

# ENGINEERING CHEMISTRY

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# Preface

One of the most common questions on the minds of all first-year engineering students is ‘Why do we need to study Chemistry to become an engineer?’ A convenient answer to this question is, ‘Chemistry is everywhere: from the air we breathe, to the food we eat.’ Moreover, engineering is a profession that requires knowledge of materials, mathematics, and fundamental sciences.

Chemical engineers find direct correlation to chemistry as they are primarily involved in process design, mass–heat transfer reactions, optimizing chemical reactions in chemical industry, food engineering, etc. A closer relation of chemistry is found in civil and environmental engineering, where engineers work with various materials (cement, glass, concrete) and also study about environmental protection and pollution control. Environmental engineers need to understand the chemical reactions and mechanisms taking place in air, soil, and water. The year 2017 saw the introduction of artificial intelligence in chemistry, when IBM researchers developed an artificial neural network algorithm that could map the synthesis of molecules as well as predict bond energies and bond angles with utmost precision. Electronics engineers need to have knowledge of diodes, liquid crystals, semiconductors, etc. Thus, a deep understanding of chemicals, their properties and reaction mechanisms, will be an added advantage in today’s competitive world.

## ABOUT THE BOOK

This book *Engineering Chemistry* is primarily written for first-year engineering students keeping in mind the new AICTE curriculum. It will help them venture into the fascinating field of applications in chemistry for their chosen engineering field. It will also serve as a preliminary text students who have taken chemistry as a diploma course at the undergraduate level.

The contents of this book are such that students can gradually move from one topic to another to obtain comprehensive knowledge of the subject. The text is written in a simple language and supported with numerous examples, figures, and tables. Moreover, the rich pedagogy enables quick assessment. Students preparing for competitive examinations will also benefit from this book.

## KEY FEATURES

- Provides comprehensive coverage of all important topics as per AICTE model curriculum and syllabi of various reputed universities
- Includes numerous self-explanatory figures, tables, and reactions that aid in the understanding of important topics
- Provides a large number of multiple-choice questions, review questions, and activity-based questions
- Includes simple as well as advanced solved numerical problems and check your progress questions interspersed in the text
- Includes summary and a list of key terms at the end of each chapter to enable recapitulation

## CONTENTS AND COVERAGE

The contents of the book are arranged in 22 chapters and divided into two parts: Part I: Basic Chemistry and Part II: Applied Chemistry.

## Part I Basic Chemistry

Chapter 1, *Atomic and Molecular Structure*, elucidates in detail the structure of atom and includes de-Broglie equation, Schrödinger equation, particle-in-a-box model, atomic orbitals, molecular orbital theory, band theory of solids and Hückel's theory of aromaticity.

Chapter 2, *Periodic Properties and Chemical Bonding*, accounts for the periodic trends observed in Modern Periodic Table. The chapter includes a brief discussion on chemical bonding as well as a detailed account of various molecular interactions and hybridization with examples.

Chapter 3, *Thermodynamics and Chemical Equilibrium*, outlines the three simple laws known as laws of thermodynamics and their potential in explaining each and every process at equilibrium. The chapter also details how to make a spontaneous process non-spontaneous and vice versa and how to shift the position of equilibrium to the product/reactant side.

Chapter 4, *Phase Rule*, details Gibbs phase rule applied to one-, two- and multi-component systems. Iron-carbon phase diagram is discussed and illustrated with phase diagrams of all-component systems and congruent and incongruent systems.

Chapter 5, *Electrochemistry*, discusses cell potentials, EMF series, concentration cells, reference electrodes, pH determination using glass, hydrogen, and quinhydrone electrodes. Nernst equation is derived in a simple manner for easy understanding. A short account on potentiometric titrations and their various graphical representations are explained. Battery technologies ranging from acid-storage, alkali-storage to fuel cells are discussed.

Chapter 6, *Chemical Kinetics*, describes the details of rates of reactions, their dependence on concentration, temperature, and other factors. Potential energy surface and transition state theory are introduced to explain the molecular picture of the rate of reaction.

Chapter 7, *Surface Chemistry*, deals with mechanism of adsorption, catalysis, emulsions, colloids, detergents and surfactants. The chapter also introduces the concept of micellization of surfactants.

Chapter 8, *Solid State Chemistry*, explains the laws of crystallography, lattice planes, Miller indices, structure of different crystal structures, X-ray diffraction studies.

Chapter 9, *Coordination Chemistry and Organometallic Compounds*, discusses the nomenclature, Werner, valence bond and crystal field theory and stability of coordination compounds. The chapter also includes a discussion on HSAB principle, EAN rule, organometallic compounds and their use as catalyst in isomerization, polymerization, hydrogenation, and hydroformylation.

Chapter 10, *Organic Reactions and Synthesis of Drug Molecules*, discusses nucleophilic, addition, elimination, oxidation, reduction, and pericyclic reactions with examples. It also details the preparation, properties, and uses of drug molecules.

Chapter 11, *Stereochemistry*, deals with the representation of three-dimensional structures, concepts of chirality, isomers, and optical activity of organic compounds. It provides a comprehensive understanding of the relative and absolute configuration of organic molecules and conformational analysis of simple alkanes.

Chapter 12, *Instrumental Methods of Analysis*, explains a variety of techniques used to separate atoms/molecules, determine their structure, and characterize them qualitatively and quantitatively. These techniques include spectroscopy, microscopy, electrochemical and thermal analyses, and chromatography.

## Part II Applied Chemistry

Chapter 13, *Water Chemistry*, details the sources of impurities in water, boiler problems, water softening methods, and desalination methods. It also discusses the significance of dissolved oxygen in water.

Chapter 14, *Corrosion*, explains the different forms of corrosion, their mechanisms and factors influencing them. The chapter also discusses various measures to control corrosion.

Chapter 15, *Metals and Alloys*, highlights the importance of metals and alloys and includes description of powder metallurgy, production of steel, metal ceramic powders and shape memory alloys.

Chapter 16, *Polymers*, explains the classification of polymers, methods of polymerization, preparation, properties and applications of commercially important polymers, compounding, plastic fabrication, and vulcanization. This chapter also includes the significance of specialty polymers in various applications.

Chapter 17, *Important Engineering Materials*, discusses the properties and applications of various types of materials such as cement, concrete, refractories, abrasives, adhesives, ceramics, glass, nanomaterials, liquid crystals, and composites. It also includes the manufacture of nanomaterials.

Chapter 18, *Lubricants*, discusses the types and properties of lubricants. The mechanism of lubrication is explained along with a note on selection of lubricants.

Chapter 19, *Energy Resources*, discusses the various renewable sources of energy, such as solar, tidal, wind, hydro, oceanic, biomass, nuclear, geothermal energy sources along with their advantages and limitations. It also includes a comprehensive account of the mechanism of nuclear fission and working of reactors.

Chapter 20, *Fuels and Combustion*, discusses different types of fuels, calorific values and their determination, coal analysis, cracking of oils, and refining processes.. It also includes a short account of explosives and propellants.

Chapter 21, *Pollution and its Control*, discusses the causes and adverse effects of various types of pollution and their remedial measures.

Chapter 22, *Green Chemistry*, elucidates the basic principles of green chemistry along with examples. The chapter discusses the synthesis of adipic acid, indigo, ibuprofen, carbaryl, and acrylamide.

Appendix -*Laboratory Experiments*- includes the principle and procedure of a few laboratory experiments as prescribed by the AICTE syllabus.

## Online Resources

The online resources centre provides resources for faculty and students using this text:

### For Faculty

- Solutions Manual
- PowerPoint Slides

### For Students

- Quizzes
- Extra Reading Material

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Suggestions and feedback are welcome and can be sent to me at: [payal.joshi@nmims.edu](mailto:payal.joshi@nmims.edu) or [payalchem@gmail.com](mailto:payalchem@gmail.com)

**Payal B. Joshi**

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# Part I: Basic Chemistry

## Atomic and Molecular Structure

### LEARNING OBJECTIVES

*After reading this chapter, you will be able to:*

- explain wave–particle duality of matter.
- deduce de Broglie relation and Schrödinger wave equation.
- understand Heisenberg’s Uncertainty Principle and Born interpretation of Schrödinger wave function.
- apply particle-in-a-box model in conjugated molecules and nanoparticles.
- sketch the atomic orbitals and radial plots of hydrogen atom.
- discuss molecular orbital theory for diatomic (homonuclear and heteronuclear) molecules.
- illustrate band theory of metals, semiconductors, and insulators.
- introduce the concept of aromaticity in benzene and cyclobutadiene.

### 1.1 STRUCTURE OF ATOM — AN OVERVIEW

Atoms and molecules are the fundamental building blocks of matter. We all have learnt about atoms in the beginning of secondary school science classes; despite this, our understanding of the structure of atom is surprisingly low. In the 19th century, scientists were facing a major challenge to reveal the structure of atoms and explain their behaviour and properties. This led to a series of postulates and experiments validating them. The earliest investigations revealed that atoms are not indivisible. Various experiments have proved that the atom consists of charged particles. An atom is composed of protons and electrons, mutually balancing their charges. Protons are in the interior of an atom surrounded by electrons. J. Dalton, J.J. Thompson, E. Rutherford, and Niels Bohr successfully postulated atomic models and described the properties of the atom. (Fig. 1.1).

#### Postulates of Bohr’s model

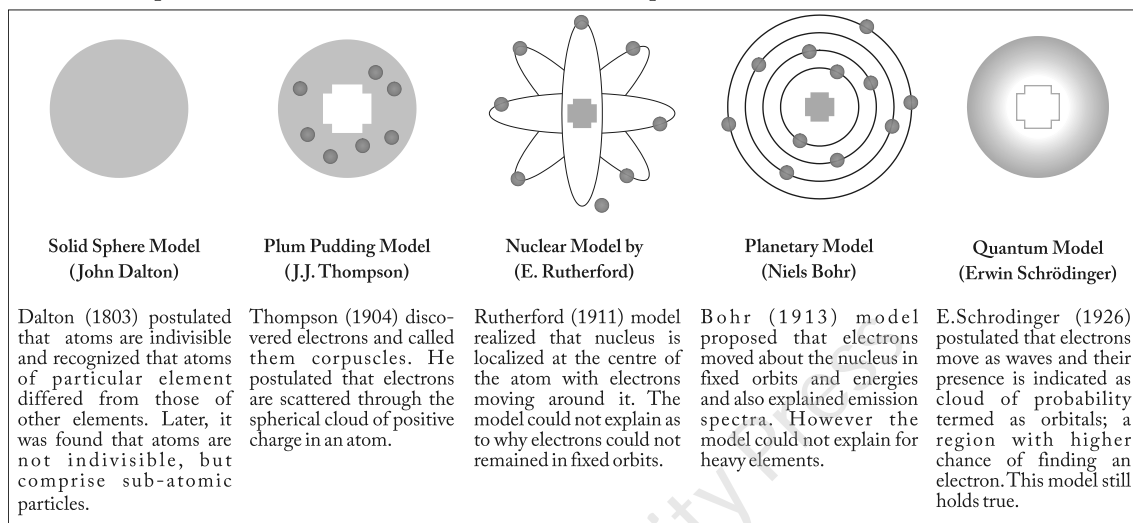
- (a) There is a small, positively charged nucleus surrounded by electrons that travel in circular orbits around the nucleus.
- (b) There is a presence of electrostatic forces between the electrons and the nucleus.
- (c) Electrons move in circular orbits of fixed sizes called stationary orbits (or energy levels) K, L, M, and N and the energy of electrons is quantized.
- (d) Atoms emit radiation: electrons jump from one orbit (allowed) to another and either absorb or emit light as electromagnetic radiation with a frequency as per Planck’s relation,  $\Delta E = E_2 - E_1 = h\nu$ , where  $h$  is Planck’s constant.

The limitations of Bohr’s model are:

- (a) The assumption of structured ‘stationary fixed orbit’ seems unjustified.
- (b) It can only explain spectral lines of hydrogen atom, but after the first 20 elements in the periodic table, Bohr’s model becomes difficult to predict the spectral details of complex atoms.

- (c) It cannot explain chemical bonding of atoms.  
 (d) There is no explanation of the distribution of electrons within an atom.

Sommerfeld attempted to improvise Bohr's theory by postulating that electrons revolved around the nucleus in elliptical orbits and also introduced additional quantum numbers.



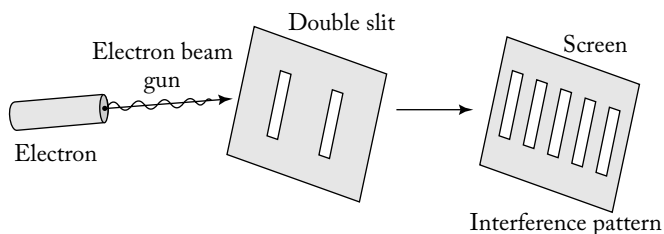
**Fig. 1.1** Various models describing the structure of atom

Further, in Bohr's theory, an assumption was made that the position and momentum of an electron were precisely known. A highly advanced theory, called 'wave mechanics' put forth by Erwin Schrödinger explained the spectra of one-electron system and even multi-electron systems. It also gave a detailed interpretation of chemical bond vibrations and other chemical phenomena.

## 1.2 DUAL NATURE OF MATTER (WAVE-PARTICLE DUALISM)

Bohr's theory was a giant step forward in understanding the atomic world; yet its limitations had to be broken down with the aid of quantum mechanics, which emerged very soon in the form of the dual nature concept. In 1905, Einstein put forth the photoelectric effect that described light as a photon. Scientists were yet debating the dual nature of light and also reluctant to accept it. Einstein further introduced the concept of light as a continuous field of waves in his paper on special relativity—a complete contradiction of light considered as a stream of particles. Experimental evidence was given by Thomas Young's double-slit experiment.

As per this experiment (Fig.1.2), light travels away from a source as an electromagnetic wave. When it passes through the slits, it gets divided into two wavefronts. These wavefronts overlap and fall on to the screen and the entire wave field disappears and a photon appears.



**Fig. 1.2** Young's double slit experiment

Experimental evidence was given by Thomas Young's double-slit experiment.

### 1.2.1 Davisson and Germer Experimental Evidence of Electron Waves

The presence of matter waves was experimentally verified by C.J. Davisson and L.H. Germer at the Bell Telephone Laboratories. They showed that the beam of electrons reflected from a metal crystal



produced a diffraction pattern. The wavelengths of electrons calculated from the experiments were found to be in agreement with de Broglie equation. G.P. Thompson demonstrated that an accelerated beam of electrons when passed through a thin gold film ( $\sim 10^{-8}$  m) strikes on to a photographic plate, a diffraction pattern is obtained.

Figure 1.3 shows the experimental arrangement used by Davisson and Germer. It consisted of an electron gun comprising a tungsten filament (F), coated with barium oxide and heated with a low-voltage power supply. The electrons emitted by the tungsten filament were accelerated to a desired velocity by applying accurate voltage. The experiment was performed by varying the accelerating voltage from 44 V to 68 V. The entire apparatus (Fig. 1.3) was placed in an evacuated chamber. Electron beams were passed through a cylinder with fine holes along its axis that produced a fine collimated beam striking on to a nickel crystal. These electrons got scattered in all directions by atoms present in the solid crystal. The intensity of the scattered electron beam in a given direction was measured by a movable electron detector and galvanometer.

The deflection of the galvanometer was found to be proportional to the intensity of the electron beam entering the collector. By moving the detector on the circular scale to different positions, the intensity of the scattered electron beam was measured for different values of angle of scattering  $\theta$ , that is, the angle between the incident and the scattered electron beams. The variation of intensity ( $I$ ) of scattered electrons with an angle of scattering  $\theta$  was obtained for different accelerating voltages.

Davisson–Germer experiment, thus, strikingly confirms the wave nature of electrons and the de Broglie relation. In 1989, the wave nature of a beam of electrons was experimentally demonstrated in a double-slit experiment, similar to that used for the wave nature of light. Moreover, in 1994, interference fringes were obtained with beams of iodine molecules that are around million times more massive than the electrons.

### 1.2.2 The de Broglie Equation and Derivation

In 1924, Louis de Broglie described the existence of matter waves. Already at that time, electromagnetic and sound waves were known. de Broglie suggested that wave–particle nature may exist even in material particles and electrons. He also derived an equation for the wavelength of photons (or particles) of light.

According to Planck's quantum theory, energy of a photon is given by  $E = h\nu$  ( $h$  is Planck's constant,  $6.626 \times 10^{-34}$  Js,  $E$  = energy and  $\nu$  = frequency of light,  $s^{-1}$ ) and Einstein's equation for mass–energy equivalence is  $E = mc^2$ , where  $c$  is the velocity of light.

$$\therefore h\nu = mc^2 \quad (1.1)$$

where  $m$  is the mass equivalent of photon. Further, it follows that

$$\frac{hc}{\lambda} = mc^2 \quad \left( \because \nu = \frac{c}{\lambda} \right)$$

$$\lambda = \frac{h}{mc} \quad (1.2)$$

The product  $mc$  is the momentum of photon. de Broglie assumed that an equation of this type is also applicable to material particles. If a particle of mass, say  $m$ , travels with a velocity  $v$ , then

$$\lambda = \frac{h}{mv} \quad (1.3)$$

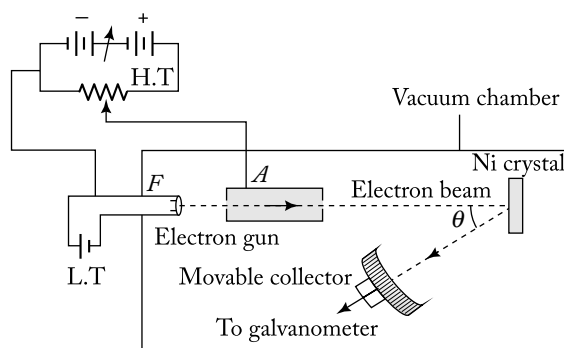


Fig. 1.3 Davisson–Germer electron diffraction arrangement

Equation (1.3) is the fundamental equation of de Broglie's theory of wave-particle duality. The wavelength of hypothetical matter waves that are called *de Broglie waves* is represented by Eq. (1.3) and is called *de Broglie equation*. de Broglie's wavelengths for moving objects are given in Table 1.1.

The de Broglie hypothesis has been the basis for the development of modern quantum mechanics leading to the field of electron optics. The wave properties of electrons have been utilized in the design of electron microscope used today.

**Table 1.1** de Broglie wavelengths for moving objects

Object (moving)	Mass (g)	Wavelength (Å)
1 volt electron	$9.11 \times 10^{-28}$	12.3
100 volt electron	$9.11 \times 10^{-28}$	1.23
Helium atom (298 K)	$6.65 \times 10^{-24}$	0.73
$\alpha$ -particle from radium	$6.65 \times 10^{-24}$	$6.6 \times 10^{-5}$
Dust particle	$\approx 10^{-6}$	$6.6 \times 10^{-13}$
Driven golf ball	45	$4.9 \times 10^{-24}$
Chemistry professor (walking)!	$8 \times 10^4$	$8.3 \times 10^{-26}$

### 1.2.3 Bohr's Theory Versus de Broglie Equation

Bohr (1913) postulated the atomic model in which nucleus of an atom is surrounded by particles known as electrons that revolve in defined shells or orbits. As per Bohr's planetary model, angular momentum is an integral multiple of  $h/2\pi$ . de Broglie gave a valid explanation supporting Bohr's model shown in Fig. 1.4.

de Broglie put forth that if one uses the wavelength associated with an electron and assume that an integral number of wavelengths must fit in the circumference of an orbit, one can deduce the same quantized orbital angular momentum postulated by Bohr's planetary model.

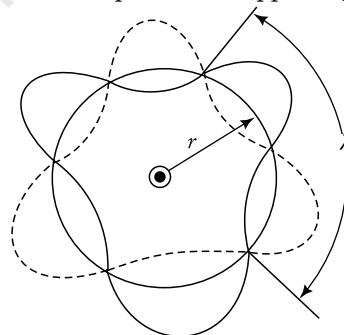
Let us say, an electron behaves as a standing wave that goes around the nucleus in a circular orbit. If one condition that the circumference of electron orbit should be equal to the integral number of wavelength of an electron (de Broglie wavelength,  $\lambda$ ) is fulfilled, the electron will undergo constructive interference. If this condition is not satisfied, the electron may suffer destructive interference. As per this argument, if  $r$  is the radius of the circular orbit, then  $2\pi r = n\lambda$ .

We know that de Broglie equation,  $\lambda = \frac{h}{mv}$ .

$$\therefore 2\pi r = \frac{nh}{mv} \text{ or, } mvr = \frac{nh}{2\pi}$$

where  $n = 1, 2, 3$ , and so on.

As  $mvr$  is the angular momentum of an electron, one can easily deduce that wave mechanical nature leads to Bohr's postulate, that is, angular momentum is an integral multiple of  $h/2\pi$  and is quantized. Hence, it is clear that de Broglie concept supports Bohr's planetary model.



**Fig. 1.4** Bohr's model of atom

### 1.3 HEISENBERG'S UNCERTAINTY PRINCIPLE

In 1927, Werner Heisenberg put forth the Principle of Uncertainty, according to which, 'the simultaneous exact determination of position and momentum or any property related to momentum such as velocity is impossible'. If  $\Delta x$  is the uncertainty regarding position and  $\Delta p$  is the uncertainty about the momentum, then

$$\Delta x \times \Delta p = h; \text{ where, } h \text{ is Planck's constant.} \quad (1.4)$$

According to Uncertainty Principle, if the position of a particle such as an electron is known precisely, then there will be uncertainty about its momentum. If an electron with an exact known momentum strikes a fluorescent screen, a flash of light is emitted so that its position at that instant is known. However,

continuous collisions of electron with the screen results in the loss of certain amount of energy and eventually the momentum of the electron will change. In an attempt to establish the precise position of the electron, an uncertainty is introduced regarding its momentum. Thus, the statements about the precise position and momentum will have no validity and shall be replaced by statements of probability that the electron has a given momentum and position. Heisenberg's Uncertainty Principle brings out the fact that nature only imposes a limit to accuracy with which the position and momentum of a particle are determinable experimentally and mathematically, stated by the equation as,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad (1.5)$$

Hence, it can be concluded that the product of uncertainties cannot be less than  $\frac{h}{4\pi}$ .

## 1.4 SCHRÖDINGER WAVE EQUATION

Erwin Schrödinger (1924) proposed and deduced the wave equation that forms the basis of the wave-mechanical behaviour of matter. It describes the particle motion and also its association to de Broglie wave. Schrödinger derived an equation for comparing the path taken by the particle with that of a ray of light and associated the wave with electromagnetic waves.

Let us consider the following equation,

$$y = f(x) g(t) \quad (1.6)$$

where,  $f(x)$  is a function of coordinate  $x$  and  $g(t)$  is a function of the time coordinate  $t$ .

For a stationary wave,

$$g(t) = A \sin(2\pi vt) \quad (1.7)$$

On substituting Eq. (1.7) in Eq. (1.6), we get,

$$y = f(x) A \sin(2\pi vt) \quad (1.8)$$

$$\frac{\partial^2 y}{\partial t^2} = f(x) 4\pi^2 v^2 A \sin(2\pi vt) = -4\pi^2 v^2 f(x) g(t) \quad (1.9)$$

Further, the one-dimensional classical wave equation is given as,

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{u^2} \frac{\partial^2 y}{\partial t^2}$$

Similarly, it follows Eq. (1.8) as,

$$\frac{\partial^2 y}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} g(t) \quad (1.10)$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2 v^2}{u^2} f(x) \quad (1.11)$$

We know, velocity  $u$  can be expressed as,  $u = v\lambda$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \quad (1.12)$$

### Check Your Progress

1. How is Heisenberg principle different from Bohr's postulates about electrons?
2. What important information is obtained from Davisson–Germer experiment?
3. Justify the statement, 'de-Broglie relation supports Bohr's model of stationary orbit.'
4. State Heisenberg Uncertainty principle. Write its expression.

Equation (1.12) for wave motion in three directions represented by the co-ordinates  $x, y$ , and  $z$  is given as,

$$\frac{\delta^2 \Psi}{\delta x^2} + \frac{\delta^2 \Psi}{\delta y^2} + \frac{\delta^2 \Psi}{\delta z^2} = -\frac{4\pi^2}{\lambda^2} \Psi \quad (1.13)$$

where,  $\Psi$  is the amplitude function of the three co-ordinates. For simplicity,  $\nabla$  is written for  $x, y$ , and  $z$  co-ordinates. Equation (1.13) can then be written as follows,

$$\nabla^2 \Psi = -\frac{4\pi^2}{\lambda^2} \Psi \quad (1.14)$$

where,  $\nabla$  is Laplacian or differential operator given by,

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

The fundamental assumption of wave mechanics is that Eq. (1.14) is applicable to all microscopic particles such as electrons, protons, and atoms. On substitution of  $\lambda$  in Eq. (1.14), de Broglie equation can be written as,

$$\nabla^2 \Psi = -\frac{4\pi^2 m^2 v^2}{h^2} \Psi \quad (1.15)$$

The kinetic energy of a particle is equal to  $mv^2/2$  and this is equal to the difference between total energy  $E$  and potential energy  $U$ .

Hence,  $E - U = \frac{mv^2}{2}$  and substitution of  $mv^2/2$  in Eq. (1.15) gives,

$$\nabla^2 \Psi = \frac{8\pi^2 m}{h^2} (E - U) \Psi$$

$$\text{or, } \frac{\delta^2 \Psi}{\delta x^2} + \frac{\delta^2 \Psi}{\delta y^2} + \frac{\delta^2 \Psi}{\delta z^2} + \frac{8\pi^2 m}{h^2} (E - U) \Psi = 0 \quad (1.16)$$

Equation (1.16) is called *Schrödinger wave equation* (time-independent). As per this equation, if a particle of mass  $m$  moving with a velocity  $v$  has total energy  $E$  and potential energy  $U$ , then the particle has an associated wave, whose amplitude is wave function  $\Psi$ . It is a second degree differential equation with several solutions, of which only some are valid. The functions are satisfactory solutions of wave equation only for certain values of energy  $E$  and such values are called *eigen values*. The corresponding functions that are satisfactory solutions of Eq. (1.16) are called *eigen functions*. Eigen functions will be single value, finite, and continuous for all possible values of the three co-ordinates, that is,  $x, y$ , and  $z$ , including infinity ( $\infty$ ).

On further solving Eq. (1.16) and introducing  $\hbar = \frac{h}{2\pi}$  we get,

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi + V = E \Psi \quad (1.17)$$

We know that Laplacian operator is,  $\nabla^2 = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}$

$$\therefore \left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right] \Psi = E \Psi$$

Further, the Hamiltonian operator can be written as,

$$\hat{H} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right] \quad (1.18)$$

On comparing Eqs (1.17) and (1.18) we get,

$$\hat{H} \psi = E \psi \quad (1.19)$$

Equation (1.19) is a compact form of Schrödinger equation.

### 1.4.1 Physical Significance of Wave Function

The function  $\psi$  is a mathematical function and is associated with moving particles and is not an observable quantity with any physical meaning. However,  $\psi^2$  has significance and can be evaluated. Max Born (1926) proposed the statistical interpretation of wave function of electrons, called *Born interpretation*. As per Born interpretation, the electron is considered as a particle, and the square of the wave function  $\psi$  at any point in space represents the probability of finding an electron at that point at a given instant. In simpler terms, if  $\psi$  is large, the probability of finding an electron is also high. Born interpretation is in agreement with the Uncertainty Principle. The function  $\psi^2$  is considered as a wave mechanical equivalent of the electron orbit of Bohr's theory and hence, the wave function is referred to as an orbital. An *orbital* represents a definite region in three-dimensional space around the nucleus where there is high probability of finding an electron of a definite energy.

### 1.4.2 Quantum Mechanical Model of Hydrogen Atom

For the hydrogen atom, Schrödinger wave equation is written as follows,

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} \left( E - \frac{Ze^2}{r} \right) \Psi = 0 \quad (1.20)$$

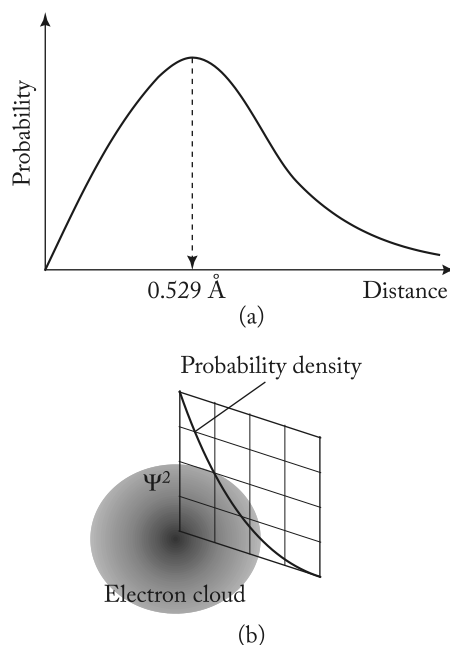
where,  $U$  (potential energy) is replaced by  $-\frac{Ze^2}{r}$ .

The solution of Schrödinger equation is a complicated one. It is sufficient to know that solution of the wave equation for an electron in a hydrogen atom involves certain integers that determine the energy and momentum of an electron. These integers correspond to quantum numbers of Bohr–Sommerfeld theory. On solving the wave equation, energy  $E$  of an electron is,

$$E = -\frac{2\pi^2 z^2 m e^4}{n^2 h^2} \quad (1.21)$$

Equation (1.21) is identical to the Bohr equation. The calculations of the values of wave functions corresponding to different values of quantum numbers have given probability distributions of an electron. These probability distributions have maxima and minima that signify that electron orbits have no significance.

For hydrogen atom, the maximum probability of finding an electron in the ground state is at a distance of  $0.529 \text{ \AA}$  from the nucleus (Fig. 1.5 (a)). This is in accordance with Bohr's theory as the distance is similar to the radius of the first orbit. Figure 1.5 (b) shows the probability of finding an electron called electron cloud (see shaded portion). The density of electron cloud is proportional to the probability of finding an electron at that point in a given instant.



**Fig. 1.5** Probability distribution of electron in hydrogen atom

### 1.4.3 Particle in a One-dimensional Box

Let us consider a particle of mass  $m$  which is allowed to freely move in a one-dimensional box of length  $l$  as shown in Fig. 1.6. The particle can only move parallel to the  $x$ -axis without friction, that is, interval of  $x = 0$  to  $x = l$ . This interval is called *one-dimensional box* or *potential well*.

The potential energy,  $V$  of an electron at the bottom of the box is constant and taken as zero. Hence, inside the box  $V = 0$ . Let the width of the box be  $a$ . Also, potential energy  $V$  becomes infinity at the walls of the box. So, let the potential energy be infinite for  $x < 0$  and  $x > l$ .

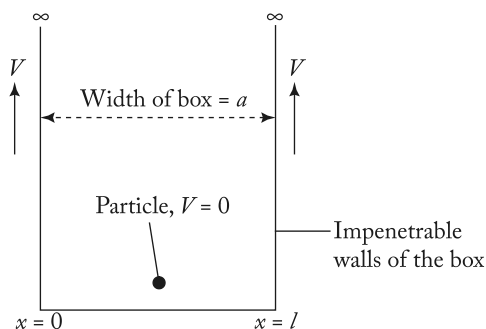


Fig. 1.6 Particle in a 1D box model

The assumptions for particle-in-a-box are as follows:

- It is assumed that the walls of the box possess infinite potential energy ensuring that the particle has zero probability of being at the walls or outside the box, called the *boundary conditions*.
- Further, the function is considered zero at  $x = 0$  and for all negative values of  $x$ , as the particle is not allowed over the walls of the box.
- The function must necessarily be zero for all values of  $x > l$ . The boundary condition is hence set in such a way that the particle is strictly confined inside the box and cannot exist outside.

Inside the box, Schrödinger equation is,

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_x \right] \Psi(x) = E\Psi(x) \quad (1.22)$$

As  $V_x = 0$ , Eq. (1.22) becomes,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = E\Psi(x) \quad (1.23)$$

For solving  $E$  and wave function  $\Psi_x$  we will mathematically rewrite Eq. (1.23) as,

$$\frac{d^2\Psi}{dx^2} + \left( \frac{2mE}{\hbar^2} \right) \Psi = 0$$

On reducing the above equation as  $k^2 = \frac{2mE}{\hbar^2}$ , we get,

$$\frac{d^2\Psi}{dx^2} + k^2\Psi = 0 \quad (1.24)$$

Now, a general solution of Schrodinger wave equation is,

$$\Psi(x) = a \cos kx + b \sin kx \quad (1.25)$$

Considering boundary conditions,  $\Psi(x) = 0$  at  $x = 0$  or  $\Psi(0) = 0$ . Outside the box,  $V_x = \infty$ .

$$\therefore \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_x \right] \Psi_x = E\Psi(x) \quad (1.26)$$

Further,

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} (E - \infty) \Psi = 0 \quad (1.27)$$

When  $\Psi = 0$  (outside the box), the particle cannot be found outside the box. Hence,  $\Psi = 0$  is considered at the walls of the box and thus  $x = 0$  and  $x = l$ . Figure 1.7 shows the wave functions of a one-dimensional particle in a box.

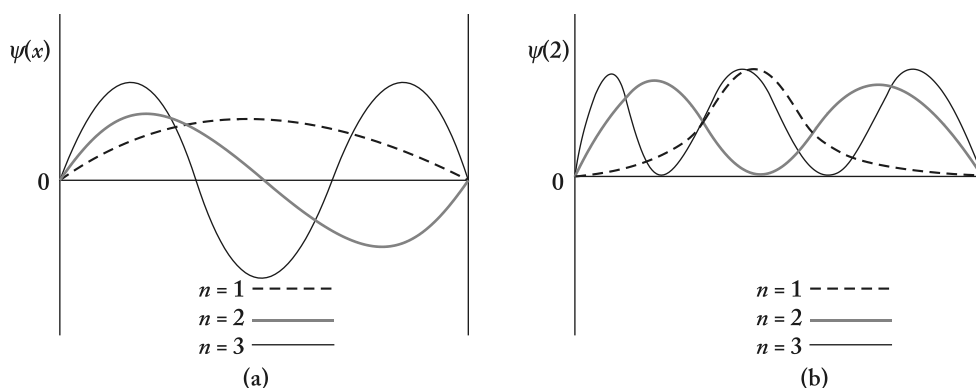


Fig. 1.7 Wave functions for one-dimensional particle in a box

From Eq. (1.25), we can say that if  $a = 0$ ,

$$\Psi(x) = a \sin kx + b \cos kx \quad (1.28)$$

As we know  $\Psi = 0$  at  $x = 0$  and  $x = l$ .

Hence, one can solve the equations as follows:  $b \sin kl = 0$

On rearranging,  $\sin kl = 0$  and also,  $kl = n\pi$  and  $k = \frac{n\pi}{l}$

we can consider  $k = \frac{n\pi}{l}$ , where,  $n = 0, 1, 2, 3$  (1.29)

Hence,  $\Psi = \Psi_n = b \sin\left(\frac{n\pi}{a}\right)$ , where,  $n = 0, 1, 2, 3$  (1.30)

The term  $\Psi_n$  is called the *eigen function*. On considering Eqs (1.29) and (1.30) we can express,

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\text{Hence, } \frac{n^2 \pi^2}{l^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2 \pi^2 \hbar^2}{l^2 2m} \quad (1.31)$$

On solving the above expressions and we know that

Total energy of an electron,  $E$  – Potential energy ( $U$ ) = Kinetic energy of the electron

$$\therefore E_n = \frac{n^2 \hbar^2}{8ml^2}, \text{ where, } n = 0, 1, 2, 3 \dots \infty \quad (1.32)$$

Equation (1.32) clearly depicts that the particle in a box consists of discrete sets of energy values (energy is quantized). Some of the energy levels, say  $E_1$ ,  $E_2$  and  $E_3$  can be written as follows:

$$E_1 = \frac{\hbar^2}{8ml^2}; \quad E_2 = \frac{4\hbar^2}{8ml^2}; \quad \text{and} \quad E_3 = \frac{9\hbar^2}{8ml^2} \quad (1.33)$$

Hence, it is proven by the above equation that a bound particle possesses quantized energy, whereas a free particle has no quantized energy.

## 1.5 SHAPES OF ATOMIC ORBITALS AND PROBABILITY DISTRIBUTION

The solution of wave function ( $\Psi$ ) of hydrogen atom led to three different types of quantum numbers that explain the spatial orientation of an electron relative to the nucleus. These solutions are called orbitals —

a term that sounds analogous to 'orbits,' in Rutherford's planetary model. An *orbital* refers to the region around the nucleus that shows the maximum probability of finding electrons. An orbital is a mathematical function that possesses finite value anywhere in space. As discussed earlier, ( $\Psi^2$ ) value at any place and instant is a measure of the probability of finding an electron of definite energy.

Before explaining the shapes of various atomic orbitals, let us quickly glance through quantum number. Each atomic orbital is specified by three quantum numbers, specified as  $n$ ,  $l$ , and  $m$ , and each electron can be designated by a set of four quantum numbers ( $n$ ,  $l$ ,  $m$ , and  $s$ ). Quantum numbers provide complete details of the position of an electron in a given atom. The various quantum numbers are: principal quantum number ( $n$ ), azimuthal quantum number ( $l$ ), magnetic quantum number ( $m$ ) and spin quantum number ( $s$ ) explained as follows:

**Principal quantum number ( $n$ )** It indicates the main energy levels in which an electron is present. These energy levels are represented as 1, 2, 3, 4, etc., for  $K, L, M, N$ , etc., Bohr orbits respectively. It specifies the energy of an electron in the given level and can be given by,  $E_n = -1312/n^2$  kJ/mol. Hence, it is clear that energy of an electron is inversely proportional to square of the principal quantum number (i.e., energy of an electron increases with increasing  $n$ ). Further, maximum number of electrons that can be added in an energy level is  $2n^2$ .

**Azimuthal quantum number ( $l$ )** It is also known as angular quantum number and was proposed by Sommerfield. It signifies the number of subshells to which the electron belongs and also the shape of the subshells. Further, it can express energies of all subshells, that is,  $s < p < d < f$  and value of  $l$  is always  $(n - 1)$ . The values of  $l$  depend directly on  $n$  value, and for a given value of  $n$ ,  $l$  can assume values as follows,

Value of $l$	0	1	2	3
Subshell	s	p	d	f
Shapes	Spherical	Dumbbell	Double dumbbell	Complex

The origin of these letters designated for subshells is from the language used to describe the lines seen in earlier studies of atomic spectra:  $s$  was 'sharp,'  $p$  was 'principal,'  $d$  was 'diffuse,' and  $f$  was 'fundamental.' After  $f$ , an alphabetical order follows for designating subshells.

**Magnetic quantum number ( $m$ )** It was proposed by Zeeman and denotes the number of permitted orientation of various subshells and also signifies the behaviour of electrons in a magnetic field. The values of  $m$  can vary from negative to positive through zero and can be calculated from  $l$  as per formula,  $m = +1, \dots, 0, \dots, 1$ . Hence, if  $l = 0$ ,  $m = 0$ , if  $l = 1$ ,  $m$  will be  $+1, 0, 1$  and if  $l = 2$ ,  $m$  will be  $+2, +1, 0, 1, 2$ , and so on.

**Spin quantum number ( $s$ )** Quantum mechanics necessitates a fourth quantum number so as to uniquely designate an electron and is termed as spin quantum number. The spin quantum number was proposed by S. Goudsmit and G. Uhlenbeck. A spin quantum number can have only two values,  $+1/2$  and  $-1/2$ . Pauli Exclusion Principle (1945) clearly expresses these theoretical restrictions and states that 'only two electrons can be accommodated by a given atomic orbital.' Further, the two electrons assigned to a specific atomic orbital must be of opposite spin quantum number, that is, their spins must be paired. This led to the development of the electronic configuration of atoms in the periodic table.

### Electronic Configuration of Atoms

An electronic configuration is defined as the distribution of electrons among the orbitals and subshells. Electrons are assigned to a specific atomic orbital one at a time so as to fill the orbitals of one energy level, before proceeding to the next higher energy level. The electrons in an atom fill the principal energy levels in order of increasing energy (the electrons get farther from the nucleus) and the order of levels filled can be depicted as:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p



We apply **Aufbau principle** to fill up the energy levels according to which a maximum of two electrons are put into orbitals in the order of their increasing orbital energy. Further, we also consider **Hund's rule** which states that when electrons go into degenerate orbitals (i.e., orbitals of same energy), they occupy them singly before pairing begins.

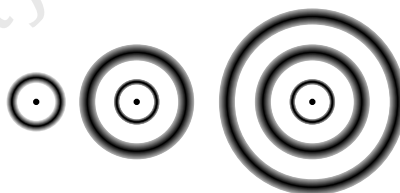
An electron is commonly depicted by an upward ( $\uparrow$ ) and downward ( $\downarrow$ ) arrow thereby showing the two possible spin states. The distribution of electrons in various quantum levels can be depicted as shown in Table 1.2.

**Table 1.2** Electron distribution in orbitals

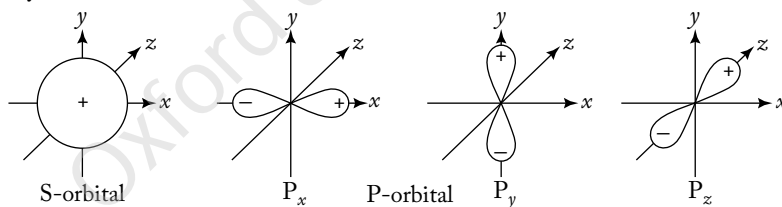
$n$	$l$	$m$	Atomic orbital	Orbitals in subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	1, 0, +1	2p	3
3	0	0	3s	1
3	1	1, 0, +1	3p	3
3	2	1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	1, 0, +1	4p	3
4	2	1, 0, +1, +2	4d	5
4	3	1, 0, +1, +2, +3	4f	7

### 1.5.1 Forms of Hydrogen Atom and Wave Functions

The solution of wave function of a hydrogen atom with its electron in the lowest quantum energy level (principal quantum number = 1) depicts a spherical region as shown in Fig. 1.8 (a) of electron probability called 1s atomic orbital. The 1s atomic orbital has more than 95 per cent probability of finding an electron within a distance of 1.7 Å (170 pm) of the nucleus. The solution of wave equation for an electron in the next higher energy level with principal quantum number 2, depicts two spherical regions of high electron probability called 2s atomic orbital. In the 2s orbital, one electron is nearer to the nucleus, similar to 1s atomic orbital, whereas the other electron is farther away from the nucleus. Similarly, the solution of wave equation depicting three spherical regions of high electron probability is called the 3s atomic orbital.

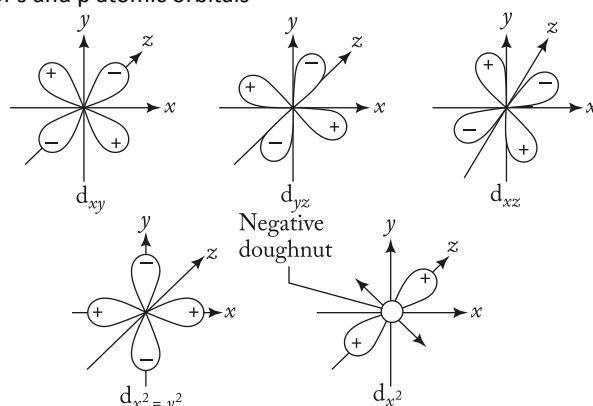


**Fig. 1.8** (a) 1s, 2s, and 3s atomic orbitals



**Fig. 1.8** (b) Shapes of s and p atomic orbitals

The solution of wave equation for the second quantum energy level of hydrogen atom described three additional atomic orbitals. These orbitals are known to be symmetrical in shape about three mutually perpendicular axes with higher electron probability in regions called *lobes* present on either side of the nucleus, as shown in Fig. 1.8 (b). One should bear in mind that  $\Psi^2 = 0$  at the nucleus clearly represents that an electron cannot be present within the nucleus at any instant. When three orbitals of equal energy (but slightly higher than 2s) are oriented at right angles ( $90^\circ$ ) to each other, they are called p levels



**Fig. 1.9** Shapes of d orbitals

(see Fig. 1.8(b)). They are designated as  $2p_x$ ,  $2p_y$ , and  $2p_z$ , at the orbitals with  $x$ ,  $y$ , and  $z$  representing the Cartesian co-ordinates in three-dimensional space. The  $p$  orbital can accommodate six electrons and have dumb-bell shape along the three axes.

The five  $d$  orbitals that can accommodate 10 electrons as shown in Fig. 1.9 are designated as five orbitals namely  $d_{(xy)}$ ,  $d_{(yz)}$ ,  $d_{(xz)}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . As shown in Fig. 1.10, the probable distances of an electron are given by radial probability distribution plots. Hence, a plot of electron probability against  $r$  (distance of electron from the nucleus) for hydrogen atom is given for  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ , and  $3d$  orbitals in this figure.

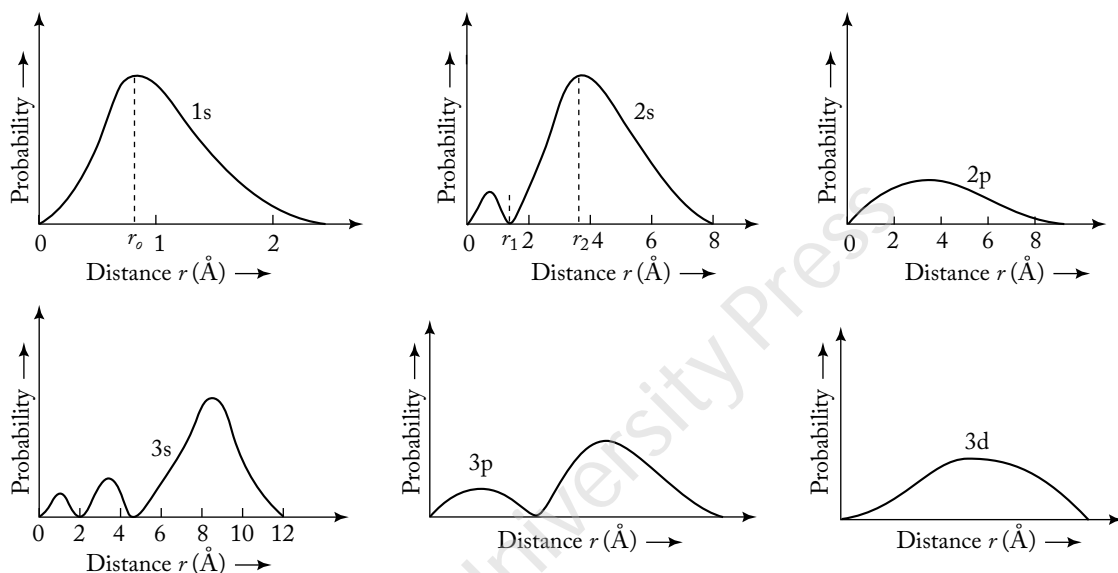


Fig. 1.10 Radial probability distribution plots for hydrogen atom

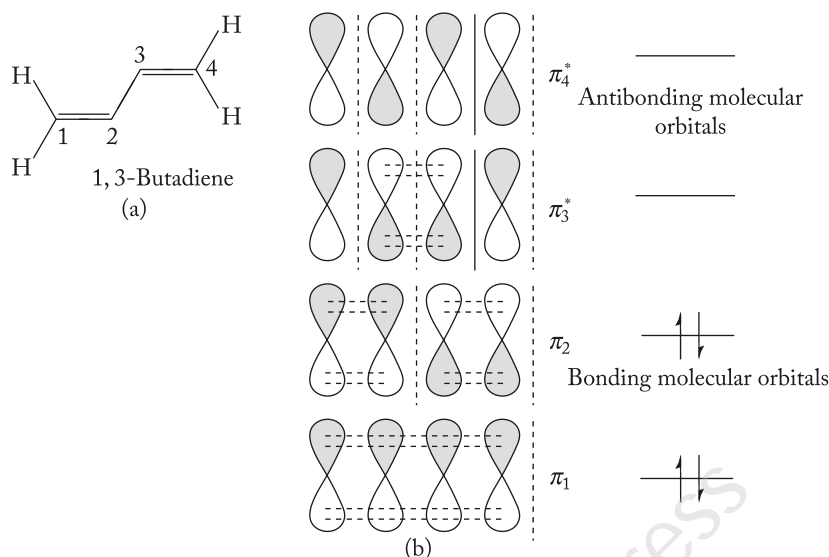
## 1.6 APPLICATIONS OF SCHRÖDINGER EQUATION

### 1.6.1 Conjugated Molecules

The chemical system that can best elucidate particle-in-a-box model is a  $\pi$ -electron moving in a conjugated system of alternate single and double bonds; for example, 1, 3-butadiene. For simplicity,  $\pi$  bonding excluding sigma ( $\sigma$ ) bonds is considered as a rigid framework of the molecule. Ethene molecule has a  $\pi$  bond in a plane perpendicular to the molecular plane, whereas in 1, 3-butadiene, the  $\sigma$  bonds and  $\pi$  bonds lie in a plane perpendicular to all the carbon and hydrogen atoms (see Fig 1.11).

### Check Your Progress

5. Distinguish between an orbit and orbital.
6. Express Schrödinger time-independent wave equation.
7. What are eigen values and eigen functions?
8. What are the possible values of eigen function?
9. What is Born interpretation?
10. Draw the radial probability distribution plots for hydrogen atom.
11. Define electronic configuration. State Hund's rules and Aufbau principle for writing the electronic configuration.



**Fig. 1.11** (a) Structure of 1,3-butadiene (b) pi-molecular orbitals of 1,3-butadiene (shaded portion represents + sign on the lobes)

The four  $\pi$  electrons move freely over the four-carbon atom framework of single bonds. One can neglect the zig-zag C – C bonds and assume a one-dimensional box. We will overlook that  $\pi$  electrons have a node in the molecular plane. Since the electron wave function extends beyond the terminal carbons, one can add approximately one-half bond length at each end. This will give a box of length equal to the number of carbon atoms times the C – C bond length. Thus, for butadiene the length will be  $4 \times 1.40 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ). In the lowest energy state of butadiene, four delocalized electrons will fill the two lowest molecular orbitals and the total  $\pi$ -electron density is given (as shown in Fig. 1.11) by,  $\rho = 2\Psi_1^2 + 2\Psi_2^2$ . Further, equations for the four  $\pi$  orbitals can be written as follows.

$$\pi_1 = 0.37 \Psi_1 + 0.60 \Psi_2 + 0.60 \Psi_3 + 0.37 \Psi_4$$

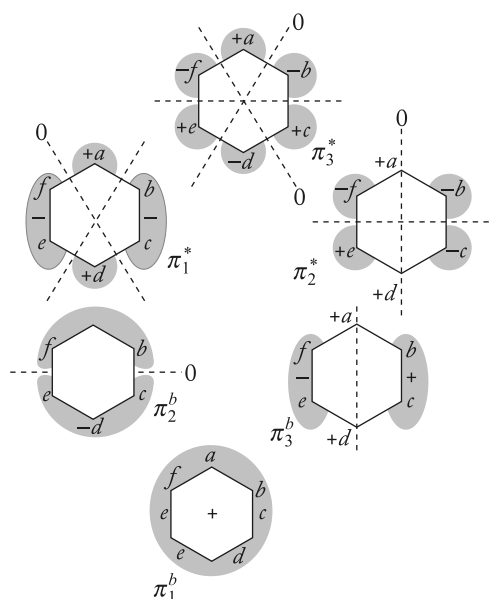
$$\pi_2 = 0.60 \Psi_1 + 0.37 \Psi_2 + 0.37 \Psi_3 + 0.60 \Psi_4$$

$$\pi_3^* = 0.60 \Psi_1 + 0.37 \Psi_2 + 0.37 \Psi_3 + 0.60 \Psi_4$$

$$\pi_4^* = 0.37 \Psi_1 + 0.60 \Psi_2 + 0.60 \Psi_3 + 0.60 \Psi_4$$

The  $\pi$ -electron density is concentrated between carbon atoms 1 and 2, and between 3 and 4; the predominant structure of butadiene has double bonds between  $C_1$ ,  $C_2$  and  $C_3$ ,  $C_4$ . Each double bond consists of a  $\pi$  bond, in addition to the underlying  $\sigma$  bond. Overall, butadiene can be described as a resonance hybrid with the contributing structures: major  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$  and, minor  $\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2$ .

In the similar manner, one can understand benzene; a cyclic ring structure with six electrons each of which is present on carbon atoms in  $\pi$  orbitals perpendicular to the molecular plane. Benzene has six p orbitals and hence it has  $6\pi$  orbitals, named  $a$  to  $f$ , as depicted in Fig. 1.12.



**Fig. 1.12** pi molecular orbitals of benzene

Let the orbitals be labelled as  $z_a, z_b, z_c, z_d, z_e$ , and  $z_f$  as depicted in Fig. 1.12 and let the sign for each orbital be either positive or negative (+ depicts p-wave function is upward and – depicts p-wave function is downward).

$$\begin{aligned}\pi_1^b &= z_a + z_b + z_c + z_d + z_e + z_f \\ \pi_2^b &= 2z_a + z_b - z_c + 2z_d - z_e + z_f \\ \pi_3^b &= z_b + z_c - z_e - z_f \\ \pi_1^* &= 2z_a - z_b - z_c + 2z_d - z_e - z_f \\ \pi_2^* &= z_b - z_c + z_e - z_f \\ \pi_3^* &= z_a - z_b + z_c - z_d + z_e - z_f\end{aligned}$$

The dashed lines in the diagram indicate nodes with zero electron density and it is evident from the above equations that there are three bonding and three antibonding orbitals in benzene. Benzene is considered an 'aromatic' compound, the additional stability of the molecule is due to the presence of  $\pi$  orbitals throughout the six carbon atoms of the cyclic ring.

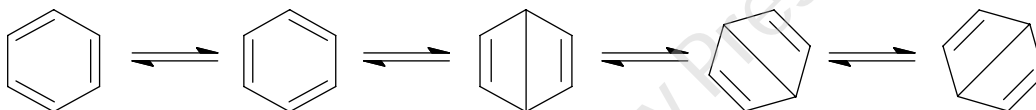


Fig. 1.13 Canonical structures of benzene

The stabilization energy of benzene is about 36 kcal and can be represented as resonance structures as shown in Fig. 1.13. Benzene represents a combination of all the above structures with the first two contributing largely.

### 1.6.2 Quantum Confinement in Nanoparticles

One of the major outcomes of size reduction of bulk materials to nanoscale levels is quantum confinement. Quantum confinement effect is a popular term in the nano world where the particle size ranges from 1–25 nm. At nanoscale levels, electron tends to 'feel' the presence of particle boundaries and respond to changes in particle size by adjusting its energy. This leads to discrete energy levels depending on the size of the structure. According to Yoffe (1993), Bohr radius of a particle can be written as,  $a_B = \epsilon m/m^* a_o$ ; where  $\epsilon$  is the dielectric constant of the material,  $m^*$  is the particle mass,  $m$  is the rest mass of an electron, and  $a_o$  is the Bohr radius of H atom. When the particle size approaches Bohr radius, the quantum confinement effect causes increased transition energy and blue shift in the absorption spectra.

As per Miller (1984), when the motion of electrons and holes is confined in one or more directions by potential barriers, they are called *quantum confined structures*. Quantum well, quantum wire, and quantum dots or nanocrystals are some examples of such structures and their Schrödinger equation can be written as follows:

$$\begin{aligned}\text{Quantum dot: } E_{n,m,l} &= \frac{\pi^2 \hbar^2}{2m^*} \left[ \frac{n^2}{L_z^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_x^2} \right], \Psi = \phi(z)\phi(y)\phi(x) \\ \text{Quantum wire: } E_{n,m}(k_x) &= \frac{\pi^2 \hbar^2}{2m^*} \left[ \frac{n^2}{L_z^2} + \frac{m^2}{L_y^2} \right] + \frac{\hbar^2 k_x^2}{2m^*}, \Psi = \phi(z)\phi(y)\exp(ik_x x) \\ \text{Quantum well: } E_n(k_x, k_y) &= \frac{\pi^2 \hbar^2 n^2}{2m^* L_z^2} + \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2), \Psi = \phi(z)\exp(ik_x x + ik_y y)\end{aligned}$$

where  $n, m, l = 1, 2, \dots$  quantum confinement numbers,  $L_x, L_y$  and  $L_z$ , are the confining dimensions,  $\exp(ik_x x + ik_y y)$  is called *wave function* that describes the electronic motion in  $x$  and  $y$  directions, same as electron wave functions.

## 1.7 MOLECULAR ORBITAL (MO) THEORY

F. Hund and R.S. Mulliken (1932) postulated the molecular orbital theory and its salient features are as follows:

- The electrons in a molecule are present in various molecular orbitals just like the electrons of atoms are present in various atomic orbitals.
- The atomic orbitals of similar energies and symmetry combine to form molecular orbitals.
- In an atomic orbital, an electron is influenced by one nucleus; it is not so in the case of molecular orbitals. As many atoms combine to form a molecule, electrons in a molecular orbital are under the influence of two or more nuclei depending on the number of combining atoms. Hence, an atomic orbital is monocentric, whereas a molecular orbital is polycentric in nature.
- When two atomic orbitals combine, two molecular orbitals are formed, namely bonding molecular orbital and antibonding molecular orbital.
- The bonding molecular orbital possess lower energy with greater stability than the corresponding antibonding molecular orbital. Electrons fill up the molecular orbitals following Pauli's, Aufbau, and Hund's rules just like atomic orbitals.

### 1.7.1 Molecular Orbitals in Homonuclear Diatomic Molecules

Generally, there are two types of diatomic molecules: homonuclear and heteronuclear molecules. If a molecule consists of two or more atoms belonging to the same element, they are called *homonuclear diatomic molecules*, for example,  $H_2, He_2, Li_2$ . The molecular orbital (MO) theory explains the formation of homonuclear diatomic molecules.

As per molecular orbital theory, when two atoms combine to form a molecule, the two nuclei are positioned at an equilibrium distance and their atomic orbitals lose their identity to form molecular orbitals. The electrons are added to these molecular orbitals which are quite similar to atomic orbitals. The  $s, p, d, f$  orbitals in atoms are determined by various sets of quantum numbers, whereas in molecules, there are  $\sigma, \pi, \delta$  molecular orbitals determined by quantum numbers. In a molecule, an electron can move in a field of more than one nucleus, hence molecular orbitals are polycentric in nature and follows Aufbau principle, Pauli Exclusion principle, and Hund's rules. Just like an atomic orbital, a molecular orbital contains a maximum of two electrons with opposite spin.

An approximate quantum mechanical picture of electrons in a chemical bond can be derived by combining hydrogen-like wave functions, namely  $\Psi_1$  and  $\Psi_2$  for two atoms. The new wave function is called the *linear combination of atomic orbitals* (also called LCAO method). As per LCAO, molecular orbitals are formed by combination of the atomic orbitals of the combining atoms. Similar to ripples formed at the water surface, the electronic wave function can interact in a constructive or destructive manner to form molecular orbitals. If there is a constructive combination of atomic orbitals, an increase in electron probability occurs between the nuclei of approaching atoms leading to the formation of energetically favourable bonding molecular orbitals denoted as  $\Psi_B$ . In destructive combination of atomic orbitals, there is a zero-electron probability between the nuclei of approaching atoms leading to the formation of energetically unfavourable antibonding molecular orbital denoted as  $\Psi_A$ . The bonding molecular orbitals are formed by adding wave functions of electrons in the two atomic orbitals, whereas antibonding molecular orbitals are formed by subtracting their wave functions as,

$$\Psi_b = \Psi_A + \Psi_B \dots (1.34) \text{ and } \Psi_a = \Psi_A - \Psi_B \quad (1.35)$$

As explained above, two atomic orbitals combine to form two molecular orbitals; hence it means that the number of molecular orbitals must always be equal to the number of atomic orbitals that are combined. The electron distribution in a given molecular orbital is obtained by squaring their wave functions, thus on squaring Eqs (1.34) and (1.35), we get,

$$\Psi_b^2 = \Psi_A^2 + 2\Psi_A\Psi_B + \Psi_B^2 \quad (1.36)$$

$$\text{and; } \Psi_a^2 = \Psi_A^2 - 2\Psi_A\Psi_B + \Psi_B^2 \quad (1.37)$$

Equations (1.36) and (1.37) depict the probability functions of bonding and antibonding molecular orbitals. The two equations differ by cross term  $2\Psi_A\Psi_B$  and integral  $\int \Psi_A\Psi_B d\tau$  is the overlap integral,  $S$ , which is infinitesimally small and hence neglected. For bonding  $S > 0$ ; antibonding  $S < 0$  and for non-bonding  $S = 0$ .

### 1.7.2 Shapes of Molecular Orbitals

Molecular orbitals can be sigma or pi depending on the mode of overlap of atomic orbitals. If a head-on collision occurs between atomic orbitals, sigma molecular orbitals will be formed. When atomic orbitals overlap laterally, pi-molecular orbitals are formed. Let us take the example of hydrogen molecule. If there is a favourable interaction between 1s atomic orbitals of two hydrogen atoms, it produces a molecular orbital cylindrically symmetrical along the inter-nuclear axis. The bond formed when two electrons occupy such a molecular orbital is called sigma ( $\sigma$ ) bond and its associated antibonding orbital is called sigma star ( $\sigma^*$ ). The electrons in such bonding orbitals are located nearer the inter-nuclear axis as shown in Fig. 1.14.

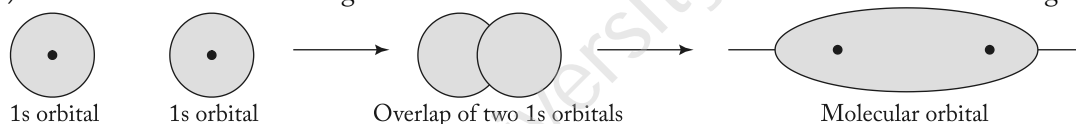


Fig. 1.14 1s orbitals leading to molecular orbital

Two different types of atomic orbitals can also result in the formation of molecular orbital of a sigma bond. Combining 1s and 2p atomic orbitals leads to the formation of molecular orbital of somewhat different shapes as shown in Fig. 1.15.

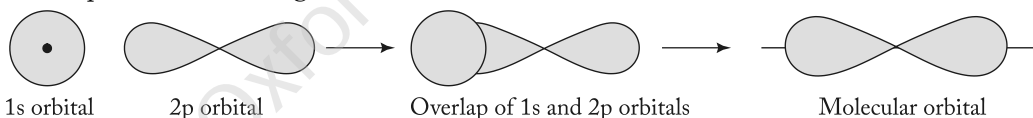


Fig. 1.15 Atomic orbital overlap leading to molecular orbital

Another type of bonding that is generally seen in organic molecules is called the pi ( $\pi$ ) bond that forms due to the interaction of parallel p orbitals located on adjacent atoms. Side-to-side interactions of p orbitals produce bonding pi ( $\pi$ ) molecular orbital and an associated antibonding pi star ( $\pi^*$ ) molecular orbital. In case of such bonding orbitals, electrons usually have the greatest probability of being located above and below the inter-nuclear axis as shown in Fig. 1.16.

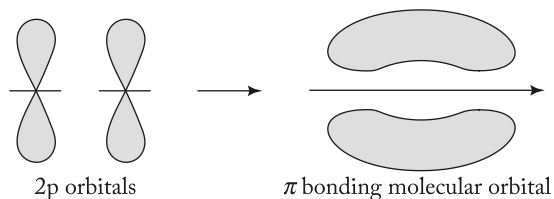


Fig. 1.16 Formation of pi bonding molecular orbital

The following conditions must be met for effective atomic orbital overlap:

- Atomic orbitals involved in linear combination must possess similar energies. Hence, no combination is possible between 1s and 2s orbitals in a homonuclear diatomic molecule.
- There must be a considerable overlap between two atomic orbitals so as to form a molecular orbital.

- (c) Atomic orbitals must have same symmetry about the molecular axes, that is, a  $2p_z$  orbital will not combine with an atomic orbital due to varying symmetries, but a  $2p_x$  orbital will combine with an s orbital to form a sigma molecular orbital. Further, a  $p_z$  orbital of one atom will not combine with a  $p_x$  or a  $p_y$  orbital of another atom.
- (d) When  $p_x$  orbitals combine, bonding and antibonding molecular orbitals that are symmetrical about the inter-nuclear axis are denoted as  $\sigma p$  and  $\sigma^* p$ , respectively. The combining  $p_y$  orbitals produces molecular orbitals of different shapes and do not remain symmetrical along the internuclear axis. They are usually denoted as  $\pi 2p_y$  and  $\pi^* 2p_y$  for bonding and antibonding molecular orbitals, respectively. Similarly, when  $p_z$  atomic orbitals combine,  $\pi 2p_z$  and  $\pi^* 2p_z$  molecular orbitals are formed.
- (e) The wave functions that refer to two or more orbitals of same energy are called *degenerate*. So,  $\pi 2p$  orbitals are *doubly degenerate* as there are two orbitals of equal energy;  $\pi 2p_y = \pi 2p_z$  and their antibonding molecular orbitals are also doubly degenerate;  $\pi^* 2p_y = \pi^* 2p_z$ .

The sequence of energy levels in the increasing order of energy that helps in predicting the electronic structure of simple molecules is as follows:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$$

### 1.7.3 Bond Order

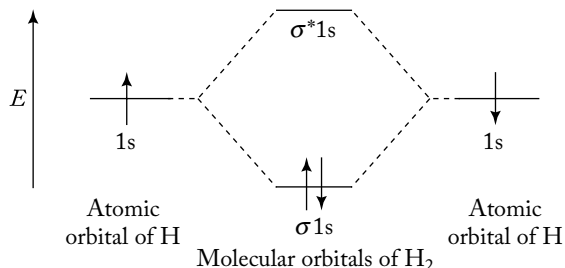
The difference between the number of bonding and antibonding electrons that is divided by 2 is called bond order.

$$\text{Bond order} = \frac{\text{Number of bonding electrons} - \text{Number of antibonding electrons}}{2}$$

The reason for dividing the total number of electrons by 2 is because we always assume bonds as a pair of electrons. Hence, for a simple molecule such as hydrogen that has two electrons, its bond order will be,  $2 - 0/2 = 1$ .

This indicates that  $H_2$  molecule has one bond. However, it is not necessary that bond order will always be a whole number.

**Dihydrogen ( $H_2$ )** The simplest homonuclear diatomic molecule is formed when atomic orbitals of two hydrogen atoms combine. The electrons occupy the molecular orbital of the lowest energy, the  $\sigma 1s$  bonding orbital. A molecular orbital can hold two electrons, so both electrons in the dihydrogen molecule are in  $\sigma 1s$  bonding orbital and the electron configuration is  $(\sigma 1s)^2$ .



**Fig. 1.17** Molecular orbital energy level diagram of dihydrogen  $H_2$  molecule

$$\text{Bond order of dihydrogen molecule} = \frac{1}{2} [N_b - N_a] = \frac{2 - 0}{2} = 1$$

**Nitrogen ( $N_2$ )** The ground state electronic configuration of nitrogen atom is  $1s^2, 2s^2, 2p^3$  and the electronic configuration of nitrogen molecule is,

$$2N (1s^2, 2s^2, 2p^3) = N_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y = \pi 2p_z)^4]$$

The  $1s$  electrons from both the nitrogen atoms are referred to as K shell electrons (closed shell electrons); they do not participate in bonding as they are in the inner shell and denoted as KK in the electronic configuration.

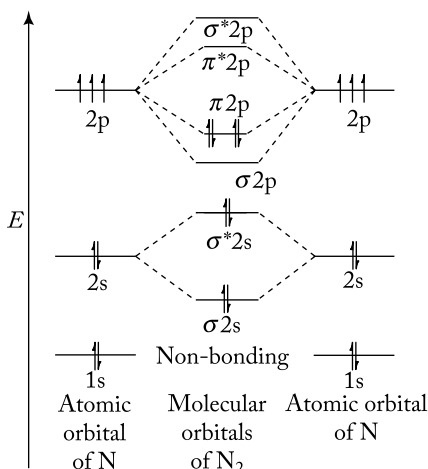


Fig. 1.18 Molecular orbital energy level diagram of  $N_2$  molecule

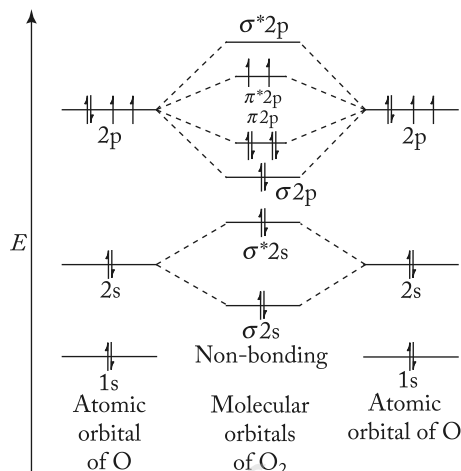


Fig. 1.19 Molecular orbital energy level diagram of  $O_2$

The bond order (i.e., number of covalent bonds) is given as:  $\frac{1}{2} [N_b - N_a] = \frac{8 - 2}{2} = 3$

Hence, nitrogen is a triple bond molecule ( $N \equiv N$ ) with one sigma and two pi bonds with diamagnetic properties.

**Oxygen ( $O_2$ )** The ground state electronic configuration of oxygen atom is  $1s^2, 2s^2, 2p^4$  and electronic configuration of oxygen molecule is,

$$2O (1s^2, 2s^2, 2p^4) = O_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y = \pi 2p_z)^4 (\pi^* 2p_y = \pi^* 2p_z)^2]$$

The 1s electrons from both oxygen atoms are referred to as K shell electrons as they do not take part in bonding since they are in the inner shell and denoted as KK in the electronic configuration.

The bond order is given as:  $\frac{1}{2} [N_b - N_a] = \frac{8 - 4}{2} = 2$

Hence, oxygen molecule has a double bond with two unpaired electrons, and thus it exhibits paramagnetism.

**Fluorine ( $F_2$ )** The ground state electronic configuration of fluorine atom is  $1s^2, 2s^2, 2p^5$ , and the electronic configuration of fluorine molecule is,  $2F (1s^2, 2s^2, 2p^5)$

$$= F_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y = \pi 2p_z)^4 (\pi^* 2p_y = \pi^* 2p_z)^4]$$

The 1s electrons from both fluorine atoms are referred to as K shell electrons since they do not take part in bonding as they are in the inner shell and denoted as KK in the electronic configuration.

The bond order is given as:  $\frac{1}{2} [N_b - N_a] = \frac{8 - 6}{2} = 1$   
Thus, fluorine molecule has a single bond with no unpaired electrons, and thereby exhibits diamagnetism.

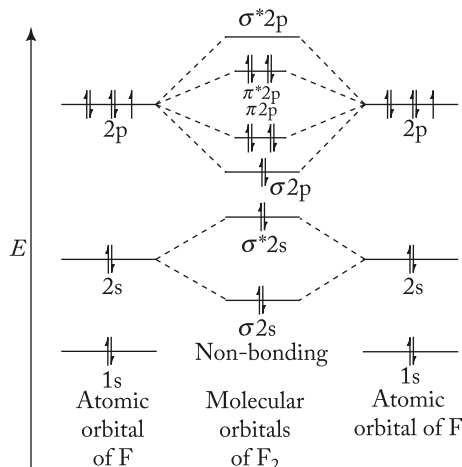


Fig. 1.20 Molecular orbital energy level diagram of  $F_2$

### 1.7.4 Molecular Orbitals in Heteronuclear Diatomic Molecules

If two bonded atoms in a molecule are of different elements, they are called *heteronuclear diatomic molecules*, for example, CO, HCl, NO. The principles of chemical bonding in heteronuclear diatomic molecule



are the same as those of the homonuclear diatomic molecules studied in the earlier section. However, some differences naturally appear in heteronuclear diatomic molecules, such as: (a) *loss of symmetry* and (b) *unequal electron cloud* due to different participating nuclei (or elements). As seen earlier, in homonuclear diatomic molecules, only the combination of atomic orbitals of equal energy and like-symmetry can form molecular orbitals. But such a limitation is not observed in heteronuclear diatomic molecules. When atomic orbitals of different elements combine, the following two factors affect the formation of molecular orbital.

**Differing electronegativities** The two atomic orbitals of the combining elements are at different energies due to differing electronegativities between atoms. When a more electronegative atom approaches a strongly electropositive atom, electron density in such molecules is significantly polarized towards the more electronegative atom.

Let us consider carbon monoxide molecule, where C and O atoms (on Pauling scale, electronegativity = 2.6 and 3.5 respectively) combine, the atomic orbitals of oxygen will be lower in energy. When such atomic orbitals overlap, the resulting bonding molecular orbitals will resemble more like atomic orbitals of oxygen, whereas the antibonding molecular orbitals will resemble the atomic orbitals of carbon. Due to differing electronegativities, the electron cloud in the molecule will be drawn towards the atom with higher electronegativity and hence the heteronuclear diatomic molecule (CO) has an unsymmetrical electron distribution.

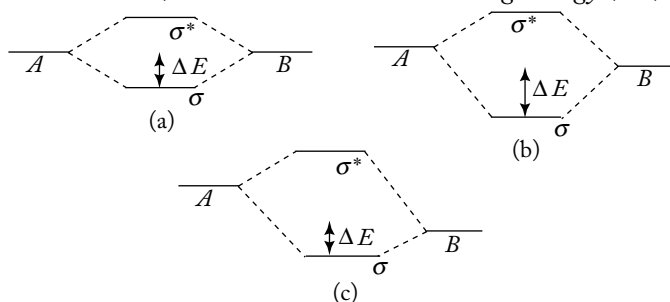
Further, the combining atomic orbitals in a heteronuclear diatomic molecule do not contribute equally to the bonding and antibonding molecular orbitals. Say, if a heteronuclear molecule AB has a more electronegative atom B, the atomic orbitals of atom B will be lower in energy than those of atom A. Thus, bonding molecular orbitals will be closer to atomic orbitals of atom B, whereas atomic orbitals will be contributing more to antibonding molecular orbitals. Hence, molecular orbitals of heteronuclear diatomic molecules can be written as:

$$\Psi_b = x\Psi_A + y\Psi_B; \text{ and } \Psi_a = y\Psi_A - x\Psi_B$$

where  $x$  and  $y$  are coefficients of atomic orbitals and  $y > x$ .

**Reduced covalent bond energy** In a heteronuclear diatomic molecule, bonds formed from atomic orbitals of differing energies have reduced covalent bond energy. As the bonding MO will have lower energy than the atomic orbitals from which it is formed, the difference is called *exchange energy* ( $\Delta E$ ).

As shown in Fig. 1.21(c), the exchange energy in a heteronuclear molecule is reduced as the atomic orbitals do not match. It is evident from Fig. 1.21(a), that there is weakening in covalent bonding, but this is not true. Whenever there is loss of covalent character, it is compensated by an increase in the ionic character of bonds. If one adds up the ionic and covalent bonding, it results in a much stronger bonding as in Fig. 1.21(b).



**Fig. 1.21** (a) Covalent energy in a homonuclear diatomic molecule, (b) covalent energy in a heteronuclear diatomic molecule and (c) heteronuclear diatomic molecule with higher electronegativity difference

**Carbon monoxide (CO)** The electronic configuration of carbon and oxygen atoms are:  ${}_6\text{C} = 1s^2, 2s^2, 2p^2$  and  ${}_8\text{O} = 1s^2, 2s^2, 2p^4$ . The number of electrons available for bonding from carbon and oxygen are 4 and 6, respectively; thereby ten electrons need to be accommodated in the molecular energy levels. Carbon monoxide can be considered isoelectronic with nitrogen molecule and the electronic configuration of CO

molecule can be expressed as,  $\text{CO} [\text{KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y = \pi 2p_z)^4]$ .

As shown in Fig. 1.22, the bonding resulting from  $\sigma 2s^2$  is effectively cancelled by antibonding  $\sigma^* 2s^2$ . This leaves  $\sigma 2p_x^2$  to provide the bonding in CO molecule. As all the six electrons are present in the bonding molecular orbitals and none of it is in the antibonding molecular orbitals, hence just like nitrogen molecule, CO molecule also shows the bond order as,

$$\frac{1}{2}[N_b - N_a] = \frac{8 - 2}{2} = 3$$

Thus, in a CO molecule, there is a triple bond  $\text{C} \equiv \text{O}$  with one  $\sigma$  and two  $\pi$  bonds with diamagnetic properties. With a high bond order of 3, CO is a stable molecule. All the electrons are paired and hence CO is a diamagnetic molecule.

**Nitric oxide (NO)** The electronic configuration of nitrogen and oxygen atoms are,  ${}_7\text{N} = 1s^2, 2s^2, 2p^3$  and  ${}_8\text{O} = 1s^2, 2s^2, 2p^4$ . The molecular energy level diagram of nitric oxide will be quite similar to nitrogen molecule (refer to Fig. 1.23). In nitric oxide, there are 11 electrons to be filled in molecular orbitals. Thus, the configuration of NO molecule can be written as

$\text{NO} [\text{KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 \pi 2p_z)^2, \pi^* 2p_y^1, \pi^* 2p_z^0]$ .

The four electrons of the two 2s orbitals fill up the bonding molecular orbitals,  $\sigma 2s^2$  and antibonding molecular orbital,  $\sigma^* 2s^2$ . Out of the remaining seven electrons: three 2p electrons of nitrogen and four 2p electrons of oxygen, only six electrons will fill up the remaining higher molecular orbitals.

The only remaining electron will occupy the antibonding orbital,  $\pi^* 2p_y^1$  and due to the presence of this single electron in the energy diagram, NO molecule exhibits paramagnetism. The presence of unpaired electron in nitric oxide molecule makes it similar to oxygen molecule that also shows paramagnetism. The bond order of NO molecule is

$$\frac{1}{2}[N_b - N_a] = \frac{6 - 1}{2} = 2.5$$

As the bond order of NO is low, bonding in NO is considerably weaker than in nitrogen molecule. The single unpaired electron occupying the  $\pi^* 2p_y$  orbital is easier to be removed forming  $\text{NO}^+$  (nitrosonium) ion having a stronger bond than NO molecule. The bond length in nitric oxide is greater than nitrogen molecule. In spite of the presence of an unpaired electron, nitric oxide molecule shows stability as this electron is well distributed over both nitrogen and oxygen atoms. The fact that nitrosonium ion can be easily obtained from nitric oxide clearly proves that  $\text{NO}^+$  ion can exist as a stable species such as  $\text{NO}^+\text{HSO}_4^-$  and  $\text{NO}^+\text{BF}_4^-$ .

**Hydrogen chloride (HCl)** The electronic configuration of hydrogen and chlorine atoms are:  ${}_1\text{H} = 1s^1$  and  ${}_{17}\text{Cl} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ . During the formation of hydrogen chloride, only three electrons of chlorine atom can combine with  $1s^1$  electron of hydrogen. As the  $3p_y$  and  $3p_z$  orbitals of chlorine atom

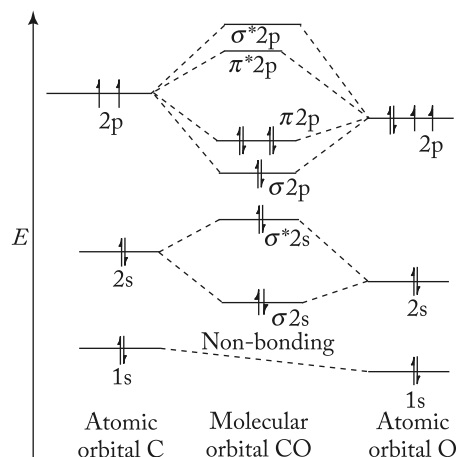


Fig. 1.22 Molecular orbital energy diagram of CO molecule

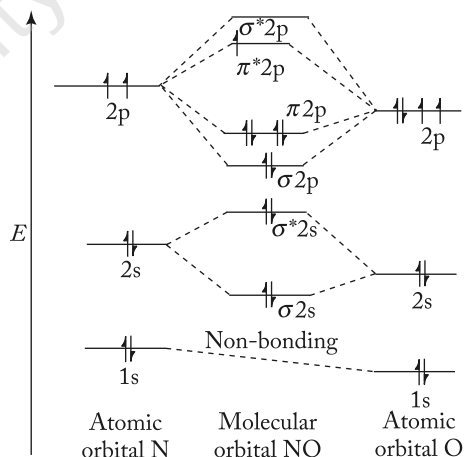


Fig. 1.23 Molecular energy level diagram of NO molecule

have no matching symmetry with 1s hydrogen orbital, there cannot be any overlap of these orbitals. The molecular energy level diagram is depicted in Fig. 1.24 considering no hybridization.

The electronic configuration of hydrogen chloride can be written as:  $\text{HCl} [\text{KK}, 2s^2, 2p^6, 3s^2, 3p_y^2, 3p_z^2]$ .

The shape of hydrogen chloride molecule clearly indicates the presence of a polar bond with a bond order of  $\frac{1}{2}[\text{N}_b - \text{N}_a] = \frac{2-0}{2} = 1$ . Since both the electrons are paired, hydrogen chloride is a diamagnetic molecule.

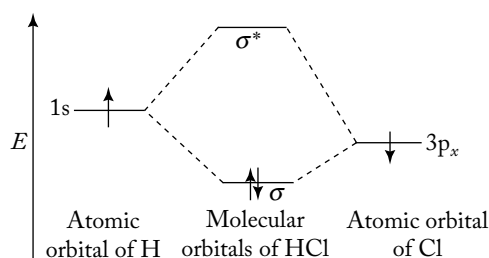


Fig. 1.24 Molecular energy level diagram of HCl molecule

## 1.8 METALLIC BOND

Metals exhibit crystalline properties possessing either body-centred cubic, face-centred cubic, or close-packed hexagonal lattices (Fig. 1.25). Each atom in the crystal lattice exhibits a high coordination number. Hence, bonding in such metallic crystalline structures cannot be explained using simple theories of bonding due to insufficient number of electrons.

It is observed that the metal atoms are closely packed in a crystal structure, which represents extensive overlap of electron orbitals such that the valence electrons are no longer associated with a particular nucleus; rather they are completely delocalized over all atoms in the crystal structure. An electrostatic attraction between metal atoms and valence electrons within its sphere of influence is called *metallic bond*. Metals are arrangements of positive ions as spheres of identical radii packed so as to completely fill the space. The theories put forth to explain bonding in metals are discussed here.

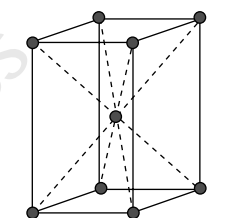
### 1.8.1 Free Electron Theory

Paul Drude (1900) put forth the free electron theory in which he considered metals as a lattice with electrons moving through it just similar to the movement of gaseous molecules. The theory was further improvized by Lorentz (1923) who stated that as metals have lower ionization potential, they easily lose valence electrons and hence are made of only a lattice of rigid spheres of positive ions and electrons delocalized in the lattice. Hence, one can model that metal behaves as an assembly of positive ions immersed in a sea of mobile, delocalized electrons as shown in Fig. 1.26.

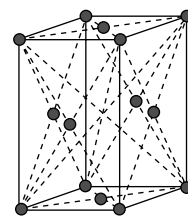
As valence electrons in a metallic bond are spread over the crystal lattice, metallic bond is non-directional in nature. Free electron theory can explain the following properties of metals.

**High strength** The metallic bonds are very strong; hence metals can maintain a regular crystal structure.

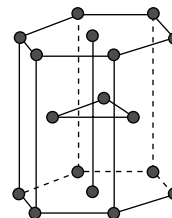
**Electrical and thermal conductivity** The high electrical conductivity of metals can be attributed to the presence of free valence electrons as they can easily move under the influence of an electric



(a) Body-centred cubic



(b) Face-centred cubic



(c) Close packed hexagonal

Fig. 1.25 Crystal structures

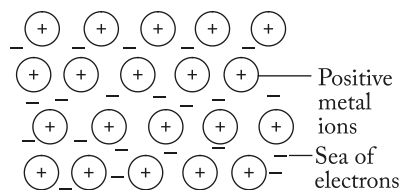


Fig. 1.26 Metal lattice showing delocalized electrons floating among positive ions

field. Higher the number of free electrons, higher will be its electric conductivity. In a similar way, metals also possess higher thermal conductivities.

**Malleability and ductility** Metallic bond is non-directional in character; hence on application of shear stress, metals are known to change their shape, this property of metals is called malleability. Further, the ease with which metal ions can glide from one lattice site to another is called ductility. Electrons in the metal lattice simply flow to follow any change in shape of the metallic crystal lattice.

**Boiling and melting point** Due to the presence of strong electrostatic attractive force between the positively charged metal ions and the surrounding valence electrons, metals exhibit higher boiling and melting points.

#### *Demerits of free electron theory*

- It fails to explain specific heat of metals, marginally lower molar heat capacity of metals as compared to non-metals.
- It also fails to distinguish between metals, insulators, and semiconductors.

The oversimplified assumption that electron is free to move anywhere within the metal crystal lattice led to the failure of this theory. In order to explain all these characteristics, band theory was postulated.

### 1.8.2 Band Theory

Felix Bloch (1928) put forth a quantum mechanical model theory to explain metal bonding. The following are the assumptions of this theory.

- All electrons present in completely filled energy levels of atoms are considered to be localized, that is, bound to the atoms with which they are associated.
- The valence electrons in the outermost energy level of atoms are free to move; however, they move in a potential field that extends over all the atoms present in the crystal lattice.
- The atomic orbitals of these free electrons can overlap with the atomic orbitals of electrons in other atoms, thereby forming delocalized molecular orbitals. Such molecular orbitals of free electrons are called *conduction orbitals* of a metal.

It is obvious that band theory is merely an extension of molecular orbital concept applicable to diatomic molecules. Let us illustrate the above concept with the example of lithium (Li) metal.

The electronic configuration of lithium atom is  $1s^2, 2s^1$  and if  $\text{Li}_2$  molecule is considered, bonding occurs using  $2s$  atomic orbitals. There are three vacant  $2p$  atomic orbitals in the valence shell and this is a prerequisite for exhibiting metallic properties. MO theory can elucidate the formation of  $\text{Li}_2$  molecule. Each lithium atom has two electrons in its inner shell, and one in its outermost shell, making a total of six electrons in its molecule. Hence, the electronic configuration of lithium molecule can be written as:  $\text{Li}_2: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$  and bonding will occur, as the  $\sigma 2s$  bonding molecular orbital is full and its corresponding antibonding orbital is vacant. If one ignores the innermost electrons, the  $2s$  atomic orbitals from each lithium atom can combine to give two molecular orbitals, one bonding and the other antibonding MOs with valence electrons occupying the bonding orbitals.

If we consider  $\text{Li}_3$  molecule, three  $2s$  atomic orbitals will combine forming three molecular orbitals, namely one bonding, one non-bonding, and one antibonding. The energy of non-bonding MO lies in between the bonding and antibonding molecular orbitals. Hence, three valence electrons from three lithium atoms tend to occupy bonding molecular orbital (2 electrons) and non-bonding molecular orbital (1 electron).

When four lithium atoms combine to form  $\text{Li}_4$ , four  $2s$  atomic orbitals with one electron each overlap, forming four molecular orbitals; two bonding and two antibonding orbitals. The presence of two non-bonding molecular orbitals between the bonding and anti-bonding molecular orbitals tends to reduce

the energy band gap between these orbitals. Hence, the four valence electrons will occupy the two lowest energy bonding molecular orbitals.

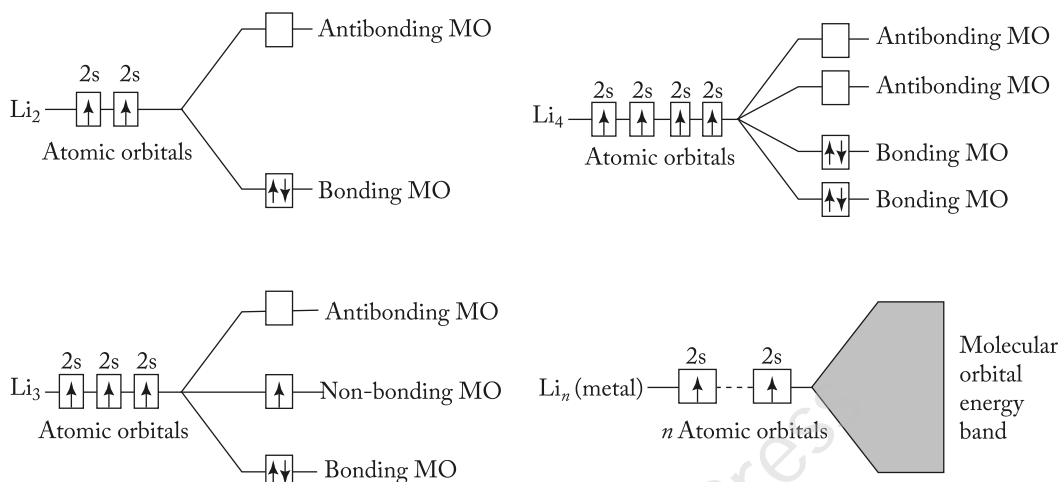


Fig. 1.27 Development of molecular orbitals into bands in metals

If  $n$  number of lithium atoms combine forming  $\text{Li}_n$ , there will be  $n$  number of  $2s$  atomic orbitals with one electron each that will overlap forming  $n$  MOs; out of which half of them will be bonding and the remaining half will be antibonding. The electrons in  $n$  orbitals will only be enough to fill the  $n/2$  number of bonding molecular orbitals, whereas antibonding molecular orbitals will remain vacant. Hence, as the number of lithium atoms increases, the spacing between the energy levels of molecular orbitals decreases, such that it virtually forms a band as in Fig. 1.27 (d). The band so formed is called the *molecular orbital energy band*.

### Explanation of Electrical and Thermal Conduction (Band Theory Concept)

Metals contain either half-filled or partially-filled valence molecular orbital energy band because of the overlap with unoccupied molecular energy band. As there is only one valence electron per atom of lithium and a molecular orbital can hold up to two electrons, it follows that only half of the molecular orbitals in the  $2s$  valence band are occupied, namely bonding molecular orbitals (Fig. 1.28 (a)). Hence, it requires only an infinitesimal amount of energy to displace an electron to an unoccupied molecular orbital. This clearly elucidates that metals exhibit high thermal and electrical conductivities.

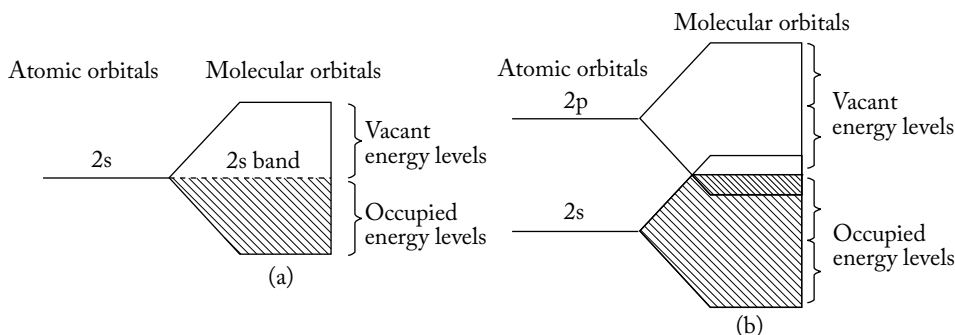


Fig. 1.28 (a) Metallic molecular orbitals of lithium showing half-filled band and (b) metallic molecular orbitals of beryllium showing overlapping bands

Beryllium has an electronic configuration  $1s^2, 2s^2$  with two valence electrons that can fill the 2s band of molecular orbitals. Similarly, 2p atomic orbitals form a 2p band of molecular orbitals. As shown in Fig. 1.28, the upper part of 2s band overlaps with the lower portion of 2p band and due to this overlap, some part of the 2p band is occupied, whereas some part of 2s band remains vacant. Due to overlapping of bands, energy gap is removed, thereby enabling free movement of electrons from the valence band to the vacant conduction band. Thus, beryllium behaves as a metal.

### Band Theory of Conductors, Insulators, and Semiconductors

According to band theory, the electronic structure of metals is considered to possess bands of electrons which are distinctly separated from each other. These bands may be completely or partially filled with free electrons whose molecular orbitals extend over the entire crystal structure. Figure 1.29 depicts the energy bands of sodium, magnesium, carbon, and germanium.

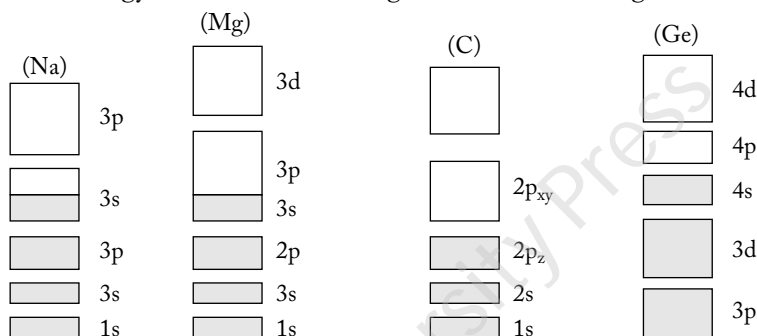


Fig. 1.29 Band models of (a) conductors (Na and Mg), (b) insulator (C), and (c) semiconductor (Ge)

**Metals (conductors)** In metals, electrical conductivities depend on the movement of electrons throughout the crystal structure under the influence of applied potential. This is possible only if electrons can be energized and jump to higher vacant band levels. As both the valence and conduction bands in metals are very close to each other, they exhibit excellent conductivity.

**Non-metals (insulators)** In this case, valence bands are fully occupied by electrons and there is a large energy gap between the valence and conduction bands. Hence, it is very difficult to excite an electron and a large amount of energy needs to be supplied for conductivity. Hence, non-metals are insulating materials.

**Semiconductors** These are materials that behave as insulators at lower temperatures and act as conductors at normal or higher temperatures. Silicon and germanium are classic examples of semiconductor materials. They have four electrons in their outermost shell and a filled band that lies below an empty  $p_{x-y}$  band. As these two bands are closer to each other, on thermal activation, electrons in the  $p_z$  band acquire sufficient energy and jump to the higher  $p_{x-y}$  band. On applying heat some covalent bonds break, thereby ejecting electrons from their regular sites which migrate, leaving behind a hole. Electrical conduction occurs due to electrons migrating in one direction and positive holes in the opposite direction; this is called *intrinsic*

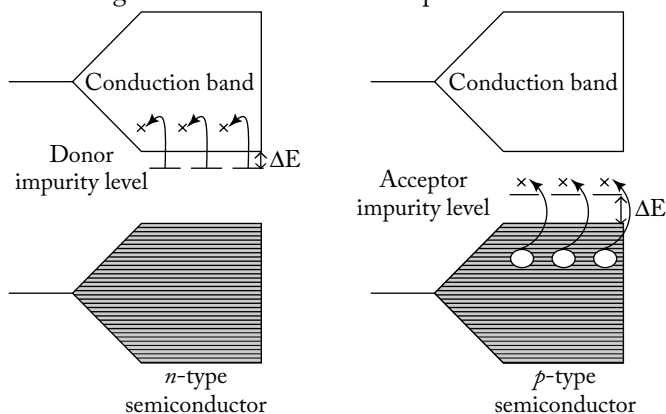


Fig. 1.30 Energy levels in n-type and p-type semiconductors

conduction. When trace impurities are added to such materials to further enhance the conductivity it is called *extrinsic conductivity*.

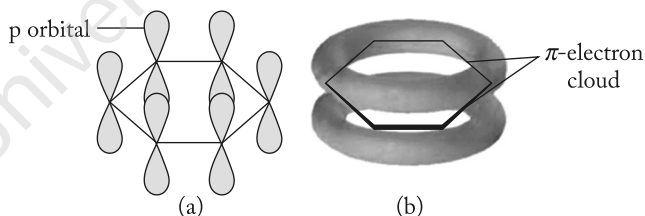
When arsenic possessing five valence electrons is doped with silicon or germanium, the four electrons of arsenic atom form a bond with four electrons of silicon, and the fifth electron is free to move. This extra electron occupies the donor impurity level just below the empty conduction band of silicon crystal. On applying thermal energy, the free electron can easily jump to the conduction band, thereby exhibiting conductivity and is termed as *n-type semiconductor*.

When indium or gallium having three valence electrons is added as an impurity, only three electrons of silicon are covalently bonded to the atoms of the dopant. Certain sites occupied by electrons are vacant called *positive holes* and occupy acceptor impurity level that lies closer to the filled valence band of silicon. On applying thermal energy, electrons get excited and jump from filled valence band to empty acceptor impurity conduction band consisting of positive holes. If a potential is applied, electrons from an adjacent atom jump and occupy the hole and in turn is replaced by an electron from another atom. It seems the positive holes are migrating and such materials are called *p-type semiconductors*.

## 1.9 CONCEPT OF AROMATICITY

Benzene (1825) was first isolated by Michael Faraday who extracted the compound from liquid residue obtained after heating whale oil under pressure. Eilhard Mitscherlich (1834) provided the molecular formula of benzene as  $C_6H_6$  and called it 'benzin' due to its relationship to benzoic acid, but later was renamed as benzene. Alchemists called such compounds aromatic, because of their pleasing odour. However, today the term 'aromatic compound' signifies some chemical structures that fulfil certain criteria.

Benzene is a planar, cyclic compound with a cyclic cloud of delocalized electrons above and below the plane of the ring (Fig. 1.31). As  $\pi$  electrons are delocalized, all the C – C bonds have the same length. Further, it is also known that benzene is quite a stable compound with large resonance energy of 36 kcal/mol. The criteria to be fulfilled for a compound to be classified as aromatic are the following.



**Fig. 1.31** Structure of benzene: (a) p orbitals on carbon atoms (b)  $\pi$ -electron cloud above and below benzene ring

- It should have an uninterrupted cyclic cloud of  $\pi$  electrons (also called  $\pi$  cloud) above and below the plane of the molecule.
- For a  $\pi$ -electron cloud to be cyclic and remain uninterrupted, the molecule must also be cyclic with every atom in the ring possessing a p orbital.
- To form an uninterrupted  $\pi$ -electron cloud, each p orbital must overlap with the p orbitals on either side of it, thus the molecule must essentially be planar with  $\pi$ -electron cloud containing an odd number of pair of electrons.

Erich Hückel (1931) was the first to recognize that an aromatic compound must possess an odd number of  $\pi$  electrons; this came to be called Hückel's rule or the  $4n + 2$  rule. Hückel's rule is a mathematical way of expressing that an aromatic compound should have an odd number of pairs of  $\pi$  electrons. According to the Rule, for a planar, cyclic compound to be aromatic, its uninterrupted  $\pi$  cloud must contain  $(4n + 2)$   $\pi$  electrons, where  $n$  is any whole number. An aromatic compound must have  $2(n = 0)$ ,  $6(n = 1)$ ,  $10(n = 2)$ ,  $14(n = 3)$ , and so on number of  $\pi$  electrons. As there are two electrons in a pair, Hückel's rule necessitates that an aromatic compound have 1, 3, 5, 7, etc. as pairs of  $\pi$  electrons.

**Antiaromatic compounds** Some compounds fulfil the first criterion of Hückel's rule (listed above), but fail to satisfy the second criterion, that is, they possess an even number of pairs of  $\pi$  electrons. Cyclobutadiene is a planar molecule with two pairs of  $\pi$  electrons. Such compounds are called *antiaromatic compounds*. They are quite unstable and difficult to isolate. Figure 1.32 depicts the distribution of electrons in benzene and cyclobutadiene.

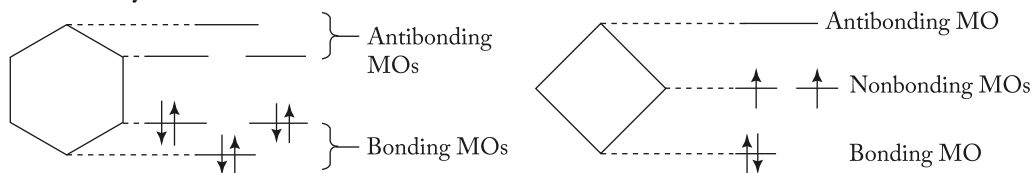


Fig. 1.32 Frost diagrams of (a) benzene and (b) cyclobutadiene

Arthur Frost proposed a simpler method to depict the distribution of electrons in aromatic systems called *Frost diagram*. In a Frost diagram, one needs to first draw the cyclic compound with one of its vertices pointed down. The molecular orbitals below the midpoint of the cyclic compound will be bonding molecular orbitals, whereas those above the midpoint are considered antibonding molecular orbitals. The midpoint of the cyclic structure in the Frost diagram will be considered as nonbonding molecular orbitals. The electrons are filled in the molecular orbitals as per Pauli Exclusion Principle and Hund's Rule, which states that if electrons are left over after filling up the bonding orbitals, they occupy non-bonding orbitals. It is evident from the diagram that in aromatic compounds such as benzene, all the bonding molecular orbitals are completely filled, whereas in a non-aromatic compound like cyclobutadiene, the presence of unpaired electrons explains its instability.

### Check Your Progress

- Distinguish between conductors and semiconductors.
- State the features of molecular orbital theory.
- What is aromaticity? Give an example of aromatic compound.
- What are the criteria for a molecule to be aromatic?
- State Hückel's rule of aromaticity.
- List the assumptions of MO theory to explain metallic bond.
- What are Frost diagrams? Illustrate Frost diagram of benzene and cyclobutadiene.
- Draw the molecular energy level diagrams of  
(a) HCl (b) NO (c) O<sub>2</sub> (d) N<sub>2</sub> (e) H<sub>2</sub> (f) CO (g) F<sub>2</sub>
- List the merits and demerits of free electron theory put forth to explain metallic bond.

### SOLVED EXAMPLES

- Calculate the wavelength of (a) a ball weighing 250 g and (b) an electron moving with a velocity of 50 m/s (Given: electron rest mass,  $m_e = 9.109 \times 10^{-31}$  kg).

**Solution:** (a) According to de Broglie equation,  $\lambda = \frac{h}{mv}$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J.s}}{2.50 \times 10^{-1} \times 50 \text{ m.s}^{-1}} \quad (\text{as } 1 \text{ kg} = 1000 \text{ g})$$

Hence,  $\lambda = 5.3 \times 10^{-35} \text{ m}$  or  $5.3 \times 10^{-25} \text{ Å}$ .

It is known that radius of an atom is in the order of  $10^{-11} \text{ m}$ ; the above value is very small and is difficult to determine by any device.



(b) For electron,

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J.s}}{9.109 \times 10^{-31} \times 50 \text{ m.s}^{-1}} = 1.46 \times 10^{-5} \text{ m} \quad (1.46 \times 10^5 \text{ Å})$$

The wavelength obtained as above falls in the infrared region of EMR spectrum.

2. Calculate the kinetic energy of a moving electron of wavelength of 5.3 pm. (Given: mass of an electron =  $9.11 \times 10^{-31} \text{ kg}$  and  $h = 6.6 \times 10^{-34} \text{ J.s}$ ).

**Solution:** The velocity of an electron can be expressed as (on rearranging de Broglie relation),

$$v = \frac{h}{m\lambda} = \frac{6.6 \times 10^{-34} \text{ J.s}}{9.11 \times 10^{-31} \text{ kg} \times 5.3 \times 10^{-12} \text{ m}} \quad (\text{as } 1 \text{ pm} = 10^{-12} \text{ m})$$

$$= 1.3682 \times 10^8 \text{ ms}^{-1}$$

As, K.E of an electron is  $\frac{1}{2}mv^2$ , thus,

$$= \frac{9.11 \times 10^{-31} \text{ kg} \times (1.3682 \times 10^8 \text{ ms}^{-1})^2}{2} = 8.524 \times 10^{-15} \text{ kg.m}^2\text{s}^{-2}$$

3. If an electron moves with a velocity of  $3.3 \times 10^7 \text{ m/s}$ , calculate the smallest possible uncertainty in its position. (Given: mass of an electron =  $9.11 \times 10^{-31} \text{ kg}$  and  $h = 1.05 \times 10^{-34} \text{ J.s}$ ).

**Solution:** As per Heisenberg's Uncertainty Principle,  $\Delta x \times \Delta p = h$

$$\text{Hence, } \Delta x = h/mv = \frac{1.05 \times 10^{-34} \text{ J.s}}{9.11 \times 10^{-31} \times 3.3 \times 10^7 \text{ m.s}^{-1}} = 3.492 \times 10^{-12} \text{ m} \quad (\text{or, } 0.0349 \text{ Å})$$

4. What is the wavelength of an electron moving at  $5.31 \times 10^6 \text{ m/s}$ ? (Given: mass of electron =  $9.11 \times 10^{-31} \text{ kg}$  and  $h = 6.626 \times 10^{-34} \text{ J.s}$ )

**Solution:** According to de Broglie's equation,

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J.s}}{9.11 \times 10^{-31} \text{ kg} \times 5.31 \times 10^6 \text{ m/s}}$$

$$= \frac{6.626 \times 10^{-34} \text{ J.s}}{4.84 \times 10^{-24} \text{ kg.m/s}} = 1.37 \times 10^{-10} \text{ m or } 1.37 \text{ Å}$$

5. Calculate the kinetic energy and de Broglie wavelength (nm) of  $\text{C}_{60}$  molecule moving at a speed of 100 m/s. (Given: atomic weight of C = 12.011 g, Avogadro's number =  $6.022 \times 10^{23}$  molecules/mol).

**Solution:** Molar mass of one  $\text{C}_{60}$  molecule =  $60 \times 12.011 = 720.66 \text{ g/mol}$

$$\text{Mass of one molecule will be} = \frac{720.66 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}} = 1.1967 \times 10^{-21} \text{ g/mol}$$

$$= \frac{1.1967 \times 10^{-21} \text{ g/mol}}{1000} = 1.1967 \times 10^{-24} \text{ kg}$$

$$\text{Kinetic energy, } E = \frac{1}{2}mv^2 = \frac{1}{2} \times 1.1967 \times 10^{-24} \times (100)^2 = 5.9835 \times 10^{-21} \text{ J}$$

According to de Broglie equation,  $\lambda = \frac{h}{mv}$

$$= \frac{6.626 \times 10^{-34} \text{ J.s}}{1.1967 \times 10^{-24} \times 100} = 5.5369 \times 10^{-12} \text{ m or } 5.537 \times 10^{-3} \text{ nm} \quad (\text{as } 1 \text{ m} = 10^9 \text{ nm})$$

6. Determine the minimum uncertainty in the velocity of a particle having a mass  $1.1 \times 10^{-27} \text{ kg}$  if uncertainty in its position is  $3 \times 10^{-10} \text{ cm}$ . (Given:  $h = 6.6 \times 10^{-34} \text{ J.s}$ )

**Solution:** According to Heisenberg's Uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{or,} \quad \Delta x \times m\Delta v = \frac{h}{4\pi}$$

On rearranging the above expression we get,

$$\Delta v = \frac{h}{4\pi m \Delta x} = \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 1.1 \times 10^{-27} \times \left( 3 \times 10^{-10} \text{ cm} \times \frac{1 \text{ m}}{10^2 \text{ cm}} \right)}$$

$$= 1.59 \times 10^4$$

Thus, the uncertainty in velocity of the particle =  $1.59 \times 10^4 \text{ ms}^{-1}$

7. Calculate the energy of an electron in ground state confined to a box of  $3\text{\AA}$  in width and moving in one-dimension ( $x$ -axis only).

**Solution:** According to particle-in-a-box model,

$$E = \frac{n^2 h^2}{8ml^2} = \frac{1^2 \times (6.6 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (3 \times 10^{-10})^2}$$

On solving the above we get,

$$\therefore E_{\text{ground state}} = 6.648 \times 10^{-19} \text{ J}$$

## SUMMARY

- Atomic and molecular structure forms the basis of chemistry. Learning about various postulates put forth by various atomic models helps us understand the structure of atoms.
- All sub-atomic particles have a wave-like nature called matter waves or de Broglie waves. The Davisson–Germer experiment practically demonstrated the wave nature of particles.
- According to Heisenberg’s Uncertainty Principle, it is impossible to simultaneously determine the position and momentum of an electron.
- Schrödinger derived an equation for comparing the path taken by the particle with that of a ray of light and the associated de Broglie wave with electromagnetic waves.
- The quantum mechanical model of hydrogen atom and particle-in-a-box are deduced using Schrödinger equation.
- The solution of  $\Psi$  led to three different types of quantum numbers. As per Pauli Exclusion Principle, only two electrons can be accommodated by a given atomic orbital.
- Schrödinger equation is well studied for hydrogen atom. It can be applied to study conjugated systems and nanoparticles.
- According to the MO theory, atomic orbitals of similar energies and symmetry combine to form molecular orbitals, one of which is bonding and the other antibonding. Also, in an atomic orbital, an electron is influenced by one nucleus; whereas in a molecular orbital, electrons are under the influence of two or more nuclei depending on the number of combining atoms.
- MO theory finds application in understanding the structures of homo and heteronuclear diatomic molecules.
- Hydrogen, nitrogen, and oxygen are examples of elements forming homonuclear molecules, while carbon monoxide, nitric oxide, and hydrogen chloride are heteronuclear molecules.
- Theories put forward to explain metallic bonds include the free electron theory and the molecular orbital or band theory.
- Though the free electron theory could account for most of the properties of metals such as their high strength, electrical and thermal conductivity, and malleability and ductility, it failed to explain the specific heat of metals and distinguish between metals, insulators, and semiconductors.
- Band theory of solids proposed by Felix Bloch addressed the shortcomings of the free electron theory.
- Hückel’s rule is a mathematical way of expressing that an aromatic compound should have an odd number of pairs of  $\pi$  electrons. According to the Rule, for a planar, cyclic compound to be aromatic, its uninterrupted  $\pi$  cloud must contain  $(4n + 2) \pi$  electrons, where  $n$  is any whole number.

## GLOSSARY

**Antibonding molecular orbital:** A molecular orbital whose occupation by electrons decreases the total energy of a molecule. Energy level of an antibonding MO lies higher than the average of the valence atomic orbitals of the atoms in a molecule.

**Aufbau principle:** A maximum of two electrons are put into orbitals in the order of increasing orbital energy.

**Bond order:** The number of chemical bonds in a molecule.

**Crystal lattice:** The 3D arrangement of atoms, ions, or molecules in a crystalline solid.

**Hückel's rule:** The mathematical expression denoting that an aromatic compound should have an odd number of pairs of  $\pi$  electrons.

**Hund's rule:** Rule for building up the electronic configuration of atoms and molecules. It states that when electrons go into degenerate orbitals, they occupy them singly before pairing begins.

**Orbital (atomic or molecular):** A wave function that depends on the spatial coordinates of a single electron.

**Pauli Exclusion principle:** A maximum of two electrons can occupy an orbital and their spins must be paired or opposed to each other.

## KEY FORMULAE

- de Broglie relation:  $\lambda = \frac{h}{mv}$
- Heisenberg Uncertainty relation:  $\Delta x \Delta p = h$
- Schrödinger equation:  $\frac{\delta^2 \Psi}{\delta x^2} + \frac{\delta^2 \Psi}{\delta y^2} + \frac{\delta^2 \Psi}{\delta z^2} = -\frac{4\pi^2}{\lambda^2} \Psi$
- Hückel's rule:  $4n + 2\pi$  electrons, where  $n$  is any whole number.

- Schrödinger equation (for hydrogen atom):

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} \left( E - \frac{Ze^2}{r} \right) \Psi = 0$$

- Bond order:  $\frac{1}{2} [N_b - N_a]$ , where  $b$  and  $a$  are bonding and antibonding molecular orbitals.

## EXERCISES

## Multiple Choice Questions

- Bohr's model of atom is supported by
  - Dalton's theory
  - de Broglie equation
  - Uncertainty principle
  - None of these
- Bohr's model of atom is contradicted by
  - Planck's quantum theory
  - Pauli Exclusion principle
  - Heisenberg Uncertainty principle
  - All of the above
- Uncertainty principle was stated by
  - de Broglie
  - Heisenberg
  - Einstein
  - Schrödinger
- The region around the nucleus where the probability of finding an electron is maximum is
  - orbit
  - energy level
  - shell
  - orbital
- Which orbital has dumb-bell shape?
  - s orbital
  - p orbital
  - d orbital
  - f orbital
- The mass of an electron ( $m_e$ ) is
  - $9.109 \times 10^{-32}$  g
  - $8.1 \times 10^{-31}$  kg
  - $9.1 \times 10^{-31}$  kg
  - $9.1 \times 10^{-31}$  mg
- The atomic orbitals that possess same energy are.
  - degenerate orbitals
  - hybrid orbitals
  - valence orbitals
  - molecular orbitals
- The size of the nucleus is approximately
  - $1/100^{\text{th}}$  of the atom
  - $1/1000^{\text{th}}$  of the atom
  - $1/10000^{\text{th}}$  of the atom
  - $1/100000^{\text{th}}$  of the atom

9. Eigen values correspond to
  - (a) definite wave function values
  - (b) quantum numbers
  - (c) definite values of total energy
  - (d) definite angular momentum of electrons
10. Which of the following statements is NOT correct about wave functions?
  - (a) It is infinite in most cases.
  - (b) It is single valued.
  - (c) It is continuous.
  - (d) It has a continuous slope.
11. In Schrödinger wave equation  $\Psi$  represents
  - (a) orbit
  - (b) wave function
  - (c) wave
  - (d) radial probability
12. Uncertainty Principle is applicable to
  - (a) measuring radii of particles
  - (b) all moving particles
  - (c) only stationary particles
  - (d) all small and fast moving particles
13. In the ground state of an atom, the electron is present
  - (a) in the nucleus
  - (b) in the second shell
  - (c) nearest to the nucleus
  - (d) farthest from the nucleus
14. The radial nodes present in 3s and 2p orbitals are
  - (a) 0, 2
  - (b) 2, 0
  - (c) 2, 1
  - (d) 1, 2
15. Quantum number denoted by symbol ' $m$ ' is
  - (a) magnetic quantum
  - (b) principal quantum
  - (c) spin quantum
  - (d) azimuthal quantum
16. A spinning electron creates
  - (a) electric field
  - (b) quantum field
  - (c) magnetic field
  - (d) atom structure
17. The quantum number that describes the shape of an electron in an atom is:
  - (a) principal quantum
  - (b) azimuthal quantum
  - (c) magnetic quantum
  - (d) spin quantum
18. The value of Planck's constant ' $h$ ' is
  - (a)  $6.625 \times 10^{-34}$  J s
  - (b)  $6.625 \times 10^{-34}$  cal
  - (c)  $6.625 \times 10^{-34}$  kJ
  - (d)  $6.625 \times 10^{-34}$  kcal
19. Stabilization energy of benzene is
  - (a) 35 kcal
  - (b) 36 kcal
  - (c) 37 kcal
  - (d) 38 kcal
20. The region where there is probability of finding an electron is
  - (a) node
  - (b) particle-in-a-box model
  - (c) electron cloud
  - (d) orbit
21. The bond order of carbon monoxide molecule is
  - (a) 2
  - (b) 2.5
  - (c) 1.5
  - (d) 3
22. Antibonding molecular orbitals are formed by
  - (a) destructive overlap of atomic orbitals
  - (b) constructive overlap of atomic orbitals
  - (c) overlap of excess negative ions
  - (d) none of these
23. Band theory of solids can satisfactorily explain
  - (a) nature of insulators
  - (b) semiconducting behaviour
  - (c) conduction in metals
  - (d) All of these
24. A vacant or partially filled band is termed as
  - (a) valence band
  - (b) conduction band
  - (c) forbidden band
  - (d) molecular band
25. The highest energy band gap is exhibited by
  - (a) semiconductor
  - (b) conductor
  - (c) insulator
  - (d) metals
26. On increasing the temperature, conductivity of an intrinsic conductor
  - (a) increases
  - (b) decreases
  - (c) remains constant
  - (d) initially decreases and then increases
27. 'No two electrons in an atom can have the same set of quantum numbers.' This statement is called
  - (a) Bohr's theory
  - (b) Pauli Exclusion principle
  - (c) Hückel's rule
  - (d) Hund's rule
28. Wave nature of electrons was first experimentally verified by
  - (a) Davisson–Germer
  - (b) Planck
  - (c) de Broglie
  - (d) Pauli
29. The quantum number that determines the shape of the subshell is
  - (a) magnetic
  - (b) principal
  - (c) spin
  - (d) azimuthal
30. The number of orientations of each subshell is given by
  - (a) magnetic quantum number
  - (b) principal quantum number
  - (c) azimuthal quantum number
  - (d) spin quantum number

31. de Broglie equation has significance in explaining  
(a) subatomic particles (b) molecules  
(c) only electrons (d) electron pairing
32. The bond order of HCl molecule is  
(a) 3 (b) 2  
(c) 1 (d) 0.5
33. The bond order and magnetism of dinitrogen molecule are  
(a) 3 and paramagnetic, respectively  
(b) 3 and diamagnetic, respectively  
(c) 2 and paramagnetic, respectively  
(d) 2.5 and diamagnetic, respectively
34. An example of antiaromatic compound is  
(a) benzene (b) naphthalene  
(c) cyclobutadiene (d) none of these
35. Bond order of NO is  
(a) 2.5 (b) 2  
(c) 1.5 (d) 0.5

## Review Questions

1. What is wave-particle dualism?
2. State and derive de Broglie equation.
3. State and explain Heisenberg's Uncertainty principle.
4. What is Bohr's frequency rule? State the difference between an orbit and an orbital.
5. How does Pauli Exclusion principle help in understanding the electronic configuration of atoms?
6. Discuss Heisenberg Uncertainty principle and Born approximation.
7. Describe Davisson-Germer experiment demonstrating the wave nature of electrons.
8. Explain the significance of  $\Psi$  and  $\Psi^2$ .
9. What are atomic orbitals? Draw the s, p, d orbitals with clear descriptions.
10. Deduce Schrödinger time-independent wave equation. Explain the terms involved in the expression and state its significance.
11. Explain Schrödinger equation for quantum model of hydrogen atom.
12. Describe the physical significance of Schrödinger wave functions.
13. Justify the statement, 'It is impossible to measure simultaneously the position and velocity of a fast moving body like an electron.'
14. Apply Schrödinger wave equation for a particle-in-a-box illustrating quantization of energy. Draw the radial plots for hydrogen atom.
15. Express Schrödinger wave equation for 1,3-butadiene and benzene using particle-in-a-box model.
16. Discuss the application of particle-in-a-box solution to conjugated butadiene and benzene systems and write the wave equations.
17. Write a short note on 'applications of particle-box model to nanoparticles.'
18. What is a metallic bond? Describe free electron theory to describe metal bonding. List their merits and demerits.
19. Discuss band theory to explain bonding in metals citing suitable examples.
20. With a neat labelled MO diagram, explain the bonding in  $F_2$  molecule.
21. Explain the electrical conductivities of conductors, insulators, and semiconductors.
22. With a neat labelled MO diagram, explain the bonding in CO molecule. State the various features of CO molecule.
23. Draw a neat labelled MO diagram of dinitrogen and explain the bonding citing its electronic configuration.
24. What is bond order of a molecule? How is it calculated? Explain bonding in HCl molecule with an MO diagram and state its characteristics.
25. What is a Frost diagram? Draw Frost diagrams for benzene and cyclobutane and show their molecular orbital configurations.
26. Draw the molecular orbital diagram for oxygen molecule and explain its paramagnetic behaviour.
27. With a neat labelled MO diagram, explain the bonding in NO molecule.
28. What is aromaticity? Explain aromaticity of benzene.
29. Discuss aromaticity of compounds. Explain the criteria for a compound to be considered as aromatic.
30. Write a short note on Hückel's rule for aromaticity and Frost diagrams.

## NUMERICAL PROBLEMS

- Calculate the wavelength (in metres) of a proton travelling at a velocity of  $2.55 \times 10^8$  m, assuming the proton mass as  $1.673 \times 10^{-27}$  kg. (Ans:  $1.533 \times 10^{-15}$  m)
- Determine the wavelength (in metres) of a wave associated with a 1 kg object moving at a speed of 1 km/h. (Ans:  $2.38 \times 10^{-33}$  m)
- What will be the wavelength (in pm) associated with an electron having a mass of  $9.11 \times 10^{-31}$  kg and travelling at a speed of  $4.19 \times 10^6$  ms<sup>-1</sup>. (Ans: 174 pm)
- Calculate the kinetic energy and de Broglie wavelength (in nm) of C<sub>60</sub> molecule moving at a speed of 200 ms<sup>-1</sup>. (Given: atomic weight of carbon = 12.011 g, Avogadro's number =  $6.022 \times 10^{23}$  molecules/mol. (Ans: KE =  $2.393 \times 10^{-20}$  J,  $2.768 \times 10^{-12}$  m)
- What is the wavelength (in angstrom) of an electron moving at  $5.31 \times 10^6$  m/s? (Ans: 1.37 Å)
- Determine the uncertainty in position of a dust particle of mass 1 mg if uncertainty in its velocity is  $5.5 \times 10^{-20}$  m/s. (assume  $h = 6.623 \times 10^{-34}$  Js) (Ans:  $9.58 \times 10^{-10}$  m)
- Calculate de Broglie wavelength (in m) of dinitrogen molecule moving at a speed of 2800 ms<sup>-1</sup>. (assume  $h = 6.626 \times 10^{-34}$  Js) (Ans:  $5 \times 10^{-12}$  m)
- If uncertainties in position and velocity of a particle are  $10^{-10}$  m and  $5.27 \times 10^{-24}$  ms<sup>-1</sup> respectively, what is the mass of the particle? (assume  $h = 6.625 \times 10^{-34}$  Js) (Ans: 0.1 kg or 100 g)
- If an electron is bound in a one-dimensional box of size  $4 \times 10^{-10}$  m, what will be its minimum energy? (assume  $h = 6.6 \times 10^{-34}$  Js) (Ans:  $E = 3.739 \times 10^{-19}$  J)
- If an electron is bound in a one-dimensional box of size  $8 \times 10^{-10}$  m, what will be its minimum energy? (assume  $h = 6.6 \times 10^{-34}$  Js) (Ans:  $E = 9.349 \times 10^{-20}$  J)

## FURTHER READING

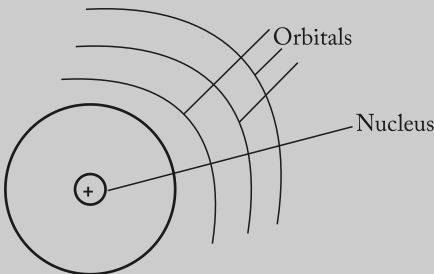
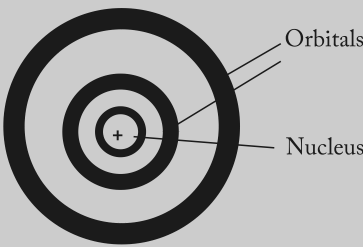
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## ANSWERS

### Check Your Progress

- According to Bohr's postulate, an electron travels a definite orbit around the nucleus, that is, the position and velocity of an electron in an atom is always known. The contradicting point by Heisenberg Uncertainty principle is that it is impossible to simultaneously determine both the position and velocity of an electron.
- Davisson-Germer practically demonstrated that particles (i.e., electrons) possess wave nature.
- According to de Broglie equation,  $\lambda = h/mv$ . We know that for a stationary orbit, its circumference must be an integer multiple of  $\lambda$ , such that  $2\pi r = n\lambda$  or  $\lambda = 2\pi r/n$ . Thus,  $h/mv = \frac{2\pi r}{n}$  or,  $mv = n h/2\pi$ . This is in accordance with Bohr's postulate, that is,  $J = n h/2\pi$  and hence the statement is justified.

4. The simultaneous exact determination of position and momentum or any property related to momentum such as velocity is impossible,  $\Delta x \times \Delta p \geq h/4\pi$

Orbit	Orbital
<p>(a) They are definite circular paths present at definite distances from the nucleus where electrons revolve.</p> 	<p>(b) They are regions around the nucleus that show the probability of finding electrons is maximum.</p> 
(b) Shape of orbit is circular.	(b) Shape of an orbital can be spherical (s orbital), dumb-bell (p orbital), or double dumb-bell (d orbital).
(c) It represents a 2-dimensional model with electrons moving in circular motion in one plane around the nucleus.	(c) It represents a 3-dimensional model with spherical movement of electrons around the nucleus.
(d) It can have $2n^2$ number of electrons, where $n$ is the number of the orbits.	(d) It can accommodate a maximum of two electrons with opposite spins.

6. 
$$\frac{\delta^2 \Psi}{\delta x^2} + \frac{\delta^2 \Psi}{\delta y^2} + \frac{\delta^2 \Psi}{\delta z^2} + \frac{8\pi^2 m}{h^2} (E - U) \Psi = 0$$
7. The functions are satisfactory solutions of Schrödinger time-independent wave equation only for certain values of energy  $E$ . Such values are called *eigen values*. The corresponding functions that are satisfactory solutions of Schrödinger equation are called *eigen functions*.
8. Eigen function is single value, finite, and continuous for all possible values of the three co-ordinates, that is,  $x$ ,  $y$  and  $z$ , including infinity  $\infty$ .
9. An electron is considered as a particle and the square of the wave function at any point in space represents the probability of finding an electron at that point at a given instant.
10. Refer to Section 1.5.1; Fig. 1.10
11. Refer to Section 1.5
12. The differences between conductors and semiconductors are as follows:

Conductor	Semiconductor
(a) No energy gap between valence and conduction band.	(a) Small energy gap between valence and conduction band.
(b) Valence band is either half-filled or partially-filled.	(b) Valence band is completely filled.
(c) Electrical conductivity decreases with increasing temperatures.	(c) Electrical conductivity increases with increasing temperatures.
(d) Impurities decrease electrical conductivity.	(d) Doping impurities enhance electrical conductivity.

13. Refer to Section 1.7
14. A compound possessing additional stability due to the presence of planar cyclic ring with uninterrupted  $(4n + 2) \pi$  electrons is called aromaticity. Benzene is an example of aromatic compound.
15. Refer to Section 1.9
16. For a planar, cyclic compound to be aromatic, its uninterrupted  $\pi$ -cloud must contain  $(4n + 2) \pi$  electrons, where  $n$  is any whole number.
17. Refer to Section 1.8.2

18. Frost diagrams are used to illustrate the distribution of electrons in aromatic systems. For illustration refer to Section 1.9
19. Refer to Figs 1.14 ( $\text{H}_2$ ), 1.15 ( $\text{N}_2$ ), 1.16 ( $\text{O}_2$ ), 1.19 ( $\text{CO}$ ), 1.20 ( $\text{NO}$ ), 1.21 ( $\text{HCl}$ ), 1.17 ( $\text{F}_2$ )
20. Refer to Section 1.7

### Multiple Choice Questions

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (c)  | 3. (b)  | 4. (d)  | 5. (b)  | 6. (c)  | 7. (a)  |
| 8. (d)  | 9. (d)  | 10. (c) | 11. (b) | 12. (d) | 13. (c) | 14. (b) |
| 15. (a) | 16. (c) | 17. (b) | 18. (a) | 19. (b) | 20. (c) | 21. (d) |
| 22. (a) | 23. (d) | 24. (b) | 25. (c) | 26. (a) | 27. (b) | 28. (a) |
| 29. (b) | 30. (a) | 31. (a) | 32. (c) | 33. (b) | 34. (c) | 35. (a) |

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