

# Chemical Bonding and Molecular Structure

## Class 11 Notes Chemistry Chapter 4

### • Chemical Bond

The force that holds different atoms in a molecule is called chemical bond.

### • Octet Rule

Atoms of different elements take part in chemical combination in order to complete their octet or to attain the noble gas configuration.

### • Valence Electrons

It is the outermost shell electron which takes part in chemical combination.

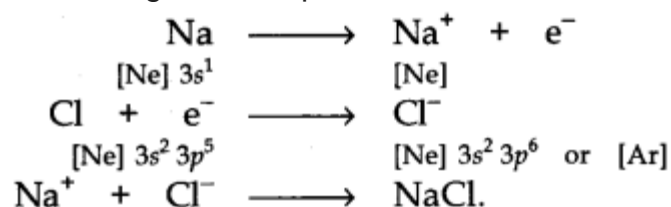
### • Facts Stated by Kossel in Relation to Chemical Bonding

— In the periodic table, the highly electronegative halogens and the highly electro-positive alkali metals are separated by noble gases.

— Formation of an anion and cation by the halogens and alkali metals are formed by gain of electron and loss of electron respectively.

— Both the negative and positive ions acquire the noble gas configuration.

— The negative and positive ions are stabilized by electrostatic attraction Example,



### • Modes of Chemical Combination

— By the transfer of electrons: The chemical bond which formed by the complete transfer of one or more electrons from one atom to another is termed as electrovalent bond or ionic bond.

— By sharing of electrons: The bond which is formed by the equal sharing of electrons between one or two atoms is called covalent bond. In these bonds electrons are contributed by both.

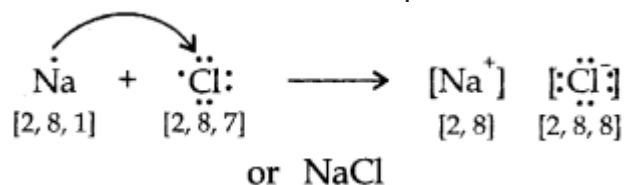
— Co-ordinate bond: When the electrons are contributed by one atom and shared by both, the bond is formed and it is known as dative bond or co-ordinate bond.

### • Ionic or Electrovalent Bond

Ionic or Electrovalent bond is formed by the complete transfer of electrons from one atom to another. Generally, it is formed between metals and non-metals. We can say that it is the electrostatic force of attraction which holds the oppositely charged ions together.

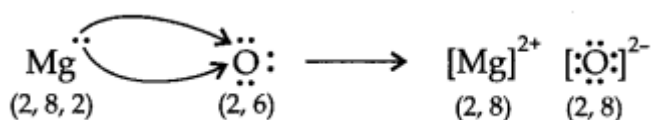
The compounds which is formed by ionic or electrovalent bond is known as electrovalent compounds. For Example, ,

(i) NaCl is an electrovalent compound. Formation of NaCl is given below:



Na<sup>+</sup> ion has the configuration of Ne while Cl<sup>-</sup> ion represents the configuration of Ar.

(ii) Formation of magnesium oxide from magnesium and oxygen.



Electrovalency: Electrovalency is the number of electrons lost or gained during the formation of an ionic bond or electrovalent bond.

• **Factors Affecting the Formation of Ionic Bond**

(i) Ionization enthalpy: As we know that ionization enthalpy of any element is the amount of energy required to remove an electron from outermost shell of an isolated gaseous atom to convert it into cation.

Hence, lesser the ionization enthalpy, easier will be the formation of a cation and have greater chance to form an ionic bond. Due to this reason alkali metals have more tendency to form an ionic bond.

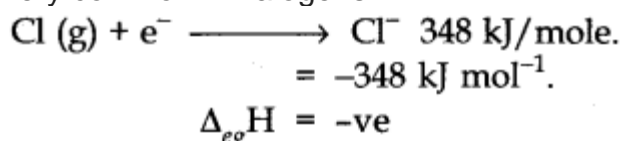
For example, in formation of Na<sup>+</sup> ion I.E = 496 kJ/mole

While in case of magnesium, it is 743 kJ/mole. That's why the formation of positive ion for sodium is easier than that of magnesium.

Therefore, we can conclude that lower the ionization enthalpy, greater the chances of ionic bond formation.

(ii) Electron gain enthalpy (Electron affinities): It is defined as the energy released when an isolated gaseous atom takes up an electron to form anion. Greater the negative electron gain enthalpy, easier will be the formation of anion. Consequently, the probability of formation of ionic bond increases.

For example. Halogens possess high electron affinity. So, the formation of anion is very common in halogens.



(iii) Lattice energy or enthalpy: It is defined as the amount of energy required to separate 1 mole of ionic compound into separate oppositely charged ions.

**Lattice energy of an ionic compound depends upon following factors:**

(i) Size of the ions: Smaller the size, greater will be the lattice energy.

(ii) Charge on the ions: Greater the magnitude of charge, greater the interionic attraction and hence higher the lattice energy.

• **General Characteristics of ionic Compounds**

(i) Physical State: They generally exist as crystalline solids, known as crystal lattice. Ionic compounds do not exist as single molecules like other gaseous molecules e.g., H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub> etc.

(ii) Melting and boiling points: Since ionic compounds contain high interionic force between them, they generally have high melting and boiling points.

(iii) Solubility: They are soluble in polar solvents such as water but do not dissolve in organic solvents like benzene, CCl<sub>4</sub> etc.

(iv) Electrical conductivity: In solid state they are poor conductors of electricity but in molten state or when dissolved in water, they conduct electricity.

(v) Ionic reactions: Ionic compounds produce ions in the solution which gives very fast reaction with oppositely charged ions.

For example,



• **Covalent Bond—Lewis-Langmuir Concept**

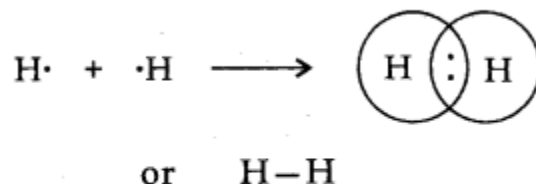
When the bond is formed between two or more atoms by mutual contribution and

sharing of electrons, it is known as covalent bond.

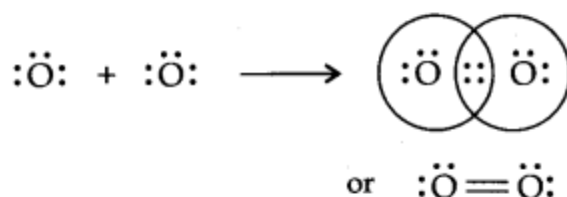
If the combining atoms are same the covalent molecule is known as homoatomic. If they are different, they are known as heteroatomic molecule.

For Example,

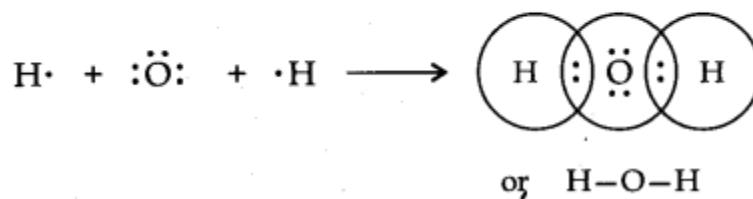
(i) Formation of hydrogen molecule.



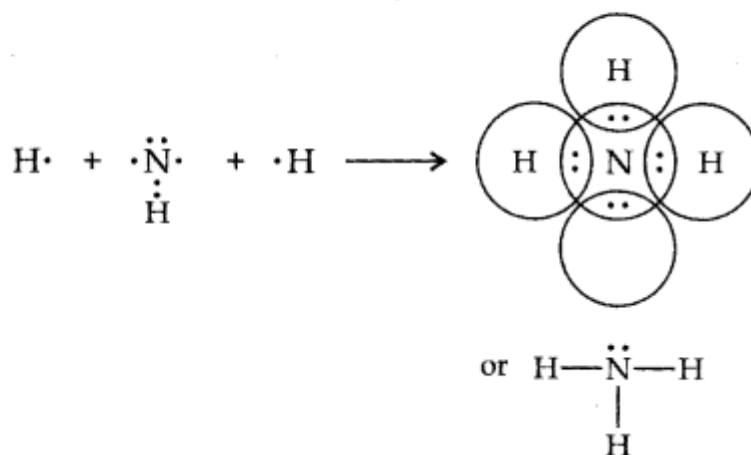
(ii) Formation of oxygen molecule.



(iii) Formation of  $\text{H}_2\text{O}$  molecule.



(iv) Formation of  $\text{NH}_3$  molecule.



• **Lewis Representation of Simple Molecules (the Lewis Structures)**

The Lewis dot Structure can be written through the following steps:

- (i) Calculate the total number of valence electrons of the combining atoms.
- (ii) Each anion means addition of one electron and each cation means removal of one electron. This gives the total number of electrons to be distributed.
- (iii) By knowing the chemical symbols of the combining atoms.
- (iv) After placing shared pairs of electrons for single bond, the remaining electrons

may account for either multiple bonds or as lone pairs. It is to be noted that octet of each atom should be completed.

### Lewis structures of some typical molecules and ions

Molecule/Ion	Lewis Representation	
(i) CO	$:\text{C}::\text{O}:$	or $:\text{C}\equiv\text{O}:$
(ii) CO <sub>2</sub>	$\ddot{\text{O}}::\text{C}::\ddot{\text{O}}$	or $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
(iii) O <sub>2</sub>	$:\text{O}::\text{O}:$	or $:\text{O}=\text{O}:$
(iv) O <sub>3</sub>	$\begin{array}{c} \ddot{\text{O}}^+ \\ \diagup \quad \diagdown \\ :\ddot{\text{O}}: \quad :\ddot{\text{O}}^- \end{array}$	or $\begin{array}{c} \text{O}^+ \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O}^- \end{array}$
(v) H <sub>2</sub> O <sub>2</sub>	$\text{H}:\ddot{\text{O}}:\ddot{\text{O}}:\text{H}$	or $\text{H}-\ddot{\text{O}}-\ddot{\text{O}}-\text{H}$
(vi) SO <sub>3</sub>	$\begin{array}{c} :\ddot{\text{O}}::\text{S}::\ddot{\text{O}}: \\ :\ddot{\text{O}}: \end{array}$	or $\begin{array}{c} :\ddot{\text{O}}=\text{S}=\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}: \end{array}$
(vii) HClO <sub>4</sub> (Perchloric acid)	$\begin{array}{c} :\ddot{\text{O}}: \\ :\text{H}:\ddot{\text{O}}::\text{Cl}::\ddot{\text{O}}: \\ :\ddot{\text{O}}: \end{array}$	or $\begin{array}{c} :\ddot{\text{O}}: \\   \\ \text{H}-\ddot{\text{O}}-\text{Cl}-\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}: \end{array}$
(viii) CN <sup>-</sup> (Cyanide ion)	$[\text{C}::\text{N}]^-$	or $[\text{C}\equiv\text{N}]^-$
(ix) NO <sub>2</sub> <sup>-</sup> (Nitrite ion)	$[\ddot{\text{O}}::\text{N}::\ddot{\text{O}}]^-$	or $[\ddot{\text{O}}=\text{N}-\ddot{\text{O}}]^-$
(x) SO <sub>4</sub> <sup>2-</sup>	$\left[ \begin{array}{c} \ddot{\text{O}} \\ :\ddot{\text{O}}::\text{S}::\ddot{\text{O}}: \\ \ddot{\text{O}} \end{array} \right]^{2-}$	or $\left[ \begin{array}{c} \ddot{\text{O}} \\   \\ \ddot{\text{O}}-\text{S}-\ddot{\text{O}}: \\   \\ \ddot{\text{O}} \end{array} \right]^{2-}$
(xi) O <sub>2</sub> <sup>2-</sup>	$[\ddot{\text{O}}::\ddot{\text{O}}]^{2-}$	or $[\ddot{\text{O}}-\ddot{\text{O}}]^{2-}$

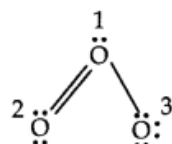
#### • Formal Charge

In polyatomic ions, the net charge is the charge on the ion as a whole and not by particular atom. However, charges can be assigned to individual atoms or ions. These are called formal charges.

It can be expressed as

$$\text{Formal charge (F.C.) on an atom in a Lewis structure} = \left[ \begin{array}{l} \text{total number of valence} \\ \text{electrons in the free} \\ \text{atom} \end{array} \right] - \left[ \begin{array}{l} \text{total number of non} \\ \text{bonding (lone pair)} \\ \text{electrons} \end{array} \right] - (1/2) \left[ \begin{array}{l} \text{total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$

It does not indicate the real charge. 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

$$= 6 - 2 - \frac{1}{2} (6) = +1$$

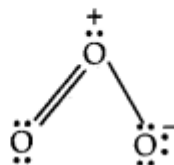
The end O atom marked 2

$$= 6 - 4 - \frac{1}{2} (4) = 0$$

The end O atom marked 3

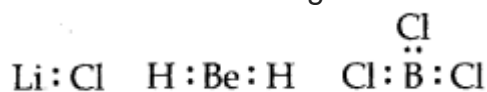
$$= 6 - 6 - \frac{1}{2} (2) = -1$$

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



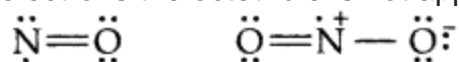
#### • Limitations of the Octet Rule

(i) The incomplete octet of the central atoms: In some covalent compounds central atom has less than eight electrons, i.e., it has an incomplete octet. For example,

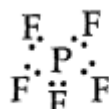


Li, Be and B have 1, 2, and 3 valence electrons only.

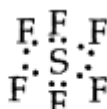
(ii) Odd-electron molecules: There are certain molecules which have odd number of electrons the octet rule is not applied for all the atoms.



(iii) The expanded Octet: In many compounds there are more than eight valence electrons around the central atom. It is termed as expanded octet. For Example,



$PF_5$  (10 electrons)



$PF_6$  (12 electrons)

#### • Other Drawbacks of Octet Theory

(i) Some noble gases, also combine with oxygen and fluorine to form a number of

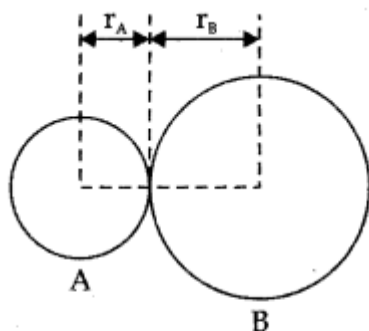
compounds like  $\text{XeF}_2$ ,  $\text{XeOF}_2$  etc.

(ii) This theory does not account for the shape of the molecule.

(iii) It does not give any idea about the energy of The molecule and relative stability.

#### • Bond Length

It is defined as the equilibrium distance between the centres of the nuclei of the two bonded atoms. It is expressed in terms of A. Experimentally, it can be defined by X-ray diffraction or electron diffraction method.



*The bond length in a covalent molecule AB.*

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

#### • Bond Angle

It is defined as -the angle between the lines representing the orbitals containing the bonding – electrons.

It helps us in determining the shape. It can be expressed in degree. Bond angle can be experimentally determined by spectroscopic methods.

#### • Bond Enthalpy

It is defined as the amount of energy required to break one mole of bonds of a particular type to separate them into gaseous atoms.

Bond Enthalpy is also known as bond dissociation enthalpy or simple bond enthalpy.

Unit of bond enthalpy =  $\text{kJ mol}^{-1}$

Greater the bond enthalpy, stronger is the bond. For e.g., the H—H bond enthalpy in hydrogen is  $435.8 \text{ kJ mol}^{-1}$ .

The magnitude of bond enthalpy is also related to bond multiplicity. Greater the bond multiplicity, more will be the bond enthalpy. For e.g., bond enthalpy of C —C bond is  $347 \text{ kJ mol}^{-1}$  while that of C = C bond is  $610 \text{ kJ mol}^{-1}$ .

In polyatomic molecules, the term mean or average bond enthalpy is used.

**Average Bond Enthalpies of some common Bonds**

Bond	Bond enthalpy ( $\text{kJ mol}^{-1}$ )	Bond	Bond enthalpy ( $\text{kJ mol}^{-1}$ )
H—H	435.8	C—C	347
Cl—Cl	239	C=C	610
Br—Br	196	C≡C	836
I—I	158	N—N	158
H—Cl	431.0	N=N	418
H—F	564	N≡N	946

#### • Bond Order

According to Lewis, in a covalent bond, the bond order is given by the number of bonds between two atoms in a molecule. For example,

Bond order of  $H_2$  ( $H-H$ ) = 1

Bond order of  $O_2$  ( $O=O$ ) = 2

Bond order of  $N_2$  ( $N=N$ ) = 3

Isoelectronic molecules and ions have identical bond orders. For example,  $F_2$  and  $O_2^{2-}$  have bond order = 1.  $N_2$ ,  $CO$  and  $NO^+$  have bond order = 3. With the increase in bond order, bond enthalpy increases and bond length decreases. For example,

For  $N_2$  B.O. = 3

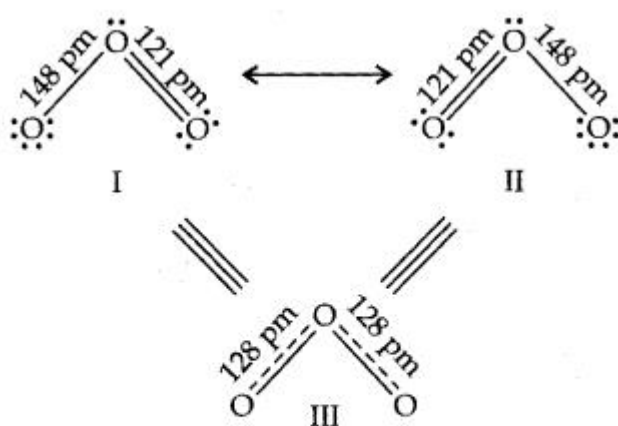
Bond enthalpy = 946 kJ/mol.

For  $O_2$ , B.O. = 2

Bond enthalpy = 498 kJ/mol.

#### • Resonance Structures

There are many molecules whose behaviour cannot be explained by a single-Lewis structure, For example, Lewis structure of Ozone represented as follows:

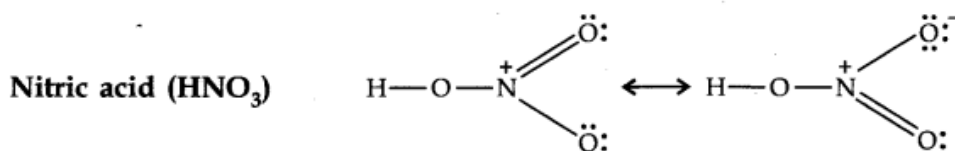
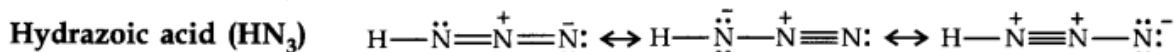
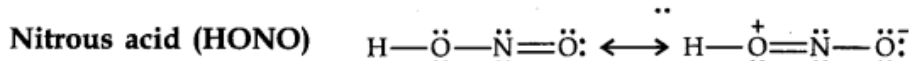
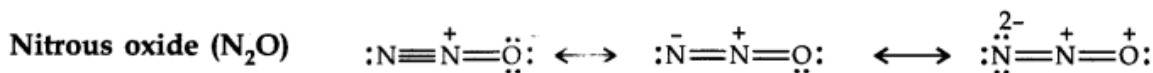
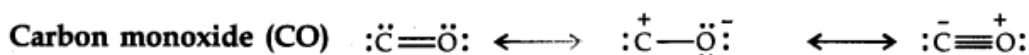
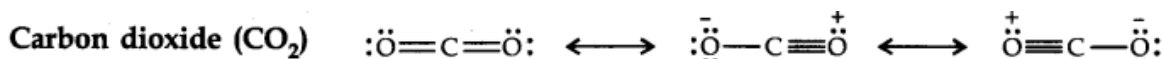


*Resonance in the  $O_3$  molecule*

*(Structures I and II represent the two canonical forms while the Structure III is the resonance hybrid)*

Thus, according to the concept of resonance, whenever a single Lewis structure cannot explain all the properties of the molecule, the molecule is then supposed to have many structures with similar energy. Positions of nuclei, bonding and nonbonding pairs of electrons are taken as the canonical structure of the hybrid which describes the molecule accurately. For  $O_3$ , the two structures shown above are canonical structures and the III structure represents the structure of  $O_3$  more accurately. This is also called resonance hybrid.

Some resonating structures of some more molecules and ions are shown as follows:



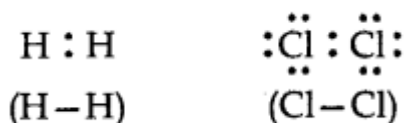
### • Polarity of Bonds

Polar and Non-Polar Covalent bonds

Non-Polar Covalent bonds: When the atoms joined by covalent bond are the same like; H<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub>, the shared pair of electrons is equally attracted by two atoms and thus the shared electron pair is equidistant to both of them.

Alternatively, we can say that it lies exactly in the centre of the bonding atoms. As a result, no poles are developed and the bond is called as non-polar covalent bond. The corresponding molecules are known as non-polar molecules.

For Example,

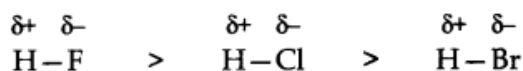


Polar bond: When covalent bonds formed between different atoms of different electronegativity, shared electron pair between two atoms gets displaced towards highly electronegative atoms.

For Example, in HCl molecule, since electronegativity of chlorine is high as compared to hydrogen thus, electron pair is displaced more towards chlorine atom, thus chlorine will acquire a partial negative charge (δ<sup>-</sup>) and hydrogen atom have a partial positive charge (δ<sup>+</sup>) with the magnitude of charge same as on chlorination. Such covalent bond is called polar covalent bond.



Greater the difference in electronegativity of the bonding atoms, more will be the polarity of the bond.



### • Dipole Moment

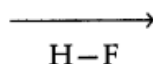
Due to polarity, polar molecules are also known as dipole molecules and they possess dipole moment. Dipole moment is defined as the product of magnitude of the positive or negative charge and the distance between the charges.

Dipole Moment ( $\mu$ ) = Charge ( $Q$ )  $\times$  ( $d$ ) (Distance of Separation)

It is expressed in Debye units (D)

$$1\text{D} = 3.33564 \times 10^{-30} \text{ cm}$$

Dipole moment is a vector quantity. It is depicted by a small arrow with tail on positive centre and head pointing towards the negative centre. For Example,



With the help of dipole moment the degree of polarity of bonds can be expressed.

#### • Applications of Dipole Moment

(i) For determining the polarity of the molecules.

(ii) In finding the shapes of the molecules.

For example, the molecules with zero dipole moment will be linear or symmetrical. Those molecules which have unsymmetrical shapes will be either bent or angular. (e.g.,  $\text{NH}_3$  with  $\mu = 1.47 \text{ D}$ ).

(iii) In calculating the percentage ionic character of polar bonds.

#### • The Valence Shell Electron Pair Repulsion (VSEPR) Theory

Sidgwick and Powell in 1940, proposed a simple theory based on repulsive character of electron pairs in the valence shell of the atoms. It was further developed by Nyholm and Gillespie (1957).

Main Postulates are the following:

(i) The exact shape of molecule depends upon the number of electron pairs (bonded or non bonded) around the central atoms.

(ii) The electron pairs have a tendency to repel each other since they exist around the central atom and the electron clouds are negatively charged.

(iii) Electron pairs try to take such position which can minimize the repulsion between them.

(iv) The valence shell is taken as a sphere with the electron pairs placed at maximum distance.

(v) A multiple bond is treated as if it is a single electron pair and the electron pairs which constitute the bond as single pairs.

#### • Valence Bond Theory

Valence bond theory was introduced by Heitler and London (1927) and developed by Pauling and others. It is based on the concept of atomic orbitals and the electronic configuration of the atoms.

Let us consider the formation of hydrogen molecule based on valence-bond theory.

Let two hydrogen atoms A and B having their nuclei  $N_A$  and  $N_B$  and electrons present in them are  $e_A$  and  $e_B$ .

As these two atoms come closer new attractive and repulsive forces begin to operate.

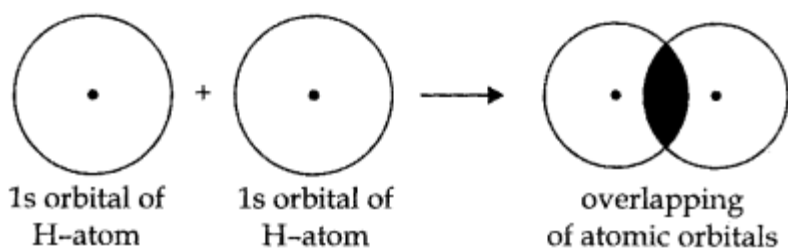
(i) The nucleus of one atom is attracted towards its own electron and the electron of the other and vice versa.

(ii) Repulsive forces arise between the electrons of two atoms and nuclei of two atoms. Attractive forces tend to bring the two atoms closer whereas repulsive forces tend to push them apart.

#### • Orbital Overlap Concept

According to orbital overlap concept, covalent bond formed between atoms results in the overlap of orbitals belonging to the atoms having opposite spins of electrons.

Formation of hydrogen molecule as a result of overlap of the two atomic orbitals of hydrogen atoms is shown in the figures that follows:



Stability of a Molecular orbital depends upon the extent of the overlap of the atomic orbitals.

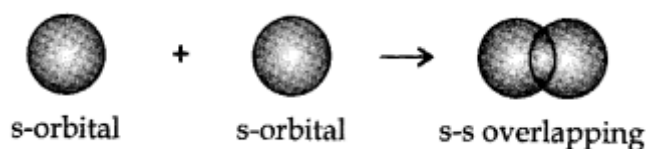
### • Types of Orbital Overlap

Depending upon the type of overlapping, the covalent bonds are of two types, known as sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds.

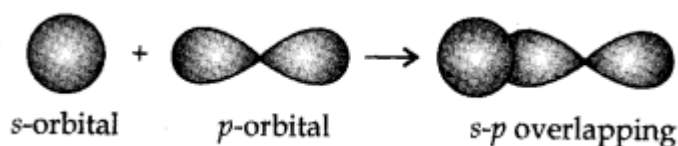
(i) Sigma ( $\sigma$  bond): Sigma bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis.

The axial overlap involving these orbitals is of three types:

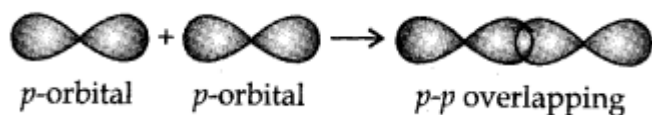
• **s-s overlapping:** In this case, there is overlap of two half-filled s-orbitals along the internuclear axis as shown below:



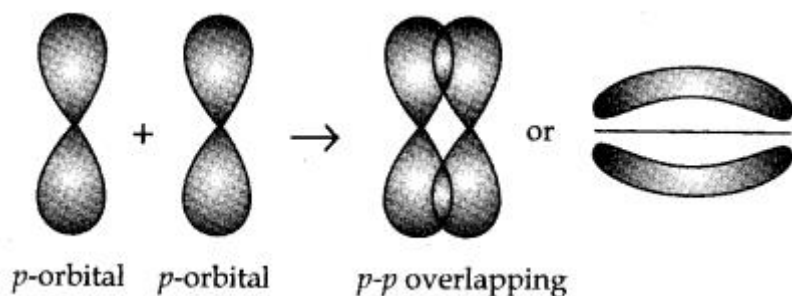
• **s-p overlapping:** This type of overlapping occurs between half-filled s-orbitals of one atom and half filled p-orbitals of another atoms.



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



(ii) pi ( $\pi$  bond):  $\pi$  bond is formed by the atomic orbitals when they overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbital formed is due to lateral overlapping or side wise overlapping.



### • Strength of Sigma and $\pi$ Bonds

Sigma bond ( $\sigma$  bond) is formed by the axial overlapping of the atomic orbitals while the  $\pi$ -bond is formed by side wise overlapping. Since axial overlapping is greater as

compared to side wise. Thus, the sigma bond is said to be stronger bond in comparison to a  $\pi$ -bond.

Distinction between sigma and  $\pi$  bonds

<i>Sigma (<math>\sigma</math>) Bond</i>	<i>pi (<math>\pi</math>) Bond</i>
(1) s-orbitals are involved in the formation of $\sigma$ bond. (2) The overlap is quite large and the bond formed is strong. (3) The bond is formed by axial overlap of atomic orbitals. (4) Only one lobe of the p-orbitals is involved (5) The electron cloud formed is symmetry.	(1) s-orbitals are not involved in the bond formation. (2) $\pi$ bond is comparatively weak. (3) The bond is formed by the sidewise overlap of atomic orbitals. (4) Both lobes of p-orbitals are involved in the overlap. (5) The electron cloud is unsymmetrical.

### • Hybridisation

Hybridisation is the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies resulting in the formation of new set of orbitals of equivalent energies and shape.

#### Salient Features of Hybridisation:

- (i) Orbitals with almost equal energy take part in the hybridisation.
- (ii) Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed,
- (iii) Geometry of a covalent molecule can be indicated by the type of hybridisation.
- (iv) The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

#### Conditions necessary for hybridisation:

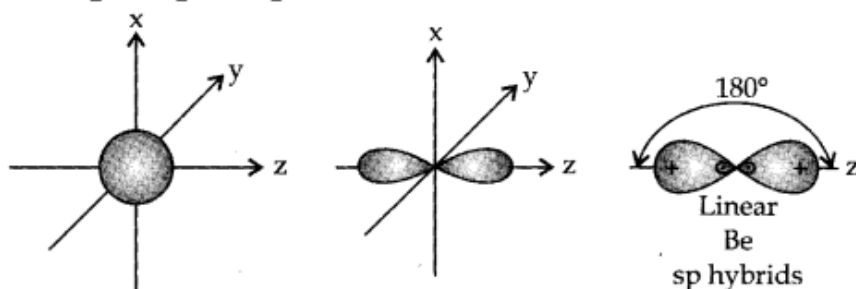
- (i) Orbitals of valence shell take part in the hybridisation.
- (ii) Orbitals involved in hybridisation should have almost equal energy.
- (iii) Promotion of electron is not necessary condition prior to hybridisation.
- (iv) In some cases filled orbitals of valence shell also take part in hybridisation.

#### Types of Hybridisation:

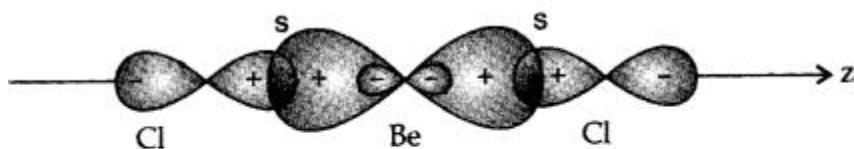
(i)  $sp$  hybridisation: When one s and one p-orbital hybridise to form two equivalent orbitals, the orbital is known as  $sp$  hybrid orbital, and the type of hybridisation is called  $sp$  hybridisation.

Each of the hybrid orbitals formed has 50% s-character and 50%, p-character. This type of hybridisation is also known as diagonal hybridisation.

*Examples:* All compounds of carbon containing  $C \equiv C$  triple bond like acetylene ( $C_2H_2$ ),  $BeCl_2$ ,  $BeF_2$ ,  $BeH_2$  etc.



(a) Formation of  $sp$  hybrids from s and p orbitals



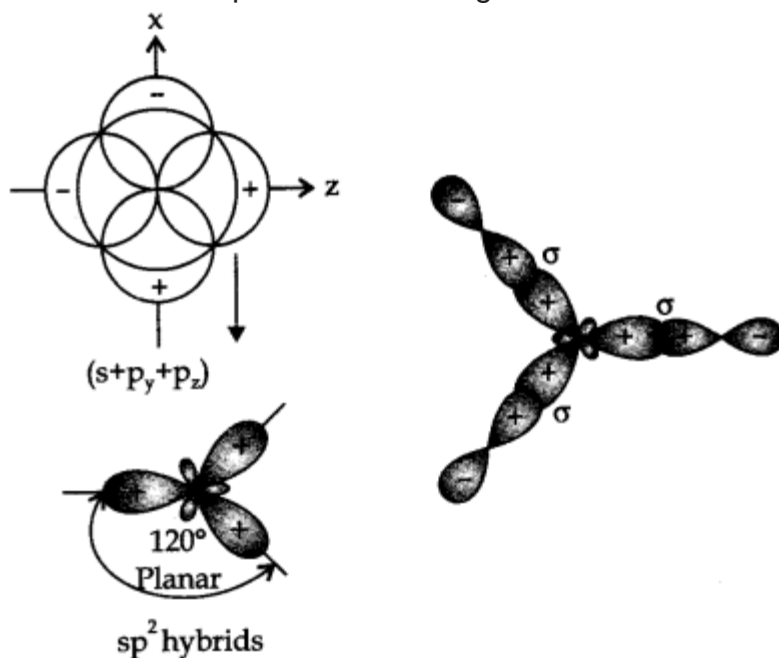
BeCl<sub>2</sub> molecule

**(b) Formation of the linear BeCl<sub>2</sub> molecule**

(ii) sp<sup>2</sup> hybridisation: In this type, one s and two p-orbitals hybridise to form three equivalent sp<sup>2</sup> hybridised orbitals.

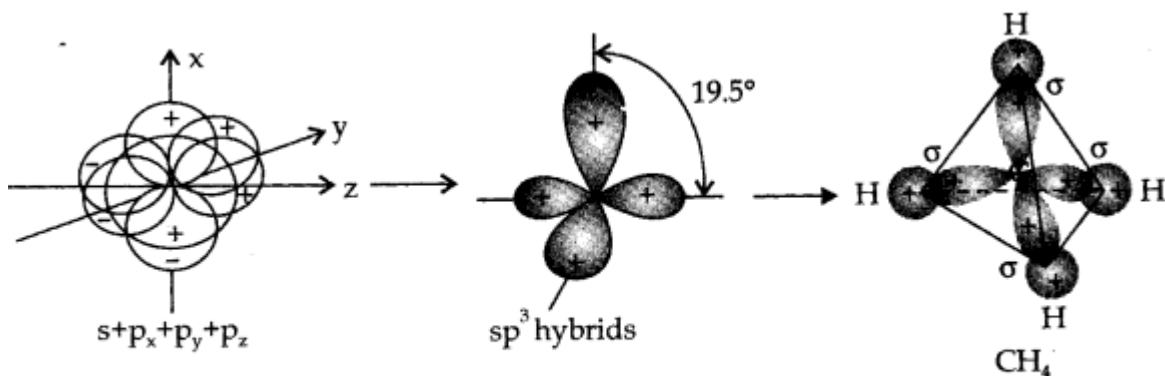
All the three hybrid orbitals remain in the same plane making an angle of 120°.

Example. A few compounds in which sp<sup>2</sup> hybridisation takes place are BF<sub>3</sub>, BH<sub>3</sub>, BCl<sub>3</sub> carbon compounds containing double bond etc.



**Formation of sp<sup>2</sup> hybrids and the BCl<sub>3</sub> molecule**

(iii) sp<sup>3</sup> hybridisation: In this type, one s and three p-orbitals in the valence shell of an atom get hybridised to form four equivalent hybrid orbitals. There is 25% s-character and 75% p-character in each sp<sup>3</sup> hybrid orbital. The four sp<sup>3</sup> orbitals are directed towards four corners of the tetrahedron.



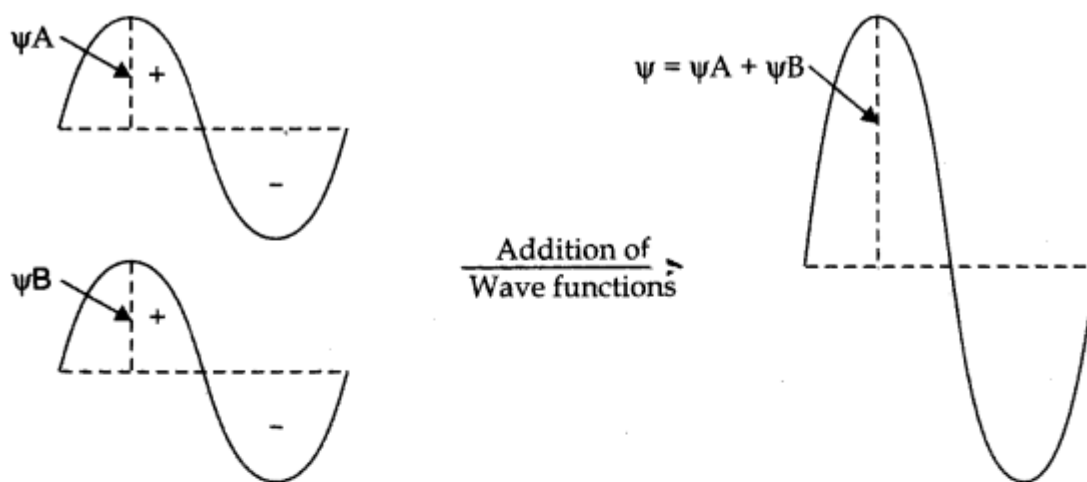
**Formation of sp<sup>3</sup> hybrids by the combination of s, p<sub>x</sub>, p<sub>y</sub> and p<sub>z</sub> atomic orbitals of carbon and the formation of CH<sub>4</sub> molecule.**

The angle between  $sp^3$  hybrid orbitals is  $109.5^\circ$ .

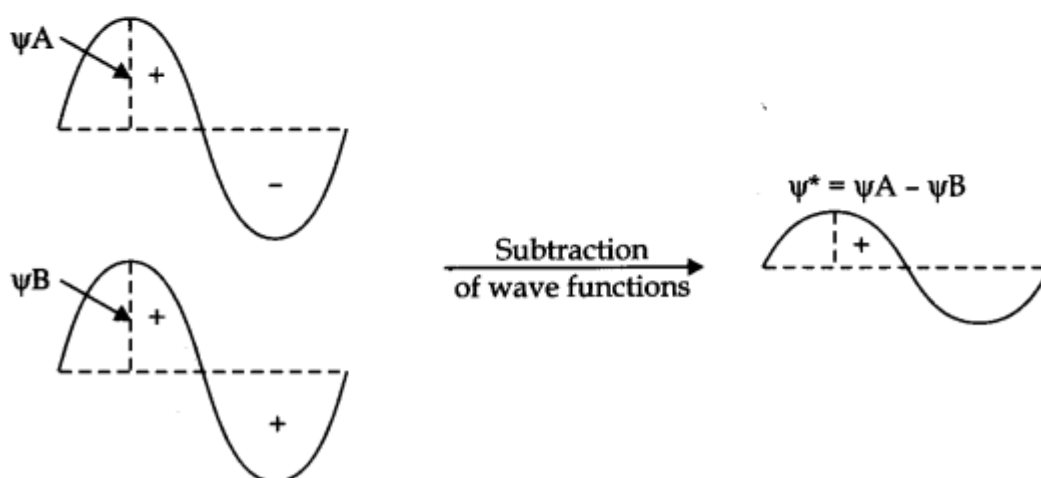
A compound in which  $sp^3$  hybridisation occurs is,  $(CH_4)$ . The structures of  $NH_3$  and  $H_2O$  molecules can also be explained with the help of  $sp^3$  hybridisation.

• **Formation of Molecular Orbitals:** Linear Combination of Atomic Orbitals (LCAO)

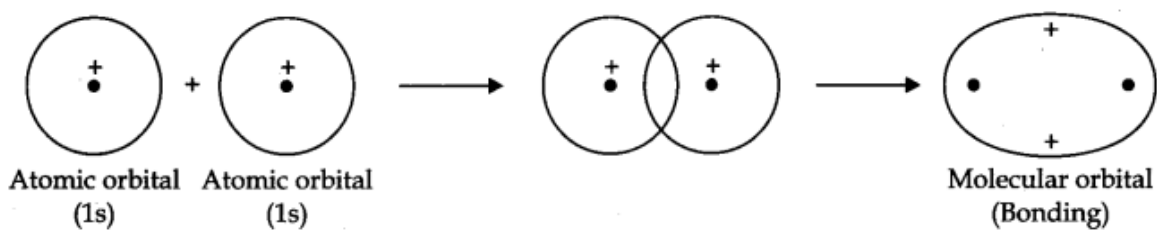
The formation of molecular orbitals can be explained by the linear combination of atomic orbitals. Combination takes place either by addition or by subtraction of wave function as shown below.



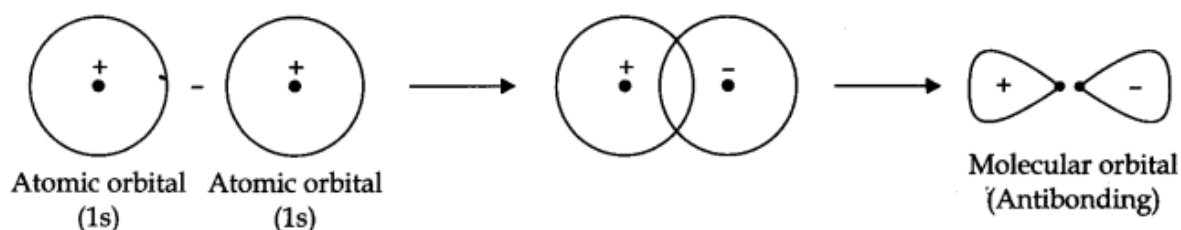
*Addition of wave functions*



*Subtraction of wave functions*



*Formation of bonding molecular orbital*



#### *Formation of antibonding molecular orbital*

The molecular orbital formed by addition of atomic orbitals is called bonding molecular orbital while molecular orbital formed by subtraction of atomic orbitals is called antibonding molecular orbital.

Conditions for the combination of atomic orbitals:

- (1) The combining atomic orbitals must have almost equal energy.
- (2) The combining atomic orbitals must have same symmetry about the molecular axis.
- (3) The combining atomic orbitals must overlap to the maximum extent.

#### • **Types of Molecular Orbitals**

**Sigma ( $\sigma$ ) Molecular Orbitals:** They are symmetrical around the bond-axis.

**pi ( $\pi$ ) Molecular Orbitals:** They are not symmetrical, because of the presence of positive lobes above and negative lobes below the molecular plane.

#### • **Electronic configuration and Molecular Behaviour**

The distribution of electrons among various molecular orbitals is called electronic configuration of the molecule.

#### • **Stability of Molecules**

If  $N_b =$  No. of electrons occupying bonding orbitals.

$N_a =$  No. of electrons occupying antibonding orbitals.

then

(i) If  $N_b > N_a$  molecule will be stable.

(ii)  $N_b < N_a$  molecule will be unstable.

#### • **Bond Order**

Bond order is defined as half of the difference between the number of electrons present in bonding and antibonding molecular orbitals.

Bond order (B.O.) =  $\frac{1}{2} [N_b - N_a]$

The bond order may be a whole number, a fraction or even zero.

It may also be positive or negative.

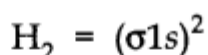
**Nature of the bond:** Integral bond order value for single double and triple bond will be 1, 2 and 3 respectively.

**Bond-Length:** Bond order is inversely proportional to bond-length. Thus, greater the bond order, smaller will be the bond-length.

**Magnetic Nature:** If all the molecular orbitals have paired electrons, the substance is diamagnetic. If one or more molecular orbitals have unpaired electrons, it is paramagnetic e.g.,  $O_2$  molecule.

#### • **Bonding in Some Homonuclear (Diatomic) Molecules**

(1) Hydrogen molecule ( $H_2$ ): It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital, so, the electronic configuration of hydrogen molecule is



$$\text{Bond order (B.O.) of H}_2 = \frac{1}{2}(2-0) = 1$$

$$= \frac{1}{2}(N_b - N_a) = 1$$

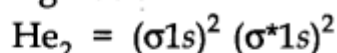
This indicates that two hydrogen atoms are bonded by a single covalent bond. Bond dissociation energy of hydrogen has been found = 438 kJ/mole. Bond-Length = 74 pm

No unpaired electron is present therefore,, it is diamagnetic.

(2) Helium molecule ( $\text{He}_2$ ): Each helium atom contains 2 electrons, thus in  $\text{He}_2$  molecule there would be 4 electrons.

The electrons will be accommodated in  $\sigma 1s$  and  $\sigma^* 1s$  molecular orbitals:

**Electronic configuration**



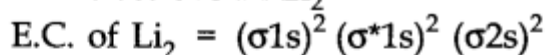
$$\text{Bond order} = \frac{1}{2}[2-2] = 0$$

$\text{He}_2$  molecule is therefore unstable and does not exist.

**(3) Lithium molecule ( $\text{Li}_2$ )**



There are 6 electrons in  $\text{Li}_2$



It can also be represented as KK  $[\sigma 2s]^2$

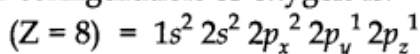
$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$

$$= \frac{1}{2}[4-2] = 1$$

Nature = Diamagnetic, since molecular orbitals are completely filled.

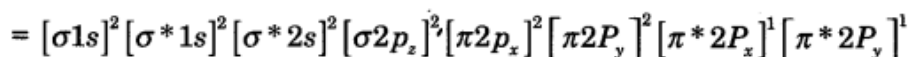
**(4) Oxygen molecule ( $\text{O}_2$ )**

The orbital configuration of oxygen is:



This means that sixteen electrons are to be filled in the molecular orbital of oxygen molecule ( $\text{O}_2$ ).

The molecular orbital configuration



It may also be written as:

$$KK[\sigma 2s]^2[\sigma^* 2s]^2[\sigma 2P_z]^2[\pi 2p_x]^2[\pi 2p_y]^2[\pi^* 2P_x]^1[\pi^* 2P_y]^1$$

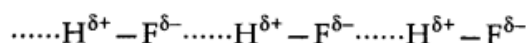
$$\text{B.O.} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[8 - 4] = 2$$

**Nature:** Paramagnetic due to the presence of two unpaired electrons.

### • Hydrogen Bonding

When highly electronegative elements like nitrogen, oxygen, fluorine are attached to hydrogen to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. Thus, partial positive charge develops on hydrogen atom which forms a bond with the other electronegative atom. This bond is known as hydrogen bond and it is weaker than the covalent bond. For example, in HF molecule, hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule.

It can be depicted as



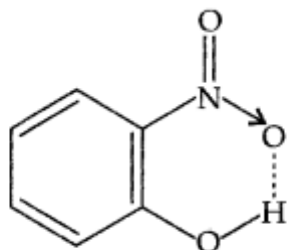
Hydrogen bond is represented by (---) dotted line, while a solid line represents the covalent bond.

### • Types of H-Bonds

(i) Intermolecular hydrogen bond (ii) Intramolecular hydrogen bond.

**(i) Intermolecular hydrogen bond:** It is formed between two different molecules of the same or different compounds. For Example, in HF molecules, water molecules etc.

**(ii) Intramolecular hydrogen bond:** In this type, hydrogen atom is in between the two highly electronegative F, N, O atoms present within the same molecule. For example, in o-nitrophenol, the hydrogen is in between the two oxygen atoms.



*Intramolecular hydrogen bonding in o-nitrophenol molecule*