2v	E	C_2	σ_{xz}	σ_{yz}		
τ_1	1	1	1	1	p_z	x^2, y^2, z^2
τ_2	1	1	-1	-1	R_z	xy
τ_3	1	-1	1	-1	$p_x R_y$	xz
τ_4	1	-1	-1	1	$p_y R_x$	yz

In the table mentioned above τ_1, τ_2, τ_3 & τ_4 are representations of C_2v point group. This type of table is known as character table.

12.5 CHARACTER TABLE

For any point group, as mentioned above in section 12.4 a table can be constructed. This type of table is known as character table and this table has six areas, as shown below :

(A)	C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
	τ_1	1	1	1	1	p_z	x^2, y^2, z^2
(C)	τ_1	1	1(D)	-1	-1	$R_z(E)$	$xy(F)$
	τ_3	1	-1	1	-1	p_x, R_y	xz
	τ_4	1	-1	-1	1	p_y, R_x	yz

Portion A : It represents the symbols of the point group in Schnoflies system

Portion B : It has the list of symmetry operations separated in different classes.

Portion C : It has symbols for irreducible representation in the Mulikan's notations.

Portion D : This portion contains characters for different irreducible representations.

Portion E : This portion contains single function space as basis of representation (such as p_x , p_y or p_z ; R_x , R_y or R_z etc.)

Portion F: This portion contains multiple function space (i.e. x^2 , y^2 , z^2 , $x^2 - y^2$, xy , xz , yz , etc.) as basis for different irreducible representations.

Character table for C_{2v} point group is :

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	p_z	x^2, y^2, z^2
A_1	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	p_x, R_y	xz
B_2	1	-1	-1	1	p_y, R_x	yz

12.6 REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS

A representation may be defined as a set of matrices or their characters which represents the operations of a point group. As mentioned earlier, the set of vectors of coordinate systems or the mathematical function space, with respect to which these matrices can be defined is the basis of representation. Let us consider x, y, z as basis of representation in case of C_{2v} point group, then the following matrices may be expressed

$$\begin{matrix} E \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{matrix}$$

Character = 3

$$\begin{matrix} \sigma_{xz} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{matrix}$$

Character = 1

$$\begin{matrix} C_2 \\ \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +1 \end{pmatrix} \end{matrix}$$

Character = -1

$$\begin{matrix} \sigma_{yz} \\ \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \end{matrix}$$

Character = 1

Therefore the cumulative representation may be represented as

C_2v	E	C_2	σ_{xz}	σ_{yz}	
$T_{x,y,z}$	3	-1	1	1	x, y, z

In any representations character of identity operation is known as the dimension of the representation. Therefore Γ_{xyz} is three dimensional representation.

We have seen earlier in section 12.5 that if individually representations or w.r.t. x, y or z are considered their dimensions are one. Therefore, Γ_{xyz} is a reducible representation and the representations corresponding to x, y & z individually (i.e. A_1 , B_1 & B_2) are irreducible representations. Therefore, this may be concluded that the representations whose dimension is high are reducible representations and the representations which have less or least dimensions are irreducible representations.

Criteria for irreducibility

For any representation if it is an irreducible representation following criteria must be obeyed.

$$\sum n_R X_a(R) X_a^*(R) = h$$

All classes

Where n_R = no. of times an operation is there in a class

$X(R)$ = character for R representation

$X^*(R)$ = character for its conjugate

If there is no. complex conjugate, then criterion is

$$\sum_{\text{all classes}} n_R [\chi(R)]^2 = h$$

Where h is order of the point group

Example 12.3 : Show that the representations Γ_{xyz} (as shown in section 12.6 above) is a reducible representation for C_{2v} point group and A_1 and B_1 are irreducible representations :

Table for C_{2v} point group is

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	p_z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	$p_x R_y$
B_2	1	-1	-1	1	$P_y R_x$
Γ_{xyz}	3	-1	1	1	xyz

Applying criteria of irreducibility to Γ_{xyz} , A_1 & B_1

Γ_{xyz} :

$$\begin{aligned} &= (1 \times (3)^2 + 1 \times (-1)^2 + 1 \times (1)^2 + 1 \times (1)^2) \\ &= 10 \neq h \text{ (i.e. 4)} \end{aligned}$$

Therefore, Γ_{xyz} is a reducible representation.

A_1 :

$$\begin{aligned} &= (1 \times (1)^2 + 1 \times (1)^2 + 1 \times (1)^2 + 1 \times (1)^2) \\ &= 4 = h \text{ (i.e. 4)} \end{aligned}$$

Therefore, A_1 is an irreducible representation

B_1 :

$$\begin{aligned} &= (1 \times (1)^2 + 1 \times (-1)^2 + 1 \times (1)^2 + 1 \times (-1)^2) \\ &= 4 = h \text{ (i.e. 4)} \end{aligned}$$

Therefore, B_1 is an irreducible representation

12.7 GREAT ORTHOGONALITY THEOREM (G.O.T.)

The statement of Great orthogonality theorem may be expressed as :

$$\Sigma [\tau_i(R)_{mn}] [\tau_i(R)m'n'] = \left(h / \sqrt{l_i l_i} \right) (\delta_{ij} \delta_{mm} \delta_{nn})$$

This theorem may be represented into following five rule, :

- (i) The number of irreducible representation in a group is equal to the number of classes of operations of that group
- (ii) The sum of squares of dimensions of the irreducible representations of a group is equal to the order of group i.e. $\sum l_i^2 = l_1^2 + l_2^2 + \dots = h$
- (iii) The sum of squares of characters in any irreducible representations in any point group is equal to the order of that group.
i.e. $\sum [X_i(R)]^2 = h$
- (iv) The characters of two different irreducible representations of a same point group are orthogonal to each other
i.e. $\sum X_i(R) X_j(R) = 0$
- (v) In a given representation (reducible or irreducible) the characters of all the matrices belonging to the same class are identical.

Example 12.4 : Prove G.O.T. (five rules of it) taking C_{2v} point group as example

Consider, the character table for C_{2v} point group given in the text above

- (i) In this character table there are 04 classes (viz E, C_2 , σ_{xz} & σ_{yz}) and 04 representations (viz. A_1 , A_2 , B_1 & B_2)
 - (ii) Sum of squares of dimensions i.e. $\sum X^2(E)$
 $= 1^2 + 1^2 + 1^2 + 1^2 = 4 = h \text{ (i.e. 4)}$
- It is equal to the order of the group

- (iii) Sum of squares of characters in any irreducible representation must be equal to order of the group, this can be shown as follows :

$$A_1 = 1^2 + 1^2 + 1^2 + 1^2 = 4 = h \text{ (i.e. order)}$$

$$A_2 = 1^2 + 1^2 + (-1)^2 + (-1)^2 = 4 = h \text{ (i.e. order)}$$

$$B_1 = 1^2 + (-1)^2 + 1^2 + (-1)^2 = 4 = h \text{ (i.e. order)}$$

$$B_2 = 1^2 + (-1)^2 + (-1)^2 + 1^2 = 4 = h \text{ (i.e. order)}$$

- (iv) Two different irreducible representations i.e. either $A_1 A_2 B_1$ or B_2 are orthogonal to each other. This can be proved by taking example of A_1 & A_2

$$1 \times 1 \times 1 + 1 \times 1 \times 1 + 1 \times 1 \times (-1) + 1 \times 1 \times (-1) = 0$$

- (v) It is obvious that in all the irreducible representation i.e. $A_1 A_2 B_1$ & B_2 characters of the matrices belonging to the operations of the same class are identical i.e. characters of the matrices belonging to E , C_2 , σ_{xz} or σ_{yz} are identical.

This proves the G.O.T. for C_2v point group.

12.8 REDUCTION FORMULA & ITS USE

Formula which is used to find out the numbers of times irreducible representations that contribute to a reducible representation is known as Reduction formula. This formula may be represented as

$$a_j = \frac{1}{h} \sum_{\text{over all classes}} n_i \chi_i(R) \chi_j(R)$$

Where a_j = no. of times that an irreducible representation with characters $X_j(R)$ appears in the reducible representation with characters $X(R)$ and n_i is the number of operations in a class.

Example 12.5 : Reduce the reducible representation Γ_{xyz} for C_{2v} point group

Please refer to character table for C_2v point group and applying reduction formula for Γ_{xyz} and considering A_1 , A_2 , B_1 & B_2 representations.

$$a_{A1} = \frac{1}{4} [1 \times 1 \times 3 + 1 \times 1 \times (-1) + 1 \times 1 \times 1 + 1 \times 1 \times 1] = 1$$

$$a_{A2} = \frac{1}{4} [1 \times 1 \times 3 + 1 \times 1 \times (-1) + 1 \times (-1) \times 1 + 1 \times (-1) \times 1] = 0$$

$$a_{B1} = \frac{1}{4} [1 \times 1 \times 3 + 1 \times (-1) \times (-1) + 1 \times 1 + 1 \times (-1) \times 1] = 1$$

$$a_{B2} = \frac{1}{4} [1 \times 1 \times 3 + 1 \times (-1) \times (-1) + 1 \times (-1) \times 1 + 1 \times 1 \times 1]$$

This shows that

$$\Gamma_{xyz} = A_1 \oplus B_1 \oplus B_2$$

12.9 CONSTRUCTION OF S.A.L.C'S (SYMMETRY ADAPTED LINEAR COMBINATIONS)

In this section, concept of projection operator and construction of symmetry adapted linearly combined orbitals i.e. S.A.L.C.'s is given.

Projection Operator : Let a projection operator P^u is operated on the function space Ψ^u , the operation may be defined as $P^u \Psi^u = (h/n_u) \Psi^u$

Where h is the order of the point group. This operation will give the result according to the above equation if projection operator and function space Ψ^u belongs to the same representation but if it belongs to the different representation the result will be zero.

$$\text{i.e. } P^u \Psi^v = 0$$

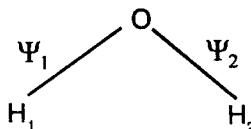
Projection operator P^u may be defined as

$$P^u = \sum X_u(R)^* O_R$$

Where O_R is the transformation operator.

Let us try to construct S.A. L.C.'s for H_2O molecule (Please refer to its character table)

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	p_z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	$p_x R_y$
B_2	1	-1	-1	1	$P_y R_x$



Effect of transformation operator O_R is

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Ψ_1	Ψ_1	Ψ_2	Ψ_2	Ψ_1
Ψ_2	Ψ_2	Ψ_1	Ψ_1	Ψ_2

Applying projection operator P^{A1} on Ψ_1 & Ψ_2

$$1 \times \Psi_1 + 1 \times \Psi_2 + 1 \times \Psi_2 + 1 \times \Psi_1 = 2(\Psi_1 + \Psi_2)$$

Therefore

$$P^A(\Psi_1 \text{ or } \Psi_2) \propto \Psi_1 + \Psi_2$$

Similarly by applying projection operators P^{A2} P^{B1} & P^{B2} on Ψ_1 & Ψ_2 following results may be obtained

$$P^{A2}(\Psi_1 \text{ or } \Psi_2) = 0$$

$$P^{B1}(\Psi_1 \text{ or } \Psi_2) = 0$$

$$P^{B2}(\Psi_1 \text{ or } \Psi_2) = 2(\Psi_1 - \Psi_2)$$

Therefore, two SALC's for H₂O molecule are $\Psi_1 + \Psi_2$ & $\Psi_1 - \Psi_2$ which on normalization becomes

$$\frac{1}{\sqrt{2}} (\Psi_1 + \Psi_2) \text{ & } \frac{1}{\sqrt{2}} (\Psi_1 - \Psi_2)$$

PROBLEMS SET-12

1. What do you understand by symmetry elements? (Section 12.1).
2. Define symmetry elements and their related symmetry operations (See section 12.1).
3. Prove that it requires $2n$ operations (if n is odd) to reach identity in S_n operation (See section 12.1).
4. Prove that it requires n operations to reach identity in S_n operation if $n = \text{even}$ (See section 12.1).
5. Find out matrix representations for
 - (a) Identity
 - (b) Reflection through σ_{xy} plane
 - (c) Reflection through σ_{yz} plane
 - (d) Reflection through σ_{xz} plane
 - (e) Proper axis of rotation with angle of rotation θ
 - (f) Improper axis of rotation (S_n axis) (See section 12.2).
6. Find out the matrices for C_2 & C_3^{-1} axis (see section 12.2).
7. Define group, sub group & class (See section 12.3).
8. What is point group ? Express the point groups for H₂O, NH₃, C₂H₂Cl₂ (Cis), C₂H₂Cl₂ (Trans), CO₂ & BF₃ (See section 12.3).
9. How will you represent a point group ? (See section 12.4).
10. What do you understand by a character table? Explain by taking example of C_{2v} (See section 12.5).
11. What do you understand by reducible and irreducible representations? (See section 12.6).
12. Prove that the following representation is reducible representation for C_{2v} point group.

C_2v	E	C_2	σ_{xz}	σ_{yz}
Γ	9	-1	1	3

13. What is criteria for irreducibility? (See section 12.6).
14. State & Explain great orthogonality theorem G.O.T. (See section 12.7)
15. Prove G.O.T. considering character table for C_{3v} point group (Pl. refer to section 12.7)

Given Character table for C_{3v} point group

C_{3v}	E	$2C_3$	3σ
A ₁	1	1	1
A ₂	1	1	-1
A ₃	2	-1	0

16. Explain reduction formula and its use (see section 12.8)
17. What is projection operator? (See section 12.9)
18. Construct S.A.L.C's for H₂O molecule (See section 12.9)

CHAPTER-13

Theories of Chemical Bonding

SYNOPSIS	
<i>Section</i>	<i>Topics</i>
13.1	LCAO – MO treatment for H_2^+ ion
13.2	LCAO – MO theory for H_2 molecule
13.3	Huckel – molecular orbital theory
13.4	Valance bond theory
13.5	Concept of hybridization

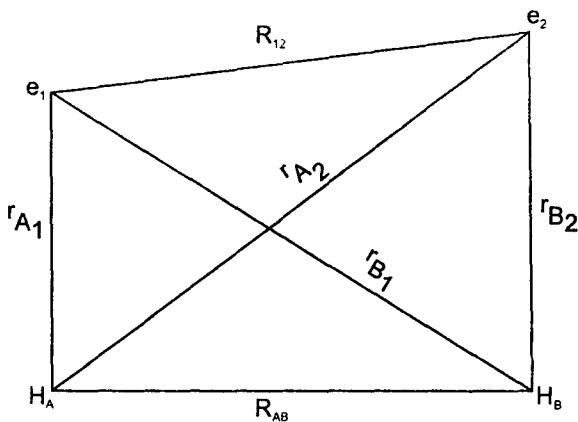
Concepts & theories of chemical bonding can be understood in a better way in the light of quantum mechanics. Linear combination of atomic orbitals, i.e., LCAO and formation of molecular orbital, i.e., LCAO – MO concept, valance bond concept as well concept of hybridization can be understood in a better manner in the light of quantum mechanics. In this chapter these concepts are included in detail.

13.1 L CAO – MO TREATMENT FOR H_2^+ ION

This concept may be treated as the consequence of variation principle. This concept is given in chapter – 8, sections 8.1, with ample mathematics and all the necessary informations related to this concept

13.2 LCAO-MO THEORY FOR H_2 MOLECULE

As one shifts from H_2^- ion to H_2 molecule the system becomes a little complicated as in this case two protons and two electrons are present. The Hamiltonian for this system may be written as :

**Fig. 13.1**

$$\hat{H}_{op} = \frac{-\hbar^2}{8\pi^2 m} \nabla_1^2 - \frac{\hbar^2}{8\pi^2 m} \nabla_2^2 - \frac{e'^2}{r_{A_1}} - \frac{e'^2}{r_{A_2}} - \frac{e'^2}{r_{B_1}} - \frac{e'^2}{r_{B_2}} + \frac{e'^2}{R_{AB}} + \frac{e'^2}{R_{12}} \quad \dots(13.1)$$

The electrons in this case will try to occupy the lowest bonding M.O. with opposite signs. The total molecular wave function will be written as

$$\Psi_{tot} = \Psi_{space} \Psi_{spin} \quad \dots(13.2)$$

Where

$$\Psi_{space} = \Psi_+^{(1)} \Psi_+^{(2)} \quad \dots(13.3)$$

For two electrons respectively and

$$\Psi_{spin} = \frac{1}{\sqrt{2}} [\alpha_{(1)} \beta_{(2)} - \alpha_{(2)} \beta_{(1)}] \quad \dots(13.4)$$

In the form of Slater determinant Ψ_{tot} may be written as

$$\Psi_{tot} = \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha_{(+)}(1) \alpha(1) & \Psi_+(1) \beta(1) \\ \Psi_+(1) \alpha(2) & \Psi_+(2) \beta(2) \end{vmatrix} \quad \dots(13.5)$$

Applying LCAO – MO Concept

$$\Psi_+ = C_1 \Psi_A + C_2 \Psi_B \quad \dots(13.6)$$

As two nuclei A & B are identical, therefore

$$C_1 = C_2 = \frac{1}{\sqrt{2(1-S_{AB})}} \quad \dots(13.7)$$

and the energy of the system can be determined by applying variation thereon as

$$E = \frac{\langle \Psi_+(1)\Psi_+(2) | \hat{H}_{\text{op}} | \Psi_+(1)\Psi_+(2) \rangle}{\langle \Psi_+(1)\Psi_+(2) | \Psi_+(1)\Psi_+(2) \rangle} \quad \dots(13.8)$$

On solution, the minimum energy for the system comes to be -30.68eV (-2.96 KJ mol^{-1}) at the stable internuclear distance, i.e., 73 pm. The bond energy of H_2 molecule is larger than that of H_2^+ - ion and the bond distance is smaller than that of H_2^+ ion.

In order to understand M.O. theory for π electron system HMO theory was proposed. This theory is given in section 13.3.

13.3 HUCKEL MOLECULAR ORBITAL THEORY (HMO THEORY)

This theory is based on following postulates :

(i) In a system σ and π electrons should be treated separately. Therefore

$$\hat{H}_{\text{tot}} = \hat{H}_\sigma + \hat{H}_\pi \quad \dots(13.9)$$

$$\Psi = \Psi_\sigma \Psi_\pi \quad \dots(13.10)$$

And $E = E_\sigma + E_\pi \quad \dots(13.11)$

As energy of π electrons is high and these electrons do not show any interaction with the nucleus because these electrons are perpendicular to the nucleus. These electrons easily take part in any chemical reaction and are more liable as compared to σ electrons. Distance between σ and π electrons remains less therefore their interaction term, i.e., $1/r_{\sigma\pi}$ will remain negligible. HMO theory, accounts for E_π energy for π electrons only.

(ii) Each and every π -electron does not interact with each other therefore, these π electrons may be treated separately. So, under free electron approximation we may write Hamiltonian as

$$\hat{H}_\pi = \hat{H}_1 + \hat{H}_2 + \dots \quad \dots(13.12)$$

$$\Psi_\pi = \Psi_1 \Psi_2 \Psi_3 \dots \quad \dots(13.13)$$

and $E = E_1 + E_2 + \dots \quad \dots(13.14)$

In order to understand this theory let us consider allyl system (only π electrons).

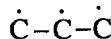


Fig. 13.2

Ψ for the allyl system may be written as

$$\Psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 \quad \dots(13.15)$$

As in allyl system each and every C-atom is sp^2 hybridized with ϕ_1, ϕ_2 and ϕ_3 as wave functions for 1,2 and 3 C-atoms respectively. Secular determinant for this system may be written as

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix} = 0 \quad \dots(13.16)$$

Where $H_{ij} = \int \phi_i \hat{H}_\pi \phi_j d\tau$ = resonance integrals = β
 $H_{ii} = \int \phi_i \hat{H} \phi_i d\tau$ = Columb integrals = α
 $S_{ij} = \int \phi_i \phi_j d\tau = 1$
 $S_{ij} = \int \phi_i \phi_j d\tau = 0$ as ϕ 's are orthonormal functions

Therefore for allyl system secular determinant will be

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad \dots(13.17)$$

Dividing the determinant by β

$$\begin{vmatrix} (\alpha - E)/\beta & 1 & 0 \\ 1 & (\alpha - E)/\beta & 1 \\ 0 & 1 & (\alpha - E)/\beta \end{vmatrix} = 0 \quad \dots(13.18)$$

Considering $(\alpha - E)/\beta = x$ the determinant will become

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \quad \dots(13.19)$$

Solution of above determinant yields $x = 0, \pm \sqrt{2}$. Therefore, three energy levels for π -electrons of allyl system may be obtained

$$E_1 = \alpha + \sqrt{2} \beta$$

$$E_2 = \alpha$$

$$\text{And } E_3 = \alpha - \sqrt{2} \beta \quad \dots(13.20)$$

MO diagram for π - electron in allyl system may be drawn as follows

On substituting the values of x one by one and solving the secular equation for C_1 & C_2

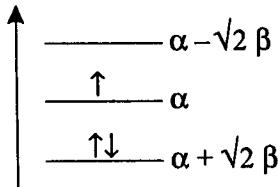


Fig. 13.3

Putting $x = -\sqrt{2}$

$$\begin{pmatrix} -\sqrt{2} & 1 & 0 \\ 1 & -\sqrt{2} & 1 \\ 0 & 1 & -\sqrt{2} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \quad \dots(13.21)$$

Solution of above equation yields $C_1 = C_3 = \frac{1}{2}$ and $C_2 = \sqrt{2}/2$. Therefore

$$\Psi_1 = \frac{1}{2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3) \quad \dots(13.22)$$

Similarly corresponding to $x = 0$

$$\Psi_2 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_3) \quad \dots(13.23)$$

And for $x = \sqrt{2}$; Ψ_3 may be obtained as

$$\Psi_3 = \frac{1}{2} (\phi_1 - \sqrt{2} \phi_2 + \phi_3) \quad \dots(13.24)$$

Charge density :

In order to calculate charge density on any atomic or molecular orbital following formula can be employed

$$Q_i = \sum_j n_j c_{ji}^2 \quad \dots(13.25)$$

Where C_{ji} is the probability of finding electrons in i^{th} level and n_j is the number of filled electrons in the level. Therefore for allyl radical charge densities for the three levels will be

$$q_1 = 2 \times \left(\frac{1}{4} \right) + 1 \times \left(\frac{1}{2} \right) = 1$$

$$q_2 = 2 \left(\frac{1}{2} \right) + 1 \times (0) = 1 \text{ and}$$

$$q_3 = 2 \times \left(\frac{1}{4} \right) + 1 \times \left(\frac{1}{2} \right) = 1$$

Bond order : Similarly charge density between two atoms i and k is bond order which may be calculated as

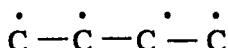
$$P_{ik} = \sum_{j=1}^{\text{all levels}} n_j C_{ji} C_{jk} \quad \dots(13.26)$$

where C_{ji} and C_{jk} are coefficient for i^{th} and k^{th} atoms and n_j is the no. of electrons filled in levels.

Applications of HMO theory :

Butadiene system : For this system secular determinant may be written as

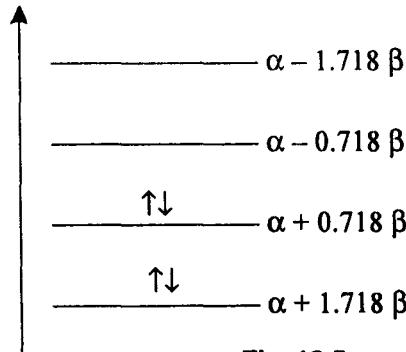
$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

**Fig. 13.4**

On solution of above determinant x will have values ± 0.718 or ± 1.718 . Therefore, energy levels for butadiene are

$$\begin{aligned} E_1 &= \alpha + 1.718 \beta \\ E_2 &= \alpha + 0.718 \beta \\ E_3 &= \alpha - 0.718 \beta \\ E_4 &= \alpha - 1.718 \beta \end{aligned} \quad \dots (13.27)$$

MO diagram for this molecule is shown below

**Fig. 13.5**

Energy for this system will be $4\alpha + 4.472\beta$

Ethylene system :

This system may be represented as

**Fig 13.6**

Secular determinant for this system may be written as

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad \dots (13.28)$$

On solving it $x = \pm 1$ and two energy levels may be obtained for the system

$$E_1 + \alpha + \beta \text{ and } E_2 = \alpha - \beta \quad \dots(13.29)$$

Its MO diagram will be

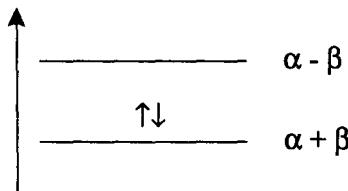


Fig. 13.7

Therefore for ethylene molecule, energy will be

$$E = 2\alpha + 2\beta \quad \dots(13.30)$$

Considering *butadiene* as combination of two ethylene molecules, energy of butadiene may be calculated as

$$E = 2(2\alpha + 2\beta) = 4\alpha + 4\beta \quad \dots(13.31)$$

As per calculation shown previously energy for butadiene is $4\alpha + 4.472\beta$

$$= \Delta E = (4 + 4.472\beta) - (4\alpha + 4\beta)$$

$$\Delta E = 0.472\beta \quad \dots(13.32)$$

This energy (ΔE) may be the stabilization energy for butadiene due to conjugation.

In case of ethylene two M.O.'s will be

$$\Psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \text{ and}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \quad \dots(13.33)$$

Charge density for both the C-atoms will be

$$2(\frac{1}{2}) = 1 \quad \dots(13.34)$$

$$\text{As } q_1^2 = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2} \text{ and } q_2^2 = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2}$$

Cyclobutadiene system :

For cyclobutadiene system secular determinant may be written as



Fig. 13.8

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0 \quad (13.35)$$

On solving this E may be obtained as $4\alpha + 4\beta$ (for four electrons). If this system would have been considered as combination of two ethylene molecules then also its energy will be $E = 4\alpha + 4\beta$. Therefore stabilization energy for cyclobutadiene will be

$$\Delta E = (4\alpha + 4\beta) - (4\alpha + 4\beta) = 0 \quad \dots (13.36)$$

Therefore, this may be concluded that cyclobutadiene is not a stable molecule

Cyclopropenyl system :

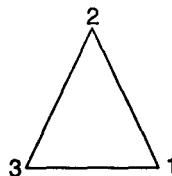


Fig. 13.9

For this system secular determinant may be written as

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0 \quad \dots (13.37)$$

On solving this determinant values for x will be -2 , 1 and 1 and the corresponding energy levels will be

$$E_1 = \alpha + 2\beta$$

and

$$E_2 = E_3 = \alpha - \beta$$

Therefore energy level diagram for cyclopropenyl cation, radical and anion are as follows :

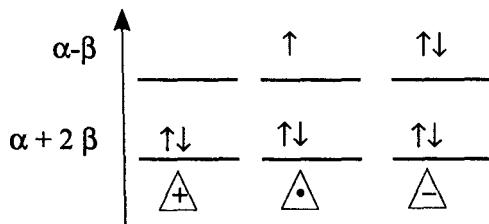


Fig. 13.10

Energy for cation will be

$$E = 2\alpha + 4\beta$$

And its stabilization energy will be 2β . Energy for radical will be

$E = 3\alpha + 3\beta$ with stabilization energy β and for anion energy will be

$E = 4\alpha + 4\beta$ with stabilization energy as zero. π wave functions for this system will be

$$\Psi_1 = \frac{1}{\sqrt{3}} (\phi_1 + \phi_2 + \phi_3)$$

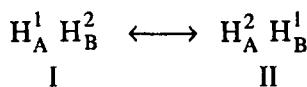
$$\Psi_2 = \frac{1}{2} (\phi_1 - \phi_2)$$

and

$$\Psi_3 = \frac{1}{\sqrt{6}} \phi_1 - \frac{2}{\sqrt{6}} \phi_2 + \frac{1}{\sqrt{6}} \phi_3 \quad \dots(13.38)$$

13.4 VALENCE BOND THEORY

This theory was given by Heitler and London. According to this theory concept of formation of H_2 molecule was explained. This theory was explained taking example of H_2 – molecule. According to this theory two hydrogen atoms which are far apart, i.e., H_A and H_B with electrons 1 and 2 can be expressed by individual wave functions Ψ_{A1} and Ψ_{B2} i.e., electron 1 is with 1s of H_A and electron 2 is around 1s of H_B atoms individually. When they come close to each other interaction between them starts and because of which their atomic orbitals Ψ_{A1} and Ψ_{B2} interact to form molecular orbital. Two possible structures can be assigned to H_2 molecule viz.



Structure I and II are covalent structures and the wave functions corresponding to these molecular structures may be written as

$$\Psi_I = \Psi_{A1} \Psi_{B2} \text{ and } \Psi_{II} = \Psi_{A2} \Psi_{B1} \quad \dots(13.39)$$

Combination of these two would yield Ψ_{MO} which may be written as

$$\Psi_{MO} = C_I \Psi_I + C_{II} \Psi_{II} \quad \dots(13.40)$$

$$\text{or} \quad \Psi_{MO} = C_I \Psi_{A1} \Psi_{B2} + C_{II} \Psi_{A2} \Psi_{B1} \quad \dots(13.41)$$

Where C_I & C_{II} are coefficient for Ψ_I and Ψ_{II} respectively, C_I & C_{II} should follow the following relation for minimum energy for the system

$$C_I^2 = C_{II}^2 \quad \dots(13.42)$$

$$C_I = \pm C_{II}$$

If $C_I = 1$; C_{II} should have values either + 1 or -1 corresponding to which symmetric and antisymmetric combinations for the functions may be obtained

$$\Psi_s = \Psi_{A1} \Psi_{B2} + \Psi_{A2} \Psi_{B1}$$

$$\text{or} \quad \Psi_s = C_I (\Psi_I + \Psi_{II}) \quad \dots(13.43)$$

and for $C_{II} = -1$

$$\Psi_{AS} = \Psi_{A1} \Psi_{B2} - \Psi_{A2} \Psi_{B1}$$

$$\text{or} \quad \Psi_{AS} = C_I (\Psi_I - \Psi_{II}) \quad \dots(13.44)$$

In case of symmetric interaction, electronic waves are in same phase in between the nuclei, i.e., the spin of two interacting electrons are opposite or this results in the lower energy state than the isolated H_A & H_B atoms. If this type of interaction is there covalent bond forms between H_A and H_B with the corresponding energy

$$E_s = \frac{\langle \Psi_I | \hat{H} | \Psi_{II} \rangle + \langle \Psi_{II} | \hat{H} | \Psi_I \rangle}{\langle \Psi_I | \Psi_{II} \rangle + \langle \Psi_I | \Psi_{II} \rangle} \quad \dots (13.45)$$

This energy of the system has been attained at stable bond distance of H_2 molecule (i.e., $r_s = 0.87 \text{ \AA}$). In case of antisymmetric interaction of orbitals as explained by Ψ_{AS} ; spin of two combining electrons are parallel, i.e., the two electronic waves results in the formation of state of higher energy. This is given by

$$E_{AS} = \frac{\langle \Psi_I | \hat{H} | \Psi_{II} \rangle - \langle \Psi_{II} | \hat{H} | \Psi_I \rangle}{\langle \Psi_I | \Psi_{II} \rangle - \langle \Psi_I | \Psi_{II} \rangle} \quad \dots (13.46)$$

E_{AS} will be the higher energy state than corresponding interacting atoms because of this antisymmetric combination formation of molecule can't take place. Pauling & Slater suggested two more ionic structures which can contribute to the formation of H_2 molecule.



According the modification suggested by them during symmetric interaction Ψ_s will be

$$\Psi_s = \Psi_{cov} + \lambda \Psi_{ionic} \quad \dots (13.47)$$

Where λ is the degree of ionic character in the bond which is 0.17 for H_2 molecule and

$$\Psi_{ionic} = \Psi_{III} + \Psi_{IV} \quad \dots (13.48)$$

Where

$$\Psi_{III} = \Psi_{A1} \Psi_{A2} \quad \dots (13.49)$$

$$\text{and } \Psi_{IV} = \Psi_{B1} \Psi_{B2} \quad \dots (13.50)$$

By this modification r_s , i.e., bond distance for symmetric combination for H_2 molecule was calculated as 0.86 \AA .

The features or significant points regarding valance bond theory are :

- (i) All atomic orbitals retain their identity during formation of valance bond but only valance electrons lose it
- (ii) During bond formation only valance electrons remain effected.
- (iii) Each and every atom involve in the valance bond formation require some energy to have unpaired electron for the formation of bond.
- (iv) Strength of bond formed depends upon the extent of overlapping. So, if the overlap integral $S > 0$ stable bond will be formed, if it is $S < 0$ no bond will be formed and if $S = 0$ there is neither attraction nor repulsion.

- (v) If there is symmetrical interaction, i.e., Ψ_s m.o. formation is there between interacting atomic orbitals, σ molecular orbital (σ_{mo}) is formed. This happens in case of s-s or $p_z - p_z$ bond formation.
- (vi) If interaction is less i.e. in case of sideways overlapping between $p_x - p_x$ or $p_y - p_y$ a.o.'s π bond is formed.
- (vii) Extent of overlapping is more in case of σ bond instead of π Bond.
- (viii) Rotation around σ bond is possible and
- (ix) Isomerism can be shown along σ bond formed

Different types of AO's interaction and formation of σ and π bond is shown in figure 13.11

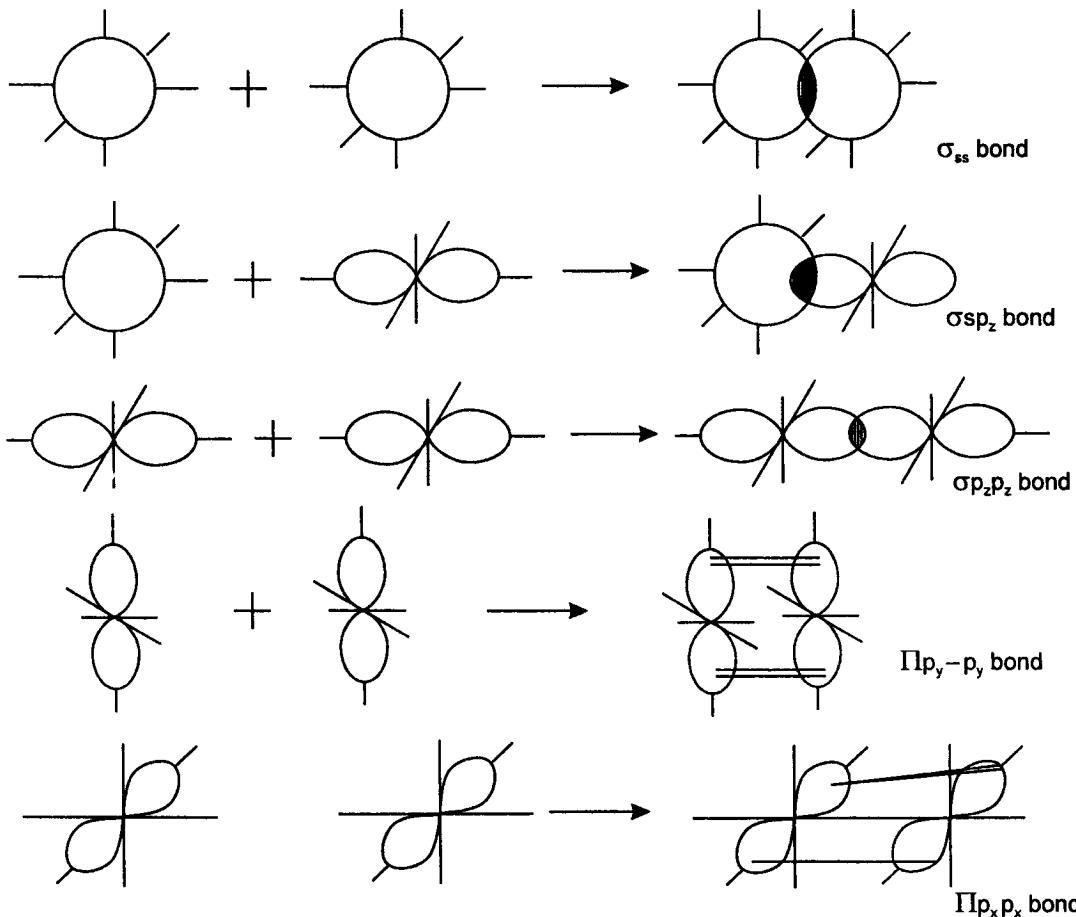
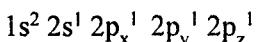


Fig. 13.11

13.5 CONCEPT OF HYBRIDIZATION

Carbon has atomic number 6 and its electronic configuration is $1s^2 2s^2 2p_x^1 2p_y^1$. This suggests that carbon should be bivalent in nature but actually carbon is a tetravalent atom in stable organic compounds. Likewise Be has electronic configuration $1s^2 2s^2$ and B has electronic configuration $1s^2 2s^2 2p_x^1$ which suggest that Be should be zerovalent and B should be monovalent but actually Be forms stable compounds in bivalent and B in trivalent states. To explain such anomalies a concept

has been introduced known as hybridization which involves the formation of hybrid orbitals. Here hybridization has been explained taking examples of Carbon atom. As mentioned above with electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1$, carbon should be taken as bivalent atom with two unpaired or uncoupled electrons with valance angle of about 90° . But it has been observed that in most of the stable organic compounds carbon is in tetravalent state with four unpaired electrons and its electronic configuration in excited state is



If it is assumed here that all the four orbitals. viz. $2s$ and $2p_x$, $2p_y$ & $2p_z$ are involved in bond formation, then the four bonds formed by carbon atom will be of different kinds on 3 bonds with p-orbitals will be of different nature is compared to 1 bond with s orbital as overlapping properties of s and p orbitals are different. But if we see the case of CH_4 and other carbon compounds it has been observed that all the four bonds of Carbon atoms are of same nature, i.e., identical bonds are formed by the carbon atom with equivalent energy at equal angles viz., $109^\circ 28'$ to each other to set up in regular tetrahedron geometry. This can be understood on the basis of hybridization. Some points or features regarding hybridization are as follows:

- (i) Hybridization is not a real physical phenomenon but it is a concept to explain the geometries or shapes of different molecules.
- (ii) AO's of central atom which have equal or comparable energies can undergo hybridization to give hybridized A.O.'s.
- (iii) No. of A.O.'s undergoing hybridization should be equal to no. of hybrid AO's formed as it is a phenomenon of intermixing of AO's of equal or nearly equal energy.
- (iv) Energy of hybrid A.O.'s formed should be equal.
- (v) Hybrid A.O.'s formed in Central atom should be mutually orthogonal and normalized set of A.O.'s, i.e., orthonormal sets of hybridized A.O.'s are formed after hybridization.
- (vi) These hybridized A.O.'s of central atom arrange themselves in space in such a way that they are far apart from each other as a result of which shape is attained by the molecule.

Carbon may have sp^3 , sp^2 and sp hybridization in its compounds. Construction of hybrid orbitals and angle between the hybrid A.O.'s can be explained as per follows :

sp^3 hybridization :

Formation of sp^3 hybrid AO's can be shown as per figure 13.12.

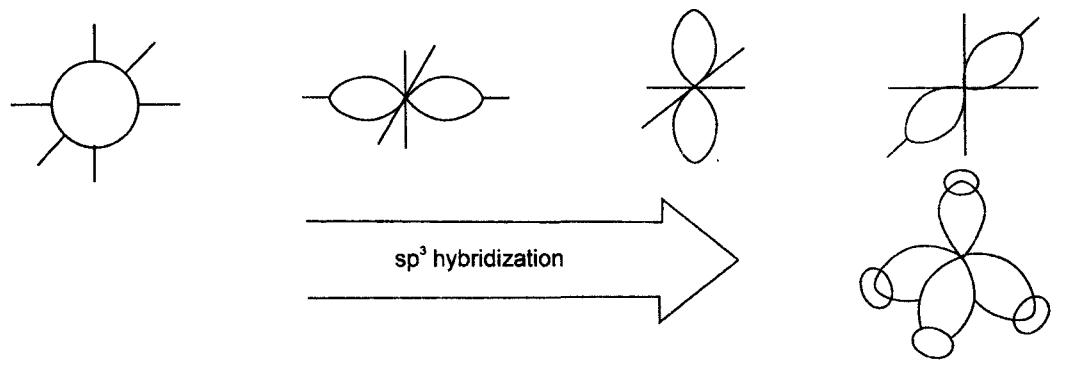


Fig. 13.12

sp^3 hybridized A.O.'s

These sp^3 hybrid A.O's are formed by the linear combinations of one 2s and three 2p orbitals of carbon atom. The wave functions of four equivalent hybrid orbitals obtained may be represented as

$$\Psi_1 = a_1 \Psi_s + b_1 \Psi_{px} + c_1 \Psi_{py} + d_1 \Psi_{pz}$$

$$\Psi_2 = a_2 \Psi_s + b_2 \Psi_{px} + c_2 \Psi_{py} + d_2 \Psi_{pz}$$

$$\Psi_3 = a_3 \Psi_s + b_3 \Psi_{px} + c_3 \Psi_{py} + d_3 \Psi_{pz}$$

And

$$\Psi_4 = a_4 \Psi_s + b_4 \Psi_{px} + c_4 \Psi_{py} + d_4 \Psi_{pz}$$

Where $a_1, a_2, a_3, a_4, b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, d_3$ and d_4 are mixing coefficients of A.O's which are involved in sp^3 hybridization. As these hybrid orbitals are completely equivalent. Their s-character must be same. This implies that

$$a_1^2 = \frac{1}{4} \text{ or } a_1 = \frac{1}{2}$$

Similar equations can be written for all the hybrid orbitals

$$a_1^2 = a_2^2 = a_3^2 = a_4^2 = \frac{1}{4}$$

$$\Rightarrow a_1 = a_2 = a_3 = a_4 = \frac{1}{2}$$

Let us assume the direction of first hybrid orbital along x-axis only. Therefore in Ψ_1, Ψ_2 py and Ψ_{2pz} will be zero i.e. these will not have any contribution in Ψ_1 , this implies that $c_1 = 0$ and $d_1 = 0$

Since Ψ_1 should be normalized

$$\Rightarrow a_1^2 + b_1^2 = 1$$

Or

$$b_1^2 = 1 - a_1^2 = 1 - \frac{1}{4} = \frac{3}{4}$$

or

$$b_1 = \frac{\sqrt{3}}{2}$$

As $\Psi_1, \Psi_2, \Psi_3, \Psi_4$, etc. should be mutually orthogonal to each other

Therefore

$$a_1 a_2 + b_1 b_2 = 0$$

$$a_1 a_3 + b_1 b_3 = 0$$

$$a_1 a_4 + b_1 b_4 = 0$$

from above equations this may be concluded that

$$b_2 = \frac{-a_1 a_2}{b_1} = \frac{-\frac{1}{2} \times \frac{1}{2}}{\sqrt{3}/2} = \frac{-1}{2\sqrt{3}}$$

$$b_3 = \frac{-a_1 a_3}{b_1} = \frac{-\frac{1}{2} \times \frac{1}{2}}{\sqrt{3}/2} = \frac{-1}{2\sqrt{3}}$$

and

$$b_4 = \frac{-a_1 a_4}{b_1} = \frac{-\frac{1}{2} \times \frac{1}{2}}{\sqrt{3}/2} = \frac{-1}{2\sqrt{3}}$$

As Ψ_2 lies in xz plane, therefore contribution of p_y in Ψ_2 is zero. Hence we may write

$$c_2 = 0$$

As Ψ_2 is itself of normalized

$$\text{Therefore } a_2^2 + b_2^2 + d_2^2 = 1$$

$$\Rightarrow d_2^2 = 1 - (a_2^2 + b_2^2) \\ = 1 - (a_2^2 + b_2^2)$$

$$= 1 - \left(\frac{1}{4} + \frac{1}{12} \right) = \frac{2}{3}$$

$$\Rightarrow d_2 = \sqrt{\frac{2}{3}}$$

Considering orthogonality of Ψ_2 , Ψ_3 and Ψ_4 wave functions

$$a_2 a_3 + b_2 b_3 + d_2 d_3 = 0$$

$$a_2 a_4 + b_2 b_4 + d_2 d_4 = 0$$

which implies that

$$d_3 = - \frac{(a_2 a_3 + b_2 b_3)}{d_2}$$

$$- \frac{\left(\frac{1}{4} + \frac{1}{12} \right)}{\sqrt{\frac{2}{3}}} = - \frac{1}{\sqrt{6}}$$

$$\text{and } d_4 = - \frac{(a_2 a_4 + b_2 b_4)}{d_2}$$

$$= - \frac{\frac{1}{4} + \frac{1}{12}}{\sqrt{\frac{2}{3}}} = - \frac{1}{\sqrt{6}}$$

As Ψ_3 and Ψ_4 are normalized functions

$$\Rightarrow a_3^2 + b_3^2 + c_3^2 + d_3^2 = 1$$

$$\Rightarrow c_3^2 = \frac{1}{2}$$

$$\text{Or } c_3 = + \sqrt{\frac{1}{2}}$$

Similarly

$$a_4^2 + b_4^2 + c_4^2 + d_4^2 = 1$$

$$\Rightarrow \left(\frac{1}{2} \right)^2 + \left(\frac{-1}{2\sqrt{3}} \right)^2 + (C_4)^2 + \left(\frac{-1}{\sqrt{6}} \right)^2 = 1$$

$$\Rightarrow c_4^2 = \frac{1}{2} \Rightarrow C_4 = \frac{-1}{\sqrt{2}}$$

c_3 and c_4 can't be same. Therefore to make Ψ_3 different from Ψ_4 root c_4 should be negative, i.e., $c_4 = -ve$ or $C_4 = -\sqrt{1/2}$

Incorporation of all the coefficients Ψ_1 , Ψ_2 , Ψ_3 , and Ψ_4 , may be written as

$$\Psi_1 = \frac{1}{2} \Psi_s + \frac{\sqrt{3}}{2} \Psi_{px}$$

$$\Psi_2 = \frac{1}{2} \Psi_s - \frac{1}{2\sqrt{3}} \Psi_{px} + \sqrt{\frac{2}{3}} \Psi_{pz}$$

$$\Psi_3 = \frac{1}{2} \Psi_s - \frac{1}{2\sqrt{3}} \Psi_{px} + \frac{1}{\sqrt{2}} \Psi_{py} - \frac{1}{\sqrt{6}} \Psi_{pz}$$

$$\text{and } \Psi_4 = \frac{1}{2} \Psi_s - \frac{1}{2\sqrt{3}} \Psi_{px} - \frac{1}{\sqrt{2}} \Psi_{py} - \frac{1}{\sqrt{6}} \Psi_{pz}$$

Calculation of angles between the hybrid orbitals

In order to calculate the angle between two sp^3 hybrid A O's and their general shape. Let us consider the orbitals in their proper coordinates

$$\Psi_s = 1$$

$$\Psi_{pz} = \sqrt{3} \cos \theta$$

$$\Psi_{px} = \sqrt{3} \sin \theta \cos \phi$$

$$\Psi_{py} = \sqrt{3} \sin \theta \sin \phi$$

Where θ is angle of a position vector with z-axis and ϕ is angle of projection of the vector on xy plane with x-axis.

Incorporating Ψ_s , Ψ_{px} , Ψ_{py} and Ψ_{pz} , hybrid orbitals Ψ_1 , Ψ_2 , Ψ_3 and Ψ_4 may be written as

$$\Psi_1 = \frac{1}{2} + \frac{\sqrt{3}}{4} (\sqrt{3} \sin \theta \cos \phi)$$

$$\Psi_2 = \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos \phi) + \sqrt{\frac{2}{3}} (\sqrt{3} \cos \phi)$$

$$\Psi_3 = \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos \phi) + \frac{1}{\sqrt{2}} (\sqrt{3} \sin \theta \sin \phi) - \frac{1}{\sqrt{6}} (\sqrt{3} \cos \theta)$$

$$\Psi_4 = \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos \phi) - \frac{1}{2} (\sqrt{3} \sin \theta \sin \phi) - \frac{1}{\sqrt{6}} (\sqrt{3} \cos \theta)$$

It was considered earlier that Ψ_2 is in xz plane therefore ϕ must be 180° . So, putting value of $\phi = 180^\circ$.

$$\begin{aligned}
 \Psi_2 &= \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos 180^\circ) + \sqrt{\frac{2}{3}} (\sqrt{3} \cos \phi) \\
 &= \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta (-1)) + \sqrt{\frac{2}{3}} \cos \theta \\
 &= \frac{1}{2} - \frac{1}{2} \sin \theta + \sqrt{\frac{2}{3}} \cos \theta
 \end{aligned}$$

Differentiating it w.r.t. θ and putting equal to zero

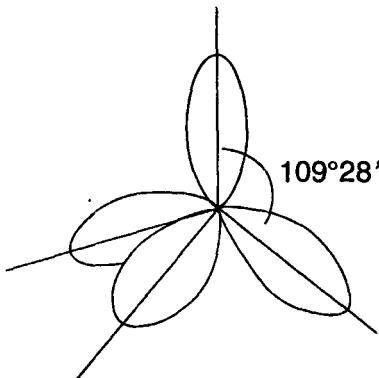
$$\frac{d\Psi}{d\theta} = \frac{1}{2} \cos \theta - \sqrt{\frac{2}{3}} \sin \theta$$

$$\Rightarrow \frac{1}{2} \cos \theta - \sqrt{\frac{2}{3}} \sin \theta = 0$$

$$\tan \theta = \frac{1}{\sqrt{\frac{2}{3}}} = 0.354$$

$$\Rightarrow \theta = 19^\circ 28'$$

Where θ is an angle between z-axis and the axis of wave function Ψ_2 . Therefore angle between Ψ_1 and Ψ_2 will be $90^\circ + 19^\circ 28' = 109^\circ 28'$ (as Ψ_1 is considered along x axis). Similarly all other angles can also be calculated as $109^\circ 28'$. This shows that sp^3 hybrid orbitals attain a regular tetrahedron geometry with angle $109^\circ 28'$ as shown below :



sp² hybridization : In this hybridization p_z orbitals do not take part or participate. Therefore, s and p_x , p_y orbitals are involved in hybridization which results in the formation of three hybrid AO's, viz., Ψ_1 , Ψ_2 & Ψ_3

$$\begin{aligned}
 \Psi_1 &= a_1 \Psi_s + b_1 \Psi_{px} + C_1 \Psi_{py} \\
 \Psi_2 &= a_2 \Psi_s + b_2 \Psi_{px} + C_2 \Psi_{py} \\
 \Psi_3 &= a_3 \Psi_s + b_3 \Psi_{px} + C_3 \Psi_{py}
 \end{aligned}$$

Where a's, b's and c's are mixing coefficients of AO's used in these hybrid orbitals. As all the hybrid orbitals are equivalent therefore each of it must have same s- character.

$$\Rightarrow a_1^2 = a_2^2 = a_3^2 = 1/3$$

Or $a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$

Let us assume Ψ_1 is along x – axis

$$\Rightarrow c_1 = 0$$

As Ψ_1 is a normalized orbital

$$\Rightarrow a_1^2 + b_1^2 = 1$$

Or $\left(\frac{1}{\sqrt{3}}\right)^2 + b_1^2 = 1$

$$\Rightarrow b_1 = \sqrt{\frac{2}{3}}$$

As Ψ_1 , Ψ_2 and Ψ_1 , Ψ_3 are orthogonal to each other

$$\Rightarrow a_1 a_2 + b_1 b_2 = 0$$

And $a_1 a_3 + b_1 b_3 = 0$

$$\Rightarrow b_2 = -\frac{a_1 a_2}{b_1}$$

$$= -\frac{\left(\frac{1}{\sqrt{3}} \times \frac{1}{\sqrt{3}}\right)}{\sqrt{\frac{2}{3}}} = \frac{-1}{\sqrt{6}}$$

And $b_3 = -\frac{a_1 a_3}{b_1}$

$$= -\frac{\frac{1}{\sqrt{3}} \times \frac{1}{\sqrt{3}}}{\sqrt{\frac{2}{3}}} = \frac{-1}{\sqrt{6}}$$

As Ψ_2 and Ψ_3 are normalized itself

$$\Rightarrow a_2^2 + b_2^2 + c_2^2 = 1$$

Or $c_2^2 = 1 - (a_2^2 + b_2^2)$

$$\Rightarrow 1 - \left\{ \left(\frac{1}{\sqrt{3}} \right)^2 + \left(\frac{-1}{\sqrt{6}} \right)^2 \right\}$$

$$\Rightarrow c_2 = \frac{1}{\sqrt{2}}$$

Similarly considering Ψ_3

$$\begin{aligned} a_3^2 + b_3^2 + c_3^2 &= 1 \\ \Rightarrow c_3^2 &= 1 - (a_3^2 + b_3^2) \\ \Rightarrow 1 - \left\{ \left(\frac{1}{\sqrt{3}} \right)^2 + \left(\frac{-1}{\sqrt{6}} \right)^2 \right\} \\ c_3 &= \pm \frac{1}{\sqrt{2}} \end{aligned}$$

Since C_2 and C_3 must have different signs therefore if c_2 is positive c_3 must be negative. Therefore hybrid orbitals Ψ_1 , Ψ_2 and Ψ_3 in this case are

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{3}} \Psi_s + \sqrt{\frac{2}{3}} \Psi_{px} \\ \Psi_2 &= \frac{1}{\sqrt{3}} \Psi_s \frac{-1}{\sqrt{6}} \Psi_{px} + \frac{1}{\sqrt{2}} \Psi_{py} \\ \Psi_3 &= \frac{1}{\sqrt{3}} \Psi_s \frac{-1}{\sqrt{6}} \Psi_{px} - \frac{1}{\sqrt{2}} \Psi_{py} \end{aligned}$$

Calculation of bond angle and shape

In order to calculate the bond angle between sp^2 hybrid orbitals, Let us take into account Ψ_s , Ψ_{px} and Ψ_{py} in terms of polar coordinates.

$$\Psi_s = 1$$

$$\Psi_{px} = \sqrt{3} \sin \theta \cos \phi \text{ and}$$

$$\Psi_{py} = \sqrt{3} \sin \theta \sin \phi$$

Therefore

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{3}} + \sqrt{\frac{2}{3}} (\sqrt{3} \sin \theta \cos \phi) \\ \Psi_2 &= \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} (\sqrt{3} \sin \theta \cos \phi) + \frac{1}{\sqrt{2}} (\sqrt{3} \sin \theta \sin \phi) \end{aligned}$$

And

$$\Psi_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} (\sqrt{3} \sin \theta \cos \phi) - \frac{1}{\sqrt{2}} (\sqrt{3} \sin \theta \sin \phi)$$

Considering Ψ_1 at x axis. Therefore to find out the direction of Ψ_2 hybrid orbital w.r.t. Ψ_1 , differentiate Ψ_2 w.r.t. angle ϕ and put it equal to zero.

$$\Rightarrow \frac{d\Psi_2}{d\phi} = \frac{1}{\sqrt{2}} \sin \phi + \sqrt{\frac{3}{2}} \cos \phi = 0$$

$$\text{or } \frac{1}{\sqrt{2}} \sin \phi = -\sqrt{\frac{3}{2}} \cos \phi$$

$$\Rightarrow \tan \phi = -\sqrt{3}$$

$$\Rightarrow \tan \phi = -1.732$$

or $\phi = 120^\circ$

Therefore considering Ψ_1 at x axis and Ψ_2 and Ψ_3 in xy plane with angle of 120° between Ψ_1 , Ψ_2 and Ψ_3 formation of sp^2 hybrid orbitals and shape (i.e., triangular planar) which results is shown in figure 13.14

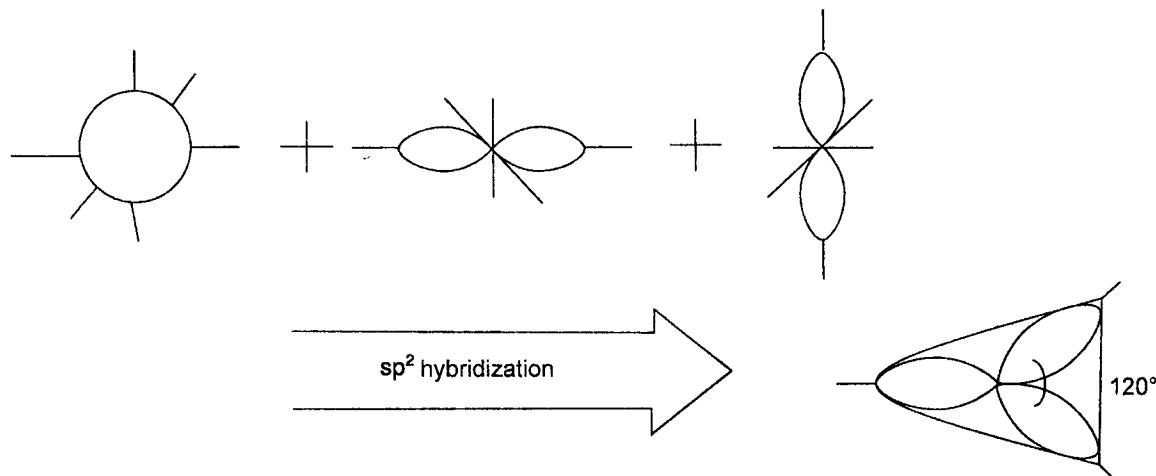


Fig. 13.14

sp – hybridization : This hybridization is also known as diagonal hybridization. In this hybridization only one s-orbital and one p orbital (i.e. p_z) intermixes to give sp hybridized A.O's wave functions for sp hybridized A.O's i.e. Ψ_1 and Ψ_2 may be written as

$$\Psi_1 = a_1 \Psi_s + b_1 \Psi_{p_z}$$

and

$$\Psi_2 = a_2 \Psi_s + b_2 \Psi_{p_z}$$

where a's and b's are mixing coefficients As both the hybrid AO's are equivalent. Therefore both of them contain equal s character and p character

$$\Rightarrow a_1^2 = a_2^2 = \frac{1}{2}$$

Or

$$a_1 = a_2 = \frac{1}{\sqrt{2}}$$

As Ψ_1 is normalized

$$\Rightarrow a_1^2 + b_1^2 = 1$$

$$\Rightarrow b_1^2 = 1 - a_1^2$$

$$\Rightarrow 1 - \frac{1}{2}$$

$$\Rightarrow b_1 = \frac{1}{\sqrt{2}}$$

As Ψ_1 , Ψ_1 are orthogonal to each other

$$= a_1 a_2 + b_1 b_2 = 0$$

$$\Rightarrow \left(\frac{1}{\sqrt{2}}\right) \left(\frac{1}{\sqrt{2}}\right) + \left(\frac{1}{\sqrt{2}}\right) b_2 = 0$$

$$\Rightarrow b_2 = -\frac{1}{\sqrt{2}}$$

Substituting a_1 , a_2 and b_1 , b_2

$$\Psi_1 = \frac{1}{\sqrt{2}} (\Psi_s - \Psi_{pz})$$

$$\text{And } \Psi_2 = \frac{1}{\sqrt{2}} (\Psi_s - \Psi_{pz})$$

Bond angle between the hybrid A.O's Ψ_1 and Ψ_2 can be calculated by considering polar coordinates

$$\Psi_s = 1$$

$$\Psi_{pz} = \sqrt{3} \cos \theta$$

On substituting Ψ_s and Ψ_{pz}

$$\Rightarrow \Psi_1 = \frac{1}{\sqrt{2}} (1 + \sqrt{3} \cos \theta)$$

$$\text{And } \Psi_2 = \frac{1}{\sqrt{2}} (1 - \sqrt{3} \cos \theta)$$

As Ψ_1 and Ψ_2 do not contain ϕ , they lie in the plane of z-axis. Therefore, condition of orthogonality between them leads to a bond angle of 180° between Ψ_1 & Ψ_2 . Hybridization of s and p_z orbitals and formation of sp hybrid A.O's with corresponding shape is shown in figure 13.15

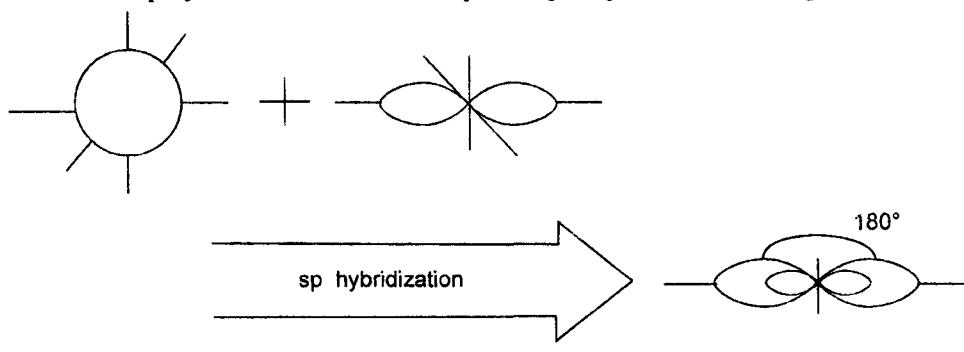


Fig.13.15

PROBLEMS SET-13

1. Explain the concept of L C.A.O. MO formation (See section 13.1)
2. Explain L.C.A.O – M.O. theory for H_2 molecule (See section 13.2)
3. List the postulates of HMO theory (See section 13.3)
4. Explain HMO theory taking suitable example of allyl system (See section 13.3)
5. How charge density and bond order can be computed on the basis of HMO concept? (See section 13.3)
6. Explain application of HMO theory taking examples of (i) Butadiene (ii) Ethylene and (iii) Cyclobutadiene system (See section 13.3)
7. What do you understand by stabilization energy? Explain giving examples of butadiene and cyclobutadiene (See section 13.3)
8. Explain valance bond theory. (See section 13.4)
9. What is concept of hybridization (See section 13.5)
10. Find out hybrid orbitals and angle between hybrid A.O's formed in case of
(i) sp^3 hybridization
(ii) sp^2 hybridization and
(iii) sp hybridization (See section 13.5)

SECTION-5

14. Introduction to use of Computers in Quantum Mechanics

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CHAPTER-14

Introduction to use of Computers in Quantum Mechanics

SYNOPSIS	
Section	Topics
14.1	A brief account of Hartree Fock self consistent field theory
14.2	Koopman's Theorem
14.3	Introduction to Quantum Chemical Packages
14.4	Applications of Quantum Chemical Softwares

Use of computer for calculations in Quantum chemistry had started since 1960's. Since then use of computer softwares and development of packages began for the quantum chemical calculations. With the advancements in technology and upgradation in hardware techniques, software packages have also improved with all generations of computers. These softwares or packages form a basis of calculations of physical properties of the molecular systems under study. These packages have been improved time to time depending upon the needs for the calculations of the parameters for molecular systems. Softwares or packages which are in use now-a-days come under either ab initio or semi – empirical categories of packages. These softwares or packages are based on Hartree Fock self consistent field theory. In this chapter introduction to (i) Hartree Fock self consistent field theory (HFSCF), (ii) Ab initio and semi – empirical packages and (iii) some applications of computer softwares or packages in theoretical or quantum chemical calculations are included

14.1 HARTREE FOCK SELF CONSISTENT FIELD THEORY

Hartree Theory : This theory was given by D.R. Hartree for n electronic molecular system. Hartree considered Ψ the wave function for n -electronic molecular system as

$$\Psi = \phi_1 (1) + \phi_2 (2) + \dots + \phi_n^{(n)} \quad \dots(14.1)$$

For such a system showing appropriate Hamiltonian, energy of the system may be given by the equation

$$E = \int \Psi^* |\hat{H}| \Psi d\tau \quad \dots (14.2)$$

As ϕ 's are normalized so, Ψ may be also considered as normalized wave function Hamiltonian including $\left(\frac{1}{r_{ij}}\right)$ potential energy interaction term may be expressed as

$$\hat{H} = \sum_i \hat{H}(i) + \frac{1}{2} \sum_i \sum_j \frac{1}{r_{ij}} \quad \dots (14.3)$$

For system to certain minimum energy

$$\partial E = 0$$

$$\text{Or} \quad \partial E = \partial \int \Psi^* |\hat{H}| \Psi d\tau = 0 \quad \dots (14.4)$$

This system can be considered having n parallel Schrodinger equations

$$\hat{H}_{(i)} \phi_i = \epsilon_i \phi_i \quad \dots (14.5)$$

$$\hat{H}(i) \phi_i = \epsilon_i \phi_i \quad (i = 1, 2, 3, \dots, N) \quad \dots (14.5)$$

Where $\hat{H}(i)$ Hamiltonian terms may be expressed as

$$\hat{H}(i) = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \hat{V}_i \quad \dots (14.6)$$

$$\text{Or} \quad \hat{H}(i) = \hat{H}^0(i) + V_i \quad \dots (14.7)$$

In above Hamiltonian V_i 's are potential terms which can be expressed as follows for 02 electrons system

$$V_{12} = \frac{q_1 q_2}{r_{12}} \quad \dots (14.8)$$

$$\text{Or} \quad V_{12} = \frac{\int (-e)(-e) |\phi_i|^2 d\tau_2}{r_{12}} \quad \dots (14.9)$$

Taking electronic charge ($e = 1 \text{ a.u.}$)

$$V_{12} = \frac{\int |\phi_i|^2 d\tau}{r_{12}} \quad \dots (14.10)$$

In the method proposed by Hartree repeated interactions have been applied to the system to get self consistent value for interaction term within the specified potential field. For this purpose trial

functions ϕ 's are chosen and applied in their respective Schrodinger equations as

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{z}{r_i} + V_i(r_i) \right] \phi'_i = E_i \phi'_i \quad \dots(14.11)$$

ϕ' can be obtained from equation 14.11 similar, equations can be employed for $\phi_2 \phi_3$ and so on within the same specified potential field to get self consistent value. Therefore, this theory is known as self consistent field theory. Probability density can be obtained cumulatively from $\phi_1 \phi'_2$ as

$$|\phi_1(r_1)|^2 + |\phi_2(r_2)|^2 + \dots + |\phi_n(r_n)|^2 \quad \dots(14.12)$$

And the total wave function for the system may be obtained as

$$\Psi = \phi'_1, \phi'_2, \phi'_3, \dots, \phi'_n \quad \dots(14.13)$$

Energy can be computed as

$$E_i = E_i^\circ + \sum_{j \neq i} J_{ij} \quad \dots(14.14)$$

Where J = average coloumbic energy which counts for average repulsion between I and j atomic enters in the system.

Hartree calculate energy and ionization potential values for various atoms, molecules and ions. Energy of some atoms do not match well with the exact value

Hartree Fock Self Consistent Field Theory (HFSCF)

Fock modified the theory proposed by Hartree & Fock used antisymmetrized wave function as

$$\Psi = \frac{1}{\sqrt{n_i}} \begin{vmatrix} \phi_1^{(1)} & \phi_1^{(2)} & \dots & \phi_{n/2}^{(2)} \end{vmatrix} \quad \dots(14.15)$$

In above Ψ 's equation $\phi_1^{(1)} \phi_1^{(2)}$ together show a complete set of spin orbital for electron 1. Combination of such similar sets of spin orbitals constitute Ψ Fock applied Fock operator which also includes electron exchange terms, with Fock operator equation may be written as

$$\hat{F}\phi_i = E_i \phi_i \quad \dots(14.16)$$

In terms of (a.u.) atomic units Fock operator may be expressed as

$$\hat{F} = -\frac{1}{2} \nabla_i^2 - \frac{z}{r_i} + \sum_{j=1}^{n/2} (2\hat{J}_i - \hat{k}_j) \quad \dots(14.17)$$

Where J operator is coloumb operator and K (i) is exchange operator. Choosing any arbitrary function of operation of $K_j(1)$ may be shown as

$$\hat{K}_j(1) f(1) = \phi_j(1) \int \frac{\phi_j^*(2)f(2)}{r_{12}} v_2 \quad \dots(14.18)$$

First term of the Fock operator may be treated as kinetic energy and second term as potential energy term for one electron numbers as (1) Collectively, with this modification, the self consistent field theory is known as Hartree Fock self consistent field Theory (HFSCF)

Roothanian Proposal :

The key development that makes feasible the calculation of accurate SCF wave function was Roothan's proposal to expand the spatial orbitals ϕ_i as linear combinations of set of one electron basis functions x_s :

$$\phi_i = \sum_{s=1}^b C_{si} X_s \quad \dots(14.19)$$

To exactly represent MO's for a molecular system ϕ_i is the basis of functions. In practice finite number of basis sets of functions are used. If b is large enough and functions X_r are well chosen M.O.'s for the molecular system can be represented with negligible error. With Roothanian's proposal Hartree Fock equation may be modified as

$$\sum_s C_{si} \hat{F} X_s = \epsilon_i \sum_s C_{si} X_s \quad \dots(14.20)$$

Multiplication by X_r^* and integration gives

$$\sum_{s=1}^b C_{si} (F_{rs} - \epsilon_i S_{rs}) = 0$$

$r = 1, 2, \dots, b \quad \dots(14.21)$

Where $F_{rs} = \langle X_r | \hat{F} | X_s \rangle$ integral and

$$S_{rs} = \langle X_r | X_s \rangle \text{ integral}$$

The equation 14.21 form a set of b simultaneous linear homogeneous equations in the b unknowns C_{si} (coefficients). $S = 1, 2, \dots, b$, that describe the M.O. ϕ_i in equation (14.19). For non trivial solution of this equation following equation must be satisfied.

$$\det(F_{rs} - \epsilon_i S_{rs}) = 0$$

This is a secular equation whose roots give us the values of ϵ_i .

14.2 KOOPMAN'S THEOREM

Hartree Fock orbital energies as calculated for various molecular orbitals system, have experimental as well as theoretical importance. Koopman gave some arguments that indicate that the energy required to remove an electron from a closed shell atom or a molecule is reasonably approximated by the minus of the orbital energy ϵ of the AO and MO from which the electron is removed. A partial justification of the results observed is the fact that if the charge in the form of the MO's that occurs when molecule is ionized, then the difference between the Hartree Fock energies of the ion and the neutral closed shell molecule can be shown equal to the orbital energy of the MO from which the electron was removed. The energy required to remove an electron from the MO of a molecule can be determined experimentally using photo electron spectroscopy. Koopman's theorem states that ionization potentials are somewhat inaccurate due to (1) neglect of the change in the form of the MO's that occur on ionization and (2) neglect of the change in correlation energy between neutral molecule and the ion formed.

14.3 INTRODUCTION TO QUANTUM CHEMICAL PACKAGES

Softwares that are in use for the purpose of calculations of wave functions and energies as well as other related properties are termed as quantum chemical softwares or packages to find out the accurate electronic wave functions for polyatomic molecules use of these softwares or packages was in practice for a long time with the development of technology and generations of computers, these packages have also been improved.

Basically these packages may be categorized as (i) ab initio and (ii) semi empirical packages. Both of these categories of packages are based on Hartree Fock theory. Any computer package optimize the geometry and minimize the energy of the molecules whose job assignment is assigned to the computer.

Basic difference between these categories is that ab-initio methods or packages use all electron Hamiltonian while semi – empirical packages and methods use only Valance electrons Hamiltonian. In this way semi – empirical methods are somewhat more trivial but the significant point to note that these methods are less time consuming and have occupied relatively less memory on the computer disk.

Some of the parameters or electronic properties can be predicted for the molecules using these quantum chemical packages. These may include (i) Heat of formation (ii) Electronic Energy (iii) Cose core repulsion energy (iv) Ionization Potentials (v) Total energy (vi) Dipole moments (vii) Eigen Values (viii) HOMO – LUMO energy gap (ix) moment of inertia and force constants and (x) normal modes analysis with reduced masses and force constants as used in spectral analysis of the molecule etc.

Some of the commonly used abinitio packages now – a- days are (i) Gauss.an and (ii) Gamess and some of the semi – empirical packages which are common in use now – a – days are (i) PC MODEL (ii) MOPAC (iii) WinMOPAC and (iv) Hyperchem etc.

Basis set of Functions

Depending upon the need basis set of functions have been employed in these quantum chemical packages. These basis set of functions have different notations. Selection of these set of functions depend upon the fact that one, two or many centre integrals are to be solved. These basis set of functions are STO type functions. Some common basis functions are 6-31G, 6-31G** etc. for GAMESSand Gaussian and AM1, PM3, etc. for semi empirical packages.

14.4 APPLICATIONS OF QUANTUM CHEMICAL SOFTWARE

Some of the applications of Quantum Chemical Softwares are as under :

(A) Study of Energy barriers for the reactions :

Energy barriers for the reactions can be studied using such quantum chemical softwares. One such study confirms the benzyne intermediate formation in the conversion of halo benzene to amino benzene. The proposed Mechanism is :

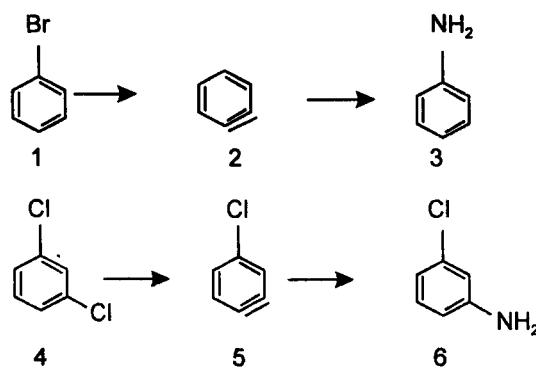


Fig. 14.1

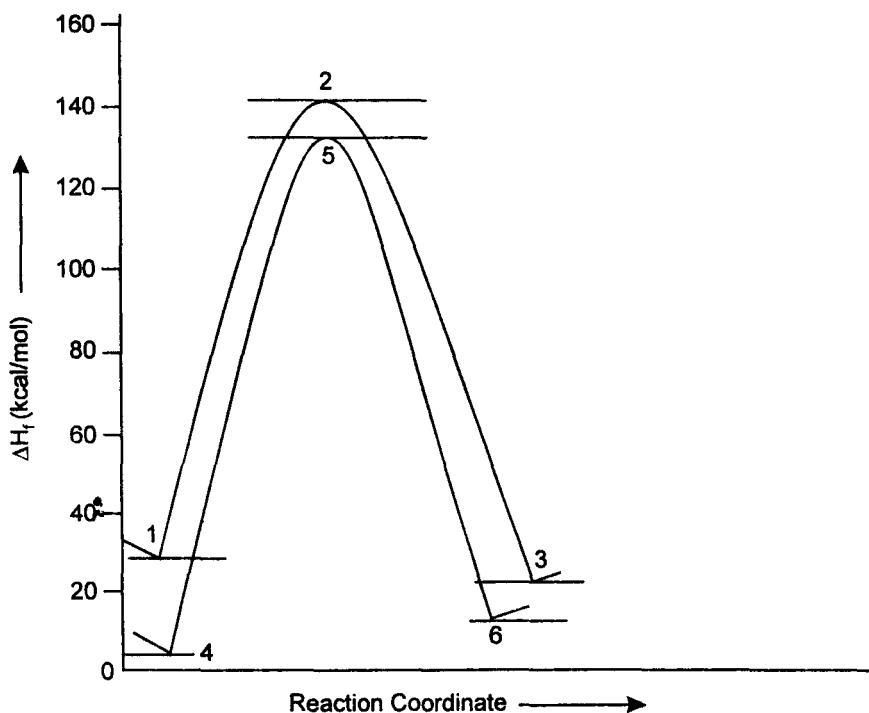


Fig. 14.2

These values shown in the above diagram are AM1 computed values using MOPAC package. Similar studies are also available in literature.

(B) Theoretical studies of electronic and geometric structures of the compounds

Theoretical studies of electronic and geometric structures of compounds can be done successfully using these packages. Some of such studies are carried out on organic compounds which are used as ligands in the formations of metal complexes. Such studies were carried out on Schiff base ligands some of them are shown below :

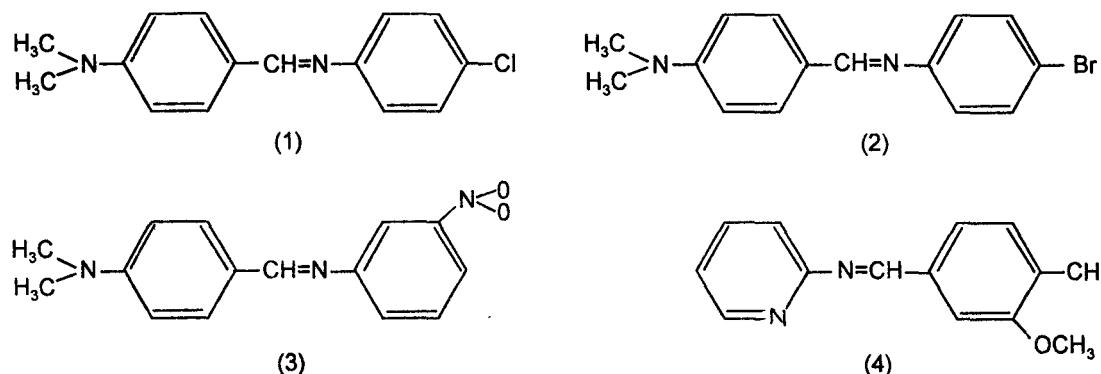


Fig. 14.3.

Such studies shows that electron densities in Schiff bases are ample and maximum on azomethinic nitrogen. This fact supports that these Schiff bases can coordinate to central metal atom through azomethinic nitrogen.

(C) Computer simulation of IR spectra using these packages :

Normal modes analysis of some of the compounds can also be performed using specific keywords with the help of these computer packages. On the basis of normal mode analysis computer simulation of IR spectra can be done. One such study for S-Benzyl 1- β -M-(2-furyl methyl ketone) dithio carbazate schiff base has been carried out with AM1, PM3 MNDO and MNDO-d methods. These computer simulated IR spectra are shown in figure below.

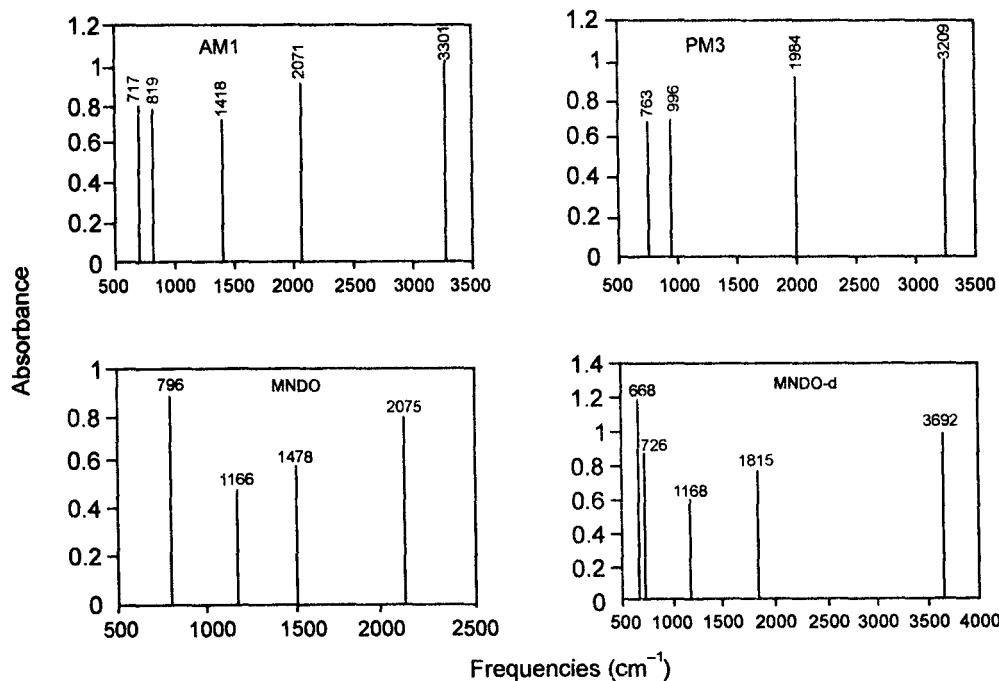
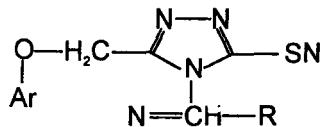


Fig. 14.4.

(D) QSAR studies of compounds of pharmacological importance :

Some of the compounds which have antimicrobial significance. Their activities can be correlated to their quantum chemically predicted structural physical parameters to perform QSAR (Quantitative structure and activity relationship) studies. One such study has been carried out on pharmacologically important Schiff base compounds mentioned in figure below and this has been shown that there is a perfect correlation between computed activity and the observed activity of such compounds.



Ar = C₁₀H₇, (CH₃)C₆H₄, (Cl)(CH₃)C₆H₃

R = C₄H₃O, (NO₂)C₄H₂O, N(CH₃)₂C₆H₄

PROBLEMS SET-14

1. Explain Hartree Theory. (See section 14.1)
2. What is Fock modification? Explain Hartree Fock Theory. (See section 14.1)
3. What do you understand by Self consistent field theory ? (See section 14.1)
4. What is Roothanian proposal ? (See section 14.1)
5. What do you understand by Koopmen's Theorem? (See Section 14.2)
6. Explain the need of Quantum Chemical Packages. (See section 14.3)
7. What do you understand by Basis set of Functions? (See Section 14.3)
8. Explain the application of Quantum chemical Softwares? (See Section 14.4)

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APPENDIX – I
TABLE FOR PHYSICAL CONSTANTS

Constant	Symbol	S.I. Value
Speed of Light In vacuum	C	$\sim 3 \times 10^8$ m/s
Electronic Charge	e	1.6×10^{-19} C
Permitivity in Vacuum	ϵ_0	8.854×10^{-12} C ² /N.m ²
Avogadro's Constant	N _A	6.023×10^{23}
Electron rest mass	m _e	9.1×10^{-31} kg
Proton rest mass	m _p	1.672×10^{-27} kg
Neutron rest mass	m _n	1.674×10^{-27} kg
Plank's constant	h	6.026×10^{-34} Js
Faraday Constant	F	96485.3 C/mol
Bohr radius	a ₀	5.29×10^{-11}
Bohr Magneton	$\beta.m.$	0.27×10^{-24} J/T
Gas constant	R	8.314 J / mol – K
Boltzman's constant	k	1.38×10^{-24} J/K
Gravitational Constant	G	6.67×10^{-11} m ³ /kg.s ²

APPENDIX – II
TABLE FOR SOME ENERGY CONVERSION FACTORS

1 erg	= 10^{-7} J
1 J	= 10^7 erg
1 cal	= 4.184 J
1 ev	= 1.602×10^{-19} J
1 ev	= 1.602×10^{-12} erg
1 ev	= 23.06 k cal/mol