

ENGINEERING CHEMISTRY

(Strictly based on the latest syllabus prescribed by
Mahamaya Technical University, Noida)



Dr. B.S. Chauhan

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by Mahamaya Technical University, Noida)*

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Preface

The present edition of the book is as per the latest syllabus of Mahamaya Technical University, Noida. The whole prescribed syllabus is divided into thirteen chapters covering all the disciplines of engineering chemistry such as inorganic, organic, synthetic, physical, applied, industrial, spectroscopic and material chemistry. This book is written keeping in mind the requirement of engineering students, *i.e.*, every aspect of a topic is dealt keeping in view its application in engineering science. Key features of the book include a simple and holistic approach with large number of illustrations and tables.

Chapter 1 Advanced Theory of Chemical Bonding explains the concepts of atoms to molecules like chemical bonding, valence bond theory, molecular orbital theory and the concepts of molecules to materials like molecular solids and supramolecular chemistry. *Chapter 2 Stereochemistry of Organic Molecules* gives an exhaustive view of three dimensional representation of organic molecules and various classes of stereoisomerism like optical and geometrical isomerism. Dynamic stereochemistry concepts like conformations, stereoselectivity, stereospecificity are discussed in depth. *Chapter 3 Intermolecular Forces and Molecular Aggregation* gives an elaborative view on intermolecular forces, molecular aggregation, micelles, functional materials and the core concepts of nanotechnology. *Chapter 4 Separation, Purification and Characterization of Materials* deals with the methodology involved in separation, purification and characterization of materials giving a detailed account of physical and chemical methods of purification, chromatography, melting and boiling point determinations and particle size measurements. *Chapter 5 Instrumental Methods of Analysis* explains various spectroscopic methods that are useful in characterization of materials. *Chapter 6 General Organic Chemistry and Reaction Mechanism*, discusses electronic displacements in organic molecules and reaction mechanism like S_N1 , S_N2 , S_Ni and S_NAr and electrophilic substitution reactions in detail along with their stereo and regiochemistry. *Chapter 7 Chemical Kinetics and Catalysis* gives an exhaustive account of reaction dynamics and catalysis. *Chapter 8 Fats, Oils, Soaps and Detergents* gives an overview of materials for controlling friction like oils, fats, detergents, soaps and lubricants. *Chapter 9 Corrosion and Electrochemical Processes* explains various aspects of metallic corrosion and prevention along with the concepts of electrolysis, industrial electrolytic processes, fuel cells and batteries. *Chapter 10 Water and Water Treatment* describes the concepts of water hardness, alkalinity, removal of hardness, boiler feed water, desalination of brackish water and water potability. *Chapter 11 Polymer Chemistry* gives an elaborative account of polymers, mechanism of polymerization, commonly used polymers, natural and synthetic rubbers, conducting and biodegradable polymers. *Chapter 12 Miscellaneous Materials (Polymer Blends, Dendrimers, Adhesives, Composites and Lubricants)* gives an overview account of polymer blends, dendrimers, silicones, composites and adhesives. *Chapter 13 Experimental Chemistry* explains safety and working in chemistry lab, preparation of solutions experiments prescribed in latest syllabus of MTU, Noida. Exhaustive discussion is given in each experiment along with important viva-voce questions. The complete information regarding laboratory accidents and first aid is provided in the same chapter.

At the end useful appendices and last two semester examination papers are given. I hope the present book will prove a useful tool for teachers and students of undergraduate engineering classes. Critical suggestions from the users on the material presented are welcome for the improvement of the book.

–Author

Syllabus

AS103/203 : ENGINEERING CHEMISTRY

UNIT-I: INTRODUCTION OF ENGINEERING CHEMISTRY

Atoms to Molecules to Materials for Engineers

Atoms combine to give molecules and how molecules aggregate to give materials.

Recapitulation of salient features of *valence bond theory*, *Hybridization*, sigma and pi bonds, Shape of the simple inorganic compound based upon concepts of hybridization and to illustrate planar, tetrahedral square planar, and octahedral geometries.

Molecular orbital theory and its application to form homo (H_2 , N_2 and O_2) and hetero (HF, NO) diatomic molecules.

Structure and Stereo-Structure of Molecules

Representing three dimensional structure of organic molecules including Conformations, Newman, Sawhorse, Fischer, projections wedge and dash structural representation, equivalence of structural representations.

Chirality, optical activity and isomerism, compounds containing one and two chiral carbons, enantiomers, *di* stereo isomers, *meso* compounds, number of chiral atoms and optical isomers, Dynamic stereochemistry, concepts of regiochemistry, stereo selectivity, Stereo specificity and enantiomeric excess R and S nomenclature.

Geometrical isomerism in simple acyclic and cyclic molecules, E and Z nomenclature.

UNIT-II: MATERIALS AND THEIR PROPERTIES

Micro and macroscopic properties of molecules, Intermolecular force, Molecular aggregation micelles.

Examples of inorganic and organic functional materials, core concepts of nanotechnology.

Purification

Physical (crystallization, fractional crystallization, distillation, fraction distillation, steam distillation) and chemical methods of purification. General chromatography (Adsorption and partition) techniques (column thin layer and paper chromatography) and their application.

Criteria of Purity

Melting and Boiling point, chromatography, particles size measurement and surface area.

Characterization

Surface tension, Viscosity, Conductivity, and Absorption Spectroscopy (IR, UV-Visible, NMR).

UNIT-III: STABILITY AND REACTIVITY OF MOLECULES : UNIT PROCESSES IN ORGANIC CHEMISTRY

Reactivity of Molecules

Electron displacement effects : inductive, electromeric, resonance and hyper-conjugation, Reactive sites in molecules-functional groups.

Reaction Mechanism

Fission of a covalent bond, types of reaction - nucleophilic (S_N1 and S_N2 , S_Ni , S_NAr) and electrophilic substitution reactions (Nitration, Sulphonation, Halogenation and Friedel Crafts reaction) and their mechanism, regio and Stereochemistry of involved reactions.

Reactions Dynamics

Chemical kinetics, Order and molecularity, zero, first and second order reactions, pseudo first order reaction, temperature dependence of reaction rates, Catalysis and some industrially important catalytic reactions.

UNIT-IV: WATER AND ITS TREATMENT

Alkalinity of water, estimation of alkalinity, Hard and soft water, hardness—units, determination of hardness by complexometric titration, Removal of hardness of water—Zeolite, ion exchange process, Boiler feed water, descaling of boilers, desalination of brackish water, Reverse osmosis, Potable water.

UNIT-V: SOME MATERIALS OF INDUSTRIAL IMPORTANCE

Polymers and Polymerization (ionic, anionic and free radical induced), Properties of polymers, Number average and Weight average, molecular weights, characterization of polymer samples, polymers blends, Stereo-structure of polymers, Dendrimers, some examples of common polymers used in Industry, Natural and Synthetic rubber, Silicones, Composites, Adhesives, Conducting polymers, Biodegradable polymers.

Metallic corrosion and its prevention, electrolysis, Industrial electrolytic processes (aluminium). Fuel cells and batteries.

Control of friction: Oils, fats and lubricants, soaps and detergents.

AS 103 P/AS 203 P: ENGINEERING CHEMISTRY (PRACTICALS)

The following representative experiments have been suggested for chemistry laboratory:

1. Introduction to safety and working in a chemical laboratory.
2. Determination of hardness of water by titration with standard EDTA solution.
3. Determination of iodide content in iodized salt through audiometric titration with sodium thiosulphate.
4. Determination of Alkalinity in water sample.
5. Determination of rate constant for acid catalyzed hydrolysis of ethyl acetate through titration.
6. Determination of glycerine content in a sample of amino acid.
7. Synthesis of benzimidazole and record of its UV spectrum.
8. Comparison of viscosity and surface tension of two liquids and their variation on addition of surfactants and soap of known concentration.
9. Determination of neutralization of a lubricant oil or iodine number of an unsaturated oil.
10. Detection of functional groups in an organic compound by wet tests.
11. Identification of an organic compound.
12. Synthesis of *p*-nitroacetanilide from acetanilide.

Chapter 1 *ADVANCED THEORY OF CHEMICAL BONDING*

1.1 FROM ATOMS TO MOLECULES

A molecule may be defined as a small electrically neutral cluster or aggregate of mutually bonded atoms. The molecule formed must be more stable than the individual atoms otherwise molecule should not be formed, *i.e.*, the process must be energetically favourable and leads to a minimum energy. A very logical question arises is 'why and how do atoms combine together to form different molecules? These cluster of atoms are met in gases, *e.g.*, hydrogen, oxygen, nitrogen, fluorine etc. have diatomic molecules. But the liquids and particularly solids cannot be generally described in terms of simple molecules having a few atoms. In diamond, for example, the carbon atoms are bonded to form bigger aggregates to give a single giant molecule. In crystalline solids, for example, sodium chloride, the situation is entirely different. In this case, the constituent units are Na^+ and Cl^- ions and not atoms. These ions are strongly held together throughout the crystal and none of them is present as separate entity. From the above discussion, it can be concluded that different types of combinations involve different number of atoms of the same or different elements and thus result in the formation of different molecules.

When two atoms tends to remain together rather than separate from each other, they are said to form a chemical bond with each other. A chemical bond may be defined as *an attractive force which holds together the constituent atoms in a molecule.*

Now we consider, what is happening in terms of electronic structure during bond formation. From the electronic theory of valency, we know that the inability of noble gases in forming compounds is because of the fact that various shells particularly the outermost (which is responsible for compound formation) has its complete octet and hence the electronic configuration ns^2p^6 for the noble gases is considered as the most stable electronic configuration. This octet is called the *stable octet*. From energy consideration, the bonds or molecules are formed only if each atom acquires a stable electronic configuration in the process.

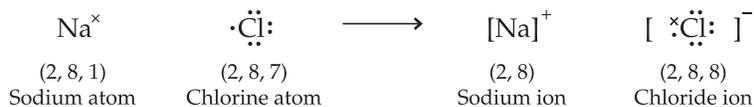
There are mainly three ways by which the atoms may obtain a stable electronic configuration, namely by gaining, losing or sharing of electrons. We divide all the known elements on electronegativity scale into (a) electropositive elements (whose atoms give up one or more electrons readily), (b) electronegative elements (whose atoms take up electrons), and (c) elements whose atoms neither gain nor lose electrons, the following three types of bonds are possible by the different types of combinations of the three types of elements.

- (i) $\begin{array}{c} \text{Electropositive element} \\ + \\ \text{Electronegative element} \end{array} \longrightarrow \text{Ionic bond}$
- (ii) $\begin{array}{c} \text{Electropositive element} \\ + \\ \text{Electronegative element} \end{array} \longrightarrow \text{Covalent bond}$
- (iii) $\begin{array}{c} \text{Electropositive element} \\ + \\ \text{Electropositive element} \end{array} \longrightarrow \text{Metallic bond}$

1.1.1 Ionic or Electrovalent Bonds

An ionic bond is formed by the complete transference of one or more electrons from the outermost energy shell of one atom to outermost energy shell of another dissimilar atom, so that both acquire stable inert gas configurations. The atom which loses the electrons, acquires a positive charge and becomes a positive ion (cation), while the atom which gains the electron, acquires a negative charge and becomes a negative ion (anion). These two oppositely charged ions combine, due to electrostatic forces of attraction, to form an electrovalent or ionic compound. An electrostatic attraction always tends to decrease the potential energy. For example,

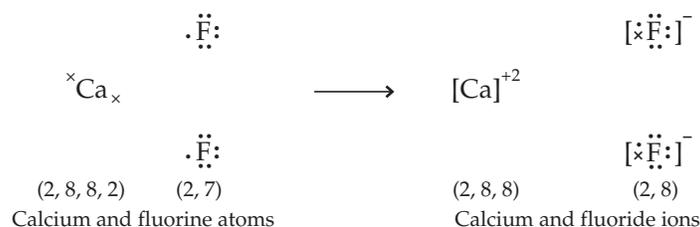
1. Formation of sodium chloride. When sodium and chlorine atoms are brought together, the outer electron of the sodium atom is transferred to the chlorine atom and the two ionic species, *viz.* Na^+ and Cl^- having inert gas configuration are held together by the electrostatic attraction of their opposite charges.



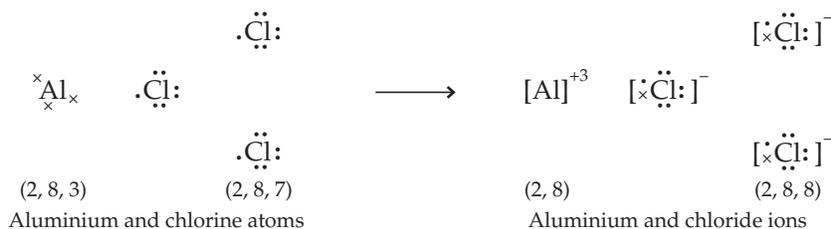
Note that on the symbols only the outermost electrons are shown, the complete configuration of the two atoms is represented below the symbols.

Lastly it must be noted that since the two atoms attain a very stable inert gas configuration by losing or gaining the electron, the process is energetically favourable, and sodium chloride $[\text{Na}^+\text{Cl}^-]$ is formed readily.

2. Formation of calcium fluoride. CaF_2 is formed by losing two electrons of calcium atom to two fluoride atoms forming a calcium ion, Ca^{+2} and two fluoride ions, F^- , which are held together by the electrostatic attraction of their opposite charges.



3. Formation of aluminium trichloride. The formation of aluminium trichloride may be represented below.



Properties of ionic compounds. The ionic compounds are found to possess the following characteristic properties:

(i) **Crystal structure.** Ionic compounds are made up of positive and negative ions (and not molecules) arranged in a regular way in lattice. These ions are held together by strong electrostatic forces of attraction.

(ii) **Electrical conductivity.** Whenever an ionic compound is put into a solvent of high dielectric constant such as water, it decomposes into ions which migrate towards the respective electrode and thus conduct electricity. Similarly, these compounds also conduct electricity in the fused state. On fusion, their electrostatic lines break and ions become free.

The failure of ionic compounds in solid form to migrate and thus conduct electricity is because of the fact that in ionic crystals the ions are trapped in fixed places in the crystal lattice.

(iii) **Melting and boiling points.** Since the attraction between ions is electrostatic, non-directional and extends equally in all directions; to melt an ionic compound it is necessary to break the lattice which requires considerable energy and hence these compounds are very hard and their melting and boiling points are considerably high.

(iv) **Non-directional character.** Each ion of an ionic compound is surrounded by uniformly distributed electric field. This electric field is non-directional and thus imparts this characteristic property also to the ionic bond.

(v) **Solubility.** Ionic compounds are generally soluble in polar solvents. The solubility is two-fold : firstly the molecules of the polar solvent interact strongly with ions of the crystal and the *solvation energy* thus produced is sufficient to overcome the attraction between the ions in the crystal lattice, and the secondly the high dielectric constant of some of the solvent such as water weakens the interionic attractions resulting in solution.

Non-polar solvents (organic solvents) such as benzene and carbon tetrachloride do not dissolve the ionic compounds since they neither possess high dielectric constant nor solvate the ions.

(vi) **Ionic reactions.** Ionic compounds exhibit ionic reactions, as these compounds form free ions in solution. Ionic reactions are usually rapid since the reacting species are to collide only.

(vii) **Isomorphism.** Ionic compounds having similar electronic configuration exhibit the phenomenon of isomorphism : examples are sodium fluoride and magnesium oxide, and potassium sulphide and calcium chloride.

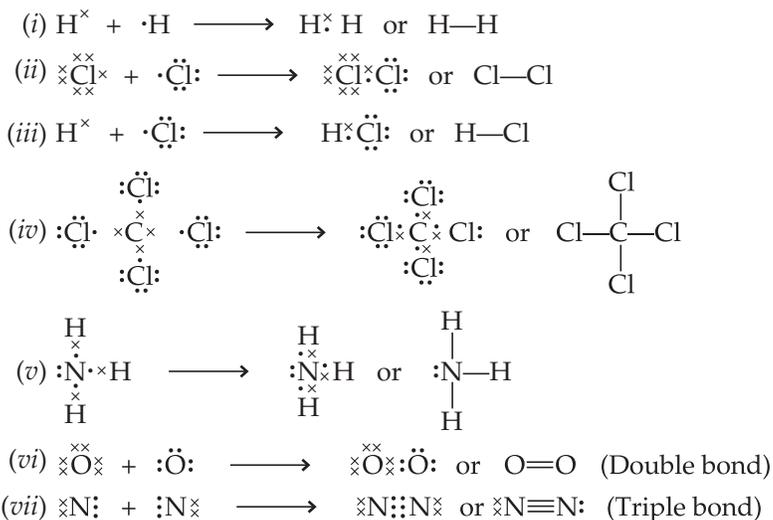
(a) Sodium fluoride	and	Magnesium oxide
Na ⁺ F ⁻		Mg ⁺² O ⁻²
2, 8 2, 8		2, 8 2, 8
(b) Potassium sulphide	and	Calcium chloride
K ⁺ S ⁻²	K ⁺	Cl ⁻ Ca ⁺⁺ Cl ⁻
2, 8, 8 2, 8, 8	2, 8, 8	2, 8, 8 2, 8, 8 2, 8, 8

1.1.2 Covalent Bond

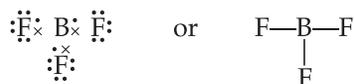
A covalent bond is formed by sharing of electrons in pairs between two atoms, both of which make equal contribution of electrons. These mutually shared electrons become the common property of both the atoms, each pair of shared electron is indicated by a line (-).

When each atom contributes one, two or three electrons such that two, four or six electrons are shared in all, the union so set-up, is called single, double or triple covalent bond respectively.

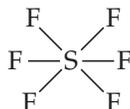
Common examples and representation of covalent compounds:



Although in all the above examples we observed that during covalent bond formation a stable octet is attained by both the atoms, it is important to note that in covalent bond formation attainment of noble gas or octet configuration by the two atoms is not an essential feature. For example, in boron trifluoride molecule although each fluorine atom has completed its octet, the boron atom has only six electrons in its outermost shell



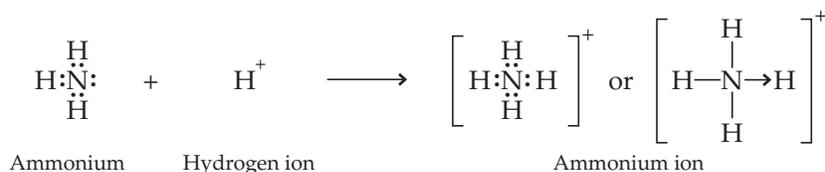
Similarly, in sulphur hexafluoride molecule, SF_6 , sulphur atom has twelve electrons in its outermost shell.



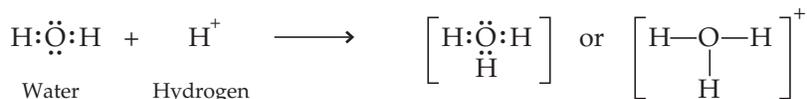
Thus the only necessary feature of a covalent bond formation between two atoms is that it must involve the pairing of two electrons with opposite spins.

Co-ordinate or Dative Bond. It is a special type of covalent bond in which the shared electrons are contributed by one atom only, while the other atom accepts the sharing electrons without any contribution of electrons. For example,

(i) Formation of ammonium ion (NH_4^+) in following manner,



(ii) Formation of hydronium ion (H_3O^+)



Properties of Covalent and Co-ordinate Compounds

1. Covalent compounds are often gases, liquids or soft solids with low melting points except compounds like SiO_2 and diamond which are very hard and have high melting points.

Since a co-ordinate linkage is considered to be formed by the combination of electrovalent and covalent linkages, compounds having co-ordinate linkage melt at higher temperatures than the covalent compounds.

2. **Electrical conductivity.** Since the covalent compounds have no electric charge, they carry no current in either the solid, liquid or gaseous state and hence they are generally used as insulators.

Since the co-ordinate linkages are partially covalent in nature, the compounds having them do not ionise and are poor conductors of electricity.

3. **Solubility.** The covalent and co-ordinate compounds are generally insoluble in polar solvents but are soluble in non-polar (organic) solvents, *i.e.*, solvents of low dielectric constant such as benzene and carbon tetrachloride. The solubility can be ascribed to similar covalent nature of the solute and solvent molecules (*i.e.*, like dissolves like).

4. **Molecular reactions.** Covalent and co-ordinate compounds usually react slowly since the reaction generally involves breaking and formation of bonds. Thus collision between the reactant molecules will cause reaction only if they have sufficient energy.

However, in case of some co-ordinate compounds such as $\text{BF}_3 \cdot \text{NH}_3$ in which the donor and acceptor are capable of independent existence, the co-ordinate linkage is readily cleaved.

5. **Directional nature.** Since the covalent bonds are formed by the overlapping of atomic orbitals which, except *s* orbital, are directional, the molecular orbitals of the bonded atoms must also be concentrated along certain directions which imports directional nature to covalent bonds.
6. **Isomerism.** Due to directional nature of covalent bonds, they show structural and space isomerism.

1.2 VALENCE BOND THEORY OF BONDING

This theory was proposed by *W. Heitler* and *F. London* in 1927 and later developed by *Pauling* and *Slater* in 1933. It is based on the Linear Combination of Atomic Orbitals (LCAO). Its salient features are:

1. A covalent bond is formed by the overlap of half filled atomic orbitals of the different atoms.
2. The overlapping atomic orbitals must have electrons with opposite spins.
3. The bonded electron pair is localized between the two linked atoms.
4. The stability of the covalent bond is due to the exchange of the valence electrons between the participating atoms, which lowers the potential energy of the bonded atoms.
5. Each atom of the covalent compound tends to acquire a noble gas configuration by sharing of electrons.

The valence bond treatment of bonding begins with the independent atoms and then considers the interaction between them. When the atoms are brought nearer to each other there is a change in energy due to the rearrangement of the electron cloud of one atom under the influence of the other atom. This theory is based on the following two principles of quantum mechanics:

1. If ψ_A and ψ_B are the wave functions for two independent atoms A and B, then the total wave function for the system of two atoms will be the product of these two wave functions, *i.e.*,

$$\Psi = \psi_A \psi_B \quad \dots(1.1)$$

The energy of the system is given by:

$$E = E_A + E_B$$

2. If there are several wave functions $\psi_1, \psi_2, \psi_3, \dots, \psi_n$ for the same system, then the wave function ψ for the system is obtained by combining the several wave functions linearly, *i.e.*,

$$\Psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \dots + C_n\psi_n \quad \dots(1.2)$$

where C_1, C_2, C_3, \dots are the various coefficients indicating the contribution of each wave function. These coefficients are so adjusted as to give a state of lowest energy, *i.e.*, maximum stability.

1.2.1 Formation of H₂ Molecule

Let there be two hydrogen atoms A and B associated with electrons 1 and 2, respectively. Such hydrogen atoms may be represented as H_A(e₁) and H_B(e₂), respectively. If their starting wave functions are $\psi_A(1)$ and $\psi_B(2)$, then the wave function of the separated atom can be given as:

$$\psi = \psi_A(1) \psi_B(2) \quad \dots(1.3)$$

Equation (1.3) can be used to calculate the energy of an H₂ molecule. The energy changes that take place are shown in Figure 1.1.

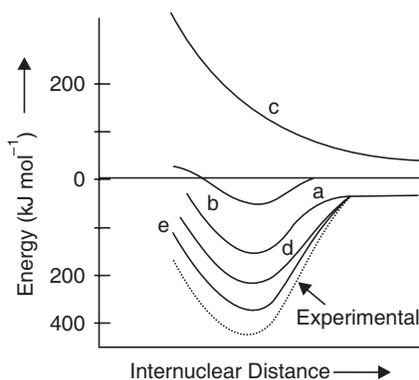
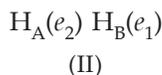
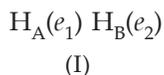


FIGURE 1.1 Change of energy with internuclear distance in the formation of H₂ molecule.

It is clear that when the two atoms of hydrogen are at an infinite distance, the total energy of the system is zero. It increases as the internuclear distance decreases, as shown in the figure. It is known that in the formation of H₂ molecule, internuclear distance (r_0) is 0.74 Å while decrease in energy is 458 kJ/mol. Curve *a* gives the value of (r_0) as 0.90 Å and decreases in energy 24 kJ/mol, which is quite different from the experimental values. Hence equation (1.3) doesn't show the wave function of an H₂ molecule. Certain improvements have been introduced to make the energy value comparable to the experimental value. These improvements are:

- 1. Exchange of electrons.** When two hydrogen atoms come close to each other then their electrons get exchanged and a bond is formed between the two hydrogen atoms and the two shared electrons become indistinguishable from each other. This state of two H atoms may be represented as:

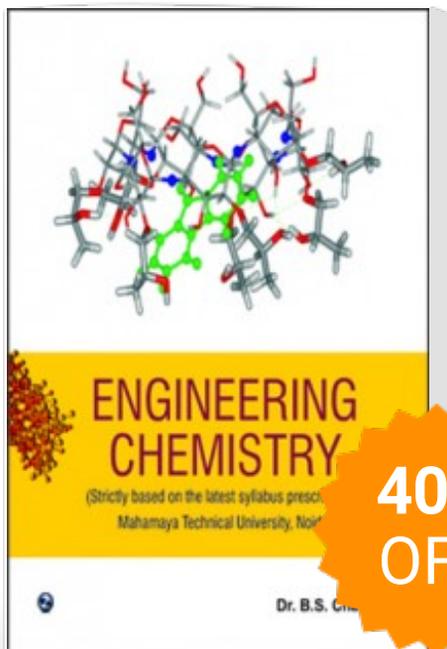


If the wave functions of the two states (I) and (II) are represented by ψ_I and ψ_{II} respectively, the wave functions may be written as:

$$\psi_I = \psi_A(1) \psi_B(2)$$

$$\psi_{II} = \psi_A(2) \psi_B(1)$$

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