

# R.K.MALIK'S

## NEWTON CLASSES

JEE (MAIN & ADV.), MEDICAL + BOARD, NDA, IX & X

### CHAPTER : 4

## CHEMICAL BONDING

In lesson 2, you have learnt about the structure of atom while in the lesson 3, you studied about the classification of elements and periodicity in properties. You know that molecules are obtained by the combination of two or more than two atoms of the same or different elements. In this lesson you will study

- Why do atoms combine?
- What are the different ways in which the atoms can combine?, and
- What are the shapes of different molecules?

The answers to these questions are of fundamental importance to the study of chemistry, as you would discover while studying the later parts of this course.

### OBJECTIVES

After reading this lesson you will be able to

- explain the formation of bond in terms of potential energy diagram and octet rule;
- list different types of bonds;
- define ionic bond and cite some examples;
- write Lewis structures of some simple molecules;
- list the characteristics of ionic compounds;
- explain Born Haber Cycle;
- define covalent bond and cite some examples;
- list the characteristics of covalent compounds;
- state valence shell electron pair repulsion (VSEPR) theory;

# Chemical Bonding

- explain bond polarity and dipole moment;
- explain bond parameters;
- predict the geometry of molecules with the help of VSEPR theory;
- explain the hybridisation of atomic orbitals involving s, p and d orbitals and illustrate with examples;
- tabulate the geometry of some molecules showing  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $dsp^2$ , and  $dsp^3$  hybridisation;
- explain the formation of  $\sigma$  and  $\pi$  bonds in  $CH_4$ ,  $C_2H_4$  and  $C_2H_2$  ;
- explain resonance;
- explain molecular orbital theory;
- write the molecular orbital configuration of  $H_2$ ,  $N_2$ ,  $O_2$  and  $F_2$  molecules;
- define bond length and bond order and relate them and
- explain hydrogen bonding with the help of examples.

## 4.1 VALENCE ELECTRONS

The electrons in the outer most shell take part in the bond formation and determine the combining capacity or the 'valency' of the atom. Therefore, the outer most shell of any atom is called its **valence shell** and the electrons present in the valence shell are called the **valence electrons**.

## 4.2 WHAT IS A CHEMICAL BOND?

When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combined or a bond is formed between the two. The bond is called a **chemical bond**. Thus *a chemical bond may be visualised as an effect that leads to the decrease in the energy*. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the constituent atoms.

A question arises, "How do atoms achieve the decrease in energy to form the bond". The answer lies in the electronic configuration. As you are aware, the noble gases do not react with other elements to form compounds. This is due to their stable electronic configuration with eight electrons (two in case of helium) in their outermost shells. The formation of a bond between two atoms may be visualised in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

# Chemical Bonding

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons. Accordingly, there are different types of chemical bonds, like,

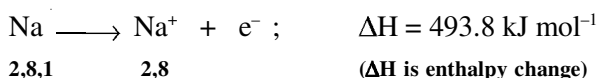
- Ionic or electrovalent bond
- Covalent bond
- Co-ordinate covalent bond

In addition to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

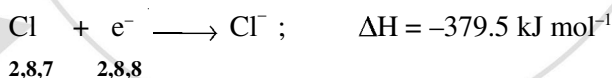
## 4.3 IONIC OR ELECTROVALENT BOND

According to Kossel's theory, in the process of formation of ionic bond the atoms acquire the noble gas electronic configuration by the gain or loss of electrons. Let us consider the formation of NaCl in terms of Kossel's Theory.

The electronic configuration of sodium atom (atomic number 11) is 2,8,1. Since it is highly electropositive, it readily loses an electron to attain the stable configuration of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation ( $\text{Na}^+$ ) in the process



On the other hand, a chlorine atom (electronic configuration: 2,8,7) requires one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion ( $\text{Cl}^-$ ) in the process.



According to **Kossel's** theory, there is a **transfer** of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.



The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an **electrovalent** or an **ionic bond**. Thus *the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together*. The compounds so formed are termed as ionic or electrovalent compounds.

# Chemical Bonding

## 4.3.1 Energetics of Ionic Compound Formation

We have just described the formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. You may raise a question here that when **more energy is required** (ionisation energy) to form a sodium ion from sodium atom, **than that released** (electron affinity) in the formation of chloride ion from chlorine atom then how do we say that the formation of NaCl is accompanied by a decrease in energy? Your question is quite justified but let us assure you that there is no anomaly. Let us look at the whole process somewhat closely to clarify your doubts.

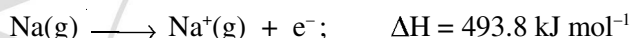
### Born Harber Cycle

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

- a) **Sublimation** of solid sodium to gaseous sodium atoms.



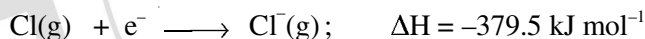
- b) **Ionization** of gaseous sodium atom to give sodium ion.



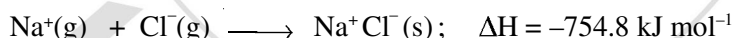
- c) **Dissociation** of gaseous chlorine molecule into chlorine atoms



- d) Conversion of gaseous chlorine atom to chloride ion (**addition of electron**)



- e) Formation of NaCl from sodium and chloride ions. (**Crystal or lattice formation**).



The energy released in this step is **lattice energy**.

The net reaction would be



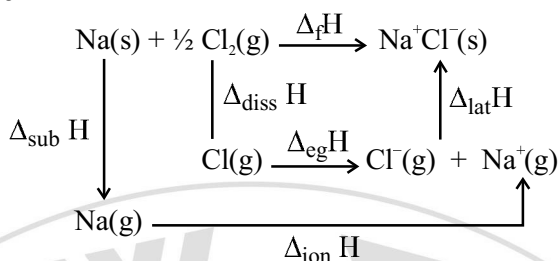
The overall energy change can be computed by taking the sum of all the energy changes:

$$\Delta H = ( 180.7 + 493.8 + 120.9 - 379.5 - 754.8 ) = - 410.9 \text{ kJ mol}^{-1}$$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

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## Born Haber Cycle



Of the five different types of energies involved, two (sublimation and dissociation energies) generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. On the basis of the above discussion we can say that the formation of an ionic compound is favoured by

- i. Low ionisation energy of the metal,
- ii. High electron affinity of the other element (non-metal), and
- iii. High lattice energy

### 4.3.2 Characteristic Properties of Ionic Compounds

- These exist as crystalline solids in which the ions are arranged in a regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explains bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. Secondly, this theory is incapable of explaining the formation of molecules like,  $\text{SO}_2$  or  $\text{O}_2$ , etc. For example in case of  $\text{O}_2$ , there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

## 4.4 COVALENT BOND

Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration is achieved, is different. Lewis proposed that this is achieved by "sharing of a pair of electrons" between the two atoms. Both the

# Chemical Bonding

atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shown as

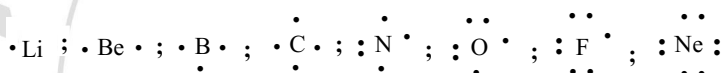


This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for 'bonding' between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called covalent compounds.

## 4.4.1 Lewis Structure

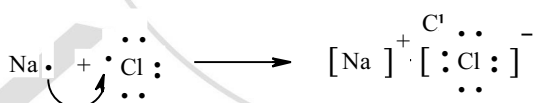
In the process of suggesting the process of chemical bonding Lewis provided a very convenient way of representing bonding in simple molecules. This is called **Lewis electron-dot structures** or simply **Lewis structures**.

In Lewis structure each element is represented by a **Lewis symbol**. This symbol consists of the normal chemical symbol of the element surrounded by number of dots representing the electrons in the valence shell. Since the electrons are represented by dots, these are called electron-dot structures. The Lewis symbols of some elements are as:



You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols

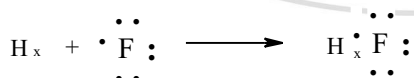
In terms of Lewis symbols the ionic bond formation in NaCl can be represented as



and the covalent bond formation in HCl is represented as



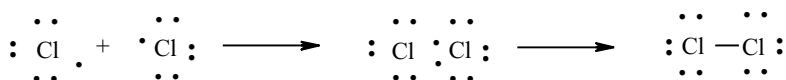
Sometimes the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as



In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no difference between electrons; it is just a presentation for the sake of convenience.

# Chemical Bonding

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as



Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.



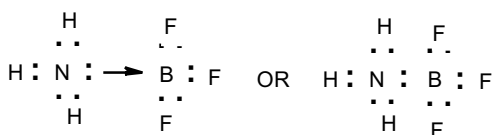
You may have noticed that in the process of bond formation, the elements of second period acquire eight electrons in their valence shell. This is called '**Octet rule**'. You may also note that in case of  $\text{H}_2$  and  $\text{Cl}_2$  the atoms are linked by a single line while in case of  $\text{O}_2$  the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said to be joined by a single bond. And when, two pairs of electrons are shared (as in case of  $\text{O}_2$ ), the two atoms are said to be bound by a double bond. In nitrogen ( $\text{N}_2$ ) the two atoms are joined by a triple bond as they share three pairs of electrons.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding electrons; the pair of electrons is called '*bond pair*' and the pairs of electrons not involved in the bonding process are called '*lone pairs*'. The nature of the electron pair plays an important role in determining the shapes of the molecules. This aspect is discussed later in Section 4.4.

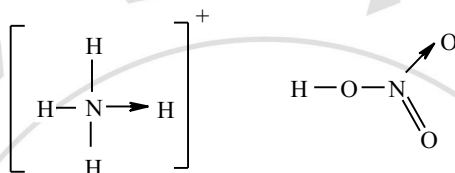
## 4.4.2 Coordinate Covalent Bond

You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair. However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion). A common example is the formation of a bond between boron trifluoride ( $\text{BF}_3$ ) and ammonia ( $\text{NH}_3$ ).  $\text{BF}_3$  is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electrons on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electrons to electron deficient  $\text{BF}_3$ . Such electron donor-acceptor bonds are called **coordinate covalent** or **dative bonds**.

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A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is identical to a covalent bond in terms of its polarity and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed.  $\text{HNO}_3$  and  $\text{NH}_4^+$  ion are some more common examples of formation of a coordinate bond.



## INTEXT QUESTION 4.1

1. Define electrovalent bond.
2. Show the formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.
3. What do you understand by a polar covalent bond? Give two examples.
4. What is a coordinate covalent bond ? How is it different from a covalent bond?

### 4.4.3 Characteristic properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

### 4.4.4 Polar Covalent Bond

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule this shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electro-



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negative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more towards more electronegative chlorine atom. As a result of this unequal sharing of the electron pair, the bond acquires polarity or partial ionic character.



In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus, though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

## 4.4.5 Bond Polarity and Dipole Moment

A covalent bond is formed by sharing of a pair of electrons by the two atoms—each one of which contributes one electron. If the two atoms have the same electronegativity, then the sharing of the two bonded atoms is equal, see Fig. 4.1. This situation is encountered when both the atoms are of the same element as in  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  etc. Such a bond is pure covalent bond. It is *non-polar* in nature. However, if the electronegativities of the two bonded atoms are different as in HCl, then the shared pair of electrons lies more towards the more electronegative atom i.e. chlorine. As a result, a small negative charge ( $\delta^-$ ) develops on Cl atom and an equal positive charge ( $\delta^+$ ) develops on H atom. The covalent bond in HCl is a *polar covalent bond*. It is not a pure covalent bond as it has some ionic character.

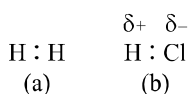


Fig. 4.1: Non-polar or pure covalent bond; (b) polar covalent bond

The extent of shift of the shared pair of electrons and hence the magnitude of ionic character depends upon the difference in electronegativities of the two bonded atoms. If it is 1.7, then the bond has 50% ionic character. If it is less than 1.7, then ionic character is less than 50% and if the difference is more than 1.7, then the ionic character is more than 50%.

## Dipole Moment

Charge separation in a covalent bond results in the formation of an electrical dipole (two equal but opposite charges with a small distance between them). Each electrical dipole is characterized by its **dipole moment** which is defined as

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Dipole Moment ( $\mu$ ) = Magnitude of charge ( $Q$ )  $\times$  Distance of Separation ( $r$ )

It is commonly measured in the unit ‘**debye**’, symbol D. The SI unit of dipole moment is Coulomb-metre (Cm). The two units are related as

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

The dipole moment depends upon the difference in electronegativities of the two bonded atoms. It can be seen from the data given below

Bond	Electronegativity of halogen atom	Dipole moment/D
H-F	4.0	1.90
H-Cl	3.0	1.04
H-Br	2.8	0.79
H-I	2.5	0.38

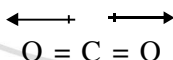
Dipole moment is a vector quantity since it has direction and magnitude both. By convention, the symbol ( $\longleftrightarrow$ ) is used to represent the dipole moment with tail on the positive centre and the head pointing towards the negative centre. The dipole moment of HCl is represented as



Like forces, dipole moment vectors can be added and subtracted. By doing so, the overall dipole moment of a molecule can be calculated. Let us consider some examples to understand it.

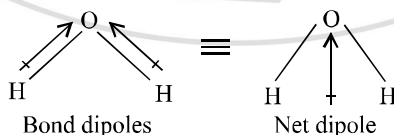
## (i) Carbon dioxide, CO<sub>2</sub>

CO<sub>2</sub> molecule is a linear triatomic molecule. Each C = O bond is polar with the oxygen atom having the negative end of the bond dipole



The dipole moments of both the C = O bonds have the same magnitude but are in opposite directions hence they cancel each other. The net dipole moment of CO<sub>2</sub> is zero.

## (ii) Water, H<sub>2</sub>O

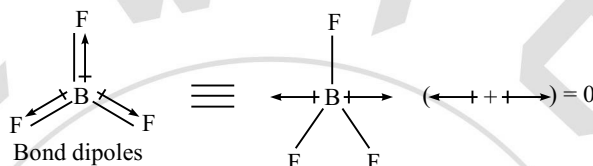


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H<sub>2</sub>O is a non-linear or bent diatomic molecule. Each H–O bond is a polar covalent bond and has a dipole moment. Although dipole moments of both the bonds are equal in magnitude, but due to non-linear shape, they do not cancel each other. The net dipole moment of H<sub>2</sub>O molecule is 1.85D (or  $6.17 \times 10^{-30}$  cm)

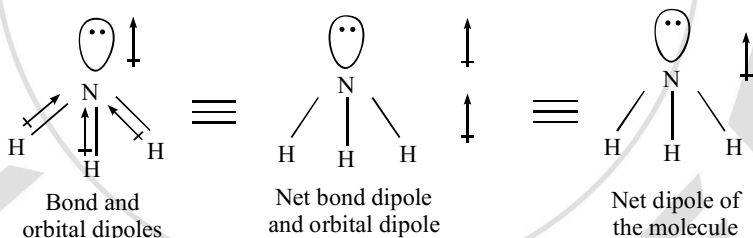
## (iii) Boron trifluoride, BF<sub>3</sub>

The net dipole moment for BF<sub>3</sub> is zero due to its symmetrical planar structure as shown below, although the B–F bonds are polar.



## (iv) Ammonia, NH<sub>3</sub>

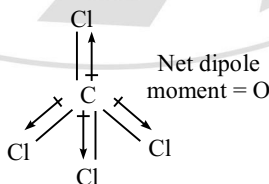
NH<sub>3</sub> has a pyramidal structure which makes the arrangement of three N–H bonds unsymmetrical. In each N–H bond, nitrogen is the negative centre and hydrogen is the positive centre. In addition to three N–H bonds, nitrogen atom has a lone pair of electrons, which also has an orbital dipole moment in which the electron pair is the negative centre.



The net dipole moment of NH<sub>3</sub> is 1.47D ( $4.90 \times 10^{-30}$  Cm).

## (v) Carbon tetrachloride, CCl<sub>4</sub>

It has a net zero dipole moment due to its symmetrical tetrahedral shape



# Chemical Bonding

## 4.4.6 Covalent Character of Ionic Bond

In the earlier discussion, we have seen that most of the covalent bonds have some ionic character. Similarly, ionic bonds also have some covalent character. The origin of covalent character of an ionic bond lies in the distortion of electron cloud under the influence of an electric charge. This property of an electron cloud to get distorted is called its **polarizability** and the process of distortion of electron cloud is called **polarization**. The power of an electric charge to distort an electron cloud is called its **polarizing power**. In an ionic compound cations and anions are formed as a result of loss and gain of electrons, respectively. Each ion tries to polarize the electron cloud of the other.

Generally, cations have greater polarizing power due to their small size and hence high charge density. Anions are more easily polarized. Due to their large size, the electrons in anions are more loosely bound to the nucleus than in cations. Cation attracts the electron cloud of the anion and this results in its polarization and the electron cloud spreads out towards cation in between the two ions. Thus the electron lost by cation does not fully belong to the anion but partially comes back towards cation and is shared by it. This results in some covalent character in the ionic bond. The more the polarization, the more is the covalent character.

Fajan proposed some empirical rules that deal with the polarization process. These rules are known as **Fajan's rules** which are given below. The following factors increase the covalent character of an ionic bond

- (i) small cation
- (ii) large anion
- (iii) high positive charge on cation
- (iv) cations with electronic configuration  $(n-1)d^xns^0$  (typically transition metal cations) as compared to cations with same size and charge but having  $ns^2np^6$  (noble gas) configuration.

## 4.4.7 Covalent Bond Parameters

Each covalent bond is characterized by the following parameters which are called covalent bond parameters.

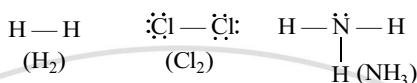
### (1) Bond order

Bond order is the number of bonds present between two atoms in a molecule or ion. Generally, bond order has an integral value. For example,

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## Bond order = 1

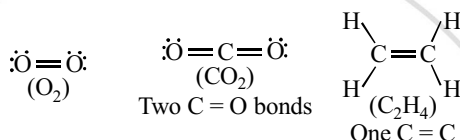
Bond order is 1 (one) when there is only **one covalent bond** (sigma bond) between the two bonded atoms.  $H_2$ ,  $Cl_2$ ,  $NH_3$  are some such examples. These are called single bonds.



In  $NH_3$  molecule, there are three single N-H bonds.

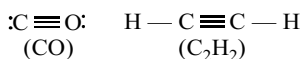
## Bond order = 2

Bond order is 2 (two) when there are **two covalent** bonds between the two bonded atoms. Of the two, one is a sigma bond and the other is a pi bond. These are called double bonds. Examples are as follows.



## Bond Order = 3

Bond order is 3 (three) when there are three bonds between the two bonded atoms. Out of these, one is a sigma bond and two are pi bonds. These are called triple bonds. Examples are given below.



## (2) Bond Length

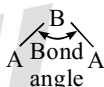
Bond length is the distance between the nuclei of the two bonded atoms. It is expressed in picometer (pm). Bond length depends upon the sizes of the bonded atoms and the bond order of the bond linking them. The greater the bond order, the smaller is the bond length.

Bond	Bond Length/pm	Bond	Bond Length/pm
H-H	74	O=O	121
H-F	92	N≡N	109
H-Cl	127	C-C	154
H-Br	141	C=C	134
H-I	160	C≡C	120
		C=O	122

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## (3) Bond Angle

It is the angle between the two bonds in a molecule. Since covalent bonds are formed through overlapping of orbitals, it may also be defined as the angle between the two orbitals that contain bonding electrons and overlap with atomic orbitals of other atoms. Bond angle between two bonds or bonding orbitals is shown below

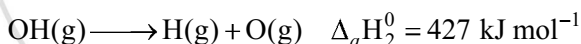
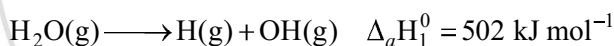


The bond angle between two O–H bonds in  $\text{H}_2\text{O}$  molecule is  $104.5^\circ$ , between N–H bonds in  $\text{NH}_3$  molecule is  $107.3^\circ$  and between C–H bonds in  $\text{CH}_4$  is  $109^\circ 28'$ .

## (4) Bond Enthalpy $\Delta_a H$

It is the amount of energy required for breaking one mole of bonds of a particular type in gaseous molecules. It is also called bond dissociation enthalpy, and is applicable to simple molecules, containing only one bond of the particular type. For example, the bond enthalpy of Cl–Cl bond in  $\text{Cl}_2$  is  $243 \text{ kJ mol}^{-1}$ , of O=O in  $\text{O}_2$  is  $498 \text{ kJ mol}^{-1}$  and of  $\text{N}\equiv\text{N}$  bond in  $\text{N}_2$  is  $946 \text{ kJ mol}^{-1}$ .

A difficulty arises in using this definition in case of molecules that contain more than one bond of the same type.  $\text{H}_2\text{O}$  molecule has two O–H bonds and the two bonds require different amounts of energies to break.



Likewise, there are three N–H bonds in  $\text{NH}_3$  and four C–H bonds in  $\text{CH}_4$ . Each one of these bonds requires a different amount of energy to break. In such cases, **average bond enthalpy** is considered. It is defined as the average energy per bond required to dissociate one mole of bonds in gaseous atoms.

$$\text{Average bond enthalpy} = \frac{\text{Total energy required to break all the bonds of a particular type in one mole of gaseous molecules}}{\text{Total no. of moles of bonds broken.}}$$

For example in case of water molecule

$$\text{Average bond enthalpy of O–H bond} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

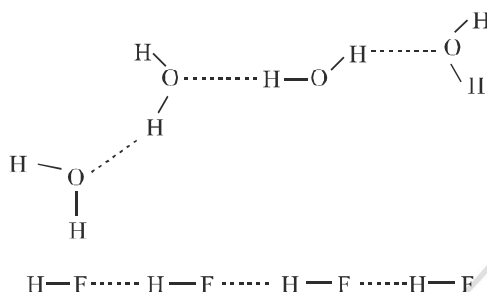
Some bond enthalpy values are given below:

# Chemical Bonding

Bond	Bond Enthalpy/kJ mol <sup>-1</sup>	Bond	Bond Enthalpy/kJ mol <sup>-1</sup>
H-H	436	N≡N	946
H-C	414	O=O	498
H-N	391	C-C	347
H-O	464	C=C	611
N-N	159	C≡C	837
O-O	138	C≡N	891
F-F	157	C-Cl	330

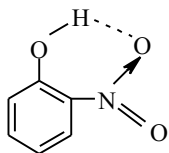
## 4.5 HYDROGEN BONDING

It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol<sup>-1</sup>. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol<sup>-1</sup> of energy to break. However, it is strong enough to be responsible for the high boiling points of H<sub>2</sub>O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.

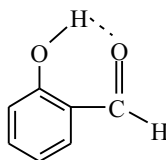


Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a partial positive charge while the electronegative atom bears the partial negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bond**. Salicylaldehyde and o-nitrophenol are two common examples of the molecules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.

# Chemical Bonding



o-nitrophenol



Salicylaldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecules like proteins and nucleic acids.

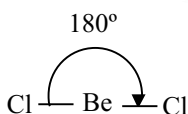
## 4.6 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in 1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

### POSTULATE 1

**The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize 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. Let us take up some examples.

**BeCl<sub>2</sub>** is one of the simple triatomic molecules. In this molecule, the central atom, beryllium has an electronic configuration of  $1s^2 2s^2$ . That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of  $180^\circ$  which gives the molecule a linear shape.



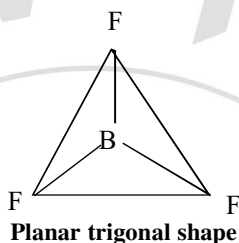
Cl — Be — Cl  
linear molecule



# Chemical Bonding

Other molecules of this type would also have a similar shape.

**BF<sub>3</sub>**: In boron trifluoride, the central atom, boron has an electronic configuration of  $1s^2 2s^2 2p^1$ . That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of  $120^\circ$  which gives the molecule a planar trigonal shape.



Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 4.1.

Table 4.1: Geometric arrangements of electron pairs around central atom.

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX <sub>2</sub>	2	Linear		HgCl <sub>2</sub> , BeCl
AX <sub>3</sub>	3	Planer trigonal		BF <sub>3</sub> , BCl <sub>3</sub>
AX <sub>4</sub>	4	Tetrahedral		CCl <sub>4</sub> , CH <sub>4</sub> , SiCl <sub>4</sub>
AX <sub>5</sub>	5	Trigonal bipyramidal		PCl <sub>5</sub> , PF <sub>5</sub>
AX <sub>6</sub>	6	Octahedral		SF <sub>6</sub> , PF <sub>6</sub> <sup>-</sup>

# Chemical Bonding

## POSTULATE 2

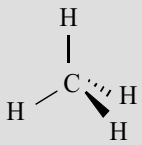
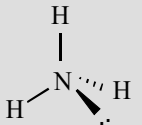
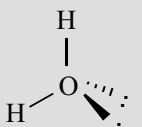
**The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than between two bond pairs.** The order of repulsive force between different possibilities is as under.

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

The shapes of the molecules given in Table 4.1. correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 4.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs, while one is a lone pair. Similarly, in case of water again there are four pairs of electrons ; two are bond pairs, while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 4.2.

**Table 4.2: Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.**

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH <sub>4</sub>	4	0	tetrahedral		109.5
NH <sub>3</sub>	3	1	trigonal pyramidal		107.3
H <sub>2</sub> O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer ( ionic bonding) or sharing (covalent bonding) of electrons.

# Chemical Bonding

The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 2. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

## INTEXT QUESTION 4.2

1. What are the basic postulates of VSEPR theory?
2. Predict the shape of methane ( $\text{CH}_4$ ) on the basis of VSEPR theory.
3. It is a molecule the difference between the electro-negativity of two atom is 1.7. How much % will be ionic and covalent character?

## 4.7 MODERN THEORIES OF CHEMICAL BONDING

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are known as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

### 4.7.1 Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

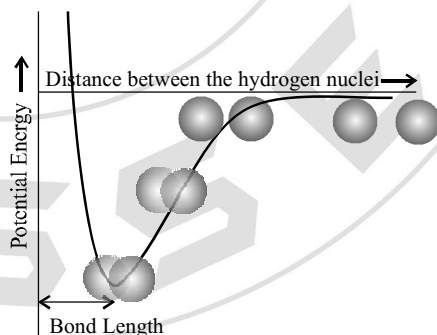


Fig. 4.2 : Formation of hydrogen molecule from overlapping of two hydrogen atoms

# Chemical Bonding

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective  $1s$  orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their  $1s$  orbitals begin to overlap which lead to decrease in energy, Fig. 4.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

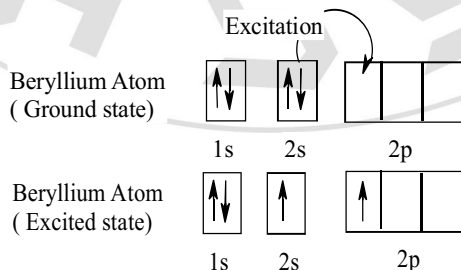
This simple approach can be used to explain the bonding in simple diatomic molecules like  $\text{HF}$ ,  $\text{F}_2$  etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridisation need to be used.

## 4.7.1.1 Hybridisation

“Hybridisation is the process of forming new orbitals by mixing of atomic orbitals in a particular atom. The new hybrid orbitals that are formed are all equivalent orbitals and have the same energy. The phenomenon is known as hybridisation”. Two main characteristics of hybridisation are:

- The number of hybrid orbitals formed is the same as the number of atomic orbitals undergoing hybridisation.
- All the new hybrid orbitals that are formed are exactly identical in their shapes and energy.

Let us take up the example of bonding in a triatomic molecule; say, beryllium hydride ( $\text{BeH}_2$ ) to understand the concept of hybridisation of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is  $1s^2 2s^2$ . In order to form bonds with two hydrogen atoms the valence electrons ( $2s^2$ ) of beryllium atom must overlap with the  $1s$  electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e.,  $2s$ ) it cannot overlap with the  $3p$  orbital of hydrogen atoms containing one electron. [You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the  $2s$  orbital of beryllium atom gets momentarily excited to the empty  $2p$  orbital as shown below.

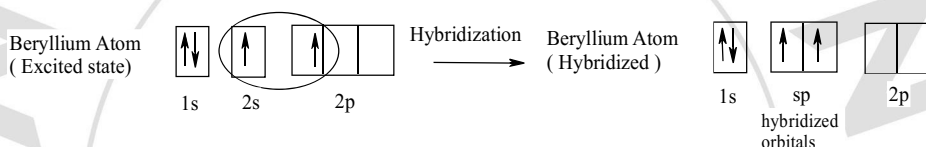


## Chemical Bonding

Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of 2s orbital of beryllium with 3p orbital of chlorine while the other would involve overlapping of 2p orbital of beryllium with 2p orbital of chlorine. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called **hybridisation** of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of  $\text{BeCl}_2$  the two singly occupied orbitals (2s and 2p) hybridize to give two  $sp$ -hybrid orbitals. This is called  **$sp$  hybridisation**. These hybrid orbitals lie along the  $z$ -direction and point in opposite directions.

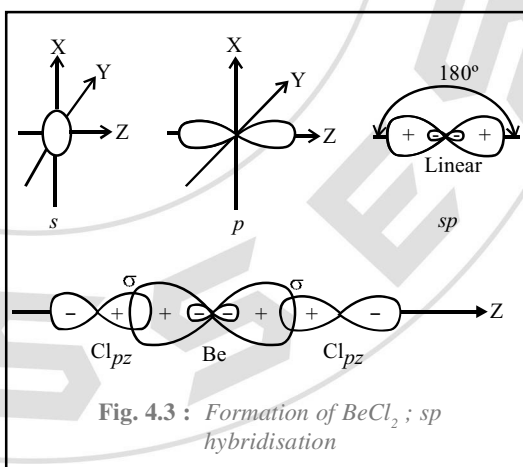


These hybrid orbitals can now overlap with the 3p orbitals of chlorine atoms to give the linear molecule of  $\text{BeCl}_2$  as shown below, Fig. 4.3.

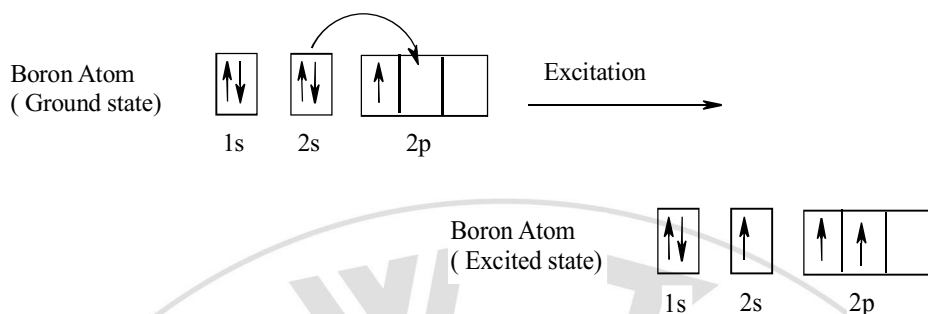
The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridisation of suitable orbitals. Let us take up some more cases involving hybridisation of  $s$  and  $p$  orbitals.

**Boron trichloride ( $sp^2$  hybridisation):** In boron there are five electrons and the electronic configuration is  $1s^2, 2s^2, 2p^1$ . There are three electrons in the valence shell of boron atom.

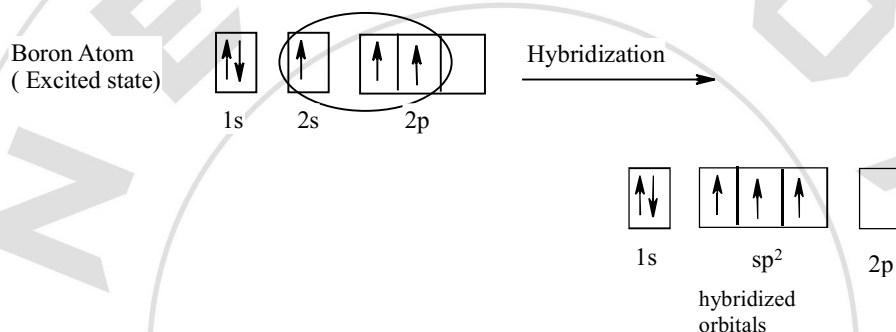
In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital.



# Chemical Bonding



One 2s orbital and two 2p orbitals hybridise to give three  $sp^2$  hybridized orbitals. This is called  **$sp^2$  hybridisation**.



The three hybridized orbitals are coplanar and directed towards the corners of an equilateral triangle. These **hybrid** orbitals then form bonds with the p-orbitals of chlorine atoms as shown below, Fig. 4.4.

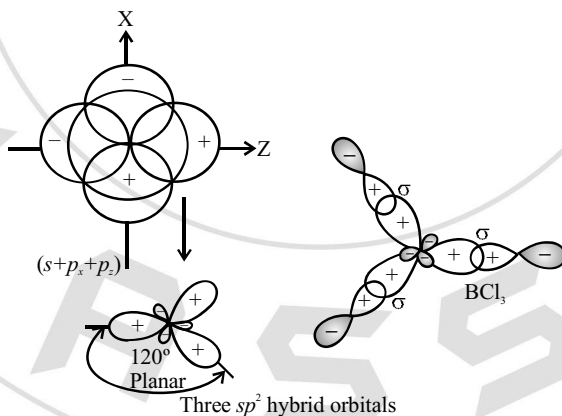
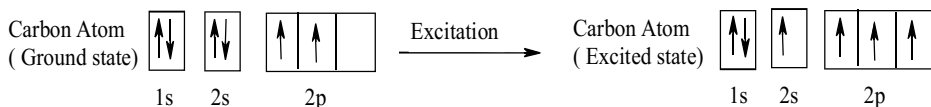


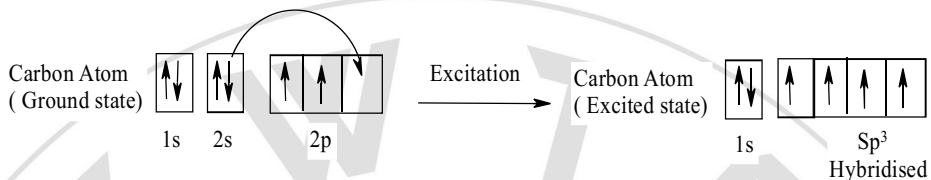
Fig. 4.4 : Formation of  $BCl_3$  ;  $sp^2$  hybridisation.

**Bonding in Methane ( $sp^3$  hybridisation) :** In case of methane the central atom, carbon, has an electronic configuration of  $1s^2, 2s^2, 2p^2$ . In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital.

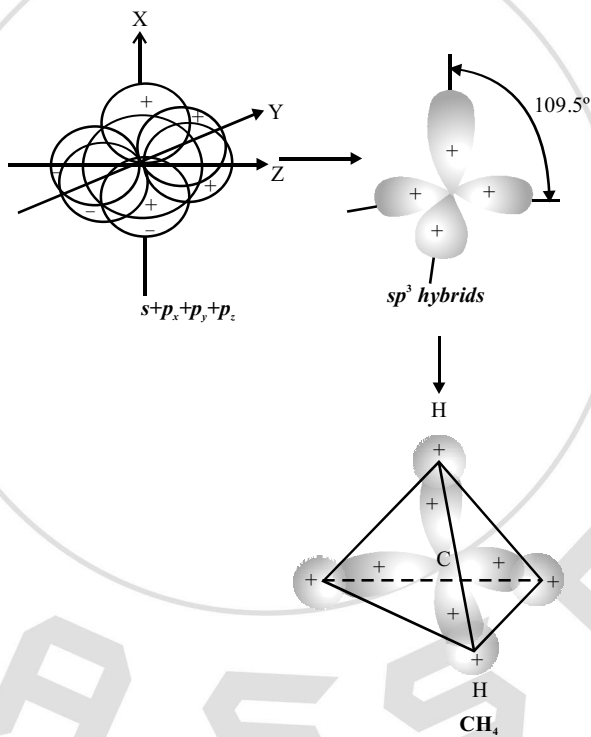
# Chemical Bonding



One 2s orbital and three 2p orbitals of the carbon atom then hybridise to give four  $sp^3$  hybridised orbitals. This is called  **$sp^3$  hybridisation**.

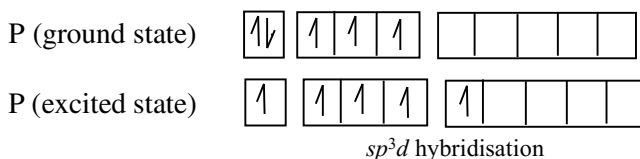


These four  $sp^3$  hybrid orbitals are directed towards the corners of a regular tetrahedron. These **hybrid** orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 4.5.



**Fig. 4.5 :** *Formation of  $CH_4$  ;  $sp^3$  hybridisation.*

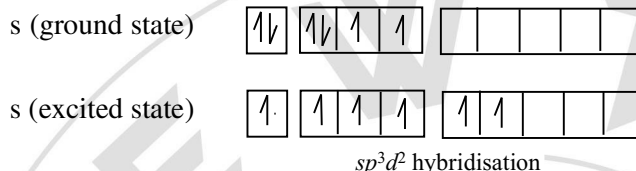
**Phosphorus pentachloride ( $sp^3d$  hybridisation):**



## Chemical Bonding

Five  $sp^3d$  hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramid (Fig. 4.5a). These orbitals overlap with singly filled  $p$ -orbitals of five chlorine atoms and five  $\sigma$  bonds are formed. Thus  $PCl_5$  molecule has a trigonal bipyramidal geometry. Three P–Cl bonds (equatorial) make an angle of  $120^\circ$  with each other and lie in one plane. The other two P–Cl bonds (axial) are at  $90^\circ$  to the equatorial plane, one lying above and the other lying below the plane.

### $SF_6$ ( $sp^3d^2$ hybridisation):



Six  $sp^3d^2$  hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form  $\sigma$  bonds giving a regular octahedral geometry (Fig. 4.5 b)

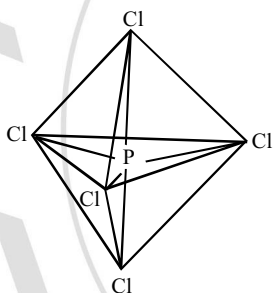


Fig. 4.5 (a) : Trigonal bipyramidal geometry of  $PCl_5$  molecule.

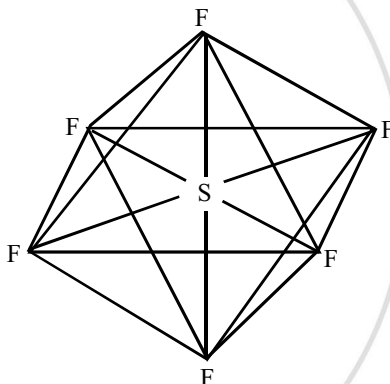


Fig. 4.5 (b) : Octahedral geometry of  $SF_6$  molecule

### 4.7.1.2 Hybridisation and Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane ( $C_2H_6$ ), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo  $sp^3$  hybridisation. In ethane each carbon atom undergoes  $sp^3$  hybridisation to give four  $sp^3$  hybridized orbitals. The two carbon atoms form a carbon – carbon bond by  $sp^3$  -  $sp^3$  overlapping. The remaining six  $sp^3$  hybridized orbitals overlap with  $1s$  orbitals of hydrogen atoms to give a molecule of *ethane*,  $C_2H_6$ , as shown in Fig.



## Chemical Bonding

4.6. The C-C bond so formed is along the internuclear axis. Such a bond is called a  **$\sigma$  bond**.

**Bonding in ethene:** In case of ethene, the relevant orbitals of the carbon atoms undergo  $sp^2$  hybridisation. Here, only two of the three  $p$  orbitals of the carbon atoms hybridize with the  $2s$  orbital to form three  $sp^2$  hybrid orbitals each. The remaining  $p$ -orbitals (one on each carbon atom) do not take part in hybridisation. A carbon – carbon bond is formed by overlapping of  $sp^2$  orbital on the two carbon atoms [Fig. 4.7(a)]. The remaining four  $sp^2$  hybridized orbitals overlap with the  $1s$  orbitals of hydrogen atoms to give the basic skeleton of the molecule. This leaves an un-hybridized  $p$  orbital each on both the carbon atoms [Fig. 4.7(b)]. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plane above and below the molecule [Fig. 4.7(b and c)]. This is called a  **$\pi$ - bond**. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

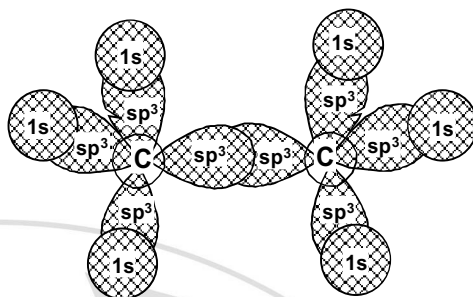


Fig. 4.6 : Formation of ethane molecule

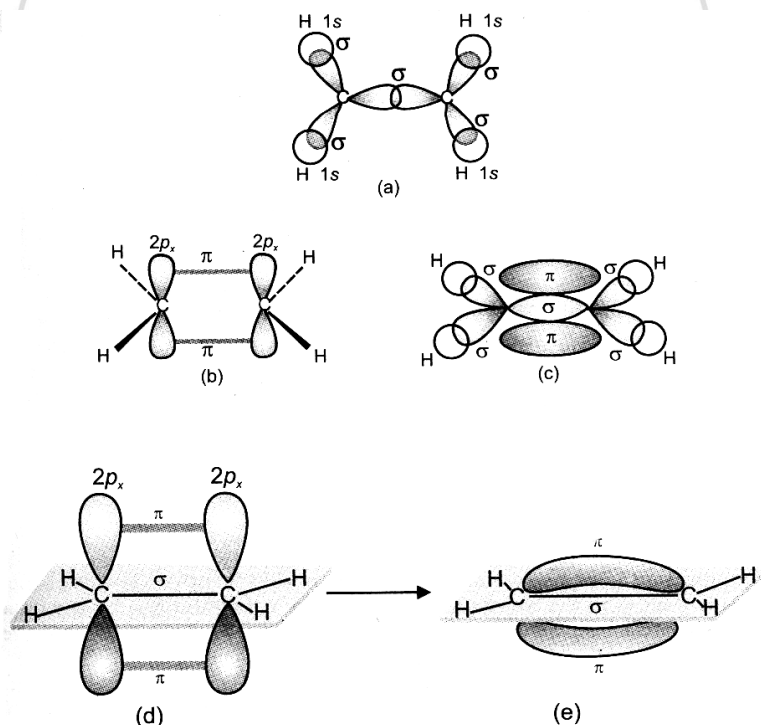
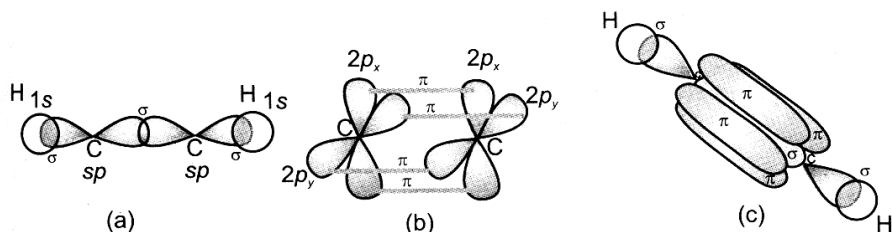


Fig. 4.7 : Formation of ethylene molecule: (a) formation of the basic skeleton of the molecule (b) sideways overlapping of the unhybridized  $p$  orbitals and (c) a  $\pi$ - bond (d) and (e) complete picture of ethylene molecule.

# Chemical Bonding

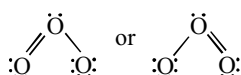
**Bonding in ethyne (acetylene):** In case of acetylene the bonding can be explained in terms of  $sp$ -hybridisation in carbon atoms. One  $2s$  and one  $2p$  orbitals hybridize to give two  $sp$ -hybridized orbitals. This leaves two mutually perpendicular unhybridised  $p$  orbitals each on both the carbon atoms. The carbon – carbon bond is formed by  $sp - sp$  overlapping with each other. The remaining  $sp$  orbital on each carbon overlaps with the  $1s$  orbital of hydrogen to give C-H bonds (Fig. 4.8). The unhybridised  $p$  orbitals each on both the carbon atoms overlap sideways to give two  $\pi$ -bonds.



**Fig. 4.8 :** Formation of acetylene molecule : (a) formation of the basic skeleton of the molecule (b) sideways overlapping of two pairs of un-hybridized  $p$  orbitals and (c) two mutually perpendicular  $\pi$ - bonds.

## 4.7.1.3 Resonance

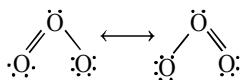
Some times it is possible to write more than one Lewis structure of a compound that agree with the electronic requirements. For example, we can write two Lewis structures for ozone molecules,  $O_3$ .



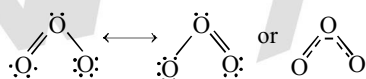
Both of these structures satisfy the octet rule and have a double bond on one side and single bond on the other side of the central oxygen. According to these structures one oxygen-oxygen bond ( $O=O$ ) would be shorter than the other ( $O-O$ ). However, this is not the case. Experimentally both the oxygen-oxygen bonds are found to have the same bond length (128 pm) which is in between the bond lengths of a ( $O=O$ ) double bond (121 pm) and a ( $O-O$ ) single bond (148 pm).

These experimental observations can be explained with the help of the concept of *resonance*. The alternate Lewis structures are called **canonical structures**. These are separated by a double headed arrow ( $\leftrightarrow$ ). All canonical structures must have similar positions of nuclei, similar number of bonding and non-bonding electrons and similar energy. The actual structure is the **resonance hybrid** of all the contributing canonical or resonating structures. The structure of  $O_3$  molecule is represented as

# Chemical Bonding



Resonance does not mean that the molecule constantly changes from one canonical structure to the other. The structure is stable and the bond lengths and energies have values which are intermediate between those of single and double bonds. The concept of the resonance is necessary because of the limitations in the way *we write* the structures. Some times the structure of a resonance hybrid is shown with help of representation of bonds by broken lines or dashes. The structure of resonance hybrid of  $\text{O}_3$  is shown below:

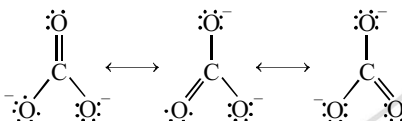


In molecules or ions containing more than two atoms and having double bonds or triple bonds, there are **pi ( $\pi$ ) bonds**. The electrons involved in  $\pi$ -bonds are not localized between two atoms, but are spread over the entire structure (or the portion of the structure) which has only sigma ( $\sigma$ ) bonds. This spreading of  $\pi$ -electrons is known as the delocalization of the electrons. Broken lines or dashes depict the region of delocalization of the  $\pi$ -electrons. Delocalization results in stabilizing the structure. Therefore, the resonance hybrid is more stable than the contributing canonical structures.

Some examples of resonance structures:

## (1) Carbonate ion ( $\text{CO}_3^{2-}$ )

The three possible canonical structures of carbonate ion are



## (2) Sulphur dioxide ( $\text{SO}_2$ )

The two canonical structures of sulphur dioxide are shown below



## (3) Dinitrogen oxide ( $\text{N}_2\text{O}$ )

The three canonical structure of dinitrogen oxide are shown below



## INTEXT QUESTION 4.3

1. What do you understand by the term, ‘hybridisation’?
2. How would you explain the shape of ammonia molecule on the basis of hybridisation?
3. Draw the canonical structures of  $\text{CO}_3^{2-}$  and  $\text{SO}_2$ .

### 4.7.2 Molecular Orbital Theory

You have just learnt about valence bond theory. It describes bond formation as a result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised. Molecular orbital theory (MOT) was developed by F.Hund and R.S.Mulliken in 1932. In contrast to the localized bonding in VBT, the molecular orbital theory visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- **The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals).** These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not “belong” to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals (LCAO) approach in which, **the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.**
- The available **electrons then fill these orbitals in the order of increasing energy as in the Aufbau principle** used in the electron configurations of atoms.

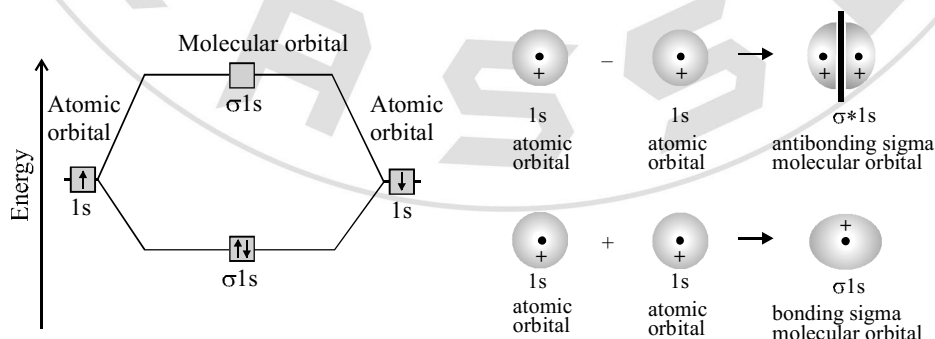


Fig. 4.9 : Formation of bonding ( $\sigma$ ) and anti bonding ( $\sigma^*$ ) molecular orbitals

# Chemical Bonding

Let us take the example of hydrogen molecule to understand the molecular orbital approach to chemical bonding. The two hydrogen atoms have one electron each in their respective 1s orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wavefunction is obtained by addition of the two atomic wave functions whereas in the other the MO is obtained by subtraction of the wave function. The combination of the 1s orbitals on the two hydrogen atoms are shown in Fig. 4.9.

The molecular orbital obtained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals and is called a **bonding orbital**. On the other hand, the orbital obtained by subtraction of atomic orbitals is of higher energy and is called an **anti-bonding orbital**. You can note here that the molecular orbitals obtained here are symmetric around the bond axis (the line joining the two nuclei). Such molecular orbitals are called **sigma ( $\sigma$ ) molecular orbitals**. The bonding orbital obtained above is denoted as  $\sigma_{1s}$  while the anti-bonding orbital is denoted as  $\sigma^*_{1s}$ . Here  $\sigma$  indicates the type of molecular orbital; 1s tells about the atomic orbital involved and \* is indicative of the anti-bonding nature of the MO. There are a total of 2 electrons in a hydrogen molecule; according to Aufbau principle these are filled into  $\sigma_{1s}$  orbital. Since the  $\sigma_{1s}$  orbital is a bonding orbital, its getting filled leads to stability or the bond formation.

Like electronic configuration of atoms we write MO electronic configuration for molecules. The MO configuration of hydrogen molecule is given as  $(\sigma_{1s})^2$ . The molecular orbital energy level diagram is given in Fig. 4.10(a).

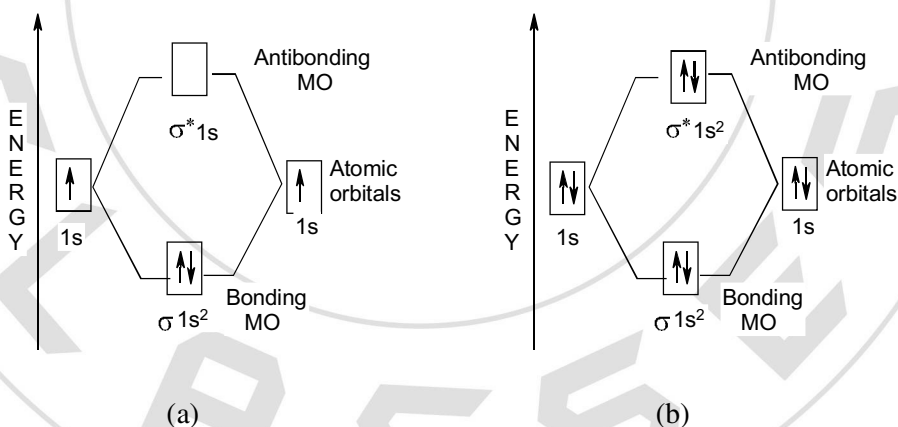


Fig. 4.10 : Molecular orbital energy level diagram for a)  $H_2$  and b)  $He_2$  molecules

**Bond Order:** we may define a new parameter called bond order as

$$\text{Bond order} = (\text{b.o.}) = \frac{1}{2}(n_b - n_a)$$

Where,  $n_b$  and  $n_a$  refer to the number of electrons present in bonding and antibonding molecular orbitals, respectively. For hydrogen molecule the bond order will be  $\frac{1}{2}(2-0) = 1$ , i.e., there is a single bond between two hydrogen atoms.

# Chemical Bonding

## Helium ( $\text{He}_2$ ) molecule

In case of  $\text{He}_2$  also, there will be linear combination of 1s orbitals leading to the formation of  $\sigma 1s$  and  $\sigma^* 1s$  orbitals. The four electrons would be distributed as per the MO electronic configuration :  $(\sigma 1s)^2 (\sigma^* 1s)^2$ . The molecular orbital energy level diagram is given in Fig. 4.10 (b). This gives a bond order of  $\frac{1}{2}(2-2) = 0$ , that is there is no bond between two helium atoms. In other words  $\text{He}_2$  molecule does not exist.

## $\text{Li}_2$ and $\text{Be}_2$ molecules

The bonding in  $\text{Li}_2$  and  $\text{Be}_2$  can be explained by combining the 1s and 2s orbitals to give appropriate MO's. The molecular orbital diagrams for  $\text{Li}_2$  and  $\text{Be}_2$  are given in Fig. 4.11.

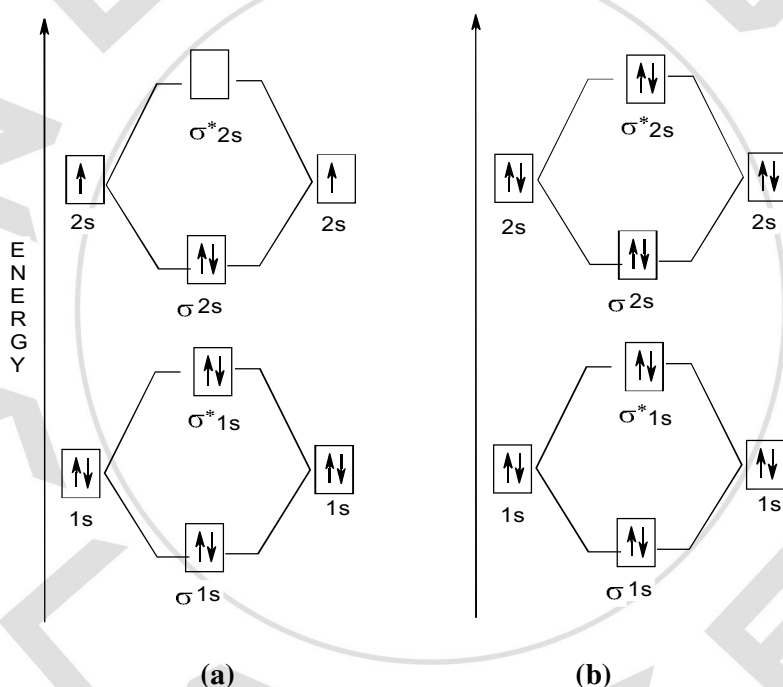


Fig. 4.11: Molecular orbital energy level diagram for a)  $\text{Li}_2$  and b)  $\text{Be}_2$  molecules

### 4.7.2.1 Molecular Orbital Bonding in Diatomic Molecules of Second Period

So far we have talked about bonding in the elements in which the MO's were obtained from the linear combination of s orbitals. In case of the atoms of second period (beyond Be) elements both s and p orbitals are involved in the formation of molecular orbitals. In such a case a number of different molecular orbitals are obtained depending on the type and symmetry of the atomic orbitals involved in

# Chemical Bonding

the process. Let us try to understand the nature of MO's obtained in this case.

Here also the 1s and 2s orbitals of the two atoms would combine to give corresponding bonding and anti-bonding molecular orbital as shown in Fig. 4.11 (b). Let us learn about the formation of MO's from the combination of p orbitals

As mentioned above, in LCAO, the atomic orbitals of **comparable energies** and of **suitable symmetry** combine to give molecular orbitals. A suitable symmetry means that the combining orbitals should have same symmetry about the molecular axis. It is normally assumed that the bond formation takes place along the z-direction. You have learnt in the first unit that the three p orbitals are directed towards three mutually perpendicular directions namely the x, y and z directions. Therefore the  $p_z$  orbitals of the two atoms would combine along the bond axis to give two molecular orbitals as shown below Fig. 4.12. Since these molecular orbitals are symmetric around the molecular axis these are called  $\sigma$  orbitals. The designation of the orbitals would be  $\sigma_{2p_z}$  and  $\sigma_{2p_z}^*$ .

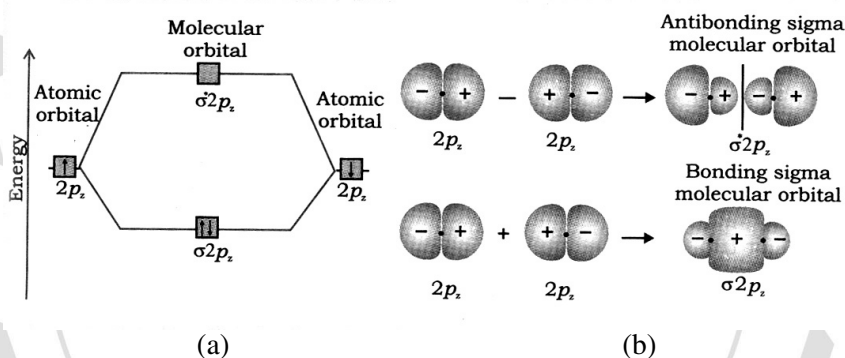


Fig. 4.12: Overlapping of two  $2p_z$  orbitals to give molecular orbitals

**Combination of a  $p_z$ -orbital with either a  $p_x$  or a  $p_y$  orbital would not lead to any bonding.** On the other hand a  $p_x$  orbital will combine with a  $p_x$  and the  $p_y$  with a  $p_y$  as shown in Fig. 4.13.

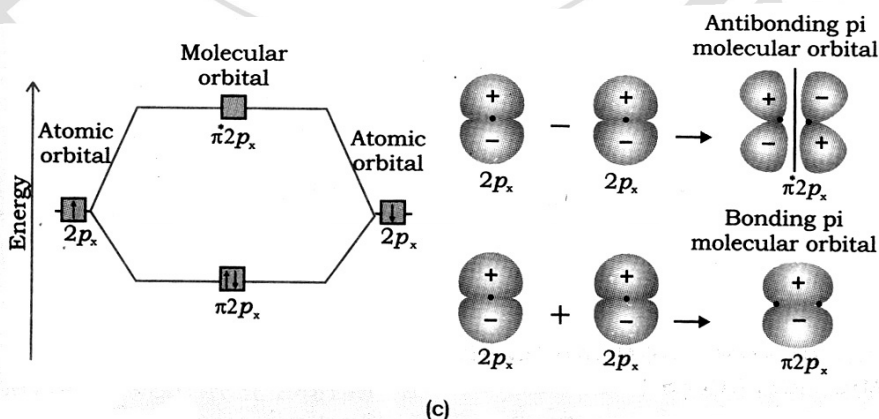


Fig. 4.13 : Formation of molecular orbitals from two  $2p_x$  atomic orbitals.

# Chemical Bonding

You may note here that these orbitals combine in a lateral fashion and the resulting molecular orbitals are not symmetric around the bond axis. These MO's are called  $\pi$ - molecular orbitals. These have large electron density above and below the internuclear axis. The anti-bonding  $\pi$  orbital,  $\pi^* 2p_x$  (or  $\pi^* 2p_y$ ) have a node (a region of zero electron density) between the nuclei.

The molecular orbitals obtained as a result of combination of respective AO's of two atoms can be represented in the form of following energy level diagram, Fig. 4.14(a). The MO's obtained from the combination of 1s orbitals are not shown. (these belong to the inner core and are completely filled) The electrons in these molecular orbitals are filled in accordance with Aufbau principle and Hund's rule.

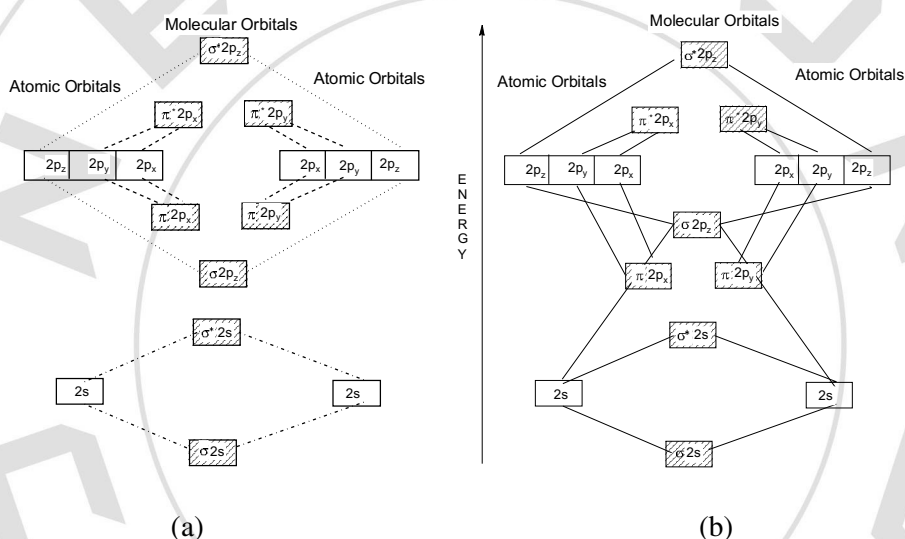


Fig. 4.14: Molecular orbital energy level diagrams a) for  $O_2$  and  $F_2$  and b) for diatomic molecules of lighter elements Li, Be, B, C and N

However, this energy level diagram is valid for the diatomic molecules  $O_2$  and  $F_2$  only; For the diatomic molecules of the lighter elements like, B, C and N this energy level diagram is somewhat modified. It is so because in case of lighter elements the difference in the energy of 2s and 2p orbitals is very low and s and p orbitals on the two atoms get mixed up. In place of normal pure 2s-2s or 2p-2p combinations we may have s-p combinations; for example 2s orbital of first atom can have a reasonable overlapping with  $2p_z$  orbital of the second atom and vice versa. The modified energy level diagram is given in Fig. 4.14 (b).

## 4.7.2.2 MO Electronic Configuration and Properties of a Molecule

The MO energy level diagram discussed above can be used to find out the MO electronic configuration of a molecule. This in turn provides the information about



# Chemical Bonding

some properties of the molecule. Let us take the example of nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's. Using Fig. 4.14, the MO electronic configuration can be written as  $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p_z^2$

**Bond order** :  $\frac{1}{2} [n_b - n_a] = \frac{1}{2} [8 - 2] = \frac{1}{2} [6] = 3$  ; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

**Magnetic nature:** molecules show magnetic behaviour depending on their MO electronic configuration. If all the MO's are **doubly occupied** the substance shows **diamagnetic** behaviour. In case one or more MO's are **singly occupied**, the substance shows **paramagnetic** behaviour. The MO electronic configuration of  $O_2$  (with 12 valence electrons) is  $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1, \pi^* 2p_y^1$ ; Since it contains unpaired electrons, oxygen shows paramagnetic behaviour. This has been found to be so experimentally also. In fact, the explanation of the paramagnetic behaviour of oxygen is an achievement of MOT.

The bond order and the magnetic behaviour of the diatomic molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +ve charge we subtract an electron. For example,  $O_2^{2-}$  (oxygen molecule dianion) would have a total of 14 valence electrons (12 + 2) while oxygen molecule cation  $O_2^+$  would have 12 - 1 = 11 valence electrons.

## INTEXT QUESTION 4.4

1. What is the basic difference between the valence bond and molecular orbital theories?
2. Calculate the bond orders for  $Li_2$  and  $Be_2$  molecules using the molecular orbital diagrams given in Fig. 4.12.
3. Predict the magnetic behaviour of  $O_2$ .

## WHAT YOU HAVE LEARNT

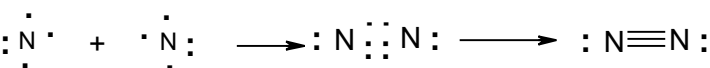
- A chemical bond may be visualised as an effect that leads to the decrease in the energy of the combination of two atoms when they come closer.
- The atoms combine in such a way so as to attain stable electronic configuration of noble gases.
- According to Kossel, transfer of an electron from one atom to the other achieves the stable configuration. This leads to formation of ions, which are held together by electrostatic interactions called ionic bond.

# Chemical Bonding

- According to Lewis, the stable configuration is achieved by sharing of electron pairs between the bonding atoms. This leads to the formation of a covalent bond.
- Bonding in simple molecules can be conveniently represented in terms of Lewis electron-dot structures.
- In some covalently bound atoms the shared pair of electron is more towards the atom with greater electronegativity and leads to partial ionic character in the molecule.
- Valence shell electron pair repulsion (VSEPR) theory is very helpful in predicting the shapes of simple molecules. It is based on the interactions between the electron pairs around the central atom in the molecule.
- Valence bond theory (VBT) and Molecular orbital theory (MOT) are two modern theories of chemical bonding. These are based on the wave mechanical model of atom.
- According to the valence bond theory the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The overlap increases the electron charge density in the inter-nuclear region.
- In order to explain bonding in molecules containing more than two atoms, Pauling proposed the concept of hybridisation. In hybridisation, the atomic orbitals of the valence shell of the central atom 'hybridise' or merge and give newer orbitals with proper orientations, which explain the shape of the molecule.
- According to the Molecular orbital theory the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals. These molecular orbitals extend over the entire region of the molecule i.e., these are delocalised over the whole molecule.
- When two atomic orbitals combine it gives a pair of molecular orbitals; one is called bonding molecular orbital of lower energy and the other of higher energy is called anti-bonding orbital.
- The electrons present in the molecule are filled in these orbitals in the order of increasing energy (Aufbau principle) to give the MO electronic configuration.
- The number of bonds between the two atoms is called bond order and is defined as  $\text{Bond order} = \text{b.o.} = \frac{1}{2}(n_b - n_a)$
- The MO electronic configuration can be used to predict the magnetic nature of the molecule. If all the MO's are doubly occupied the substance shows diamagnetic behaviour and if one or more MO's are singly occupied the substance shows paramagnetic behaviour.

## ANSWERS TO INTEXT QUESTIONS Chemical Bonding

An electrovalent bond is formed when one or more electrons are transferred from one atom to another atom or atoms.



In a covalent bond the shared pair of electrons is closer to the more electronegative atom. This leads to charge separation in the molecule and the bond becomes polar

A bond in which both the bonding electrons are contributed by one atom only.

The two postulates of VSEPR theory are

- i) The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion
- ii) The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is stronger 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

In methane the central carbon atom would have four pairs of electrons in its valence shell. According to VSEPR theory these would be placed tetrahedrally around the carbon atom. Hence the methane molecule would have a tetrahedral shape.

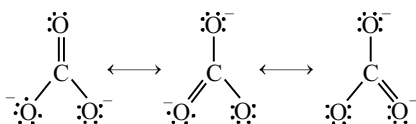
50% ionic and 50% covalent character.

Hybridisation is a concept which is quite useful in explaining the shapes of molecules. According to this two or more than two non equivalent orbitals with comparable energies and different shapes mix and give rise to an equal number of equivalent hybrid orbitals in an atom. The hybrid orbitals have identical energies and shapes.

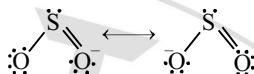
In ammonia the 2s and three 2p orbitals hybridize to give four  $sp^3$  hybridized orbitals. Three of these overlap with the 1s orbitals of hydrogen and one remains nonbonding containing a lone pair. The  $sp^3$  hybridized orbitals are directed towards the corners of a regular tetrahedron. But due to the difference in the repulsion between lone pair - bond pair and bond pair - bond pair the ammonia molecule has a distorted tetrahedral shape which is somewhat like a trigonal pyramid.

## Chemical Bonding

3. The Canonical structure of  $\text{CO}_3^{2-}$  ion are represented as.



Sulphur dioxide is as—



### 4.4

1. Valence bond theory visualises the bond formation to be localized whereas according to MOT it is delocalised.
2. Bond order =  $\text{b.o.} = \frac{1}{2}(n_b - n_a)$   
for  $\text{Li}_2$  ; Bond order =  $\frac{1}{2} [ 4 - 2 ] = \frac{1}{2} [ 2 ] = 1$   
for  $\text{Be}_2$  ; Bond order =  $\frac{1}{2} [ 4 - 4 ] = \frac{1}{2} [ 0 ] = 0$
3. MO configuration of  $\text{O}_2$  is  $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2$   
 $\pi^* 2p_x^1 = \pi^* 2p_y^1$

Due to 2 unpaired electrons  $\text{O}_2$  molecule is paramagnetic.