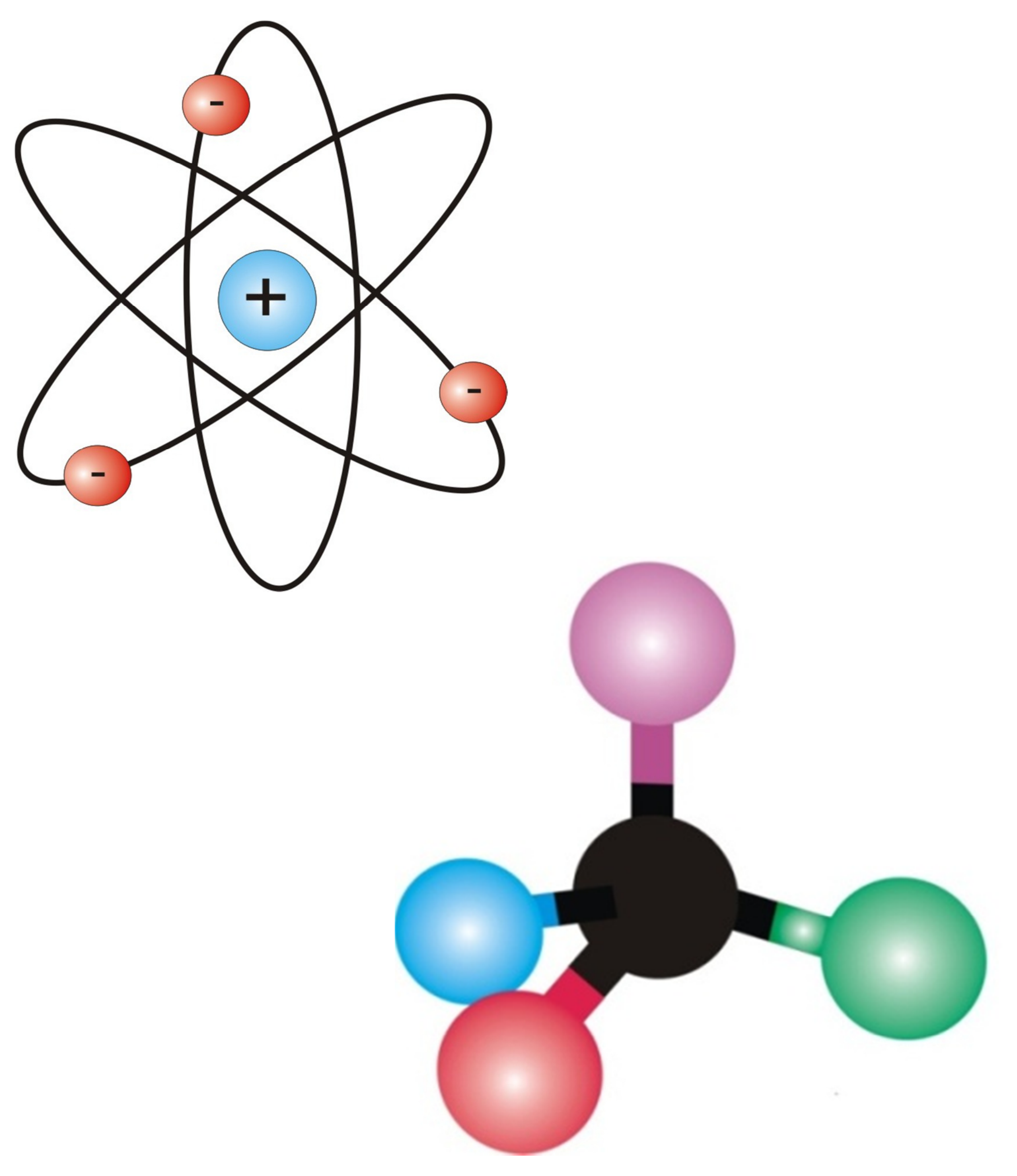
Indira Gandhi National
Open University
School of Sciences

BCHCT-131

ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS



CHEMICAL BONDING AND MOLECULAR STRUCTURE

2

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Block

2

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Course Design Committee

Prof. H. B. Singh (Retd.)
Dept. of Chemistry,
University of Delhi,
Delhi

Prof. A. K. Bakhshi
Dept. of Chemistry,
University of Delhi,
Delhi

Prof. Amir Azam
Dept. of Chemistry,
Jamia Millia Islamia,
New Delhi

Prof. Tabrez Alam
Dept. of Chemistry,
Jamia Millia Islamia,
New Delhi

Prof. J. M. Khurana
Dept. of Chemistry,
University of Delhi,
Delhi

School of Sciences,
IGNOU

Prof. Vijayshri
Prof. Sunita Malhotra
Prof. Javed A. Farooqi
Dr. Lalita S. Kumar

Block Preparation Team

Prof. Sunita Malhotra (Unit 9)
School of Sciences, IGNOU

Prof. Bharat Inder Fozdar (Unit 6)
School of Sciences, IGNOU

Prof. Lalita S. Kumar (Unit 7)
School of Sciences, IGNOU

Prof. Kamalika Banerjee (Unit 8)
School of Sciences, IGNOU

Prof. B. S. Saraswat (Retd.) (Editor)
School of Sciences, IGNOU

Course Coordinators: Prof. Sunita Malhotra and Prof. Javed A. Farooqi

Production

Mr. Sunil Kumar
Assistant Registrar (Pub.)

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BLOCK 2: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Units 1 to 5 of Block 1 were devoted to the old theories of atomic structure, the basic principle of quantum mechanics and their applications to atomic structure. The knowledge of atomic structure will now be used to understand the process of combining of atoms to form molecules. The focus of Block 2 is on the fundamental concepts of chemical bonding and molecular structure. The first unit of this block, Unit 6, begins with some of the basic ideas about bonding in molecules. The rest of the unit is devoted to ionic bonding and characteristics of ionic compounds. In Unit 7, we discuss the Lewis theory in explaining the covalent linkages. In this unit, we have also given detailed description of the VSEPR theory and its use in explaining the shapes of molecules. In Unit 8, we discuss the valence bond theory in detail to explain the covalent linkages in molecules. The main features of resonance and hybridisation in the light of molecular parameters such as bond length and bond angle have also been discussed. Unit 9 covers the molecular orbital theory as another profile of covalent linkages. The course contents given in Blocks 1 and 2 would be particularly helpful in understanding the structure and reactivity patterns of chemical compounds.

Expected Learning Outcomes

After reading this block; you should be able to:

- describe the salient features of ionic and covalent linkages;
- explain the shapes of molecules and ions on the basis of VSEPR theory;
- explain the principle of valence bond theory and use it to derive the structure of molecules;
- describe the main aspects of hybridisation and resonance; and
- explain bonding in simple molecules using molecular orbital theory.


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UNIT 6

IONIC BOND

Structure

6.1 INTRODUCTION

In earlier Units 1-5, concepts regarding atomic structure have been discussed in detail. These ideas naturally lead you to think as to why; the atoms of elements combine among themselves or with those of others, to form stable structures, called molecules. Hydrogen gas, for example, consists of H_2 molecules, each of which is made up of two atoms of hydrogen. In contrast to this, the He_2 molecule is not formed by the combination of two atoms of helium. You may like to know the nature of attractive forces, known as chemical bonds, which are responsible for the stability of some structures. Such an analysis can also help you in correlating the physical and chemical characteristics of molecules to the type of bonding present in them.

Many attempts were made in the past to explain the formation of stable molecules. On the basis of electrolysis experiments, Berzelius (1812) concluded that some elements have a positive electric charge and some a negative charge and that the attraction between these opposite charges holds the elements together. This dualistic theory was proposed before the discovery of electrons and protons. But Cannizzaro (1860) showed that the elements like oxygen, hydrogen etc., are diatomic. This fact could not be explained by the dualistic theory of Berzelius. In 1852, Frankland proposed the theory that elements have a definite capacity for combining to which the name valency was given later. It was for Kossel and Lewis (1916) to put forward theories of ionic (electrovalent) and covalent compounds, respectively.

In this unit and the next unit, we shall study the theories of Kossel and Lewis. In this unit we shall also learn the properties of ionic compounds, the importance of the ratio of ionic radii of combining ions in deciding the crystal geometry and the significance of lattice energy, solubility and solvation energy of ionic compounds. We shall explain some of the characteristics associated with the ionic compounds, such as polarising power and polarisability along with Fajan's rules. Finally we shall discuss the relationship between the bond polarity and dipole moment. In the next unit we will take up another important type of bonding i.e. covalent bond.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define the terms such as effective nuclear charge, ionisation energy, electron affinity, electronegativity and utilise them in predicting bond character;
- define ionic bond and list the properties of ionic compounds;
- explain the role of ionic radii in deciding crystal geometry;
- calculate lattice energy and explain its importance in deciding stoichiometry, stability and solubility of a crystal;
- define solubility and solvation energy;
- explain the polarising power and polarisability;
- state Fajan's rules; and
- correlate bond polarity and dipole moments.

6.2 CHEMICAL BONDING: BASIC CONCEPTS

Atoms can combine with each other in different ways to form a large variety of molecules. Really speaking the description of chemical bonds between atoms in a molecule is essentially the description of electron distribution around nuclei of the atoms in a molecule. There are three main types of bonding in molecules. One of them is ionic bonding and it arises when one or more valence electrons are transferred from one atom to another, resulting in the formation of positively and negatively charged ions.

The second type of arrangement that holds atoms together in a molecule is known as covalent bond. In this case, the bond results from the mutual sharing of electrons between atoms of the same or different elements. The formation of H_2 molecule is a case of covalent bond formation. Third type of bonding is coordinate bond and it arises when both the shared electrons are provided by one atom only, known as the donor. A coordinate bond differs from the covalent bond only in the mode of formation. Once a coordinate bond is formed, there is no way to distinguish it from the covalent bond. The salient features of the three types of bonds described above are listed in Table 6.1.

Table 6.1: Bonding in Molecules

Bonding type	**Type of electronic interaction**	**Examples**
Ionic bond	Transfer of electron(s) from one atom to another	Na^+Cl^-, K^+Cl^- Cs^+Cl^-
Covalent bond	Equal contribution and sharing of electrons between atoms	H_2, F_2, CH_4
Coordinate bond	Contribution of electrons by one atom and sharing by both the bonding atoms	$(CH_3)_3NO, NH_4^+$

One would like to know the factors on which the tendency of an atom to transfer or share one or more of its electrons depends. There are various factors such as effective nuclear charge, ionisation energy, electron affinity and electronegativity which determine the above tendency. We shall explain the salient features of these factors before going into the details of chemical bonding.

6.2.1 Effective Nuclear Charge

The hold the nucleus has over an electron in a particular level is decreased by other electrons in the same and lower levels. In an atom with atomic number *Z*, the effect of nuclear charge is not felt uniformly by the electrons in the various orbitals. The extent to which other electrons decrease the nuclear charge over a particular electron is given by screening constant, *S*. Hence the effective nuclear charge, *Z**, is given by the equation,

The outermost shell in an atom is called the valence shell. The electrons in this shell are called valence electrons.

$$Z^* = Z - S \qquad ...(6.1)$$

It is possible to calculate *Z** from the values of *Z* and *S*. It is observed that there is a steady increase in *Z** across the elements in a period. The values of effective nuclear charge felt by electrons in the valence shell of some elements are given in Table 6.2.

Table 6.2: Effective Nuclear Charge Felt by Valence Shell Electrons

H							He
1							1.7
Li	Be	B	C	N	O	F	Ne
1.3	1.95	2.6	3.25	3.9	4.55	5.2	5.85
Na	Mg	Al	Si	P	S	Cl	Ar
2.2	2.85	3.5	4.15	4.8	5.45	6.1	6.75

Screening constant value for a particular electron indicates how much, the other electrons in the same and lower levels decrease the nuclear charge due to *Z* protons in the atom.

The high value for the effective nuclear charge felt by an electron signifies that the nucleus exhibits more attraction towards such an electron and hence more energy is needed in removing that electron from the atom. From effective nuclear charge values given in Table 6.2, you can infer that the loss of valence shell electron is more difficult for Ar than for Na. That is, formation of Na^+ is easier than the formation of Ar^+. **Anyhow values of Z^* alone are not sufficient to make generalisation regarding cation or positively charged ion formation.** You shall study about other factors concerning cation formation, in Subsec. 6.2.2. Before that, try the following SAQ.

SAQ 1

Justify the fact that Li^+ ion formation is easier than that of Ne^+ ion.

6.2.2 Ionisation Energy

Ionisation energy, in electron volt (eV), is known as ionisation potential.

1 eV = 96.5 kJ mol^{-1}

Ionisation energy is defined as the minimum energy required removing the least tightly bound electron from a gas phase atom. The unit for ionisation energy is kJ mol^{-1} and we use the symbol '*I*' for representing ionisation energy of an element.

For an element X, the formation of singly charged cation can be represented by the following equation

$$X(g) \rightarrow X^+(g) + e^-$$

In a chemical reaction, 'g' stands for gaseous state, 'l 'for liquid state and 's' for solid state.

The energy required for the above process, *I*(X), is called first ionisation energy of X.

In the case of multielectron atoms, more than one electron can be removed; that is, second, third and higher ionisation energies are also possible.

It is also observed that the second ionisation energy is larger than the first ionisation energy, since during the second ionisation, the electron is to be removed from a positively charged ion against forces of attraction. Normally ionisation energy means first ionisation energy only. In Table 6.3, the ionisation energy values of some elements are given. The values with * mark indicate second ionisation energies.

Energy required to form a dipositive ion in the gaseous state is the sum of first and second ionisation energies.

Table 6.3: Ionisation Energy Values in kJ mol^{-1}

H							He
1312							2372
Li	Be	B	C	N	O	F	Ne
520	900	800	1086	1403	1314	1681	2081
	1757*						
Na	Mg	Al	Si	P	S	Cl	Ar
495	738	577	787	1060	1000	1255	1520
	1450*						
K						Br	Kr
418						1142	1350
Rb						I	Xe
403						1007	1170
Cs							Rn
374							1037

In Table 6.2, we studied that effective nuclear charge increases along the elements of a period. We would expect ionisation energy also to increase accordingly. But a scrutiny of first ionisation energies of second period elements shows that the values increase from lithium to beryllium, decrease for boron, and increase up to nitrogen, again decrease in oxygen and finally increase up to neon, Fig. 6.1. At the outset this seems difficult to understand. But you can correlate the dependence of ionisation energy on electron configuration as discussed below:

We consider the predominant influence of one of more of the following factors while trying to explain the variation of ionisation energy across the elements in a period:

i) The increase in the effective nuclear charge across the elements in a period.

ii) The high energy level of the electrons in *np* as compared to those in *ns* orbitals.

iii) The stability associated with the half-filled and fully filled orbitals.

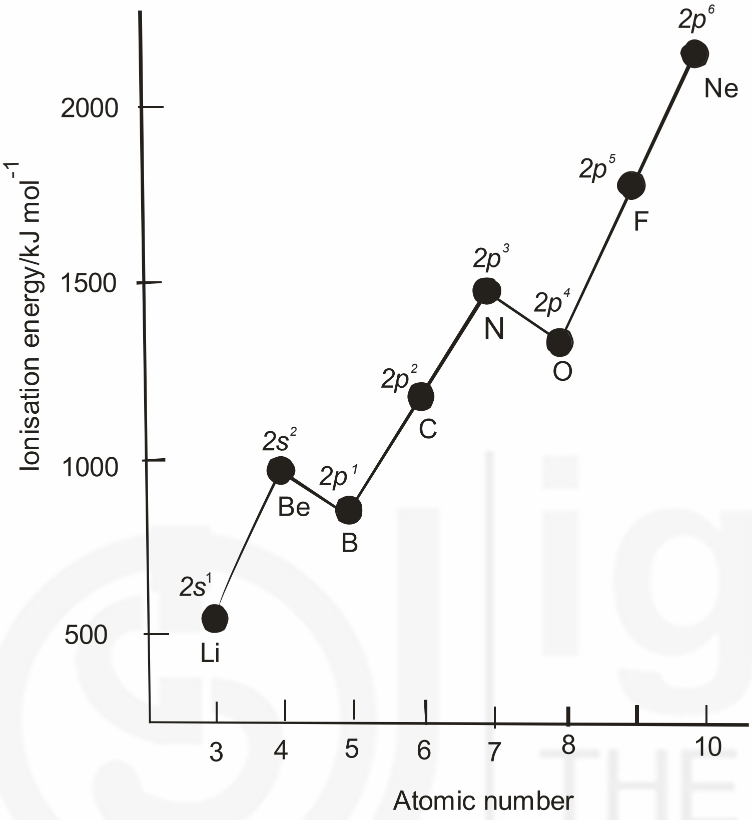
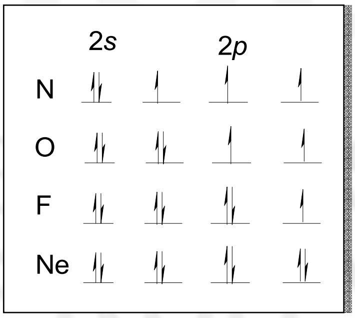


Fig. 6.1: Ionisation energy of second period elements; only the orbital involved in ionisation indicated.



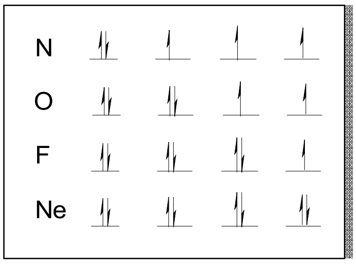
i) The electrons in *np* orbitals are in higher energy level than those in *ns* level. Hence it is easier to remove *np* electron than *ns* electron. Thus boron needs lower ionisation energy than beryllium.

ii) The half-filled and fully filled orbitals are more stable than partially filled orbitals. Thus nitrogen, with exactly half-filled *p* orbitals, is more stable than carbon and oxygen, with partially filled orbitals.

Low ionisation of an element indicates that positive ion i.e. cation can form of easy.

Hence, ionisation energy of nitrogen is larger than that of carbon and oxygen. For the same reason, neon with fully filled orbitals has larger ionisation energy than fluorine with partially filled orbitals.

Within a group, the ionisation energy decreases as atomic number increases. It is so since, increasing the energy level and increasing the average distance from the nucleus cause reduction of attraction between nucleus and the electron. With this background, you can understand the decrease in ionisation energies of group 1 elements, from hydrogen to caesium, as shown in Table 6.3.



Ionisation energy values of elements are useful in deciding their electron configuration

The high ionisation energies of noble gases indicate the greatest stability of ns^2np^6 configuration (except in the case of helium having $1s^2$ configuration) known, in general, as **noble gas configuration**. You will soon see that **attainment of noble gas configuration** is one of the guiding factors in bond formation. When elements of group 1 (except hydrogen) lose their single ns^1 electron, their configuration becomes that of the preceding noble gas. Hence ionisation energy is low for alkali metals and they form cations easily.

Ionisation energies can be measured experimentally. In Unit 1, you have studied how ionisation energy of hydrogen can be determined from the atomic spectra of hydrogen.

6.2.3 Electron Affinity

In the preceding subsection, we studied about ionisation energies which tell us about cation forming tendency of elements. Now we turn our attention to electron affinity values of elements which inform us about the ability of elements to form negatively charged ions, known as anions. **The energy change associated with the gain of an electron by a gaseous atom in its ground state is defined as electron affinity of an element.** It is expressed in kJ mol^{-1} and is represented by the symbol E_a. For an element X, the formation of X$^-$ can be represented as,

Since, the removal of an electron from an atom or ion needs energy, which*I* is always positive. The electron addition may be energy demanding or releasing, hence E_a may be positive or negative.

$$X(g) + e^- \rightarrow X^-(g)$$

Energy change = First electron Affinity of X = $E_a(X)$

The electron affinity value defined above is, in fact, first electron affinity of an element. The second electron affinity is the energy change associated with the formation of X^{2-} ion from X$^-$ ion.

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

Energy change = Electron affinity of X$^-$ = Second electron affinity of X = $E_a(X^-)$

The electron affinity values of halogens are large and negative indicating that a large amount of energy is evolved in the formation of halide ion from halogen. For example, the electron affinities of chlorine and bromine are – 348 and – 325 kJ mol^{-1}, respectively. This is due to the following factors:

i) The addition of an electron to a halogen is relatively easy as it leads to the stable noble gas configuration s^2p^6. For example, compare the electron configuration of chloride ion with that of argon.

$$Cl^-: 1s^22s^22p^63s^23p^6 \qquad Ar: 1s^22s^22p^63s^23p^6$$

ii) The effective nuclear charge of halogens is fairly high (Table 6.2). Therefore, halogens have a rather strong attraction for electrons. The ease of formation of halide ions, especially chloride, explains their abundant occurrence in ores.

The formation of oxide and sulphide ions is interesting since their first electron affinities are negative. That is, addition of first electron results in release of energy. But the second electron affinities are positive, which means, the addition of second electron is an energy demanding process. This is understandable since addition of an electron to O^{-} (g) or S^{-} (g) must overcome repulsion between like charges.

	O	S
First electron affinity (E_{a1})/(kJ mol^{-1})	− 141	− 200
Second electron affinity (E_{a2})/(kJ mol^{-1})	+ 701	+ 565

The energy required for the formation of O^{2-} (g) ion from oxygen atom can be calculated as follows:

$O(g) + e^{-} \rightarrow O^{-}(g)$ First electron Affinity (E_{a1}) = − 141 kJ mol^{-1}

$O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$ Second electron Affinity of oxygen (E_{a2}) = + 701 kJ mol^{-1}

Adding both,

$O(g) + 2e^{-} \rightarrow O^{2-}(g)$ Total energy for the = + 560 kJ mol^{-1}

Electron affinity values indicate anion forming capacity of an element. Born-Haber cycle is used for determining electron affinity values of elements.

Similarly, the transformation $S(g) + 2e^{-} \rightarrow S^{2-}(g)$ requires a total energy of (− 200 + 565 = + 365 kJ mol^{-1}. These values indicate that the reaction, $O(g) + 2e^{-} \rightarrow O^{2-}(g)$ or $S(g) + 2e^{-} \rightarrow S^{2-}(g)$ is energetically unfavourable. Even then, many metallic oxides and sulphides occur natively as ores. We shall explain this in the Subsec. 6.3.3.

SAQ 2

Electron affinity of carbon is − 122 kJ mol^{-1}, while that of nitrogen is + 9 kJ mol^{-1}. Explain.

6.2.4 Electronegativity

The use of values of ionization energies and electron affinities to express the tendency of isolated atoms to lose or gain electrons is somewhat cumbersome in practice. To reduce this difficulty, Linus Pauling and Robert Mulliken, developed empirical expressions for the attraction of bonding electrons to each of the two bonded atoms based upon the concept of electronegativity.

Electronegativity is not a directly measurable quantity but it is a concept that a chemist uses frequently on an intuitive basis.

Electronegativity is the attraction of an atom for bonding electrons in a chemical bond. It can be defined as a measure of the tendency of an atom to attract the electrons which bind it to another atom. In a molecule containing two different atoms, one may have more attraction for the shared electrons, and that atom is said to be more electronegative. For example, in the molecule hydrogen fluoride, fluorine is more electronegative than hydrogen. Hence, the shared electron pair is attracted by fluorine to a greater extent. In the case of molecules composed of two identical atoms like H_2, F_2 etc., the shared pair is pulled equally by both the atoms, since there is no difference in electronegativity.

There are different scales for electronegativity like Pauling scale, Allred and Rochow scale etc. The electronegativity values of some elements are given in Table 6.4 on Pauling scale. Electronegativity is represented by the symbol χ (chi). It is expressed as a number only.

Table 6.4: Electronegativity values of Elements on Pauling Scale

H						
2.1						
Li	Be	B	C	N	O	F
1.1	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca					Br
0.8	1.0					2.8
Rb	Sr					I
0.8	1.0					2.5
Cs	Ba					
0.7	0.9					

From Table 6.4, you can understand that electronegativity increases from left to right along a period and decreases in a group from top to bottom in the periodic table. It is seen that oxygen group elements and halogens have higher electronegativities than alkali and alkaline earth metals. Caesium is the least electronegative element while fluorine is the most electronegative.

Electronegativity has been proved to be an extremely useful concept in the estimation of molecular properties such as ionic character of bonds, dipole moments, bond dissociation energies, covalent radii etc. We shall soon define ionic and covalent bonding on the basis of electronegativity values of atoms.

6.3 IONIC BOND

In ionic bonding, there is complete transfer of one or more electrons from one atom to another.

Low ionisation energy for the metal and high, negative electron affinity for the nonmetal favour ionic bonding.

Before trying to understand ionic bonding using basic concepts, let us know how it was formulated originally. Kossel pointed out that the ions are formed by the loss or gain of electrons and that they would be stable, if they attain noble gas electron configuration, ns^2np^6. A reaction between sodium and chlorine results in the formation of sodium ions and chloride ions both types being held together by electrostatic attraction. In this process one mole electrons are transferred from one mole atoms of sodium to one mole atoms of chlorine. The resulting Na^+ and Cl^- ions have stable inert gas configurations:

$$\mathrm{Na}(1s^22s^22p^63s^1) \; + \; \mathrm{Cl}(1s^22s^22p^63s^23p^5) \rightarrow$$

$$\mathrm{Na}^+(1s^22s^22p^6) \quad + \quad \mathrm{Cl}^-(1s^22s^22p^63s^23p^6)$$

Electron configuration of neon	Electron configuration of argon

Compounds like potassium chloride, magnesium oxide, calcium fluoride and cesium chloride are also formed similarly. In all these compounds, the positive and negative ions are held together by strong electrostatic attraction known as ionic bond.

From what you have studied in Subsecs. 6.2.2, and 6.2.3, you can infer that alkali and alkaline earth elements, which have low ionisation energies, can combine with halogens, which have large negative electron affinity values forming ionic compounds. Even oxides and sulphides of metals are known to have ionic character to a large extent, although second electron affinity values for oxygen and sulphur are positive.

This is facilitated by higher lattice energy values of metallic oxides and sulphides. You will study about this aspect in section 6.3.3.

On the basis of electronegativity values, it has been observed that if the difference in electronegativity between two elements is more than 1.7, these two elements form compounds which are largely ionic in character. If the difference between electronegativities of two atoms has $\Delta\chi < 1.7$, the bond between them has large covalent character. The differences in electronegativity values, $\Delta\chi$, for some ionic compounds are given below:

$$\Delta\chi(\mathrm{NaCl}) = \chi(\mathrm{Cl}) - \chi(\mathrm{Na}) = 3.0 - 0.9 = 2.1$$

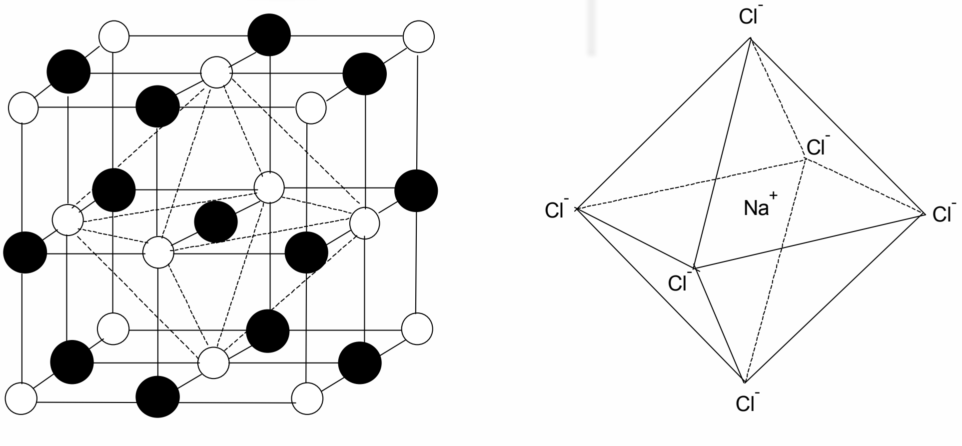
$$\Delta\chi(\mathrm{CsCl}) = \chi(\mathrm{Cl}) - \chi(\mathrm{Cs}) = 3.0 - 0.7 = 2.3$$

$$\Delta\chi(\mathrm{KBr}) = \chi(\mathrm{Br}) - \Delta\chi(\mathrm{K}) = 2.8 - 0.8 = 2.0$$

Ionic substances exist as charged particles whether in solid or liquid state. In solids, these charged particles form an array or a three-dimensional crystal lattice, as shown for sodium chloride crystal in Fig. 6.2(a). X-ray analysis of sodium chloride crystal has established the presence of Na^+ and Cl^- ions. In ionic crystal lattice, each ion is attracted by several ions of opposite charge. In sodium chloride crystal, each Cl^- ion is surrounded octahedrally by six Na^+ ions and *vice versa*, Figs. 6.2(a) and (b). In this context, it is apt to point out that a molecule of NaCl does not exist as such. The formula of an ionic substance is the lowest ratio of the component ions and can be determined from the charges of the respective ions. Thus in sodium chloride crystal, electrical neutrality is maintained if Na^+ and Cl^- ions are present in the ratio 1:1.

An octahedron has eight faces and six corners. Each face is an equilateral triangle.

Six Na^+ ions surrounding a Cl^- ion or six Cl^- ions surrounding a Na^+ ion prefer an octahedral arrangement, since, then the repulsion between like charges is minimum.



(a) **(b)**

Fig. 6.2: (a) Arrangement of Na^+ (○) and Cl^- (●) ions in sodium chloride crystal. Note the central Cl^- ion is surrounded by six Na^+ ions as indicated by dotted lines. (b) Octahedral arrangement of six Cl^- ions around a Na^+ on.

We shall next take up some characteristics of ionic compounds.

SAQ 3

Predict the bond nature between two bonded atoms in the following compounds: (Hint: use the electronagativity values given in the Table 6.4)

i) CS_2; ii) CO; iii) NaF

6.3.1 Properties of Ionic Compounds

Ionic compounds conduct electricity when melted or in solution. But in solid state, they are generally insulators due to very low mobility of the ions. The migration of ions towards electrodes explains their conducting capacity. The ionic compounds are usually soluble in solvents like water.

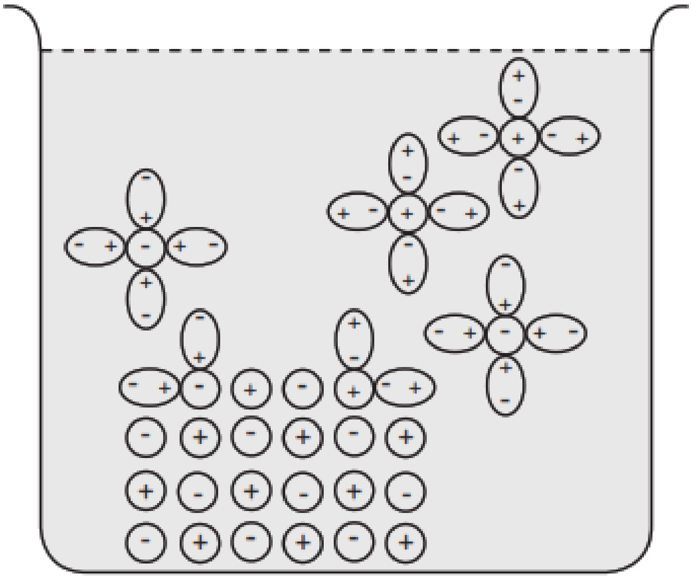


Fig. 6.3: Solution of an ionic crystal in water; ⊕ and ⊖ indicate ions from the crystal, while ± stands for water. The collection of ions at the bottom represents the undissolved solid.

In Fig. 6.3, we see that positive and negative ions of an ionic substance are surrounded by a sheath of water molecules in such a way that oxygen, the negative end of water, is directed towards cation and hydrogen the positive end of water, is directed towards anion. This type of solute-solvent interaction is called ion-dipole interaction and it reduces the force of attraction between the cation and anion. Solvents like water are called polar solvents.

In Fig. 6.2, you have seen alternating layers of structure containing sodium ions and chloride ions, one around the other. Due to strong electrostatic forces operating in ionic compounds, higher energy is required to overcome such electrostatic forces. Hence melting and boiling points of ionic substances are high. The stabilisation, an ionic crystal lattice attains due to electrostatic forces, is usually described in terms of lattice energy about which we will study in a detailed way in Subsec 6.3.3 after understanding the importance of ionic radii.

Let us see, if you can answer the following SAQ.

SAQ 4

Sodium chloride does not have high solubility in benzene. What do you infer from this?

6.3.2 Ionic Radii

The geometrical arrangement of ions in a crystal lattice depends on the relative sizes of cation and anion which are theoretically referred to in terms of ionic radii. The principles of quantum mechanics do not allow assigning definite size to an atom or ion. However, for the purposes of defining crystalline shape, cations and anions are assumed to be spherical, incompressible and having a sharply defined surface. Radius of an ion then becomes the radius of such a spherical charge, Fig. 6.4.

Using X-ray diffraction methods, a large number of ionic crystals have been studied and their interionic distances determined. For an ionic substance, AB, the interionic distance, a_{AB}, is assumed to be equal to the sum of the ionic radii, $(r_{A^+} + r_{B^-})$.

$$a_{AB} = r_{A^+} + r_{B^-} \qquad ...(6.2)$$

It has been experimentally found that for a pair of ions having same electron configuration (for examples: ions in NaF and KCl), known as isoelectronic pair, there is an inverse relationship between effective nuclear charge felt by an outermost electron of an ion and its radius. Let us assume that the ions A^+ and B^- are isoelectronic.

$$\frac{r_{B^-}}{r_{A^+}} = \frac{Z^*_{A^+}}{Z^*_{B^-}} \qquad \ldots(6.3)$$

Where $Z^*_{A^+}$ and $Z^*_{B^-}$ − Effective nuclear charge value felt by an electron in the outermost shell of cation and anion.

r_{A^+} and r_{B^-} − Radius values of cation and anion.

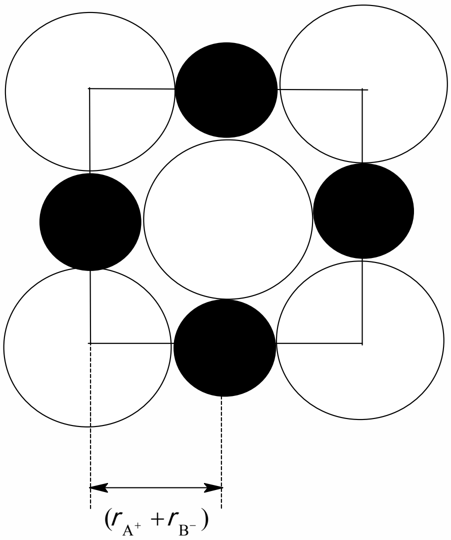


Fig. 6.4: Hard sphere model radii; here r_{A^+} and r_{B^-} are radii of cation and anion.

The above equation has been used by Pauling in estimating individual ionic radii and some of the values are given in Table 6.5. For your easy identification, isoelectronic ions are grouped together.

Table 6.5: Ionic Radii Values

Number of electrons in the ion	Anionic radii (pm)		Cationic radii (pm)	
2	H^-	208	Li^+	60
			Be^{2+}	31
10	F^-	136	Na^+	95
	O^{2-}	140	Mg^{2+}	65
			Al^{3+}	50
18	Cl^-	181	K^+	133
	S^{2-}	184	Ca^{2+}	99
36	Br^-	195	Rb^+	148
54	I^-	216	Cs^+	169

In an isoelectronic system of ions, the anion with largest charge has the largest radii value while cation with the largest charge has the smallest radii.

Thus, $r_{O^{2-}} > r_{F^-} > r_{Na^+} > r_{Mg^{2+}} > r_{Al^{3+}}$

Two factors responsible for this trend among isoelectronic ions are as follows:

i) The effective nuclear charge felt by the valence electrons is more for the cation than for the anion. Due to greater attraction from the nucleus, cation is smaller than the anion.

ii) In a highly charged anion, interelectronic repulsion is partly decreased by increase in size.

The ratio of cationic radius to anionic radius is useful in determining crystal geometry. Based on principles of geometry and X-ray diffraction experiments, the relationship among radius ratio, coordination number and crystal shape is given in Table 6.6. The terms r_A^+ and r_B^- refer to cationic and anionic radius, respectively. Coordination number is the greatest number of oppositely charged ions surrounding a particular ion. In Fig. 6.2, you saw that each Cl^- ion is surrounded octahedrally by six Na^+ ions and *vice versa*. It means coordination number for this system is six.

Table 6.6: Radius Ratio and Crystal Geometry

Coordination number	Structure types	Limiting value of radius ratio (r_{A^+}/r_{B^-})	Example
3	Triangular	0.155-0.225	BN
4	Tetrahedral	0.225 – 0.414	ZnS
6	Octahedral	0.414 – 0.732	NaCl
8	Cubic	0.732 – 1.000	CsCl

Let us see whether we get the same conclusion by using Tables 6.5 and 6.6.

r_{Na^+} = 95 pm; r_{Cl^-} = 181 pm

r_{Na^+}/r_{Cl^-} = 95/181 = 0.525

Hence in sodium chloride crystal, each ion is octahedrally surrounded by six ions of opposite charge, as per Table 6.6.

For greater clarity on this generalisation, consider other types of crystal structures such as tetrahedral and cubical types. Best examples of these types of crystal structures are ZnS and CsCl. The radius ratio values in these cases are $r_{Zn^{2+}}/r_{S^{2-}}$ = 74/184 = 0.40 and r_{Cs^+}/r_{Cl^-} = 169/181 = 0.93, respectively. On the basis of these radius ratio values, we can predict that ZnS crystal will prefer tetrahedral structure and CsCl crystal will prefer cubic structure. Hence, in ZnS crystal structure, each zinc ion is surrounded tetrahedrally by four sulphide ions and *vice versa*. In CsCl crystal structure, each caesium ion is surrounded by a cube of eight chloride ions and *vice versa*. You can see that there is fair agreement between the predicted shapes and the crystal structures as shown in Fig. 6.5 and 6.6.

A tetrahedron has four faces and four corners, each face being an equilateral triangle.

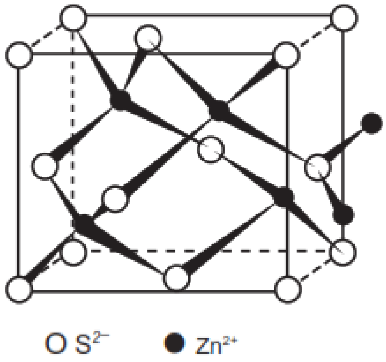


Fig. 6.5: Tetrahedral structure; Zinc sulphide (zinc blende).

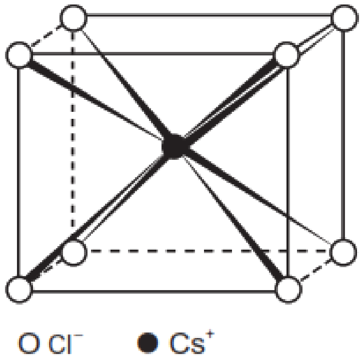


Fig. 6.6: Cubic structure; Caesium chloride.

Larger size of Cs^+, compared to Na^+, is responsible for the difference in crystal geometry between NaCl and CsCl.

But radius ratio need not be overemphasised since other factors such as lattice energy and pressure also play a role in determining the crystal shape.

SAQ 5

Predict the coordination number of Ca^{2+} in CaO crystal and also its crystal structure, if ionic radii for Ca^{2+} =99 pm and O^{2-} = 140 pm.

6.3.3 Lattice Energy

In the last section, we saw, how in an ionic crystal the geometrical shape depends on radius ratio. In this section, we focus our attention on lattice energy which is an important factor in lattice formation and stability.

For an ionic crystal to be formed, its lattice energy and enthalpy of formation must be negative.

In Table 6.3, the first and second ionisation energies of magnesium are given as 738 and 1450 kJ mol^{-1}, respectively. The sum of these two values, that is 2188 kJ mol^{-1}, is the energy required to form Mg^{2+} ion. In Subsec.6.2.3, it has been calculated that the formation of O^{2-} ion needs 560 kJ mol^{-1} energy. Thus energy is needed for the formation of both Mg^{2+} and O^{2-} ions. Yet solid magnesium oxide is actually formed along with the liberation of heat and light, when a magnesium wire is ignited. The interesting feature in the formation of magnesium oxide is that energy liberated in the lattice arrangement of magnesium oxide crystal, known as its lattice energy, is more than the energy required for the formation of Mg^{2+} and O^{2-} ions. The arrangement of positive and negative ions alternately in a three-dimensional lattice is a stabilising structural feature due to strong electrostatic attraction.

Before defining lattice energy of a crystal, it is better we know the significance of enthalpy change in a reaction. Heat change accompanying a reaction at constant pressure is represented as enthalpy change and is represented by the symbol ΔH. It is expressed in kJ mol^{-1} units. As you know, in exothermic reactions, heat is evolved and ΔH is negative; in endothermic reactions, heat is absorbed and ΔH is positive. You may recollect that a reaction is feasible if the change in free energy, ΔG, is negative. Using the values of change in enthalpy, ΔH, and the change in entropy, ΔS, and the value of ΔG is calculated from the following equation:

$$\Delta G = \Delta H - T\Delta S$$

In this expression, T is the temperature. For the type of reactions discussed in this unit it is assumed that exothermic reactions are feasible. It is allowed since the entropy change is too small for such reactions.

Lattice energy, ΔH_L, is the energy released when one mole of an ionic compound is formed from its constituent gaseous ions. Remember, lattice energy is different from the enthalpy of formation, ΔH_f, of the ionic compound in that the ΔH_f refers to the energy involved in the formation of the ionic compound from its elements. Lattice energy and enthalpy of formation of sodium chloride are the heat changes accompanying the reactions represented below:

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ Heat change = Lattice energy of NaCl = $\Delta H_L(NaCl)$

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$ Heat change = Enthalpy of formation of NaCl = $\Delta H_f(NaCl)$

The formation of a stable crystal from the elements or ions is exothermic; hence the values of ΔH_f and ΔH_L for such a crystal are negative. Let us now study about the methods of determining lattice energy.

Calculation of Lattice Energy

Two of the important methods for obtaining lattice energy values of crystals are based on electrostatic model and Born-Haber cycle. The electrostatic model is a theoretical approach and it is based on the assumption that the bond is wholly ionic in the crystal. In 1918 Max Born and Alfred Landé derived Eq. 6.4, on the basis of electrostatic model.

$$\text{Lattice energy}, U = \frac{-1.389 \times 10^{-4} A Z^+ Z^-}{a}\left(\frac{n-1}{n}\right) \text{kJ mol}^{-1} \qquad \ldots(6.4)$$

The Eq. 6.4 is called **Born–Landé equation,** in this equation, *A* and *n* are known as Madelung constant and Born constant, respectively and for each crystalline shape, their values are available in literature. The quantities *a*, Z^+, Z^- are characteristic of a particular compound; *a* = internuclear distance, which is equal to the sum of ionic radii; Z^+ and Z^- = positive integers representing the positive and negative charges on the ions. For example, in NaCl crystal, $Z^+ = Z^- = 1$ and in CaF_2 crystal, $Z^+ = 2$ and $Z^- = 1$.

Let us calculate the lattice energy value of NaCl crystal using Eq. 6.4. The literature values of *A*, *a* and *n* for NaCl crystal are given below:

$a = 276$ pm; $A = 1.748$; $n = 9.1$

$$\text{Lattice energy of NaCl} = \frac{-1.389 \times 10^{-4} \times 1.748 \times 1^2 \times 8.1}{276 \times 10^{-12} \times 9.1} = -783\,\text{kJ mol}^{-1}$$

The second method, Born-Haber cycle, is a thermochemical method of calculating lattice energy and it is based on Hess' law of heat summation which states that the heat change in a reaction is same, whether it takes place in one or in many steps. In Table 6.7, the formation of sodium chloride crystal is depicted in two ways; first through five stages, (i) through (v), and the second directly by the reaction between solid sodium and gaseous chlorine namely through step (vi). According to Hess' law, the heat change either way is equal. That is, total heat change for the steps (i) through (v) is equal to the heat change in step (vi). Let us calculate lattice energy of sodium chloride using data in Table 6.7.

Table 6.7: Born-Haber Cycle for Sodium Chloride Crystal

Stages	**Name of the reaction**	**Reaction**	**Heat change** **Name**	**Term**	**ΔH, kJ mol^{-1}**
i	Sublimation of solid sodium	$Na(s) \rightarrow Na(g)$	Heat of sublimation or enthalpy of atomization	ΔH_s	+108
ii	Formation of sodium ions in gaseous state	$Na(g) \rightarrow Na^+(g) + e^-$	Ionisation energy of sodium	$I(Na)$	+495
iii	Dissociation of chlorine	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	Heat of dissociation or enthalpy of atomisation	$\frac{1}{2}\Delta H_d$ (one mole of atoms results from half a mole of chlorine)	$(\frac{1}{2} \times 242) = +121$
iv	Formation of chloride ions in gaseous state	$Cl(g) + e^- \rightarrow Cl^-(g)$	Electron affinity of chlorine	$E_a(Cl)$	–348
v	Formation of solid sodium chloride from gaseous ions	$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	Lattice energy of sodium chloride	ΔH_L	To be calculated
vi	Formation of solid sodium chloride from the elements[(i) + (ii) + (iii) + (iv) + (v)]	$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$	Heat of formation of sodium chloride	ΔH_f	–411

$$\Delta H_f = \Delta H_s + I(\mathrm{Na}) + \frac{1}{2}\Delta H_d + E_a(\mathrm{Cl}) + \Delta H_L$$

$$\Delta H_L = \Delta H_f - [\Delta H_s + I(\mathrm{Na}) + \frac{1}{2}\Delta H_d + E_a(\mathrm{Cl})]$$

$$= -411 - (108 + 495 + 121 - 348)\ \mathrm{kJ\ mol^{-1}}$$

$$= -787\ \mathrm{kJ\ mol^{-1}}$$

It is usual to express the changes given in the Table 6.7 above in a cyclic way as given in Fig. 6.7.

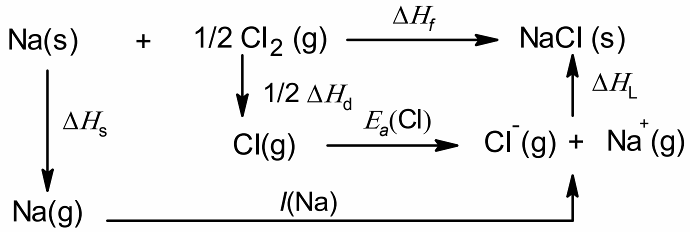


Fig. 6.7: Born-Haber cycle for the formation sodium chloride

Ionic compounds usually have high melting points because the electrostatic interactions that hold the ions together are very strongly.

You can see that there is fair agreement between the lattice energy values derived from the two methods discussed above. A still better agreement between the values is possible if some refinements suggested for electrostatic model are taken into account. A large disparity between the values from the two methods suggests that bonding in the crystal is not wholly ionic and some covalent character may also be present. Thus for cuprous bromide, the electrostatic model gives a value of –882 kJ mol^{-1} whereas Born-Haber cycle value is –956 kJ mol^{-1}. Poor agreement hints at low ionic character of cuprous bromide.

Now, consider the Eq. 6.4 again to understand the trend of lattice energy in different ionic compounds. It is clear from this equation that lattice energy are largest when the internuclear distance, *a*, is small and when the charge Z^+ and Z^- are large. Smaller internuclear distance (i.e. ionic radii) means ions are closer to each other and larger the electrostatic attraction among ions. For example, consider the ionic compounds such as LiF, NaF, KF. In these compounds cation size follows the order $K^+ > Na^+ > Li^+$. So lattice energies follow the order LiF > NaF > KF. Lattice energies of some ionic compounds are listed in Table 6.8.

Table 6.8: Lattice energies of some ionic compounds (kJmol^{-1})

Anion					
Cation	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1036	853	807	757	2953
Na^+	923	787	747	704	2695
K^+	821	715	682	649	2360
Be^{2+}	3505	3020	2914	2800	4443
Mg^{2+}	2957	2524	2440	2327	3791
Ca^{2+}	2630	2258	2176	2074	3401
Al^{3+}	5215	5492	5361	5218	15916

Table 6.8 also indicates that compounds of ions with higher charges have larger lattice energies than compounds of ions with lower charge. For

example, in compounds like NaCl, $MgCl_2$ and $AlCl_3$, the order of lattice energies is $AlCl_3 > MgCl_2 > NaCl$.

Lattice energy calculations help us in predicting the stability and stoichiometry of compounds. Let us assume that we want to find the stoichiometric formula for magnesium chloride. We suggest three tentative formulae, MgCl, $MgCl_2$ and $MgCl_3$, and corresponding to each formula, lattice energy is calculated using Eq. 6.4. These lattice energy values are then used in Born-Haber cycles designed individually for the three formulae and the enthalpies of formation of magnesium chloride corresponding to the three formulae are calculated. Of the different stoichiometric formulae available, we can choose the one giving rise to largest negative value for the enthalpy of formation; it is so since a large negative enthalpy value corresponds to a stable structure. Thus, of the various suggested formulae for magnesium chloride, $MgCl_2$ is acceptable since it corresponds to the largest negative enthalpy of formation, as given below:

$MgCl = -130$ kJ mol^{-1}

$MgCl_2 = -642$ kJ mol^{-1}

$MgCl_3 = +3909$ kJ mol^{-1}

Lattice energy values play an important role in deciding the solubility of ionic solids. Higher lattice energy value means, necessity of larger energy to break the crystal lattice. Thus alkali metal chlorides are more soluble than alkaline earth chlorides since for the latter class, lattice energy values, given in kJ mol^{-1}, are high.

$NaCl = -787$	$KCl = -718$
$MgCl_2 = -2525$	$CaCl_2 = -2253$

There is also another factor which also affects the solubility of ionic solids; this factor will be discussed in following section.

SAQ 6

i) Write down Born-Haber cycle for $BaCl_2$ formation.

ii) Arrange the following ionic compounds in the order of their decreasing lattice energies. Also justify your answer.

LiCl, LiF, LiI and LiBr

6.4 SOLUBILITY AND SOLVATION ENERGY

We have discussed earlier that solubility of ionic solids in water is a result of an interaction between polar water molecule and the ions which make up an ionic solid. Basically solubility depends on the balance of two factors: the lattice energy and **hydration energy** or **Enthalpy of Hydration** of ions, if water is involved as solvent system otherwise in general hydration energy is called as **solvation energy** or **solvation enthalpy**. Hydration energy may be defined as the amount of energy released when a mole of the gaseous ion dissolved in a large amount of water forming an infinitely dilute solution. To further understand this relationship, consider the dissolving process of sodium chloride in water:

$NaCl\,(s) \longrightarrow Na^+(g) + Cl^-(g)$ $\Delta H'_L$ Lattice dissociation energy (equal to lattice energy of crystal)

$Na^+(g) + H_2O \longrightarrow Na^+(aq)$ $\Delta H_{hyd}(Na^+)$ Hydration energy of Na^+

$Cl^-(g) + H_2O \longrightarrow Cl^-(aq)$ $\Delta H_{hyd}(Cl^-)$ Hydration energy of Cl^-

$NaCl\,(s) + H_2O \longrightarrow Na^+(aq) + Cl^-(aq)$ ΔH_{sol} Enthalpy of Solution

The enthalpy changes in this process may also be represented by a simple cycle diagram such as Fig. 6.8.

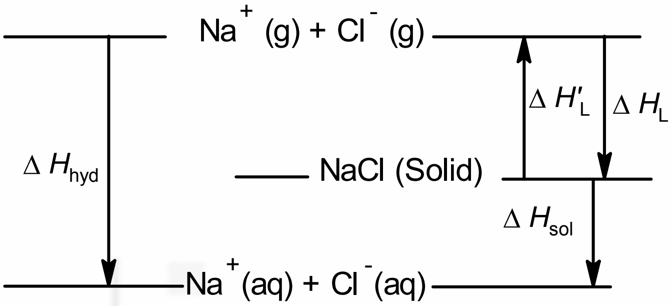


Fig. 6.8: Enthalpy changes in the dissolution process of NaCl

The hydration process of ionic solid occurs in two steps: In first step, the ions in the solid are separated to gaseous ions, which requires the input of energy equal to the lattice energy, ΔH_L. This heat energy is called lattice dissociation energy or lattice dissociation enthalpy. Unlike lattice energy, lattice dissociation has positive value. In second step, the separated gaseous ions are hydrated (solvated) by the water molecules with the evolution of the hydration energy, ΔH_{hyd}, of the cation and anion. The enthalpy of solution, ΔH_{sol}, is the difference between the lattice energy and hydration energy (see Fig. 6.7). It is the energy change associated with the dissolution of a mole ionic solid in a water or solvent to give a solution of infinite dilution. If three of the four enthalpies are known the fourth one can be calculated similar to Born-Haber cycle. Thus for NaCl:

$$\Delta H_{sol} = [\Delta H_{hyd}(Na^+) + \Delta H_{hyd}(Cl^-)] - \Delta H_L$$

The factors affecting the lattice energy were discussed earlier. It may be recalled that the lattice energy is greatest for small ions of high charge. The solvation energy (hydration energy) of the gaseous ions arises from the electrostatic attraction between the ionic charges and the dipole of the water molecules. These interactions are shown schematically in Fig. 6.3. The strength of the ions interaction with the water molecules increases with the charge on the ions and inversely proportional to their size.

However, it is not easy to estimate the relative magnitudes of these two factors or to quantitatively predict water solubilities of ionic solids. But based on experimentations, we can generalise:

- Salts in which both the anion and cation are singly charged are generally soluble (exception silver halids, AgX).
- Salts in which both the cations and anions are multiply charged are generally insoluble.
- Salts that have degree of covalency often have low solubility in water e.g. AgX, FeS etc.

The exceptional behaviour of solubility of some ionic salts in water can be explained on the basis of Fajan's rules which predict the covalent character in ionic compounds. As the covalent character increases the solubility in polar solvent definitely decreases. In next Sec. we will take up this phenomenon in more detail.

SAQ 7

Lattice energy for KCl is −715 kJ mol^{-1}. The enthalpies of hydration for potassium and chloride ions are −322 and −363 kJ mol^{-1}, respectively. From these values calculate the enthalpy of solution for KCl.

6.5 POLARISING POWER AND POLARISABILITY OF IONS

In the preceding sections we have noticed some exceptions of radius-ratio rules and solubility of some ionic salts. The possible explanation we have given is the degree of covalent character present between ions. When an ionic bond is formed, the cation attracts the electrons of the anion and at the same time it repels the nucleus, thus distorting or polarising the anion. In the same way negative ion will also polarise the positive ion, but usually anions are larger than cations. This effect is not much significant in cations as electrons are more firmly bound because of the higher effective nuclear charge. Now there are two situations (i) if the degree of polarisation is quite small between two ions, then the bond remain largely ionic, (ii) if the degree of polarisation is large, electrons are drawn from the anion, towards the positive cation resulting a high electron density between the two nuclei and a significant degree of covalent character is generated in the bond i.e., the electron density of anion is distorted toward the cation. This distortion from the spherical shape of the ideal anion is referred to as polarisation and the extent to with distortion occurs depends on the power of a cation to distort i.e. its polarising power and how easily anion is distorted i.e. its polarisability. In general, the polarising power of cation increases as they become smaller and more highly charged. On the other hand polarisability of anion is more with the larger size. In Fig. 6.9 we have shown diagrammatic representation of polarisation in LiI. Here small lithium ion polarising large polarisable Iodide ion. Polarisation concept is a departure from purely ionic bonding in the compounds. Thus, the idea of ions as hard sphere has to be modified by allowing for distortions of the spherical electron cloud around ions.

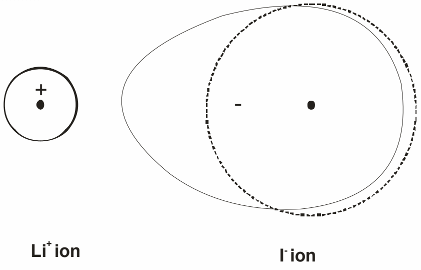


Fig. 6.9: Polarisation in LiI

6.5.1 Fajan's Rules

Fajan's developed the following rules which summarise the factors favouring polarisation of ions and hence the increase in covalent character in bonding.

1. A cation will be more polarising power, if it is small and highly positively charged.

2. An anion will be more easily polarised, if it is large and highly negatively charged.

3. Polarisation is favoured, if the cation does not have a noble gas configuration. This rule is particularly important for the *d* block elements.

To further illustrate these rules, let us discuss a few examples.

Along with the size of ion charge density can also be employed to measure the polarising power of a cation. The change density of an ion is expressed by following formula

$$\text{Charge density} = \frac{\text{unit charge} \times \text{charge of proton in Coulombs}}{\text{volume of ion in mm}^3} \quad \ldots(6.5)$$

Therefore, for the Na^+ ion which is having ionic radius 116 pm., the charge density will be

$$\text{Charge density} = \frac{1 \times 1.60 \times 10^{-19}\,\text{C}}{(4/3) \times \pi \times (1.16 \times 10^{-7}\,\text{mm})^3}$$

$$= 24\ \text{C mm}^{-3}$$

Similarly we can calculate the charge density of Al^{3+} ion which comes out 364 C mm^{-3}. This is much greater than the charge density of sodium ion, therefore the aluminum ion has much more polarising power than the sodium ion and so more likely to favour covalency in its bonding. These observations are consistent with the Fajan's first rule. We can even generalise that in determining the degree of covalency in a compound with a cation change of 1+ or 2+, ionic behaviour will usually predominant. With a cation change of 3+ only compounds with poorly polarisable anions, such as fluoride, are likely to be ionic. Cations that theoretically have charge of 4+ or above, their compounds can always be considered to have mainly a covalent character.

To illustrate Fajan's second rule, i.e. the effects of anion size, consider aluminum fluoride [m.p 1563 K (1290° C)] and aluminum iodide [m.p 463 K (190°)]. In these compounds fluoride ion has ionic radius of 117 pm and iodide ion has ionic radius 206 pm. In fact iodide ion volume is five times of fluoride ion volume. Because of the smaller size of F^- ion, it cannot be polarised significantly by the Al^{3+} ion. Hence, the bonding in AlF_3 is essentially ionic. On the other hand iodide ion is distorted towards the high-charged Al^{3+} ion to such an extent that covalently bonded aluminum iodide (AlI_3) is formed. Therefore, melting point of aluminum fluoride is higher than the melting point of aluminum iodide. Low solubility of sulphate salts can also be explained on this basis as the size of sulphate ion is large and it is dinegative. Due to high polarisability of sulphate ions, their salts have considerable covalent character specially salts like $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$ etc.

One of the simplest ways of distinguishing ionic behaviour from covalent behaviour is by observing melting points. Ionic compounds and networking covalent compounds like diamond tend to have higher melting points than those of small molecule covalent compounds.

The Fajan's third rule is related to cations that do not have a noble gas electron configuration. As we know noble gas configuration is the most effective at shielding the nuclear charge, so ions which do not have noble gas configuration are more likely to be more polarsable, i.e. have greater tendency towards covalency. Consider the examples of silver ion (Ag^+), which has electronic configuration [Kr] $4d^{10}$ and potassium ion, which has noble gas electronic configuration [$3s^2\ 3p^6$]. The charge density and ionic radius of silver ion are comparable with that of potassium ion (charge density of Ag^+ = 15 C mm^{-3}, r_{Ag^+} = 126 pm, and charge density of K^+ = 11 C mm^{-3} and r_{K^+} = 133 pm). Therefore, their salts should also have close melting points. But, it is observed that the melting point of AgCl is considerably lower than that of potassium chloride. The melting points of AgCl and KCl are 718 K (445 °C) and 1043 K (770 °C), respectively. These melting points indicate that AgCl has partially covalent character. Similar behaviour is also observed with salts of Cu^+, Sn^{2+} and Pb^{2+} ions. Presence covalent character in AgCl also explains low solubility of AgCl in water.

SAQ 8

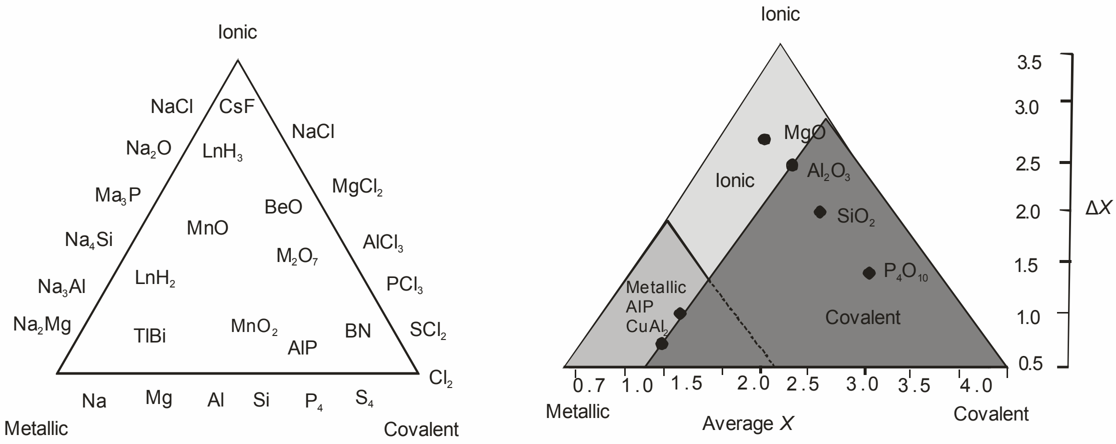
i) Between chloride ion and fluoride ion which one would be more polarisable? Explain.

ii) Explain the difference between the melting points of tin(II) chloride, $SnCl_2$ [500 K (227°C)] and tin(IV) chloride $SnCl_4$ [243 K (–33°C)].

6.6 THE BONDING CONTINUUM

In the beginning of our discussion on bonding, we have mentioned that three are three types of bonding: ionic, covalent and coordinate. Coordinate bonds, now consider as another types of covalent bond. There is another type of bonding, called metallic bonding, which exists between two electropositive elements. In the metallic bonding the electrons of outer most orbital are free to move throughout the whole crystal. These bonds, i.e. ionic, covalent and metallic bonds are called ideal types. In fact, there are few cases of pure ionic compounds having ideal ionic bond and similar is true for covalent bonds and metallic bonds. While discussing Fajan's rules, we have illustrated how polarisation of ions can result in covalent character of ionic bonds. Thus, in realty, we do not see a rigid ionic-covalent divide but a bonding continuum. The bonding continuum is not confined to two dimensions i.e. ionic or covalent.

For better understanding the types of bonding, we can construct a triangular diagram whose corners represent the three extremes of ‘pure’ or ‘ideal’ covalent, Ionic and metallic bondings.



(a) (b)

Fig. 6.10: Diagrammatic illustration of bond types using van Arkel-Ketelaar bond triangle

Fig. 6.10(a) represents bond triangle, which is also known as van Arkel-Ketelaar triangle. In this diagram three extreme types of bonds are placed at the corner of the triangle. Compounds having bonding predominantly of one type are represented by points near the vertices of the bond triangle and the compounds with bonding intermediate between the two types are represented by points along an edge of the triangle. The majority of compounds are represented by points within the area of the triangle, showing that the bonding has some of the characteristics of all three types. In another diagram Fig. 6.10(b) we have shown a rough division into metallic, ionic and covalent zones. Any binary compound can be located on this triangle by plotting the average electronegativity of the two atoms against their electronegativity difference.

Generally the bonding and general properties of most of the compounds discussed at this level can be explained in terms of one bonding type or, at most, a combination of two bonding types: ionic and covalent.

6.7 BOND POLARITY

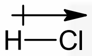
We just have mentioned above that there are three idealised extremes of chemical bonding. i.e. (i) ionic bonding: in which one or more electrons are transferred completely from one atom to another, and resulting ions are held together by purely electrostatic forces, (ii) covalent bonding in which electrons are shared equally between two atoms, and (iii) metallic bonding: this type of bonding occurs among metal atoms. Instead of a bond between just two atoms, a metallic bond is a sharing of electrons between many atoms of a metal element. However, bonding in most compounds is intermediate among these three ideal situations. The intermediate bonding between purely ionic and purely covalent is called polar bond or polar covalent bond. The extent of the ionic character in a covalent bond is called ‘**bond polarity**’. Bond polarity is a measure of how equally or unequally the electrons in any chemical bond are shared.

Bond polarity is determined generally by relative electronagativities of the bonded atoms. A bond is nonpolar, if the bonded atoms have equal electronagativities, for example bonds in O_2, Cl_2, N_2 etc., in these cases bonding electrons are equally shared between two atoms. A bond is a polar, if the electronagativities of the bonded atom are not equal. In this case the bonding electrons are not shared equally. For example, in HCl, the chlorine atom being more electronegative ($\chi_{Cl} = 3.16$) than hydrogen ($\chi_H = 2.20$), it will exert a greater attraction for the bonding electrons than hydrogen atom. As a consequence, the more electronegative chlorine atom attracts electron density away from the less electronegative hydrogen atom, leaving a partial positive charge on the hydrogen atom and a partial negative charge on the chlorine atom. The charge distribution can be represented as:

Polarity in a chemical bond is due to the difference in electronegativity between the atoms forming bond.

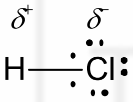
$$\overset{\delta^+}{\mathrm{H}}-\overset{\delta^-}{\mathrm{Cl}}$$

Where symbols lowercase delta with positive sign (δ^+) and negative sign (δ^-) indicate partial positive and negative charges, respectively. In a polar bond charges on atoms are less than the full charges of the ions. The bond polarity shown above can also be represented by placing a small arrow near covalent bond, with head towards the more electronegative atom and a cross at other end of the arrow indicating more electropositive atom.



Equal and unequal sharing of bonding electrons can be shown by Lewis structures in Cl_2 and HCl molecules:

Nonpolar bond
Bonding pair (:)
equally shared



Plar bond
Bonding pair (:)
unequally shared

The results of the calculation of electron density distribution around Cl_2 and HCl are illustrated in Fig. 6.11. You can see that in Cl_2 the distribution of electron density is symmetrical, in HCl this is clearly shifted towards chlorine atom and thus creating positive and negative centres in HCl molecule.

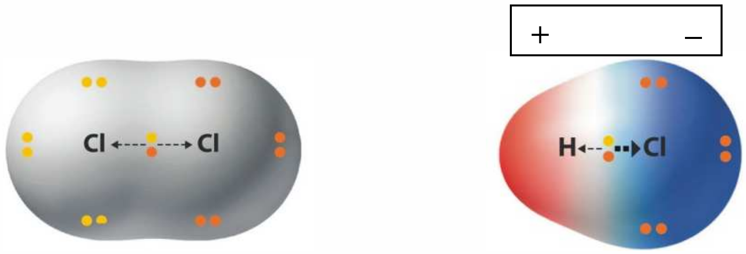


Fig. 6.11: The electron density distribution: This shows the calculated electron density distribution of the Cl_2 and HCl molecules.

In a chemical bond, centre of positive and negative charge do not coincide, is a polar bond.

Bond polarity and ionic character increase with an increasing difference in electronegativities ($\Delta\chi$) between two bonded atoms. If the difference is large enough, an ionic bond is formed. Remember that electronegativities are difficult to measure precisely and therefore polarity is measured in terms of dipole moment.

6.7.1 Dipole Moments

As we have just seen, there is a difference in electronegativity between hydrogen and chlorine atoms, which leads to a polar covalent bond in the HCl molecule. As a result, there is a concentration of negative charge on the more electronegative Cl atom, leaving the less electronegative H atom at the positive end of the molecule. A molecule such as HCl in which the centres of positive and negative charge do not coincide is said to be a **polar molecule.** Thus, we not only describe bonds as polar and nonpolar, but we also describe entire molecules this way as well. The polarity of HCl molecule can be expressed as:

$$\overset{\delta^+}{\mathrm{H}}\text{—}\overset{\delta^-}{\mathrm{Cl}} \quad \text{or} \quad \overset{+\!\!\!\longrightarrow}{\mathrm{H}\text{—}\mathrm{Cl}}$$

Polar molecules align themselves with respect to each other and with respect to ions. The negative end of one molecule and the positive end of another attract each other. Polar molecules are likewise attracted to ions. The negative end of a polar molecule is attracted to a positive ion, and the positive end is attracted to a negative ion (as illustrated in Fig. 6.3). These interactions help us in explaining many physical and chemical properties of inorganic and organic compounds.

Dipole moment can occur between two ions in ionic bond or between atoms in covalent bond. The dipole moment is a measure of the polarity of the molecule.

How can we determine the polarity of a diatomic molecule such as HCl? Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a dipole is established. The quantitative measure of the magnitude of a dipole is called its dipole moment, denoted symbol lowercase mu (μ). If two equal and opposite charges, q^+ and q^- are separated by a distance r, the magnitude of the dipole moment is the product of q and r:

$$\mu = qr$$

We see that the dipole moment will increase in size as the quantity of charge that is separated increases, and as the distance between the charges increases.

Let us consider the general case of a chemical bond, constituted by two atoms of different electronegativities. An electric dipole results with charges $+q$ and $-q$ (say) separated by the interatomic distance r.

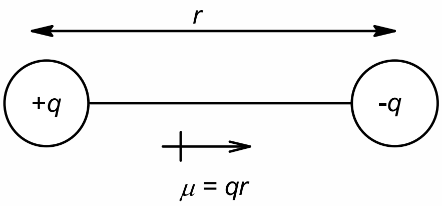


Fig. 6.12: Representation of a dipole

Dipole moment, associated with such a system can be given by

$$\mu = qr \qquad \text{...(6.6)}$$

It is diagrammatically represented by an arrow pointing from the positive to negative pole (see Fig. 6.12). The SI unit is C m (Coulomb meter). If a negative charge equivalent to that of an electron (of magnitude 1.602×10^{-19} C) is separated from a positive charge of equal magnitude at a distance of 10^{-10} m (100 pm), then dipole moment would be,

$$\mu = 1.602 \times 10^{-19} \text{ C} \times 1 \times 10^{-10} \text{ m}$$

$$= 16.02 \times 10^{-30} \text{ C m}$$

In literature, the dipole moment values are given in Debye (D) units.

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

Therefore,

$$\mu = 16.02 \times 10^{-30} \text{ C m} \times \frac{1 \text{ D}}{3.36 \times 10^{-30} \text{ C m}} == 4.80 \text{ D}$$

Measurement of the dipole moments of molecules can provide us with valuable information about the charge distributions in molecules. If the values of dipole moment and bond length are known, than charges on bonded atoms can be calculated. For example, the experimentally measured dipole moment of HCl (g) is 1.07 D and bond length is 127.5 pm. The magnitude of charge on the hydrogen and chlorine atoms can be calculated as follows:

$$q = \frac{\mu}{r} = \frac{1.07 \text{ D}}{127.5 \times 10^{-12} \text{ m}} \times \frac{3.336 \times 10^{-30} \text{ C m}}{1 \text{D}}$$

$$= 2.80 \times 10^{-20} \text{ C}$$

Charge in units of electron, *e,*

$$q = 2.80 \times 10^{-20} \text{ C} \times \frac{1e}{1.60 \times 10^{-19} \text{ C}} = 0.175\, e$$

Thus, the experimental dipole moment indicates the following charge separation in the HCl molecule:

$$\overset{+0.175}{\text{H}} - \overset{-0.175}{\text{Cl}}$$

Charges on the atoms are less than a full electronic charge. Therefore, we can conclude that HCl bond is polar covalent bond rather than pure ionic.

We saw that the dipole moment of a diatomic molecule is a quantitative measure of the amount of charge separation in the molecule. For a molecule with more than two atoms, the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule as bond dipole moments (bond dipoles) are vector quantities; that is, they have both a magnitude and a direction.

The overall dipole moment of a polyatomic molecule is the sum of its bond dipoles. Both the magnitudes and the directions of the bond dipoles must be considered in this sum of vectors. These factors help us in predicting correct molecular polarity and the geometry of the compounds as well.

In the next section, we study how dipole moment is estimated for polar molecules but before that you try the following SAQ, using Eq.6.6.

SAQ 9

The dipole moment and the bond distance in hydrogen iodide are 0.44 D and 161.0 pm. Calculate the magnitude of charges on hydrogen and iodide atoms. Compare the result with the charge on an electron.

6.7.2 Determination of Dipole Moments

As mentioned above dipole moments provide valuable information about charge distribution in the molecules and their geometry. Let' us briefly discuss how dipole moments are determined. Dipole moments are experimentally measurable. This is done by determining molar polarisation at different temperature using experimentally measured relative permittivity and density at different temperature.

When a polar molecule is subjected to an electric field, the positive and negative charge distribution in the molecule is disturbed which is known as polarisation. Polarisation is a threefold disturbance caused by an electric field in a molecule. This disturbance is in the alignment of dipoles, electronic distribution and in the nuclear skeleton. Let us briefly understand some terms used above.

Polarisability is a measure of how easily an electron cloud is distorted by an electric field. Polarisability is experimentally measured as the ratio of induced dipole moment μ' to the electric field E that induces it:

$\alpha = \mu'/E$

Molar Polarisation: The polarisation so caused is quantified in terms of molar polarisation (P_M), which is the polarisation for one mole of a substance. This can be expressed by following relation:

$$P_M = \frac{N_A}{3\varepsilon_o}\left(\alpha + \frac{\mu^2}{3kT}\right) \quad ...(6.7)$$

Here N_A, μ, ε_o, k, T *and* α stand for Avogadro number, dipole moment of the molecules, permittivity of vacuum, temperature and polarisability, respectively. When a polar molecule immersed in medium as air or liquid we use term relative permittivity, ε_r in place of ε_o, which can be expressed as:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o} \quad ...(6.8)$$

where ε_o *and* ε are the permittivity values in vacuum and in the medium. ε_r is dimensionless quantity. The relative permittivity of a molecule is large if a molecular polar or highly polarisable. It can be related to molar polarisation by Debye equation:

$$P_M = \frac{\varepsilon_r - 1}{\varepsilon_r - 2} \cdot \frac{M}{\rho} \quad ...(6.9)$$

Here. M and ρ stand for molar mass of the molecule (in kg mol^{-1}) and density of the medium (in kg m^{-3}), respectively. The relative permittivity can be experimentally measured by comparing the capacitance of a capacitor with the sample present (C) and without (C_o); using relation $\varepsilon_r = C/C_o$.

Equation 6.7 can also be written as:

$$P_M = \frac{N_A \alpha}{3\varepsilon_O} + \frac{N_A \mu^2}{9k\,\varepsilon_o} \times \frac{1}{T} \qquad \text{...(6.10)}$$

This equation is similar to linear equation, thus it can also be written as:

$$P_M = A + \frac{B}{T} \qquad \text{...(6.11)}$$

If P_M is plotted against $1/T$, It will yield a straight line as per Eq. 6.10. The slope of the straight line (B) is equal to $\frac{N_A \mu^2}{9\varepsilon_O k}$ and intercept (A) equal to $\frac{N_A \alpha}{3\varepsilon_O}$.

Hence, dipole moment

$$\mu = \sqrt{\frac{9\varepsilon_O k \times \text{slop}}{N_A}} \qquad \text{...(6.12)}$$

The slope of P_M against $1/T$ plot is to be substituted in above Eq. 6.12 to calculate the dipole moment of polar molecules.

Having studied the method of finding out the dipole moment of molecules, let us now take up some of its applications. Before that, attempt the following SAQ.

SAQ 10

Using Eq. 6.11, show that molar polarisation has the unit, $m^3 \, mol^{-1}$.

6.7.3 Applications of Dipole Moment Studies

First let us see how dipole moment studies help us redefine polar and nonpolar molecules.

Polar and Nonpolar Molecules Redefined

So far we have defined polar and nonpolar molecules based on electronegativity. Now let us define them in a different way. In Fig. 6.12 the P_M vs $1/T$ curves a, b and c are drawn for CH_3Cl, HCl and CCl_4 molecules, respectively.

You can see that total molar polarisation (P_M) increases with $1/T$ for CH_3Cl and HCl (as shown by the rising curves a and b). That is, for CH_3Cl and HCl, P_M against $1/T$ curves have finite**, positive slope**. Such behaviour is characteristic of polar molecules. Since the polar molecules have a finite positive slope for the plot, P_M against $1/T$, these molecules have a finite dipole moment value too, as per Eq.6.13. But, for CCl_4, the molar polarisation is constant at all temperatures (as shown by the curve c which is parallel to *x*-axis, denoting zero slope value), and such molecules are nonpolar.

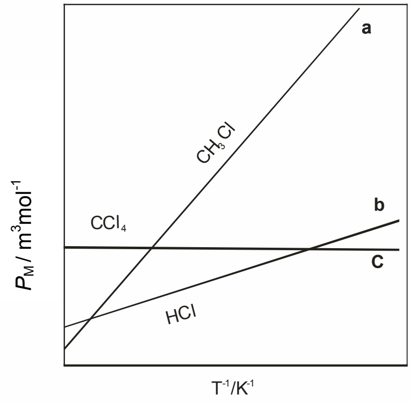


Fig. 6.13: P_M against $1/T$ plot for CH_3Cl (a), HCl (b), and CCl_4 (c).

In other word, for polar molecule, the molar polarisation increases with decrease in temperature; for nonpolar molecules, the molar polarisation does not depend on temperature.

Percentage Ionic Character

In the last sub-section, we defined polar and nonpolar molecules based on dipole moment values. It is interesting to see how percentage ionic character of a polar molecule can be calculated using dipole moment values. Consider for example, HCl molecule again, for which the observed dipole moment (μ_{observed}) is 3.57×10^{-30} C m. But, if it were 100% ionic, the bonding electron pair should have completely moved to chlorine. Then there should be a negative charge (of magnitude 1.602×10^{-19} C) on chlorine and an equal positive charge on hydrogen, both being separated by the bond distance of 127.5 pm. We have seen the actual charge on hydrogen and chlorine in hydrogen chloride molecule is less than 1 electron charge. For this situation, dipole moment can be calculated using Eq. 6.6 and represented as $\mu_{\text{calculated}}$.

A polar molecule has a permanent dipole moment and for a nonpolar molecule, $\mu = 0$.

$$\mu_{\text{calculated}} = 1.602 \times 10^{-19}\ \text{C} \times 127.5 \times 10^{-12}\ \text{m} = 20.42 \times 10^{-30}\ \text{C m}$$

Thus, values of observed dipole moment and calculated dipole moment are not same.

We can estimate the % ionic character using the relationship,

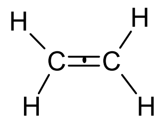
$$\text{Percentage Ionic character} = \frac{\mu_{\text{observed}} \times 100}{\mu_{\text{calculated}}}\,\% \qquad \text{...(6.13)}$$

$$\text{Hence, ionic character in HCl} = \frac{3.57 \times 10^{-30}\ \text{C m} \times 100}{20.42 \times 10^{-30}\ \text{C m}} = 17.5\,\%$$

Structure Elucidation

As mentioned earlier for polyatomic molecules, different bonds have different dipole moments. It must be borne in mind that the dipole moment is a vector quantity and in a molecule, it is the vector sum of dipole moments of all bonds. By bond dipole moment or bond dipole, we mean the moment associated with a chemical bond. Again, the absence of a permanent dipole moment in a molecule may be due to the fact that either all the bonds present are nonpolar or the individual bond dipoles add vectorially to zero. In the case of a molecule with a centre of symmetry, dipole moment will be zero. Therefore dipole studies can help us in predicting correct molecular polarity and the geometry as well if we know the dipole values.

If at equal distances from a particular point in the structure of a substance, you find identical groups in opposite directions, the structure is said to have centre of symmetry. Ethylene molecule has a centre of symmetry. In its structure, atoms which are identical and equidistant from the centre as shown below:



It is quite easy to calculate dipole moment for diatomic molecules using Eq. 6.6. For a simple triatomic molecule like H_2O or CO_2, the dipole moment can also be calculated using the parallelogram method of addition of vectors. This method provide following equation to calculate angles between two dipoles (bond angle) to understand the structure of triatomic molecules:

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta \qquad \text{...(6.14)}$$

Where *μ is the dipole of a triatomic molecule,* μ_1 and μ_2 are dipoles of two bonds, if, μ_1 and μ_2 are equal than Eq. 6.14 can be written as:

$$\cos\theta = \frac{\mu^2 - (2\mu_1^2)}{2\mu_1} \qquad \text{...(6.14)}$$

Usually, bond angle values calculated using dipole moments in such cases are close agreement with theoretical values and thus quite useful in predicting structure of such molecules. But for higher poly atomic molecules, such predictions are not as accurate.

Let us consider some examples of tratomic molecules.

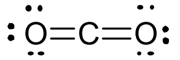
i) Let us take up the structure of carbon dioxide. The bond dipole moment C=O bond ($\mu_{C=O}$) is 7.67×10^{-30} C m. But the dipole moment of carbon dioxide (μ_{CO_2}) is zero. It implies that the two C=O bond moments nullify each other, acting in opposite directions. To prove this fact, the bond angle between carbon and two oxygens, θ can be calculated using Eq. 6.14:

$$\cos\theta = \frac{\mu_{CO_2}^2 - 2\mu_{CO}^2}{2\mu_{CO}^2}$$

$$\text{or} \qquad \cos\theta = \frac{\mu_{CO_2}^2}{2\mu_{CO}^2} - 1 = \frac{(0\ \text{C m})^2}{2(7.67\times10^{-30}\ \text{C m})^2} - 1 = -1$$

$$\theta = \cos^{-1}(-1) = 180^\circ$$

That is, carbon dioxide molecule is linear. It is worth noting that this molecule has a centre of symmetry and evidently its dipole moment is zero.



Carbondioxide

In the structure of CO_2, the carbon atom is at the centre of symmetry.

ii) Let us now study the structure of water. The bond moment, μ_{OH} and the dipole moment μ_{H_2O} are reported to be 5.02×10^{-30} C m and 6.14×10^{-30} C m, respectively. Again using Eq. 6.14 of dipole moments, we can calculate the bond angle θ between oxygen and two hydrogens.

$$\cos\theta = \frac{\mu_{H_2O}^2 - 2\mu_{OH}^2}{2\mu_{OH}^2}$$

$$\text{or } \cos\theta = \frac{\mu^2_{H_2O}}{2\mu^2_{OH}} - 1 = \frac{(6.14\times10^{-30}\ \text{Cm})^2}{2\times\ (5.02\times10^{-30}\ \text{Cm})^2} - 1 = -0.2520$$

$$\theta = \cos^{-1}(-\ 0.2520) = 104^{\circ}.36'$$

Thus water molecule has angular structure.

The above conclusions regarding the structure of carbon dioxide and water are in keeping with the predictions of valence shell electron pair repulsion (VSEPR) theory (This will be discussed in next unit).

iii) Again based on VSEPR theory, it is mentioned in next unit that boron trifluoride (with three bond pairs) has a planar triangular structure, whereas ammonia (with three bond pairs and one lone pair) has a trigonal pyramidal structure. Based on these structures and the vector addition of moments, boron trifluoride must have zero dipole moment whereas ammonia must have a finite dipole moment. The experimental dipole moment value for boron trifluoride and ammonia are zero and 4.871×10^{-30} C m, respectively. This proves the validity of the shapes of these molecules assigned on the basis of VSEPR theory.

SAQ 11

Is it true to say that the sulphur dioxide a liner molecule?

SAQ 12

Calculate the dipole moment of 1,3-dichlrobenzene if the dipole of the C–Cl bond 1.60 D.

6.8 SUMMARY

In this unit, we have explained some of the basic concepts of bonding with more emphasis on ionic bonding. You have learnt the following aspects of chemical bonding:

- Various factors such as effective nuclear change, ionisation energy, electron affinility and electronegativity which determine the nature of bonding in atoms.
- Characteristics of ionic solids with special reference to radius ratio rules and lattice energy.
- Continuum of bonding types.
- The difference in electronegativity between the atoms forming a bond causes polarity.
- Dipole moment is a measure of the polarity of the bond; it is related to the molar polarisation of the substance.
- Dipole moment serves as a support for VSEPR prediction.

6.9 TERMINAL QUESTIONS

1. In each of the following pairs, pick out the one with higher ionisation energy and justify your answer:
   a) K or Rb
   b) Si or Cl
2. Why are the electron affinities of noble gases positive?
3. How do you define an ionic compound, based on the concept of ionisation energy, electron affinity and electronegativity?
4. How do you predict geometry of ionic crystals?
5. Define the following terms:
   a) ion-dipole interaction
   b) radius ratio
   c) polarisation
   d) Polarising power and polarisability
   e) hydration energy
6. Which one on the following pairs would be expected to have the higher melting point? Explain
   a) NaCl or NaI
   b) NaCl or KCl
7. Between NaCl and $CaCl_2$ which one would be expected to have the higher solubility? Explain
8. Which one would be more polarisable between following pairs?
   a) fluoride ion or iodide ion
   b) O^{2-} or S^{2-}
9. Explain the reason for the following:
   a) Ionic radius of H^- ion is greater than that of F^-
   b) MnO is having higher melting point than Mn_2O_7
10. Calculate the lattice energy of magnesium chloride using the following energy values given in kJ mol^{-1}

    $\Delta H_s(Mg) = 150$; $I\,(Mg) = 738$; $I\,(Mg^+) = 1450$; $\Delta H_d(Cl_2) = 242$

    $E_A(Cl) = -348$; $\Delta H_f = -642$
11. Calculate the dipole moment of sodium chloride molecule at an intenuclear separation of 500 pm.

    [Hint: Assume $q = 1.602 \times 10^{-19}$ C].
12. The dielectric constant of carbon tetrachloride is 2.238 at 293 K. Its density is 1.595×10^3 kg m^{-3}. Calculate its molar polarisation.

    [Hint: Its molecular mass is 0.154 kg mol^{-1}]

9.10 ANSWERS

Self-Assessment Questions

1. Z^* values increase along a period; that is $Z^*_{Ne} > Z^*_{Li}$. Hence, formation of Li^+ is easier than that of Ne^+.

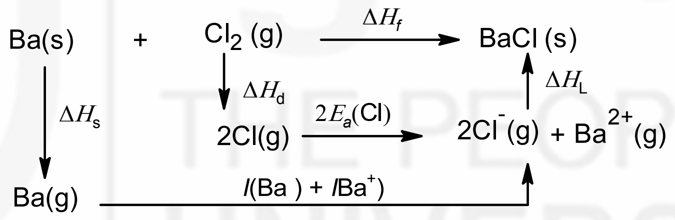
2. Carbon by accepting an electron becomes C^- ion which is now having half filled p^3 configuration on the other hand nitrogen atom is already having this stable configuration. But on adding an electron to nitrogen, it becomes partially filled and attains less stable p^4 configuration. Thus, the E_a of nitrogen is less favourable than that of carbon.

3. i) In CS_2, C-S bonds are covalent since the electronegativities of C and S are both 2.5; ii) CO bond is also covalent since the difference in electronagativities is lesser than 1.7, you can also extend your answer: as the electronegativities of C and O are not equal therefore this bond has some ionic character or in other wards it is a polar covalent bond; iii) In NaF, Na–F bond is ionic bond since the difference between electronagativities is greater than 1.7.

4. Benzene is a nonpolar solvent and cannot solvated ions as water can do.

5. The radius ratio for CaO is $r_+/r_- = 99/140 = 0.707$. Therefore, Coordination number for Ca^{2+} will be 6. This will have NaCl structure i.e. octahedral.

6. i) Born-Haber cycle for $BaCl_2$



   ii) LiF > LiCl > LiBr > LiI

   Lattice energy increases as anion size decreases. In these compounds anion size follows the order $I^- > Br^- > Cl^- > F^-$

7. The enthalpy of hydration for KCl is estimated to be

$$\Delta H_{hyd} = -322 + (-363) = -685 \text{ kJ mol}^{-1}$$

   Thus, the enthalpy of solution is

$$\Delta H_{sol} = -685 - (-715) = 30 \text{ kJ mol}^{-1}$$

   This value indicates that in this case solvation process is an endothermic cprocess. This reason when KCl is dissolved in water the temperature of solution is decreased.

8. i) Chloride ion as its size bigger than the fluoride ion.

   ii) Compounds of ions such as Sn^{4+} are always be considered to have a predominantly covalent character, therefore $SnCl_4$ is having low melting point than the $SnCl_2$.

9. The charge on iodine or hydrogen, $q = \mu/r$

   $= [0.44 \text{ D} \times 3.336 \times 10^{-30} \text{ C m} / 1 \text{ D}] / 162.0 \times 10^{-12} \text{ m} = 9.118 \times \text{I}0^{-21} \text{ C}.$

   Compared to the magnitude of the charge of an electron (1.602×10^{-19} C), the negative charge on iodine atom of HI is less than the charge of electron,

   $= 9.118 \times \text{I}0^{-21} \text{ C} / [1 \text{ e} / 1.60 \times \text{I}0^{-19} \text{ C}] = 0.057 \text{ e}$

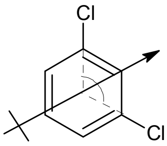
   Therefore, in the molecule, HI, the partial charge on H is +0.057 and that on the I = 0.057. Both the charges are very less than charge on an electron. This indicates that charge separation in HI is not completed similar to an ionic compound. See Subsec. 6.7.1 for more detail.

10. The units of M and ρ are kg mol^{-1} and kg m^{-3}, respectively. Relative permittivity is dimensionless. Substituting only the relevant units in Eq. 6.9, we get,

   $$P_{\text{M}} = \frac{\text{kg mol}^{-1}}{\text{kg m}^{-3}} = \text{m}^3 \text{ mol}^{-1}$$

11. Not true; it has finite dipole moment value since SO_2 is angular.

12. Consider the structure of 1,3-dichlorobenzene:



Bond angle between C-Cl bonds 120°

   Structure of 1,3-dichlorobenzene indicates that bond angle between two bond is 120°.

   Use Eq. 6.14 to calculate dipole moment of 1,3-dichlorobenzene

   $$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta = 2(1.6)^2 + 2 \times 1.60 \times 1.60 \times \cos\theta$$

   $$= 5.12 + 5.12(-0.5)$$

   $$\mu = \sqrt{2.56} \text{ D} = 1.60 \text{ D } (\mu_{\text{observed}} = 1.48 \text{ D})$$

Terminal Questions

1. a) I(K) > I(Rb); since the 4*s* electron of K, being nearer to the nucleus, is more difficult to remove than the 5*s* electron of Rb.

   b) I(Cl) > I(Si); effective nuclear charge on the valence electrons is higher for chlorine than for silicon.

2. An electron is added to a system which is already stable due to fully filled orbitals. The added electron has to go to (n +1)*s* orbital.

3. An element of low I value combines with an element of high negative E_a value, to form an ionic compound. Two elements, differing in electronegativity by more than 1.7 form an ionic compound.

4. Using radius ratio, ionic crystal geometry can be predicted.

5. i) The binding of an ion, such as Na^+, with a polar molecule, such as water, is an example of an ion-dipole interaction.

   ii) Radius ratio: in an ionic compound, the radius of the positive ion, r_+, divided by the radius of the negative ion, r_-.

   iii) This distortion from the spherical shape of the ideal anion is called polarisation.

   iv) The extent to with distortion in an anion occurs depends on the power of a cation to distort i.e. its polarising power and how easily anion is distorted i.e. its polarisability.

   v) Hydration energy of an ion is the amount of energy released when a mole of the ion dissolved in a large amount of water forming an infinite dilute solution.

6. As we know the melting process involves partially overcoming the strong ionic attraction and allowing the free movement of the ions in the liquid phase. The smaller the ions, the shorter the interionic distance, hence the stronger the electrostatic attraction among ions, and higher the melting point of ionic solids. In NaCl and NaI pair, I^- ion is having larger radius than Cl^- ion. In NaCl and KCl pair, K is having higher ionic radius. Therefore, NaCl is having higher melting points in both (a) and (b) cases.

7. NaCl is having higher solubility than $CaCl_2$. This can be explained on the basis of lattice energy values. In the case of NaCl, lattice energy value is -787 kJ mol^{-1} and in case of $CaCl_2$ it is -2258 kJ mol^{-1}. High lattice energy value means, necessity of large energy to break the crystal lattice.

8. Larger ions are easily polarisable than the smaller, therefore I^- and S^{2-} are more polarisable.

9. a) The effective nuclear charge on the valence electrons of H^- ion is less than that for F^- ion.

   b) This can be explained using Fajan's first rule. Mn (II) oxide forms ionic crystal lattice (Mn has 2+ charge), whereas Mn (VII) oxide is covalent in nature (Mn has more than 3+ charge).

10. Use Born-Haber cycle for calculation of lattice energy; lattice energy of $MgCl_2 = -2524$ kJ mol^{-1}.

11. $\mu = q \times r$

    $= 1.602 \times 10^{-19}\ (\text{C}) \times 500 \times 10^{-12}\ (\text{m}) = 8.010 \times 10^{-29}\ \text{C m}.$

12. Molecular mass of carbon tetrachloride 0.154 kg mol^{-}1 and its density is 1.595×10^3 kg m^{-3}.

$$P_{\text{M}} \frac{\varepsilon_r - 1}{\varepsilon_r - 2} \times \frac{M}{\rho} = \frac{(2.238 - 1)}{(2.238 + 1)} \times \frac{0.154\,\text{kg mol}^{-1}}{1.595 \times 10^3\,\text{kg m}^{-3}} = 2.820 \times 10^{-5}\ \text{m}^3\,\text{mol}^{-1}$$

UNIT 7

COVALENT BOND

Structure

7.1 INTRODUCTION

In the previous unit you have learnt about ionic bond which, according to Kossel's theory of bonding, is formed when one or more electrons are transferred from one atom to another atom in the process of bond formation. However, the vast majority of chemical substances are not ionic in nature. It was proposed by G.N. Lewis that an atom might attain a stable noble gas electron configuration by sharing electrons to form a covalent bond. In this unit you will learn about the formation of a covalent bond and writing the Lewis structure of a covalent molecule. The Valence Shell Electron Pair Repulsion Theory (VSEPR) that describes the shapes of molecules is explained in detail. The covalent bond parameters like length and strength and the properties exhibited by the covalent compounds would also be discussed here.

In addition to the classical approaches of Kossel and Lewis towards chemical bonding, based on attainment of stable noble gas configuration, two new theories emerged to explain the process of chemical bond formation on the basis of quantum mechanical approach. These modern theories called the Valence Bond Theory and The Molecular Orbital Theory will be explained in the next two units of this block.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define covalent bond and state the characteristics of covalent compounds,
- compare the properties of covalent compounds with those of ionic compounds,
- describe Lewis concept of covalent bond formation,
- draw Lewis structures for simple molecules and ions,
- define formal charge and determine formal charge on different atoms in simple molecules and ions,
- explain the covalent bond parameters like bond length, bond strength and bond energy,
- describe the postulates of valence shell electron pair repulsion theory, and
- predict the shapes of molecules on the basis of valence shell electron pair repulsion theory.

7.2 CLASSICAL THEORY OF COVALENT BOND

Gilbert N. Lewis
(1875–1946)

You have read in the previous unit that Kossel proposed the theory of ionic bond formation. According to that theory, the bond formation is achieved by transfer of electron from one atom to the other. The electron transfer occurs in such a way that the atoms involved in the bonding acquire stable noble gas configuration. Alike Kossel, G. N. Lewis assumed that atoms attain the electronic configuration of the noble gases in the process of bond formation. However, he proposed, "sharing of a pair of electrons" between atoms as a means to achieve stable electronic configuration to form a covalent bond. This shared pair of electrons contributes towards the stability of both the atoms. Let us understand the Lewis concept of covalent bond.

7.2.1 Lewis Concept of Covalent Bond

The diatomic hydrogen molecule (H_2) is the simplest example of a molecule with covalent bond, and its formation can be represented as given below.

$$H\cdot + \cdot H \longrightarrow H:H$$

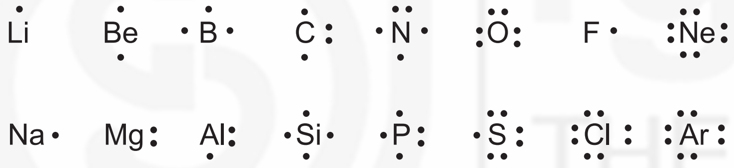
Covalent bond formation between two H atoms

In this representation both the hydrogen atoms share their valence electron to form a pair of shared electrons. This shared pair of electrons provides each hydrogen atom with two electrons in its valence shell (the 1*s* orbital). We can say that both the hydrogen atoms have the electron configuration of the noble gas helium. The electron density due to the shared pair of electrons is concentrated between the two nuclei. The attraction of the positively charged nuclei and the negatively charged electron cloud located between them is responsible for bonding of two hydrogen atoms to give H_2 molecule. A shared pair of electrons is also called the **bonding pair**. The shared pair of electrons between the bonded atoms is represented in terms of a single line between them. Thus, the covalent bond in the hydrogen molecule is represented as H-H.

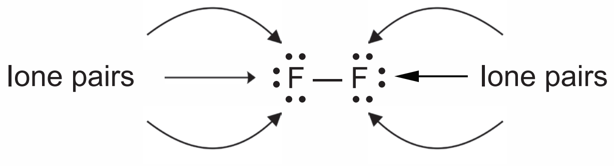
In case of many-electron atoms, only the valence electrons are involved in bonding. For example, the formation of fluorine molecule (F_2) by bonding between two fluorine atoms involves the sharing of unpaired electron in the 2*p* orbitals of fluorine atoms. The other electrons (i.e., 2*s* and remaining 2*p*) of the valence shell stay as lone pairs on fluorine atoms; there are three lone pairs of electrons on fluorine atom. The inner low energy 1*s* electrons do not participate in bond formation and stay near the nucleus. The formation of F_2 molecule can be represented as:

Covalent bond formation in many-electron atoms

You would note here that in representing the covalent bond formation between atoms, we have used Lewis electron – dot symbols. These symbols were introduced by G.N. Lewis to represent valence electrons in an atom and are called **Lewis symbols**. The symbol of the element is surrounded by the number of dots equal to the number of valence electrons in the atom. The Lewis symbols for the elements of second and third period are given as follows.



In a molecule the lone pairs belong to only one atom and are also called **nonbonding electron pair.** These lone pairs of electrons are not directly involved in bonding but are very important in affecting the shape of molecules.



We have taken the examples of two homonuclear molecules; the molecules formed by bonding between two atoms of the same element. Let us take bonding between atoms of different elements say oxygen and hydrogen to form a water molecule. The electronic configuration of oxygen is $1s^2 2s^2 2p^4$ and that of hydrogen is $1s^1$. Since, the bond formation involves the valence electrons, the unpaired 2*p* electrons of oxygen atom and the 1*s* electrons of hydrogen would be involved. The inner *s* electrons of oxygen atom do not participate in bonding. The bonding can be represented as follows.

Bonding between two different atoms

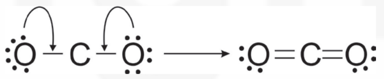
Multiple bonds

The sharing of a single pair of electrons between two atoms represents a single covalent bond, usually referred to as a single bond. In many molecules atoms attain complete octets (noble gas configuration) by sharing more than one pair of electrons between them. Sharing of two pairs of electrons gives a double bond whereas three pairs of shared electrons give a triple bond. For example, nitrogen contains 5 valence electrons and it needs to share 3 electrons to attain inert gas electronic configuration. Thus, in N_2 molecule, there is a triple bond between two nitrogen atoms.

A nitrogen molecule with three bonds

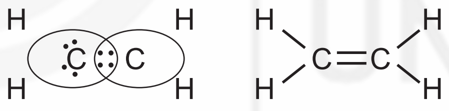
The double and triple bonds are also called multiple bonds. Nitrous acid, HNO_2, contains a N=O double bond, and hydrogen cyanide, HCN, a triple bond. A molecule may have more than one multiple bond, for example, in carbon dioxide, the central carbon atom is double bonded to two oxygen atoms.

HNO_2 with a double bond HCN with a triple bond

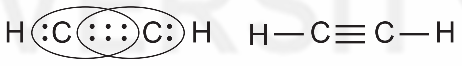


Two double bonds in a CO_2 molecule

The multiple bond formation in unsaturated hydrocarbons, ethylene and acetylene is shown below.



Double bond in ethylene



Triple bond in acetylene

As a consequence of multiple bond formation between atoms, the interatomic distance (bond distance) decreases. Therefore in N_2, where the two atoms are bonded by a triple bond, the bond distance is fairly short (110 pm) as compared to N-N single bond (147 pm). As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases. The average N-N bond distance in molecules having single, double or triple bonds are as follows:

$$\mathrm{N-N}\ (147\ \mathrm{pm}) \qquad \mathrm{N{=}N}\ (124\ \mathrm{pm}) \qquad \mathrm{N{\equiv}N}\ (110\ \mathrm{pm})$$

The representation of single, double or triple bonds between different atoms in a molecule becomes easy by writing its Lewis structure. How do we write a Lewis structure? This is discussed in detail in the next subsection. Before starting to read, try to answer the following SAQ.

SAQ 1

Draw the electron dot structure and identify the type of bond (single, double or triple) in the following molecules.

Phosphine, Bromine, Formaldehyde and Carbon monoxide

7.2.2 Writing Lewis Structures

The representation of bond formation in case of simple diatomic or triatomic molecules is quite simple and straight forward as shown above. How do we represent the bonding in larger polyatomic molecules or ions? For this we need to learn about how to write a Lewis structure that provides information about the relative placement of atoms in a molecule or ion and shows which atoms are bonded to each other. However, these do not indicate the three-dimensional shape of the molecule.

The following guidelines may be followed to write Lewis structures for polyatomic molecules or ions.

Step1 The first step is to count the total number of valence electrons present in the molecule or the ion. The number of valence electrons for an element of the main group is the same as its group number in the periodic table (or the last digit of the group number in case of IUPAC group numbers). The valence electrons of all the atoms are added to get the total number. For polyatomic anions, the number of negative charges is added to the total and for cations the number of positive charges is subtracted from this total.

Remember to put the Lewis structures for polyatomic ions in brackets and show the charge on the outside upper right(as shown in the margin).

$[:C\equiv N:]^-$

Lewis structure of anion

Generally only one arrangement of atoms is possible however; in some cases two or more structures are possible. In such cases some chemical or physical properties may be used to decide the correct structure.

Step2 The next step is to write the skeletal structure of the compound and place the bonded atoms next to one another. For this to be done we need to determine the central atom(s) of the molecule or ion. The central atom is usually the least electronegative atom of the species. The hydrogen atom being an exception as it is never the central atom in amolecule. Similarly, fluorine also occupies the terminal positions in the Lewis structure of the molecule.

Step3 As the atoms must be bonded by at least a single bond, draw a single covalent bond between the central atom and each of the surrounding atoms. Subtract two valence electrons for each bond so formed from the total number of valence electrons obtained is Step 1 and distribute the remaining electrons (in pairs) to atoms surrounding the central atom (or atoms)so as to complete their octets (duet in case of hydrogen).While completing octets, the shared electrons are counted for both of the bonded atoms.

Step4 Distribute the remaining electrons in pairs to the central atom or atoms after subtracting the number of electrons already distributed from the total valence electrons. The distribution is first done on the peripheral atoms and then on the central atom.

Step5 If the central atom has lesser than eight electrons, it indicates the presence of multiple bond(s). If the central atom is short of octet by two electrons, there may be a double bond and if the shortage is of four electrons, it may be a triple bond or two double bonds. The octet on the central atom can be completed by moving one or more lone pairs of electrons from the surrounding atoms to make double or triple bonds as required.

Step 6 This step is to be applied if all the atoms have completed their octets (duet for H) and some valence electrons are still left. The leftover electrons are placed on the central atom even if they get more than 8 electrons. [The atoms from the third or a higher period can accommodate more than 8 electrons.]

Let us illustrate these guidelines with the help of examples.

Example1: Carbon dioxide (CO_2)

Step1. Total number of valence electrons:

4 (C) + (2 x 6) (O) = 16

Step2. Skeletal structure

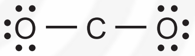
O C O (∵C is central atom as it has lower electronegativity than O)

Step3. Draw single bonds between the atoms; calculate remaining electrons

O—C—O

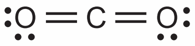
Remaining valence electrons = $16-(2\text{x}2)=12$

Step 4. Distribute the remaining valence electrons on the atoms (from periphery inwards) to complete their octets

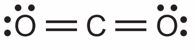


Step5. Central carbon atom has four electrons; it is short of four electrons for the octet.

We move two lone pairs (one from each O atom) to the central C atom and create double bonds.



This gives the desired Lewis structure for CO_2 molecule.



Example2: Sulphur tetrafluoride (SF_4)

Step1. Total number of valence electrons

6 (S) + (4 x 7) (F)= 34

Step2. Skeletal structure

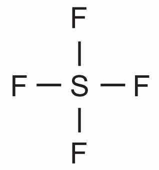
F

F S F

F

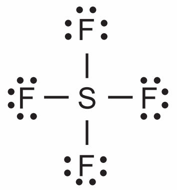
(∵ S has lower electronegativity than F, so it is the central atom)

Step3. Draw single bonds between the atoms; calculate and distribute remaining electrons



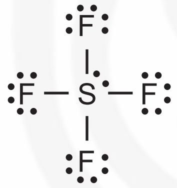
(Remaining valence electrons = 34 – (2 x 4)= 26

Step4. Distribute the remaining valence electrons on the atoms (from periphery inwards) to complete their octets



Step5. Not required as the central atom has complete octet

Step6. After completing the octets of all the atoms we are still left with two electrons (1 lone pair). This is placed on the central S atom. We get the following Lewis structure.



You can practice and remember the guidelines for writing the Lewis structure of many more molecules. You can try a few by answering the following SAQ.

SAQ 2

Draw the Lewis structures for the following molecule and ions.

i) HNO_3 ii) CO_3^{2-} iii) NH_4^+

7.2.3 Formal Charge: Predicting Preferred Lewis Structure

You have learnt above that the Lewis structures depict the distribution of valence electrons in a molecule or ion. For some molecules or ions, it may be possible to write more than one Lewis structure, each of which is consistent with the octet rule. The question arises that in such a case which of the structures is preferred? In order to write the preferred structure we can make use of the formal charges. Formal charge is a calculated quantity and is defined as the charge an atom in a molecule would appear to have if the electrons are counted in a particular way. The concept of formal charge is based on the following three assumptions:

i) All bonding electrons are shared equally between the bonded atoms irrespective of their electronegativities,

ii) The lone pairs (if any) on the bonded atom belong exclusively to it.

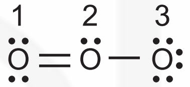
iii) The sum of the formal charges on all the atoms must be equal to the actual charge on the species; for molecules it is zero and for an ion it is equal to the charge on the ion.

On the basis of these assumptions, the formal charge on an atom in a molecule can be calculated as per the following formula:

Formal charge = No. of valence electrons of the atom – No. of unshared electrons – No. of bonding pairs

Let us take an example to learn about the application of the formula.

1. One of the Lewis structures for ozone is given below. Calculate the formal charge on different atoms in the molecule.



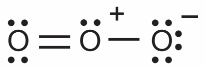
Solution: Let us label the atoms as 1, 2 and 3 starting from the left and calculate the formal charge on each one of them as per the formula.

Formal charge (atom 1) = 6 – 4 – 2 = 0

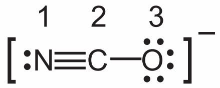
Formal charge (atom 2) = 6 – 2 – 3 = 1

Formal charge (atom 3) = 6 – 6 – 1 = –1

The total formal charge on all the atoms adds to zero as required and the molecule with the formal charges can be represented as:



2. Let us take another example and calculate the formal charges on the atoms of an ion. The Lewis structure for cyanate ion is:



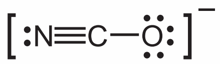
Solution: Let us label the atoms as 1, 2 and 3 starting from the left and calculate the formal charge on each one of them as per the formula.

Formal charge (atom 1) = 5 – 2 – 3 = 0

Formal charge (atom 2) = 4 – 0 – 4 = 0

Formal charge (atom 3) = 6 – 6 – 1 = –1

The total formal charge on all the atoms adds to -1, the charge on the ion. The ion with the formal charges can be represented as:



Rules for determining the preferred Lewis structure are as follows.

- Lewis structure in which there are no formal charges is preferable over the one with formal charges.
- Lewis structures with small formal charges are preferable over the ones with larger formal charges.
- Amongst the Lewis structures having similar distributions of formal charges, the one with negative formal charges on more electronegative atoms is preferred.

Example

Two possible Lewis structures for **NO** molecule are given below. Calculate the formal charge on both the atoms for the two structures and identify the preferred Lewis structure for NO on the basis of the rules outlined above.

Structure 1 **Structure 2**

Solution

Calculating the formal charges on the different atoms in structure 1 we get,

Formal charge (atom 1) = 5 – 3 – 2 = 0

Formal charge (atom 2) = 6 – 4 – 2 = 0

Calculating the formal charges on the atoms in structure 2 we get,

Formal charge (atom 1) = 5 – 4 – 2 = –1

Formal charge (atom 2) = 6 – 3 – 2 = 1

The structure 1 with no formal charges is the preferred structure.

In the next subsection, you will learn about a special type of covalent bond called the coordinate bond. This type of bond is concerned with donating or accepting a pair of shared electrons.

7.2.4 Coordinate Covalent Bonds

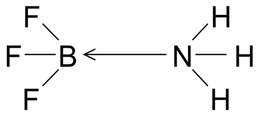
You have learnt above, that a covalent bond is formed between two atoms as a consequence of sharing of an electron each by these. In some cases a covalent bond between two atoms can arise as a consequence of the shared pair of electron being contributed by any one of the atoms. As mentioned above, this special type of covalent bond is known as **coordinate covalent bond or dative bond.** This type of bonding can happen if one of the atoms has a nonbonding pair of electrons which can be contributed for bonding and the other atom has an empty orbital that can accommodate this electron pair. The covalent and coordinate bond formation can be comparatively depicted as follows.

$A\cdot + B\cdot \longrightarrow A{:}B$ $\quad\quad$ $A + {:}B \longrightarrow A{:}B$

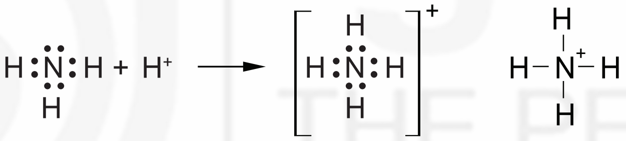
Covalent bond formation **Coordinate bond formation**

The atom contributing the lone pair is called the **donor** and the one accepting it is called the **acceptor**. The donor atom has complete octet in its configuration and the octet of the acceptor gets completed in the process of sharing. A coordinate bond between two atoms A and B is represented by an arrow pointing from the donor atom towards the acceptor atom as in $A \rightarrow B$. If in a molecule A-B, the atom A provides the electrons for bonding then it will have a formal positive charge and the acceptor atom B would have a formal negative charge. In such a case the molecule can be represented as $A^+– B^–$.

Let us consider the coordinate bond formation between the boron atom of boron trifluoride and nitrogen atom of ammonia molecule. One of the 2*p* orbitals on boron in BF_3 is empty and can accommodate the lone pair donated by the nitrogen atom of ammonia as shown below.



The difference between the coordinate bond and covalent bond is only in the way these are formed; that is, whether each atom contributes one electron or one atom contributes both the electrons of the shared pair. Once the bond is formed a covalent bond cannot be differentiated from the coordinate bond since electrons are identical regardless of their source. For example, ammonium ion is formed by the donation of a pair of electrons by ammonia molecule to a proton, once ammonium ion is formed, all four N – H bonds are equivalent.

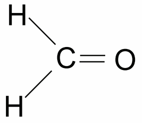


Having discussed about the formation of a covalent bond and coordinate bond as proposed by Lewis, let us look into some of the characteristics of the covalent compounds so formed. Before reading further, try to answer the following SAQ.

SAQ 3

The two possible structures of formaldehyde are given below. Calculate the formal charges and identify the more stable structure.

H–C=O–H and



7.3 CHARACTERISTICS OF COVALENT COMPOUNDS

The properties of covalent compounds are distinctly different from those of ionic compounds due to the difference in the nature of bonding and the forces of interaction between different species. In ionic compounds the ions are held together by electrostatic interactions whereas in case of covalent compounds there are two types of forces involved. These are the strong covalent bonds between the atoms and the weak van der Waal's interactions between different molecules. As the intermolecular forces are quite weak as compared to the forces holding atoms together within a molecule, molecules of a covalent compound are not held together tightly. As a consequence the covalent compounds have low melting and boiling points as compared to the ionic compounds. The organic compounds, which are largely covalent in nature are the examples. For the same reason the covalent compounds are usually gases, liquids, or low-melting solids whereas the ionic compound are usually solids at room temperature and have high melting points.

Another consequence of the difference in the nature of interactions involved is that the covalent molecules dissolve mostly in non-polar solvents like benzene, carbon tetrachloride etc., but not in polar solvents like water. On the other hand the ionic solids are more soluble in water. The water molecule although covalent has some polar character due to difference in electronegativity between oxygen and hydrogen. Therefore the ionic substances interact favourably with water and dissolve in it. We can conclude from these that the dissolution proceeds well if the solute and solvent molecules have similar type of bonding.

The ionic substances when dissolved in water generate ions as these are strong electrolytes and as a consequence the solutions are conducting in nature. On the other hand the covalent substances when dissolved in water give neutral molecular species. The interaction with water causes the disruption of weak intermolecular interactions. As a consequence the covalent substances are nonconducting in solution. A comparison of the general properties of ionic and covalent compounds is given in Table 7.1.

Table 7.1: Comparison of the Properties of Ionic and Covalent Compounds

Physical Property	Ionic Compounds	Covalent Compounds
Force of attraction	Strong force of attraction between constituent ions	Relatively weak force of attraction between molecules (van der Waals)
State of existence	Generally exist as solids e.g., common salt (NaCl(s)	Can exist as solids, liquids, or gases for example, $C_6H_{12}O_6$(s), H_2O (l), CO_2 (g). Some of the covalent substances exist as giant network structures e.g., diamond, silica (SiO_2), graphite, etc.
Boiling and Melting points	High melting and boiling points due to strong Coulombic interactions between ions	Low melting and boiling points due to weak intermolecular interactions (often exist as a liquid or gas at room temperature)

Solubility	Generally dissolve in polar solvents like water	Generally dissolve easily in nonpolar solvents like benzene
Conductance	Conducting in solid state as well as in solution due to the presence of positive and negative ions, e.g., Na^+Cl^-.	Nonconducting as consist of neutral molecules e.g., glucose, $C_6H_{12}O_6$.

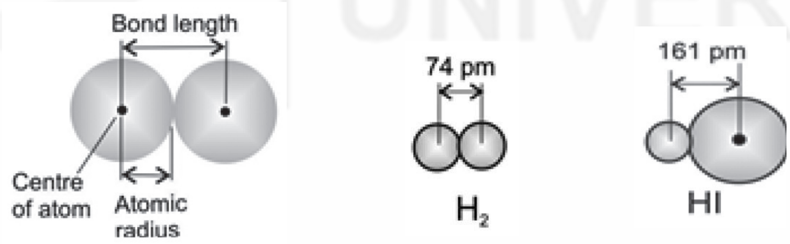
7.3.1 Bond Parameters

The covalent bonds are characterised in terms of a number of parameters. Some of these are bond length, bond strength, bond polarity and bond multiplicity. Let us understand the meaning and significance of these parameters. Let us begin with bond length.

Bond Length

As is obvious from the name, the bond length concerns the length of the bond formed between two atoms in a molecule. You have learnt in the previous unit that the ionic radii of the ions are related to interionic distance in an ionic compound. Similarly, the bond length and covalent radii of the bonded atoms are related in covalent molecules. The distance between centres of covalently bonded atoms is called **bond length or bond distance.** Bond lengths are determined by X-ray diffraction of solids, by electron diffraction, and by spectroscopic (study of light absorbed or emitted by molecules) methods. The bond lengths range from the shortest of 74 pm for H–H to some 200pm for molecules with large atoms. Half of the bond length of a single bond of two similar atoms is called covalent radius. The C–C bond distance of 154 pm in diamond is taken as standard value for C–C bond length and half its value i.e. 77 pm is the single bond covalent radius of carbon.

Bond length in diamond



Bond length in a covalent bond

The sum of covalent radii of two atoms is usually the single bond length. For example, the covalent radii of H and C are 37 and 77 pm, respectively. The C-H bond is thus (37+77) 114 pm. Similarly, the covalent radii of chlorine and bromine are 99 and 114pm, respectively. Hence, the calculated bond distance for Cl-Br (99 +114=213pm) agrees well with the experimental bond length of Cl-Br, viz., 214pm. Multiple bond radii, like C=C and C≡C, are obtained by studies in alkenes and alkynes, respectively. Some of the typical bond lengths are given in Table 7.2.

In case of multiple bond formation between two atoms, the bond length decreases. This is so because due to multiple bond formation the electron density between the atoms increases and as a consequence the atoms are pulled together more strongly. The bond lengths of the carbon-oxygen single, double and triple bonds are 143, 122 and 113 pm, respectively.

Table 7.2: Bond length (pm) and bond energy (kJ/mol) of some molecules

Bond	Length	Energy	Bond	Length	Energy
H—H	74	436	H—C	109	413
C—C	154	348	H—N	101	391
N—N	145	170	H—O	96	366
O—O	148	145	H—F	92	568
F—F	142	158	H—Cl	127	432
Cl-Cl	199	243	H—Br	141	366
Br-Br	228	193	H—I	161	298
C—N	147	308	C=C	134	614
C—O	143	360	C≡C	120	839
C—S	182	272	O—O	148	145
C—F	135	488	O=O	121	498
C—Cl	177	330			
C—Br	194	288	N—N	145	170
C—I	214	216	N=N	110	945

Bond Strength

The strength of a covalent bond is a measure of how strongly the two bonded atoms are held together? This can be expressed in terms of the amount of energy required to break a bond i.e., the bond-dissociation energy (or “bond energy”). The larger the bond energy, the stronger is the bond. The bond energy can be defined as the average enthalpy change (ΔH, heat input) associated with the breaking of a particular type of bond (in 1 mole of a gaseous substance). For example the dissociation of Cl-Cl bond in chlorine molecule can be represented in terms of the following thermochemical equation.

$$:\underset{..}{\ddot{Cl}}-\underset{..}{\ddot{Cl}}:(g) \longrightarrow 2\ :\underset{..}{\ddot{Cl}}\ (g) \qquad \Delta H = D\,(Cl-Cl) = 242\ kJ$$

As discussed above, the length of a bond between a pair of atoms decreases when the number of bonding electrons between them increases i.e., formation of the multiple bonds. This decrease is due to a stronger interaction between the atoms due to the increased electron density between these. The stronger interaction implies a stronger bond. Therefore, the multiple bonds are stronger than single bonds. This argument is supported by the experimental data as given in Table 7.2.

So far you have studied the Lewis concept of covalent bond formation, the characteristics of covalent compounds and some of their parameters. The Lewis concept is not able to explain the shapes of molecules in relation to the number of shared and lone pairs around the central atoms. Valence shell electron pair repulsion theory (VSEPR) is used to explain this. In the next section, you will learn to apply this theory in predicting the shapes of various molecules. Before that try to answer the following SAQs.

SAQ 4

In the following statements write “T” for true and “F” for false:

i) Covalent compounds are by and large soluble in nonpolar solvents.

ii) Graphite owes its electric conduction to the availability of electrons.

iii) Tap water is able to conduct electricity.

iv) Multiple bonds lead to larger bond length and lower bond enthalpy.

SAQ 5

Determine the carbon-chlorine bond length in CCl_4 and carbon–oxygen bond length in CO_2. Compute the required covalent radii using Table 7.2.

7.4 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Molecular geometry refers to the general shape of a molecule, as determined by the relative positions of the atomic nuclei.

The atoms in a molecule combine in such a manner that each atom has a definite position relative to other atoms and give rise to the specific three-dimensional structure of a molecule called the **molecular geometry.** The molecular geometry can be determined experimentally. The experiments reveal that molecules with similar formulae have distinctly different shapes. For example, BF_3 is a planar molecule whereas PF_3 has trigonal pyramidal shape. Further, the geometry of the molecule plays an important role in the reactivity and the properties of the molecule. It is, therefore, important to understand and predict the shapes of the molecules. However, the theories of bonding discussed so far do not explain anything about the shape of the molecules. The electron dot structures given by Lewis theory have no geometrical significance other than depicting the order in which the various atoms are connected to one another. **The Valence Shell Electron Pair Repulsion (VSEPR)** theory provides a way or is an approach that allows us to predict the probable structure for the molecules. The VSEPR theory was put forth by **Sidgwick** and **Powell in 1940** and was later refined and extended by **Nyholm** and **Gillespie in 1957.** This theory explains the molecular geometry by considering the nature of the central atom, the bonding electrons and the lone pairs around it and has two postulates. Let us learn about the postulates of VSEPR theory.

POSTULATE 1

The bonding and nonbonding electron pairs in the valence shell of the central atom in amolecule arrange themselves in space in such a way that they minimise their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible.

POSTULATE 2

The repulsion between two lone pairs of electrons in a molecule is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs. The order of repulsive force between different possibilities is as under.

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

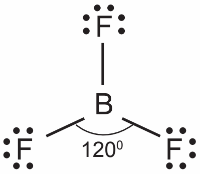
On the basis of these postulates, we can systematically predict the geometry of molecules and ions. In order to understand the approach better, it is convenient to divide molecules into following categories,

- Molecules with central atom having only bond pairs
- Molecules with central atom having bond pairs and lone pairs
- Molecules with central atom having multiple bonds

7.4.1 Central Atom Having Only Bond Pairs

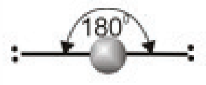
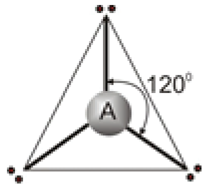
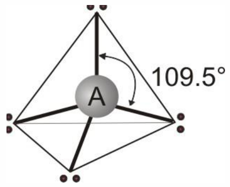
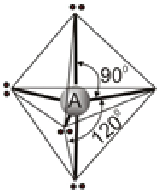
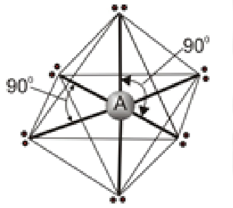
Let us take the simplest case of a molecule like $BeCl_2$having only two bond pairs in the valence shell of the central atom. In order to maximise the repulsion [postulate 1] these would try to be at the opposite sides of the beryllium atom thereby giving a linear arrangement of atoms in which the Be–Cl bonds will form an angle of 180° to one another.

You may note that the lone pairs on the Cl atoms of $BeCl_2$ are not involved in determining the molecular shape; only the bond pairs around the central atom are involved. In case the molecule has three pairs of bond pairs around the central atom (e.g., BF_3) the energetically favourable arrangement would have these bond pairs directed towards the corners of an equilateral triangle.



Similarly we can work out the energetically favourable arrangements for other molecules having molecular formula AX_n and different number of bond pairs around the central atom. The relationship between the number of bond pairs and their geometrical arrangement around a central atom is given in Table 7.3.

Table7.3: Geometric arrangements of electron pairs around central atom

Molecule type	Number of bond pairs	Predicted geometry	Examples
AX_2	2	 Linear	$BeCl_2$ $HgCl_2$
AX_3	3	 Planar trigonal	BF_3, CO_3^{2-} and NO_3^-
AX_4	4	 Tetrahedral	CH_4
AX_5	5	 Trigonal bipyramidal	PCl_5
AX_6	6	 Octahedral	SF_6

7.4.2 Central Atom Having Bond Pairs and Lone Pairs

In case of molecules with the central atom having one or more pairs of lone pair electrons in addition to the bond pairs of electrons, we have to use both the postulates. The first postulate decides the location of the electron pairs (bond pair and lone pair) around the central atom. In other words it determines the electron pair geometry i.e. the location of electron pairs around the central atom. As per the second postulate the electron pair geometry gets altered due to the difference in the extent of repulsion between the lone pairs and bond pairs etc. This determines the final molecular geometry i.e. the location of atoms around the central atom.

Let us take an example wherein we take different systems containing four electron pairs each with different combinations of lone pairs and bond pairs and look at their shape and bond angles. Methane (CH_4) contains a carbon atom to which four hydrogen atoms are connected i.e., the central atom (C) has four pairs of bonding electrons around it. As per postulate 1, the energetically favourable arrangement would be a regular tetrahedron as it would lead to the largest possible separation between the electron pairs and the corresponding bonds. The H─C─H angle would be 109.5°.

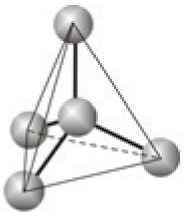
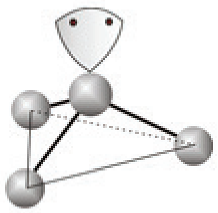
The positions of the bond pairs define the shape of the molecule although bond angle values depend on the number of both the bond pairs and lone pairs around the central atom.

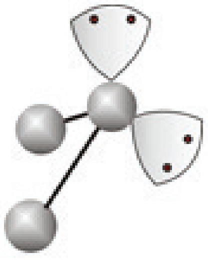
A molecule of ammonia (NH_3) contains a nitrogen atom bound to three hydrogen atoms i.e. the central atom has three pairs of bonding electrons around it. In addition, the nitrogen atom would have a pair of nonbonding electrons, completing the octet. Thus in ammonia the central atom (N) contains a total of four electron pairs i.e. three bond pairs and one lone pair. We can predict that the three bond pairs will occupy three corners of a tetrahedron centred on the nitrogen atom while the lone pair orbital will point towards the fourth corner of the tetrahedron. But due to the difference in the repulsive force between bond pair ─ bond pair and lone pair ─ bond pair, the NH_3 molecule does not have a tetrahedral shape instead it takes a pyramidal shape or a trigonal pyramid to be more accurate. The hydrogen atoms are all in the same plane with the nitrogen above or below the plane and the H─N─H bond angles are 107° each.

The single lone pair on nitrogen of ammonia and two lone pairs on oxygen of water occupy more space than the bond pairs; hence the bond pairs are compressed resulting in a bond angle reduction in ammonia and water from the regular tetrahedral angle of 109°28'.

Now we consider H_2O molecule in which the central oxygen atom is bound to two hydrogen atoms and also contains two pairs of nonbonding electrons. The four pairs of electrons (2 bonding and 2 nonbonding) would be pointed towards the four corners of the tetrahedron. But as in case of ammonia, the molecule of water will also not have pure tetrahedral shape. Due to the different order of repulsive forces between lone pair─lone pair; lone pair─bond pair and bond pair─bond pair electrons the shape acquired by water molecule at best be called as **a bent shape**. The H–O–H bond angle in water is 104.5° somewhat less than even the H─N─H angle of 107° in ammonia. The results of these examples are summarised in Table 7.4.

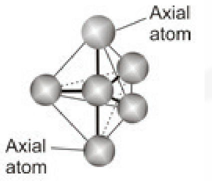
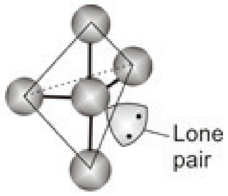
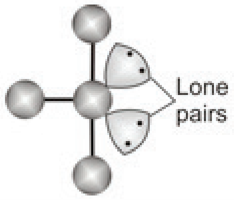
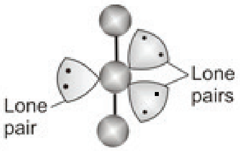
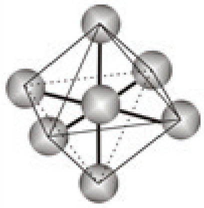
Table 7.4: Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs

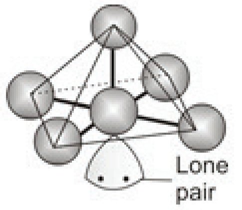
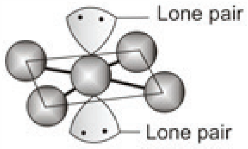
Molecule	No. of bond pairs	No. of lone pairs	Molecular geometry	Molecular shape	Bond angle in degree)
CH_4	4	0	Tetrahedral		109.5
NH_3	3	1	Trigonal pyramidal		10

H_2O	2	2	Angular or Bent		104.5

In case of elements belonging to third period and onwards, there is a possibility of expansion of octet due to the presence of empty *d*-orbitals. As a consequence there can be 5 or even 6 electron pairs around the central atom. Further, these electron pairs could be all bond pairs or a combination of bond pairs and lone pairs. Some such possibilities, their examples and the corresponding shapes predicted on the basis of the postulates of VSEPR are compiled in Table 7.5.

Table 7.5: Molecular geometries of molecules with a total of 5 and 6 electron pairs with different combinations of lone pairs and bond pairs

No. of electron pairs			**Molecular geometry**	**Molecular shape**	**Examples**
Total	**Bond pairs**	**Lone pairs**			
5	5	0	trigonal bipyramidal		PCl_5, $SnCl_5^-$
5	4	1	see-saw		$TeCl_4$, IF_4^+, SF_4
5	3	2	T-shaped		ClF_3, BrF_3
5	2	3	Linear		XeF_2, ICl_2^-
6	6	0	Octahedral		SF_6, PF_6^-

6	5	1	square pyramidal		IF5, SbF_5^{2-}
6	4	2	square planar		BrF_4^- XeF_4

As you can observe from Table 7.5, in a trigonal bipyramidal structure the lone pairs prefer more spacious equatorial positions. Thus SF_4 has see-saw shape with the lone pair occupying an equatorial position of the trigonal bipyramid. Similarly ClF_3 is T-shaped with two lone pairs occupying two equatorial positions of trigonal bipyramid while XeF_2 is linear with three lone pairs occupying three equatorial positions.

In case of octahedral geometry, a lone pair of electrons can occupy any of the six positions, since all of them are equivalent. But if there are two lone pairs, these orient themselves as far apart as possible i.e. at an angle of 180°. Thus IF_5 and XeF_4 with one and two lone pairs around the central atom have square pyramidal and square planar structures, respectively.

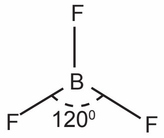
7.4.3 Central Atom Having Multiple Bonds

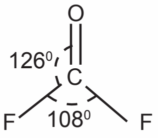
As expected, the electron pairs of multiple bonds occupy more space and are larger; the three electron pairs of a triple bond occupy more space than two electron pairs of a double bond which in turn occupy more space than the single electron pair of a single bond. However, it has been found experimentally that the two or three electron pairs of a multiple bond behave as a single electron pair in establishing molecular geometry. For example, beryllium difluoride, carbon dioxide, and hydrogen cyanide, are linear in shape.

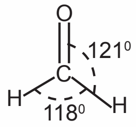
$:\underset{..}{\overset{..}{F}}-\mathrm{Be}-\underset{..}{\overset{..}{F}}:$ $\underset{..}{\overset{..}{O}}=C=\underset{..}{\overset{..}{O}}$ $H-C\equiv N:$

The linear geometry of BeF_2 is obvious as per the first postulate. In case of CO_2 the central carbon atom is surrounded by two double bonds whereas in case of HCN the carbon atom is bonded by a triple bond. It clearly shows that the molecular geometry is determined solely by the first bond pair between the bonded atoms, the second and third electron pairs in double and triple bonds do not affect the molecular geometry. Therefore, in order to qualitatively predict the geometry of a molecule, as an approximation, the double and triple bonds are treated like single bonds. The difference in the sizes of electron pair for single and multiple bonds causes deviations in the regular geometries. Let us try to illustrate this with the help of examples.

In **COF_2**, there are three effective electron pairs around the central atom and the molecule has triangular shape, like BF_3. However, in BF_3 all the bond angles are equal whereas in COF_2, the bond angles are different. The two electron pairs in C=O occupy more space and compress the F-C-F angle.







The bond pair size and also the bond angle decrease with increasing electro negativity of the atoms connected to the central atom. You can compare the bond angles in H_2CO with those of F_2CO given above. The reason for the lower value of the angle between the two C–F bonds than that between the two C-Cl bonds is the higher electronegativity of fluorine than chlorine.

As discussed above, the formation of bond in terms of sharing of a pair of electrons between the constituent atoms as proposed by Lewis, followed by the VSEPR approach provide a reasonably satisfactory idea about the number of bond pairs and lone pairs of electrons and the shape of the molecule. However, these methods do not explain how does the sharing of electrons lead to bonding or what type of electrons (e.g., *s, p* or *d*) are involved in bonding and what is the nature of the orbitals occupied by the shared electrons? These aspects are explained by modern theories of chemical bonding. These theories would be explained in the subsequent units of this block.

SAQ6

X and Y atoms have 2 and 6 valence electrons in their outermost shells, respectively, the compound which X and Y are likely to form is:

(a) XY_2 (b) XY

(c) YX_2 (d) YX_3

7.5 SUMMARY

Let us summarise that has been discussed in this unit about the covalent bond.

According to the classical theory of bonding a covalent bond is formed by the sharing of electrons between two or more atoms as a result of which the molecule attains stability. The electrons shared come from the atoms involved. The sharing leads to a single, double or a triple bond depending on whether there is one, two or three pairs of electrons shared, respectively between the two atoms. When the sharing is between two atoms of different electronegativities a polar covalent bond is obtained. When the shared pair of electrons is donated by one atom only then a coordinate covalent bond is formed. The covalent compounds have different physical properties as compared to the ionic compounds. For example, the covalent compounds have lower melting and boiling points whereas ionic compounds have higher melting and boiling points. Similarly, covalent compounds dissolve in nonpolar solvents whereas ionic compounds dissolve in polar solvents. The behaviour is explained on the basis of the forces of attraction that exist between the atoms involved in bond formation.

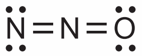
The characteristic parameters of the covalent bond include mainly the bond length and strength. Bond length is the distance between centres of covalently bonded atoms that depends on factors like the bond order. The bond length of a single bond is more than that of a double bond which is more than that of a triple bond. Bond strength is a measure of the strength of a chemical bond. The larger the bond energy, the stronger is the bond.

The classical theory of covalent bond is not able to predict the shape of the molecules. The valence shell electron pair repulsion (VSEPR) theory given by Gillespie explains molecular geometry or the three dimensional structure of a molecule considering the nature of the central atom, and the number of bonding pairs and the lone pairs of electrons around it. The shapes of the molecules vary depending on the presence of number of lone pairs of electrons. The shapes of molecules include linear, trigonal, square planar, tetrahedral, bipyramidal, octahedral, etc. The multiple bonds also show similar types of variations. There are certain shortcomings in the VSEPR approach like, it does not explain the type of electrons involved and the shape of the orbitals involved. These aspects are explained by the modern theories.

7.6 TERMINAL QUESTIONS

1. Calculate the number of covalent bonds and lone pairs on all the atoms of CH_3Br, N_2H_4 and CN^-.
2. Calculate the formal charges on the central atoms in the following:

   Carbonate ion and Xenon tetrafluoride.
3. Why tap water is able to conduct electricity?
4. Why does wax melt easily whereas the table salt does not?
5. Three possible Lewis structures for N_2O molecule are given below.

   a)  b)  c) 

   Calculate the formal charge on all the atoms for the structures and identify the preferred Lewis structure for N_2O.
6. Arrange the following four compounds in the increasing order of stability:

   CF_4, CI_4, CBr_4, and CCl_4
7. Use VSEPR theory to predict the shapes of the following:

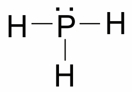
   (i) AsF_5 (ii) SO_4^{2-} (iii) CO_3^{2-}
8. Predict the shapes of the following ions:

   (i) BeF_3^- (ii) BeF_4^- (iii) IF_4^- (iv) IBr_2^- (v) GeF_3^-

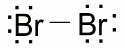
7.7 ANSWERS

Self Assessment Questions

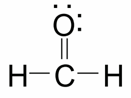
1.



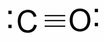
(3 single bonds)



(one single bond)

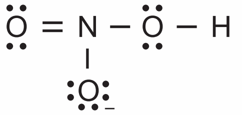


(2 single bonds
1 double bond)

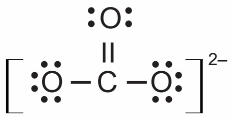


(1 triple bond)

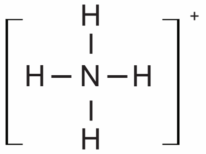
2. i)



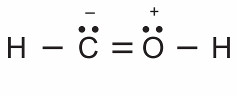
ii)



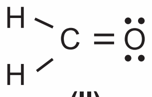
iii)



3.



(I)



(II)

Structure II being with no formal charges is more stable.

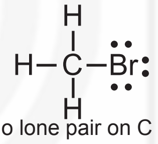
4. i) √ ii) √ iii) √ iv) ×

5. Covalent radii of single bond is half of C bond length i.e. 154/2 = 77 and Cl–Cl = 177/2 = 88.5.
Therefore bond length of C–Cl = 77 + 88.5 = 165.5 pm
Covalent radii of C=C is 134/2 = 67
Covalent radii of O=O is 121/2 = 60.5
Therefore, bond length of CO = 67 + 60.5 = 127.5 pm

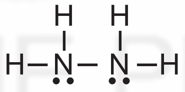
6. (b)

Terminal Questions

1.



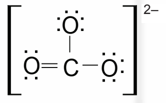
(No lone pair on C and
3 lone pairs on Br) Total
– 4 single bonds

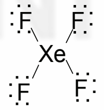


(One lone pair on N)
total – 4 single bonds
– 1 double bonds

(One lone pair on C
One lone pair on N)
total – 1 triple bonds

2.





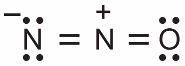
Formal charge on C = 4–0–4 = 0

Xe = 8–0–4 = 4

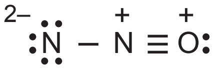
3. The tap water consists of ionisable salts from various sources which make it conducting in nature.

4. Wax is made up of organic molecules with covalent bonds in between the constituent atoms. In the compound the molecules are held together by weak intermolecular interactions that make it low melting. However, table salt is chemically sodium chloride, an ionic compound. The constituent species are held tightly by strong electrostatic interactions making it high melting.

5. The structure (c) is the most stable as the negative charge is on more electronegative O atom.



(a)



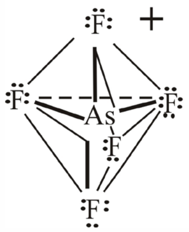
(b)

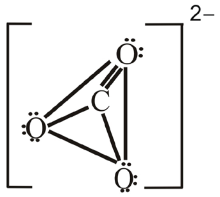
(c)

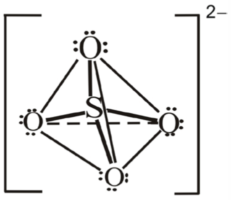
6. The stability increases in the following order:

   $CI_4 < CBr_4 < CCl_4 < CF_4$; the conclusion is based on bond enthalpy values of C – X bonds.

7. i) Trigonal bipyramidal ii) Tetrahedral iii) Triangular Planar







8. i) Planar Triangular ii) Tetrahedral iii) Square Planar iv) Linear v) Trigonal Pyramidal

UNIT 8

VALENCE BOND THEORY

Structure

8.1 INTRODUCTION

In Unit 7, covalent bond formation was explained on the basis of Lewis theory. For the same purpose, two quantum mechanical approaches namely valence bond theory and molecular orbital theory are available. These two theories seek to describe the structure of molecules, their shape and their energy. Valence bond method, proposed by Heitler and London (1927), is based on the assumption that a molecule is formed by the interaction of valence electrons and that atoms in a molecule maintain their individuality so far as the inner electrons are concerned. Molecular orbital theory, developed by Hund, Mulliken and Hückel (1930) considers the entire molecule as a new unit with all the electrons moving under the influence of all the nuclei and all the other electrons. Molecular orbital theory will be discussed in Unit 9; here we concentrate on valence bond theory.

In this unit, we shall explain the main principles of valence bond approach and apply the same to describe the structural aspects of hydrogen and other simple molecules. The concepts, resonance and hybridisation, are explained as developments in the evolution of valence bond theory. In Unit 7, shapes of some molecules were derived by using VSEPR theory. It is interesting to see how same conclusions are arrived at in a different way using hybridisation concept.

Expected Learning Outcomes:

After studying this unit, you should be able to :

- explain the principles of valence bond method and apply the same to derive the structure of hydrogen molecule,
- list and illustrate the rules of resonance,
- explain the term hybridisation and list its types, and
- explain the structures of methane, ethane, ethylene and acetylene using hybridisation theory.

8.2 THE ORIGIN OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

The two approaches, valence bond theory and molecular orbital theory, arise by the different ways of arriving at the solution of the Schrödinger equation for the molecules. The Schrödinger equation (Eq. 8.1) can be written for the molecules as in the case of atoms.

$$H\psi = E\psi \qquad \text{.... (8.1)}$$

Here *H* is the Hamiltonian operator for the system and *E* is the energy of the system.

The exact solution of Eq. 8.1 in the case of any molecule is impossible. Even for the simplest molecule hydrogen, *H* has the form,

$$H = -\frac{h^2}{8\pi^2 m}\left[\nabla_1^2 - \nabla_2^2\right] - \frac{e^2}{4\pi \in_0}\left(\frac{Z_a}{r_{a1}} + \frac{Z_b}{r_{b1}} + \frac{Z_a}{r_{a2}} + \frac{Z_b}{r_{b2}} - \frac{Z_a Z_b}{R} - \frac{1}{r_{12}}\right)$$

where,

1 and 2 denote the two electrons and *a* and *b* the two nuclei,

R is the internuclear distance,

r_{a1} distance between electron 1 and nucleus a etc.,

r_{12} is the interelectronic distance between the electrons 1 and 2,

Z_a is the charge on nucleus *a* etc.,

h is the Planck's constant

m is the mass of the electron.

In the above *H*, the kinetic energy of nuclei has not been considered as they, being too massive relative to electrons, are assumed to be stationary. This is known as **Born Oppenheimer Approximation**. The solution of Eq. 8.1 is impossible due to the presence of $1/r_{12}$ term in the Hamiltonian *H*. Therefore, one has to solve Eq. 8.1 by an approximate method.

Two types of mathematical approaches are used to solve the Eq. 8.1. These approaches differ in the manner of choosing ψ. Once ψ is constructed, the average energy *E* of the molecule can be calculated using the equation,

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad \text{... (8.2)}$$

Also E is calculated as a function of the internuclear distance R. In Eq. 8.2, ψ^* is the complex conjugate of the wave function, ψ.

In one of the approaches, known as Valence Bond (VB) method, approximate wave functions are constructed from those of the separate atoms. This approach is, in a sense, the quantum mechanical description of the Lewis concept of electron pair bond; hence the name – valence bond method. In the second approach, the Molecular Orbital (MO) method, the approximate wave functions are constructed from the molecular orbitals which in turn are constructed from the atomic orbitals of the constituent atoms. The electrons of the molecule are then assigned to these molecular orbitals on the basis of Aufbau principle. In this unit, we take up the study of valence bond approach and its application to simple molecules. We shall study the details of the molecular orbital theory in Unit 9.

8.3 PRINCIPLES OF VALENCE BOND THEORY

The main steps used in valence bond method, in arriving at the structure of a molecule, are given below :

i) Molecular wave function for the combining electrons is formed as a product of wave functions of electrons of the constituent atoms. For example, if the wave functions for 1*s* electron on each of the two hydrogen atoms are ψ_A and ψ_B, then the molecular wave function ψ is given by,

$$\psi = \psi_A . \psi_B \qquad \text{...(8.3)}$$

In other words, the **constituent atoms retain their identity** when they combine to form a molecule.

ii) Various trial functions ψ are designed, depending on the assumptions regarding molecule formation. Setting up different trial functions, indicates our attempts to describe the structure of molecule in different ways, taking into account various factors such as effective nuclear charge, resonance, indistinguishability of bonding electrons etc.

iii) Each trial function is fitted into an appropriate Schrödinger equation (Eq. 8.2) and the energy values, E, are obtained as a function of interatomic distance, R.

iv) E vs R diagrams, known as energy diagrams, are drawn for each trial function (Fig. 8.1). The curves with minima represent stabilising features for molecule formation. The difference between the total energy of the two isolated atoms and the energy corresponding to minima of the curve, gives the bond energy, calculated according to a particular trial function. The value of R at the minima point is the equilibrium interatomic distance or bond distance.

These steps are repeated for various trial functions. That trial function, for which calculated bond energy and bond distance values, agree closely with experimental values, is taken as the correct one, and the structural features assumed in designing such a trial function, are also considered valid.

In the next section, the above procedure is applied to determine the structural features of hydrogen molecule. Before we take that up, you can try the following SAQ.

SAQ 1

What are the deciding factors in choosing a particular trial function for a molecule?

8.4 VALENCE BOND THEORY OF HYDROGEN MOLECULE

In this section, we will apply the principles of valence bond theory, discussed in the last section, to the case of H_2 molecule.

We shall begin with two hydrogen atoms far apart so that no appreciable interaction between them occurs. Let us assume that the total energy of these two hydrogen atoms is represented by the point L in Fig. 8.1. Arbitrarily this has been placed on the zero of the scale. Although the two hydrogen atoms are identical, for the sake of convenience, we may label the electrons as 1 and 2 and the nuclei as A and B; the orbital wave functions of the two electrons 1 and 2 contained in two hydrogen atoms A and B would then be given by $\psi_A(1)$ and $\psi_B(2)$, respectively. Using Eq. 8.3, the trial molecular wave function for the hydrogen molecule (in reality a system of two separated H atoms) can be written as,

$$\psi_1 = \psi_A(1).\psi_B(2)$$

Using the above wave function in Eq. 8.2, the energy *E* of the system comprising two identical hydrogen atoms can be calculated as a function of the internuclear distance *R*. From the values of *E* and *R*, energy diagram 8.1a is drawn. The energy difference between L (total energy of the two isolated hydrogen atoms) and the minima of the curve 8.1a, gives the calculated bond energy of 24 kJ mol^{-1}. The equilibrium interatomic distance is calculated to be 90 pm. But the actual bond energy and interatomic distance for hydrogen molecule are 436 kJ mol^{-1} and 74 pm, respectively.

At the equilibrium interatomic distance r_0, a molecule has a stable existence. At interatomic distance greater than or less than r_0, it is less stable.

This means that the assumption used in trial function ψ_1 that electron 1 resides on hydrogen atom A and electron 2 resides on hydrogen atom B is not acceptable.

A refined wave function, ψ_{cov} , is then designed which allows for either of the electrons to reside on either of the hydrogen atoms. Also it is assumed that the two electrons are shared equally since the atoms are identical. This trial function is called ψ_{cov} to denote covalent bonding.

$$\psi_{cov} = \psi_A(1).\psi_B(2) + \psi_A(2).\psi_B(1) \quad ...(8.4)$$

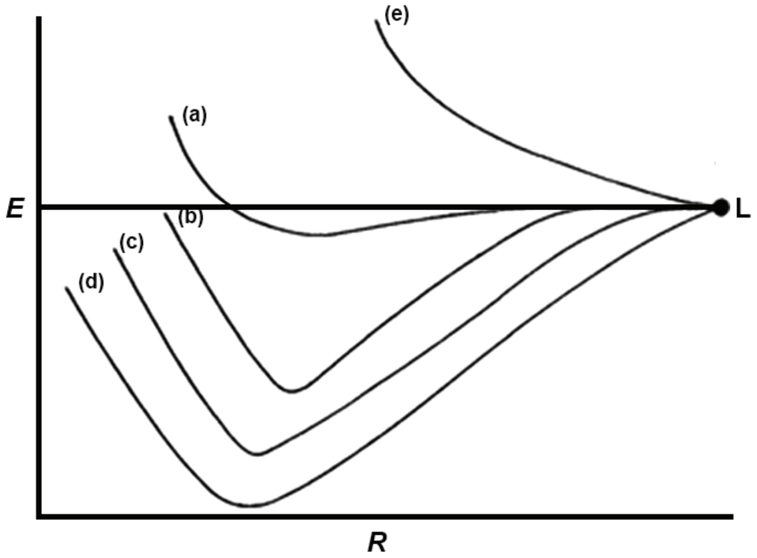


Fig. 8.1 : Theoretical energy curves (a-c, e) for hydrogen molecule compared with the experimental curve (d).

This trial function ψ_{cov} is tried in Eq. (8.2) in place of ψ and energy values at different R values are obtained. The bond energy and bond distance, according to this calculation are 303 kJ mol^{-1} and 86.9 pm, respectively. The E vs R curve is shown in Fig. 8.1(b). This trial function again requires further refinement.

A wave function ψ_2, is then designed keeping in mind the following features:

i) The two electrons mutually shield one another from the nuclear charge. Hence, the effective nuclear charge value Z^* must be used, instead of $Z = 1$.

ii) Hydrogen molecule can be given covalent structure (I) and ionic structures (II and III) as shown below :

$$\underset{\text{I}}{H:H} \qquad \underset{\text{II}}{\overset{-}{H}:\overset{+}{H}} \qquad \underset{\text{III}}{\overset{+}{H}:\overset{-}{H}}$$

The wave function corresponding to ionic forms is given by,

$$\psi_{ion} = \psi_A(1).\psi_A(2) + \psi_B(1).\psi_B(2) \qquad \ldots (8.5)$$

The first term in the right hand side denotes a situation, when both the electrons are on hydrogen atom A, and the second term, when the two electrons are on hydrogen atom B. The structures (I - III) are called canonical or resonating structures and the actual structure is the resonance hybrid of all these three structures. You will study more about resonance in the next section. This mixing of ionic and covalent forms is called ionic - covalent resonance.

A combined wave function ψ_2 is formed using ψ_{cov} and ψ_{ion} as follows :

$$\psi_2 = C_1\,(C_2\,\psi_{cov} + C_3\,\psi_{ion}) \qquad ..(8.6)$$

In this equation, C_1, C_2 and C_3 are constants depending on how much of the ionic wave function is mixed with the covalent wave function. When the wave function ψ_2 is used in Eq. 8.2, and energy values calculated for various values of R, curve of the type 8.1(c) is obtained. The bond energy and bond distance values, according to this calculation, are found to be 388 kJ mol^{-1} and 74.9

pm, respectively. Thus the addition of new terms to the trial function, brings the bond energy and bond distance values closer to experimental values. The resonance structures (I - III) seem to describe the structure of hydrogen molecule much better than covalent structure (I) alone. In Table 8.1, a summary of bond energy and bond distance values, obtained for trial functions mentioned above, is given.

Table 8.1 : Bond Energy and Bond Distance For Various Trial Functions of Hydrogen Molecule

	Trial Function	**Energy**	**Distance**	**Curve representing trial function**
Type	**Significance**	**(kJ mol^{-1})**	**(pm)**	
ψ_1	A system of two isolated H atoms; two electrons are distinguishable	24	90	8.1a
ψ_{cov}	Covalent structure and indistinguishable electrons	303	86.9	8.1b
ψ_2	Effective nuclear charge and ionic-covalent resonance recognized.	388	74.9	8.1c
Experimental curve		436	74	8.1d

A trial function, combining as much as 100 terms, has been found to yield bond energy and bond distance values almost equal to experimental values. The energy diagram corresponding to experimental values is given in Fig. 8.1(d).

Valence bond theory throws light on the fact that no bond is 100% ionic or 100% covalent. It is further inferred that the electron density distribution is symmetrical about the axis passing through the nuclei, Fig. 8.2. Such bonds, with symmetrical electron density about internuclear axis, are called σ bonds.

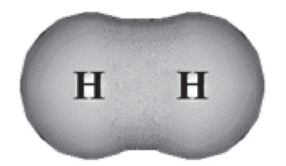


Fig. 8.2: σ bond in hydrogen molecule.

In constructing atomic wave functions such as $\psi_A(1).\psi_B(2)$ etc., the spins of combining electrons have been assumed to be opposite. Hence hydrogen molecule formation can also be considered as a process of spin pairing. On the other hand, if the two H atoms approach in such a way that the spins are in the same direction, then the net force of interaction is strongly repulsive. As two hydrogen atoms having same spin value approach each other, the energy of the system increases. This situation is indicated by the curve 8.1 (e). Try the following SAQ, to see if you have understood the ideas developed above.

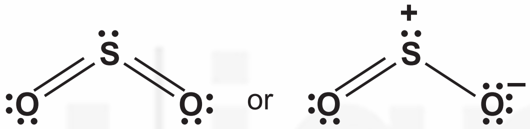
SAQ 2

Explain the fact that for H_2 molecule, covalent structure is more important than ionic structures. (Hint: Use the bond energy values).

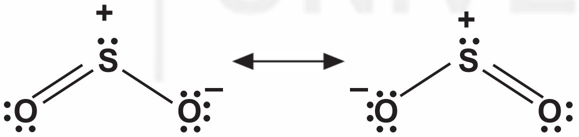
8.5 RESONANCE OR ELECTRON DELOCALISATION

Sometimes the properties of a molecule or ion are not adequately represented by a single Lewis structure. In the last section, we saw how the structure of hydrogen could not be represented by one of the three structures (I), (II) and (III) alone and had to be conceived on the basis of contribution from all the three. Such structures are known as resonance structures. They differ in the arrangement of electrons, keeping the atomic arrangement the same.

Let us take another example; say sulphur dioxide.



The charges represented are formal charges, which you studied in section 7.2.3 of Unit 7. According to the above structure, the two sulphur-oxygen bonds must be of different types, one being a single bond and the other a double bond. But in sulphur dioxide molecule, both the bonds are of same length. So in the case of this molecule also, two or more valence bond structures such as (IV) and (V), have to be used to depict the molecule. The molecule is said to be a resonance hybrid of the structures (IV) and (V), which are in turn known as resonating or canonical structures.



IV **V**

The actual structure of sulphur dioxide does not correspond to either of the resonance structures alone; but it is intermediate between these two resonance structures. There is only one type of sulphur dioxide molecule and it can have only one structure. The electrons do not flip within the molecule; i.e., for no moment of time, the molecule has any one resonance structure. The two resonance structures of sulphur dioxide are equivalent. But in some cases, like hydrogen chloride, all the resonance structures may not be equivalent.

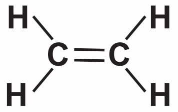
A π bond is formed by the lateral (sideways) overlap of atomic orbitals. The electrons giving rise to a π bond arc called π electrons

VI **VII** **VIII**

The ionic - resonance structures, having lower bond order value than covalent structures, are of less importance. Thus, ionic structures (VII) and (VIII) of hydrogen chloride having zero bond order are of less importance than covalent structure (VI) having bond order value of one. This is due to the involvement of σ electrons which is rarely significant in resonance structures. Resonance structures in majority of cases, involve variable distribution of π electrons. Hence, resonance is also known as delocalisation of π electrons.

Localisation of π electrons means fixing π electrons between two particular atoms, as in ethylene

Double bond in alkenes is said to be localised since its location is fixed between two particular carbon atoms.



Ethylene

Compounds like benzene and naphthalene have a delocalised π electron structure which means π electrons are not fixed between any two particular carbon atoms.

The percentage contribution each resonating structure makes to the resonance hybrid indicates how far the characteristics of the molecule are explained by a particular structure.

Benzene **Naphthalene**

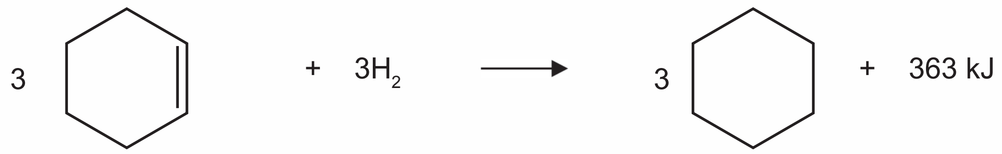
π electron delocalised over all the carbon atoms.

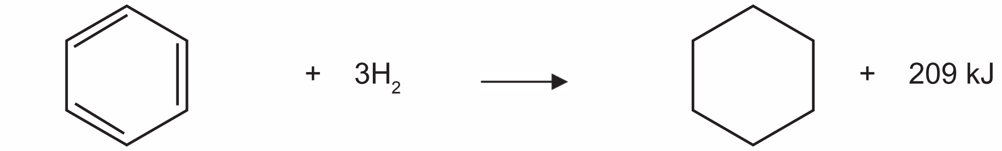
Some structures may be of lower energy than others and hence make major contribution to the hybrid. The resonance forms must be evaluated to determine their importance and relative contribution to the resonance hybrid. The percentage contribution, that each resonance structure makes to the resonance hybrid, is derived by the solution of Schrödinger equation, set up for the molecule.

The stabilisation, a molecule or ion attains, due to contributing resonance structures, is described in terms of resonance energy. A substance that has a considerable resonance energy is said to be resonance stabilised. As an illustration, let us calculate resonance energy for benzene. The resonance energy for benzene is the difference between the heat of hydrogenation calculated for a structure with three localised double bonds and the experimental value. The heat of hydrogenation for the localised structure of benzene is calculated on the assumption that the three double bonds of benzene add on hydrogen like three molecules of cyclohexene. That is, the calculated heat of hydrogenation of benzene is thrice the heat of hydrogenation of cyclohexene (363 kJ). But the experimentally determined heat of hydrogenation of benzene is 209 kJ mol^{-1}.

The heat of hydrogenation is the quantity of heat evolved or absorbed when one mole of an unsaturated compound adds on hydrogen.

The difference between the calculated and the experimental values of heat of hydrogenation for benzene is (363 -209 =) 154 kJ mol^{-1}. Thus, the resonance energy of benzene is 154 kJ mol^{-1}. Compared to this, the resonance energy of naphthalene is 315 kJ mol^{-1}. Hence, naphthalene has greater resonance





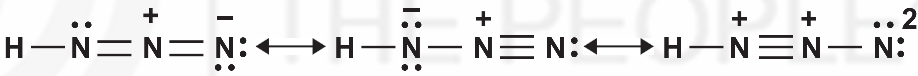
stability than benzene.

Let us now see the rules that are useful in deciding the relative importance of resonance structures of a molecule or ion.

1) The resonance forms of a given species differ in the arrangement of electrons, and not in the arrangement of nuclei.

   Thus for carbon dioxide, having the arrangement of atoms as OCO, the structure, OOC, is not a resonance structure.

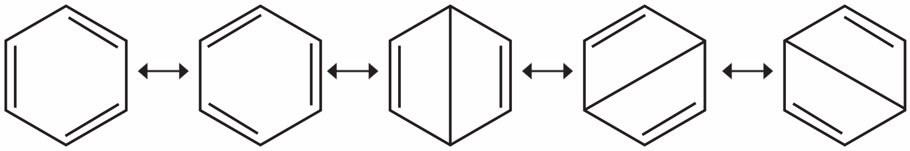
2) In case resonance structures have charge separation, two atoms that are bonded together should not have formal charges with the same sign. The contributing structures should be so written that unlike charges reside on neighboring atoms. This rule can be illustrated by writing various resonance structures for HN_3 . The last structure is quite insignificant because of the positive charge on adjacent N atoms and double negative charge on the third nitrogen atom.



$$H-\ddot{N}=\overset{+}{N}=\overset{-}{\underset{\cdot\cdot}{N}}\!: \longleftrightarrow H-\overset{-}{\underset{\cdot\cdot}{\ddot{N}}}-\overset{+}{N}\equiv N\!: \longleftrightarrow H-\overset{+}{N}\equiv\overset{+}{N}-\overset{2-}{\ddot{N}}\!:$$

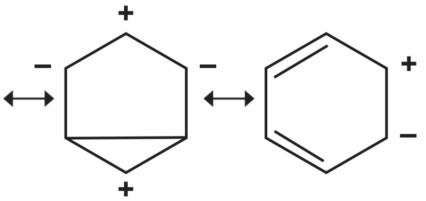
IX **X** **XI**

3) The structures without formal charges are more important than those with formal charges. For benzene, the resonance structures of Kekule (XII and XIII) and Dewar types (XIV-XVI) which do not have formal charges are more important than the ionic structures (XVII and XVIII).



XII **XIII** **XIV** **XV** **XVI**

Kekule structures **Dewar structures**

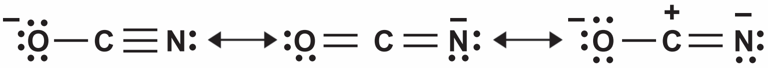


XVII **XVIII**

Ionic structures

4) While giving formal charges, the more electronegative atom should carry a formal negative charge and the less electronegative atom should carry a formal positive charge. Thus, of the resonance structures of hydrogen chloride, structure (VIII) is less important since the more electronegative atom chlorine has a formal positive charge.

5) The resonance forms of a molecule or ion have usually the same number of shared electrons. Of the three structures (XIX - XXI) for cyanate ion, (XXI) is less important as a resonance structure, since it has only three shared pairs. The other two structures (XIX) and (XX) have four shared pairs each.



XIX XX XXI

6) Resonance hybrid is said to be stabilised if two or more of its resonating structures are energetically equivalent. The two Kekule structures of benzene which are equivalent are largely responsible for its considerable resonance energy and resonance stabilisation.

7) Delocalisation of electrons in an unsaturated system is maximum when the molecule is coplanar.

Isomers have individual existence; resonating structures do not have.

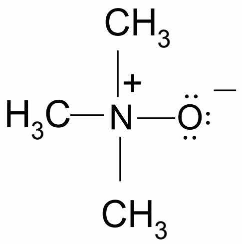
Diffraction is the bending of light rays over the edges of an object. The diffraction of X-rays is maximum in places of atomic sites. X-ray diffraction helps in the location of atomic sites.

Benzene, a resonance stabilised molecule, has been found to be a planar molecule with equal electron density around six carbon atoms, as per X-ray diffraction studies. On the other hand, bicyclohexadiene, an **isomer of benzene**, is not much resonance stabilised due to its nonplanarity.

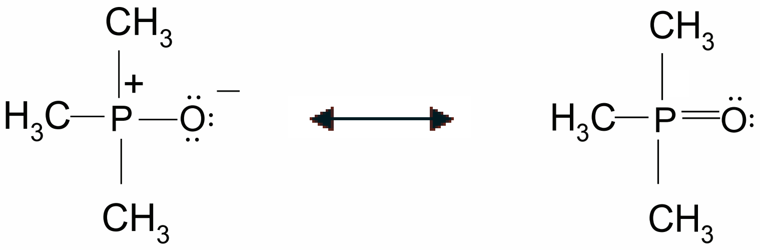
Bicyclohexadiene **Very minor**

8) The compounds of third and higher period elements can have resonance structures involving *d* orbitals whereas those of second period elements do not have. The compounds of phosphorus and sulphur, for example, exhibit resonance structures involving *d* orbitals. These two elements in their compounds can expand their outer shells to more than eight electrons. This behaviour is not expected of compounds of second period elements such as nitrogen due to nonavailability of *d* orbitals.

Trimethylamine oxide, for example has only a single structure while trimethylphosphine oxide has two resonance structures.

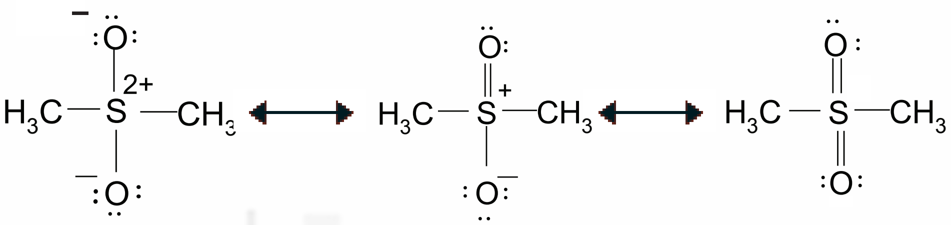


Trimethylamine oxide; resonance structures not possible.



Trimethylphosphine oxide

Similarly, dimethylsulphone has the following resonance structures :



Dimethylsulphone

Using the above rules, attempt the following SAQ

SAQ 3

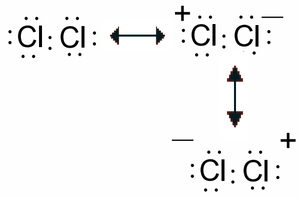
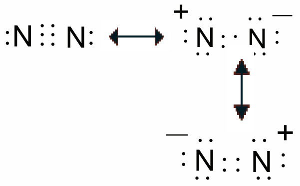
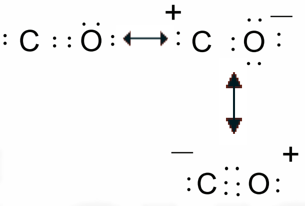
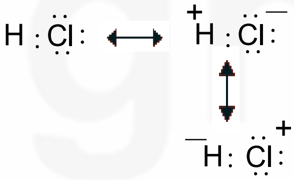
Write the resonance structures of nitrate ion. (Hint: Start with Lewis structure of NO_3^- ion).

8.6 VALENCE BOND DESCRIPTION OF SOME MORE MOLECULES

Valence bond method can be applied to describe the structure of many covalent molecules. According to valence bond method, whenever we have two atoms, each with at least one unpaired electron, they may unite to form a bond in which these two electrons are paired. In order to arrive at the structure of a molecule, various trial functions are designed, as was done in the case of hydrogen molecule, till a satisfactory trial function, which can explain the properties of the molecule, such as bond energy and bond length, is obtained. The structural features corresponding to the acceptable trial function are taken into account while describing the actual molecular structure.

The resonance structures of some molecules, obtained using the above procedure, are given in Table 8.2.

Table 8.2: Valence Bond Structures of Some Molecules

Molecule	Electron configuration of the combining atoms	Unpaired electrons	Resonance Structures
Cl_2	Cl $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$	$3p_z$ electron in each chlorine atom	
N_2	N $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	$2p_x$,$2p_y$,$2p_z$ electrons in each nitrogen atom	
CO	C $1s^2 2s^2 2p_x^1 2p_y^1$ O $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	$2p_x$ and $2p_y$ electrons of carbon and $2p_y$ and $2p_z$ electron of oxygen	
HCl	H $1s^1$ Cl $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$	$1s^1$ electron of hydrogen and $3p_z$ electron of chlorine	 **(VIII)** VIII is of little importance since chlorine has higher electronegativity

Based on the above principles, we would be tempted to give the following structures for oxygen molecule:

But these structures do not explain the experimentally known paramagnetic character of oxygen. Let us see if molecular orbital theory, which we are going to study in next unit, is able to explain this behaviour of oxygen.

In the next section, we shall see hybridisation of orbitals which is another aspect of valence bond theory. Using the above principles, attempt the following SAQ.

SAQ 4

Explain valence bond structures of fluorine molecule.

8.7 HYBRIDISATION OF ORBITALS

Principles of valence bond theory used so far in describing the structure of molecules, are not sufficient to explain the structure of methane. The electron configuration of carbon in the ground state is $ls^2 2s^2 2p_x^1 2p_y^1$. The concepts of valence bond approach enunciated above predict the pairing of two unpaired electrons in $2p_x$ and $2p_y$ orbitals of carbon with 1*s* electron of each of the two hydrogen atoms to form CH_2 molecule. But CH_2 is not a stable molecule. The simplest stable hydrocarbon is methane, CH_4. How are we to explain this?

To reconcile the valence bond theory with experimental evidence, Pauling devised a model in which one of the 2*s* electrons of carbon atom is promoted to the empty $2p_z$ orbital. The 2*s* and three 2*p* orbitals of carbon atom are mixed to form four equivalent orbitals, known as sp^3 hybrid orbitals. The axes of sp^3 orbitals are oriented in space, toward the corners of a regular tetrahedron. That is, the angle between any two orbital axes is 109° 28' [Fig. 8.3(a)]. The process of mixing two or more orbitals of different energies to give an equal number of new hybrid orbitals of lower energy is known as hybridisation. Anyhow, it should be remembered that hybridisation is a mathematical concept. The promotion of electrons to higher levels and mixing of orbitals are both mental construction which are useful in thinking about bond formation.

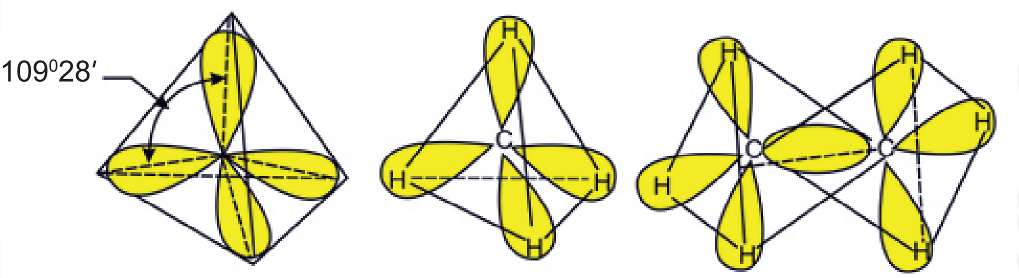


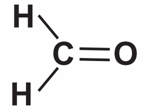
Fig. 8.3 **a) Four sp^3 atomic orbitals for carbon (small back lobes of orbitals omitted)** **b) Tetrahedral structure of methane** **c) Structure of ethane**

The most acceptable trial function for methane indicates that the hybrid orbital has one-fourth *s* character and three-fourth *p* character. The four unpaired electrons in the four sp^3 hybrid orbitals of carbon, combine with 1*s* electron of each of the four hydrogen atoms, to form four σ bonds. The energy liberated in the formation of four C–H bonds is more than that required for:

i) the promotion of 2*s* electron to $2p_z$ orbital.

ii) mixing *s* and *p* orbitals.

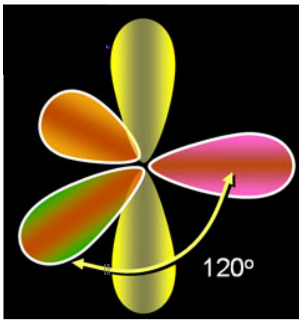
iii) keeping the four unpaired electrons free from mutual or orbital spin interactions.



Formaldehyde

Methane is tetrahedral in shape, Fig. 8.3b, with a bond angle of 109°28'. In section 7.4 of last unit, we derived the same conclusion based on VSEPR theory. In ethane, (Fig. 8.3c), and in other higher alkanes also, carbon atoms are in sp^3 hybridised state. The C–C bond length in ethane has been found to be 154 pm. The covalent radius for sp^2 hybridised carbon is 77 pm.

Let us now focus our attention on the structure of ethylene. One of the 2*s* electrons in each of the two carbon atoms is promoted to the empty $2p_z$ level as before. The 2*s*, $2p_x$ and $2p_y$ orbitals are hybridised to yield three sp^2 hybrid orbitals (Fig. 8.4a). The $2p_z$ orbital is not used for hybridisation. Each sp^2 hybrid orbital has one-third *s* character and two-third *p* character.



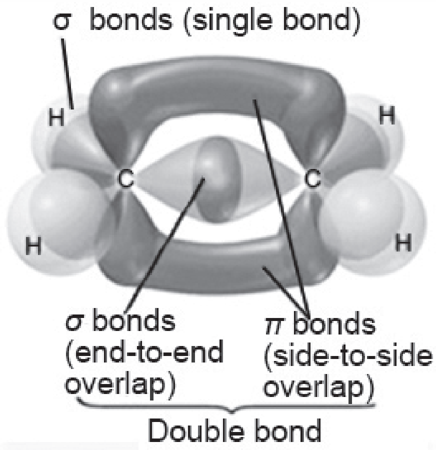
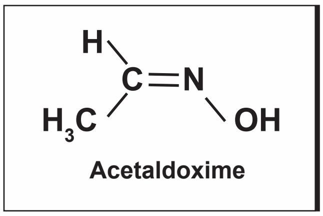


Fig. 8.4 **a) Diagram illustrating the three trigonal *sp*² hybrid orbitals of the carbon atom (coloured), which lie in the same plane and the one unhybridised *p* orbital which is perpendicular to the plane.**

b) Structure of ethylene



Acetaldoxime

Each of the two carbon atoms in ethylene forms three σ bonds, two σ bonds being formed with two hydrogen atoms and one σ bond with the other carbon atom. The fourth bond, a π bond, is formed by the lateral overlap of the $2p_z$ orbitals of the two carbon atoms. Ethylene, therefore, has a double bond between the two carbon atoms [Fig. 8.4(b)], one being a σ bond and the other a π bond, the latter being perpendicular to the plane of the molecule. The C=C bond length is 134 pm which is less then C—C bond length in ethane. The covalent radius for sp^2 hybridised double bonded carbon is 67 pm. The bond angle in ethylene and other sp^2 hybridised systems is approximately 120° and the molecule is said to have trigonal shape. That is, the orbitals around each carbon atom are directed towards the vertices of a triangle. On the basis of VSEPR theory also, the same conclusion can be obtained. The structural aspects around the double bonded carbon atoms in other alkenes also are similar to those in ethylene. In compounds like formaldehyde and acetaldoxime, double bonded carbon atom is in sp^2 hybridised state.

In the next section, you will see as to how sp^2 hybridisation concept is used in combination with resonance to explain the structure of benzene.

In acetylene, the carbon atoms are in *sp* hybridised state. Again one of 2*s* electrons is promoted to empty $2p_z$ level in each of the two carbon atoms. The mixing of 2*s* orbital and $2p_x$ orbital produces two *sp* hybrid orbitals with their axes arranged in a linear fashion [Fig. 8.5(a)]. Each *sp* hybrid orbital has 50% *s* character and 50% *p* character. The two *sp* hybrid orbitals of each of the carbon atoms form two σ bonds, one between each carbon and a hydrogen and another between the two carbon atoms. The two $2p_y$ and $2p_z$ orbitals of

Wherever carbon atom is attached to four other atoms, it is sp^3 hybridised. When it is attached to three other atoms it is sp^2 hybridised and, if attached to two other atoms, it is sp hybridised.

each carbon atom, which are not used in hybridisation, combine to give two π bonds, which are perpendicular to each other and also to the plane of the molecule. The two π bonds are represented as a cylindrical envelope around the two carbon atoms. Thus, in acetylene, there is a triple bond between the two carbon atoms, Fig. 8.5(b). The bond angle is 180° and the molecule is linear; VSEPR theory, also could be used to get the same conclusion. The $C \equiv C$ length is 120 pm and the covalent radius for *sp* hybridised triple bonded carbon is 60 pm.

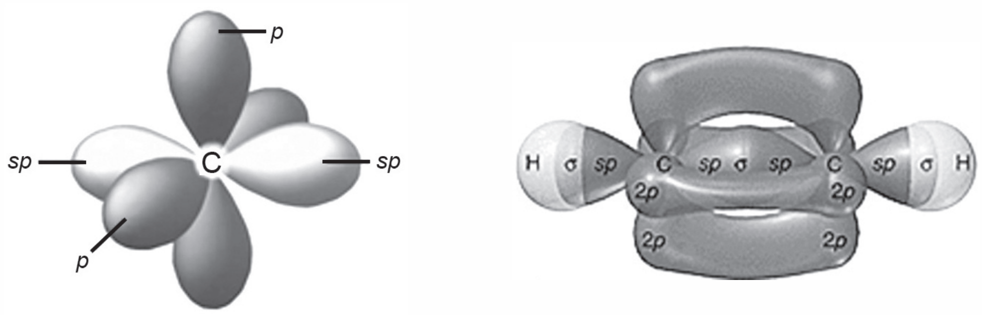


Fig. 8.5 a) Diagram of the two linear *sp* hybrid orbitals of the carbon atom, which lie in a straight line(shown grey in colour) and the two unhybridised *p* orbitals (shown black in colour) **b) structure of acetylene**

You can see that among sp^3, sp^2 and *sp* hybridised carbon atoms, covalent radius is the highest for sp^3 and least for *sp* hybridised state; *s* character is the highest for *sp* and least for sp^3 . Increase of *s* character in the hybridised carbon atom causes a decrease in its covalent radius since *s* electrons are more tightly held than *p* electrons. It is worth remembering that in section 7.4 of the previous unit, we have mentioned that the bond length decreases as bond order increases. From Table 8.3, you can have a comparative account of ethane, ethylene and acetylene with respect to structural features.

Carbon-carbon bond lengths given in Table 8.3 correspond to single, double and triple bonds formed by sp^3, sp^2 and *sp* carbon atoms, respectively. But single bond can occur between any two similarly or dissimilarly hybridised carbon atoms. Similarly double bonds of the type sp^2 - sp^2, sp^2 - *sp* and *sp*- *sp* are possible. Some examples are given below:

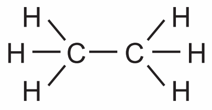
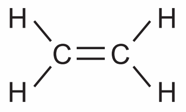
$H_3C—CH_3$ $H_3C—CH=CH_2$ $H_2C=C=CH_2$

sp^3 sp^3 sp^3 sp^2 sp^2 sp^2 sp sp^2

$H_3C—C\equiv CH$ $H_2C=CH—CH=CH_2$

sp^3 sp sp sp^2 sp^2 sp^2 sp^2

Table 8.3 : Comparison of Ethane, Ethylene and Acetylene

Name of the Compound	Hybridi-sation type	Structure	No. & Type of bonds for each carbon atom	Bond Angle	Carbon-carbon bond	
					Bond type	**Bond length/pm**
Ethane	sp^3		4 σ bonds	109°28’	Single bond	154
Ethylene	sp^2		3 σ bonds & 1 π bond	120°	Double bond	134
Acetylene	sp	H — C≡C — H	2 σ bonds & 2 π bonds	180°	Triple bond	120

Carbon-carbon bond lengths depend both on bond type and hybridisation state of linked carbon atoms, as given in Table 8.4.

Table 8.4 : Hybridisation States, Bond Types and Bond Lengths

Bond type	(Bond length) /pm	Bond type	(Bond length) /pm	Bond type	(Bond length) /pm
C-C		C = C		C-H	
sp^3 — sp^3	154	sp^2 — sp^2	134	C_{sp^3} - H	111
sp^3 — sp^2	150	sp^2 — sp	131	C_{sp^2} – H	110
sp^3 — sp	146	sp — sp	128	C_{sp} - H	108
sp^2 — sp^2	148				
sp^2 — sp	143	C≡C			
sp — sp	138	sp — sp	120		

Hybridisation is not limited to *s* and *p* orbitals only but may, in general, involve the mixing of other types of orbitals also, provided energy difference is not much. Hybrid orbitals involving *d* orbitals occur quite commonly among the heavier elements and are particularly important in complexes of the transition elements. Although hybrid orbitals are generally equivalent, in some cases nonequivalent hybrid orbitals also occur. Thus, in dsp^3 hybridisation, whether it is trigonal bipyramid or square pyramid, two types of bonds, axial (a) and equatorial (e) are seen. Under VSEPR theory of the previous unit, you studied that two types of bonds, axial and equatorial are present in a molecule having a total of five electron pairs around the central atom. In Table 8.5, hybridisations involving *d* orbitals are given.

Table 8.5 : Hybridisations Involving *d* Orbitals

Type	**Orbitals used**	**Electronic Geometry**	**Bonding pairs**	**Molecular Shape**	**Hybrid orbitals equivalent (E) or nonequi-valent (N)**	**Example**
sp^3d^2	s, p_x, p_y, p_z, $d_{x^2-y^2}$, d_{z^2}	Octahedron	4	Square	E	XeF_4
			5	Square pyramid	E	BrF_5
			6	Octahe-dron	E	SF_6
d^2sp^3	$d_{x^2-y^2}$, d_{z^2}, s, p_x, p_y, p_z	Octahedron	6	Octahe-dron	E	$[Fe(CN)_6]^{4-}$
sp^3d	s, p_x, p_y, p_z, d_{z^2}	Trigonal bipyramid	2	Linear	N	XeF_2
			3	T-shape	N	$SbCl_3$
			4	Seesaw	N	SF_4
			5	Trigonal bipyramid	N	PF_5, PCl_5
dsp^3	$d_{x^2-y^2}$, s, p_x, p_y, p_z	Square pyramid	5	Square pyramid	N	$[Co(CN)_5]^{3-}$
dsp^2	$d_{x^2-y^2}$, s, p_x, p_y	Square planar	4	Square planar	E	$[Ni(CN)_4]^{2-}$

The structure of many of the coordination complexes and of molecules like phosphorus pentachloride and sulphur hexafluoride can be explained using hybridisation theory. Earlier you studied in Unit 7, based on VSEPR theory, that sulphur hexafluoride is octahedral in shape. We can arrive at this conclusion using the concept of hybridisation also. For sulphur, the ground state configuration is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p_x^2$, $3p_y^1$, $3p_z^1$. The $3s$ and $3p_x$ electrons are unpaired, excited to $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals and the six orbitals, namely, $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{x^2-y^2}$ and $3d_{z^2}$ are hybridised to obtain six orbitals of sp^3d^2 type. Each of these six orbitals has an unpaired electron. Pairing of these six unpaired electrons with the $2p_z$ electron in each of the six fluorine atoms gives rise to sulphur hexafluoride molecule. This is diagrammatically illustrated below:

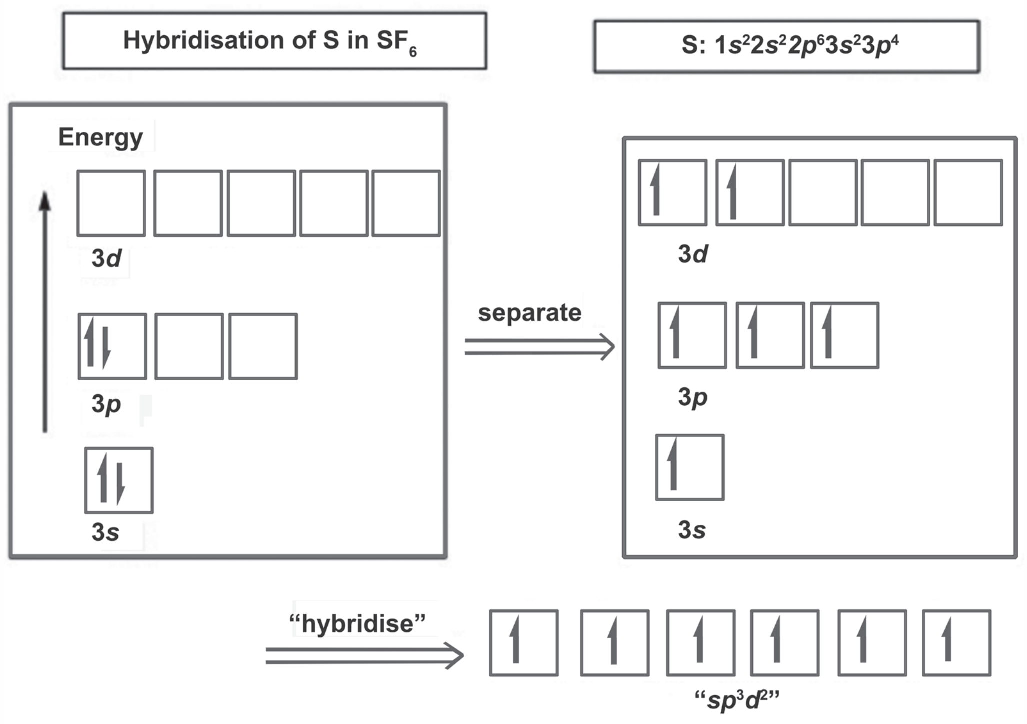


Fig. 8.6: sp^3d^2 hybridisation in sulphur atom; six unpaired electrons available for pairing with $2p_z$ electrons of six fluorine atoms.

Fig. 8.7: Structure of sulphur hexafluoride.

The orbitals of sp^3d^2 type have lobes directed to the vertices of an octahedron. In other words, sulphur hexafluoride is octahedral (Fig. 8.7).

Using the above ideas, why don't you try the following SAQ?

SAQ 5

Explain the type of hybridisation in phosphorus pentachloride.

8.8 SUMMARY

In this unit, we have described the development of valence bond theory and its applications to simple molecules. The concepts of resonance and hybridisation have also been explained. Using the principles of valence bond theory, the structures of methane, ethylene and acetylene are discussed. In the next unit, you will study the structure of molecules like hydrogen, oxygen and carbon monoxide in the light of molecular orbital theory.

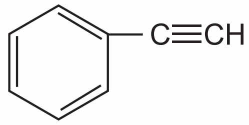
8.9 TERMINAL QUESTIONS

1) What are the essential steps involved in arriving at the structure of a molecule using valence bond theory?

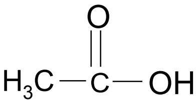
2) Identify the type of hybridisation for each of the carbon atoms:

    i) $H_3C—CH = CH_2$

    ii)



    iii)



$$H_3C-\overset{\overset{\displaystyle O}{||}}{C}-OH$$

3) Explain the shape of CCl_4 molecule on the basis of VSEPR and hybridisation theories.

4) For the following statements, mark T for correct statements and F for false ones.

    a) Electrons in a hydrogen molecule are distinguishable

    b) More terms in the trial function lead to a more acceptable bond energy value

    c) Homonuclear molecules like N_2, O_2 etc. do not have ionic terms in their valence bond structures

    d) Carbon atom, in carbonate ion, is in sp^2 hybridised state

    e) Covalent radius of carbon increases with increase of *s* character in different hybridisation states

5) Explain the structure of mercuric chloride on the basis of hybridisation theory.

6) Differentiate between the following isomers on the basis of theoretical carbon-carbon bond lengths :

$H_3C-CH_2-CH=CH_2$	$H_3C-CH=CH-CH_3$
1-Butene	2-Butene

7) Carbon dioxide is linear as per VSEPR theory. Explain the type of hybridization of the carbon atom in this molecule, in keeping with its linear structure.

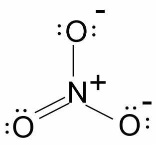
8.10 ANSWERS

Self Assessment Questions

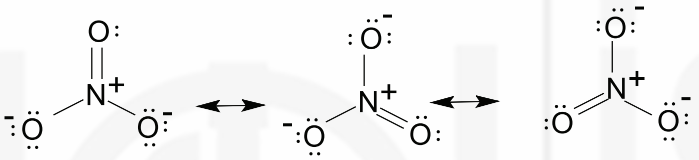
1) That trial function, for which bond energy and bond length values are closest to experimental values, is accepted as the correct one.

2) By assuming a covalent structure with indistinguishable electrons, the bond energy calculation is further improved from a value of 24 kJ mol^{-1} to 303 kJ mol^{-1}. But this value is improved further to only 388 kJ mol^{-1} by taking into account the screening effect of the electron and the possibility of ionic and covalent structures. Hence, covalent structure has greater importance than other factors.

3) Lewis structure for nitrate ion is



The resonance structures are



4) The 2p_z electrons in the two fluorine atoms get paired to give fluorine molecule. The following resonance structures are possible :

5) The five unpaired electrons in the sp^3d hybrid orbitals pair up with five unpaired electrons, one from each of the five chlorine atoms.

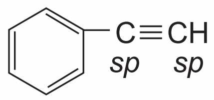
Terminal Questions

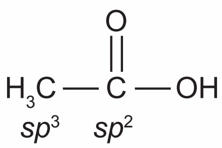
1) Molecular wave functions are formed and E vs R curves are drawn. The wave function giving E and R values, agreeing closely with experimental bond energy and bond distance, is taken as the acceptable wave function. The structural features assumed in arriving at the wave function are assumed to be correct.

2) i) $H_3C - CH = CH_2$

sp^3 sp^2 sp^2

ii) all the carbon atoms of benzene ring are sp^2 hybridised.



iii) 

$$\underset{sp^3}{H_3C}-\underset{sp^2}{\overset{\overset{\displaystyle O}{||}}{C}}-OH$$

3) Tetrahedral on the basis of both the concepts.

4) (a) F (b) T (c) F (d) T (e) F.

5) From an *s* orbital of Hg and *p* orbital of chlorine, *sp* hybrid orbitals are formed, two such hybrid orbitals forms linear structure.

6) The bond lengths are given in Table 8.4.

$CH_3 - CH_2 - CH = CH_2$: $C_1 - C_2$ 134pm;
4 3 2 1 $C_2 - C_3$ 150 pm;
$C_3 - C_4$ 154 pm.

$CH_3 - CH = CH - CH_3$: $C_1 - C_2$ 150 pm;
4 3 2 1 $C_2 - C_3$ 134 pm;
$C_3 - C_4$ 150 pm.

7) Carbon atom is *sp* hybridised.

UNIT 9

MOLECULAR ORBITAL THEORY

Structure

9.1 INTRODUCTION

You have learnt the basic concepts of atomic structure in Units 1 to 5 of Block 1 and you know that the electrons occupy different orbitals namely *s, p, d,* and *f* depending upon their energy. These orbitals are filled up in accordance with various rules like Pauli exclusion principle, *aufbau* principle and Hund's rule. Let us now extend these ideas to molecules and try to understand the molecular structure on the basis of formation of molecular orbitals.

When we talk about molecules, we know that molecules are made of atoms and in a molecule, the constituent atoms are held together by forces of attraction. In covalent molecules, the atoms share the electron pairs. In the last unit, the formation of covalent linkage has been explained on the basis of valence bond theory. You will now study an alternative approach for the formation of molecules which is called Molecular Orbital Theory.

Here, you will first learn about the nature of molecular orbital. Then, Linear Combination of Atomic Orbitals (LCAO) method will be explained for various combinations of atomic orbitals. We will deal here with *s-s, s-p, p-p* combinations of atomic orbitals and understand the type of molecular orbitals resulting from these combinations. The non-bonding combination of atomic orbitals will also be discussed. After that various rules for linear combination of atomic orbitals will be described.

After understanding the above concepts, molecular orbital configuration for various simple homonuclear molecules will be arrived at and the energy level diagram will be drawn for such molecules. Then, molecular orbital configuration of simple heteronuclear molecules such as carbon monoxide, nitrogen oxide etc. will be discussed. You will also learn how can the bond order of a molecule be calculated from its molecular orbital configuration. The molecular configuration is also helpful in knowing the magnetic characteristics of a molecule.

Expected Learning Outcomes

After studying this unit, you should be able to:

- describe molecular orbital theory;
- explain linear combination of atomic orbitals;
- discuss bonding, antibonding and nonbonding orbitals;
- illustrate the molecular orbitals derived from various combinations of *s* and *p* atomic orbitals with suitable diagrams;
- write various molecular orbitals of homonuclear diatomic molecules according to the increasing order of energy and draw their energy level diagram;
- state the molecular orbital configuration for simple homonuclear diatomic molecules;
- write the molecular orbital configuration for simple heteronuclear diatomic molecules; and
- calculate the bond order of a molecule from its molecular orbital configuration and predict its magnetic behaviour.

9.2 MOLECULAR ORBITAL THEORY

A molecule is defined as a stable combination of two or more atoms. By stable combination, we mean that when two atoms form a molecule, the energy of the new entity is less than the sum of the energies of the isolated atoms. In case the atoms constituting a molecule are identical, they form the **homonuclear molecules**. Their examples are molecules of various elements, like H_2, N_2 and O_2. In other cases, when the atoms constituting a molecule are of different elements, they form **heteronuclear molecules**. The examples of such molecules being the molecules of compounds, like HCl and H_2O. Molecules of varying complexities exist in nature including the simple ones like CO_2, SO_2, CH_4, NH_3 and the complex polyatomic molecules like proteins and carbohydrates. Whatever be the nature of molecules, they are built up from the atoms according to certain basic laws.

In the last unit, you have already read about the valence bond approach. Let us now study the molecular orbital theory which also deals with the formation of the molecules from the atoms from a different angle. Consider a system in which the nuclei are in their equilibrium positions and the electrons occupy the molecular orbitals. These molecular orbitals are similar to atomic orbitals. The procedure for constructing the molecular orbitals is given below:

1) The molecular orbital will be polynuclear, i.e., it will be associated with all the nuclei present in the molecule and the wave function for the molecular orbital will have the same significance that it has for the atom, which means that $\psi^2 d_T$ is proportional to the probability of finding the electron in a given volume d_T. Each electron is placed in a molecular energy level or orbital which is determined by the sets of various quantum numbers.

2) Each molecular wave function corresponds to a definite energy value and the sum of the individual energies of electrons in the molecular orbitals, after correction for interaction, represents the total energy of the molecule.

3) The electrons occupy the available molecular orbitals one at a time; the lowest energy molecular orbital being filled first. In assigning configuration to the electrons, the *aufbau* principle and Hund's rule are applied. Also, according to the Pauli exclusion principle, each molecular orbital can accommodate a maximum of two electrons, provided their spins are opposite.

We can write SchrÖdinger equation for molecules also, as in case of atoms. Again, the exact solutions cannot be obtained and some approximations are to be made. There are two approximation methods, one is Linear Combination of Atomic Orbitals or the LCAO method and the other is United Atom method. Here, we will study only the LCAO method.

9.2.1 LCAO Method

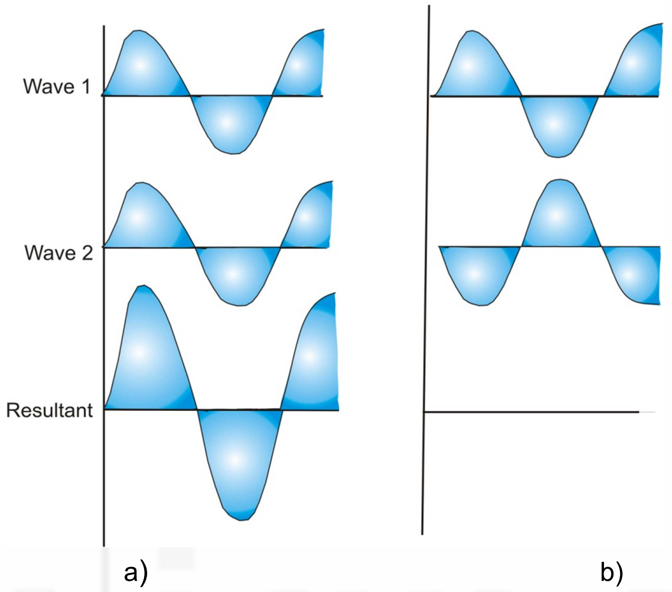
Consider two atoms A and B having atomic orbitals of similar energy and described by the wave functions ψ_A and ψ_B, respectively. When these atoms form a bond, the electrons of the atoms occupy moleclular orbitals. These molecular orbitals can be written using linear combination of atomic orbitals. The number of molecular orbitals produced is always equal to the sum of the number of atomic orbitals involved. Hence, we can write the molecular orbitals as

$$\psi_{(g)} = \psi_A + \psi_B \qquad \dots(9.1)$$

$$\psi_{(u)} = \psi_A - \psi_B \qquad \dots(9.2)$$

where '*g*' stands for **gerade**(even) and '*u*' for **ungerade**(odd). The letters *g* and *u* refer to the symmetry of the orbital about its centre. If the sign of the wave function ψ is unchanged when the orbital is reflected about its centre (i.e., axes *x*, *y* and *z* are replaced by *-x,-y* and *-z*), it is called **gerade.** If you recall the types of atomic orbitals from Unit 4 (Fig. 4.11), you will agree that *s* orbital is symmetrical about its centre; hence it will be **gerade**. Similarly, an **ungerade** orbital is one which changes sign on reflection about the centre; for example, each *p* orbital having lobes with different signs representing different symmetry (Fig. 4.11, Unit 4) is **ungerade**. Can you guess about the *d* orbitals? Yes, they are all **gerade**.

Let us assign a positive sign for ψ_A .Then, ψ_B may be positive or negative. Wave functions of the same sign represent the waves that are *in phase* and such waves combine by constructive interference to give a wave, whose amplitude is the sum of amplitudes of ψ_A and ψ_B at every point (see Fig. 9.1a). Similarly, wave functions of opposite sign represent the *out of phase* waves which on combination will cancel each other by destructive interference (see Fig. 9.1b).



a) b)

Fig. 9.1: Superposition of Waves: a) Constructive Interference and b) Destructive interference.

9.2.2 Bonding and Antibonding Molecular Orbitals

When ψ_A and ψ_B having same symmetry combine, the resulting molecular orbital would be ψ_A and $\psi_{(g)}$ leading to an increased electron density *in between* the nuclei. This is called the **bonding molecular orbital** and it is lower in energy than the atomic orbitals ψ_A and ψ_B. Conversely, $\psi_{(u)}$ will result when ψ_A and ψ_B, having different symmetry combine, resulting in zero electron density in between the nuclei. This type of molecular orbital is known as the **antibonding molecular orbital** and it is higher in energy, as compared to the atomic orbitals ψ_A and ψ_B. We can represent these ideas pictorially using Fig. 9.2.

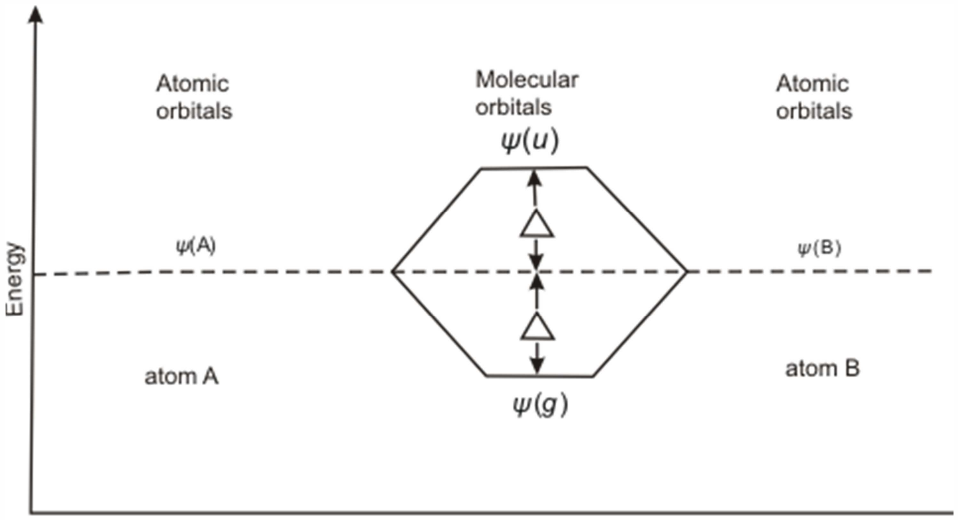


Fig. 9.2: Energy levels of atomic and molecular orbitals.

The energy of the bonding molecular orbital $\psi_{(g)}$ is lower than that of the constituent atomic orbitals by an amount of Δ, known as the **stabilisation energy**. Similarly, the energy of the antibonding molecular orbital is higher by the same amount Δ, as compared to the parent atomic orbitals.

Let us now study how various combinations of *s* and *p* atomic orbitals yield different types of molecular orbitals.

9.2.3 Molecular Orbitals and their Characteristics

In this sub-section, we will study about various molecular orbitals obtained by the combinations of *s* and *p* orbitals and their characteristics.

i) *s-s* Combination of Atomic Orbitals

Consider the case of hydrogen molecule ion H_2^+. This ion is formed when hydrogen is subjected to an electrical discharge under reduced pressure and can be detected spectroscopically. It has a bond length of 106 pm and a bond energy of 269.5 kJ mol^{-1}. Here, there are two protons and one electron; thus, ψ_A and ψ_B in this case are two 1*s* orbitals. Their linear combination will produce two molecular orbitals: one bonding and the other antibonding. The single electron in the ground state occupies the bonding orbital. You can visualise the shape of molecular orbitals formed by the combination of two 1*s* orbitals as shown in Fig. 9.3.

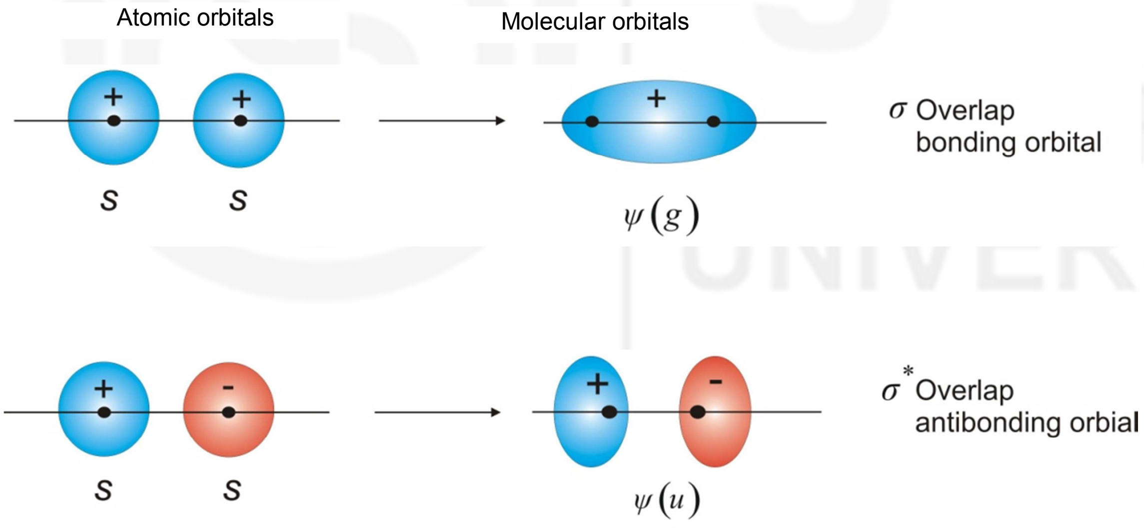


Fig. 9.3: *s-s* combination of atomic orbitals.

We represent the molecular orbitals formed from the 1*s* atomic orbitals as σ1*s* and σ*1*s*. The former is a bonding orbital and the latter, an antibonding orbital. One typical feature of σ orbitals is that they are symmetrical about the molecular axis.

The electron probability density graphs for bonding and antibonding combinations are given in Fig. 9.4.

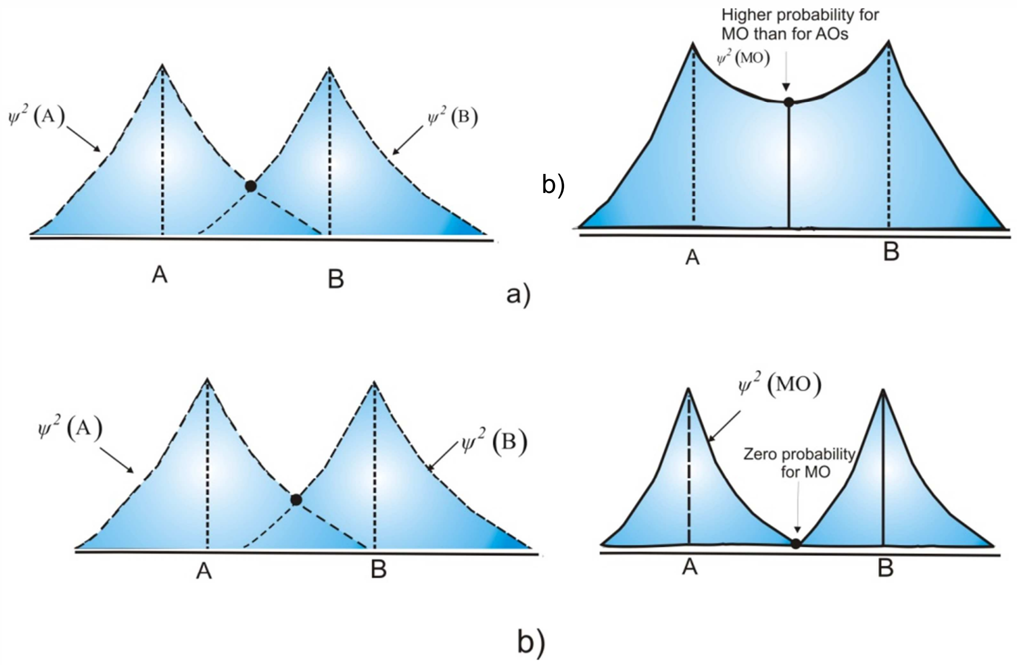


Fig. 9.4: a) Individual electron densities of atoms A and B and bonding orbital showing increased electron density the atoms A and B and b) Antibonding orbital showing decreased electron density between the atoms A and B.

ii) *s-p* Combination of Atomic Orbitals

Next let us study the molecular orbitals obtained by the combination of *s* and *p* atomic orbitals. There are three equivalent *p* orbitals for a given principal quantum number, namely p_x, p_y and p_z. An *s* orbital may combine with a *p* orbital, provided that the lobes of the *p* orbital are pointing along the axis joining the nuclei. Let us first consider s-p_x combination of orbitals. When the lobes of *s* and p_x orbitals have the same sign, the molecular orbital produced is bonding molecular orbital, whereas the antibonding molecular orbital results when the lobes of these orbitals are of opposite sign, (Fig. 9.5).The other combinations, i.e., combination of *s* orbital with p_y and p_z orbitals will be discussed later.

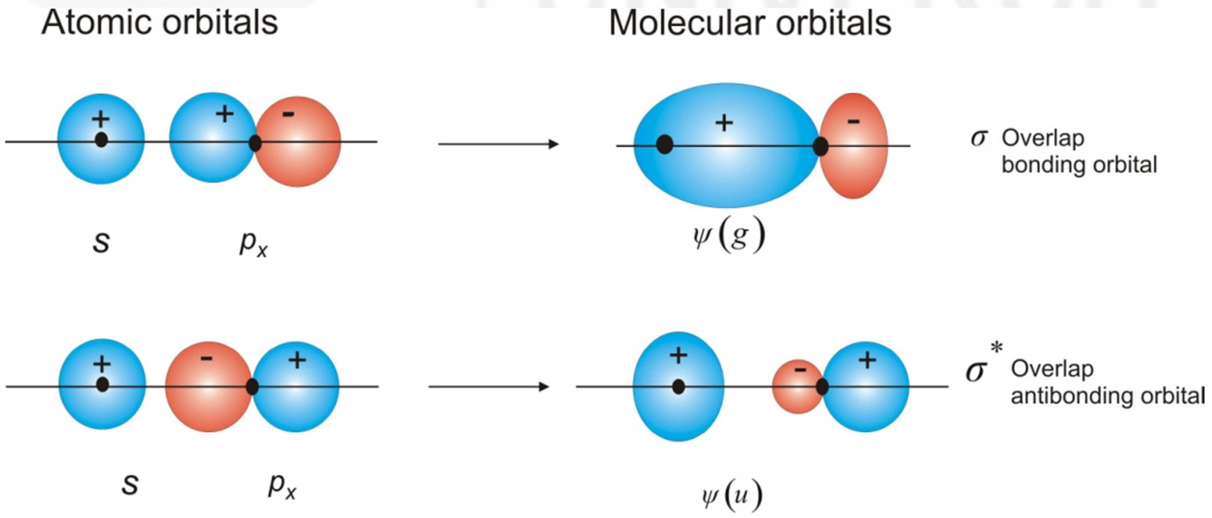


Fig. 9.5: s–p_x combination of atomic orbitals

You have already studied in Unit 4 that + and – signs of the orbitals refer to the symmetry of the wave function and have nothing to do with the electrical charges because the electron cloud is always negatively charged.

Note that the combination of s and p_x atomic orbitals gives σ type of molecular orbitals, as they are symmetric about the internuclear axis.

iii) *p-p* Combination of Atomic Orbitals

As the lobes of a p orbital are of opposite sign, the combination of two p_x orbitals, which have lobes pointing along the axis joining the nuclei, lead to σ bonding as well as σ^* antibonding orbitals depending on the nature of the sign of the wave functions. This is shown below in Fig. 9.6.

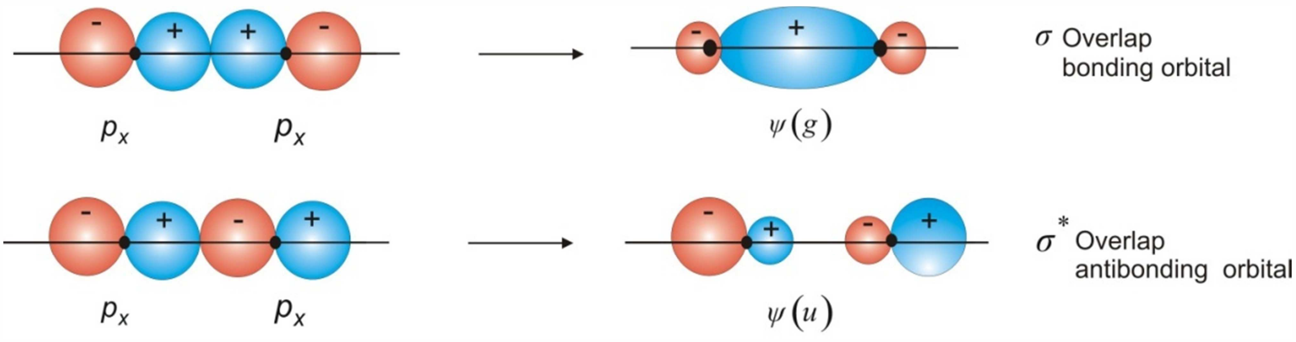


Fig. 9.6: p_x–p_x combination of atomic orbitals.

Let us now focus our attention on the combination of two p orbitals which have their lobes perpendicular to the axis joining the nuclei. Lateral overlap of these orbitals will result in the π *(pi) bonding* and π^* *(pi star) antibonding* molecular orbitals. Both p_y and p_z orbitals form π and π^* orbitals in the above fashion. In Fig. 9.7, the *p-p* combination using p_y orbitals is depicted. Similarly, you can draw the π and π^* orbitals using p_z orbitals. You will be studying about compounds like ethylene, acetylene and benzene which contain π bonds in Units 16 to 20 in Block- 4 of this course.

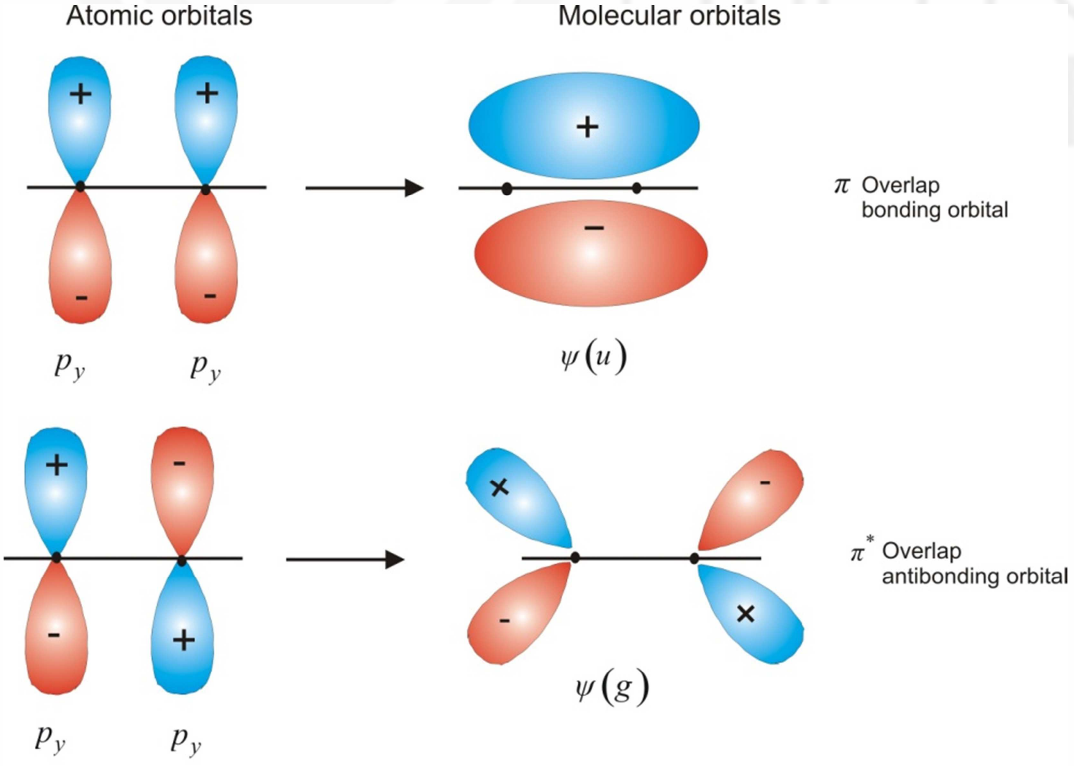


Fig. 9.7: p_y–p_y combination giving *pi* bonding.

Similarly, a *p* orbital can overlap with a *d* orbital giving bonding and antibonding combinations. The *d-d* combination of orbitals is also possible and it produces δ bonding and δ^* antibonding orbitals.

iv) Non-bonding Combination of Atomic Orbitals

Upto this stage, you have learnt about two types of molecular orbitals viz. bonding and antibonding. There is a third category called **nonbonding molecular orbitals** which can be understood when we consider the combination of an s-p_y or s-p_z atomic orbitals as shown in Fig. 9.8.

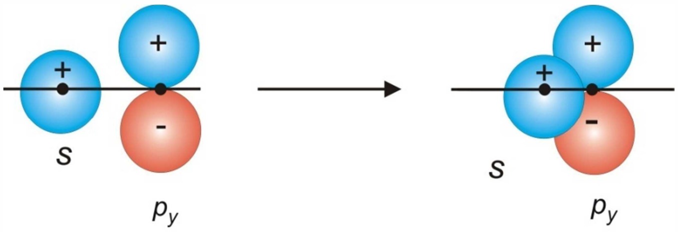


Fig. 9.8: *s* and p_y combination of atomic orbitals leading to nonbonding situation; *s* and p_z orbitals also combine in a similar way

In this type of combination, any stabilisation from overlapping of + and + lobes of atomic orbitals is cancelled by the equal amount of overlapping between + and – lobes of atomic orbitals. This evidently indicates that there is no net change in energy by combination of atomic orbitals and hence no bonding occurs. Thus, this situation is called **nonbonding combination of orbitals.**

After studying various combinations of atomic orbitals, let us now sum up the rules governing the linear combination of the orbitals.

9.3 RULES FOR LINEAR COMBINATION OF ATOMIC ORBITALS

1) The constituent atomic orbitals must be of similar energy, i.e., combination of 1*s* and 2*s* or 1*s* and 2*p* orbitals will not give any effective combination in case of homonuclear diatomic molecules because they are of different energy. However, such combinations may be possible in heteronuclear molecules, since the energies of the orbitals of atoms A and B may become comparable in such cases, e.g., in HF molecule.

2) The atoms must be close enough to give effective overlap, i.e., the radial distribution functions $R_{(r)}$ must be similar at this distance. You are already familiar with the radial distribution functions, discussed in Unit 4.

3) In order to produce bonding and antibonding molecular orbitals, either the symmetry of the two atomic orbitals must remain unchanged (as in the case of $p_x - p_x$ combination) when rotated about the internuclear axis, or both atomic orbitals must change symmetry in an identical manner (as the case of $p_y - p_y$ or $p_z - p_z$ combinations). For example, in Fig. 9.6 when p_x orbitals are rotated along the internuclear axis, no change in their symmetry is observed, hence the bonding and antibonding molecular orbitals are produced as shown in Fig. 9.6.

But in the case of $p_y - p_y$ combination of orbitals leading to π bonding, if the p_y orbitals (Fig. 9.7) are rotated about the intermolecular axis, the atomic orbitals obtained after rotation will yield the molecular orbital as shown in Fig. 9.9 a). Similarly, for the other combination, the rotation of orbitals will yield the antibonding orbitals as given in Fig. 9.9 b.

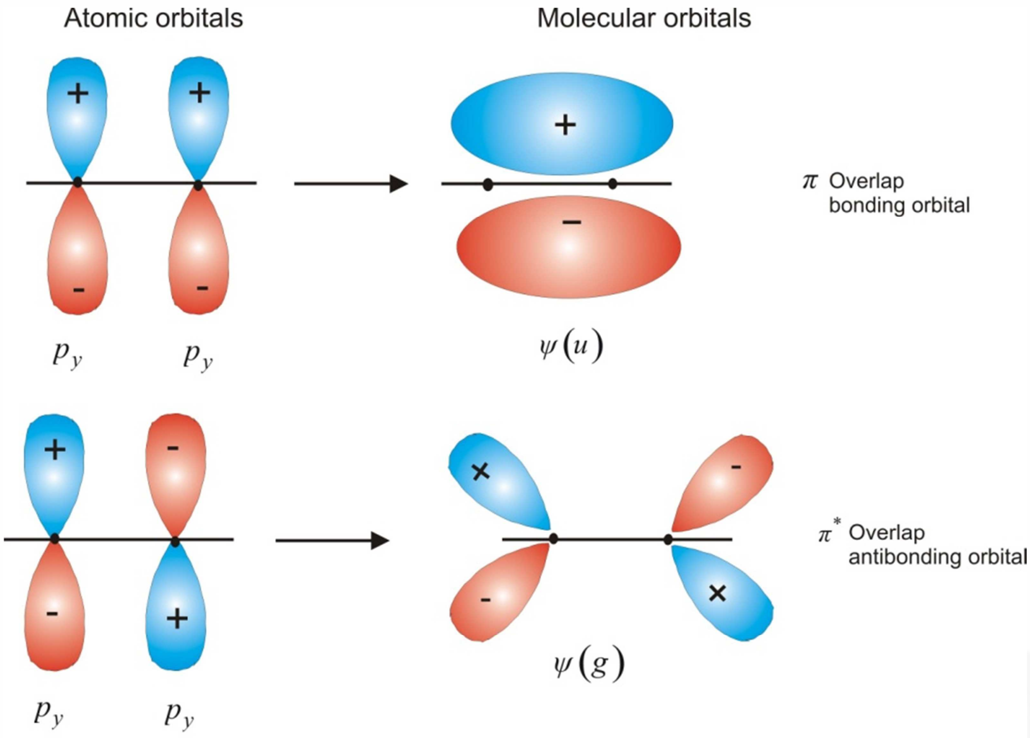


Fig. 9.9: p_y–p_y combination after rotation of p_y orbitals around the internuclear axis giving: a) π bonding orbital and b) π^* antibonding orbital.

SAQ 1

Assume that you are starting with two p_y orbitals. Show the type of molecular orbitals formed under the hypothetical situation when only one of the two p_y atomic orbitals changes symmetry, on rotation, about the internuclear axis.

Various molecular orbitals have different energies and are represented by the four quantum numbers similar to atomic orbitals. The principal quantum number, n and the subsidiary or azimuthal quantum number, m_l are retained from the atomic orbitals and have the same significance here also. But the magnetic quantum number, m_l is replaced by a new quantum number, λ. In case of diatomic molecules, the internuclear axis is taken as the reference axis and the quantisation of angular momentum in $h / 2\pi$ units is represented with respect to this axis similar to the case of atoms. λ can take same values for molecules as m_l has for the atoms, i.e.,

$$\lambda = -l \ldots -2, -1, 0, 1, 2, \ldots l.$$

When $\lambda = 0$, orbitals are symmetrical about the internuclear axis and hence are called σ orbitals. When $\lambda = \pm 1$, orbitals are known as π orbitals. Similarly, $\lambda = \pm 2$, represents the δ orbitals. The spin quantum number, m_s, is similar to that for the atomic orbitals and can take the values $\pm 1/2$.

The order of energy of molecular orbitals has been determined from the spectroscopic data. For homonuclear diatomic molecules, the order of increasing energy of various molecular orbitals is as shown below.

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_x, \begin{cases} \pi 2p_y \\ \pi 2p_z \end{cases}, \begin{cases} \pi^* 2p_y \\ \pi^* 2p_z \end{cases}, \sigma^* 2p_x$$

The energy level diagram for homonuclear diatomic molecules is shown in Fig. 9.10.

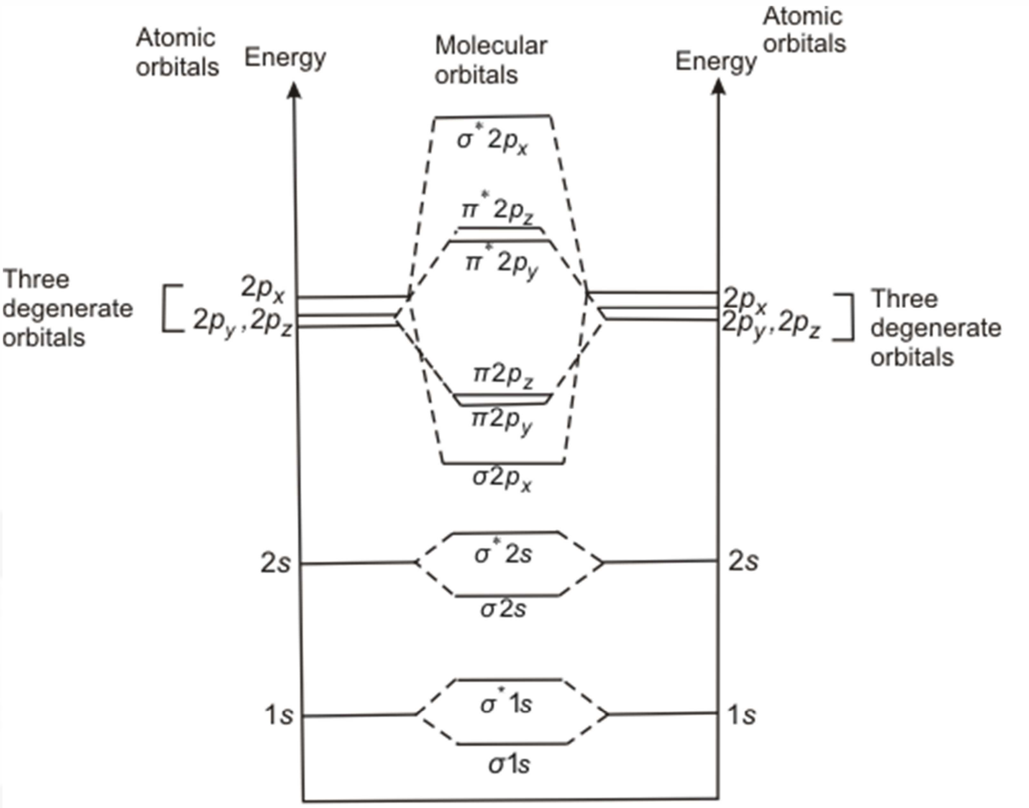


Fig. 9.10: Energy pattern for homonuclear diatomoic molecules; although three 2*p* orbitals are degenerate, for the sake of clarity, p_x has been shown slightly above p_y and p_z orbitals.

Here, the energies of the $\pi 2p_y$ and $\pi 2p_z$ orbitals are the same and hence, they are called **degenerate orbitals**. Similarly, $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals constitute another set of **degenerate orbitals**. The energies of $\sigma 2p_x$ and $\pi 2p_y / \pi 2p_z$ orbitals are very close to one another; and hence in some cases, the above order is reversed, i.e., in some molecules $\pi 2p_y$ and $\pi 2p_z$ orbitals are lower in energy than $\sigma 2p_x$ orbital.

SAQ 2

Fill in the blanks using appropriate words:

i) In case of σ overlap, the lobe of atomic orbitals point ………………the internuclear axis whereas for π overlap, the lobes are…………..to the line joining nuclei.

ii) In contrast to σ orbitals, π orbitals have both ψ and ψ^2…………..along the internuclear axis.

SAQ 3

Classify the following molecular orbitals as gerade or ungerade:

i) π bonding orbital

ii) σ bonding orbital

iii) σ^* antibonding orbital

iv) π^* antibonding orbital

9.4 HOMONUCLEAR DIATOMIC MOLECULES

By now, you are familiar with details of the LCAO method. Let us apply these ideas to some simple homonuclear diatomic molecules, i.e., the molecules containing both the atoms of the same nuclei.

H_2^+ molecular ion: As studied before, it has only one electron, so you can write its molecular orbital configuration as $\sigma 1s^1$. This means, H_2^+ ion has one electron in $\sigma 1s$ bonding orbital.

H_2 molecule: Each hydrogen atom contributes one electron. So the two electrons go to the lower energy $\sigma 1s$ bonding orbital and the electron configuration can be written as $\sigma 1s^2$. The bond energy of H_2 is 436 kJ mol^{-1} and bond length is 74 pm. On comparing these data with those of H_2^+ given in sub-Sec. 9.2.3, you will realise that placement of an additional electron in the bonding $\sigma 1s$ orbital of the H_2 molecule has resulted in a more stable arrangement; hence, the bond energy of H_2 is more and bond length is less than those of H_2^+ ion.

He_2^+ ion: Since He_2^+ has three electrons, its configuration is, $\sigma 1s^2$, $\sigma^* 1s^1$. Here, one electron is in antibonding orbital and it reduces the bond strength. The bond energy in this case is 238 kJ mol^{-1} and the internuclear distance is 108 pm.

He_2 molecule: Theoretically, each He atom contributes two electrons giving a total of four electrons which can be accommodated into the molecular orbitals as follows:

$$\sigma 1s^1,\ \sigma^* 1s^2$$

Since, both the bonding and antibonding orbitals are equally filled, there is no net decrease in energy as compared to the helium atoms and hence, He_2 does not exist under ordinary conditions.

We can introduce a term **bond order** here. As you know, the two bonding electrons constitute a bond; the bond order is one half the difference between the number of electrons in bonding orbitals (N_b) and the number of electrons in antibonding orbital (N_a), i.e.,

$$\text{Bond Order} = 1/2\ (N_b - N_a)$$

For He_2, N_b and N_a are both equal to two; hence its Bond Order =1/2 (2–2) = 0 i.e., there is no bond between the two He atoms and He_2 does not exist. However, He_2 is detected in discharge tubes and is formed there due to the promotion of two electrons from $\sigma^* 1s$ level to $\sigma 2s$ level. Thus, it has a configuration $\sigma 1s^2, \sigma 2s^2$ which corresponds to higher energy than that of two normal uncombined helium atoms. But, it appears to be more stable than two separate excited atoms.

Li_2 molecule — Each lithium atom has two electrons in its inner 1*s* orbital and one in the outer 2*s* orbital, making a total of six electrons in Li_2 which can be arranged as $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$.

The filled $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals do not contribute to the bonding as explained above in the case of He_2. The electrons in these orbitals could be collectively represented as *KK* and hence the configuration of Li_2 is *KK*, $\sigma 2s^2$. Here, bonding occurs due to the filling $\sigma 2s$ orbital and Li_2 has been found to exist in the vapour state.

Be_2 molecule — Combination of four electrons from each Be atom leads to eight electrons in Be_2 molecule which can be arranged as

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \quad \text{or} \quad or\ KK, \sigma 2s^2, \sigma^* 2s^2$$

Again, the effect of bonding and antibonding 2*s* levels would cancel each other, so there is no net stabilisation and the molecule would not be expected to be stable.

B_2 molecule: B_2 molecule has a total of ten electrons and its molecular orbital configuration is

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi 2p_y^1 \\ \pi 2p_z^1 \end{cases}$$

In case of B_2 and C_2, $\sigma 2p_x$ is of higher energy as compared to the $\sigma 2p_y$ and $\sigma 2p_z$ orbitals due to the repulsion among 2*s* and $2p_x$ orbitals as they tend to occupy the same region of space. This effect decreases for the higher elements and in O_2 and F_2, $\sigma 2p_x$ orbital is of lower energy than $\sigma 2p_y$ and $\sigma 2p_z$ orbitals.

Note, that the $\pi 2p$ orbitals here are lower in energy than $\sigma 2p_x$ orbital. Since $\pi 2p_y$ and $\pi 2p_z$ are degenerate, they are singly occupied in accordance with the Hund's rule. Here, the stabilisation occurs due to the filling of $\pi 2p$ orbitals and B_2 molecule is known to exist. Since, two unpaired electrons have parallel spins, B_2 molecule is paramagnetic in nature.

C_2 molecule: It has 12 electrons as each carbon atom is contributing six electrons to the molecule. So filling of molecular orbitals can be represented as follows:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

Here again, as in the case of B_2, the $\pi 2p$ orbitals are lower in energy as compared to $\sigma 2p_x$ orbital which is in contrast to the general order of filling of electrons in molecular orbitals according to the sequence given before.

N_2 molecule: In the nitrogen molecule, there are fourteen electrons arranged in the molecular orbitals as,

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

Assuming that the inner orbitals do not participate in bonding, stabilsation will be produced by filling of six electrons in the bonding $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals. Hence, the bond order will be $\frac{1}{2}(N_b - N_a) = \frac{1}{2}(6 - 0) = 3$.

O_2 molecule: Each oxygen atom has eight electrons. Thus, total sixteen electrons are present in the oxygen molecule which can occupy the molecular orbitals as shown below.

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{cases}$$

The $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals are singly occupied according to the Hund's rule. Since, the two unpaired electrons have parallel spins, oxygen is paramagnetic in nature.

Paramagnetic substances are those which have unpaired electron spins and they have a tendency to be drawn into a magnetic field.

Bond order in oxygen molecule is two because there are six electrons in $\sigma 2p_x$ and $\pi 2p$ bonding orbitals and two electrons in the π^* antibonding orbitals.

F_2 molecule: Flourine molecule has a total of eighteen electrons and the filling of molecular orbitals can be represented as given below,

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases} \begin{cases} \pi * 2p_y^2 \\ \pi * 2p_z^2 \end{cases}$$

The inner shell is nonbonding and the filled bonding $\sigma 2s$, $\pi 2p_y$, $\pi 2p_z$ orbitals are cancelled by their corresponding antibonding orbitals. This leaves only filled $\sigma 2p_x$ orbital to contribute for bonding. Since there are two electrons in the bonding $\sigma 2p_x$ orbital, bond order is one in F_2 molecule.

In Unit 7, Sec. 7.2, we have indicated that as the bond order increases, bond length decrease and bond energy increases; the same has again been emphasised in Sec. 8.6 of Unit 8. The molecular orbital theory predicts bond orders of fluorine, oxygen and nitrogen as 1, 2 and 3, respectively. You can see from Table 9.1 that this prediction is in keeping with the bond length and bond energy values of these molecules.

Table 9.1: Bond Length, Bond Energy and Bond Order

Molecule	**Bond order as per M.O. theory**	**Experimental Values**	
		Bond Length (pm)	**Bond Energy (kJ mol^{-1})**
F_2	1	144	155
O_2	2	121	497
N_2	3	110	945

SAQ 4

Calculate the bond order for the following:

a) H_2^+ b) H_2 and c) He_2^+

SAQ 5

Which of the following is paramagnetic and why?

a) O_2 b) O_2^{2-}

9.5 HETERONUCLEAR DIATOMIC MOLECULES

The principles which apply to the homonuclear molecules are valid for heteronuclear molecules also. You may recollect that heteronuclear molecules contain two different nuclei. To form the molecular orbitals, the atomic orbitals must have

1) similar energies,

2) charge clouds that overlap as much as possible, and

3) the same symmetry properties with respect to the internuclear axis.

Let us consider **HF molecule**. The electron configuration of the atoms are

H — $1s^1$

F — $1s^2 2s^2 2p^5$

The inner 1*s* and 2*s* electrons of fluorine do not participate in bonding since they are much lower in energy as compared to the 1*s* orbital of hydrogen. The effective overlap is possible between 1s orbital of hydrogen and only $2p_x$ orbital of fluorine because the $2p_x$ orbital points along the intermolecular axis. This leads to the bonding and antibondingmolecular orbitals as shown earlier in Fig. 9.5 for s-p_x combination of orbitals.

The other possibilities, i.e., s–p_y and s–p_z combinations will lead to the nonbonding situation as was shown earlier in Fig. 9.8. Thus, we can write the configuration of ten available electrons in HF molecule as given below.

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2$$

As the electrons in the inner $\sigma 1s$ and $\sigma^* 1s$ orbitals do not participate in bonding and the stabilisation of filled $\sigma 2s$ orbital is cancelled by the filling of $\sigma^{*} * 2s$ orbital; the two electrons in the bonding $\sigma 2p_x$ orbital lead to the bond order of one, as shown below.

$$\begin{aligned} \text{Bond order} &= 1/2(N_b - N_a) \\ &= 1/2(2-0) \\ &= 1 \end{aligned}$$

Let us next consider **CO molecule**. Here, carbon and oxygen atoms contribute six and eight electrons, respectively, making a total of fourteen electrons which can be arranged in molecular orbitals as

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \left\{\begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix}\right., \sigma 2p_x^2$$

Again, the inner electrons do not contribute to bonding and $\sigma 2s^2$ orbital is cancelled by $\sigma^* 2s^2$. We are now left with six electrons in the bonding $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals. This leads to a bond order of 3. Here, due to different electronegativities of carbon and oxygen, the constituent atomic orbitals are of different energies, i.e., the 2*s* atomic orbital of oxygen is lower in energy than the analogous carbon orbital, see Fig. 9.11.

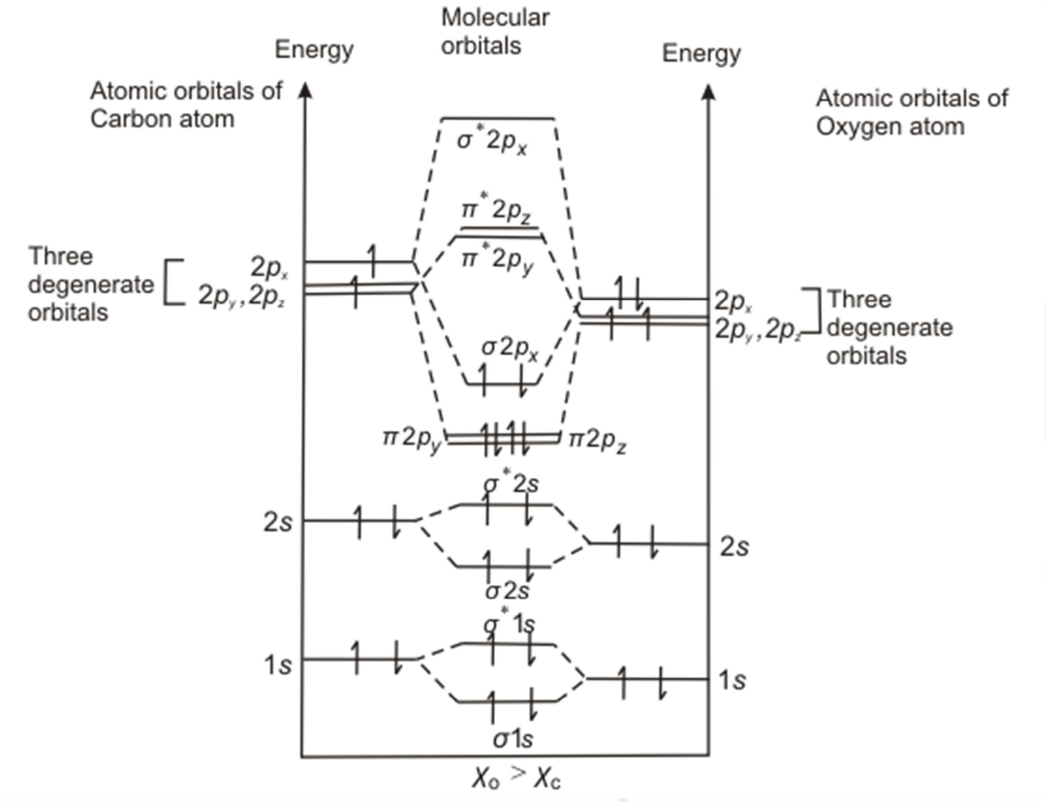


Fig. 9.11: Molecular orbitals for carbon monoxide.

Note that the bonding $\pi 2p$ orbitals of carbon monoxide are lower in energy than the $\sigma 2p_x$ orbital.

Let us next understand the molecular orbital configuration of **NO molecule**. In case of NO molecule, nitrogen gives seven electrons and oxygen gives eight electrons. So, the NO molecule has a total of fifteen electrons and its molecular orbital configuration can be given as follows:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,\ \sigma 2p_x^2, \left\{\begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix}\right., \left\{\begin{matrix} \pi^* 2p_y^1 \\ \pi^* 2p_y^0 \end{matrix}\right.$$

The energy pattern for this molecule is shown in Fig. 9.12.

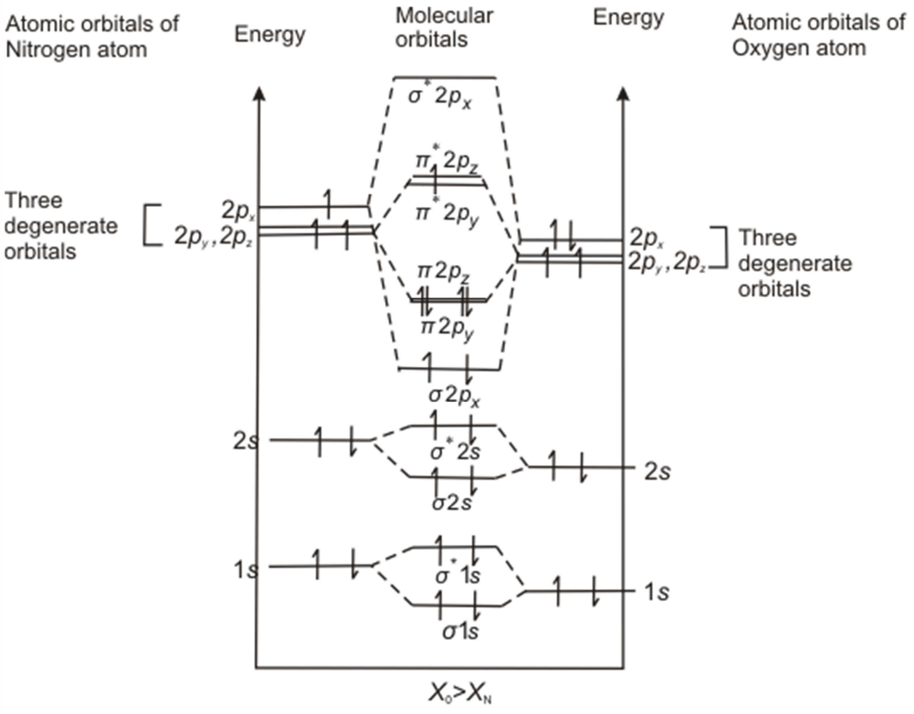


Fig. 9.12: Energy pattern for NO molecule

Let us consider NO^+. It has one electron less than NO. Hence, number of electrons in NO^+ is 14. These fourteen electrons can be arranged in various molecular orbitals as given below:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,\ \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

The energy level diagram of NO^+ according to the above molecular orbital configuration is given below in Fig 9.13.

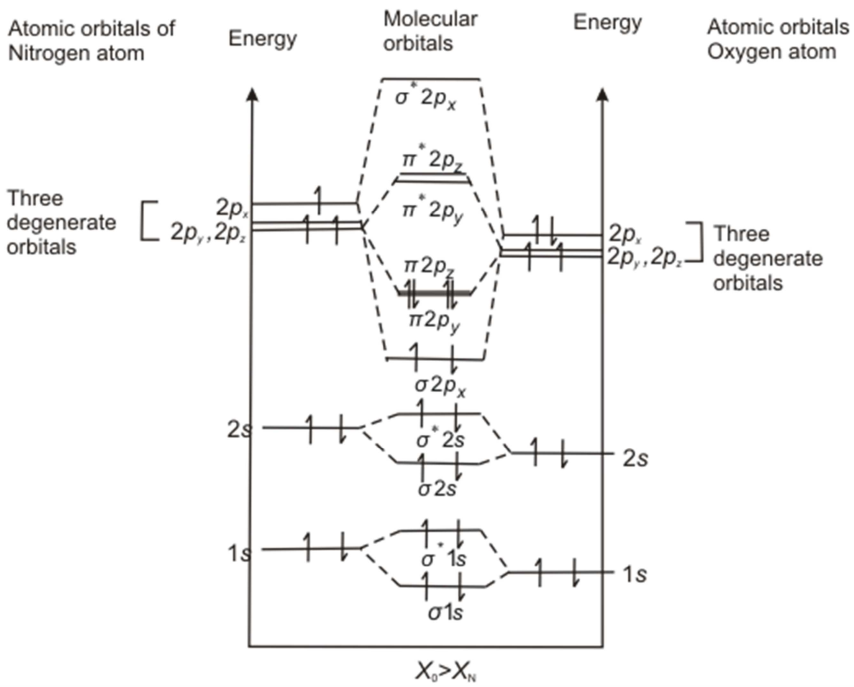


Fig. 9.13: Energy level diagram of NO^+.

You can see from above that ten electrons are present in the bonding molecular orbitals and four electrons occupy the antibonding molecular orbitals. Thus, the bond order of NO^+ can be calculated as shown below:

$$\begin{aligned}\text{Bond Order} &= \frac{1}{2}(N_b - N_a)\\ &= \frac{1}{2}(10-4)\\ &= 3\end{aligned}$$

After understanding the above concepts, answer the following SAQs.

SAQ 6

Calculate the bond order of NO molecule.

SAQ 7

State whether NO is paramagnetic or not. Give reason in support of your answer.

9.6 COMPARISON OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

You have studied in the last unit about the valence bond theory and you are now familiar with the molecular orbital approach also. Let us now compare these two approaches. The principles which govern the filling of orbitals in both the theories are same, i.e., Hund's rule and *aufbau* principle. The valence bond theory retains the individuality of the atoms but the bonding is described in terms of the pairing of unpaired electrons. The molecular orbital theory states that molecular orbitals are formed by the linear combination of atomic orbitals. These molecular orbitals are similar to the atomic orbitals but they encompass all the nuclei and hence are polycentric in nature. Thus, according to this approach the atoms do not retain their individuality and all the nuclei are assumed to behave as a single unit around which the electrons are present in molecular orbitals. This approach uses the linear combination of atomic orbitals or the LCAO method, whereas the valence bond approach utilises the resonance and hybridization concepts to explain the structures of molecules. However, unlike the valence bond theory, the molecular orbital theory explains the paramagnetic character of oxygen molecule on the basis of the presence of two unpaired electrons.

9.7 SUMMARY

You have learnt in this unit about the molecular orbital theory which involves the linear combination of atomic orbitals to give molecular orbitals. You studied about various combinations of *s* and *p* atomic orbitals to yield bonding, antibonding and nonbonding orbitals. Then, a description was given regarding the energies of these molecular orbitals and their filling. These ideas were applied to various simple homonuclear and heteronuclear diatomic molecles and electron configurations were assigned to them. The electron configurations were used to calculate the bond order and comparative stability in some cases. Finally, we compared the valence bond approach which you studied in the previous unit, with the molecular orbital theory.

9.8 TERMINAL QUESTIONS

1. Draw $p_y - d_{xy}$ bonding and antibonding molecular orbitals.
2. a) Define bond order.

   b) Calculate the bond order for the following:

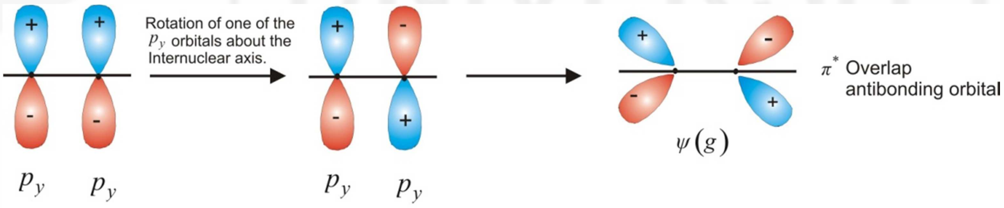
   i) He_2^{2+} ii) Li_2

   iii) B_2 iv) C_2
3. Arrange the following in increasing order of their stabilities:
   $O_2, O_2^+, O_2^-, O_2^{2-}$.
4. Write molecular orbital configuration of Na_2.
5. Discuss the molecular orbitals of the HCl molecule, considering that the 1*s, 2s, 2p* and 3*s* atomic orbitals of chlorine are of lower energy as compared to 1*s* atomic orbital of hydrogen.
6. Comment on the paramagnetic nature of NO^+.

9.9 ANSWERS

Self-Assessment Questions

1.



When only one p_y orbital changes sign on rotation as shown in above figure, the resultant combination will lead to the antibonding situation.

2. i) along, perpendicular

   ii) Zero
3. i) Ungerade

   ii) Gerade

   iii) Ungerade

   iv) Ungerade
4. a) 1/2 b) 1 c) ½

5. O_2- $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \left\{\begin{matrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{matrix}\right., \left\{\begin{matrix}\pi^* 2p_y^1 \\ \pi^* 2p_z^1\end{matrix}\right.$

   It has two unpaired electrons and hence, is paramagnetic. And,

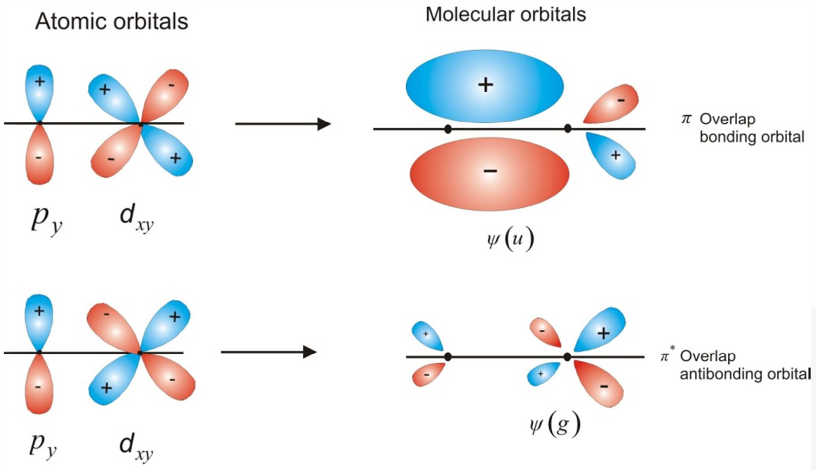
   $O_2^{2-} - \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \left\{\begin{matrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{matrix}\right., \left\{\begin{matrix}\pi^* 2p_y^2 \\ \pi^* 2p_z^2\end{matrix}\right.$

   It has no unpaired electron and hence, is not paramagnetic.

6. 2.5

7. It is paramagnetic due to one unpaired electron in $\pi^* 2p_y$ level.

Terminal Questions

1. 

2. a) It is half of the difference of number of electrons occupying bonding and antibonding orbitals.

   b) i) 1 ii) 1 iii) 1 iv) 2

3. $O_2^{2-} < O_2^{2-} < O_2 < O_2^+$

   First calculate the bond order which is as follows:

   $O_2 - 2,\ O_2^+ - 2.5,\ O_2^- 1.5,\ O_2^{2-} - 1$

   and then arrange according to the increasing bond order.

5. Out of the three available 3*p* orbitals of chlorine, the combination of $3p_y$ *or* $3p_z$ orbital with 1*s* orbital of hydrogen will lead to the nonbonding situation. Hence, effective overlap is possible only with $3p_x$. Here, all the atomic orbitals of chlorine except $3p_x$ will retain their original atomic orbital status and electrons in *3s*, $3p_y$ and $3p_z$ orbitals will be regarded as *nonbonding or lone pairs* of electrons. The combination of 1*s* and $3p_x$ atomic orbitals will give a bonding orbital which is occupied by the two electrons; and the corresponding antibonding orbital is empty. Hence, in HCl bond order is one according to molecular orbital theory.

6. It is evident from the molecular orbital configuration of NO^+ that it has no unpaired electrons. Hence, it is not paramagnetic in nature.

FURTHER READING

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