

# 14.

# CHEMICAL BONDING

## 1. INTRODUCTION

A chemical bond consists of an attraction between atoms that allows the formation of chemical substances which contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction.

There are many approaches to understand the bonding in molecules as explained in the following topics.

## 2. LEWIS DOT DIAGRAM

Lewis postulated that atoms achieve the stable octet (i.e. 8 electrons in their outer most shells), when they are linked by chemical bonds. This can happen (i) by the transfer of electrons(s) from one atom to another, and (ii) by the sharing of a pair of electrons between the atoms. In Lewis Diagrams we represent the outer shell electrons by dots around atom represented by its symbol.

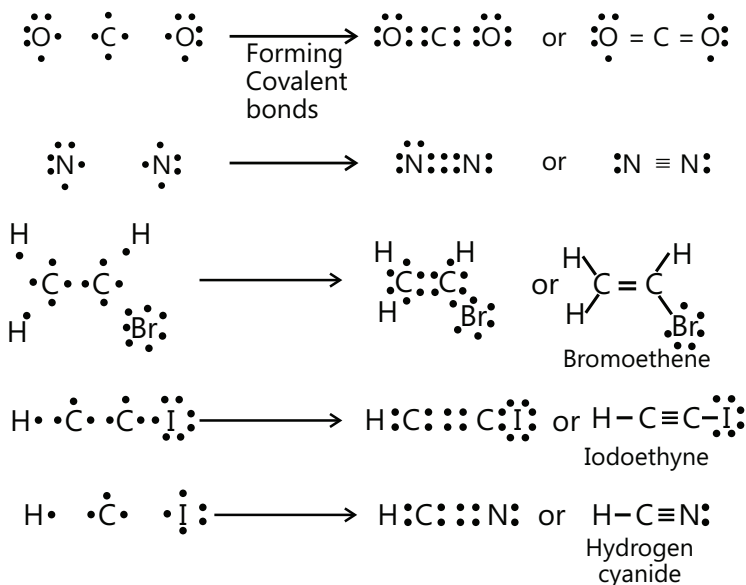
For many common elements, the number of dots corresponds to the element's group number.

For e.g:       $\text{Li}$     $\text{Be}$     $\text{B}$     $\text{C}$     $\text{N}$     $\text{O}$     $\text{F}$     $\text{Ne}$

**Lewis Diagrams for Molecules:** Molecules can be depicted by Lewis Diagrams by placing dots or lines around the constituent elemental symbols. Once again, only valence electrons are shown. Lines denote bonded electron pairs, whereas dots are reserved for only unbound electrons. The following algorithm can be used to construct Lewis diagrams of most molecules.

- Find the total number of electrons:** Determine the total number of valence electrons by reading the group number for each element.
- Draw a first tentative structure:** Frequently the central element is the one with least atoms in the molecule. In your first draft, attach the atoms with single bonds.
- Add electrons as dots to get octets around atoms:** Each atom must have its valence shell completely filled. Remember to count bonds and lone electrons.
- Count the total number of electrons:** Ensure the number of electrons displayed in the symbol agree with the calculation from step 1.
- Cycle through steps 3 and 4:** By way of trial and error, repeat the steps above until a conclusion is reached.

For e.g.



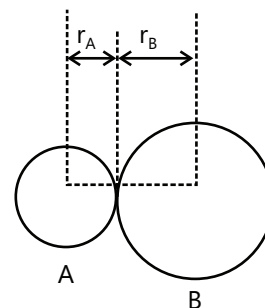
### 3. BOND PARAMETERS

#### 3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques, about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (figure). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms that are joined by a covalent bond.

( $R$  is the bond length and  $r_A$  and  $r_B$  are the covalent radii of atoms A and B respectively.)

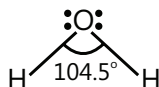


**Figure 14.1:** Bond length in covalent molecule AB.

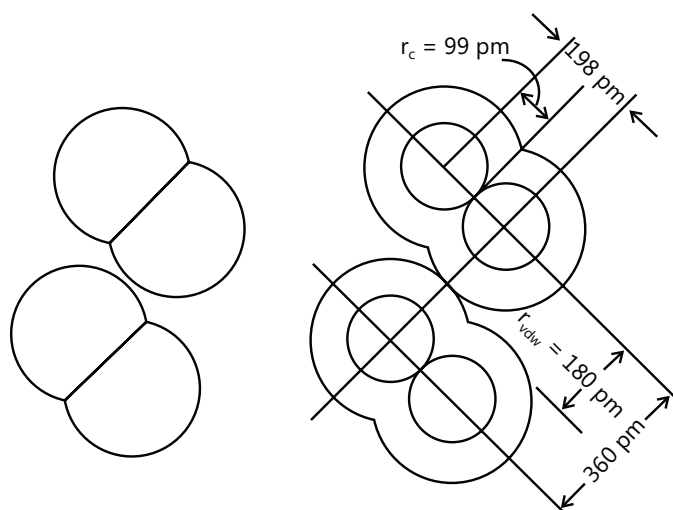
$$R = r_A + r_B$$

#### 3.2 Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree and can be experimentally determined by spectroscopic methods. It gives an idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under:



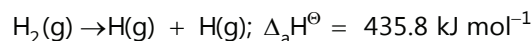
Covalent bond in the same molecule. The van der Waals radius represents the overall size of the atom which includes its valence shell in a non-bonded situation. Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in figure.



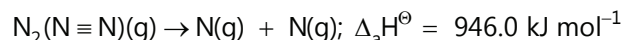
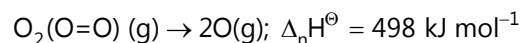
**Figure 14.2:** Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom ( $r_{\text{vdw}}$  and  $r_c$  are van der Waals and covalent radii respectively)

### 3.3 Bond Enthalpy

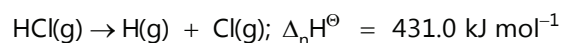
It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is  $\text{kJ mol}^{-1}$ . For example, the H-H bond enthalpy in hydrogen molecule is  $435.8 \text{ kJ mol}^{-1}$ .



Similarly the bond enthalpy for molecules containing multiple bonds, for example  $\text{O}_2$  and  $\text{N}_2$  will be as under:



It is important to note, that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a hetero-nuclear diatomic molecules like HCl, we have



In case of polyatomic molecules, the measurement of bond strength is more complicated. For example, in case of  $\text{H}_2\text{O}$  molecule, the enthalpy needed to break the two O-H bonds is not the same.

### 3.4 Bond Order

In the Lewis description of a covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in  $\text{H}_2$  (with a single shared electron pair), in  $\text{O}_2$  (with two shared electron pairs) and in  $\text{N}_2$  (with three shared electron pairs) is 1, 2, 3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For  $\text{N}_2$ , bond order is 3 and its  $\Delta_{\text{a}}\text{H}^{\ominus}$  is  $946 \text{ kJ mol}^{-1}$ ; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example,  $\text{F}_2$  and  $\text{O}_2^{2-}$  have bond order 1.  $\text{N}_2$ , CO and  $\text{NO}^+$  have bond order 3.

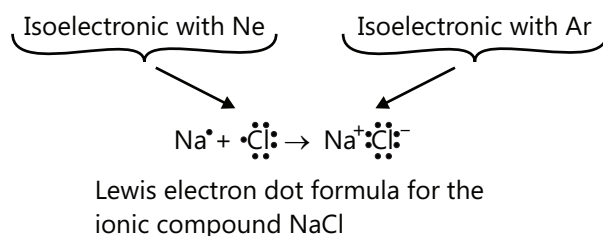
A general correlation useful for understanding the stabilities of molecules is that: with increase in the bond order, the bond enthalpy increases and the bond length decreases.

## 4. TYPES OF BONDING

### 4.1 Ionic Bond

The transfer of electrons from one atom to another results in an ionic bond.

An electron transfer that results in an ionic bond is more likely to occur when an atom with a low ionization energy reacts with an atom that has a large electron affinity.



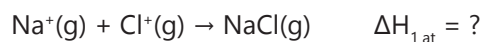
**Figure 14.3** Lewis electron dot formula for the ionic compound NaCl

#### MASTERJEE CONCEPTS

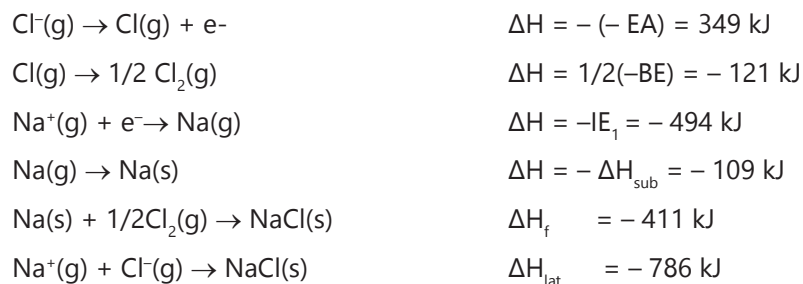
- An ionic bond forms when electrons are transferred from one atom to another. During ionic bonding, the atoms become oppositely charged ions.
- Ionic bonding usually occurs between atoms of metals and atoms of non-metals.
- Energy is needed to remove electrons from metal atoms. Energy is released when most Non-metal atoms gain electrons.
- Ionic compounds form solids by building up a three-dimensional repeating pattern called a crystal lattice.
- Ionic compounds are brittle and highly soluble, with high melting and boiling points.

**Vaibhav Krishnan (JEE 2009 AIR 22)**

**Lattice Energy:** How much energy is released when the gaseous ions  $\text{Na}^+$  and  $\text{Cl}^-$  form the ionic solid NaCl ?



Where  $\Delta H_{\text{lat}}$  is called the lattice energy:

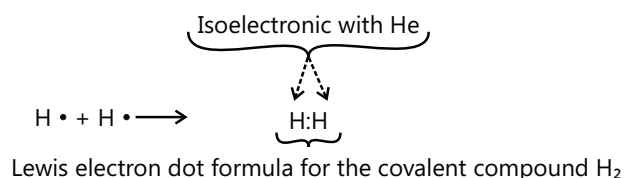


Where, EA is the electron affinity for  $\text{Cl}(\text{g})$ , BE is the bond energy for the Cl-Cl bond,  $IE_1$  is the first ionization for  $\text{Na}(\text{g})$ , and  $\Delta H_{\text{sub}}$  is the enthalpy of sublimation.

## 4.2 Covalent Bond

The sharing of an electron pair results in a covalent bond.

The covalency of an atom is the number of covalent bonds formed by the atom.



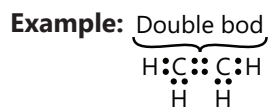
**Figure 14.4:** Covalent bonding in hydrogen molecule

**Table 14.1:** Valencies of some elements

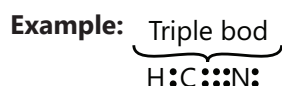
Element	Common Covalency
H	1
F, Cl, Br, I	1
O, S, Se	2
N, P, As	3
C, Si, Ge	4

## 4.3 Multiple Bonds

Multiple bonds result from the sharing of more than one pair of electrons by two atoms. Sharing of two pairs of electrons results in a double bond.



**Sol:** Each atom satisfies the octet rule and is consistent with the common covalency of the element.



Generally, only elements in the second period and sulphur form multiple bonds and maintain an octet of electrons.

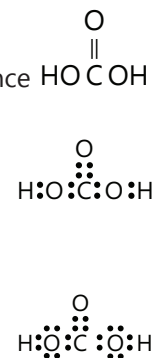
**Illustration 1:** Write the Lewis electron dot formula for carbonic acid, OC(OH)<sub>2</sub>.

**Sol:** In these notes the formula OC(OH)<sub>2</sub> indicates that the atoms are arranged in the following sequence HO C OH

- Number of bonding electrons

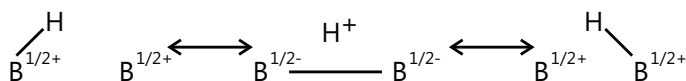
$$\begin{aligned} \sum_f^{\text{all atoms}} (\text{octet of electron})S_1 - \sum_f^{\text{all atoms}} (\text{valence electron})S_1 \\ = [8_c + 3(8_o) + 2(2_H)] - [4_c + 3(6_o) + 2(1_H)] \\ = 36 \text{ electrons} - 24 \text{ electrons} = 12 \text{ bonding electrons} \end{aligned}$$

- Number of remaining electrons = Total number of valence electrons - number of bonding electrons = 24 - 12 = 12 electrons



## 4.4 Bridge Bonding

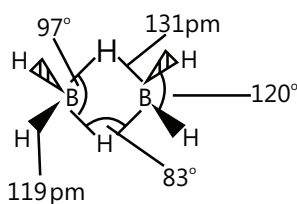
Boron compounds



Resonance structures of 3c-2e bond in diborane.

Three-centre-two-electron bonds are seen in many boron compounds, such as diborane ( $B_2H_6$ ). The monomer  $BH_3$  is unstable, since the boron atom is only surrounded by six valence electrons, and thus, to form a stable electron configuration closer to an octet, shares electrons with a B–H bond on another boron atom, forming a B–H–B 3-center-2-electron bond. In diborane, there are two such bonds: two H atoms bridge the two B atoms, leaving two additional H atoms in ordinary B–H bonds on each B.

The two electrons (corresponding to one bond) in a B–H–B bonding molecular orbital are spread out across three internuclear spaces. The reported bond order for each B–H interaction is 0.5, so that the bridging B–H bonds are weaker and longer than the terminal B–H bonds, as shown by the bond lengths in the structural diagram.



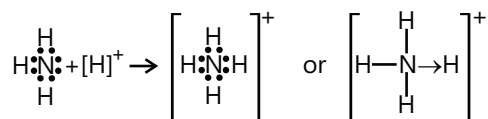
This bonding pattern is also seen in tri methyl aluminium, which forms a dimer  $Al_2(CH_3)_6$  with the carbon atoms of two of the methyl groups in bridging positions. This type of bond also occurs in carbon compounds, where it is sometimes referred to as a hyper conjugation; another name for asymmetrical three-centre two-electron bonds.

**Subdivision of covalent bonds:** There are three types of covalent substances: individual molecules, molecular structures, and macromolecular structures. Individual molecules have strong bonds that hold the atoms together, but there are negligible forces of attraction between molecules. Such covalent substances are usually gases, for example,  $HCl$ ,  $SO_2$ ,  $CO_2$ , and  $CH_4$ . In molecular structures, there are weak forces of attraction. Such covalent substances are low-boiling-temperature liquids (such as ethanol), and low-melting-temperature solids (such as iodine and solid  $CO_2$ ). Macromolecular structures have a large number of atoms linked in chains or sheets (such as graphite), or in 3-dimensional structures (such as diamond and quartz). These substances have high melting and boiling points, are frequently brittle, and tend to have high electrical resistivity. Elements that have high electronegativity, and the ability to form three or four electron pair bonds, often form such large macromolecular structures.

## 4.5 Coordinate Bonding

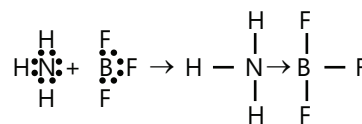
A covalent bond results from the sharing of a pair of electrons between two atoms, where each atom contributes one electron to the bond. It is also possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called coordinate bonds or dative bonds. Since, in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds only in the way they are formed, and once formed they are identical to normal covalent bonds.

Even though the ammonia molecule has a stable electron configuration, it can react with a hydrogen ion  $H^+$  by donating a share in the lone pair of electrons, forming the ammonium ion  $NH_4^+$  :

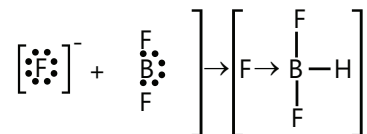
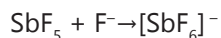
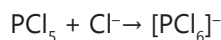


Covalent bonds are usually shown as straight lines joining the two atoms, and coordinate bond as arrows indicating which atom is donating the electrons. Similarly, ammonia may donate its lone pair to boron trifluoride, and through this means the boron atom attains a share in eight electrons:

In a similar way, a molecule of  $\text{BF}_3$  can form a coordinate bond by accepting a share in a lone pair from a  $\text{F}^-$  ion.



There are many other examples, including:



## 4.6 Metallic Bond

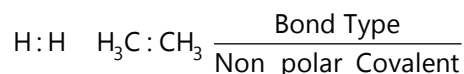
Metals are made up of positive ions packed together, usually in one of the three following arrangements:

1. Cubic close-packed (also called face-centered cubic).
2. Hexagonal close-packed.
3. Body-centered cubic.

Negatively charged electrons hold the ions together. The number of positive and negative charges is exactly balanced, as the electrons originated from the neutral metal atoms. The outstanding feature of metals is their extremely high electrical conductivity and thermal conductivity, both of which are because of the mobility of these electrons through the lattice.

## 5. POLAR COVALENT BONDS, ELECTRONEGATIVITY, AND OXIDATION NUMBERS

### 5.1 Polar Covalent Bonds



The fractional charge,  $d$ , is the charge that results from the unequal sharing of electrons. In heteronuclear bonds, one of the bonding atoms attracts the bonding pair of electrons more strongly than the other bonding atom. The numerical value of  $d$  is the fraction of the charge ( $4.80 \times 10^{-10}$  esu) on an electron.

The unequal sharing of an electron pair results in a polar covalent bond.

**Table 14.2:** Different types of bond and characteristics

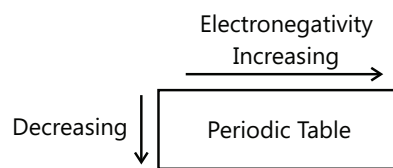
Increasing Bond Polarity $\longrightarrow$			
Type	Nonpolar	Polar Covalent	Ionic
Example	$\text{H} : \text{H}$	$\begin{array}{c} \text{H} \\   \\ \text{H} : \text{C} : \text{H} \\   \\ \text{H} \end{array} : \begin{array}{c} \text{H} \\   \\ \text{H} : \text{C} : \text{H} \\   \\ \text{H} \end{array} : \text{Cl} : \text{Cl} : \text{Cl} :$	$\text{Na}^+ : \left[ \begin{array}{c} \text{Cl} \\ \vdots \\ \text{Cl} \end{array} \right]^-$
$d$	0	0.07 0.17	1.00
$\Delta\chi = \chi_B - \chi_A$	0	0.30 0.74	2.21

## 6. ELECTRONEGATIVITY

Electronegativity,  $\chi$ , is a measure of the relative tendency of a bonded atom to attract electrons. The electronegativity of an atom is not experimentally measured, but calculated from bond energies, ionization energies, and electron affinities.

A rough approximation of Bond Type for AB Based on  $\Delta_x$

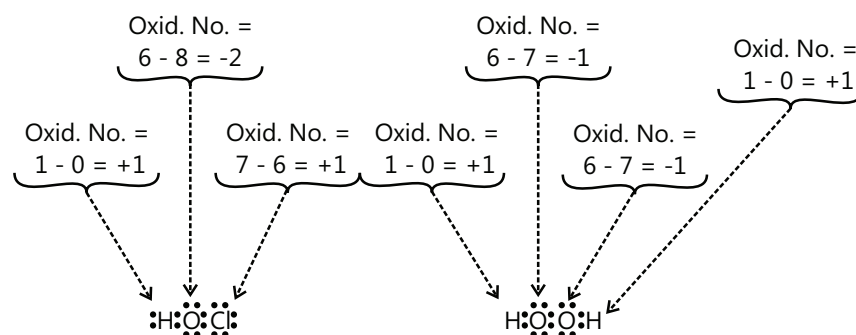
$\Delta_x = \chi_B - \chi_A$	Bond Type
$\geq 1.7$	Ionic
$< 1.7$	Polar covalent
0	Nonpolar covalent



**Figure 14.5:** Trends of electronegativity in the periodic table

## 7. OXIDATION NUMBER

The oxidation number (oxid. No.) of an atom, is the number of valence electrons on the neutral atom minus the number of valence electrons assigned to the atom in the compound on the basis that the bonding electrons belong to the more electronegative atom.



**Figure 14.6:** Illustration of oxidation number

## 8. DIPOLE MOMENTS AND POLARITY

### 8.1. Bond Dipole

An electric dipole is a positive charge,  $q$ , and a negative charge,  $q$ , of equal magnitude that are separated by a distance,  $r$ .

The dipole moment,  $\mu$ , is  $\mu = qr$

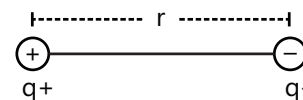
where,  $q$  is the magnitude of the charge in esu (electrostatic units) and  $r$  is the distance between the positive and negative charges in centimeter.

**Note:** A polar covalent bond is a dipole and has a dipole moment.

**Illustration 2:** Calculate the dipole moment,  $\mu_{\text{HCl}}$  for HCl. The magnitude of the fraction charge  $d$ , is 0.17 and the bond distance,  $r_{\text{HCl}}$  is 1.27 Å.

**Sol:**  $q = d(4.80 \cdot 10^{-10} \text{esu}) = (0.17)(4.80 \cdot 10^{-10} \text{esu}) = 8.16 \times 10^{-11} \text{esu}$

$$\mu_{\text{HCl}} = qr = (8.16 \cdot 10^{-11} \text{esu})(1.27 \text{ \AA}) \left( 1.10^{-8} \frac{\text{cm}}{\text{Å}} \right) = 1.03 \times 10^{-18} \text{esu} - \text{cm}$$



**Figure 14.7:** Electrical dipole



1D = 1Debye =  $1.10^{-18}$  esu-cm

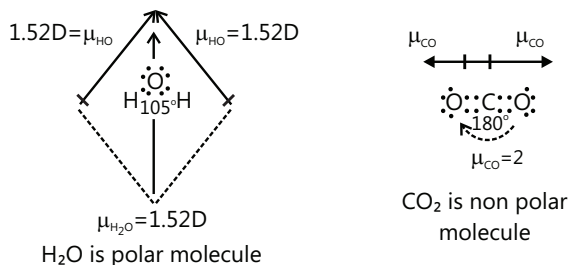
$$\mu_{\text{HCl}} = (1.03 \cdot 10^{-18} \text{ esu-cm}) \left( \frac{1\text{D}}{10^{-18} \text{ esu-cm}} \right) = (1.03\text{D})$$

The magnitude and direction of the dipole moment is represented by the vector,  $\rightarrow$

## 8.2. Molecular Dipole

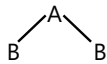
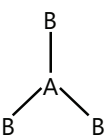
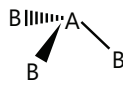
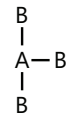
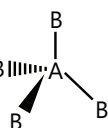
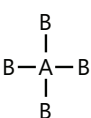
The dipole moment for a molecule is the resultant dipole moment obtained from the vector sum of the individual bond dipole moments. Molecules that have a dipole moment are said to be polar. Molecules with  $\mu = 0$  are said to be nonpolar.


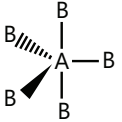
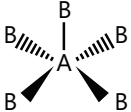
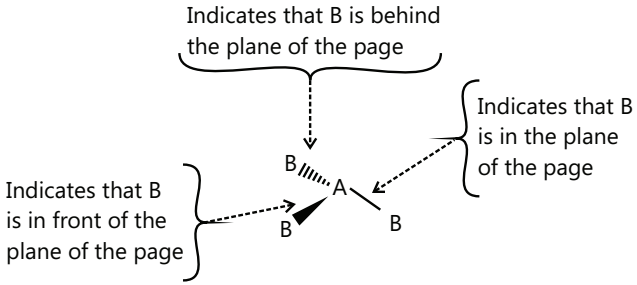
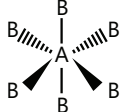
Example



The polarity of a molecule depends on its bond dipole moments and molecular geometry.

**Table 14.3:** Molecular Geometries and Polarities

Formula	Molecular Geometry	Polarity	Example (Exception)
AB	linear A — B	Polar	HCl
AB <sub>2</sub>	Linear B—A—B	Nonpolar	CO <sub>2</sub> (HCN)
AB <sub>2</sub>	Bent 	Polar	H <sub>2</sub> O
AB <sub>3</sub>	Trigonal planar 	Nonpolar	BF <sub>3</sub> (BCl <sub>2</sub> )
AB <sub>3</sub>	Trigonal pyramidal 	Polar	NH <sub>3</sub>
AB <sub>3</sub>	T-shaped 	Polar	ClF <sub>3</sub>
AB <sub>4</sub>	Tetrahedral 	Nonpolar	CH <sub>4</sub> (CCl <sub>4</sub> )
AB <sub>4</sub>	Square planar 	Nonpolar	XeF <sub>4</sub>

Formula	Molecular Geometry	Polarity	Example (Exception)
$AB_4$	Distorted tetrahedral 	Polar	$SF_4$
$AB_5$	Trigonal bipyramidal 	Polar	$PF_5$ ( $F_3PCl_2$ )
$AB_5$	Square pyramidal 	Polar	$BrF_5$
			
$AB_6$	Octahedral 	Nonpolar	$SF_6$

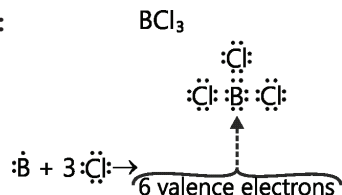
\* Valid when the bonds are covalent,  $\chi_B \neq \chi_A$  and all AB bonds in the nonpolar cases are identical in all respects, i.e. the same bond energies and bond lengths.

## 9. EXCEPTIONS TO THE OCTET RULE

### 9.1 Less than an Octet of Electrons

Atoms that have less than four valence electrons and form covalent bonds may not satisfy the octet rule.

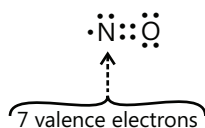
**Example:**



### 9.2 Free Radicals

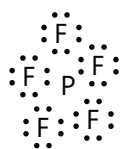
Free radicals are compounds with one or more unpaired electrons.

**Example:** NO.



### 9.3 More than an Octet of Electrons

**Example:** PF<sub>5</sub>

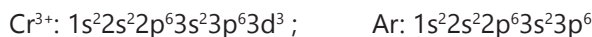


The phosphorus atom in PF<sub>5</sub> has ten valence electrons.

Atoms in the second period never exceed an octet of electrons.

### 9.4 Ions of the Transition and Post-Transition Metals

**Example:** Cr<sup>3+</sup> is not isoelectronic with Ar.



### 9.5 Method for the Determination of Lewis Electron Dot Formula for Covalent Compounds

When the central atom is in the third, fourth, etc. period, determine the total number of valence electrons and distribute them as follows.

- Place two electrons between each bonding pair of atoms.
- Place sufficient electrons around each terminal atom so that the terminal atoms satisfy the octet rule.
- Assign the remaining valence electrons to the central atom.

**Example :** ClF<sub>3</sub>



Twenty-four of the twenty-eight valence electrons are displayed in (ii). Four valence electrons remain and these electrons are assigned to the central atom in (iii).

## 10. NO MOLECULE (IMPORTANT)

In NO molecule, nitrogen contains 5 electrons in outermost shell and oxygen 6. Now oxygen gives 2 electrons for bonding and now nitrogen has 3 electrons for bonding out of which 2 of them form complete bond with oxygen while the odd electron just wanders, contributing partially to the bond. Hence, NO has 2.5 bond order.

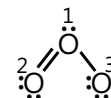
## 11. FORMAL CHARGE

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom.

It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as:

Formal charge (F.C.) On an atom in a Lewis Structure	=	$\left[ \begin{array}{l} \text{Total number of valence} \\ \text{electron in the free atom} \end{array} \right] - \left[ \begin{array}{l} \text{Total number nonbonding} \\ \text{(lonepair) electrons} \end{array} \right] - (1/2) \left[ \begin{array}{l} \text{Total number of} \\ \text{bonding (shared) electrons} \end{array} \right]$
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Let us consider the ozone molecule ( $O_3$ ). The Lewis structure of  $O_3$ , may be drawn as:



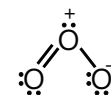
The atoms have been numbered as 1, 2 and 3. The formal charge on.

The central O atom marked 1 =  $6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 =  $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 =  $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent  $O_3$  along with the formal charges as follows:



### MASTERJEE CONCEPTS

It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally, the lowest energy structure is the one with the smallest formal charges on the atoms.

**Misconception:** The formal charge is a factor based on a pure covalent view of bonding and not ionic. Hence, never apply this concept on ionic compounds where electron pairs are equally shared by neighboring atoms.

**Aman Gour (JEE 2012, AIR 230)**

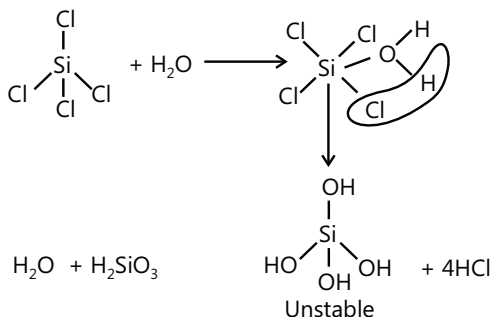
## 12. HYDROLYSIS

**Hydrolysis** means a reaction with water molecules ultimately leading to the breaking of O–H bond into  $H^+$  and  $OH^-$  ions. While the term hydration means the surrounding of polar molecule or ions by polar molecules of water. In hydrolysis, there is a complex formation with a water molecule or reaction with a water molecule.

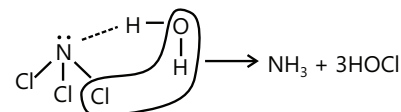
Hydrolysis in covalent compounds takes place generally by two mechanisms:

- (a) By Coordinate bond formation. Generally in halides of atoms having vacant d-orbitals or of halides of atoms having vacant orbitals.
- (b) By H-bond formation: For example in nitrogen trihalides.

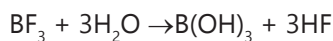
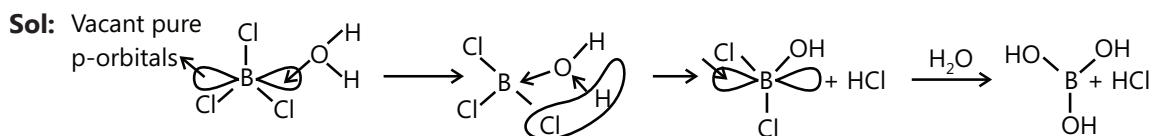
**(a) Hydrolysis via coordinate bond formation:** Hydrolysis of  $\text{SiCl}_4$  (due to presence of vacant d-orbitals on silicon)



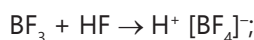
**(b) By H-bond formation:** Hydrolysis of  $\text{NCl}_3$  (N has no vacant orbitals). By a similar mechanism there will be hydrolysis of  $\text{NBr}_3$  and  $\text{NI}_3$ , but  $\text{NF}_3$  does not undergo hydrolysis mainly because it is a polar molecule and also the hydrolysis product FOH is an unstable compound.



**Illustration 3:** Explain the hydrolysis in  $\text{BCl}_3$  and  $\text{BF}_3$ .



But the HF produced will react with the reactant  $\text{BF}_3$  to form  $\text{BF}_4^-$  ion



hydrogen tetrafluoroborate (III) (stable species)

## 13. COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE)

When an anion and cation approach each other, the valence shell of the anion is pulled towards the cation's nucleus and thus the shape of anion gets deformed. This phenomenon of deformation of an anion by a cation is known as polarisation, and the ability of a cation to polarize a nearby anion is called as the polarizing power of the cation.

Fajan's rule points out that greater the polarization of an anion in a molecule, the more covalent it is of character..

### MASTERJEE CONCEPTS

More the distortion of anion, more the polarization and covalent character will increase.

**Vaibhav Krishnan (JEE 2009, AIR 22)**

Fajan gives some rules which govern the covalent character in the ionic compounds, which are as follows:

**(a) Size of cation:** Smaller the cation, more is its polarizing power and thus more will be the polarization of an anion. Hence, greater will be the covalent character of the compound.

Size of cation  $\propto$  (1/polarisation)

e.g.  $\text{BeCl}_2$        $\text{MgCl}_2$        $\text{CaCl}_2$        $\text{SrCl}_2$

Size of cation increases      Polarisation decreases      Covalent character decreases

**(b) Size of anion:** Larger the anion, greater is its polarisability and, therefore, more will be the polarization. Thus, greater will be the covalent character in the compound.

Size on anion  $\propto$  polarisation

e.g. LiF LiCl LiBr LiI

→  
 -Size of anion increases  
 -Polarisation increases  
 -Covalent character increases

**(c) Charge on cation:** Higher the oxidation state of the cation, more will be the deformation of anion and thus, greater will be the covalent character in the compound.

**(d) Charge on anion:** Higher the charge on the anion, more will be the polarisation of anion and thus, greater will be the covalent character in the compound.

Charge on cation  $\propto$  polarisation

e.g. NaCl MgCl<sub>2</sub> AlCl<sub>3</sub>

Na<sup>+</sup> Mg<sup>2+</sup> Al<sup>3+</sup>

→  
 -Charge of cation increases  
 -Polarisation increases  
 -Covalent character increases

Charge on anion  $\propto$  polarisation

e.g. AlF<sub>3</sub> Al<sub>2</sub>O<sub>3</sub> AlN

F<sup>-</sup> O<sup>2-</sup> N<sup>3-</sup>

→  
 -Charge of anion increases  
 -Polarisation increases  
 -Covalent character increases

**(e) Pseudo inert gas configuration of cation:** A cation having pseudo inert gas configuration has more polarizing power than a cation with inert gas configuration. Thus, NaCl having inert gas configuration will be more ionic, whereas CuCl having a pseudo inert gas configuration will be more covalent by nature.

Charge on cation  $\propto$  polarization.

Cu<sup>+</sup> = [Ne] 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup>

18e<sup>-</sup>

Pseudo inert gas configuration

(Poor shielding of d-electrons)

Na<sup>+</sup> = 1s<sup>2</sup> 2s<sup>2</sup> p<sup>6</sup>

8e<sup>-</sup>

Inert gas configuration

(More shielding of s and p electrons)

### 13.1 Application and Exceptions of Fajan Rule

(i) Ag<sub>2</sub>S is less soluble than Ag<sub>2</sub>O in H<sub>2</sub>O because Ag<sub>2</sub>S is more covalent due to bigger S<sup>2-</sup> ion.

(ii) Fe(OH)<sub>3</sub> is less soluble than Fe(OH)<sub>2</sub> in water because Fe<sup>3+</sup> is smaller than Fe<sup>2+</sup> and thus charge is more. Therefore, Fe(OH)<sub>2</sub> is more covalent than Fe(OH)<sub>3</sub>.

(iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

**For example:**

AgCl is white AgBr, AgI, Ag<sub>2</sub>CO<sub>3</sub> are yellow. Similarly, SnCl<sub>2</sub> is white but SnI<sub>2</sub> is black, PbCl<sub>2</sub> is white but PbI<sub>2</sub> is yellow. The bigger anions are more polarised and hence their electrons get excited by the partial absorption of visible light.

(iv) Variation of melting point [melting point of covalent compound < melting point of ionic compound]:

BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub>, BaCl<sub>2</sub>

→

Ionic character increases, melting point increases; since size of cation increases and size of anions is constant.

CaF<sub>2</sub>, CaCl<sub>2</sub>, CaBr<sub>2</sub>, CaI<sub>2</sub>

→

Covalent character increases, melting point decreases; since size of anions increases and size of cations is constant.

**Illustration 4:** Explain why AgCl is colourless whereas AgI is yellow.

**Sol:** The bigger anions are more polarized and hence their electrons get excited by the partial absorption of visible light. AgCl is colourless whereas AgI is yellow, because of:

- (A)  $\text{Ag}^+$  has 18 electron shell to screen the nuclear charge.
- (B)  $\text{Ag}^+$  shows pseudo inert gas configuration.
- (C) Distortion of  $\text{I}^-$  is more pronounced than  $\text{Cl}^-$  ion.
- (D) Existence of d-d transition.

## 14. THEORIES OF BONDING

Lewis approach helps in writing the structure of molecules, but it fails to explain the formation of a chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like  $\text{H}_2$  (435.8 kJ mol<sup>-1</sup>, 74 pm) and  $\text{F}_2$  (150.6 kJ mol<sup>-1</sup>, 42 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly, the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

### 14.1 Valence Bond Theory (Modern Concept of Covalent Bond)

Introduced by Heitler and London (1927) and developed further by Pauling and others, discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configuration of elements, the overlapping criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. Consider two hydrogen atoms A and B approaching each other having nuclei  $N_A$  and  $N_B$  and electrons present in them are represented by  $e_A$  and  $e_B$ . When the two atoms are at a large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

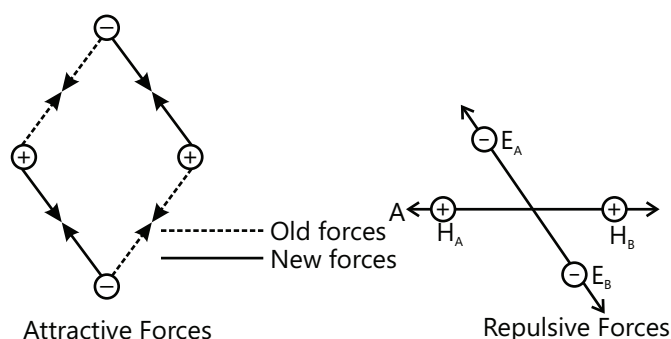
**Attractive forces arise between:**

- (a) Nucleus of one atom and its own electron i.e.,  $N_A - e_A$  and  $N_B - e_B$
- (b) Nucleus of one atom and electron of other atom i.e.,  $N_A - e_B$ ,  $N_B - e_A$ .

**Similarly repulsive forces arise between:**

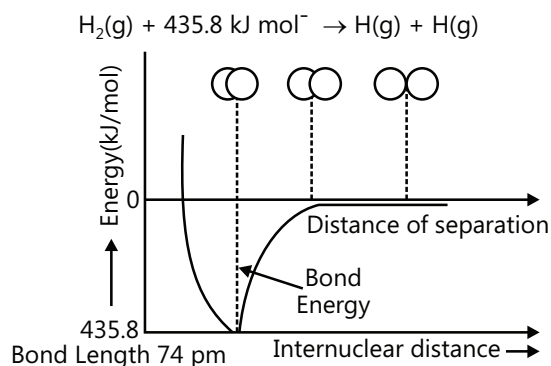
- (a) Electrons of two atoms like  $e_A - e_B$
- (b) Nuclei of two atoms  $N_A - N_B$ .

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 14.8)



**Figure 14.8:** Force of attraction and repulsion during the formation of  $\text{H}_2$  molecule

Experimentally, it has been found that the magnitude of new attractive forces is more than the new repulsive forces. As a result, two atoms approach each other and the potential energy decreases. Ultimately, a stage is reached where the net force of attraction balances the force of repulsion and the system acquires minimum energy. At this stage, two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.



**Figure 14.7:** The potential energy curve for the formation of  $\text{H}_2$  molecule as a function of intermolecular distance of H atoms. The minimum in the curve corresponds to the most stable state of  $\text{H}_2$

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in figure. Conversely 435.8 kJ of energy is required to dissociate one mole of  $\text{H}_2$  molecule.

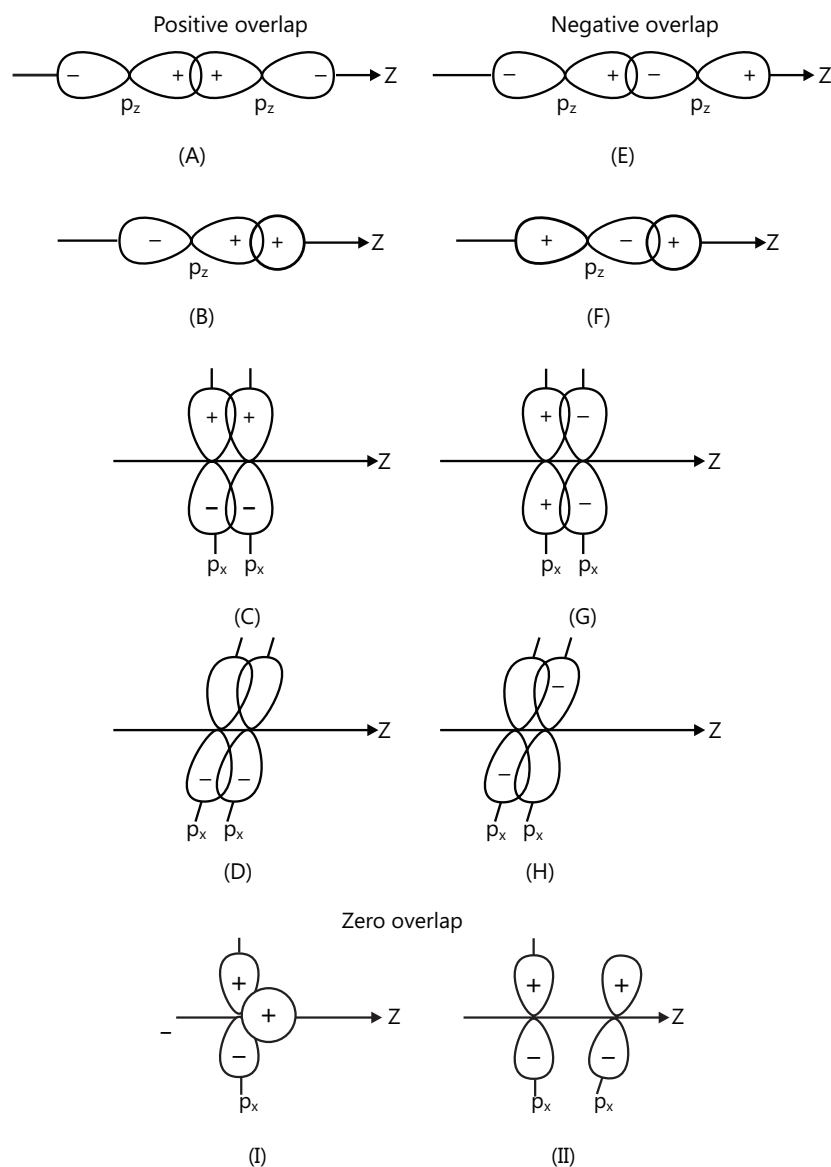
**Orbital Overlap Concept:** In the formation of hydrogen molecule there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals, which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap, the stronger is the bond formed between two atoms. Therefore, according to the orbital overlap concept, the formation of a covalent bond between two atoms results by the pairing of electrons present in the valence shell having opposite spins.

**Directional Properties of Bonds:** The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , etc. in terms of overlap and hybridisation of atomic orbitals.

**Overlapping of Atomic Orbitals:** When two atoms come close to each other there is an overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in the given figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , the VB theory has to account for their characteristic shapes as well. We know that the shapes of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  molecules are tetrahedral, pyramidal and bent respectively.



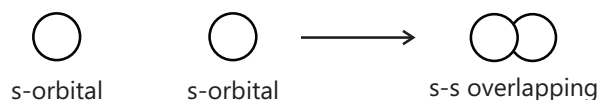


**Figure 14.8(a):** Positive, Negative and zero overlaps of s and p atomic orbital

**Types of overlapping and nature of covalent bonds:** The covalent bond may be classified into two types depending upon the types of overlapping: (i) Sigma ( $\sigma$ ) bond, and (ii) pi ( $\pi$ ) bond

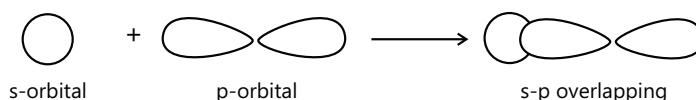
**(a) Sigma( $\sigma$ )bond:** This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the internuclear axis. This is called the head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

**s-s overlapping:** In this case, there is an overlap of two half-filled s-orbitals along the internuclear axis as shown below:



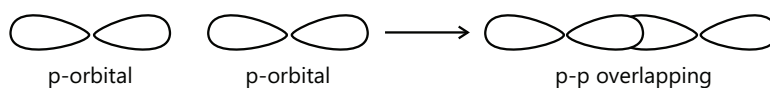
**Figure 14.8(b):** s-s overlapping

**s-p overlapping:** This type of overlap occurs between half-filled s-orbitals of one atom and half-filled p-orbitals of another atom.



**Figure 14.8 (c):** s-p overlapping

**p-p overlapping:** This type of overlap takes place between half-filled p-orbitals of the two approaching atoms.



**(b) Pi ( $\pi$ ) bond:** In the formation of  $\pi$  bond, the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals are formed due to sideways overlapping, and consists of two saucer type charged clouds above and below the plane of the participating atoms.

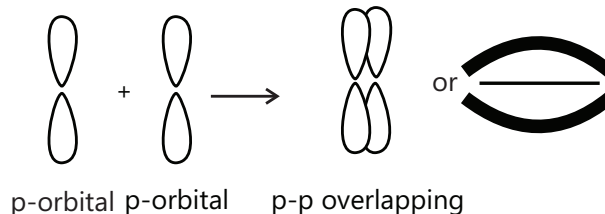
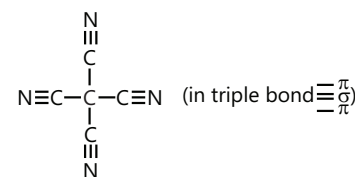


Figure 14.8 (d): p-p overlapping

**Strength of Sigma and pi Bonds:** Basically, the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that a pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

**Illustration 5:** What are the total number of  $\sigma$  and  $\pi$  bonds in tetracyanomethane.



**Sol:** From the structure it is clear that it has  $8\sigma$  and  $8\pi$  bonds.

### MASTERJEE CONCEPTS

**Bent's rule:** In a molecule, smaller bond angles are formed between electronegative ligands, since the central atom to which the ligands are attached tend to direct bonding hybrid orbitals of greater p character towards its more electronegative substituents.

**Reason:** The rule states: "Atomic s character tends to concentrate in orbitals that are directed toward electropositive groups and atomic p character tends to concentrate in orbitals that are directed toward electronegative groups". Bent based his rule on the perturbation theory, and suggested that isovalent orbital hybridization should transfer more s character to the more electropositive bonding orbital to maximize bonding energy, hybrid orbitals for main group elements consist of one s and three p orbitals, with the s orbital having lower energy. To have more s character means that the bonding orbital is lower in energy and shaped more like an s orbital rather than a p orbital. In other words, ligand orbitals tend to be rich in p character because of higher electronegativity, with s character concentrated on the central metal. However, in cases where the metal has a lone pair, the lone pair orbital is high in s character. This is because s orbitals are closer to the nucleus, allowing for greater stabilization of the lone pair.

Nikhil Khandelwal (JEE 2009, AIR 94)

## 14.2 Valence Shell Electron Pair Repulsion (VSEPR) Theory

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

**The main postulates of VSEPR theory are as follows:**

**(a)** The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.

- (b) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- (c) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- (d) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- (e) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- (f) When two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

**The repulsive interaction of electron pairs decreases in the order:**

lone pair ( $\ell$ p)-lone pair( $\ell$ p) > lone pair (p)-bond pair(bp) > bond pair (bp)-bond pair(bp)

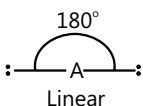
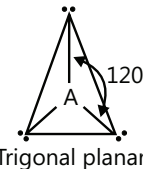
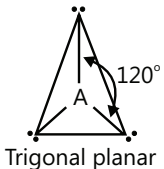
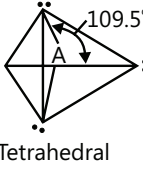
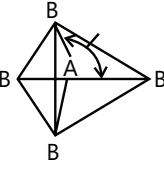
### MASTERJEE CONCEPTS

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localized on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs, electrons as compared to the lone pair-bond pair and bond pair-bond pair repulsions. These repulsion effects result in deviations from idealized shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair, and (ii) molecules in which the central atom / ion has one or more lone pairs.

**Rohit Kumar (JEE 2012, AIR 79)**

**Table 14.4:** Shape (molecular geometry) of some simple molecules / ions with central atom / ion having no lone pairs of electrons (E)

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
2	 <p style="text-align: center;">Linear</p>	$B - A - B$ Linear	$BeCl_2, HgCl_2$
3	 <p style="text-align: center;">Trigonal planar</p>	 <p style="text-align: center;">Trigonal planar</p>	$BF_3$
4	 <p style="text-align: center;">Tetrahedral</p>	 <p style="text-align: center;">Tetrahedral</p>	$CH_4, NH_4^+$

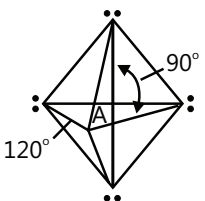
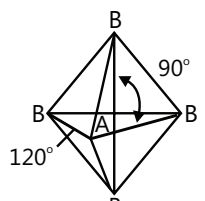
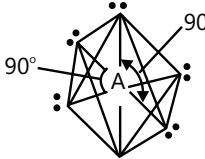
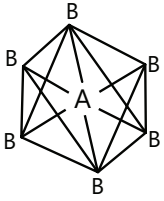
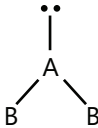
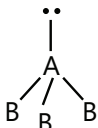
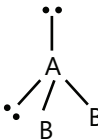
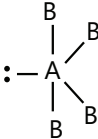
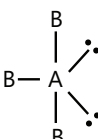
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
5	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	$\text{PCl}_5$
6	 <p>Octahedral</p>	 <p>Octahedral</p>	$\text{SF}_6$

Table 14.5: Electron pair geometries of some simple molecules

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement electron pairs of	Shape	Examples
$\text{AB}_1\text{E}$	2	1		Bent	$\text{SO}_2, \text{O}_3$
$\text{AB}_1\text{E}$	3	1		Trigonal pyramidal	$\text{NH}_3$
$\text{AB}_2\text{E}_2$	2	2		Bent	$\text{H}_2\text{O}$
$\text{AB}_4\text{E}$	4	1		See saw	$\text{SF}_4$
$\text{AB}_3\text{E}_2$	3	2		T-shape	$\text{ClF}_3$

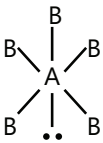
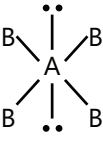
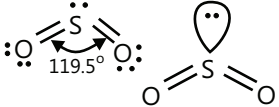
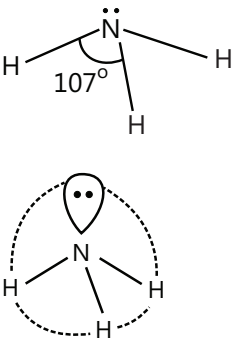
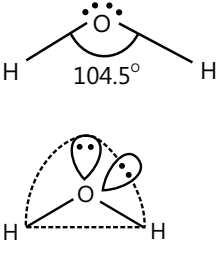
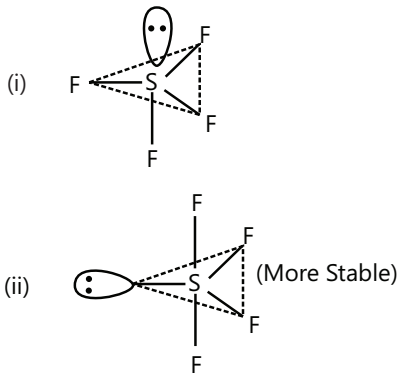
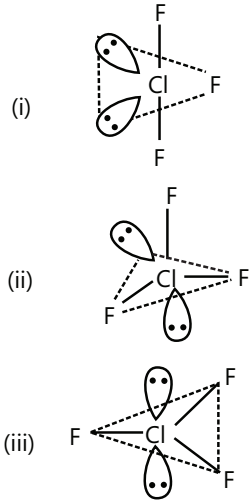
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement electron pairs of	Shape	Examples
$AB_5E$	5	1		Square pyramidal	$BrF_5$
$AB_4E_2$	4	2		Square planar	$XeF_4$

Table 14.6: Molecular shape of some simple compounds

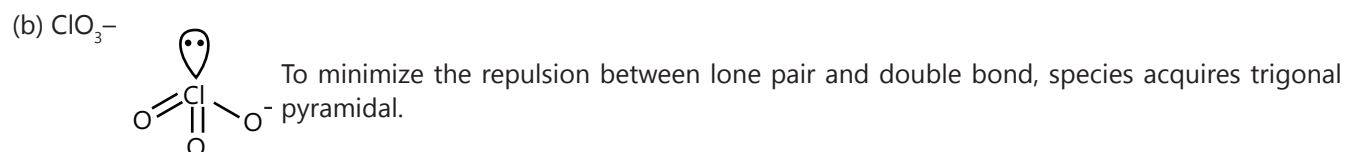
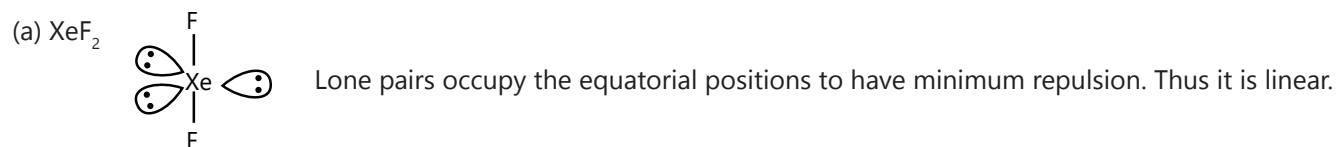
Molecule type	No. of bonding pairs	No. of lone pairs		Shape	Reason for the shape acquired
$AB_2E$	4	1		Bent	It is found to be bent or v-shaped. The reason being the lone pair- bond pair repulsion is much more as compared to the bond pair - bond pair repulsion. So the angle is reduced to $119.5^\circ$ from $120^\circ$ .
$AB_3E$	3	1		Trigonal pyramidal	It is found to be trigonal pyramidal due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to $107^\circ$ to $109.5^\circ$
$AB_2E_2$	2	2		Bent	The shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion. Thus, the angle is reduced to $104.5^\circ$ from $109.5^\circ$

Molecule type	No. of bonding pairs	No. of lone pairs		Shape	Reason for the shape acquired
$AB_4E$	4	1		See saw	In (i) the lp is present at axial position so there are three lp-bp repulsion at $90^\circ$ . In (ii) the lp is an equatorial position and there are two lp-bp repulsion. Hence, arrangement (ii) is more stable. The shape shown in (ii) is called as a distorted tetrahedron, a folded square or a see-saw.
$AB_3E_2$	3	2		T-shape	In (i) the lone pairs are at equatorial position ( $120^\circ$ ), so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (i) is most stable. (T shaped)

The VSEPR Theory is able to predict the geometry of a large number of molecules, especially the compounds of p-block elements accurately.

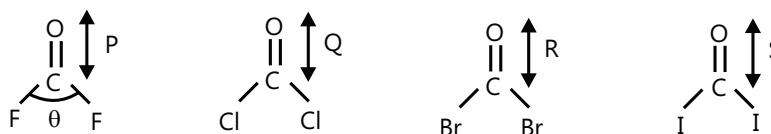
**Illustration 6:** Use the VSEPR model to predict the geometry of the following (a)  $XeF_2$  (b)  $ClO_3^-$

**Sol:**



**Illustration 7:** Discuss the bond angle in carbonyl halides  $COF_2$ ,  $COCl_2$ ,  $COBr_2$ ,  $COI_2$

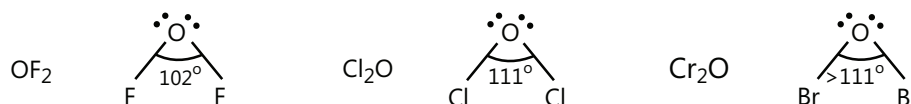
**Sol:** Extent of electronegativity and the steric crowding of the large halogen atoms contributes in the increasing bond angles.



Double bonds require more room than single bonds. Hence, C = O group compresses the molecule and bond angle decreases maximum in  $\text{COF}_2$ , as bond pairs of electrons are closer to fluorine atoms because of high electronegativity of fluorine. As the size of halogen atoms increase and their electronegativity decreases repulsion between bond pairs increases and therefore  $\theta$  increases.

**Illustration 8:** Compare bond angle of  $\text{OF}_2$ ,  $\text{Cl}_2\text{O}$  and  $\text{Br}_2\text{O}$ .

**Sol:** Extent of electronegativity and the steric crowding of the large halogen atoms contributes in the increasing bond angles.



Bond pair electrons are closer to the fluorine atoms (because of high electronegativity of fluorine). So the lp-lp repulsion is more than bp-bp. Thus the F—O—F bond angle decreases to  $102^\circ$  from  $109.5^\circ$ . In  $\text{Cl}_2\text{O}$ , the bond pair are closer to the oxygen atom because of the high electronegativity of oxygen. So the bp-bp repulsion is more than lp-lp. Thus, the bond angle Cl—O—Cl increases to  $111^\circ$  due to bp-bp repulsion and repulsion between larger Cl atoms.

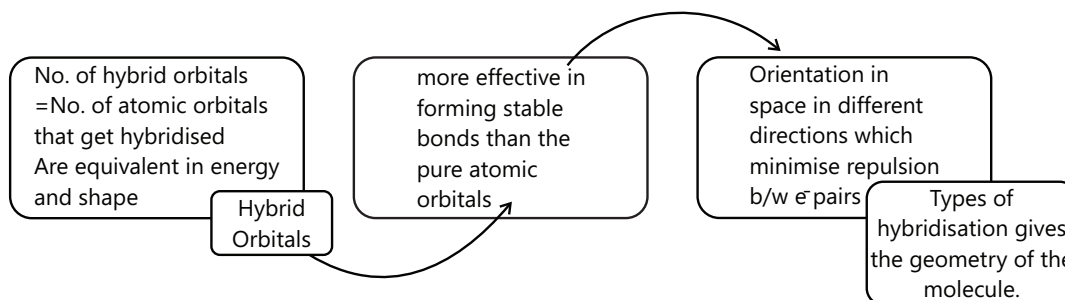
**Note :** The steric crowding of the large halogen atoms also contributes in the increasing bond angles.

## 15. HYBRIDISATION

Valence bond theory (overlapping concept) explains the formation of various molecules but it fails to account for geometry and shapes of various molecules. In order to explain the cases of linear  $\text{BeCl}_2$ , planar  $\text{BF}_3$  and other such structures, the VBT has been supplemented by the concept of hybridization. This is a hypothetical concept and was introduced by Pauling and Slater.

According to them, the atomic orbitals combine to form a new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation, which can be defined as the process of intermixing of the orbitals of slightly different energies in the formation of a new set of orbitals of equivalent energies and shape.

For example, when one 2s and three 2p-orbitals of carbon hybridise, there is a formation of four new  $\text{sp}^3$  hybrid orbitals.



**Flowchart 14.1:** Salient features of hybridisation

## MASTERJEE CONCEPTS

**Drago's rule:** For any Group in general, the formula for calculating the number of hybrid orbitals in a group is the number of the central element + no. of atoms surrounding the central element (except oxygen) - charge on the central element (consider the charge including its sign) whole divided by 2.

Aman Gour (JEE 2012, AIR 230)

### Important conditions for hybridisation:

- The orbitals present in the valence shell of the atom are hybridised.
- The orbitals undergoing hybridization should have almost equal energy.
- Promotion of electron is not an essential condition prior to hybridization.
- It is the orbital that undergoes hybridization and not the electrons. For example, for orbitals of N atom ( $2s^2 2p_x^1 2p_y^1 2p_z^1$ ) belonging to valence shell, when hybridized to form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each, it is not necessary that only half filled orbitals participate in hybridization. In some cases, even fully filled orbitals of the valence shell take part in hybridization.

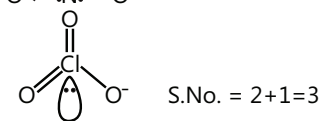
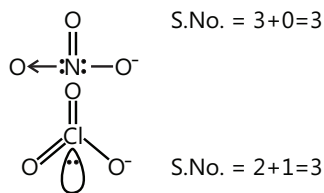
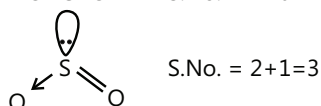
### Determination of hybridisation of an atom in a molecule or ion:

#### Steric number rule (given by Gillespie):

Steric no. of an atom = Number of the atom bonded with that atom + Number of lone pair(s) left on that atom.

**Note:** This rule is not applicable to molecules/ions which have odd  $e^-$  ( $\text{ClO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ), free radicals and compounds like  $\text{B}_2\text{H}_2$ , which involve 3 centre  $2e^-$  bond (banana bond).

**For example:**  $\text{O}=\text{C}=\text{O}$       S.No. =  $2+0=2$



**Table 14.7:** Determination of hybridisation of an atom using steric number

Steric number	Types of Hybridisation	Geometry
2	$sp$	Linear
3	$sp^2$	Trigonal planar
4	$sp^3$	Tetrahedral
5	$sp^3d$	Trigonal bipyramidal
6	$sp^3d^2$	Octahedral
7	$sp^3d^3$	Pentagonal bipyramidal

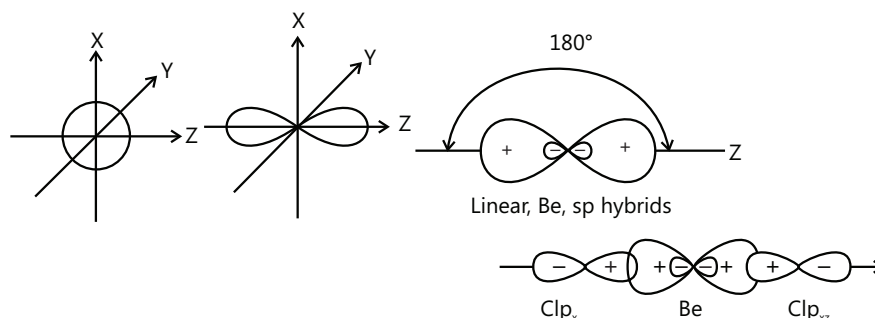


## 15.1 Types of Hybridisation

(a) **sp hybridisation:** Mixing of one s + one p = Two sp hybrid orbitals. Each sp hybrid orbital has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation. The two sp hybrids point in the opposite direction along the Z-axis with projecting bigger positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

### Example of a molecule having sp hybridisation

**BeCl<sub>2</sub>:** The ground state electronic configuration of Be is 1s<sup>2</sup> 2s<sup>2</sup>. In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its divalency. Once 2s and 2p-orbitals get hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and forms two Be-Cl sigma bonds.

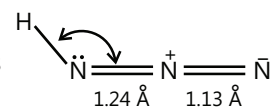


**Figure 14.9:** Figure (A) formation of sp hybrids from s and p orbitals; (B) Formation of the linear BeCl<sub>2</sub> molecule.

### More examples of sp hybridisation:

- (a) C  $\equiv$  N,      H – C  $\equiv$  C – H  
 (b) H<sub>2</sub>C = C = CH<sub>2</sub>  
 (c) N<sub>3</sub><sup>-</sup> (azide ion), BeF<sub>2</sub>, HgCl<sub>2</sub>, NO<sub>2</sub><sup>-</sup> (nitronium ion), N<sub>2</sub>O

**Note:** In N<sub>3</sub><sup>-</sup> there is a total of two  $\sigma$  and two  $\pi$  bonds giving N = N = N and a bond order of two. Both N – N bonds are of the same length, 1.16 Å. The hydrogen azide molecules have a bent structure and two N–N bond lengths are different.



**Illustration 9:** Which is linear PH<sub>4</sub><sup>+</sup>, H<sub>3</sub>S<sup>+</sup> or NO<sub>2</sub><sup>+</sup>?

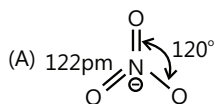
- (A) Phosphonium ion (PH<sub>4</sub><sup>+</sup>)    (B) Sulphonium (H<sub>3</sub>S<sup>+</sup>)    (C) Nitronium ion (NO<sub>2</sub><sup>+</sup>)    (D) None of these

**Sol:** Phosphonium ion (PH<sub>4</sub><sup>+</sup>) is tetrahedral, sulphonium (H<sub>3</sub>S<sup>+</sup>) is pyramidal, but nitronium ion (NO<sub>2</sub><sup>+</sup>) is linear; O = N<sup>⊕</sup> = O (sp hybridisation)      **Ans. (C)**

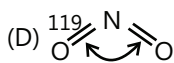
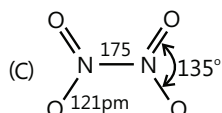
**Illustration 10:** The ONO angle is maximum in

- (A) NO<sub>3</sub><sup>-</sup>    (B) NO<sub>2</sub><sup>+</sup>    (C) N<sub>2</sub>O<sub>4</sub>    (D) NO<sub>2</sub>

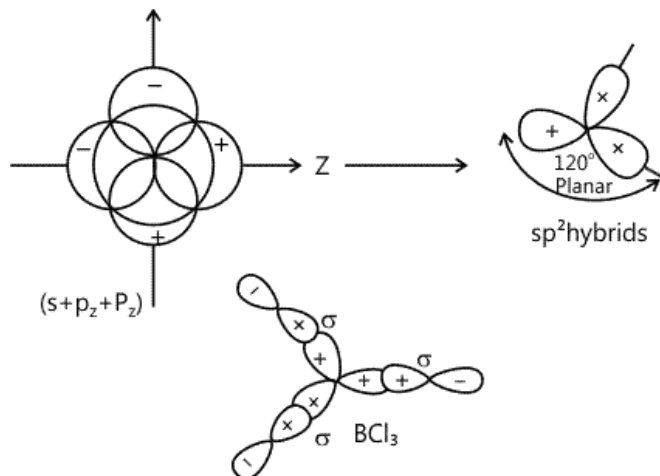
**Sol:**



(B) O = N<sup>⊕</sup> = O Bond angle is 180° because of sp hybridisation of nitrogen  
115pm



(b)  **$sp^2$  hybridisation** : Mixing of one  $s$ +two  $p$ =Three  $sp^2$  hybrid orbitals. For example, in  $BCl_3$  molecule, the ground state electronic configuration of central B(boron) atom is  $1s^2 2s^2 2p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbital. As a result, boron has three unpaired electrons. These three orbitals (one  $2s$  and two  $2p$ ) hybridise to form three  $sp^2$  hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with  $2p$  orbitals of chlorine to form three B–Cl bonds. Therefore, in  $BCl_3$ , the geometry is trigonal planar with ClBCl bond angle of  $120^\circ$ .

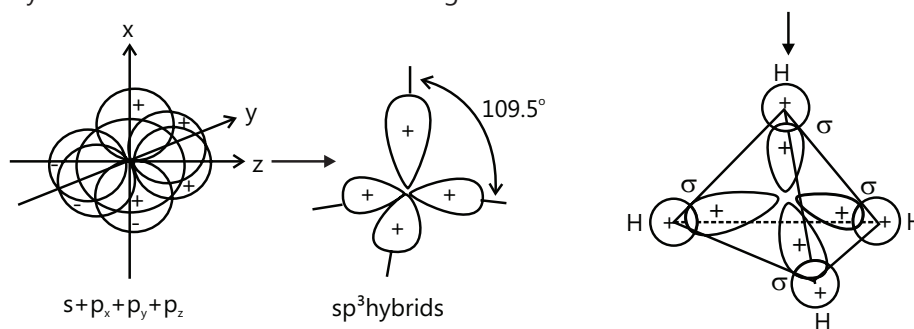


**Figure 14.10:** Formation of  $sp^2$  hybrids and then  $BCl_3$  molecule steric no-3, Geometry=Trigonal planar, Ideal bond angle= $120^\circ$

**Table 14.8:** Examples of molecules showing  $sp^2$  hybridisation

Shape	Trigonal	V-shaped (bent)
Example	$\text{>C}=\text{CH}_2, \text{CH}_3\text{CH}_2$ $\text{C}_6\text{H}_6, \text{CO}_3^{2-}, \text{HCO}_3^-$ $\text{H}_2\text{CO}_3, \text{graphite}, \text{BF}_3$ $\text{B(OH)}_3, \text{SO}_3, \text{NO}_3^-$ $\text{C}_{60}$ (Fullerene)	$\text{O}_3, \text{SO}_2, \text{SnCl}_2$ $\text{NOCl}, \text{O}_3, \text{NO}_3$ $\text{NO}_2^-$

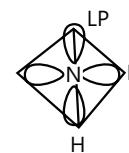
(c)  **$sp^3$  hybridisation**: This type of hybridisation can be explained by taking the example of  $CH_4$  molecule in which there is mixing of one  $s$ -orbital and three  $p$ -orbitals of the valence shell to form four  $sp^3$  hybrid orbitals of equivalent energies and shape. There is 25%  $s$ -character and 75%  $p$ -character in each  $sp^3$  hybrid orbital. The four  $sp^3$  hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between  $sp^3$  hybrid orbital is  $109.5^\circ$  as shown in figure.



**Figure 14.11:** Shape of  $sp^3$  hybridised orbital

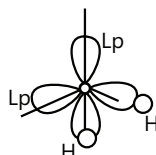
The structure of  $NH_3$  and  $H_2O$  molecules can also be explained with the help of  $sp^3$  hybridisation.

In  $\text{NH}_3$ , the valence shell (outer) electronic configuration of nitrogen in the ground state is  $2s^2 2p_x^1 2p_y^1 2p_z^1$  having three unpaired electrons in the  $sp^3$  hybrid orbitals and a lone pair of electrons is present in the fourth one. Overlapping of these orbitals with s-orbitals of 3 Hydrogen atoms gives 3 bonds. Since lone pair-bond pair repulsion is more than bond pair-bond pair, the molecule gets distorted and the bond angle is reduced to  $107^\circ$  from  $109.5^\circ$  giving it a pyramidal geometry.



**Figure 14.12:** Formation of  $\text{NH}_3$  molecule

In case of  $\text{H}_2\text{O}$  molecule, the four oxygen orbitals (one 2s and three 2p) undergo  $sp^3$  hybridisation forming four  $sp^3$  hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four  $sp^3$  hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to  $104.5^\circ$  from  $109.5^\circ$  and the molecule thus acquires a V-shape or angular geometry.



**Figure 14.13:** Formation of  $\text{H}_2\text{O}$  molecule

Steric No. = 4

Geometry = tetrahedral

Ideal bond angle =  $109^\circ 28'$

**Table 14.9:** Examples of molecule showing  $sp^3$  hybridisation

Type	Shape	Example
$\text{AB}_4$	Tetrahedral	$\text{CH}_4$
$\text{AB}_3\text{L}$	Pyramidal	$\text{XeO}_3$
$\text{AB}_2\text{L}_2$	V-shape or bent	$\text{OBr}_2$
$\text{ABL}_3$	Linear	$-\text{OCl}$

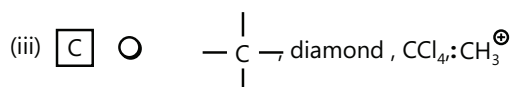
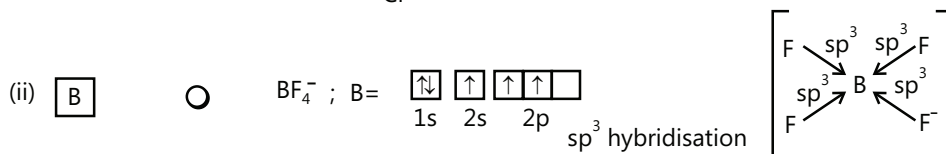
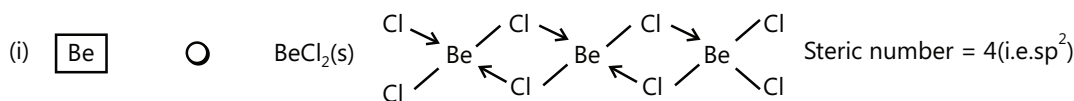
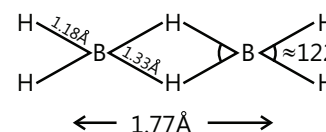
### Some other Examples of $sp^3$ hybridisation

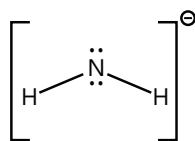
This molecule does not have any B–B bond like C–C bond in  $\text{C}_2\text{H}_6$  (ethane). Therefore, there is no scope of any conformations in the molecules of  $\text{B}_2\text{H}_6$ .

Both the B atoms are in  $sp^3$  hybridization state and each boron contains two types of boron hydrogen bond lengths.

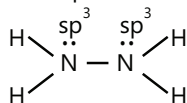
This is an example of 3-centre  $2-e^-$  bond which is also known as Banana bond.

The bridging hydrogen atoms are not in the plane of the molecule, one is above the plane and the other is below the plane.

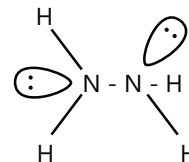
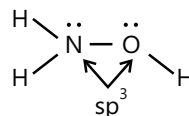


(v) N ○  $\text{NH}_2^-$  (amide ion)

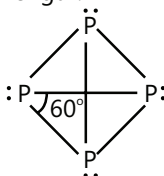
V-shape

○  $\text{NH}_2\text{-NH}_2$  or  $\text{N}_2\text{H}_4$  (hydrazine)

Structure is similar to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecules are rotated  $95^\circ$  about N–N bond and occupy a gauche (non-eclipsed) conformation. The bond length is  $1.45 \text{ \AA}$ .

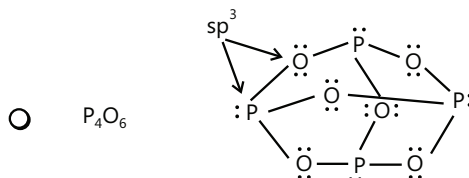
○  $\text{NH}_2\text{OH}$  (hydroxylamine)

lp-lp repulsion increases the N-O bond length.

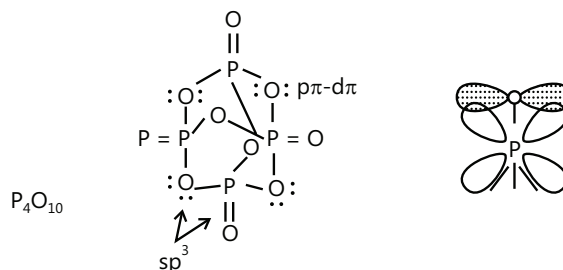
(vi) P ○  $\text{P}_4$  (white phosphorus)

All phosphorus atoms occupy all four vertexes of tetrahedron. There are six P–P bonds and  $\angle \text{PPP}$  is  $60^\circ$ .

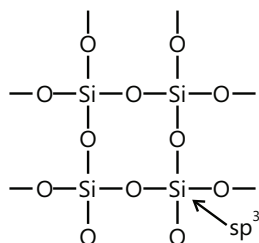
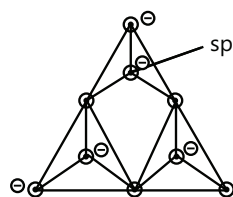
Since bond angle is  $60^\circ$  (against normal tetrahedral bond angle,  $109.5^\circ$ ) so,  $\text{P}_4$  molecule is a strained molecule. So it is chemically very reactive.



P–O bond length shows that the bridging bonds on the edges are  $1.65 \text{ \AA}$  and are normal single bonds. There is no P–P bonds.



The P–O bond lengths shows that the bridging bonds on the edges are  $1.60 \text{ \AA}$  but the P=O bonds on the corners are  $1.43 \text{ \AA}$  and the P = O is formed by p – d back bonding. A full p orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is  $127^\circ$  and there is no P – P bond.

(vii) Si ○  $\text{SiO}_2$  is a covalent network solid like diamond○ Structure of cyclic silicates :  $[\text{Si}_3\text{O}_9]^{6-}$ 

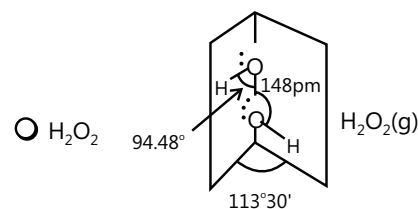
• = Silicon ; ○ = Oxygen

**Note:** Oxygen atom bonded with two Si atoms cannot have a negative charge. There is no oxygen-oxygen bond. All silicates contain only Si-O bond and there is no Si-Si bond.

O – O bond length (148 pm) is larger than the expected due to the repulsion between the lone pairs on the two oxygen atoms.

It has book like structure (angle between the two pages of the book =  $94^\circ$ ) and both the O atoms have two lone pairs each.

The  $\text{H}_2\text{O}_2$  is the smallest molecule known to show restricted rotation about the O–O bond and this is presumably due to repulsion between the OH groups. A similar structure is retained in the liquid and solid, but bond lengths and angles are slightly changed because of hydrogen bonding.



**Table 14.10:** Hybridization Involving d-orbital

$sp^3d$	$d_z^2$
$sp^3d^2$	$d_{x^2-y^2}$ & $d_z^2$
$sp^3d^3$	$d_{xy}$ , $d_{yx}$ , $d_{zx}$
$dsp^2$	$d_{x^2-y^2}$

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

Steric number = 5

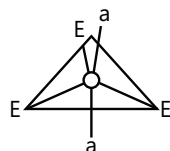
Geometry = trigonal bipyramidal

**Table 14.11:** Examples of molecule showing  $sp^3d$  hybridisation

Type	$AB_5$	$AB_4L$	$AB_3L_2$	$AB_2L_3$
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	$\text{PCl}_5$ , $\text{PBr}_5$ , $\text{PF}_5$ etc	$\text{SF}_4$ , $\text{XeO}_2\text{F}_2$	$\text{ClF}_3$ , $[\text{XeF}_3]^+$	$\text{XeF}_2$ , $\text{I}_3^-$ , $[\text{ICl}_2]^-$

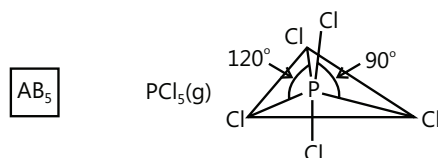
Important points regarding  $sp^3d$  :

(i) According to VSEPR theory, a lone pair will occupy equatorial positions but not axial.



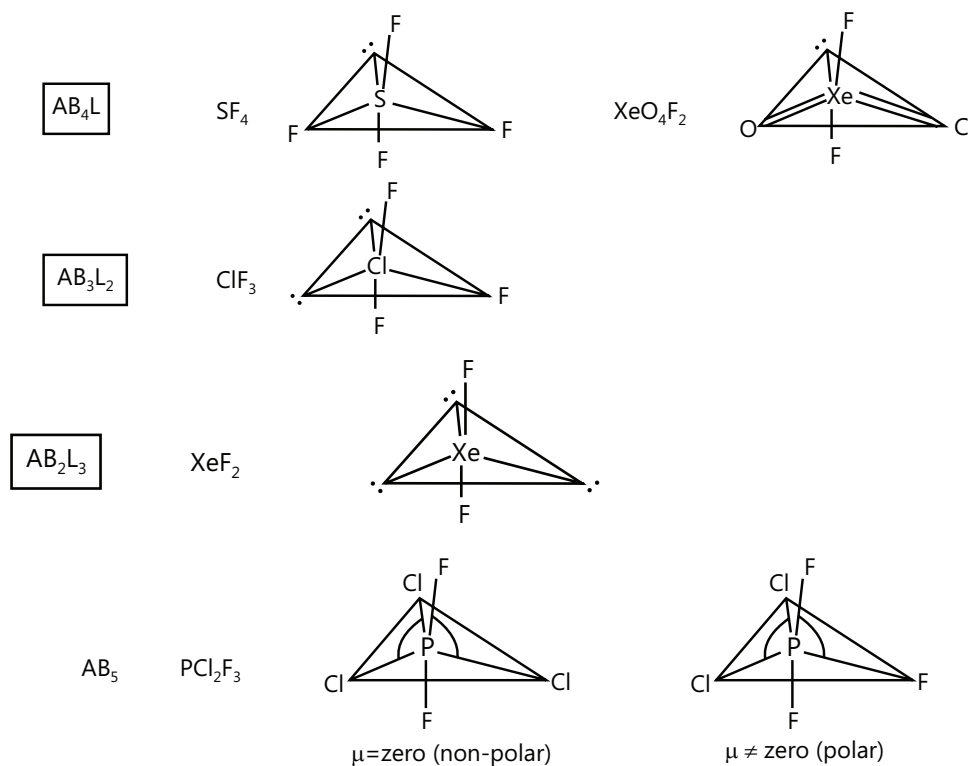
(ii) More electronegative atoms will prefer to occupy axial positions.

(iii) Since, double bonds occupy more space. Therefore, they will also prefer equatorial positions.



It is covalent in the gas but in solid state exists as an ionic solid consisting of  $[\text{PCl}_4]^-$  (tetrahedral) and  $[\text{PCl}_6]^-$  (octahedral). All P–Cl bonds are not of equal lengths. Here, axial bonds are longer and weaker than equatorial bonds.

Note:  $\text{PF}_5$  (g) is trigonal bipyramidal and the electron diffraction shows that some bond angles are  $90^\circ$  and others are  $120^\circ$ , and axial P – F bond lengths are  $1.58 \text{ \AA}$ , whilst the equatorial P – F lengths are  $1.53 \text{ \AA}$ . But NMR studies suggest that all five atoms are equivalent because of pseudo rotation.  $\text{PF}_5$  remains covalent and is trigonal bipyramidal in the solid state.  $\text{PBr}_5$ (s) exists as  $[\text{PBr}_4]^+ \text{Br}^-$  and  $\text{PI}_5$  as  $[\text{PI}_4]^+ \text{I}^-$  in solution.



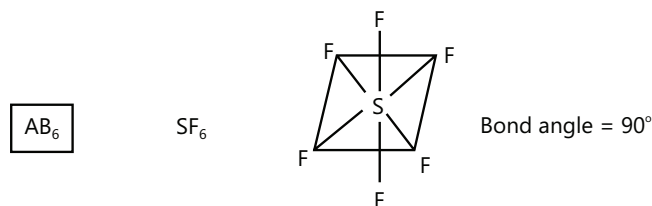
(e)  $sp^3d^2$  hybridization: Steric Number = 6 Geometry = octahedral

**Table 14.12:** Examples of molecules showing  $sp^3d^2$  hybridisation

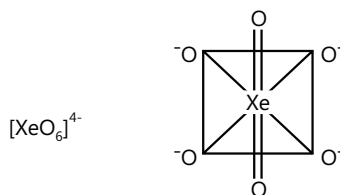
Type	$AB_6$	$AB_5L$	$AB_4L_2$
Shape	Octahedral	Square Pyramidal	Square Planar
Example	$SF_6$ , $PF_6^-$ , $[SiF_6]^{2-}$ $[AlF_6]^{3-}$ , $[XeO_6]^{4-}$	$BrF_5$ , $IF_5$ $XeOF_4$	$ICl_4^-$ $XeF_4$

**Important :** Since, octahedral is a symmetrical figure, hence

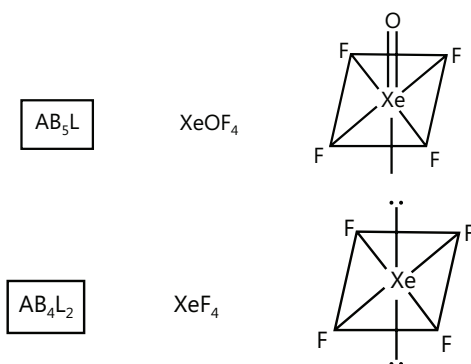
- Position of a lone pair can be anywhere,
- But if there are two lone pairs (max.) then these must be in the trans positions.



Due to over-crowding and maximum valency of S,  $SF_4$  is much less active (almost inert) than  $SF_6$



$[\text{XeO}_6]^{4-}$  is the perxenate ion and  $\text{H}_4\text{XeO}_6$  is called perxenic acid. But  $\text{H}_2[\text{X}^{4-}\text{eO}_4]$  is called xenic acid.



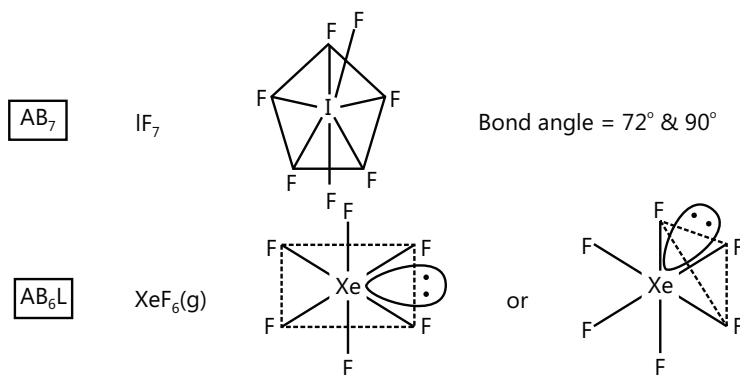
**(f)  $sp^2d^3$  Hybridization:**

Steric number = 7

Geometry = Pentagonal bi-pyramidal

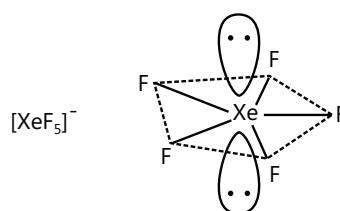
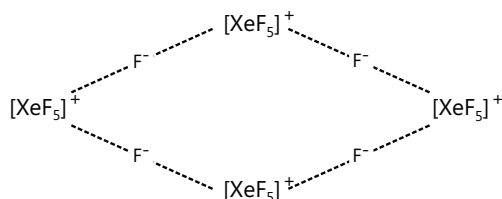
**Table 14.13:** Examples of molecules showing  $sp^3d^3$  hybridisation

Type	$\text{AB}_7$	$\text{AB}_6\text{L}$
Shape	Pentagonal bi-pyramidal	Distorted octahedral
Example	$\text{IF}_7$	$\text{XeF}_6$



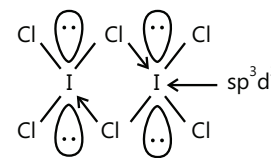
Distorted octahedral with a nonbonding electron pair either at the center of a face or the midpoint of an edge.

- $\text{XeF}_4(\text{s})$  is found to be ionic solid, consisting of  $[\text{XeF}_5]^+$  and  $\text{F}^-$  ions. It is found that  $\text{F}^-$  is forming a bridge between two  $\text{XeF}_5^+$  ions.

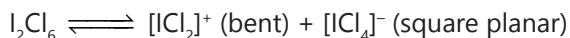


Pentagonal planar ion with two nonbonding electron pairs above and below the plane of the pentagon.

- $\text{ICl}_3$  does not exist, but the dimer  $\text{I}_2\text{Cl}_6$  is a bright yellow solid. Its structure is planar. The terminal I – Cl bonds are normal single bonds of length 2.38 Å and 2.39 Å. The bridging I – Cl bonds are appreciably longer (2.68 Å and 2.72 Å) suggesting delocalized bonding, rather than a simple halogen bridge formed by coordinate bonds from  $\text{Cl}_2$  to I.



The liquid has an appreciable electrical conductance due to self-ionization.



**Illustration 11:** The triodes ion  $[\text{I}_3]^-$  in which the I atoms are arranged in a straight line is stable, but the corresponding  $\text{F}_3^-$  ion does not exist.

**Sol:**  $\text{F}_3^-$  and  $\text{I}_3^-$  are of same group. Iodine can expand its octet but F cannot and thus, in  $\text{I}_3^-$  octet rule is not violated, but in  $\text{F}_3^-$ , the octet rule is violated.

## 15.1 Molecular Orbital Theory (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

- Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule.

Thus an atomic orbital is monocentric, while a molecular orbital is polycentric.

- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called bonding molecular orbital and anti-bonding molecular orbitals are formed.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by the molecular orbital.
- The molecular orbitals like the atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli Exclusion Principle and the Hund's Rule of Maximum Multiplicity. But the filling order of these molecular orbitals is always experimentally decided, there is no rule like  $(n + 1)$  rule in case of atomic orbitals.

### Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

Let us begin by discussing the case of molecular hydrogen. An approximate description of the molecular orbitals in  $\text{H}_2$  can be obtained by considering them as a Linear Combination of Atomic Orbitals (LCAOs). Let us label the nuclei A and B. The lowest energy orbital associated with each nucleus is the 1s orbital, and each of these atomic orbitals may be represented by wave function  $\varphi_A$  or  $\varphi_B$ . Now each molecular orbital may also be represented by a wave function which is a suitable linear combination of atomic orbitals; since A and B are identical atoms, their atomic orbitals obviously contribute equally to molecular orbitals. In this case we can write down two molecular orbitals derived by combining the 1s atomic orbitals, these being represented by:

$$\varphi_m = [\varphi_A + \varphi_B] \quad \varphi_m = [\varphi_A - \varphi_B]$$

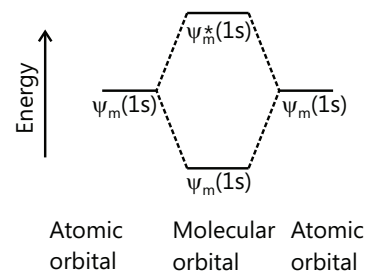
The molecular wave functions  $\varphi_m$  and  $\varphi_m^+$  are bonding and antibonding molecular orbitals; orbitals of the type, in which the line joining the two nuclei is a symmetrical axis for the electron distribution, are known as  $\sigma$  orbitals if bonding and  $\sigma^*$  orbitals if antibonding, so we may alternatively denote them as  $\sigma_{1s}$  and  $\sigma_{1s}^*$  orbitals. When the



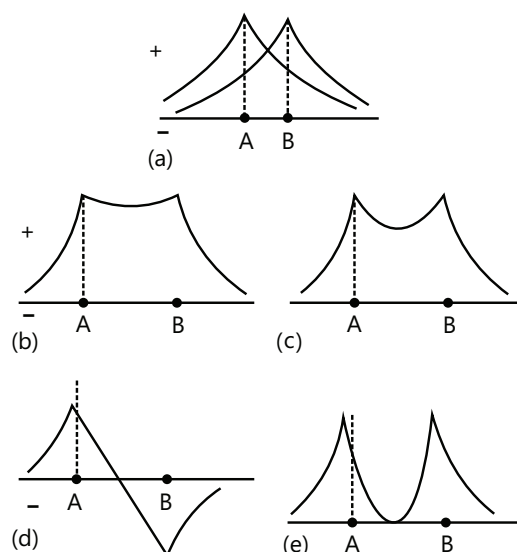
two 1s wave functions are added, they reinforce one another everywhere, and especially in the region between the two nuclei; the build-up of electron density, there diminishes the internuclear repulsion and a strong bond results. When one of the two 1s wave functions is subtracted from the other, they exactly cancel in a plane, midway between the nuclei, and the molecular wave function changes sign at this nodal plane. This lack of electron density raises the internuclear repulsion, the total energy becomes higher, the two nuclei are not bonded together, and the orbital is described as antibonding.

Pictorial representations of this LCAO method are given in figure, in the first of these, the relative energies of 1s molecular orbitals and their constituent atomic orbitals are shown, note that the antibonding orbital is correctly shown as somewhat more destabilised relative to the atomic orbitals than the bonding orbital is stabilised (N is not strictly equal to  $N^+$ , but is rather smaller, as we mentioned earlier).

In the hydrogen molecule in its ground state, both electrons occupy the  $\sigma$  1s orbital in the hydrogen molecule ion,  $H_2^+$ . Formed by the action of an electric discharge on hydrogen at low pressures, only a single electron is in this orbital and the total bonding energy being  $269 \text{ kJ mol}^{-1}$  compared with  $458 \text{ kJ mol}^{-1}$  for  $H_2$ .



**Figure 14.14:** The relative energy levels of molecular orbitals and their constituent atomic orbitals for  $H_2$



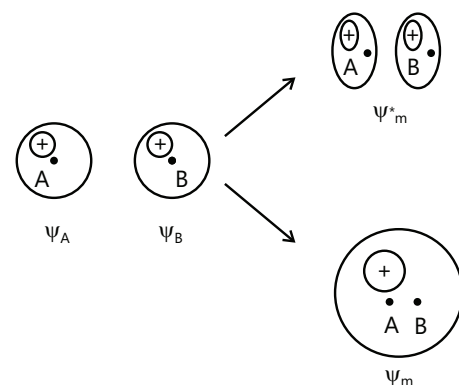
**Figure 14.15:** The formation of molecular orbitals for  $H_2$ . (a)  $\Psi_A$  and  $\Psi_B$  for individuals. (b)  $\Psi_A + \Psi_B = \Psi_m$ . (c) Probability function for the bonding orbital,  $(\Psi_m)^2$ .  $\Psi_A - \Psi_B = \Psi_m^*$ . (e) Probability function for the antibonding orbital,  $(\Psi_m^*)^2$ .

**Figure:** Another representation of the formation of molecular orbitals for  $H_2$ . Since the  $\sigma$  and  $\sigma^*$  orbitals are respectively centrosymmetric and non-centrosymmetric these orbitals may also be denoted by the symbols  $\sigma_g$  and  $\sigma_u^*$ .

Molecular orbital wave functions are designated as  $\phi_g$  and  $\phi_u$ , g and u refer to the symmetry of the orbital about its centre. If the wave function is centrosymmetric, i.e., has the same sign at the same distance in opposite directions from the centre of symmetry. The orbitals is said to gerade (German, even); if it changes sign on inversion about the centre, it is said to ungerade (German, uneven).

Alternative method for determining the symmetry of the molecular orbital is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remain the same, the orbital is gerade, and if the sign changes, the orbital is ungerade.

Thus  $\sigma$  and  $\pi^*$  molecular orbitals are gerade and  $\sigma^*$  and  $\pi$  molecular orbitals are ungerade.



**Figure 14.16 :** Combination of atomic orbital

**Condition for the combination of atomic orbitals:** The linear combination of atomic orbitals to form molecular orbital takes place only if the following conditions are satisfied.

- 1. The combining atomic orbitals must have the same or nearly the same energy.** This means that the 1s orbital can combine with another 1s orbital but not with the 2s orbital because the energy of the 2s orbital is appreciably higher than that of the 1s orbital. It, therefore, means that only a limited number of combinations of atomic orbitals are possible.
- 2. The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having the same or nearly the same energy will not combine if they do not have the same symmetry. For example,  $2p_z$  orbitals of one atom can combine with  $2p_z$  orbital of the other atom but not with the  $2p_x$  or  $2p_y$  orbitals because of their different symmetries.
- 3. The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

**Types of molecular orbitals:** Molecular orbitals of diatomic molecules are designated as  $\sigma$  (sigma),  $\pi$  (pie),  $\delta$  (delta) etc. In this nomenclature, the sigma ( $\sigma$ ) molecular orbitals are symmetrical around the bond-axis, while pi ( $\pi$ ) molecular orbitals are not symmetrical. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the  $\sigma$  type and are designated as  $\sigma 1s$  and  $\sigma^* 1s$ . If internuclear axis is taken to be in the direction, it can be seen that a linear combination of  $2p_z$ -orbitals of two atoms also produces two sigma molecular orbitals designated as  $\sigma 2p_z$  and  $\sigma^* 2p_z$ . [Fig.(b)]. Molecular orbitals obtained from  $2p_x$  and  $2p_y$  orbitals are not symmetrical around the bond axis because of the presence of a positive lobes plane. Such molecular orbitals, are labelled as  $\pi$  and  $\pi^*$  [Fig(c)]. A  $\pi$  bonding MO has large electron density above and below the internuclear axis. The  $\pi^*$  anti-bonding MO has a node between nuclei and  $\delta$ -type of molecular orbitals are obtained by involvement of d-orbitals into bonding.

#### Difference between $\pi$ molecular orbitals and the $\sigma$ orbitals

- For  $\pi$  overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for  $\sigma$  overlap the lobes point along the line joining the two nuclei.
- For  $\pi$  molecular orbitals,  $\Psi$  is zero along the internuclear line and consequently the electron density  $\psi^2$  is also zero. This is in contrast to  $\sigma$  orbitals.
- The symmetry of  $\pi$  molecular orbitals is different from that shown by  $\sigma$  orbitals. If the bonding  $\pi$  MO is rotated about the internuclear line, a change in the sign of lobe occurs. The  $\pi$  bonding orbitals are therefore ungerade, whereas all bonding MO's are gerade. Conversely, the antibonding  $\pi$  MO's are gerade, while all  $\sigma$  antibonding MO's are ungerade.

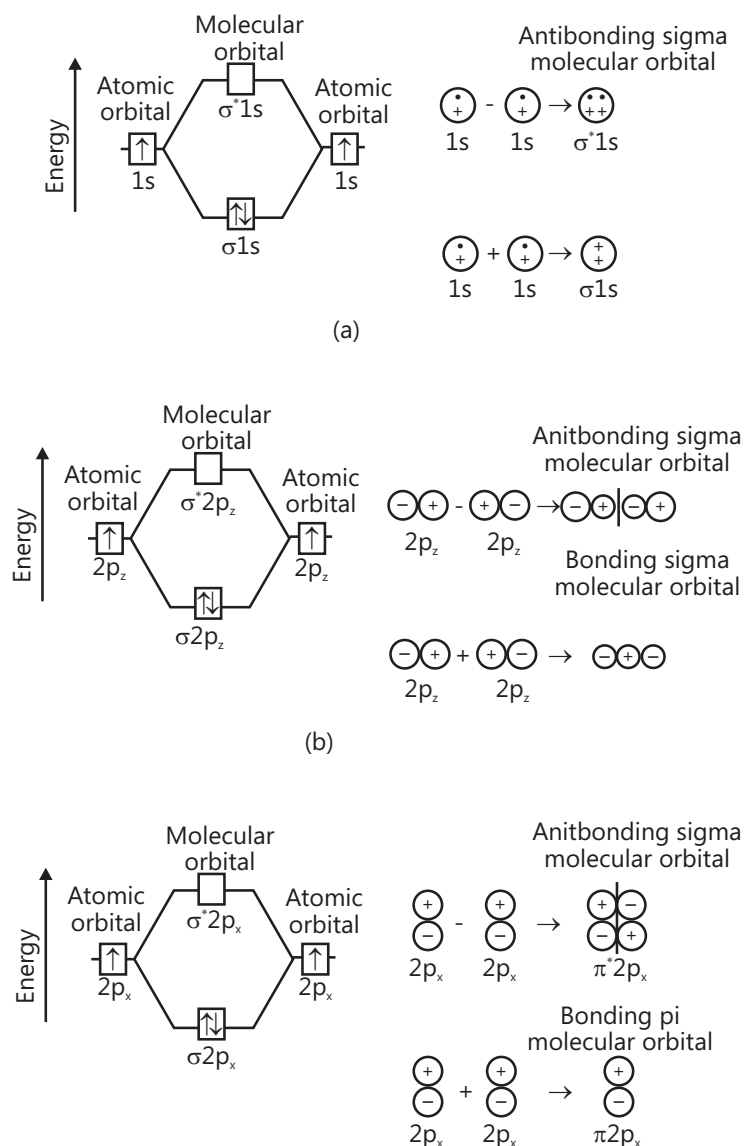
**Energy level diagram for molecular orbitals:** The energy level of molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for  $O_2$  and  $F_2$  is given below :

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

The increasing order of energies of various molecular orbitals for  $Be_2$ ,  $B_2$ ,  $C_2$ ,  $N_2$  etc. is :

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

The important characteristic feature of this order in that the energy of  $\sigma 2p_z$  molecular orbital is higher than that of  $\pi 2p_x$  and  $\pi 2p_y$  molecular orbitals.



**Figure 14.17:** Bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals (b)  $2p_z$  orbital and (c)  $2p_x$  atomic orbitals

**Electronic configuration and molecular behaviour:** The distribution of electrons among molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecules as discussed below:

- (i) The molecule is stable, if  $N_b$  is greater than  $N_a$  and
- (ii) The molecule is unstable, if  $N_b$  is less than  $N_a$

In (i) more bonding orbitals are occupied, so the bonding influence is stronger and a stable molecule results. In (ii) antibonding influence is stronger and therefore the molecule is unstable.

$N_b$  is the number of electrons in bonding molecular orbitals and  $N_a$  is the number of electrons in antibonding molecular orbitals.

**Bond order:** Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e., Bond order (b.o.) =  $\frac{1}{2}(N_b - N_a)$ .

A positive bond order (i.e.  $N_b > N_a$ ) means a stable molecule while a negative (i.e.  $N_b < N_a$ ) or zero (i.e.,  $N_b = N_a$ ) bond order means an unstable molecule.

**Nature of the bond:** Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

**Bond-Length:** The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

**Magnetic nature:** If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g.,  $N_2$  molecule. However if one or more molecular orbitals are single occupied it is paramagnetic (attracted by magnetic field), e.g.  $O_2$  molecule.

### Bonding in Some Homonuclear Diatomic Molecules:

(a) **Hydrogen molecule ( $H_2$ ):**  $H_2 : (\sigma 1s)^2$

$$\text{Bond order} : \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be  $438 \text{ kJ mol}^{-1}$  and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

(b) **Helium molecule ( $He_2$ ):**  $He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$

$$\text{Bond order of } He_2 \text{ is } \frac{1}{2}(2 - 2) = 0$$

The molecular orbital description of  $He_2$  predicts two electrons in a bonding orbital and two electrons in an antibonding orbital, with a bond order of zero, in other words, no bond. This is what is observed experimentally. The noble gas He has not a significant tendency to form of free atoms.  $He_2$  has a very low binding energy, approximately  $0.01 \text{ J/mol}$ ; for comparison,  $H_2$  has a bond energy of  $436 \text{ kJ/mol}$ .

(c) **Lithium molecule ( $Li_2$ ):**  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

Its bond order, therefore is  $\frac{1}{2}(4 - 2) = 1$ . It means that  $Li_2$  molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic  $Li_2$ , the molecules are known to exist in the vapour phase. The M.O. model predicts a single Li-Li bond in  $Li_2$ , in agreement with gas phase observations of the molecule.

(d) **Beryllium ( $Be_2$ ):**  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$

$Be_2$  has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like  $He_2$ , Be is not a stable chemical species.

(e) **Boron ( $B_2$ ):**  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x^1 = \sigma 2p_y^1) (\sigma 2p_z)^0$

Here is an example in which the Molecular orbital model has distinct advantage over the Lewis dot picture.  $B_2$  is found only in the gas phase, solid boron is found in several very hard forms with complex bonding, primarily involving  $B_{12}$  icosahedra,  $B_2$  is paramagnetic. This behaviour can be explained if its two higher energy electrons occupy separate p-orbitals. The Lewis dot model cannot account for the paramagnetic behaviour of this molecule.

$B_2$  is also a good example of the energy level shift caused by the mixing of s and p orbitals. In the absence of mixing, the  $\sigma_g(2p)$  orbital is expected to be lower in energy than the  $\pi_u(2p)$  orbitals and the resulting molecule would be diamagnetic. However, mixing of  $\sigma_g(2s)$  orbital with the  $\sigma_g(2p)$  orbital lowers the energy of  $\sigma_g(2s)$  orbital and increases the energy of the  $\sigma_g(2p)$  orbital to a higher level than the  $\pi$  orbitals, giving the order of energies shown above. As a result, the last two electrons are unpaired in the degenerate (having the same energy)  $\pi$  orbitals, and the molecule is paramagnetic. Overall, the bond order is 1, even though the two p electrons are in different orbitals. The bond order of  $B_2$  is  $1/2(6 - 4) = 1$ .

- (f) **Carbon molecule ( $C_2$ ):**  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$  or  $(\sigma 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ . The simple MO picture of  $C_2$  predicts a doubly bonded molecule with all electrons paired, but with both the highest occupied molecular orbitals (HOMOs) having  $\pi$  symmetry. It is unusual because it has two  $\pi$  bonds and no  $\sigma$  bond. The bond dissociation energies of  $B_2$ ,  $C_2$  and  $N_2$  increase steadily, indicating single, double, and triple bond with increasing atomic number. Although  $C_2$  is not a commonly encountered chemical species (carbon is more stable as diamond, graphite, and fullerene), the acetylide ion,  $C_2^{2-}$ , is well known, particularly in compounds with alkali metals, alkaline earths, and lanthanides. According to the molecular orbital model,  $C_2^{2-}$  should have order of 3 (configuration  $\pi_a^2 \pi_u^2 \sigma_g^2$ ). This is supported by the similar C–C distances in acetylene and calcium carbide (acetylide).

**Table 14.14:** C–C bond distance in different molecule

C – C Distance (pm)	
H – C = C – H	120.5
CaC <sub>2</sub>	119.1

The bond order of  $C_2$  is  $1/2 (8 - 4) = 2$  and  $C_2$  should be diamagnetic.  $C_2$  molecules have indeed been detected in the vapour phase. It is important to note that double bond in  $C_2$  consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

- (g) **Nitrogen molecule ( $N_2$ ):**  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$

$N_2$  has a triple bond according to both the Lewis and the molecular orbital models. This is in agreement with its very short N–N distance (109.8 pm) and extremely high bond dissociation energy (942 kJ/mol). Atomic orbitals decrease in energy with increasing nuclear charge  $Z$ ; as the effective nuclear charge increases, all orbitals are pulled to lower energies. The shielding effect and electron–electron interactions cause an increase in the difference between the 2s and 2p orbital energies as  $Z$  increases, from 5.7 eV for boron to 8.8 eV for carbon and 12.4 eV for nitrogen. As a result, the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  levels of  $N_2$  interact (mix) less than the  $B_2$  and  $C_2$  levels, and the  $\sigma_g(2p)$  and  $\pi_u(2p)$  are very close in energy and  $C_2$  levels. And the  $\sigma_g(2p)$  and  $\pi_u(2p)$  are very close in energy. The bond order of  $N_2$  is  $1/2 (10 - 4) = 3$ . It contains one sigma and two  $\pi$  bonds.

- (h) **Anionic nitrogen species ( $N_2^-$ ):** Though 15 electrons, but derived from  $N_2$ . Hence electronic configuration will be according to  $N_2$ .

Electronic configuration:  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2, (\pi^* 2p_x)^1$  The bond order of  $N_2^-$  is  $1/2(10 - 5) = 2.5$ . It is a paramagnetic species.

- (i)  **$N_2^+$ :** Bond order = 2.5. Out of  $N_2^+$  and  $N_2^-$ ,  $N_2^-$  is less stable though both have equal bond order but  $N_2^-$  has greater number of antibonding electrons.

- (j) **Oxygen molecule ( $O_2$ ):**  $O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$   $O_2$  is paramagnetic. This property, as for  $B_2$ , cannot be explained by the traditional Lewis dot  $\ddot{O}=\ddot{O}$  structure, but is evident from the molecular orbital picture, which assigns two electrons to the degenerate  $\pi_g$  orbitals. The paramagnetism can be demonstrated by pouring liquid  $O_2$  between the poles of a strong magnet: some of the  $O_2$  will be held between the pole faces until it evaporates. The bond order of  $O_2$  is  $\frac{1}{2} [N_b - N_a] - \frac{1}{2} [10 - 0] = 2$ .

So in the oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in  $\pi^* 2p_x$  and  $\pi^* 2p_y$  molecular orbitals, therefore,  $O_2$  molecule should be paramagnetic, a prediction that corresponds to the experimental observations. Several ionic forms of diatomic oxygen are known, including  $O_2^+$  and  $O_2^{2-}$ . The internuclear O – O distance can be conveniently known, including  $O_2^-$  and  $O_2^{2-}$ . The internuclear O – O distance can be conveniently correlated with the bond order predicted by the molecular orbital model, as shown in the following table.

**Table 14.15:** Bond order predicted by the molecular orbital model

	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
$O_2^+$ (dioxygenyl)	2.5	112.3	1
$O_2$ (dioxygen)	2.0	120.07	2
$O_2^-$ (superoxide)	1.5	128	1
$O_2^{2-}$ peroxide	1.0	149	0

**Note :** Oxygen-oxygen distances in  $O_2^-$  and  $O_2^{2-}$  are influenced by the cation. This influence is especially strong in the case of  $O_2^{2-}$  and is one factor in its unusually long bond distance. The extent of mixing is not sufficient in  $O_2$  to push the  $\sigma(2p)$  orbital to higher energy than the  $\pi_g(2p)$  orbitals. The order of molecular orbitals shown is consistent with the photoelectron spectrum.

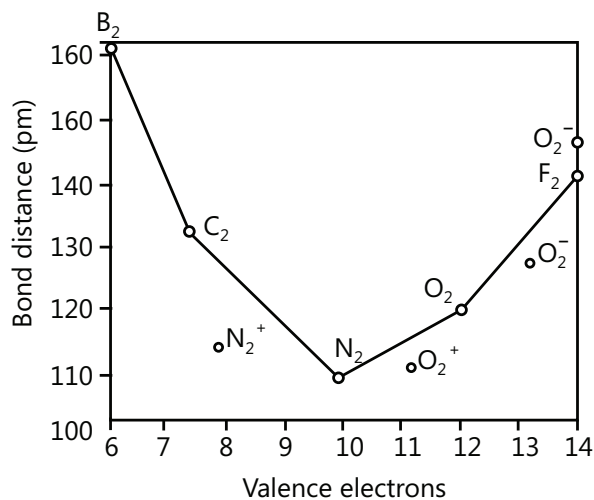
**(k) Fluorine molecule ( $F_2$ ):**  $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x^2 = \pi 2p_y^2)(\pi^*2p_x^2 = \pi^*2p_y^2)$  The molecular orbital picture of  $F_2$  shows a diamagnetic molecule having a single fluorine-fluorine bond, in agreement with experimental data on this very reactive molecule.

The net bond order in  $N_2$ ,  $O_2$  and  $F_2$  is the same whether or not mixing is taken into account, but the order of the filled orbitals is different. The switching of the order of the  $\sigma_g(2p)$  and  $\pi_u(2p)$  orbitals can occur because these orbitals are so close in energy ; minor changes in either orbital can switch their order. The energy difference between the 2s and 2p orbitals of the atoms increases with increasing nuclear charge, from 5.7 eV in boron to 27.7eV in fluorine. Because the difference becomes greater, the s-p interaction decreases and the normal order of molecular returns in  $O_2$  and  $F_2$ . The higher  $\sigma_g$  orbital is seen again in CO.

**(l) Neon molecule ( $Ne_2$ ):**  $(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x^2 = \pi 2p_y^2)(\pi^*2p_x^2 = \pi^*2p_y^2)(\sigma^*2p_z)^2$  All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons and the bond order is therefore zero. The  $Ne_2$  molecule is a transient species, if it exists at all.

**Note:** HOMO : Highest Occupied Molecular Orbital, LUMO : Lowest Unoccupied Molecular Orbital

**Bond lengths in homonuclear diatomic molecules:** Figure shows the variation of bond distance with the number of valence electrons in the second period, p block homonuclear diatomic molecules. As the number of electrons increases, the number in bonding orbitals also increases, the bond strength becomes greater, and the bond length becomes shorter. This continues with up to 10 valence electrons in  $N_2$  and then the trend reverses because the additional electrons occupy antibonding orbitals. The ions  $N_2^+$ ,  $O_2^+$ ,  $O_2^{2+}$  are also shown in the figure and follow a similar trend.

**Figure 14.18:** Plot of Bond distance Vs Valence electrons for homonuclear diatomic orbital

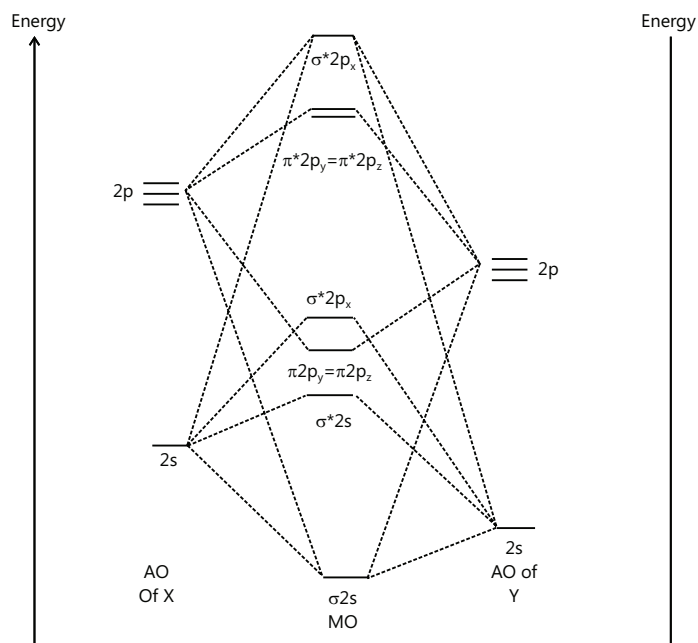
The same principles apply when combining atomic orbitals from two different atoms as applied when the atoms are identical, that is:

- (1) Only atomic orbitals of about the same energy can combine effectively.
- (2) They should have the maximum overlap.
- (3) They must have the same symmetry.

Since the two atoms are different, the energies of their atomic orbitals are slightly different. A diagram showing how they combine to form molecular orbitals after considering the symmetry interaction of 2s and 2p<sub>x</sub> orbitals is given in figure (where the molecule is XY and Y is more electronegative than X).

There are a total of 15 electrons in the molecule and the order of energy levels of the various MOs is

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



**Figure 14.19:** Electronic configuration, atomic and molecular orbital for a heteronuclear molecule XY

An unpaired electron is present in the  $\pi^*$  orbital and is delocalized over the whole molecule, hence NO molecules is paramagnetic. Since the highest occupied molecular orbital (HOMO) is  $\pi^*$  and the energy of which is higher than the atomic orbitals of N atom and O atom, the ionization energy of NO is less than that of both N and O atoms.

**Table 14.16:** Ionization enthalpies of some elements

Species	Ionization energy (in kJ mol <sup>-1</sup> )
N	1402
O	1314
NO	894

On ionization, the bond order 2.5 of NO is increased to 3.0 in NO<sup>+</sup>, as a result of which bond length decreases from 113 pm in NO to 106 pm in NO<sup>+</sup>.

Some special features are introduced in the MO diagram of CO because the electronegativity difference between C and O atom is large. Since the  $\Delta E_{(2p-2s)}$  for C atom (5.3 eV) is much less compared to  $\Delta E_{(2p-2s)}$  for O atom (15.0 eV), the participation of s-p hybrid orbitals are considered for the formation of MO diagram of CO, which is shown in the figure.

In ionization of CO, i.e. CO → CO<sup>+</sup>, the removal of the electron takes place from the non-bonding orbital of C atom (HOMO). Hence the interelectronic repulsion decreases and finally the bond length decreases from 112.8 pm to 111.5 pm.

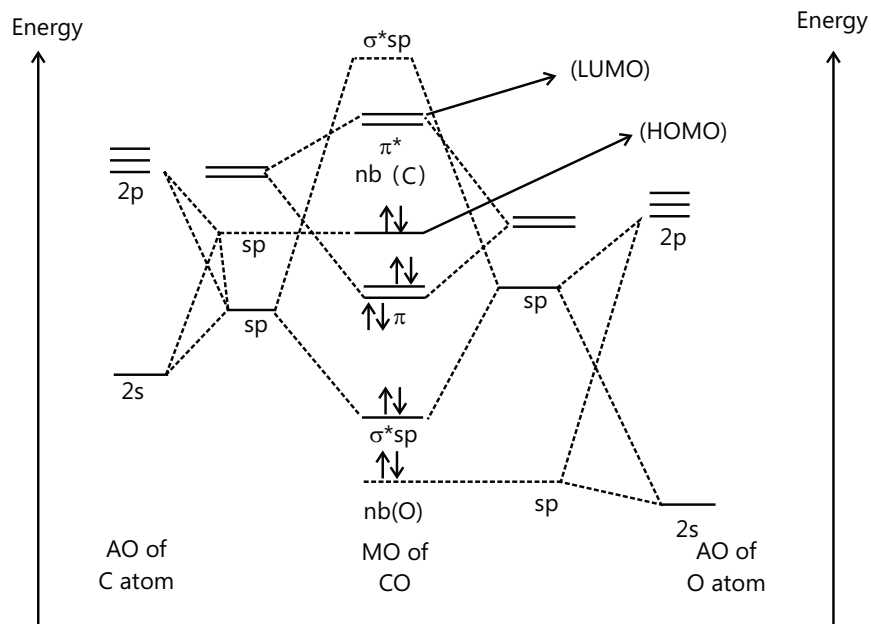


Figure 14.20: Molecular orbital diagram for CO molecule

**Illustration 12:** Though  $O_2$  molecule is paramagnetic yet it is a colourless gas. Why ?

**Sol :** It is because the energy gap between HOMO and LUMO levels in  $O_2$  molecule is so large that the radiation of visible light cannot excite  $e^-$  from HOMO to LUMO. In fact  $O_2$  gas shows absorption in UV zone. So it is colourless.

**Illustration 13:** Correct order of bond energy is-

- (A)  $N_2 > N_2^+ > N_2^- > N_2^{2-}$       (B)  $N_2^+ > N_2^- > N_2^{2-} > N_2$   
 (C)  $N_2 > N_2^- = N_2^+ > N_2^{2-}$       (D)  $N_2^- > N_2 = N_2^+ > N_2^{2-}$

**Sol:** (A) Bond order is directly proportional to the bond energy.

$$\text{Bond order of } N_2 = 3, N_2^- = 2.5 \quad N_2^{2-} = 2$$

But  $N_2^-$  has more electrons in antibonding MO's and thus  $N_2^+$  is more stable than  $N_2^-$ . So correct order of bond energy will be  $N_2 > N_2^+ > N_2^- > N_2^{2-}$

**Illustration 14:** Which of the following species have a bond order of 3 ?

- (A) CO      (B)  $CN^-$       (C)  $NO^+$       (D)  $O_2^-$

**Sol:** Bond order =  $\frac{1}{2} [N_b - N_a]$

Where  $N_b$  - No of electron in bonding energy level

$N_a$  - no of electron in anti-bonding level.

(A, B, C). Species CO,  $CN^-$ ,  $NO^+$  are isoelectronic with 14 electrons to  $N_2$  which has bond

order of 3 (i.e.  $\frac{10-4}{3} = 3$ ), so their bond order will be equal to three.



**Illustration 15:** Which of the following are diamagnetic ?

- (A)  $C_2$       (B)  $O_2^{3-}$       (C)  $Li_2$       (D)  $N_2^+$

**Sol:** (A, B, C). Species  $C_2$ ,  $O_2^{2-}$ ,  $Li_2$  have all the electrons paired but  $N_2^-$  has one unpaired electron in the bonding molecular orbital, it is paramagnetic.

**Polarity of bonds:** In reality no bond or compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, for example in  $H_2$ ,  $O_2$ ,  $Cl_2$ ,  $N_2$  or  $F_2$  the shared pair of electrons is equally attracted by the atoms. As a result, electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine, since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

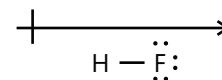
As a result of polarisation, the molecule possesses the dipole moment which can be defined as the product of magnitude of the partial charge ( $\delta^+$  or  $\delta^-$ ) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment ( $\mu$ ) = Magnitude of charge ( $q$ )  $\times$  distance of separation ( $d$ )

Dipole moment is usually expressed in Debye units (D). The conversion factors are  $1D = 3.33564 \times 10^{-10}$  Cm, where C is coulomb and m is meter.

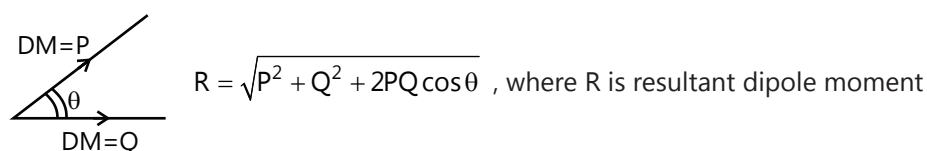
$$1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u. cm.}$$

Further dipole moment is a vector quantity and is depicted by a small arrow with a tail on the positive centre and the head pointing towards the negative centre. For example, the dipole moment of HF may be represented as

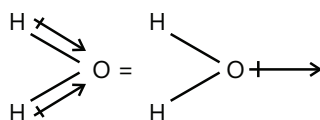


The shift in electron density is represented by crossed arrow ( $\rightarrow$ ) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules, the dipole moment not only depends upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such a case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e., a molecule will have a dipole moment if the summation of all of the individual vectors is non-zero.

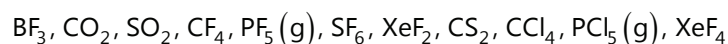


For example,  $H_2O$  molecule, which has a bent structure, the two O–H bonds are oriented at an angle of  $104.5^\circ$ . Net dipole moment of  $6.17 \times 10^{-30}$  cm ( $1D = 3.33564 \times 10^{-30}$  cm) is the resultant of the dipole moments of two O–H bonds.



Net dipole moment,  $\mu = 1.85 D = 1.85 \times 3.33564 \times 10^{-30} \text{ cm} = 6.17 \times 10^{-30} \text{ cm}$ .

Following compounds have zero dipole moment:

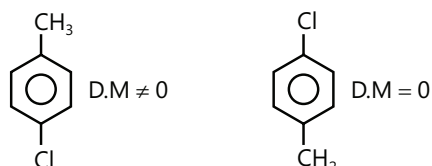


Some important orders

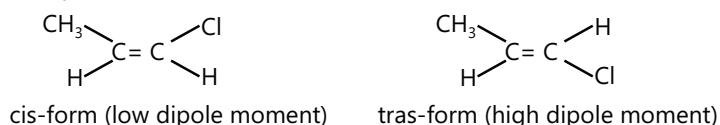
HF	>	HCl	>	HBr	>	HI
1.92 D		1.08		0.78		0.38
CH <sub>3</sub> Cl	>	CH <sub>2</sub> Cl <sub>2</sub>	>	CHCl <sub>3</sub>	>	CCl <sub>4</sub>
1.86		1.6		1.0		0

Usually for distributed Benzene order is o > m > p

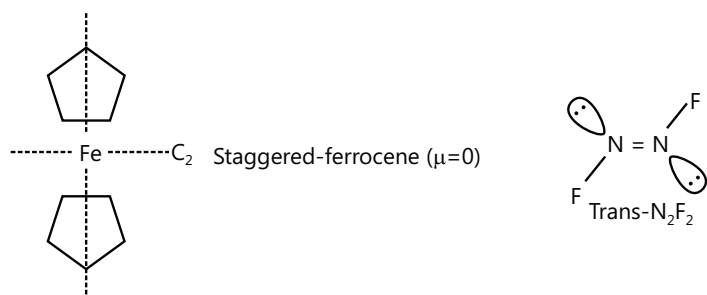
But it all depends on the substituents



**Note:** For geometrical isomers, usually the dipole moment of cis is more than trans, but again there can be exceptions.



**For example:** The presence of a centre of symmetry, *i*, requires that the dipole moment be zero, since any charge on one side of the molecule is cancelled by an equal charge on the other side of the molecule. Thus, [CoF<sub>6</sub>]<sup>3-</sup>, trans-N<sub>2</sub>F<sub>2</sub> and the staggered conformer of ferrocene do not have moments.



**Some Important points about dipole moment:** A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B-F bonds are polar in BF<sub>3</sub>, but BF<sub>3</sub> has  $\mu = 0$  due to its symmetrical geometry.

If the molecule has  $\mu \neq 0$ , then it should be linear or having symmetrical geometry.

E.g. linear – CO<sub>2</sub>, CS<sub>2</sub>, BeCl<sub>2</sub>(g) ; symmetrical geometry –BF<sub>3</sub>, CH<sub>4</sub>, PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>, XeF<sub>4</sub>

If the molecule has  $\mu = 0$ , then it should be angular or having unsymmetrical geometry

SnCl<sub>2</sub>, PbCl<sub>2</sub>, SO<sub>2</sub>, angular molecular geometry NH<sub>3</sub>, H<sub>2</sub>O, NF<sub>3</sub>, SF<sub>4</sub>, H<sub>2</sub>S, unsymmetrical molecular geometry

$$\bigcirc \quad \% \text{ Ionic character} = \frac{\mu_{\text{experimental}}}{\mu_{\text{theoretical}}} \times 100 = \frac{\mu_{\text{(Observed)}}}{\mu_{\text{(100\% ionic compound)}}} \times 100$$

**Illustration 16:** The resultant dipole moment of water is 1.85 D, ignoring the effects of lone pair calculate, the dipole moment of each OH bond (given that bond angle in H<sub>2</sub>O = 104°, cos 104° = -0.25)

**Sol:**  $R^2 = P^2 + Q^2 + 2PQ \cos$

$$(1.85)^2 = x^2 + x^2 + 2x^2 \left( -\frac{1}{4} \right)$$

$$(1.85)^2 = 2x^2 - \frac{x^2}{2} \Rightarrow \frac{3x^2}{2}$$

$$\therefore x = 1.51 \text{ D}$$

**Illustration 17:** For a HCl molecule, the observed dipole moment is 1.03 D and bond length is 1.275Å. Calculate % ionic character.

**Sol:** first determine the theoretical dipole moment by using distance of separation and magnitude of charge.

% ionic character can be calculated as follows :

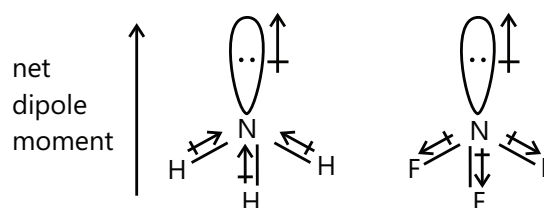
$$\frac{\text{experimental dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

$$\text{Dipole moment} = 4.8 \times 10^{-8} \times 1.275 \times 10^{-8} = 4.8 \times 1.275$$

$$\% \text{ ionic character} = \frac{1.03 \times 100}{1.275 \times 4.8} \approx 17\%$$

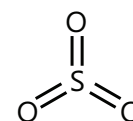
**Illustration 18:** Why does  $\text{NH}_3$  have more dipole moment than  $\text{NF}_3$ ?

**Sol:** In  $\text{NH}_3$  molecule, nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards nitrogen atom, but in  $\text{NF}_3$  molecule, fluorine is more electronegative than nitrogen so that net dipole moment is towards fluorine atoms. In  $\text{NH}_3$ , the bond pair moments and lone pair moments are in the same direction, while in  $\text{NF}_3$ , the lone pair moment and bond pair moments are in opposite direction.



**Illustration 19:** The geometry of  $\text{SO}_3$  and its dipole moment are :

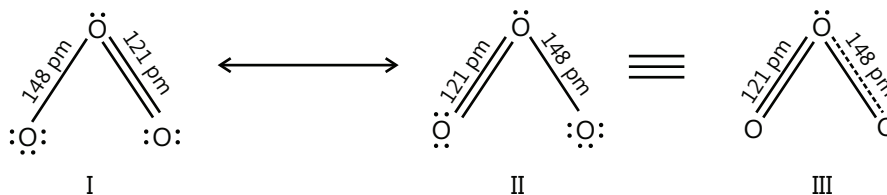
- (A) pyramidal and non-zero      (B) trigonal and non-zero  
(C) trigonal planar and zero      (D) T-shaped and zero



**Sol: (C)** The steric number of sulphur = 3 ; so hybridization in  $sp^2$ . There is no lone pair on sulphur atom., therefore, according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence, the molecule will be symmetrical (trigonal planar) with zero dipole moment.

## 16. RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone,



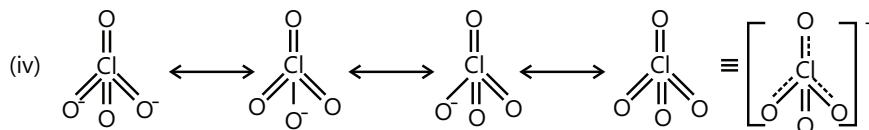
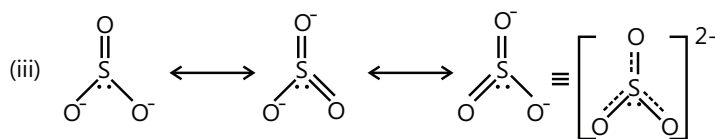
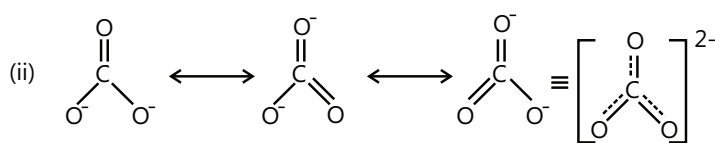
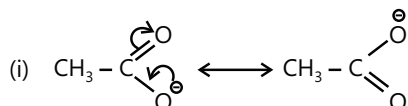
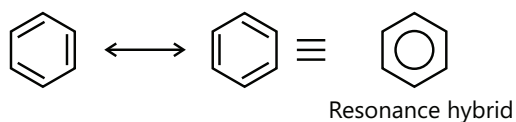
(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O–O single bond and a O = O double bond. The normal O – O and O = O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the  $\text{O}_2$  molecule are same (128 pm). Thus, the oxygen-oxygen bonds in the  $\text{O}_2$  molecule are intermediate between a double and a single bond.

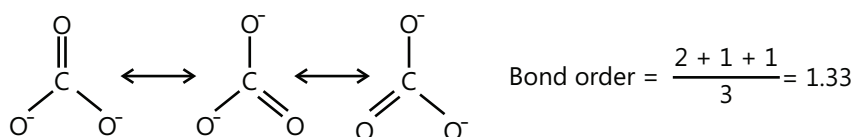
Obviously, this cannot be represented by either of the two Lewis structures shown above. The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like  $O_3$ .

**Definition:** Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound.

**Resonance Hybrid:** It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



**Example:**



Resonance energy = Actual bond energy – Energy of most stable resonating structure.

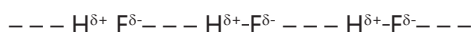
Stability of molecule of resonance energy.

More the number of covalent bonds in a molecule, greater will be its resonance energy.

(Resonance energy)  $\propto$  (number of resonating structures).

## 17. HYDROGEN BOND

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied to a hydrogen atom to form a covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially, positively charges the hydrogen atom forming a bond with the other more electronegative atom. This bond is called a hydrogen bond and is weaker than a covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below :



Here, the hydrogen bond acts as a bridge between atoms which holds one atom by covalent bond and the other by a hydrogen bond. Hydrogen bond is represented by a dotted line (---), while a solid line represents the covalent

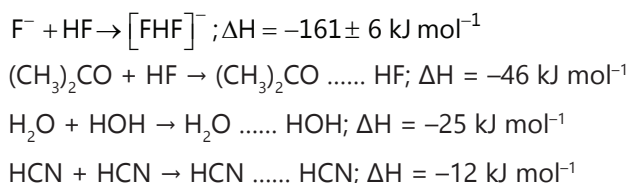
bond. Thus, hydrogen bond can be defined as the attractive force which binds the hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pair tend to line up and hold the molecules together. Other atom with high electronegativity, such as Cl, can also form hydrogen bonds in strongly polar molecules such as chloroform,  $\text{CHCl}_3$ .

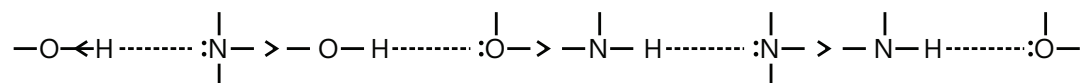
### Conditions required for H-bond :

- (i) Molecule should have a more electronegative atom (F, O, N) linked to H-atom.
- (ii) Size of electronegative atom should be smaller.
- (iii) A lone pair should be present on a electronegative atom.

**Strength of H-bond:** The strength of H-bond is usually very low (5 – 10 kJ/mol,) but in some cases this value may be as high as 50 kJ/mol. The strongest H-bonds are formed by F atoms. Deuterium is more electropositive than H, therefore it also forms stronger bonds. The strength of the H-bond can be compared by the relative bond energies and the geometry of the various compounds as given below :



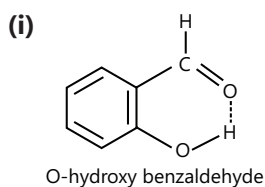
The magnitude of H-bonding depends on the physical state of the compounds. H-bonding is maximum in the solid state and minimum in the gaseous state. Thus, hydrogen bonds have a strong influence on the structure and properties of the compounds. Order of H-bond strength



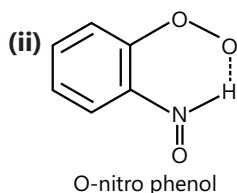
### Types of H-Bonds:

#### (a) Intramolecular H-Bonding:

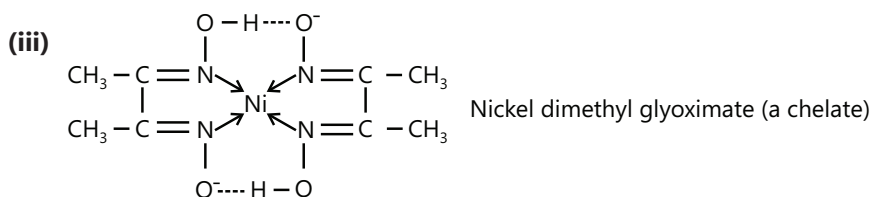
This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.



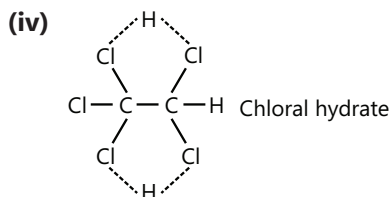
It has a lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.



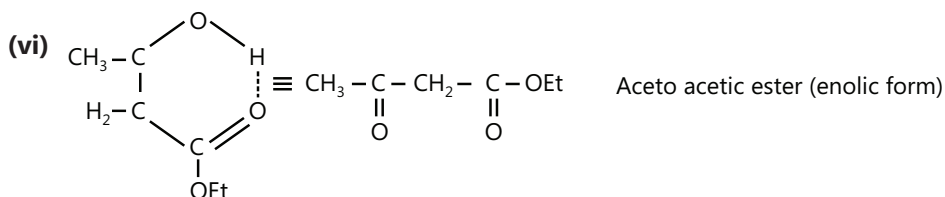
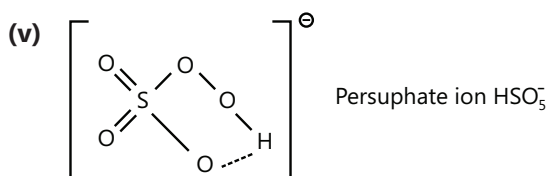
It has a lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.



Extra stability of the complex is because of intermolecular hydrogen bonding in addition to the chelating effect.



Chloral hydrate is stable only on account of intramolecular hydrogen bonding.

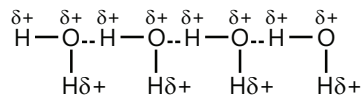


$K_1$  of peroxomono sulphuric acid (i.e., caros acid) is greater than  $K_2$ . After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult. The intramolecular hydrogen bonding attributes the stability of the enolic form of acetoacetic ester.

### Necessary conditions for the formation of intramolecular hydrogen-bonding:

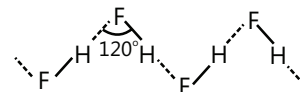
- The ring formed as a result of hydrogen bonding should be planar.
  - a 5- or 6- membered ring should be formed.
  - Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.
- (a) **Intermolecular H-Bonding:** Exists between the negative and positive ends of different molecules of the same or different substances i.e., it is formed between two different molecules of the same or different compounds.

- (i) In water molecules due to the polar nature of  $\text{H}_2\text{O}$  there is an association of water molecules giving a liquid abnormally high boiling point.



When ice is formed from liquid water, some air gaps are formed (in tetrahedral packing of water molecules). The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules. Due to this, volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Conversely when ice melts, density increases but only upto  $4^\circ\text{C}$ , after this intermolecular H-bonding between water molecules breaks. Hence, volume increases and density decreases. Thus, water has maximum density at  $4^\circ\text{C}$ .

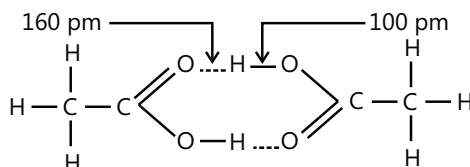
- (ii) The hydrogen bonds in HF link the F atom of one molecules with the H-atom of another molecule, thus forming a zig-zag chain  $(\text{HF})_n$  in both the solid and also in the liquid.



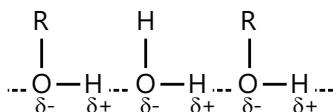
Some hydrogen bonding also occurs in the gas, which consists of a mixture of cyclic  $(\text{HF})_6$  polymers, dimeric  $(\text{HF})_2$ , and monomeric HF. Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula  $\text{M}(\text{HF})_2$ ; For example, in  $\text{KHF}_2$  an X-ray diffraction study together with a neutrons diffraction study shows that there is a linear symmetrical anion having an over all, F–H–F distance of 2.26 Å, which may be compared with the H–F bond length of 0.92 Å in hydrogen fluoride monomer.

(iii) There is also similar H-bonding in alcohol (R–OH), ammonia ( $\text{NH}_3$ ) and phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) molecules

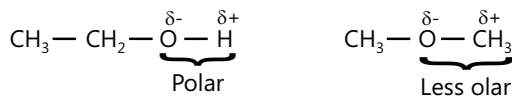
(iv) Carboxylic acid dimerises in gaseous state due to H-bonding



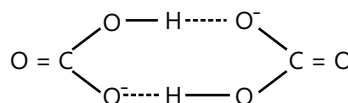
(v) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding  $\text{H}_2\text{O}$  and R–OH molecules)



However, isomeric ether is less soluble in water due to the less polar nature of ether.



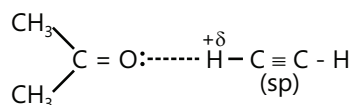
(vi)  $\text{HCO}_3^-$  ions exist as dimer in  $\text{KHCO}_3$



In  $\text{NaHCO}_2^-$ , the  $\text{HCO}_3^-$  ions are linked in to an infinite chain through intermolecular H-bonding.

**Illustration 20:**  $\text{C}_2\text{H}_2$  is not soluble in  $\text{H}_2\text{O}$ , but it is highly soluble in acetone.

**Sol:** As %s character increases, electronegativity increases, due to Hydrogen bonding  $\text{C}_2\text{H}_2$  becomes soluble in acetone



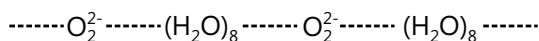
In hybridisation, as s character increases, electronegativity increases, hence  $\text{C}_2\text{H}_2$  forms H-bonds with O-atom of acetone and dissolves. But  $\text{H}_2\text{O}$  molecules are so linked that it is not possible for  $\text{C}_2\text{H}_2$  molecules to break that association, hence  $\text{C}_2\text{H}_2$  is not soluble in  $\text{H}_2\text{O}$ .

**Illustration 21:** Why  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  readily loses one molecule of water at  $80^\circ\text{C}$  ?

**Sol :** One water molecule is coordinated to a lone pair of electrons on  $\text{SnCl}_2$  and the other is hydrogen bonded to coordinate water molecules.

**Illustration 22:** Why does crystalline sodium lose one molecule of water at  $80^\circ\text{C}$  ?

**Sol :**  $\text{Na}_2\text{O}_2$  forms stable hydrates on account of H-bonding



**Illustration 23:** Explain why tetramethyl ammonium hydroxide is a stronger base than trimethyl ammonium hydroxide.



**Sol :** Due to hydrogen bonding in trimethyl ammonium hydroxide, ionization becomes difficult and thus  $\text{OH}^-$  is not formed with ease.

In the trimethyl compound, the O–H group is hydrogen bonded to  $\text{Me}_3\text{NH}$  group and this makes it more difficult for the OH group to ionize and hence it is a weak base.

In the tetramethyl compound, hydrogen bonding cannot occur, so the  $\text{OH}^-$  group ionizes easily and thus it is a much stronger base.

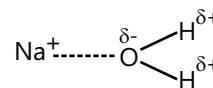
## 18. INTERMOLECULAR FORCES (VAN DER WAAL'S FORCES)

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of the following types.

- Ion-dipole attraction,
- Dipole-dipole attraction,
- Ion-induced dipole attraction,
- Dipole-induced dipole attraction,
- Instantaneous dipole-Instantaneous induced dipole attraction (Dispersion force or London forces)

Strength of Van der Waal's forces  $a > b > c > d > e$

**(a) Ion-dipole attraction:** Exists between an ion and a polar molecule. Its strength depends on (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule. It is thought to be directional. Ion-dipole forces are important in solutions of ionic compounds in polar solvents, where solvated species such as  $\text{Na}(\text{OH}_2)_x^-$  and  $\text{F}(\text{H}_2\text{O})_y^+$  (for solution of NaF in  $\text{H}_2\text{O}$ ) are found. Hence, this force is responsible for hydration.

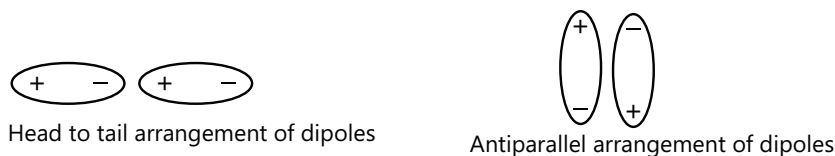


**(b) Dipole-dipole attraction:** These are electrostatic attractions between the oppositely charged ends of permanent dipoles. Exists between polar molecules and due to this force, gas can be liquefied.

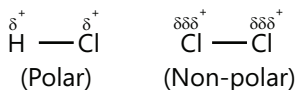


**(c) Ion-induced dipole attraction:** Exists between ion and non-polar molecules (e.g. an atom of a noble gas such as Xenon)

**(d) Dipole-induced dipole attraction:** Exists between polar and non-polar molecules.



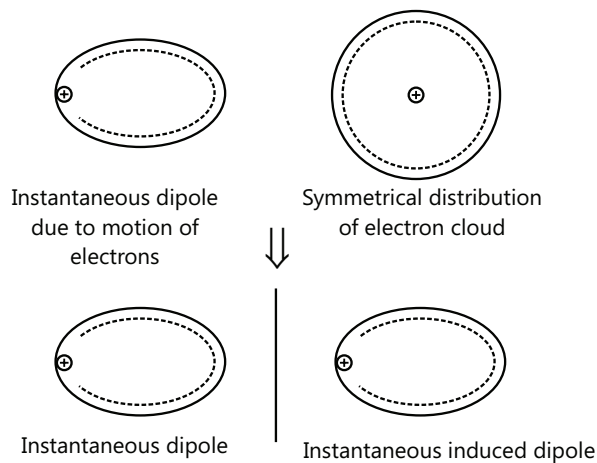
**Figure 14.17:** Different arrangements of dipole





(e) **Instantaneous dipole-Instantaneous induced attraction:** Exists among the non-polar molecules like  $H_2$ ,  $O_2$ ,  $Cl_2$  etc. in solid or liquid states. Even in atoms or molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary unbalances in electron distribution.

London forces are extremely short range in action and the weakest of all attractive forces. The London forces increase rapidly with molecular weight, or more properly with the molecular volume and the number of polarizable electrons.



**Figure 14.18:** Instantaneous dipole-Instantaneous induced attraction

**Note :** Fluoro carbons have usually low boiling points because tightly bound electrons in the fluorine atoms have a small polarizability.

- Strength of Van der waal force  $\propto$  molecular mass.
- van der Waal's force  $\propto$  boiling point.

**Illustration 24:** Give the order of boiling point of following  $Cl_2$ , HCl.

**Sol:**  $Cl_2 - Cl_2 < HCl - HCl$  (boiling point)

As dipole-dipole attraction is stronger than dispersion force.

**Illustration 25:** Arrange the inert gases, according to their increasing order of boiling points.

**Sol :** strength of van der Waal's force increases down the group with increase in molecular mass.

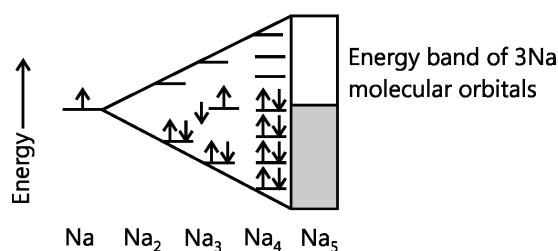
$He < Ne < Ar < Kr < Xe$  (boiling point)

**Metallic bond:** Most metals crystallise in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electron interactions among 8 to 12 nearest neighbours (which is also called coordination number). Bonding in metals is called metallic bonding. It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole. Two models are considered to explain metallic bonding:

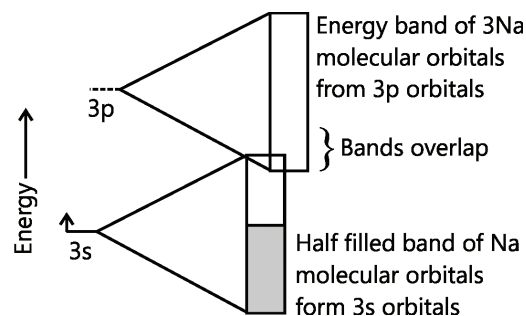
- Band model
- Electron-sea model

(a) **Band Model:** The interaction of two atomic orbitals, say the 3s-orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one antibonding orbital. If N atomic orbitals interact, N molecular orbitals are formed. Atoms interact more strongly with nearby atoms than with those farther away. The energy that separates bonding and antibonding molecular orbitals decreases as the interaction (overlap) between the atomic orbitals decreases. When we consider the possible interactions among one mole of Na atoms,

there is a formation of a series of very closely spaced molecular orbitals ( $3\sigma_s$  and  $3\sigma^*$ s). They consist of a nearly continuous band of orbitals belonging to the crystal as a whole. One mole of Na atoms contributes one mole ( $6.02 \times 10^{23}$ ) of valence electrons, thus  $6.02 \times 10^{23}$  orbitals in the band are half-filled.



**Figure 14.19:** The band of orbitals resulting from interaction the 3s-orbitals in a crystal of sodium.



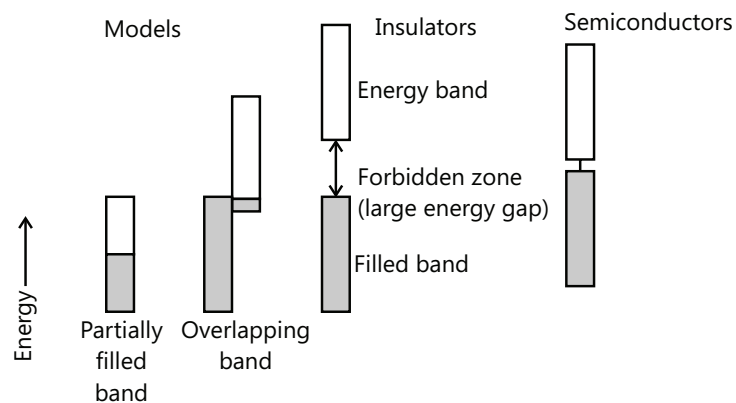
**Figure 14.20:** Overlapping of a half-filled 3s band with an empty 3p band of Na crystal.

The empty 3p atomic orbitals of Na atoms also interact to form a wide band of  $3 \times 6.07 \times 10^{23}$  orbitals. The 3s and 3p atomic orbitals are quite close in energy, so that these bands of molecular orbitals overlap. The two overlapping bands contain  $4 \times 6.02 \times 10^{23}$  orbitals. Because each orbital can hold two electrons, the resulting combination of bands is only-eight full.

According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band which (or into which) electrons must move to allow electrical conduction is called a conduction band. The electrical conductivity of a metal decreases as temperature increases. The increases in temperature cause thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

Crystalline non-metals, such as diamond and phosphorus, are insulators, they do not conduct electricity. It is due to the fact their highest-energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty band (conduction band) by an energy difference called the band gap. In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band.

Elements that are semiconductors have filled bands that are only slightly below, but do not overlap with empty bands. They do not conduct electricity at low temperature, but a small increase in temperature is sufficient to excite some of the highest-energy electrons into the empty conduction band.



**Figure 14.21:** Distinction among metal, insulator and semiconductors.in each case an unshaded area represents a conduction band.

**(b) Electron-Sea Model:** Metals have the ability to conduct electricity, ability to conduct heat, ease of deformation that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility) and a lustrous appearance.

One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured as a network of positive ions immersed in a "sea of electrons". In lithium, the ions would be  $\text{Li}^+$  and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

In thermal conductivity, no electrons leave or enter but those in the region being heated gain kinetic energy and transfer this to other electrons.

According to the electron-sea model, the case of deformation of metals can be thought of in this way : If one layer of metal ions is forced across another, perhaps by hammering, the structure remains unchanged as the sea of electrons rapidly adjusts to the new situation.

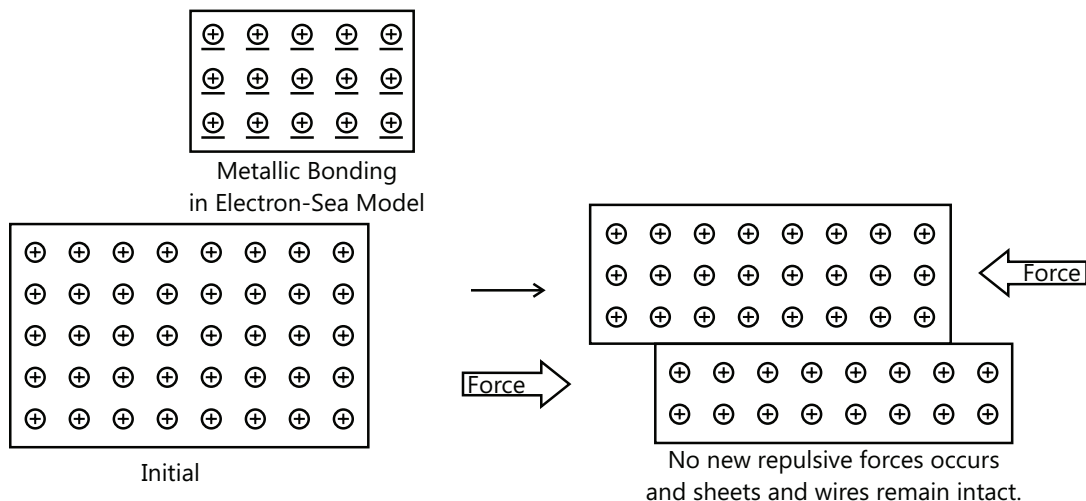
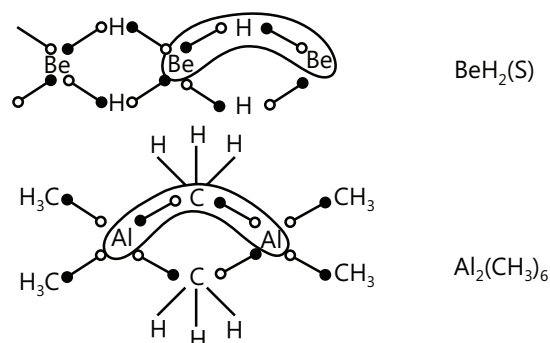


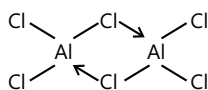
Figure 14.22: Effect of distortion on metal sheet

### Some Special Bonding Situations:

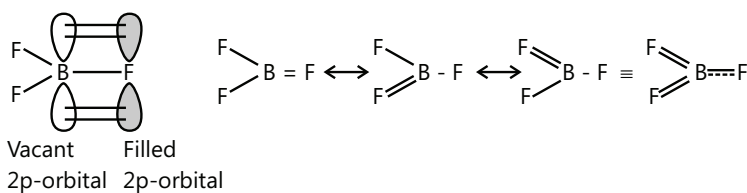
- (a) **Electron deficient bonding:** There are many compounds in which some electron deficient bonds are present from normal covalent bonds or coordinates which are 2c-2e bonds (two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected, such as three centre-two electron bonds (3c-2e) present in diborane  $B_2H_6$ ,  $Al_2(CH_3)_6$ ,  $BeH_2(s)$  and bridging metal carbonyls.



But  $Al_2Cl_6$  has a covalent bond only and there is no electron deficient bonding as depicted in the given structure.



- (b) **Back Bonding:** Back bonding generally takes place when out of two bonded atoms has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair (generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in  $BF_3$ , the boron atom completes its octet by accepting two 2p-electrons from fluorine into 2p empty orbital.



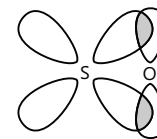
- (i) Decrease in B – F bond length is due to delocalised  $p\pi-p\pi$  bonding between filled p-orbitals of F atom and vacant p-orbital of B atom. The extent of back bonding is much larger if the orbitals involved in the back are of same size, for example the extent of back bonding in boron trihalides is as follows:  $BF_3 > BCl_3 > BBr_3$

There is  $p\pi-p\pi$  back bonding in boron trihalide. The extent of back bonding decreases from  $\text{BF}_3$  to  $\text{BI}_3$  because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

- (ii) The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pair on it. So among the atoms of third period the extent of back bonding follows the order

$\text{Si} > \text{P} > \text{S} > \text{Cl}$ . The extent of  $p\pi-p\pi$  overlapping  $\propto \frac{1}{\text{Lewis acid character}}$

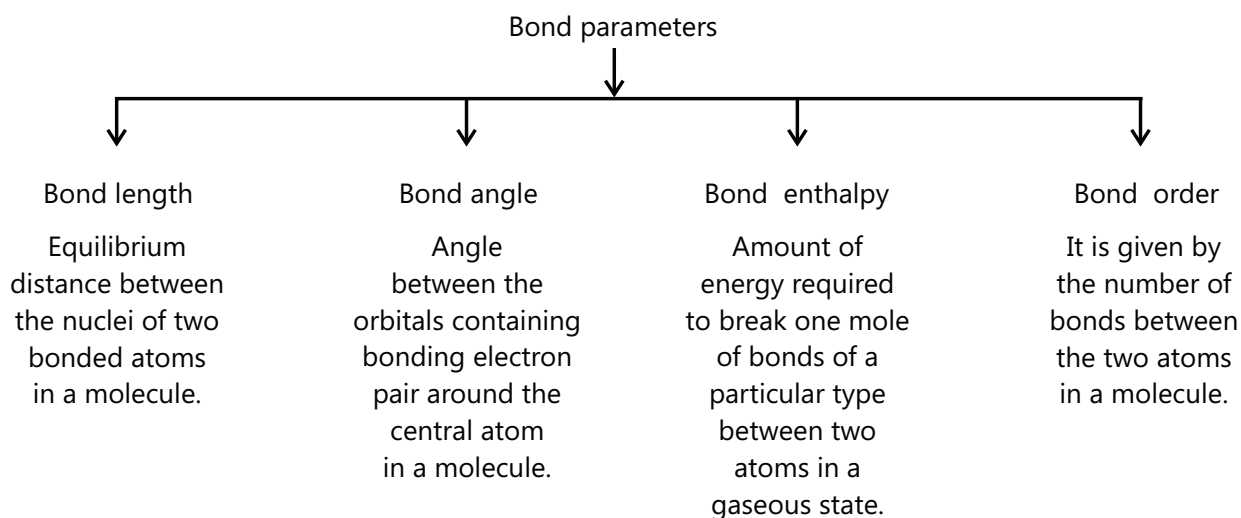
- (c) **Bond Lengths and  $p\pi-d\pi$  bonding:** The bonds between S and O, Se and O, are much shorter than might be expected for a single bond. In some cases, they may be formulated as localized double bonds. A  $\sigma$  bond is formed in the usual way. In addition a  $\pi$  bond is formed by the sideways overlap of a p orbital on the oxygen with a d orbital on the sulphur giving a p-d interaction. This  $p\pi-d\pi$  bonding is similar to that found in the oxides and oxo-acids of phosphorus, and is in contrast to the more  $p\pi-d\pi$  type double bond found in ethene.

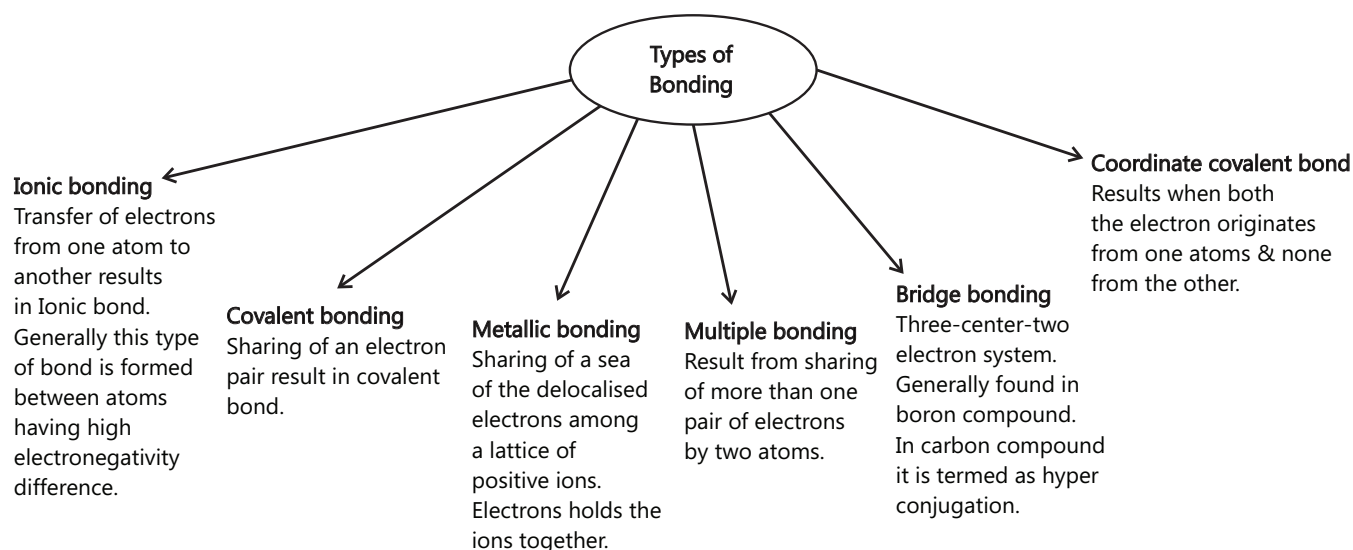


**Figure 14.23:**  $p$ - $d$  interaction between S and O

To obtain effective  $p\pi-d\pi$  overlap the size of the d orbital must be similar to size of the p orbital. Thus sulphur forms stronger  $\pi$  bonds than the larger elements in the group. On crossing a period in the periodic table, the nuclear charge is increased, as more s and p electrons are added. Since, these s and p electrons shield the nuclear charge incompletely, the size of the atom and the size of the 3d orbitals in this series of elements leads to progressively stronger  $p\pi-d\pi$  bonds. Thus, in the silicates there is hardly any  $p\pi-d\pi$  bonding and  $\text{SiO}_4^{4-}$  units polymerize into an enormous variety of structures by  $\text{Si-O-Si}$   $\sigma$  bonds. In the phosphates,  $\pi$  bonding is stronger, but a large number of polymeric phosphates exist. In the oxo-acids of sulphur,  $\pi$  bonding is even stronger and has become a dominant factor. Thus only a small amount of polymerization occurs, and only a few polymeric compounds are known with  $\text{S-O-S}$  linkages. For chlorine,  $p\pi-d\pi$  bonding is so strong that no polymerization of oxo-anions occurs.

## POINTS TO REMEMBER





- **Electronegativity:** Electronegativity is a measure of the relative tendency of a bonded atom to attract electrons.
- **Oxidation Number:** The oxidation number (oxid. No.) of an atom is the number of valence electrons on the neutral atom minus the number of valence electrons assigned to the atom in the compound on the basis that the bonding electrons belong to the more electronegative atom.
- **Dipole Moment:**  $\mu = q \times r$   
Where,  $q$  is the magnitude of the charge in esu (electrostatic units) and  $r$  is the distance between the positive and negative charges in centimeter.
- **Formal Charge** = (Total no. of valence electron in the free atom) - (Total no of nonbonding electron) -  $1/2$  (Total no of bonding electron)
- **Polarization :** When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarization and the ability of cation to polarize a nearby anion is called as polarizing power of cation.
- **Fajan's Rule :** Greater is the polarization of anion in a molecule, more is covalent character in it.
- **Theories of Bonding :**
  - (a) Valence Bond Theory
  - (b) Valence shell Electron Pair repulsion theory
  - (c) Molecular Orbital theory
- **Hydrogen bond:** Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pair tend to line up and hold the molecules together.
- **Back Bonding:** Back bonding generally takes place when out of two bonded atoms has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair (generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length.