

5. Chemical Bonding

5.1 Introduction : Why are atoms held together in chemical compounds ? There must be some force that holds them together. You have already learnt in lower classes that the forces holding atoms together in a compound are the chemical bonds.

How are chemical bonds formed between two atoms ? There are two ways of formation of chemical bonds (i) by loss and gain of electrons (ii) by sharing a pair of electrons between the two atoms. In either process of formation of chemical bond each atom attains a stable noble gas electronic configuration.

Which electrons are involved in the formation of chemical bonds ? The electrons present in the outermost shell of an atom are involved in the formation of a chemical bond.

5.2 Kossel and Lewis approach to chemical bonding : Number of attempts were made to explain the formation of chemical bond in terms of electrons, but the first satisfactory explanation was given by W.Kossel and G.N. Lewis independently. They gave a logical explanation of valence which was based on the inertness of noble gases. On the basis of this they proposed a theory of valence known as Electronic theory of valence in 1916.

According to Lewis, the atom can be pictured in terms of a positively charged 'kernel' (the nucleus plus inner electrons) and outer shell that can accommodate a maximum of eight electrons. This octet of electrons represents a stable electronic arrangement.

Lewis stated that each atom achieves stable octet during the formation of a chemical bond. In case of sodium and chlorine this can be achieved by transfer of one electron from sodium to chlorine. Thus Na^+ (2, 8) and Cl^- (2, 8, 8) ions are formed which held together. In case of other molecules like H_2 , F_2 , Cl_2 , HCl etc. the bond is formed by the sharing of a pair of electrons between the atoms. In this process each atom attains a stable outer octet of electrons.

Octet rule : In 1916 Kossel and Lewis proposed an important theory for explaining the formation of chemical bond known as Electronic Theory of Valence. This theory is mainly based on octet rule developed by Lewis. Octet rule is based on stability of noble gases due to presence of eight electrons (ns^2np^6) in the valence shell.

This rule states that during the formation of chemical bond, atom loses, gains or shares electrons so that its outermost orbit (valence shell) contains eight electrons. Therefore the atom attains the nearest inert gas electronic configuration.

The octet rule is found to be very useful in explaining the normal valence of elements and in the study of the chemical combination of atoms leading to the formation of molecule. However it should be noted that octet rule is not valid for H and Li atoms. These atoms tend to have only two electrons in their valence shell similar to that of Helium ($1s^2$) which called duplet.

5.2.1 Ionic bond

I. Formation of sodium chloride (NaCl)

The electronic configurations of Sodium and Chlorine are :

Na ($Z = 11$) $1s^2 2s^2 2p^6 3s^1$ or 2, 8, 1

Cl ($Z = 17$) $1s^2 2s^2 2p^6 3s^2 3p^5$ or 2, 8, 7

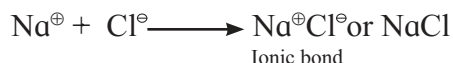


Internet my friend

Search more atoms which complete their octet during chemical combinations.

Sodium has one electron in its valence shell. It has a tendency to lose one electron to acquire the configuration of the nearest noble gas Ne (2, 8). Chlorine has seven electrons in its valence shell. It has a tendency to gain one electron and thereby acquire the configuration of the nearest noble gas Ar (2, 8, 8). During the combination of sodium and chlorine atoms, the sodium atom transfers its valence electron

to the chlorine atom, sodium atom changes into Na^{\oplus} ion while the chlorine atom changes into Cl^{\ominus} ion. The two ions are held together by strong electrostatic force of attraction. The formation of ionic bond between Na and Cl can be shown as follows.



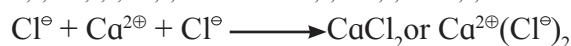
II. Formation of calcium chloride (CaCl_2)

: The following representation shows the formation of compound calcium chloride from the elements calcium and chlorine :

Electronic configuration of

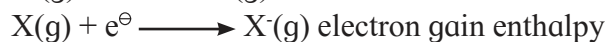
Calcium : $1s^2 2s^2 2p^6 3s^2 3p^4 4s^2$

Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$



5.1.2 Ionic solids and Lattice Enthalpy :

Ionic solids are solids which contain cations and anions held together by ionic bonds. Kossel treatment helps us to understand the formation of ionic bonds between ions of different elements. Formation of ions depends on the ease with which an atom can lose or gain electrons.

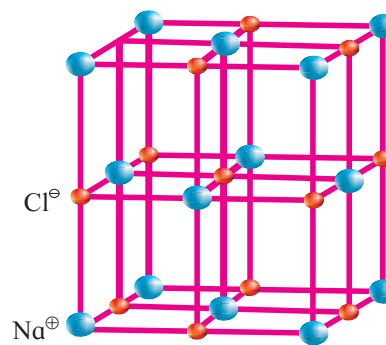


Do you know ?

CsF is the most ionic compound. Because Cs is the most electropositive while F is the most electronegative element. The electronegativity difference between them is the largest. Hence ions are easily separable, the bond is weakest and the compound is least stable ionic compound.

Ionization is always an endothermic process while electron gain process can be exothermic or endothermic. Based on the ionisation enthalpy ($\Delta_i H$) and electron gain enthalpy, we can predict which elements can form ionic compounds.

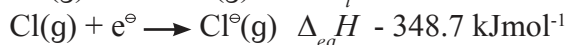
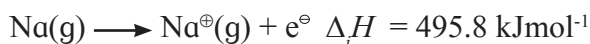
Elements having low ionization enthalpy can readily form ionic bond with elements having a high negative value of electron gain enthalpy. Both these processes take place in gaseous phase. All ionic compounds in the solid state have each cation surrounded by a specific number of anions and vice versa.



NaCl crystal lattice

The arrangements of cations and anions in a crystalline solid is ordered and they are held together by coulombic forces of attraction. During their formation, these compounds crystallize from the gaseous state ($\text{MX(g)} \longrightarrow \text{MX(s)}$) to the solid state. The structure in which they crystallize depends upon the size of the ions, their packing arrangement and other factors. The overall stability of the ionic solid depends upon the interactions between all these ions and the energy released during the formation of the crystal lattice.

Let us consider the formation of NaCl ionic solid.



Conversion of $\text{NaCl(g)} \longrightarrow \text{NaCl(s)}$ is associated with release of energy which is -788 kJ mol^{-1} . This released energy is much more than the absorbed energy. Thus stability of an ionic compound can be estimated by knowing the amount of energy released during lattice formation and not just by energy associated with completion of octet around the ionic species in the gaseous state alone.

Lattice Enthalpy : Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of solid

ionic compound into the gaseous components. Lattice enthalpy of NaCl is -788 kJ mol^{-1} which means that 788 kJ of energy is required to separate 1 mole of NaCl into one mole of gaseous $\text{Na}^+(\text{g})$ and $\text{Cl}^-(\text{g})$ to an infinite distance.

Table 5.1 : Lattice Enthalpy values of some ionic Compounds

Compound	Lattice enthalpy kJmol^{-1}
LiCl	853
NaCl	788
BeF_2	3020
CaCl_2	2258
AlCl_3	5492

For same anion and different cations :

1. Cations having higher charge have large lattice energies than compounds having cations with lower charge. $\text{AlCl}_3 > \text{CaCl}_2 > \text{NaCl}$
2. As size of cation decrease, lattice energy increases.
 $\text{LiF} > \text{NaF} > \text{KF}$.

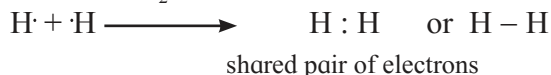
5.2.2 Covalent bond : In 1919 Lewis suggested that there are atoms which attain inert gas configuration (i.e. $1s^2$ or ns^2np^6 configuration) by sharing one or more electron pairs with similar or dissimilar atoms. Each atom contributes one electron to the shared electron pair and has equal claim on the shared electron pair. Langmuir called the Lewis electron pair bond a covalent bond. Thus the concept of covalent bond is known as Lewis Langmuir concept. A shared pair of electron is represented as a dash (–) and is responsible for holding the two atoms together.

A covalent bond may be defined as follows :

The attractive force which exists due to the mutual sharing of electrons between the two atoms of similar electronegativity or having small difference in electronegativities is called a covalent bond.

I. Formation of H_2 molecule : The electronic configuration of H atom is $1s^1$. It needs one more electron to complete its valence shell. When two hydrogen atoms approach each

other at a certain internuclear distance they share their valence electrons. The shared pair of electrons belongs equally to both the hydrogen atoms. The two atoms are said to be linked by a single covalent bond and a molecule H_2 is formed.



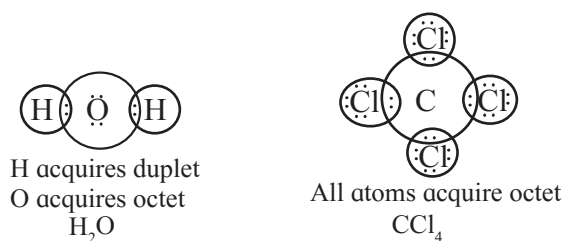
II. Formation of Cl_2 : The Lewis-Langmuir theory can explain the formation of chlorine molecule, Cl_2 . The Cl atom with electronic configuration $[\text{Ne}]3s^23p^5$ is one electron short of Argon configuration. The formation of Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between two chlorine atoms. Each chlorine atom contributes one electron to the shared pair. In the process both the chlorine atoms attain the valence shell octet of the nearest noble gas (i.e. Argon)



The dots represent the electrons. Such structures are referred to as Lewis structures. The Lewis dot structure can be written for other molecules also in which the combining atoms may be identical or different. Following are the important features of covalent bond.

- Each bond is formed as a result of sharing of electron pair between the two atoms.
- When a bond is formed, each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer shell noble gas configuration as a result of the sharing of electrons.

Thus in H_2O and CCl_4 the formation of covalent bonds can be represented as,



III. Formation of Multiple bond : When two atoms share one electron pair they are said to be joined by a single covalent bond. When two combining atoms share two pairs of electrons, the covalent bond between them is called a double bond. For example a double bond between two carbon atoms in ethylene molecule. When two combining atoms share three electron pairs a triple bond is formed as in the case of two nitrogen atoms in the N_2 molecule [Fig 5.1(a)]. Some other examples of multiple bonds are CO_2 and C_2H_2 [Fig 5.1]

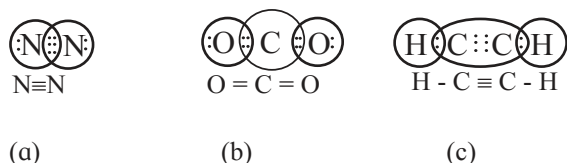


Fig 5.1 Multiple bonding

5.2.3 Lewis structures (Lewis representations of simple molecules) : Lewis dot structures show a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. Although such a picture does not explain completely the bonding and behaviour of a molecule, it helps to understand the formation and properties of molecule.

5.3.1 Steps to write Lewis dot structures

1. Add the total number of valence electrons of combining atoms in the molecule.
2. Write skeletal structure of the molecule to show the atoms and number of valence electrons forming the single bond between the atoms.
3. Add remaining electron pairs to complete the octet of each atom.
4. If octet is not complete form multiple bonds between the atoms such that octet of each atom is complete.
5. In anions add one electron for each negative charge.
6. In cations remove or subtract one electron from valence electrons for each positive charge.
7. In polyatomic atoms and ions, the least electronegative atom is the central atom for eg. 'S' is the central atom in SO_4^{2-} , 'N' is the central atom in NO_3^- .

8. After writing the number of electrons as shared pairs forming single bonds, the remaining electron pairs are used either for multiple bonds or remain as lone pairs.

Table 5.2 includes Lewis representation of some molecules.

Table 5.2 Lewis dot structures of some molecules/ions

Molecule/Ion	Lewis Representation
H_2	$H:H, H-H$
O_2	$\ddot{O}::\ddot{O}$
O_3	$\begin{array}{c} \oplus \\ \text{O} \\ \diagup \quad \diagdown \\ \text{:O:} \quad \text{:O:}^- \end{array}$
NF_3	$\begin{array}{c} \text{:F:} \\ \text{:F:N:F:} \\ \text{:F:} \end{array}$
CO_3^{2-}	$\left[\begin{array}{c} \text{:O:} \\ \parallel \\ \text{:O:} - \text{C} - \text{:O:}^- \end{array} \right]^{2-}$
HNO_3	$\begin{array}{c} \ominus \\ \text{:O:} \\ \text{:O:} \cdot \text{N} \cdot \text{:O:} \text{H} \\ \oplus \end{array}$

Problem 5.1 : To write Lewis structure of nitrite ion NO_2^- .

Solution

Step I : Count the total number of valence electrons of nitrogen atom, oxygen atom and one electron of additional negative charge.

$N(2s^2 2p^3)$, $O(2s^2 2p^4)$

$5 + (2 \times 6) + 1 = 18$ electrons

Step II : The skeletal structure of NO_2^- is written as O N O

Step III : Draw a single bond i.e. one shared electron pair between the nitrogen and each oxygen atoms completing the octet on oxygen atom. This does not complete the octet of nitrogen. Hence, there is a multiple bond between nitrogen and one of the oxygen atoms (a double bond). The remaining two electrons constitute a lone pair on nitrogen. Following are Lewis dot structures of NO_2^- .

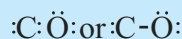


Problem 5.2 : Write the Lewis structure of CO molecule.

Solution :

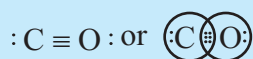
Step - I : Count number of electrons of carbon and oxygen atoms. The valence shell configuration of carbon and oxygen atoms are : $2s^2 2p^2$ and $2s^2 2p^4$ respectively. The valence electrons available are $4 + 6 = 10$

Step - II : The skeletal structure of CO is written as



Step - III : Draw a single bond (One shared electron pair) between C and O and complete the octet on O. The remaining two electrons is a lone pair on C.

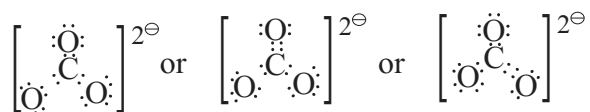
The octet on carbon is not complete hence there is a multiple bond between C and O (a triple bond between C and O atom). This satisfies the octet rule for carbon and oxygen atoms.



Each H atom attains the configuration of helium (a duplet of electrons)

5.4.1 Formal charge

The Lewis dot diagrams help us to get a picture of bonding in molecules which obey the octet rule. In case of polyatomic molecules double bonds or some times triple bonds are present and can be represented by more than one Lewis structure. In the case of CO_3^{2-} we can have three dot diagrams.



Double bonds can be present between Carbon and any one of the three oxygen atoms. Formal charges can help us in assigning bonds when several structures are possible. Formal charge is the charge assigned to an atom in a molecule, assuming that all electrons are shared equally between atoms, regardless of their relative electronegativities. While determining the best Lewis structure per molecule the structure is chosen such that the

formal charge is as close to zero as possible. Formal charge is assigned to an atom based on electron dot structures of the molecule/ion. e.g. O_3 , NH_4^+ , $[N \equiv C \equiv O]^+$, $[S \equiv C \equiv N]^+$

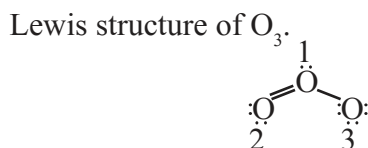
Formal charge on an atom in a Lewis structure of a polyatomic species can be determined using the following expression.

$$\left[\begin{array}{l} \text{Formal charge} \\ \text{on an atom in a} \\ \text{Lewis structure} \end{array} \right] = \left[\begin{array}{l} \text{Total no. of} \\ \text{valence electrons} \\ \text{in free atom} \end{array} \right] - \left[\begin{array}{l} \text{Total no. of non} \\ \text{bonding or lone} \\ \text{pairs of electrons} \end{array} \right] - \frac{1}{2} \left[\begin{array}{l} \text{Total no. of} \\ \text{bonding or} \\ \text{shared electrons} \end{array} \right]$$

$$\text{or } FC = VE - NE - (BE/2)$$

The structure having the lowest formal charge has the lowest energy.

1. Let us consider ozone molecule O_3



Here three oxygen atoms are numbered as 1, 2, 3. The formal charge on the central oxygen atom no.1 = $6 - 2 - 1/2(6) = +1$

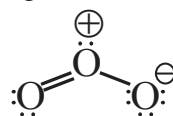
Formal charge on the end oxygen atoms is marked as 2

$$= 6 - 4 - 1/2(4) = 0$$

Formal charge on the end oxygen atoms marked as 3

$$= 6 - 6 - 1/2(2) = -1$$

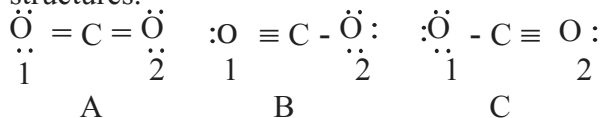
Hence, O_3 molecule can be represented along with formal charge as follows :



The lowest energy structure can be selected using formal charges from the number of possible Lewis structures, for a given species.

2. Let us take the example of CO_2 .

CO_2 can be represented by the following structures.



Assigning the formal charges on the carbon atom and the two oxygen atoms numbered 1 and 2

Structure A

Number of electrons: 4 from carbon and 6 from each Oxygen

So total number of electrons = $4 + 6 + 6 = 16$

Formal charge on C = $4 - 0 - 1/2(8) = 0$

Formal charge on O-1 and O-2 = $6 - 4 - 1/2(4) = 0$

In this structure formal charge on all atoms is zero.

Structure B.

Formal charge on C = $4 - 0 - 1/2(8) = 0$

Formal charge on O - 1 = $6 - 2 - 6/2 = 4 - 3 = +1$

Formal charge on O - 2 = $6 - 6 - 2/2 = -1$

Structure C.

Formal charge on C = $4 - 0 - 1/2(8) = 0$

Formal charge on 1st O = $6 - 6 - 2/2 = -1$

Formal charge on 2nd O = $6 - 2 - 6/2 = 4 - 3 = +1$

We find that in structure A the formal charge on all atoms is 0 while in structures B and C formal charge on Carbon is 0 while Oxygens have formal charge -1 or +1. So the possible structure with the lowest energy will be Structure A.



Use your brain power

Which atom in NH_4^+ will have formal charge +1?

Generally the lowest energy structure has the smallest formal charges on the atoms.

5.4.2 Limitation of octet rule :

1. Octet rule does not explain stability of some molecules.

The octet rule is based on the inert behaviour of noble gases which have their octet complete i.e. have eight electrons in their valence shell. It is very useful to explain the structures and stability of organic molecules. However there are many molecules whose existence cannot be explained by the octet theory. The central atoms in these molecules does not have eight electrons in their valence shell, and yet they are stable. eg. BeCl_2 , PF_5 etc such molecules can be categorized as having

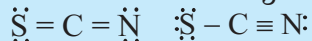
Problem 5.3 :

Find out the formal charges on S, C, N.
 $(\text{S} = \text{C} = \text{N})^\ominus$; $(\text{S} - \text{C} \equiv \text{N})^\ominus$; $(\text{S} \equiv \text{C} - \text{N})^\ominus$

Solution :

Step I

Write Lewis dot diagrams for the structure



A

B

C

Step II

Assign formal charges

$\text{FC} = \text{V.E} - \text{N.E} - 1/2 \text{B.E.}$

Structure A :

Formal charge on S = $6 - 4 - 1/2(4) = 0$

Formal charge on C = $4 - 0 - 1/2(8) = 0$

Formal charge on N = $5 - 4 - 1/2(4) = -1$

Structure B :

Formal charge on S = $6 - 6 - 1/2(2) = -1$

Formal charge on C = $4 - 0 - 1/2(8) = 0$

Formal charge on N = $5 - 2 - 1/2(6) = 0$

Structure C :

Formal charge on S = $6 - 2 - 1/2(6) = +1$

Formal charge on C = $4 - 0 - 1/2(8) = 0$

Formal charge on N = $5 - 6 - 1/2(2) = -2$

i. Incomplete octet

ii. Expanded octet

iii. Odd electrons

i. Molecules with incomplete octet :

eg. BF_3 , BeCl_2 , LiCl

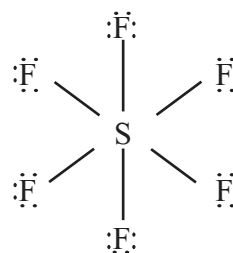
In these covalent molecules the central atoms B, Be and Li have less than eight electrons in their valence shell but are stable.

Li in LiCl has only two electrons

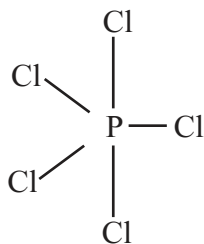
Be in BeCl_2 has four electrons while

B in BF_3 has six electrons in the valence shell.

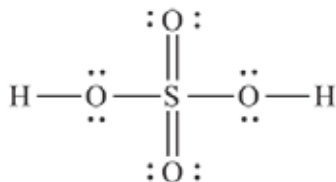
ii. Molecules with expanded octet : Some molecules like SF_6 , PCl_5 , H_2SO_4 have more than eight electrons around the central atom.



SF_6 ; 12 electrons around sulfur

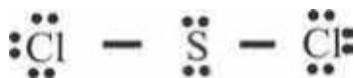


PCl₅; 10 electrons around Phosphorus



H₂SO₄; 12 electrons around sulfur

It must be remembered that sulfur also forms many compounds in which octet rule is obeyed. For example, sulfur dichloride the sulfur atom has eight electrons around it.



SCl₂ 8 electrons around sulfur

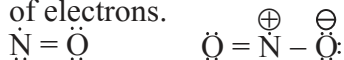


Use your brain power

How many electrons will be around I in the compound IF₇?

iii. Odd electron molecules

Some molecules like NO (nitric oxide) and NO₂ (nitrogen dioxide) do not obey the octet rule. Both N and O atoms, have odd number of electrons.



2. The observed shape and geometry of a molecule, cannot be explained, by the octet rule.

3. Octet rule fails to explain the difference in energies of molecules, though all the covalent bonds are formed in an identical manner that is by sharing a pair of electrons. The rule fails to explain the difference in reactivities of different molecules.



Use your brain power

Why is H₂ stable even though it never satisfies the octet rule?

5.5 Valence Shell Electron Pair Repulsion Theory (VSEPR) :

Properties of substances are dependent on the shape of the molecules. Lewis concept is unable to explain the shapes of molecules. Shapes of all molecules cannot be described completely by any single theory. One of the popular models used earlier to predict the shapes of covalent molecules is the valence shell electron pair repulsion theory proposed by Sidgwick and Powell. It is based on the basic idea that the electron pairs on the atoms shown in the Lewis diagram repel each other. In the real molecule they arrange themselves in such a way that there is minimum repulsion between them.

The arrangement of electrons is called as electron pair geometry. These pairs may be shared in a covalent bond or they may be lone pairs.

Rules of VSEPR :






1. Electron pairs arrange themselves in such a way that repulsion between them is minimum.
2. The molecule acquires minimum energy and maximum stability.
3. Lone pair of electrons also contribute in determining the shape of the molecule.
4. Repulsion of other electron pairs by the lone pair (L.P) stronger than that of bonding pair (B.P)

Trend for repulsion between electron pair is
L.P - L.P > L.P - B.P > B.P - B.P

Lone pair -Lone pair repulsion is maximum because this electron pair is under the influence of only one nucleus while the bonded pair is shared between two nuclei.


Thus the number of lone pair and bonded pair of electrons decide the shape of the molecules. Molecules having no lone pair of electrons have a regular geometry.


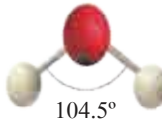


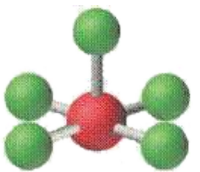
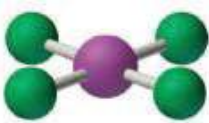
Table 5.3 : Geometry of molecules (having no lone pair of electrons)

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	Linear CO ₂ 	Linear	BeBr ₂ , CO ₂
3	Trigonal planar BCl ₃ 	Trigonal planar	BF ₃ , BCl ₃ , BH ₃
4	Tetrahedral 	Tetrahedral	CH ₄ , NH ₄ ⁺ SiCl ₄
5	Trigonal bipyramidal 	Trigonal bipyramidal	PCl ₅ , SbF ₅ , AsF ₅
6	octahedral 	octahedral	SF ₆ , TeF ₆ , SeF ₆

Depending on the number of lone pair and bonded pairs of electrons the molecules can be represented as AB₂E, AB₃E, AB₂E₂, AB₄D, AB₃E₂, AB₅E, AB₄E₂ where A is the central atom, B - bonded atom E - lone pair of electrons. examples of the above type of molecules are given in table 5.7.

Table 5.4 : Geometry of some molecules (having one or more lone pairs of electrons)

Molecule type	No. of lone pairs	No. of bonding pairs	Arrangement of bonded electron pairs	shape	examples
AB ₂ E	1	2	SO ₂ 	Bent	SO ₂ , O ₃

AB_3E	1	3		Trigonal pyramidal	NH_3, PCl_3
AB_2E_2	2	2		Bent	H_2O, OF_2, H_2S, SCl_2 , etc.
AB_4E	1	4		See saw	SF_4
AB_3E_2	2	3		T-shape	ClF_3, BrF_3, ICl_3 , etc
AB_5E	1	5		square pyramid	BrF_5, IF_5
AB_4E_2	2	4		square planar	XeF_4

The VSEPR theory is therefore able to predict and also explain the geometry of large number of compounds, particularly of p-block elements.

Let us explain the bond angles in NH_3 and H_2O .

1. Ammonia NH_3 : Expected geometry is tetrahedral and bond angle $109^\circ 28'$. Central nitrogen atom has in all 8 electrons in its valence shell, out of which 6 are involved in forming, three N-H covalent bonds the remaining pair forms the lone pair. There are two types of repulsions between the electron pairs.

- Lone-pair-bond pair
- Bond pair - bond pair

The lone-pair-bond pair repulsions are stronger and the bonded pairs are pushed inside thus reducing the bond angle to $107^\circ 18'$. and shape of the molecules becomes pyramidal.

2. Water molecule H_2O : The central atom oxygen has six electrons in its valence shell. On bond formation with two hydrogen atoms there are 8 electrons in the valence shell of oxygen. Out of these two pairs are bonded pairs and two are lone pairs.

Due to lone pair - lone pair repulsion the lone pairs are pushed towards the bond pairs and bond pair- Lone pair repulsions becomes stronger thereby reducing the HOH bond angle from the tetrahedral one to $104^\circ 35'$ and the geometry of the molecule is angular.

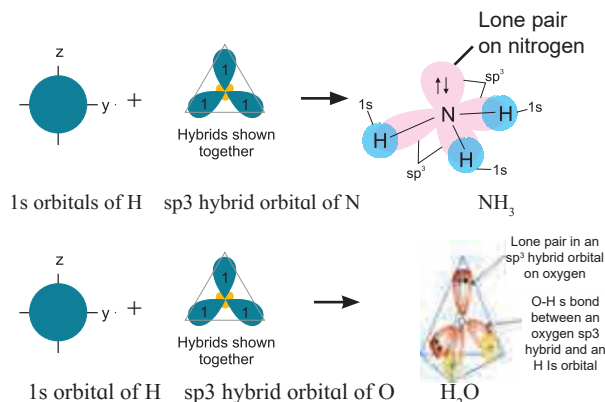


Fig 5.1 : Formation and orbital pictures of NH_3 and H_2O molecules

Advanced theories of Bonding :

The Kossel and Lewis approach to chemical bonding is the first step in understanding the nature of chemical bond. More advanced theories of bonding were put forth to account for the newly discovered properties of compounds in the light of quantum mechanical theory of atomic structures. Two important approaches regarding nature of chemical bond are **valence bond theory** and **molecular orbital theory**.

5.4 Valence Bond Theory :

In order to explain the covalent bonding, Heitler and London developed the valence bond theory on the basis of wave mechanics. This theory was further extended by Pauling and Slater.

5.4.1 Postulates of Valence Bond Theory :

- A covalent bond is formed when the half-filled valence orbital of one atom overlaps with a half filled valence orbital of another atom.
- The electrons in the half-filled valence orbitals must have opposite spins.
- During bond formation the half-filled orbitals overlap and the opposite spins of the electrons get neutralized. The increased electron density decreases the nuclear repulsion and energy is released during overlapping of the orbitals.
- Greater the extent of overlap stronger is the bond formed, however complete overlap of orbitals does not take place due to internuclear repulsions.

- If an atom possesses more than one unpaired electrons, then it can form more than one bond. So number of bonds formed will be equal to the number of half-filled orbitals in the valence shell i.e. number of unpaired electrons.
- The distance at which the attractive and repulsive forces balance each other is the equilibrium distance between the nuclei of the bonded atoms. At this distance the total energy of the bonded atoms is minimum and stability is maximum.
- Electrons which are paired in the valence shell cannot participate in bond formation. However in an atom if there is one or more vacant orbital present then these electrons can unpair and participate in bond formation provided the energies of the filled and vacant orbitals differ slightly from each other.
- During bond formation the 's' orbital which is spherical can overlap in any direction. The 'p' orbitals can overlap only in the x, y or z directions. [similarly 'd' and 'f' orbitals are oriented in certain directions in space and overlap only in these direction]. Thus the covalent bond is directional in nature.

5.4.2 Interacting forces during covalent bond formation : By now we have understood that a covalent bond is formed by the overlap of two half filled atomic orbitals and the bonded atoms are stable than the free atoms and the energy of the bonded atoms is less than that of free atoms. So lowering of energy takes during bond formation. How does this happen ?

This happens due to interactive forces which develop between the nuclei of the two atoms and also their electrons. These forces may be attractive and repulsive between nuclei of A and electrons of B and those arising from attraction between nuclei of atom A and electrons of B and the repulsion between electrons.

The balance between attractive and repulsive forces decide whether the bond will be formed or not.

When the attractive forces are stronger than the repulsive forces overlap takes place between the two half filled orbitals a bond is formed and energy of the system is lowered.

This lowering of energy during bond formation is depicted in the potential energy diagram. To understand this let us consider the formation of H_2 molecule from atoms of hydrogen each containing one unpaired electrons. When the two atoms are far away from each other there are no interactions between them. The energy of the system is the sum of the potential energies of the two atoms which is arbitrarily taken as zero.

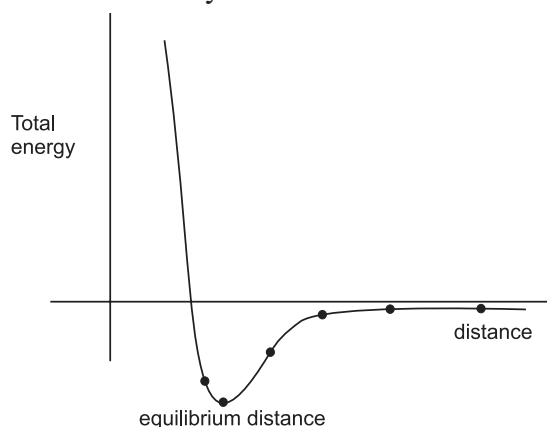


Fig. 5.2 : Potential energy diagram for formation hydrogen molecule

Repulsive forces be stabilize the system with increase energy of the system while attractive forces decrease the energy. Experimentally it has been found that during formation of hydrogen molecule the magnitude of the newly developed attractive forces contribute more than the newly developed repulsive forces. As a result the potential energy of the system begins to decrease.

As the atoms come closer to one another the energy of the system decreases. The overlap increases only upto a certain distance between the two nuclei, where the attractive and repulsive forces balance each other and the system attains minimum energy (see Fig 5.3). At this stage a bond is formed between the two atoms of hydrogen. If the two atoms are further pushed closer to each other the repulsive forces become more predominant and the energy of the system starts increasing

and stability decreases. (See Fig. 5.2 potential energy diagram)

If atoms containing electrons with parallel spins are brought close to each other, the potential energy of the system increases and bond formation does not take place.

5.4.3 Overlap of atomic orbitals : Formation of a bond has been explained on the basis of overlap of atomic orbital having same energy and symmetry. In the preceding section, we have seen that the strength of the bond depends on the extent of overlap of the orbitals. Greater the overlap stronger is the bond.

The orbitals holding the electrons vary in shape, energy and symmetry. So the extent of overlap depends on the shape and size of the orbital

On the basis of the above considerations we have 2 types of bonds.

- i. sigma bond (σ)
- ii. pi bond (π)

i. Sigma Bond :

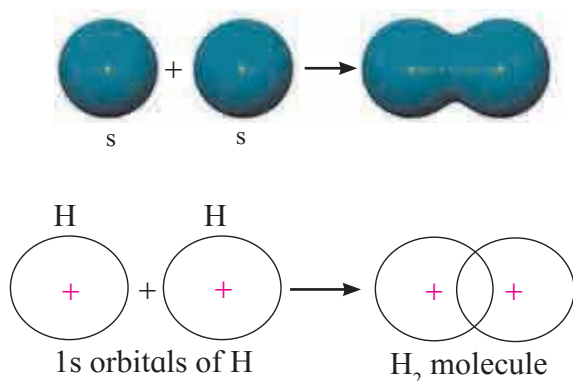
When the overlap of the bonding orbitals is along the internuclear axis it is called as sigma overlap or sigma bond.

The σ bond is formed by the overlap of following orbitals.

- a. Two 's' orbitals
- b. One 's' and one p_z orbital
- c. Two 'p' orbitals

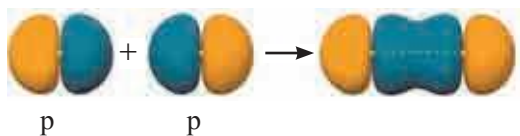
a. s-s overlap : eg. H_2

The $1s^1$ orbitals of two hydrogen atoms overlap along the internuclear axis to form a σ bond between the atoms in H_2 molecule. electronic configuration of H : $1s^1$



b. p-p overlap

This type of overlap takes place when two p orbitals from different atoms overlap along the internuclear axis eg. F_2 molecule.

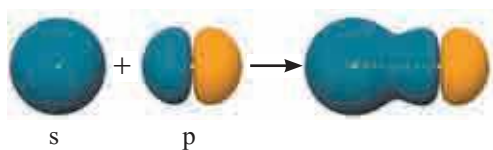


Electronic configuration of fluorine $1s^2, 2s^2, 2p_x^2, p_y^2, p_z^1$. The $2p_z$ orbitals of the fluorine atoms overlap along internuclear axis to form p-p σ overlap.

F_2 molecule: $1s^2, 2s^2, 2p_x^2, p_y^2, p_z^1$

c. s-p σ bond

In this type of overlap one half filled 's' orbital of one atom and one half filled 'p' orbital of another orbital overlap along the internuclear axis. eg. HF molecule



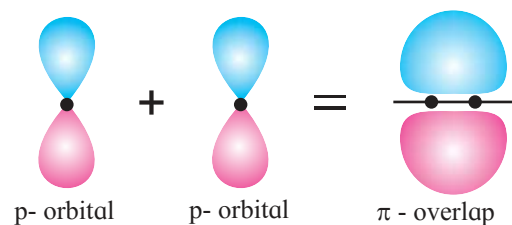
Electronic configuration :

$H \rightarrow 1s^1$; $F : 1s^2, 2s^2, 2p_x^2, p_y^2, p_z^1$

$1s^1$ orbital of hydrogen and $2p_z^1$ of fluorine overlap to form s - p σ overlap.

ii. p-p overlap/ π overlap/ π bond :

When two half filled orbitals of two atoms overlap side ways (laterally) it is called π overlap and it is perpendicular to the internuclear axis.



5.4.4 Hybridization : The valence bond theory explained well the formation of covalent bond by the overlap of orbitals in case of simple molecules like H_2 , F_2 , H-F etc. Accordingly the maximum number of covalent bonds which an atom can form equals the number of unpaired electrons present in its valence shell. But the theory does not explain how beryllium forms two covalent bonds or how boron shows

trivalency, carbon shows tetravalency in spite of their electronic configuration e.g. BeH_2 , BF_3 , CH_4 , CCl_4 etc.

Be : $1s^2, 2s^2$

B : $1s^2, 2s^2, 2p^1$

C : $1s^2, 2s^2, 2p_x^1, 2p^1$

In order to explain the observed valency in these and such other compounds a concept of hybridization was put forward.

It was suggested that one electron in '2s' orbital is promoted to the empty '2p' orbital. Thus in the excited state Be, B and C have two, three and four half filled orbitals, respectively.

Electronic configurations in excited state :

	1s	2s	2p
Be	$\uparrow\downarrow$	\uparrow	$\uparrow \quad \square \quad \square$
B	$\uparrow\downarrow$	\uparrow	$\uparrow \quad \uparrow \quad \square$
C	$\uparrow\downarrow$	\uparrow	$\uparrow \quad \uparrow \quad \uparrow$

In the excited state Be, B and C have 2, 3 and 4 half filled orbitals. So Be, B and C can form 2, 3 and 4 bonds respectively. This concept helps to understand how Be forms 2 bonds whereas B and C form 3 and 4 bonds, respectively but it cannot explain how all bonds have same bond length and bond strength.

For example, in BeF_2 beryllium will use one s and one half-filled p orbitals to overlap with two half filled 'p' orbitals on fluorine, so in the molecule there will be one s-p bond and one p-p bond. which will not be of equal strength, but actually both Be-F bonds are of the same strength. Similar situation is seen in BF_3 , BH_3 , CH_4 , CCl_4 . In CH_4 all bonds are of equal strength although the overlaps are between s, p_x, p_y, p_z orbitals of carbon and 's' orbital of hydrogen, experimentally all C-H bond lengths bond strengths and bond angles are found to be identical.

This can be explained using another concept. "**Hybridization**" in the valence bond theory. This concept helps to explain the observed structural properties of many molecules.

Hybridization refers to mixing of valence orbitals of same atom and recasting them into equal number of new equivalent orbitals-**Hybrid orbitals**.

Steps considered in Hybridization

- Formation of excited state
- Mixing and Recasting of orbitals

i. Formation of the excited state : The paired electrons in the ground state are uncoupled and one electron is promoted to the a vacant orbital having slightly higher energy. Now total number of half filled orbitals is equal to the valency of the element in the stable compound. e.g. in BeF_2 , valency of Be is two. In the excited state one electron from 2s orbital is uncoupled and promoted to 2p orbital.

	2s	2p
Ground state	$\uparrow\downarrow$	$\square \square \square$
Excited state	\uparrow	$\uparrow \square \square$

ii. Mixing and Recasting : In this step the two 's' and 'p' orbitals having slightly different energies mix with each other. Redistribution of electron density and energy takes place and **two new orbitals having exactly same shape and energy are formed.**

These new orbitals arrange themselves in space in such a way that there is minimum repulsion and maximum separation between them.

So during formation of sp hybrid orbitals as in Be the two sp hybrid orbitals are 180° .

Conditions for hybridization :

- Orbitals belonging to the same atom can participate in hybridization.
- Orbitals having nearly same energy can undergo hybridization, so 2s and 2p orbitals undergo hybridization but 3s and 2p orbitals do not.

Characteristic features of hybrid orbitals :

- Number of hybrid orbitals formed is exactly the same as the participating atomic orbitals.
- They have same energy and shape.
- Hybrid orbitals are oriented in space in such a way that there is minimum repulsion and thus are directional in nature.
- The hybrid orbitals are different in shape from the participating atomic orbitals, but they bear the characteristics of the atomic orbitals from which they are derived.
- Each hybrid orbitals can hold two electrons with opposite spins.

- A hybrid orbital has two lobes on the two sides of the nucleus. One lobe is large and the other small.
- Covalent bonds formed by hybrid orbitals are stronger than those formed by pure orbitals, because the hybrid orbital has electron density concentrated on the side with a larger lobe and the other is small allowing greater overlap of the orbitals.

5.4.5 Types of Hybridization and Geometry of Molecules : Different types of hybrid orbitals are obtained from the atomic orbitals that participate in hybridization.

s and p orbitals can hybridize to form the following hybrid orbitals

i. sp^3

ii. sp^2

iii. sp

i. sp^3 Hybridization : In this type one 's' and three 'p' orbitals having comparable energy mix and recast to form four sp^3 hybrid orbitals. It should be remembered that 's' orbital is spherically symmetrical while the p_x , p_y , p_z orbitals have two lobes and are directed along x, y and z axes, respectively.

The four sp^3 hybrid orbitals formed are equivalent in energy. and shape. They have one large lobe and one small lobe. They are at an angle of $109^\circ 28'$ with each other in space and point towards the corners of a tetrahedron CH_4 , NH_3 , H_2O are examples where the orbitals on central atom undergo sp^3 hybridization.

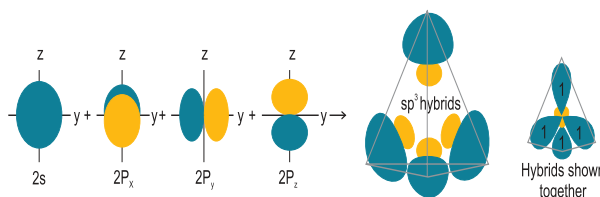


Fig 5.3 : Formation of sp^3 hybrid orbitals

Formation of methane (CH_4) molecule :

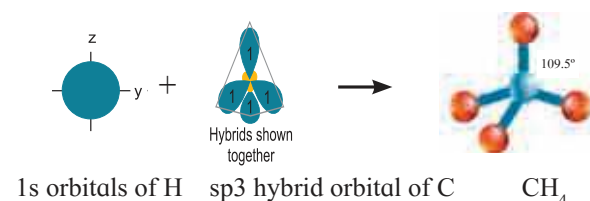
Ground state electronic configuration of Carbon is $1s^2, 2s^2, 2p_x^1, p_y^1, p_z^0$. In order to form four equivalent bonds with hydrogen the 2s and 2p orbitals undergo hybridization.

Electronic configuration of carbon	1s	2s	2p
Ground state	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow$
Excited state	$\uparrow\downarrow$	\uparrow	$\uparrow\uparrow\uparrow$
sp^3 Hybrid orbitals	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow\uparrow$	

(four sp^3 hybrid orbitals.)

One electron from the 2s orbital of Carbon atom is excited to the $2p_z$ orbital. Then the four orbitals 2s, p_x , p_y , p_z mix and recast to form four new sp^3 hybrid orbitals having same shape and equal energy. They are maximum apart and have tetrahedral geometry. Each hybrid orbital contains one unpaired electron.

Each of these sp^3 hybrid orbitals with one electron overlap axially with the 1s orbital of hydrogen atom to form one C-H sigma bond. Thus in CH_4 molecule we have four C-H bonds formed by the sp^3 -s overlap.



ii. sp^2 Hybridization : This hybridization involves the mixing of one s and two p orbitals to give three sp^2 hybrid orbitals of same energy and shape. The three orbitals are maximum apart and oriented at an angle of 120° and are in one plane. The third p orbital does not participate in hybridization and remains at right angles to the plane of the sp^2 hybrid orbitals. BF_3 , C_2H_4 molecules are examples of sp^2 hybridization.

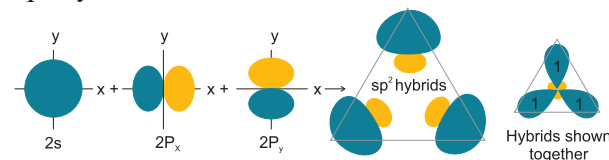


Fig 5.4 : Formation of sp^2 hybrid orbitals

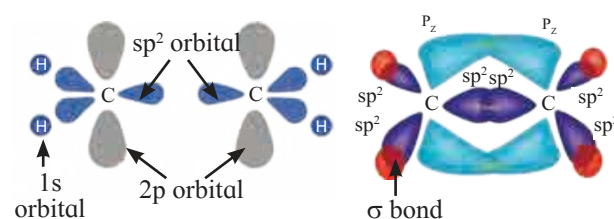
Formation of C_2H_4 molecule : This molecule contains two carbon atoms each bound to two hydrogen. Each carbon atom undergoes sp^2 hybridization. One 's' orbital and two 'p' orbitals on carbon hybridize to form three sp^2 hybrid orbitals of equal energy and symmetry.

Two sp^2 hybrid orbitals overlap axially two 's' orbitals of hydrogen to form sp^2 -s σ bond. The unhybridized 'p' orbitals on the two carbon atoms overlap laterally to form a lateral π overlap. Thus the C_2H_4 molecule has four sp^2 -s σ bonds. One sp^2 - sp^2 σ bond one p-p π bond.

Electronic configuration of carbon

	1s	2s	2p
Ground state	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow$
Excited state	$\uparrow\downarrow$	\uparrow	$\uparrow\uparrow\uparrow$
sp^2 Hybridized	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$	\uparrow

sp^2 hybrid orbitals pure 'p' orbital



Formation of Boron trifluoride (BF_3) molecule :

1. Need of hybridisation : Observed valency of boron in BF_3 is three and its geometry is triangular planar which can be explained on the basis of sp^2 hybridisation.
- 2, sp^2 hybridisation of Boron atom : In BF_3 molecule central boron atom undergoes sp^2 hybridisation. The ground state electronic configuration of Boron ($z = 5$) is $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$

$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow		
$1s^2$	$2s^2$	$2p_x^1$	$2p_y^0$	$2p_z^0$

To explain valency of boron in BF_3 one electron from 2s orbital of boron atom is uncoupled and promoted to vacant $2p_y$ orbital. Thus excited state electronic configuration of boron becomes $s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

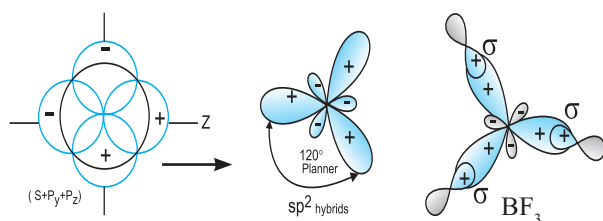
$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	
$1s^2$	$2s$	$2p_x^1$	$2p_y^1$	$2p_z^0$

The three orbitals i.e. 2s, $2p_x$ of and $2p_y$ of boron undergoes sp^2 hybridisation to form three sp^2 hybrid orbitals of equivalent energy which are oriented along the three corners of an equilateral triangle making an angle of 120° .

Thus boron in hybridised state has electronic following configuration.



- orbital overlap : Each sp^2 hybrid orbital of boron atom having unpaired electron overlaps axially with half filled $2p_z$ orbital of fluorine atom containing electron with opposite spin to form three B-F sigma bond by sp^2 -p type of overlap.
- Bond angle : Each F-B-F bond angle in BF_3 molecule is 120° .
- Geometry : The geometry of BF_3 molecule is trigonal planar.



iii. sp hybridization : In this type one 's' and one 'p' orbital undergo mixing and recasting to form two sp hybrid orbitals of same energy and shape. The two hybrid orbitals are placed at an angle of 180° . Other two p orbitals do not participate in hybridization and are at right angles to the hybrid orbitals. For example : $BeCl_2$ and acetylene molecule $HC \equiv CH$,

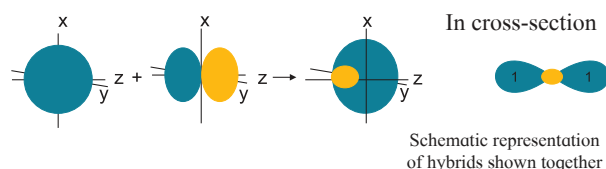


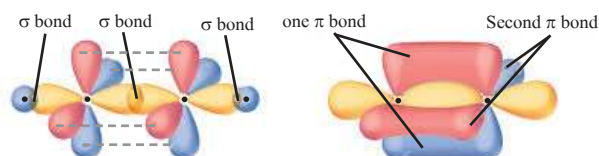
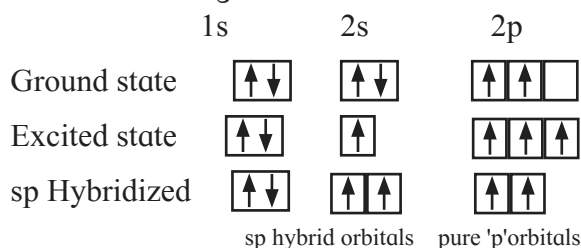
Fig 5.5 : formation of sp hybrid orbitals

Formation of acetylene molecule : This molecule contains two carbon and two hydrogen atoms. Each carbon atom undergoes sp hybridization. One s and one p orbitals mix and recast to give two sp hybrid orbitals arranged at 180° to other.

Out of the two sp hybrid orbitals of carbon atom one overlaps axially with 's' orbital of hydrogen while the other sp hybrid orbital overlaps with sp hybrid orbital of other carbon atom to form the sp-sp σ bond. The C-H σ bond is formed by sp-s overlap.

The remaining two unhybridized p orbitals overlap laterally to form two p-p π bonds. So there are three bonds between the two carbon atoms : one C-C σ bond (sp-sp) overlap, two C-C π bonds (p-p) overlap and fourth sp-s σ bond between C and H satisfy the fourth valency of carbon.

Electronic configuration of carbon



5.4.6 Importance and limitation of valence bond theory

Importance of valence bond theory (V.B)

V.B. theory introduced five new concepts in chemical bonding.

- Delocalization of electron over the two nuclei.
- shielding effect of electrons.
- covalent character of bond.
- partial ionic character of a covalent bond.
- The concept of resonance and connection between resonance energy and molecular stability.

5.4.7 Limitations of valence bond theory

- V.B. Theory explains only the formation of covalent bond in which a shared pair of electrons comes from two bonding atoms.

However, it offers no explanation for the formation of a co-ordinate covalent bond in which both the electrons are contributed by one of the bonded atoms.

- Oxygen molecule is expected to be diamagnetic according to this theory. The two atoms in oxygen molecule should have completely filled electronic shells which give no unpaired electrons to the molecule making it diamagnetic. However, experimentally the molecule is found to be para-magnetic having

two unpaired electrons. Thus, this theory fails to explain paramagnetism of oxygen molecule.

Problem 5.4

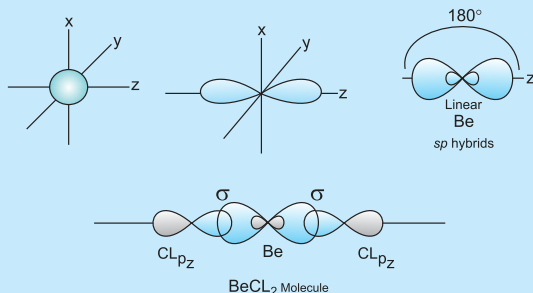
Explain the formation of BeCl_2

Electronic configuration of beryllium

	1s	2s	2p
Ground state	$\uparrow\downarrow$	$\uparrow\downarrow$	$\square\square\square$
Excited state	$\uparrow\downarrow$	\uparrow	$\uparrow\square\square$
sp Hybridized	$\uparrow\downarrow$	$\uparrow\uparrow$	$\square\square$
		sp hybrid orbitals	pure 'p' orbitals

Formation of BeCl_2 molecule.

This molecule has one Be atom and two chlorine atoms. Electronic configuration of Be is $1s^2, 2s^2, 2p_z^0$. The 2s and $2p_z$ orbitals undergo sp hybridization to form two sp hybrid orbitals oriented at 180° with each other. $2p_z$ orbitals of two chlorine atoms overlap with the sp hybrid orbitals to form two sp-p σ bond.



iii. Valence bond theory does not explain the bonding in electron deficient molecules like B_2H_6 in which the central atom possesses less number of electrons than required for an octet of electron.

5.5 Molecular orbital theory : You are familiar with the valence bond theory which describes the formation of covalent bonds by overlap of half filled atomic orbitals. This theory is successful to give satisfactory electronic description for a large number of molecules. In some cases it gives to incorrect electronic description. Therefore another bonding description called Molecular Orbital Theory (MO) has been introduced.

It has been found that the MO theory gives more accurate description of electronic structure of molecules.

The concept of an orbital is introduced by quantum mechanics. The quantum mechanical wave equation is a differential equation and its solution is called wave function. The square of the wavefunction gives a measure of probability of finding an electron within a certain region of space of an atom. It is nothing but an atomic orbital.

MO theory does not concentrate on individual atoms. It considers the molecule as a whole rather than an atom for the bonding. Accordingly a molecular orbital MOT is the property of a molecule similar to what an atomic orbital is to an atom. Hence, molecular orbital can be depicted through a square of wavefunction that gives the probability of finding an electron within a certain region of space in a molecule. Like atomic orbitals, molecular orbitals have energy levels and definite shapes. They also contain maximum two electrons with opposite spins.

5.5.1 Formation of molecular orbitals :

According to the MO theory the formation of molecular orbitals from atomic orbitals is expressed in terms of Linear Combination of Atomic Orbitals (LCAO). Formation of molecular orbitals can be understood by considering the interference of the electron waves of combining atoms. Interference of electron waves can be constructive or destructive i.e. the waves can reinforce each other or cancel each other. So we can say that. Two atomic orbitals combine in two ways to form molecular orbitals. 1. By addition of their wave functions. 2. By subtraction of their wave functions. Addition of the atomic orbitals wave functions results in formation of a molecular orbital which is lower in energy than atomic orbitals and is termed as Bonding Molecular Orbital (BMO). Subtraction of the atomic orbitals results in the formation of a molecular orbital which is higher in energy than the atomic orbitals and is termed as Antibonding Molecular Orbital (AMO).

In bonding molecular orbital the large electron density is observed between the nuclei of the bonding atoms than the individual atomic orbitals. On the other hand in the antibonding orbital the electron density is nearly zero between the nuclei.

So placing an electron in bonding orbital leads to formation of a covalent bond. While placing electron in antibonding orbital makes the bond unstable.

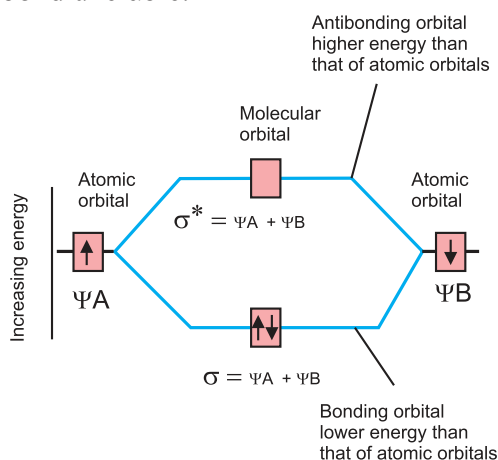


Fig. 5.5 : formation of MOs

5.5.2 Conditions for the combination of Atomic Orbitals : Atomic orbitals can be combined linearly which give molecular orbitals only if following conditions are fulfilled.

- The combining atomic orbitals must have comparable energies.

So 1s orbitals of one atom can combine with 1s orbital of another atom but not with 2s orbital, because energy of 2s orbital is much higher than that of 1s orbital.

- The combining atomic orbitals must have the same symmetry along the molecular axis. Conventionally z axis is taken as the internuclear axis. So even if atomic orbitals have same energy but their symmetry is not same they cannot combine. For example, 2s orbital of an atom can combine only with $2p_z$ orbital of another atom, and not with $2p_x$ or $2p_y$ orbital of that atom because the symmetries are not same. p_z is symmetrical along z axis while p_x is symmetrical along x axis.
- The combining atomic orbitals must overlap to the maximum extent. Greater

the overlap, greater is the electron density between the nuclei and so stronger is the bond formed.

5.5.3 Types of molecular orbitals : In diatomic molecules, molecular orbitals formed by combination of atomic orbitals are of two types (i) σ (ii) π .

According to this nomenclature a σ designates a molecular orbital which is symmetrical around the bond axis and π designates a molecular orbitals those are unsymmetrical.

This is clear if we consider a linear combination of i. two 's' orbitals ii. two p orbitals.

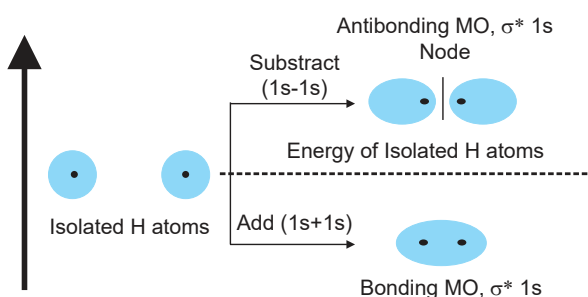


Fig 5.6 : Linear combination of two s orbitals

- The s orbitals are spherically symmetric along x, y and z axes, combination of two '1s' orbitals centred on two nuclei of two atoms, led to two σ molecular orbitals which are symmetrical along the bond axis. One of which is σ bonding and other σ^* antibonding (Fig. 7)
- If we consider 'z' to be internuclear axis then linear combination of p_z orbitals from two atoms can form $\sigma 2p_z$ bonding $\sigma^*(2p_z)$ molecular orbitals.

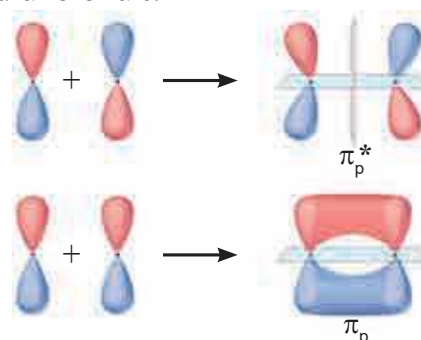


Fig 5.7 : Formation of π and π^* molecular orbitals

The p_x, p_y orbitals are not symmetrical along the bond axis, they have a positive lobe above the axis and negative lobe below the axis. Hence linear combination of such orbitals leads to the formation of molecular orbitals with positive and negative lobes above and below the bond axis. These are designed as π bonding and π antibonding orbitals. The electron density in such π orbitals is concentrated above and below the bond axis. The π molecular orbitals has a node between the nuclei (fig. 5.9)

5.5.4 Energy levels and electronic configuration : We have seen earlier that on combination of two 1s orbitals; two molecular orbitals σ 1s and σ^* 1s are formed. Similarly two 2s orbitals yield σ^* 2s and σ 2s molecular orbitals.

The three 2p orbitals on one atom combine with three 2p orbitals on another atom forming six molecular orbitals, designated as σ 2p_z, π p_x, π p_y and σ^* 2p_z, π^* p_x, π^* p_y

The molecular orbitals in homonuclear diatomic molecules have been determined experimentally.

For diatomic molecules of second row elements except O₂ and F₂ the rank order of energies is σ 1s < σ^* 1s < σ 2s < σ^* 2s < π 2p_x = π 2p_y < σ 2p_z < (π^* 2p_y = π^* 2p_x) < σ^* 2p_z

For O₂ and F₂ increasing order of energies was found to be :

σ 1s < σ^* 1s < σ 2s < σ^* 2s < σ 2p_z < (π 2p_x = π 2p_y) < (π^* 2p_x = π^* 2p_y) < σ^* 2p_z

The sequence of filling the molecular orbitals give electronic configuration of molecules. The electronic configuration of molecules provides the following information.

a. Stability of molecules : If the number of electrons in bonding MOs is greater than the number in antibonding MOs the molecule is stable.

b. Magnetic nature of molecules : If all MOs in a molecule are completely filled with two electrons each, the molecule is diamagnetic (i.e. repelled) by magnetic field.

However, if at least one MO is half filled with one electron, the molecule is paramagnetic (i. e. attracted by magnetic field).

c. Bond order of molecule : The bond order of the molecule can be calculated from the number of electrons in bonding N_b and antibonding MOs (N_a).

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

5.5.5 Key ideas of MO theory :

- MOs in molecules are similar to AOs of atoms. Molecular orbital describes region of space in the molecule representing the probability of an electron.
- MOs are formed by combining AOs of different atoms. The number of MOs formed is equal to the number of AOs combined.
- Atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- MOs those are lower in energy than the starting AOs are bonding (σ) MOs and those higher in energy are antibonding (σ^*) MOs.
- The electrons are filled in MOs beginning with the lowest energy.
- Only two electrons occupy each molecular orbital and they have opposite spins that is, their spins are paired.
- The bond order of the molecule can be calculated from the number of bonding and antibonding electrons.

5.5.6 MO description of simple diatomic Molecules

1. Hydrogen molecule.-H₂

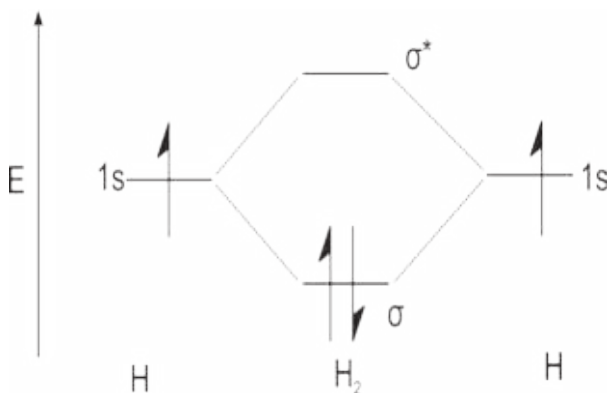


Fig. 5.8 : MO diagram for H₂ molecule

Hydrogen molecule is formed by the linear combination of two Hydrogen atoms, each having one electron in its 1s orbital. Linear combination of two 1s orbitals gives two molecular orbitals σ_{1s} and σ^*_{1s} . The two electrons from the hydrogen atoms occupy the σ_{1s} molecular orbital and σ^*_{1s} remains vacant.

Electronic configuration of Hydrogen molecule is written as σ_{1s}^2

Bond order = (bonding electron – antibonding electrons) ÷ 2

For hydrogen Bond order = $(2-0) \div 2 = 1$

So in H_2 molecule there exists one covalent bond between the two hydrogen atoms. The bond length is 74 pm and the bond dissociation energy is 438 kJ mol. As there are no unpaired electrons present the H_2 molecule is diamagnetic.

2. Lithium molecule. Li_2 :

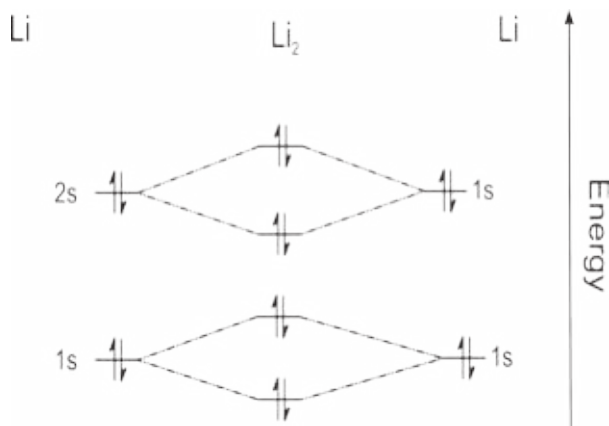


Fig. 5.9 : MO diagram for Li_2

Each Lithium atom has 3 electrons with electronic configuration $1s^2, 2s^1$, so Li_2 molecule will have 6 electrons. Linear combination of atomic orbitals gives four molecular orbitals σ_{1s} , σ^*_{1s} , σ_{2s} , σ^*_{2s}

Electronic configuration of Li_2 molecule will be $(\sigma_{1s})^2, (\sigma^*_{1s})^2, (\sigma_{2s})^2$

Bond order = $(4-2) \div 2 = 1$,

This means in Li_2 molecule there is one bond between the two Lithium atoms. Such Li_2 molecules are found in the vapour state. As there are no unpaired electrons the molecule is diamagnetic.

3. N_2 molecule :

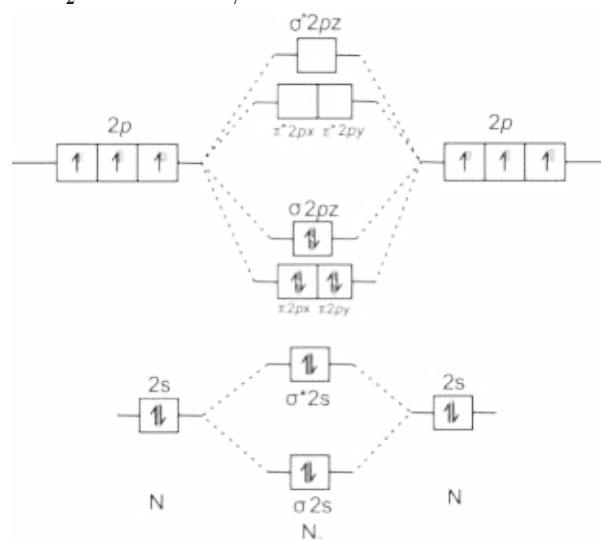


Fig. 5.10 : MO diagram for N_2

$N : 1s^2 2s^2 2p^3$

Electronic configuration of N_2 molecule (14 electrons) is

$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_x)^2 (\pi_y)^2 (\sigma_{2p})^2$

Bond order of N_2 molecule = $\frac{10-4}{2} = 3$

N_2 molecule is diamagnetic.

4. O_2 molecule :

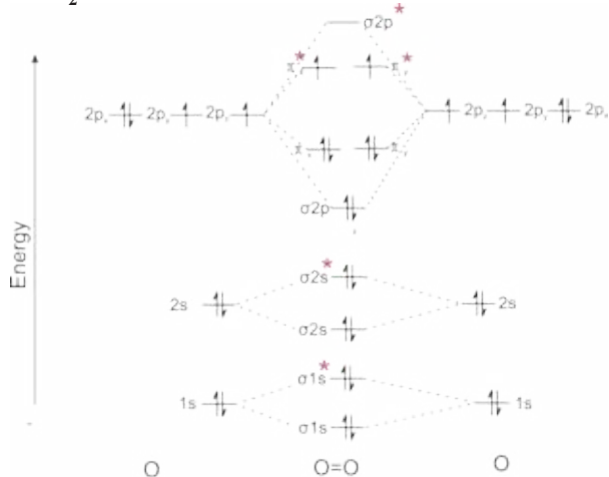


Fig. 5.11 : MO diagram for O_2

$O : 1s^2 2s^2 2p^4$

The electronic configuration of O_2 molecule (16 electrons) is

$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_x)^2 (\pi_y)^2 (\sigma_z)^2 (\pi_x^*)^2 (\pi_y^*)^2$

Bond order of O_2 molecule = $\frac{10-6}{2} = 2$

O₂ molecule is paramagnetic due to presence of 2 unpaired electrons in the π^* orbitals.

5. F₂ molecule :

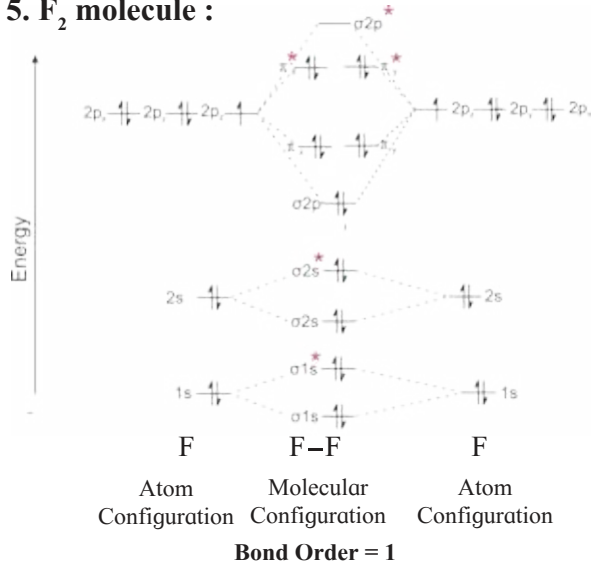
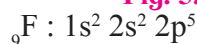


Fig. 5.12 : MO diagram for F₂



The electronic configuration of F₂ molecule (18 electrons) is $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi_x)^2 (\pi_y)^2 (\sigma_z)^2 (\pi_x^*)^2 (\pi_y^*)^2$

$$\text{Bond order of F}_2 \text{ molecule} = \frac{10 - 8}{2} = 1$$

F₂ molecule is diamagnetic

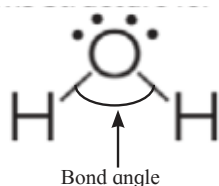


Can you tell?

Why He₂ molecule is not stable ?
Draw MO diagram for it

5.6 Parameters of covalent bond : A covalent bond is characterised by different parameters. These parameters help to understand how strong is the bond between the two atoms, what is the distance between them and what is the shape of the molecule.

5.6.1 Bond angle : The electrons which participate in bond formation are present in orbitals. The angle between the orbitals holding the bonding electrons is called the bond angle.



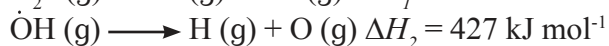
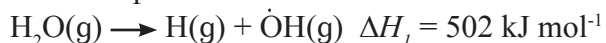
Bond angle can be determined experimentally using spectroscopic techniques. Value of bond angle gives an idea about the arrangement of orbitals around the central atom and the shape of the molecule.

Table 5.5 bond angles of some molecules

	Molecule	Bond of angle
1	H ₂ O	104°28'
2	NH ₃	107
3	BF ₃	120

5.6.2 Bond Enthalpy : The amount of energy required to break one mole of bond of one type, present between two atoms in the gaseous state is termed as Bond Enthalpy. For diatomic molecules the dissociation energy is the same as bond enthalpy. Bond enthalpy for H₂ molecule is 435.8 kJ mol⁻¹. The bond enthalpy is a measure of strength of the bond between two atoms and can be measured experimentally. N-N bond in N₂ is stronger than the O-O bond in O₂. Larger is the bond dissociation energy stronger is the bond in the molecule. For heteronuclear diatomic molecule HCl the bond enthalpy was found to be 431.0 kJ mol⁻¹.

In case of polyatomic molecules the bond enthalpy and bond dissociation energy are not identical. Bond enthalpy is the average of the sum of successive bond dissociation energies. For example dissociation of water.



Average bond enthalpy of O-H bond in H₂O :

$$\Delta_a H = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}.$$

In both the above equations the bond between O and H is broken but the amount of energy required to break the bond is different, i.e. enthalpies of two O-H bonds in water are different.

This difference arises due to the fact that cleavage of the two O-H bonds in water takes place in two steps. In the first step one O-H bond breaks leaving behind OH radical. Now the electronic environment around oxygen to

which hydrogen is attached is different than that around oxygen in H_2O molecule and this causes a change in the successive bond dissociation energy.

Same difference is observed in enthalpy values of O-H bond in $\text{C}_2\text{H}_5\text{OH}$. Oxygen here is attached to C_2H_5 group therefore hydrogen of O-H is in different environment than hydrogen of H-O-H.

In the same way, the bond enthalpy value of any covalent bond is slightly different for each bond of that kind in a given molecule and also different molecules. The average values of bond enthalpy, $\Delta_a H$, are determined from the experimentally measured values of large number of compounds containing a particular bond. Average bond enthalpy data are given in Table 5.4. In general stronger bond implies larger bond enthalpy.



Do you know ?

Among diatomic molecules the bond order and bond enthalpy of N_2 is highest. Bond order = 3, Bond enthalpy = 946 kJ mol^{-1}

Table 5.6 Bond enthalpies

Bond	$\Delta_a H / \text{kJ mol}^{-1}$
C - H	400 - 415
N - H	390
O - H	460-464
C - C	345
C - N	290 -315
C-O	355 - 380
C - Cl	330
C - Br	275
O - O	175 - 184
C = C	610 - 630
$\text{C} \equiv \text{C}$	835
C = O	724 - 757
$\text{C} \equiv \text{N}$	854

5.6.3 Bond length : Bond length implies the equilibrium distance between the nuclei of two covalently bonded atoms in a molecule. Bond lengths are measured by X-ray and Electron diffraction techniques.

Table 5.7 Average bond lengths for some single, double and triple bonds

Type of bond	Covalent bond length (pm)	Type of bond	Covalent bond length (pm)
O-H	96	$\text{H}_2(\text{H-H})$	74
C-H	107	$\text{F}_2(\text{F-F})$	144
N-O	136	$\text{Cl}_2(\text{Cl-Cl})$	199
C-O	143	$\text{Br}_2(\text{Br-Br})$	228
C-N	143	$\text{I}_2(\text{I-I})$	267
C-C	154	$\text{N}_2(\text{N} \equiv \text{N})$	109
C = O	121	$\text{O}_2(\text{O}=\text{O})$	121
N = O	122	HF (H-F)	92
C = C	133	HCl (H-Cl)	127
C = N	138	HBr (H -Br)	141
$\text{C} \equiv \text{N}$	116	HI (H-I)	160
$\text{C} \equiv \text{C}$	120		

Each atom of the bonded pair contributes to the bond length. Bond length depends upon the size of atoms and multiplicity of bonds.

It increases with increase in size of atom and decreases with increase in multiplicity of bond. It is generally measured in picometre (pm) or in Angstrom unit (\AA) – $> = > \equiv >$, so C - C single bond is longer and $\text{C} \equiv \text{C}$ triple bond is shorter.

Some typical average bond lengths of C - C single double and triple bond and others are shown in table 5.4.

5.6.4 Bond Order : According to the Lewis theory the bond order is equal to the number of bonds between the two atoms in a molecule. The bond order in H_2 , O_2 and N_2 is 1, 2 and 3 respectively. Isoelectronic molecules and ions have identical bond order. For example N_2 , CO and NO^+ each have bond order 3. F_2 whereas O_2^{2-} has bond order 1. Stabilities of molecules can be determined by knowing the bond order. As bond order increases, bond enthalpy increases and bond length decreases.

H : H	H-H
electron pair at the centre	Non polar covalent bond

$$\text{H} : \text{F} \quad \delta^+ \text{H} - \text{F} \delta^- \quad \text{H-F}$$

Polar covalent bond

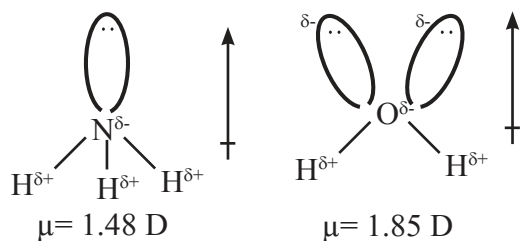


Which molecules are polar ?
H-I, H-O-H, H-Br, Br₂, N₂, I₂, NH₃

unit of dipole moment is Debye (D)

Lone pairs and dipole moment : In some molecules the central atom has unshared or lone pairs of electrons. These lone pairs also contribute to overall dipole of the molecule. Nitrogen in NH_3 and Oxygen in H_2O posses

lone pairs, these reinforce the dipoles due to N-H and O-H bonds. Both these molecules are highly polar.

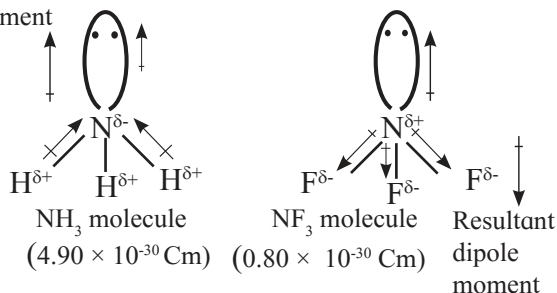


Nitrogen has only one lone pair while oxygen has two lone pairs which reflects in the higher dipole moment of water.

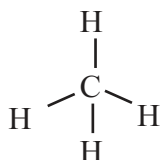
Consider NH_3 and NF_3

Both have pyramidal shape with a lone pair of electrons on nitrogen atom. Here hydrogen is less electronegative while, fluorine is more electronegative than nitrogen. The resultant dipole moment of NH_3 is $4.90 \times 10^{-30} \text{ Cm}$ while that of NF_3 is $0.80 \times 10^{-30} \text{ Cm}$. This difference is because in case of NH_3 the orbital dipole due to lone pair is in the same direction as that of resultant dipole moment of N-H bonds hence gets added whereas in NF_3 , the orbital moment is in the direction opposite to the resultant dipole moment of three N-F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N-F bond moments, which results in its low dipole moment.

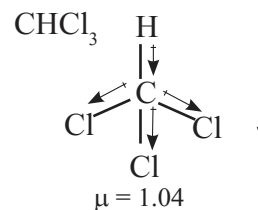
Resultant
dipole
moment



CH_4 : The central atom carbon has no lone pair and the molecule is non-polar.



In CHCl_3 the dipoles are not equal and do not cancel hence CHCl_3 is polar with a non zero dipole moment.



Dipole moments of some molecules are shown in table 5.8.

Table 5.8 dipole moments and geometry of some molecules

Types of molecule	Example	Dipole moment μ (D)	Geometry
Molecule AB	HF	1.91	linear
	HCl	1.03	linear
	HBr	0.79	linear
	H_2	0	linear
Molecule AB_2	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule AB_3	NH_3	1.47	trigonal pyramidal
	NF_3	0.23	trigonal pyramidal
	BF_3	0	trigonal planar
Molecule AB_4	CH_4	0	tetrahedral
	CHCl_3	1.04	tetrahedral
	CCl_4	0	tetrahedral

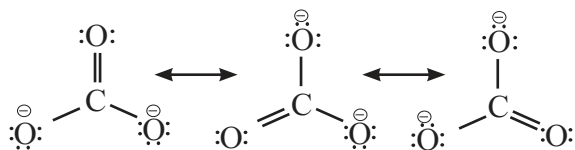
5.8.7 Covalent character of ionic bond :

Several ionic compounds possess partial covalent character and show properties similar to covalent compounds. For example LiCl is ionic but it is more soluble in organic solvents than water. To explain the partial covalent character in ionic bonds Fajans put forth the following rules :

1. The smaller size of the cation and larger the size of the anion renders, greater covalent character to ionic bond. For example Li^+Cl^- is more covalent than Na^+Cl^- . Similarly Li^+I^- is more covalent than Li^+Cl^- .
2. Greater the charge on cation, more is covalent character of the ionic bond. For example, covalent character of AlCl_3 , MgCl_2 and NaCl decreases in the following order $\text{Al}^{3+}(\text{Cl}^-)_3 > \text{Mg}^{2+}(\text{Cl}^-)_2 > \text{Na}^+\text{Cl}^-$
3. A cation with the outer electronic configuration of the $s^2p^6d^{10}$ type possess a greater polarising power compared to the cation having the same size and same charge but having outer electronic configuration of s^2p^6 type.

This is because d- electrons of the $s^2p^6d^{10}$ shell screen nuclear charge less effectively compared to s and p electrons of s^2p^6 shell. Hence the effective nuclear charge in a cation having $s^2p^6d^{10}$ configuration is greater than that of the one having s^2p^6 configuration. For example : Cu^+Cl^- is more covalent than Na^+Cl^- . Here ($\text{Cu}^+ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$; $\text{Na}^+ 1s^2 2s^2 2p^6$)

5.8 Resonance : Many polyatomic molecules can be represented by more than one Lewis structures. Consider for example, three structures written for CO_3^{2-} . Each structure differs from the other only in the position of electrons without changing positions of the atoms.



None of these individual structures is adequate to explain the properties. The actual structure of CO_3^{2-} is a combination of three Lewis structures and is called as the **resonance hybrid**. Resonance signifies that there is more than one possible way in which the electrons can be assigned in a Lewis structure. The various structures are called canonical forms.

Now consider the example of O_3 . It is the resonance hybrid of the following structures.

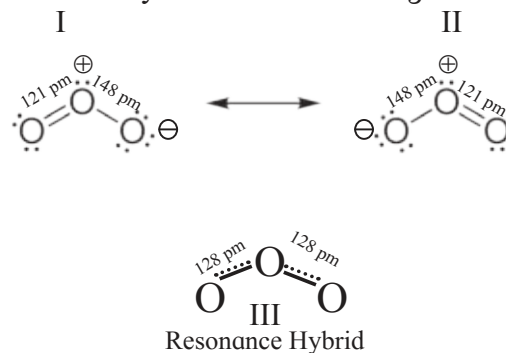


Fig. 5.13 Resonance in the O_3 molecule

(structure I and II are canonical forms while structure III is the resonance hybrid.)

Resonance Energy :

We have seen that many polyatomic ions and molecules can be represented by different canonical forms and each form has a different energy. Energy of the resonating forms is different from the most stable structure, **resonance hybrid**. The difference in energy of the stable contributing structure and the resonating forms is usually defined as Resonance energy.

To summarize it can be stated that

- a. Energy of the resonance hybrid structure is less than the energy of any single canonical form hence, resonance stabilizes certain polyatomic molecules or ions.
- b. The average of all resonating structures contributes to overall bonding characteristic features of the molecule.

This will be clear from the example of ozone. Ozone can be represented by two canonical forms (shown earlier) I and II. III is the resonance hybrid. The energy of III is less than that of I and II.



Exercises

1. Select and write the most appropriate alternatives from the given choices.

- A. Which molecule is linear?
 a. SO_3 b. CO_2
 c. H_2S d. Cl_2O
- B. When the following bond types are listed in decreasing order of strength (strongest first). Which is the correct order ?
 a. covalent > hydrogen > vander waals'
 b. covalent > vander waal's > hydrogen
 c. hydrogen > covalent > vander waal's
 d. vander waal's > hydrogen > covalent.
- C. Valence Shell Electron Pair repulsion (VSEPR) theory is used to predict which of the following :
 a. Energy levels in an atom
 b. the shapes of molecules and ions.
 c. the electronegativities of elements.
 d. the type of bonding in compounds.
- D. Which of the following is true for CO_2 ?

	C=O bond	CO_2 molecule
A	polar	non-polar
B	non-polar	polar
C	polar	polar
D	non-polar	non-polar

- E. Which O_2 molecule is paramagnetic. It is explained on the basis of :
 a. Hybridisation b. VBT
 c. MOT d. VSEPR
- F. The angle between two covalent bonds is minimum in:
 a. CH_4 b. C_2H_2
 c. NH_3 d. H_2O

2. Draw

- A. Lewis dot diagrams for the following
 a. Hydrogen (H_2)
 b. Water (H_2O)
 c. Carbon dioxide (CO_2)
 d. Methane (CH_4)
 e. Lithium Fluoride (LiF)
- B. Diagram for bonding in ethene with sp^2 Hybridisation.
- C. Lewis electron dot structures of
 a. HF b. C_2H_6 c. C_2H_4
 d. CF_3Cl e. SO_2
- D. Draw orbital diagrams of
 a. Fluorine molecule
 b. Hydrogen fluoride molecule

3. Answer the following questions

- A. Distinguish between sigma and pi bond.
- B. Display electron distribution around the oxygen atom in water molecule and state shape of the molecule, also write H-O-H bond angle.
- C. State octet rule. Explain its inadequacies with respect to
 a. Incomplete octet b. Expanded octet
- D. Explain in brief with one example:
 a. Ionic bond b. covalent bond
 c. coordinate bond
- E. Give reasons for need of Hybridisation
- F. Explain geometry of methane molecule on the basis of Hybridisation.
- G. In Ammonia molecule the bond angle is 107° and in water molecule it is $104^\circ 35'$, although in both the central atoms are sp^3 hybridized Explain
- H. Give reasons for:
 a. Sigma (σ) bond is stronger than Pi (π) bond.
 b. HF is a polar molecule
 c. Carbon is a tetravalent in nature.
- I. Which type of hybridization is present in ammonia molecule? Write the geometry and bond angle present in ammonia.
- J. Identify the type of overlap present in
 a. H_2 b. F_2 c. H-F molecule.
 Explain diagrammatically.
- K. F-Be-F is a linear molecule but H-O-H is angular. Explain.
- L. BF_3 molecule is planar but NH_3 pyramidal. Explain.
- M. In case of bond formation in Acetylene molecule :
 a. How many covalent bonds are formed ?
 b. State number of sigma and pi bonds formed.
 c. Name the type of Hybridisation.
- N. Define :
 a. Bond Enthalpy
 b. Bond Length
- O. Predict the shape and bond angles in the following molecules:
 a. CF_4 b. NF_3
 c. HCN d. H_2S

4. Using data from the Table, answer the following :

Examoles	C ₂ H ₆ Ethane	C ₂ H ₄ Ethene	C ₂ H ₂ Ethyne
Structure	$\text{>C}-\text{C}<$	$\text{>C}=\text{C}<$	$\text{-C}\equiv\text{C}-$
Type of bond between carbons	single	double	triple
Bond length (nm)	0.154	0.134	0.120
Bond Enthalpy kJ mol ⁻¹	348	612	837

- What happens to the bond length when unsaturation increases?
- Which is the most stable compound?
- Indicate the relation between bond strength and Bond enthalpy.
- Comment on overall relation between Bond length, Bond Enthalpy and Bond strength and stability.

5. Complete the flow chart

Molecular Formula	Structural Formula	Shape/Geometry	Bond angle
BeCl ₂	<input type="text"/>	<input type="text"/>	180°
<input type="text"/>	O=C=O	Linear	<input type="text"/>
C ₂ H ₂	<input type="text"/>	<input type="text"/>	<input type="text"/>

7. Answer in one sentence:

- Indicate the factor on which stability of ionic compound is measured?
- Arrange the following compounds on the basis of lattice energies in decreasing (descending) order: BeF₂, AlCl₃, LiCl, CaCl₂, NaCl
- Give the total number of electrons around sulphur (S) in SF₆ compound.
- Covalent bond is directional in nature. Justify.
- What are the interacting forces present during formation of a molecule of a compound ?
- Give the type of overlap by which pi (π) bond is formed.
- Mention the steps involved in Hybridization.
- Write the formula to calculate bond order of molecule.
- Why is O₂ molecule paramagnetic?
- What do you mean by formal charge ? Explain its significance with the help of suitable example.



Activity :

Practice the bonding structure with the help of structure set of chemistry.

6. Complete the following Table

Molecule	Type of Hybridisation	Type of bonds	Geometry	Bond angle
CH ₄	-	4C-H 4σ bonds	Tetrahedral	-
NH ₃	sp ³	3N-H 3σ bonds 1 lone pair	-	-
H ₂ O	-	-	angular	104.5°
BF ₃	sp ²	-	-	120°
C ₂ H ₄	-	-	-	120°
BeF ₂	-	2 Be-F	Linear	-
C ₂ H ₂	sp	(3σ+2π) 1C-C σ 2C-H σ 2C-C π	-	-