

# CHEMICAL BONDING

## SESSION - 1

### AIM

- To define Chemical Bond
- To understand the reason for chemical bond formation
- To introduce Ionic bond

CHEMICAL BOND is an attractive force which holds various constituents (atoms, molecules or ions) together in different species.

Chemical bonds divided into two types:

- a) Bonds which constitute molecules or formula units. These are ionic bonds, covalent bonds and co-ordinate or dative bonds.
- b) Bonds which hold various particles in solid or liquid state of the substances. These are also called **INTERMOLECULAR FORCES**. These are: metallic bonds, dipole-dipole forces, van der Waal forces, hydrogen bonds.

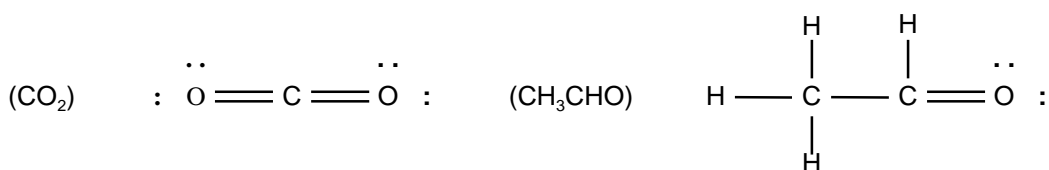
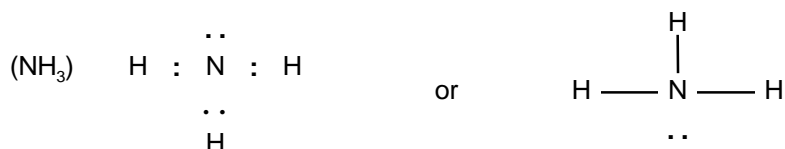
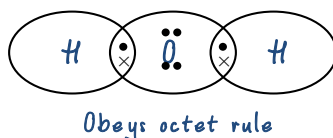
Cause of Chemical Combination: Chemical bonding takes place due

- To acquire a state of minimum energy and maximum stability
- To convert atoms into molecule to acquire stable noble gas configuration.

### LEWIS THEORY

Lewis theory gave the first explanation of a covalent bond in terms of electrons that was generally accepted. If two electrons are shared between two atoms, this constitutes a bond and binds the atoms together. For many light atoms, a stable arrangement is attained when the atom is surrounded by eight electrons.

OCTATE RULE- 'Atoms combine with each other either by sharing or by the transference of electrons to attain stable noble gas configuration in outer most shell.'



## LEWIS DOT STRUCTURES

The formula of a molecule shows the number of atoms of each element but does not show the bonding arrangement of the atoms.

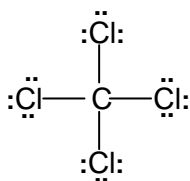
For example,  $\text{F}_2$  is  $:\ddot{\text{F}}:\ddot{\text{F}}:$  or  $:\ddot{\text{F}}-\ddot{\text{F}}:$  and a molecule of hydrogen fluoride is shown as  $\text{H}:\ddot{\text{F}}:$  or  $\text{H}-\ddot{\text{F}}:$

Arrangement of valence electrons and symbol of elements in a molecules are called Lewis structures.

(i) In water ( $\text{H}_2\text{O}$ ), one  $\text{H}$  and two  $\cdot\ddot{\text{O}}\cdot$  complete their  $\begin{array}{c} \ddot{\text{O}} - \text{H} \\ | \\ \text{H} \end{array}$  duet and octet respectively

(ii) In ammonia ( $\text{NH}_3$ ), three  $\text{H}$  and one  $\cdot\ddot{\text{N}}\cdot$  fit together and  $\begin{array}{c} \text{H} - \ddot{\text{N}} - \text{H} \\ | \\ \text{H} \end{array}$  satisfy their duet and octet respectively as

(iii) In carbon tetrachloride ( $\text{CCl}_4$ ), four  $:\ddot{\text{Cl}}\cdot$  and one  $\cdot\ddot{\text{C}}\cdot$  complete their octet as

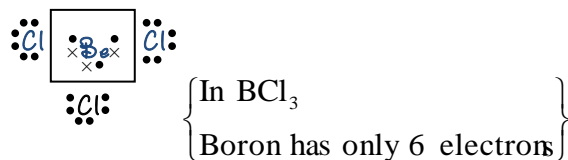
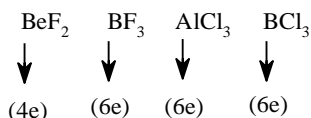


### Limitations of Octate rule

- It is failed to explain the **stability of incomplete octate**.

For example,  $\text{BH}_3$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{GaCl}_3$  etc.

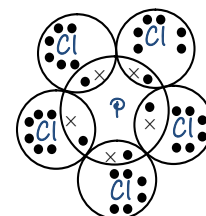
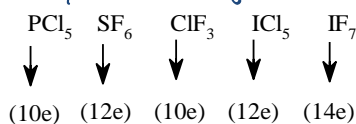
i.e., contraction of octet  $< 8e^-$



- It is failed to explain the **stability of extended octate**. It is possible in those molecules having vacant *d*-orbitals.

For example,  $\text{PCl}_5$ ,  $\text{SF}_6$  etc.

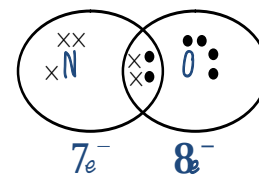
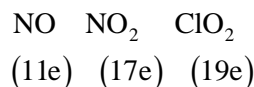
i.e., Expansion of octet  $> 8e^-$



Electron dot formula of  $\text{PCl}_5$

- It is failed to explain the **stability of odd electron species**.

For example,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{ClO}_2$ .



- It is failed to explain the stability of duplet structure of Hydrogen atom.
- It is failed to explain the stability of Cations of transition metals, which contains **18** electrons in outermost orbit

Examples :  $Ga^{+3}$ ,  $Cu^+$ ,  $Ag^+$ ,  $Zn^{+2}$ ,  $Cd^{+2}$ ,  $Sn^{+4}$ ,  $Pb^{+4}$  etc.

Electronic configuration of Ga -  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$

Electronic configuration of  $Ga^{+3}$  -  $1s^2, 2s^2 2p^6,$

- Octate rule based on the chemical inertness of noble gases but some noble gases able to form compounds like  $XeF_2$ ,  $KrF_2$  etc
- Failed to explain the geometry of molecules.
- It is failed to explain the relative stability of molecules.

### METHOD OF DRAWING LEWIS STRUCTURES of polyatomic species

(i) First calculate  $n_1$ .

$n_1 =$  Total valence electron of all the atoms of the species  $\pm$  net charge on the species.

For anion, electrons are added and for cations electrons are subtracted.

(ii) Then calculate  $n_2$ .

$n_2 = (8 \times \text{no, of atoms other than H}) + (2 \times \text{no, of H atoms})$

(iii) Subtract  $n_1$  from  $n_2$ , which gives  $n_3$ .

$n_3 = n_2 - n_1 =$  number of electrons shared between atoms = number of bonding electrons.

$$\frac{n_3}{2} = \frac{n_2 - n_1}{2} = \text{number of shared electron or bps} = \text{number of bonds.}$$

(iv) Subtracting  $n_3$  from  $n_1$  gives  $n_4$ .

$$n_4 = n_1 - n_3 = \text{number of unshared electrons or non-bonding electrons.}$$

$$\frac{n_4}{2} = \frac{n_1 - n_3}{2} = \text{no. of unshared electron pairs} = \text{number of lone pairs.}$$

(v) Identify the least electronegative atom in a molecule as central atom, when the other atoms do not contain hydrogen.

When other atoms are hydrogen only, then the central atom would be the more electronegative atom.

(vi) Now around the central atom, place the other atoms and distribute the required number of bonds (as calculated in step (iii)) & required number of lone pairs (as calculated in step (iv)), keeping in mind that every atom gets an octet of electrons except hydrogen.

(vii) Calculate the formal charge on each atom.

(ix) Lewis structure should obey like resonance (delocalization), bond length,  $p\pi-d\pi$  back bonding etc.

Exp- Determine Lewis structure of  $\text{NO}_3^-$  ion.

$$(i) n_1 = 5 + (6 \times 3) + 1 = 24$$

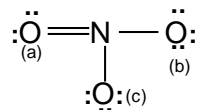
$$(ii) n_2 = (4 \times 8) = 32$$

$$(iii) n_3 = n_2 - n_1 = 32 - 24 = 8$$

$$\therefore \text{Number of bonds} = \frac{8}{2} = 4$$

$$(iv) n_4 = n_1 - n_3 = 24 - 8 = 16 \quad \therefore \text{Number of lone pairs} = \frac{16}{2} = 8$$

(v) Nitrogen is central atom (less electronegative than O). Arranging three O atoms around it and distributing 4 bonds and 8 lone pairs as



(vi) Calculating formal charge on each atom.

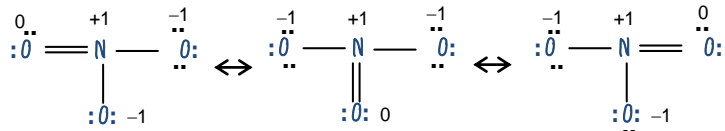
$$\text{Formal charge on N} = 5 - 4 - 0 = +1$$

$$\text{Formal charge on O (a)} = 6 - 2 - 4 = 0$$

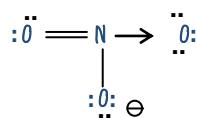
$$\text{Formal charge on O (b)} = 6 - 1 - 6 = -1$$

$$\text{Formal charge on O (c)} = 6 - 1 - 6 = -1$$

Thus, the structures can now be shown as

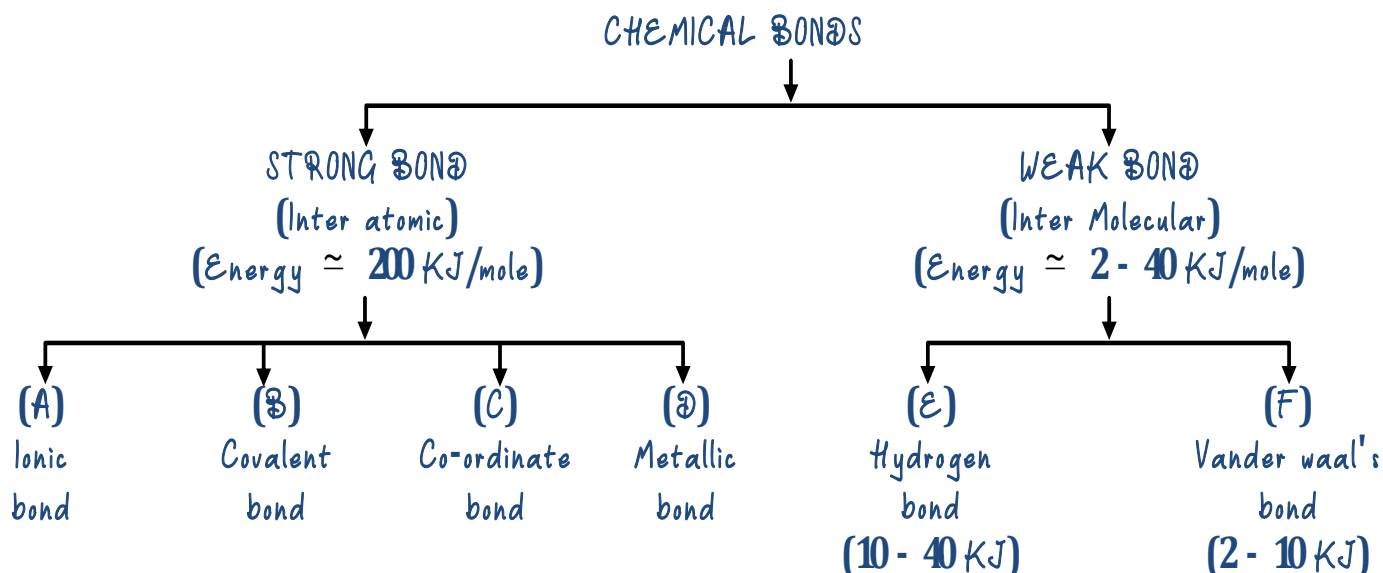


Final structure of  $\text{NO}_3^-$  is therefore shown as



which even accounts for resonance in  $\text{NO}_3^-$  ion.

## Classification of bonds :-



### • IONIC or ELECTROVALENT BOND

Ionic bond is formed by transference of electrons from electropositive atom to electronegative atom.

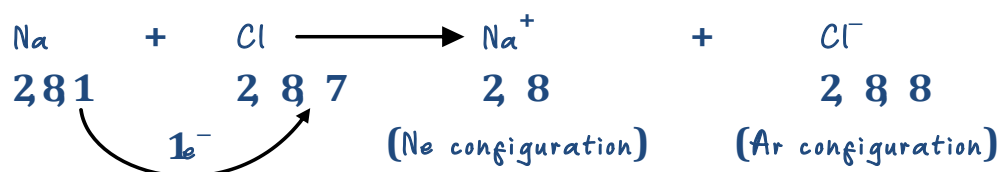
Atom losing electrons becomes cation while the atom gaining electrons becomes anion.

Electro +ve atom loses electron (group IA to IIIA)

Electro -ve atom gains electron (group VA to VIIA)

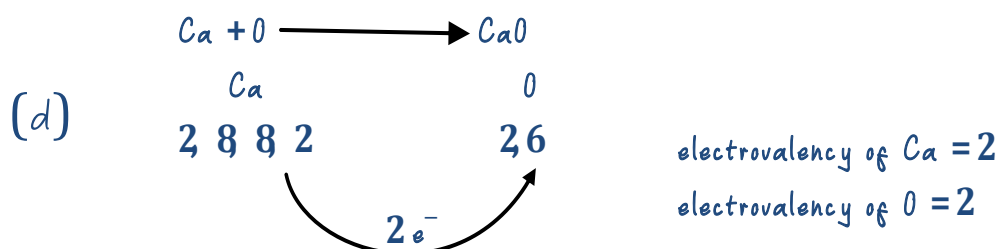
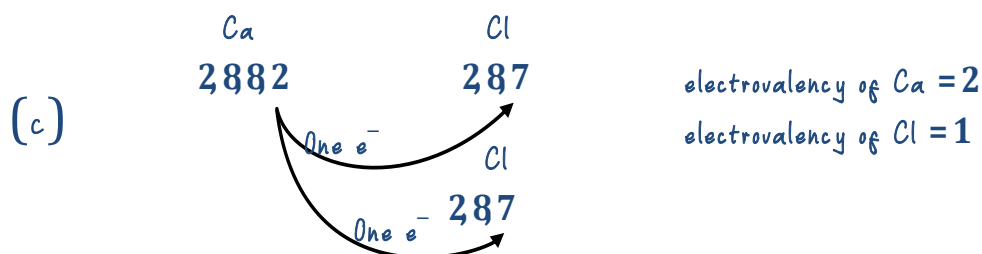
'The electrostatic force of attraction holding the oppositely charged ions' is called electrovalent bond or ionic bond.

Exp- \*IA and VIIA group elements form maximum ionic compound.



- More the distance between two elements in periodic table more will be ionic character of bond.
- Total number of electron lose or gained by an atom during the formation of ionic bond is called **electrovalency**.

(a) In  $MgCl_2$  formation, electrovalency of Mg and Cl are 2 and 1 respectively.



### Factors favouring formation of ionic bond:

- **Atomic Size:** Larger atoms can easily form cations.  
i.e., form ionic compounds easily, due to decrease in force of attraction of the nucleus on the valence electrons.

Order of formation of alkali metal cations is:  $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Smaller atoms can easily form anions.

Ex: The ease of formation of halide ions is:  $F^- > Cl^- > Br^- < I^-$

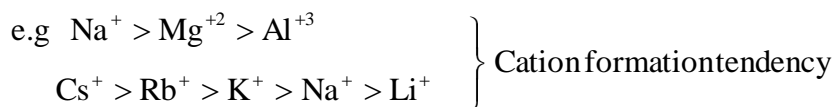


- **Ionisation Potential:** Atoms with low I.P can easily form cations.

Lesser i.e.  $\longrightarrow$  Greater tendency to form cation.

Ex: The I.P of Na is 117.3 Kcal / mole, while that of K is 100 Kcal/mole.

Therefore  $K^+$  ion is formed more easily than  $Na^+$  ion.



- **Charge of the ion:** Cations with low charge are formed more easily than the cations with high charge.

Ex: Ease of formation:  $Na^+ > Mg^{2+} > Mg^{3+}$

- **Electronic Configuration:** Cations with inert gas configuration are formed more easily than the cations with pseudo inert gas configuration. (18 valence electrons).

Ex:  $Ca^{2+}$  ion (2, 8, 8) is formed more easily than  $Zn^{2+}$  ion (2, 8, 8).

- **Electron Affinity/Electronegativity:** Atoms with high electron affinity are able to form anion more easily.

Ex: halogens possess high electron affinity. So the formation of their ions is very common.

Higher electron affinity  $\longrightarrow$  Greater tendency to form anion



- **Charge of the ion:** Anions with low charge are formed more easily than the anions with high charge. Vice versa for cation.

Ex: Ease of formation:  $F^- > O^{2-} > N^{3-}$

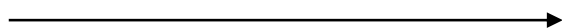
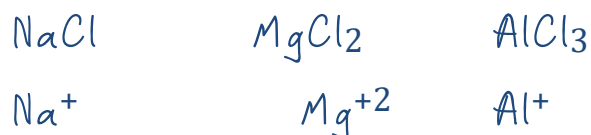
- Lattice energy — 'Amount of energy released when one mole of crystal product is formed from gaseous reactants'. Or  
'Amount of energy absorbed when one mole of ionic crystal is dissociated into its gaseous reactants'.

### Factors affecting lattice energy :

(i) Magnitude of charge  $\rightarrow U \propto z^+ z^-$  (Ionic charge)

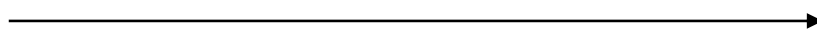
High lattice energy  $\rightarrow$  Greater stability of ionic compound.

- Lattice energy  $\propto$  Magnitude of charge



- Lattice energy increases
- Size of cation decreases.

- Size of Cation : — Lattice energy



- Size of cation increasing
- Size of anion is constant
- Lattice energy decreases

## SESSION - 2

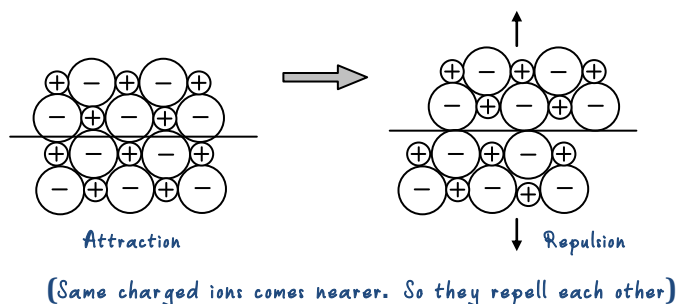
**AIM**

1] To understand the properties of ionic compounds

2] To introduce lattice energy

**PROPERTIES OF IONIC COMPOUNDS**

- **Physical state** - They are hard, crystalline and brittle solids due to strong electrostatic force of attraction.



- **Isomorphism** Ionic compounds are isomorphous i.e., they have same no. of electrons. (similar configuration of their cation and anion) with same crystal structure.

Example -	Na <sup>+</sup>	F <sup>-</sup>	Mg <sup>+2</sup>	O <sup>-2</sup>
Valency	+ 1, -1		+ 2,	- 2
electronic configuration	2, 8,	2, 8	2, 8	2, 8

- **Boiling point and melting point** is high due to strong electrostatics force of attraction among oppositely charged ions.
- **Conductivity** depends on ionic mobility.

In solid state - No free ions - Bad conductor of electricity.

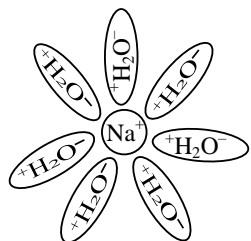
In fused state or aqueous solution Due to free ions - Good conductor of electricity.

conductivity order : Solid state > Fused state < Aqueous solution

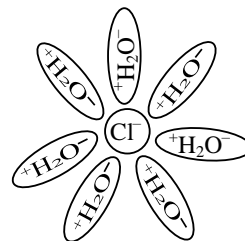
- \* **Reactivity:** Ionic compounds undergo ionic reactions which have very high reaction rates. i.e., quite fast
- \* They do not exhibit isomerism due to non-directional nature of the polar bonds present in these compounds.
- \* **Solubility** Highly soluble in water (Polar solvents) with high value of dielectric constant but insoluble in non-polar solvents due to low dielectric constant. The solubility of ionic compounds decreases with increase in covalent character of ionic compounds.

Example : NaCl in water

- (I) The  $\text{Na}^+$  ions get associates with  $-$ vely charged 'O' of water
- (II) And  $\text{Cl}^-$  ions associates with  $+$ vely charged 'H' of water.



Oxygen atom of  $\text{H}_2\text{O}$  give its electron to  $\text{Na}^+$



H atom of  $\text{H}_2\text{O}$  gain electron from  $\text{Cl}^-$

Solubility of ionic compound is governed by

- Lattice energy:** Larger the lattice energy, the lesser is the solubility. e.g., sulphates and phosphates of Ba & Sr are insoluble in water due to high lattice energy.
- Heat of hydration:** Larger the heat of hydration, the more is the solubility of ionic compound. e.g.,  $\text{AlCl}_3$ , though covalent in nature is soluble in water due to high

## Born - Haber Cycle

(Energy changes involved in the formation of an ionic bond):

The energy changes which take place in the formation of an ionic compound from its component elements can be studied with the help of a thermochemical cycle known as Born-Haber cycle.

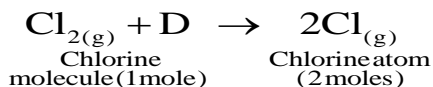
For example, in the formation of one mole of sodium chloride from sodium and chlorine the following steps are involved.

- Conversion of metallic sodium (solid) into gaseous sodium atoms:



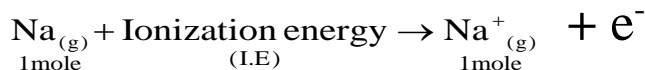
where  $\Delta H_{\text{sub}}$  is the enthalpy of sublimation of sodium. It is the amount of energy required for converting one mole of solid sodium into gaseous sodium atoms.

- Dissociation of chlorine molecules into chlorine atoms:

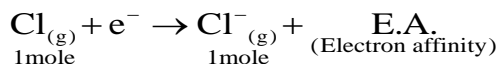


where  $\mathcal{D}$  is dissociation energy (bond energy) of  $\text{Cl}_2$ . It is clear that the energy needed for the formation of one mole of chlorine atoms is  $\mathcal{D}/2$ .

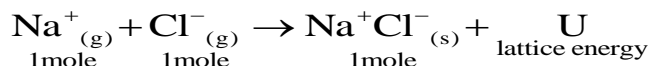
- Conversion of gaseous sodium atoms into gaseous sodium ions:



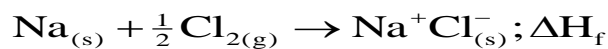
- Conversion of gaseous chlorine atoms into gaseous chloride ions:



- Combination of gaseous sodium ions, chloride ions to give solid crystal.

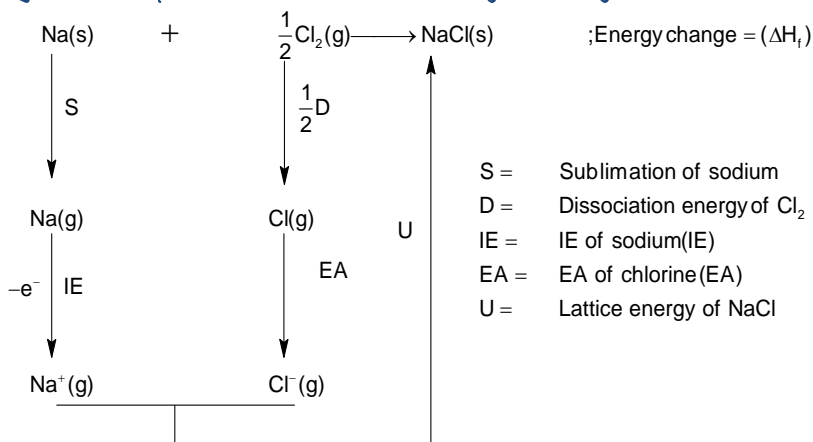


The overall formation of ionic solid may be represented as below:



Where  $\Delta H_f$  is the heat of formation of 1 mole of  $\text{Na}^+ \text{Cl}_{(s)}^-$ .

Steps may be represented in the form of Born-Haber cycle.



According to Hess law of constant heat summation, the heat of formation of one mole of  $\text{Na}^+ \text{Cl}_{(s)}^-$  should be the same whether its formation takes place directly in a single step or through a number of steps.

Hence, 
$$\Delta H_f = \Delta H_{\text{sub}} + \text{IE} + \frac{1}{2} D + (-\text{EA}) + (-U)$$

On substituting values in the above expression,

we get: 
$$\Delta H_f = (+108.5) + 495.2 + \frac{1}{2} (243.0) + (-348.3) + (-758.7) = -381.8 \text{ kJ mole}^{-1}$$

The **negative sign** in the values shows the **energy released**, while the **positive signs** indicate that the **energy is absorbed**.

Formation of NaCl molecule, involves **net fall** in the energy of the system, hence  $\text{Na}^+ \text{Cl}_{(s)}^-$  is quite stable.

**Higher the negative values** of heat of formation, **greater will be the stability** of the resulting ionic compound.

SESSION - 3

## AIM

- 1] To introduce covalent bond
- 2] To explain covalent bond formation and types of covalent bond
- 3] To explain Lewis -dot structures.

COVALENT BOND - The bond is formed by mutual sharing of electrons between the atoms. The atoms participating in bonding contribute equal number of electrons for mutual sharing.

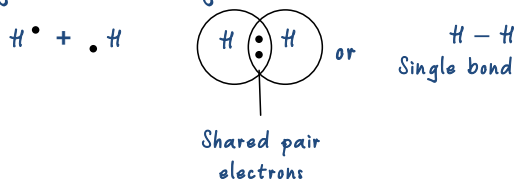
It is of 3 types

a) **Single covalent bond**: Here covalent bond formed by sharing of two electrons (i.e., 1 electron pair).

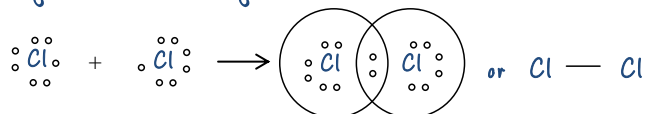
It is represented by a single line between two atoms.

Example :

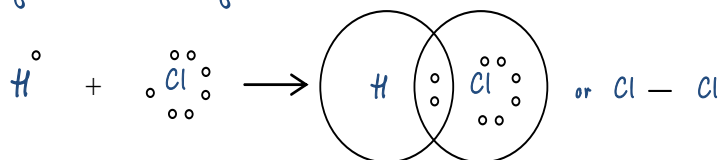
- formation of  $H_2$  molecule



- formation of  $Cl_2$  molecule:

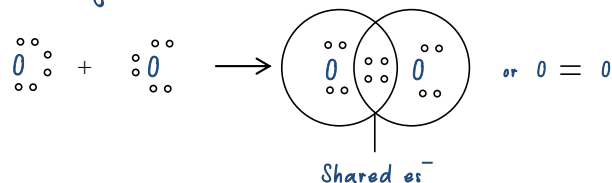


- formation of  $HCl$  :



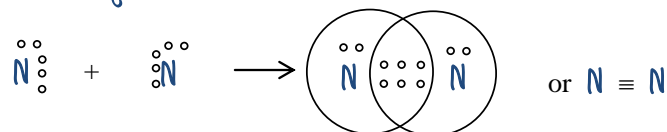
**b) Double bond or double covalent bond** formed by sharing of two electron pairs, between two atoms, it is represented by a double line ( = ) between two atoms.

Example . Formation of  $O_2$  molecule :



**c) Triple covalent bond** formed by sharing of three electron pairs. It is represented by a triple line (  $\equiv$  ) between two atoms.

Example. Formation of  $N_2$  molecule

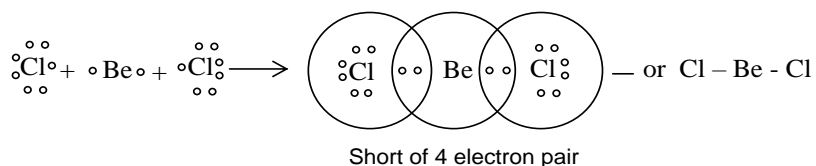


Thus, the number of covalent bonds formed by an atom depend on

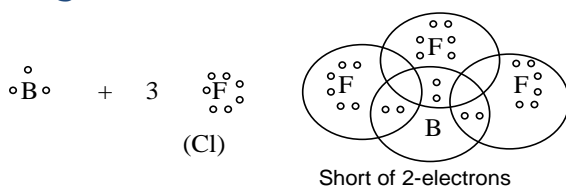
- i) the number of unpaired electrons in their valency shell.
  - ii) the number of electrons required to attain inert gas configuration.
- Generally p block elements are involved in the covalent bond formation.

**Some more examples of formation of covalent Bonds:**

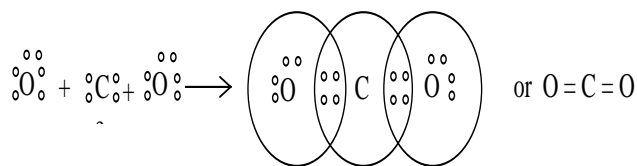
•  $BeCl_2$ :



•  $BF_3$  or  $BCl_3$ :

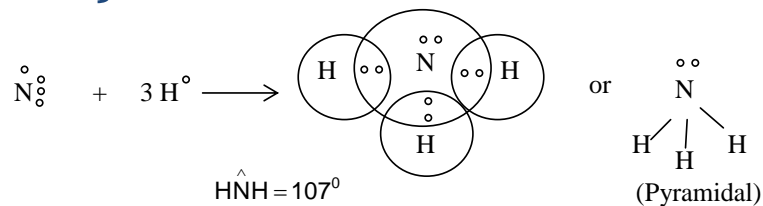




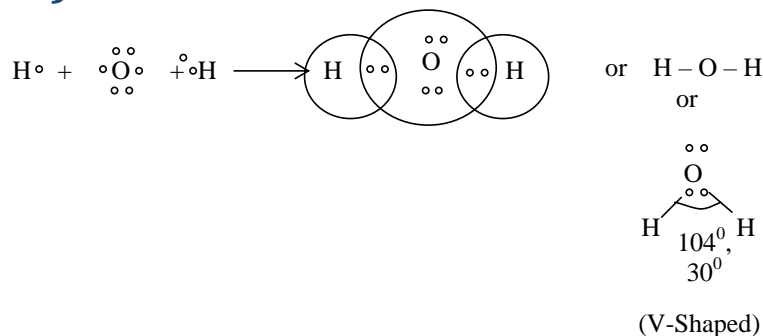


•  $\text{CO}_2$ :

•  $\text{NH}_3$  (Pyramidal):

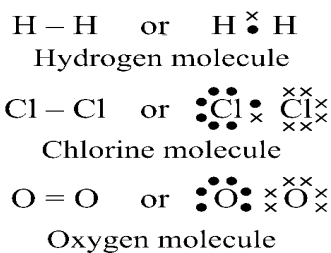


•  $\text{H}_2\text{O}$  (Angular) :



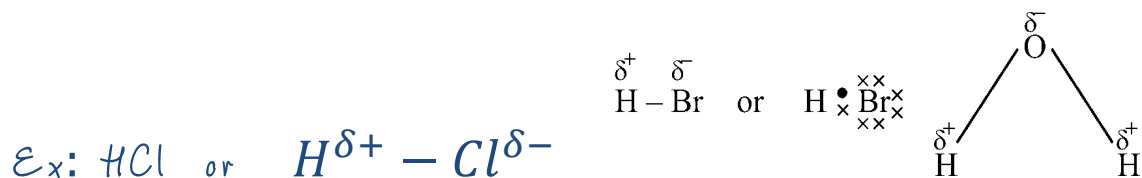
Based on nature of atoms b/w electrons, covalent bonds divided into

1. **Non-Polar Covalent Bonds:** Here bond is formed between similar atoms, shared pair of electrons lies almost in the centre and electron cloud is uniformly distributed around the two atoms.



2. **Polar Covalent Bonds** bond is formed between dissimilar atoms having different electro negativities, the bond pair is displaced towards more electronegative atoms creating partial positive charge on the less

electronegative atom and partial negative charge on more electronegative atom. Such a bond develops some ionic character.



## SESSION - 4

**AIM 1]** To introduce properties of covalent compounds

2] To introduce dative bond

3] To introduce Fajan's rules

### Characters of Covalent compounds

\* **Constituents:** They are made with discrete molecules and strong bonding forces exist between the atoms of a covalent compound.

\* **Physical State:** They occur as liquids or gases or soft solids (e.g., sulphur, phosphorus and iodine).

The various molecules are held together by weak van der Waal's forces.

\* **Solubility:** They dissolve in non-polar solvents (organic solvents) like ethanol, ether, benzene, chloroform etc. and insoluble in polar solvents. Some of the covalent compounds like alcohols, amines dissolve in water due to hydrogen bonding.

\* **Electrical Conductivity:** Covalent compounds contain neither ions nor mobile electrons, so they are unable to conduct electricity in either the solid, liquid or gaseous state.

\* **Melting and Boiling Points :** is low bcz in covalent compounds, molecules are held together by weak van der Waal's forces.

Some giant molecules (eg. diamond, SiC & Silica have high MP and BP.

\* **Nature of Reaction:** is molecular reactions which are slow and complex.

\* Covalent compounds show structural and space isomerism because covalent bonds is rigid and directional.

**Covalency :** It is defined as the number of electrons contributed by an atom of the element for sharing with other atoms to achieve noble gas configuration.

If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

**Variable valency in covalent bonds :**

(1) Variable valencies are shown by those elements which have empty orbitals in outermost shell.

(II) Lone pair electrons gets excited in the subshell of the same to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

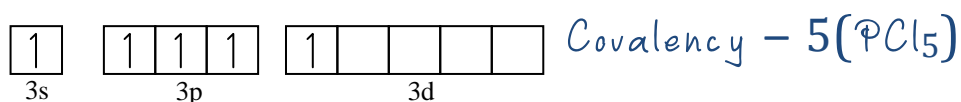
(III) The energy required for excitation of electrons is called promotion energy.

(IV) Promotion rule – Excitation of electrons in the same orbit.

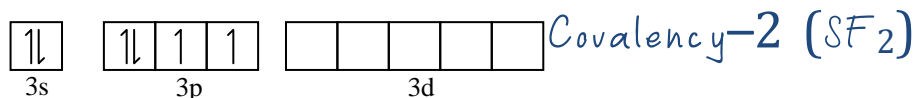
(a) Phosphorus → Ground state



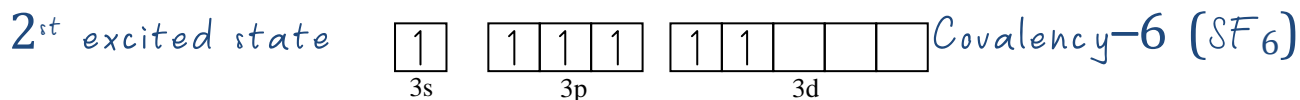
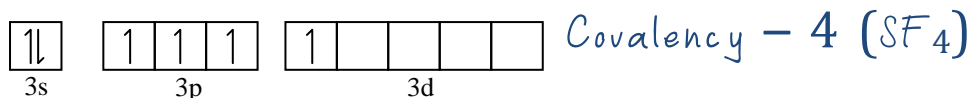
Phosphorus → Excited state



(b) Sulphur → Ground state.



Sulphur → Excited state 1<sup>st</sup> excited state

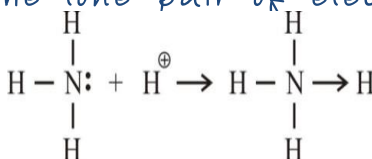


So variable covalency of S is 2, 4 & 6.

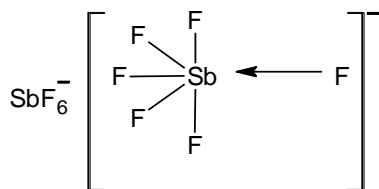
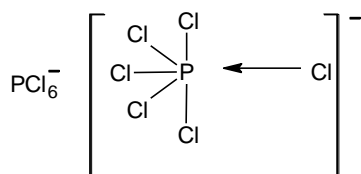
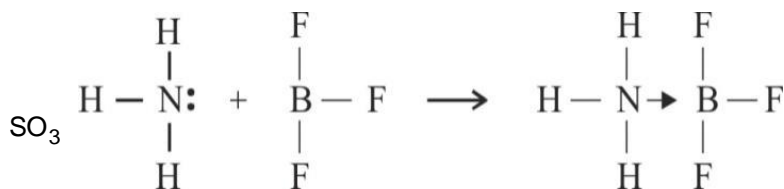
CO-ORDINATE BOND OR DATIVE BOND “ a covalent bond in which both electrons of the shared pair are contributed by one of the two atoms”. It is represented by an arrow ( $\rightarrow$ ) pointing its head towards the acceptor atoms.

The atom which supplies the electron pair (a lone pair) is called **donor (Lewis base)** and the other atom accepting the share in this lone pair is called the **acceptor (Lewis acid)**.

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



**Ex:  $NH_3$  reacts with  $BF_3$  by its lp, to form a complex  $[NH_3 \rightarrow BF_3]$ .**



Comparison of ionic, covalent & coordinate compounds

Property	Ionic	Covalent	Coordinate
binding force	Between ions strong (coulombic)	Between molecules smaller (Vander Waal's)	in between
mp/bp	High	less than ionic	in between
condition	conductor of electricity in fused state & in aqueous solution	bad conductor	Greater than covalent
solubility in polar solvent (H <sub>2</sub> O)	High	Less	in between
Solubility in non polar solvent (ether)	Low	High	in between
6. Physical state	generally solid	liquid & gaseous	solid, liquid gas

## POLARISATION OF IONS

### (Fajan's Rule) (Covalent nature in ionic bond)

In ionic compound, cation approaches an anion closely, positive charge on the cation attracts the electron cloud of the anion towards itself due to electrostatic force of attraction.

At the same time the cation also tends to repel the positively charged nucleus of the anion. As a result electron cloud of the anion no longer remains symmetrical and elongated towards the cation is called deformation or Polarization of the anion by the cation and the anion is said to be polarised.

The ability of a cation to polarise a nearby anion is called its polarization power.



Polarizability is the ability of anion to get polarised by the cation.

- Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.

i.e., Polarisation  $\propto$  Covalent character

## Factors affecting the polarisation of an ion: (Fajan's Rule)

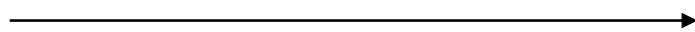
- Charge on the ions: Charge on the cation increases, its tendency to polarize the anion increases and covalent nature increases in ionic compound.

Whereas with the increasing charge of anion, its ability to get polarized, by the cation, also increases.

i.e., Polarisation  $\propto$  charge on cation anion

Charge on cation  $\propto$  Polarisation (covalent character)

eg. NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>
Na <sup>+</sup>	Mg <sup>++</sup>	Al <sup>+++</sup>	Si <sup>++++</sup>



- Charge on cation increases
- Covalent character increases
- Ionic character decreases (M.P. decreases)

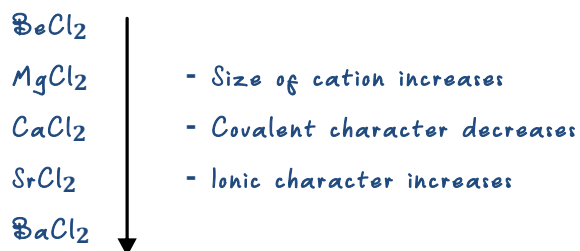
Charge on anion  $\propto$  polarisation  $\propto$  covalent nature  $\propto \frac{1}{M.P.}$

- Among PbCl<sub>2</sub> and PbCl<sub>4</sub> having charges +2 and +4 respectively. PbCl<sub>4</sub> shows covalent nature.
- Among NaCl, Na<sub>2</sub>S, Na<sub>3</sub>P, the charge of the anions are increasing, so order of covalent character is NaCl < Na<sub>2</sub>S < Na<sub>3</sub>P
- Size of the cation: Smaller the size of cation more will be the polarizing power and higher is its covalent nature.



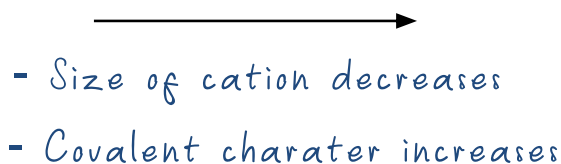
$$\text{Polarisation} \propto \frac{1}{\text{size of cation}}$$

- In a group -



Greatest polarising power of  $\text{Be}^{2+}$ , shows its maximum covalent character.

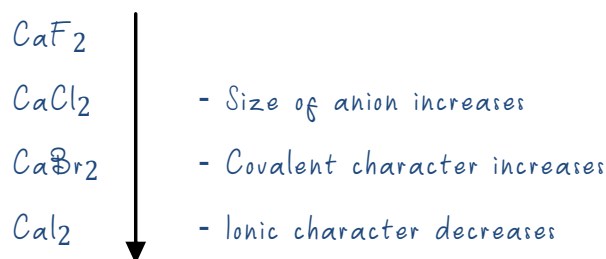
- In a period -  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Si}^{+4}$



- Size of anion: Larger the size of the anion, polarized by the cation and covalent character increases.

$$\text{Polarisation} \propto \text{size of anion}$$

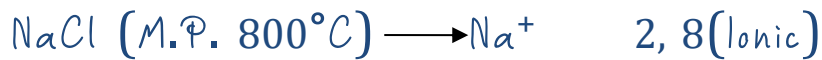
For example, in the case of halides of calcium, the covalent character increases from  $\text{F}^-$  anion to  $\text{I}^-$  anion i.e.



Similarly,  $\text{AlF}_3$     $\text{AlCl}_3$     $\text{AlBr}_3$     $\text{AlI}_3$  →  
 Covalent character increases as the size of the halide ion increases

- Nature or Electronic configuration of cation :-

Polarisation capacity of cation having pseudo inert gas configuration is high. If the size of cations is same than that of cation having inert gas configuration.



$\text{Cu}^+$  and  $\text{Na}^+$  both the cation (Pseudo & inert) have same charge and size but polarising power of  $\text{Cu}^+$  is more than  $\text{Na}^+$ .

So  $\text{CuCl}$  has more covalent character than  $\text{NaCl}$ .

SESSION - 5

**AIM** - To introduce VBT

Valency Bond Theory: VBT was proposed by Heitler and London. It was modified by Pauling and Slater. (According to this theory, a covalent bond is formed by overlapping of atomic orbitals).

- A covalent bond is formed by overlapping of unpaired atomic orbitals of two atoms.

After overlapping both orbitals got common region of electron density.

- Overlapping of orbitals causes delocalisation of electrons which in turn, lowers the energy and increases the stability.

Resulting bond acquires a pair of electrons with opposite spins to get stability.

- The strength of the bond depends on the extent of overlapping. Overlapping of orbitals is higher, the bond formed is stronger.

Order of overlapping  $s-s > s-p > p-p$

The direction of the bond formed is the direction in which the bonding orbitals are oriented.

- As the value of  $n$  increases, bond strength decreases.

$$1-1 > 1-2 > 2-2 > 2-3 > 3-3$$

If  $n$  is same  $2p-2p > 2s-2p > 2s-2s$

$$1s-2p > 2s-2p > 3s-3p$$

- Orbitals can overlap in 2 ways,

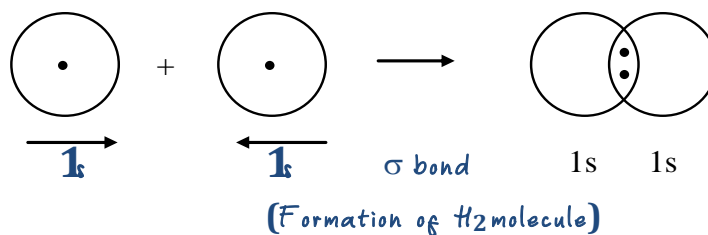
Axial overlapping results in **sigma ( $\sigma$ ) bond** here atomic orbitals overlap along the inter-nuclear axis and involve end to end or head on overlap. Here electron cloud is cylindrically symmetrical about inter-nuclear axis. The electrons constituting sigma bond are called sigma electrons.

### Three types of axial overlapping

- s-s overlapping - Overlapping of two half-filled s-orbitals of the atoms approaching to form a bond s-s  $\sigma$  bond.

#### Formation of $H_2$ molecule:

Hydrogen atom has one electron in 1s orbital.  $H \rightarrow (1) 1s^1$ . This orbital having unpaired electron overlaps axially with 1s orbital of another H atom to form a sigma bond. H-H molecule is thus formed.



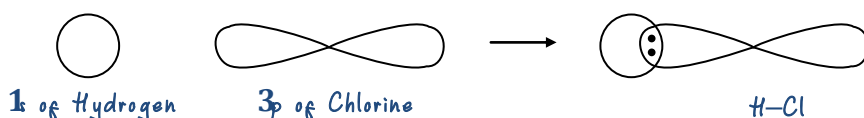
- s-p overlapping. involves overlapping of half-filled s-orbital of the one atom with half-filled p-orbital of the other, bond formed is called s-p bond.

Formation of HCl molecule:

Electronic configuration of H is  $1s^1$  with  $1s$  orbital.

Electronic configuration of chlorine is  $1s^2 2s^2 2p^6 3s^2 3p^5$  with unpaired electron in  $3p_z$  orbital.

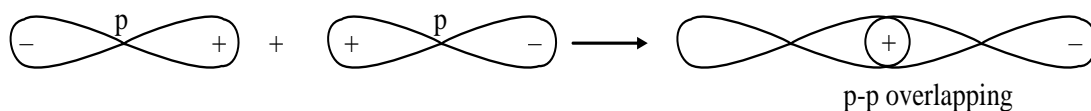
- Hydrogen's  $1s$  orbital and chlorine's  $3p_z$  orbital overlap with each other axially to form a sigma bond.



- p-p overlapping involves overlapping of half-filled p-orbitals of the two atoms. The bond so formed is called p-p bond.

Formation of Cl<sub>2</sub> molecule:

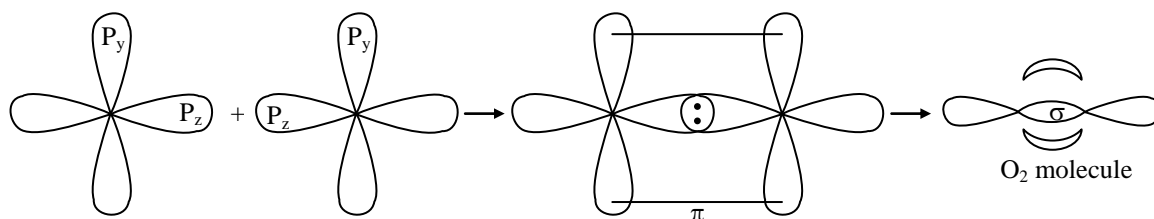
The electronic configuration of chlorine atom is  $1s^2 2s^2 2p^6 3s^2 3p^5$  with an unpaired electron in  $3p_z$  orbital.  $3p_z$  orbital of two chlorine atoms overlap with each other axially to form a sigma bond.



- Side ways overlapping of orbital is called  $\pi$  (Pi) bond. Here electrons are oriented above and below the inter nuclear axis.

- Formation of O<sub>2</sub> molecule: Electronic configuration of oxygen  $1s^2 2s^2 2p^4$ . It has 2 unpaired electrons in  $2p_y$  and  $2p_z$  orbitals.

$2p_x$  orbitals of each oxygen atoms overlap each other axially to form a sigma bond,  $2p_y$  orbitals of the oxygen atoms are perpendicular to the axis. So they overlap laterally to form  $\pi$  bond. Thus  $O = O$  is formed.



- $\sigma$  bond stronger than  $\pi$  bond due to higher overlapping of orbitals.
- In a  $\sigma$  bond, the electrons are oriented along the inter nuclear axis but in a  $\pi$  bond,
- Free rotation of molecule about  $\sigma$  bond is possible but free rotation of molecule about  $\pi$  bond is not possible.

<u>Sigma Bond</u>	<u>Pi Bond</u>
It is a stronger bond.	It is a weaker bond.
It can exist independently.	It exists along with bond
It allows the free rotation of bonded atoms.	It restricts the free rotation of bonded atoms.
The electron cloud of sigma bond is along the inter nuclear axis of the bonded atoms.	The electron cloud of the bond lies above and below this axis.
All orbitals s, p, d..... can form sigma bond.	Except 's' orbital, all other orbitals can form bond
Both pure and hybrid orbitals can form bond.	Hybrid orbitals cannot form bond
This bond is formed by the axial overlapping of orbitals.	This is formed by the lateral overlapping of orbitals.

## SESSION – 6

**AIM** - To introduce VSEPR Theory

### VALENCE SHELL ELECTRON PAIR REPULSION THEORY:

VSEPR theory was proposed by Gillespie and Nyholm. This theory helps us to predict the shape of covalent molecules based on the repulsive interactions of valence electrons.

- The shape of the molecule depends upon the number and nature of electron pairs present in the valency shell of the central atom.
- Electron pairs around the central atom of a molecule repel one another bcz negative charge on the electron cloud.
- In order to minimise the repulsion and to maximise the stability, valence electron pairs arranged away from each other around the central atom in a space.
- Central atom in a molecule surrounded with 2 types of electrons.
  - Bonding or shared electrons(bond pair)
  - Non-bonding electrons(lone pair)
- Bond pair of electrons are under the influence of two nuclei but the lone pairs are under the influence of only one nucleus. Hence lone pairs are spread around the central atom and occupy more space
- If central atom surrounded with only bond pair electrons, molecules shows definite geometry.

If central atom surrounded by at least one lone pair electrons, molecules shows altered or distorted or indefinite geometry.

ie. the original bond angle will disturbed due to repulsion between lone pair of electrons. Bond angle  $\propto \frac{1}{\text{No. of lone pair of electron}}$

- The various repulsive forces experienced by these electron pairs is of the order l.p - l.p > l.p - b.p > b.p - b.p repulsions

### Shape of molecule having only bond pairs

<u>No. of bp e<sup>-</sup></u>	<u>Shape</u>	<u>Molecule</u>
2	Linear	BeF <sub>2</sub> , BeCl <sub>2</sub> , CO <sub>2</sub>
3	Triangular	BF <sub>3</sub> , BCl <sub>3</sub> , SO <sub>3</sub> , CO <sub>3</sub> <sup>2-</sup>
4	Tetrahedral	CH <sub>4</sub> , CCl <sub>4</sub> etc
5	Trigonal bipyramidal	PF <sub>5</sub> , PCl <sub>5</sub> etc
6	Octahedral	SF <sub>6</sub> , SiF <sub>6</sub> <sup>2-</sup>
7	Pentagonal bipyramidal	IF <sub>7</sub>

### Shape of molecule having bond pairs as well as lone pair electrons.

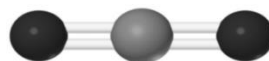
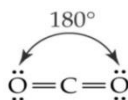
bond pairs	lone pairs	Total No.	Shape of Molecule		Example
			basic shape	actual shape	
2	1	3	Triangular	Angular	SnCl <sub>2</sub> , SO <sub>2</sub>
3	1	4	Tetrahedral	Pyramidal	NH <sub>3</sub> , H <sub>3</sub> O <sup>+</sup>
2	2	4	Tetrahedral	Angular	H <sub>2</sub> O
4	1	5	Folded square	See Saw	SF <sub>4</sub>
3	2	5	Trigonal bipyramidal	T-shaped	ClF <sub>3</sub>
2	3	5	Trigonal bipyramidal	Linear	XeF <sub>2</sub>
5	1	6	Octahedral	Square pyramidal	IF <sub>5</sub> , BrF <sub>5</sub>
4	2	6	Octahedral	Square planar	XeF <sub>4</sub>



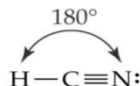
## GEOMETRY OF MOLECULES

- **Two Charge Clouds:** When there are two charge clouds, as in carbon atoms (two double bonds) and HCN (one single bond and one triple bond), the clouds are far apart or in opposite directions. Thus, CO<sub>2</sub> and HCN are linear molecules with bond angles of 180°.

A CO<sub>2</sub> molecule is linear, with a bond angle of 180°.

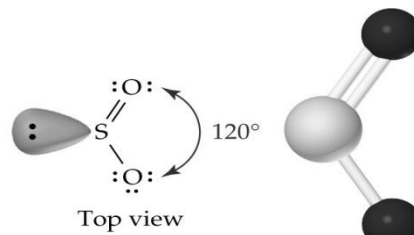


An HCN molecule is linear, with a bond angle of 180°.



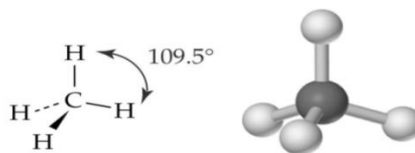
- **Three Charge Clouds:** When 3 charge clouds, as in carbon atom of formaldehyde (two single bonds and one double bond) and the sulfur atom of SO<sub>2</sub> (one single bond, one double bond, and one lp), the clouds are farthest apart when they lie in the same plane and point to the corners of an equilateral triangle with bond angle 120° rather than 180°.

An SO<sub>2</sub> molecule is bent with a bond angle of approximately 120°.



- **Four Charge Clouds:** is occurs on the central atoms in CH<sub>4</sub> (four single bonds), NH<sub>3</sub> (three single bonds and one lone pair), and H<sub>2</sub>O (two single bonds and two lone pairs), the clouds are farthest apart if they extend toward the corners of a regular tetrahedron with bond angle 109.5°.

A methane molecule is tetrahedral, with bond angles of  $109.5^\circ$ .



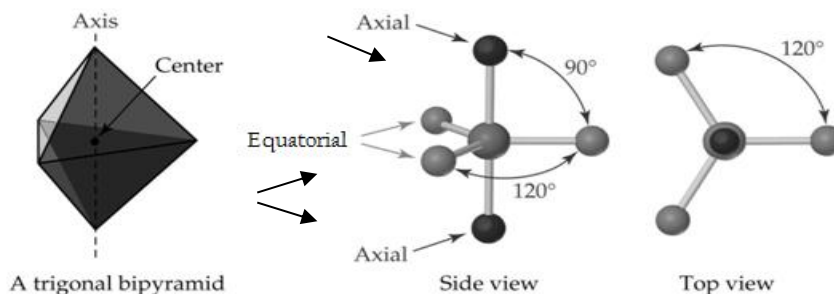
An ammonia molecule is trigonal pyramidal, with bond angles of  $107^\circ$ .



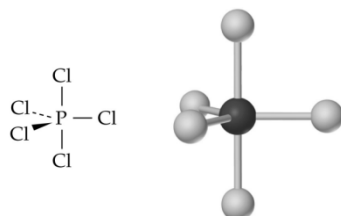
A water molecule is bent, with a bond angle of  $104.5^\circ$ .



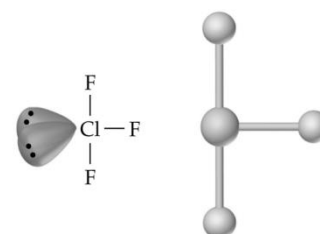
- Five Charge Clouds: found in central atoms in  $\text{PCl}_5$ ,  $\text{SF}_4$  and  $\text{ClF}_3$  are oriented toward the corners of trigonal bipyramidal. Three clouds lie in a plane and point toward the corners of an equilateral triangle, the fourth cloud points directly up, and the fifth cloud points down:



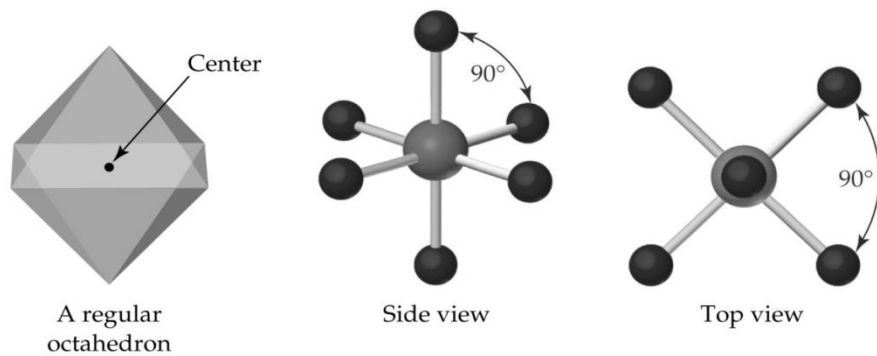
A  $\text{PCl}_5$  molecule is trigonal bipyramidal.



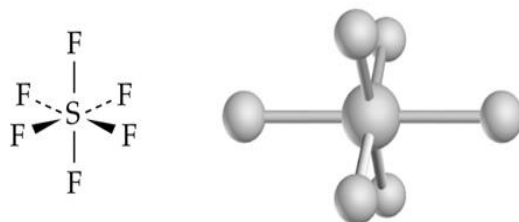
A  $\text{ClF}_3$  molecule is T-shaped (turn  $90^\circ$  to see it).



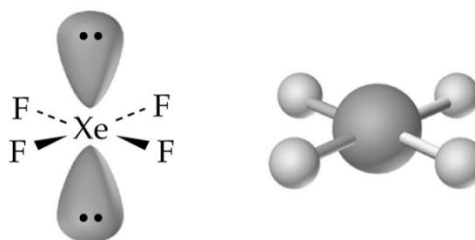
- Six Charge Clouds: shows regular octahedron,



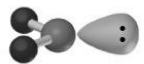

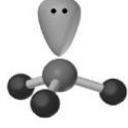
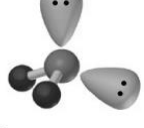


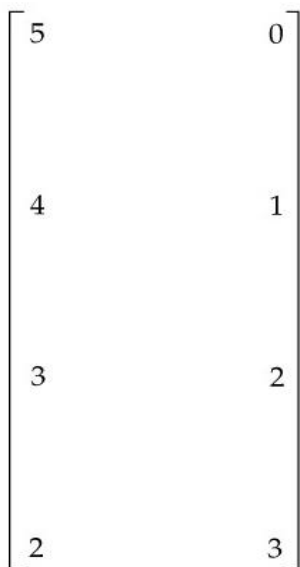
An  $\text{SF}_6$  molecule is octahedral.



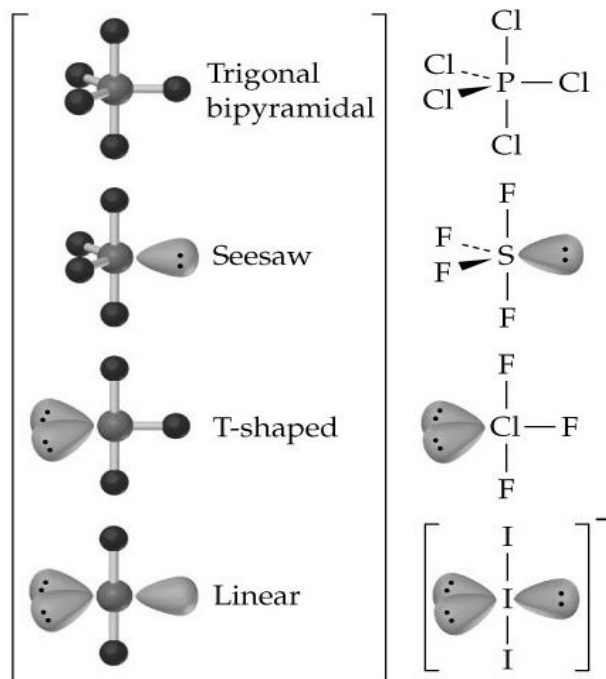
An  $\text{XeF}_4$  molecule has a square planar shape.



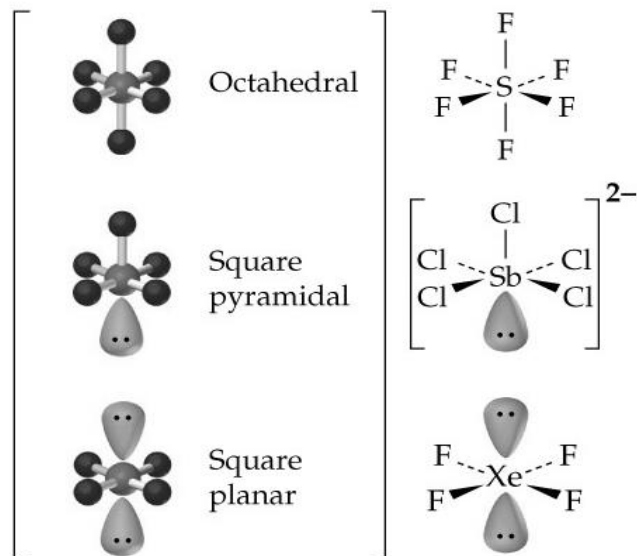
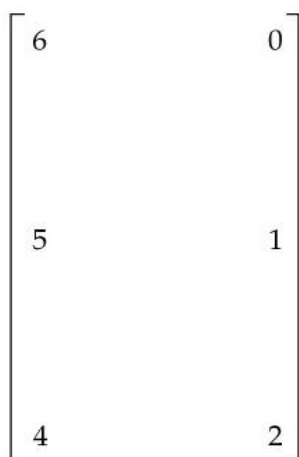
Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	 Linear	$O=C=O$
$\left[ \begin{array}{c} 3 \\ 2 \end{array} \right]$	0	3	 Trigonal planar	$H-C=O$
	1		 Bent	$O-S$
$\left[ \begin{array}{c} 4 \\ 3 \\ 2 \end{array} \right]$	0	4	 Tetrahedral	$H-C-H$
	1		 Trigonal pyramidal	$H-N-H$
	2		 Bent	$H-O$



5



6



## SESSION - 7 AND 8

**AIM** - To introduce hybridization

### HYBRIDIZATION

The intermixing up of pure atomic orbitals of an atom having nearing energies to give a set of equal number of identical hybrid orbitals of same energy is called Hybridization.

This is a hypothetical concept and was proposed by Pauling and Slater

### Rules for Hybridization:

- Atomic orbitals of an atom can intermix
- Atomic orbitals having nearing energy can intermix
- Vacant, half-filled or completely filled atomic orbitals can intermix to form hybrid orbitals
- No. of hybrid orbitals formed is equal to number of atomic orbitals intermixing
- Hybrid orbitals are identical in shape and have same energies but differ in orientation in space.
- The electrons are redistributed in these hybrid orbitals following Hund's rule and Pauli's exclusion principle
- Atomic orbitals only participating in Hybridization but not electrons.
- Hybrid orbitals form  $\sigma$  bonds, unhybridized orbitals form  $\pi$  bonds. Molecule has a regular geometry, when hybrid orbitals contain shared pair of electrons if one or more lone pairs of electrons in the valence shell, molecule shows **distorted geometry**.
- Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- The hybrid orbitals are oriented in space as far apart as possible. Thus, they help in determining the shape or geometry of a molecule.

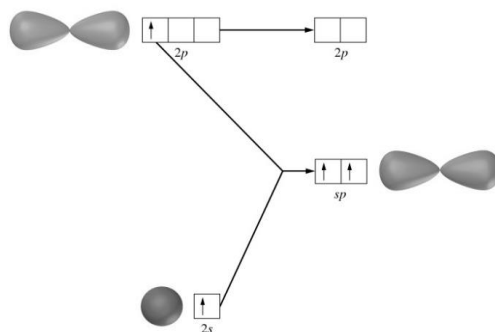
## Difference between hybridisation & overlapping

<u>Overlapping</u>	<u>Hybridisation</u>
<ul style="list-style-type: none"> <li>• It occurs between orbitals of two atoms</li> <li>• Only half filled orbitals takes part in overlapping</li> <li>• It occurs during bond formation bond formed after hybridization</li> <li>• Orbital of different energies may participate in excited states.</li> <li>• Molecular orbitals are formed</li> </ul>	<ul style="list-style-type: none"> <li>• It occurs among orbitals of the same atom</li> <li>• Any type of orbital can participate</li> <li>• Process, just before overlapping.</li> <li>• It may take place in ground or in excited state In ground state— <math>\text{NH}_3</math>, <math>\text{NCl}_3</math>, <math>\text{PH}_3</math>, <math>\text{PCl}_3</math>,</li> <li>• Hybridised orbitals are formed</li> </ul>

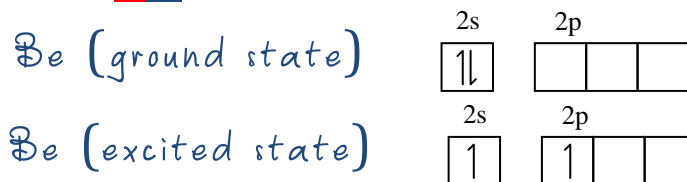
## TYPES OF HYBRIDISATION:

### • sp Hybridization:

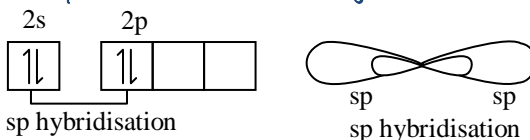
One s & one p orbital intermix to form two sp hybrid orbitals. This process is called sp hybridization. sp-hybridised orbitals of equivalent shapes and energies and arrange in straight line (linear shape) with angle of  $180^\circ$ . Each sp hybrid orbital having 50% s-character and 50% p-character



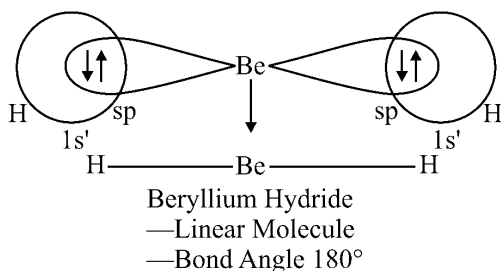
Example:  $\text{BeH}_2$  - central atom is  $\text{Be}$ .



$\text{Be}$ -atom accepts 2 electrons from  $\text{H}$  in  $\text{BeH}_2$ ,

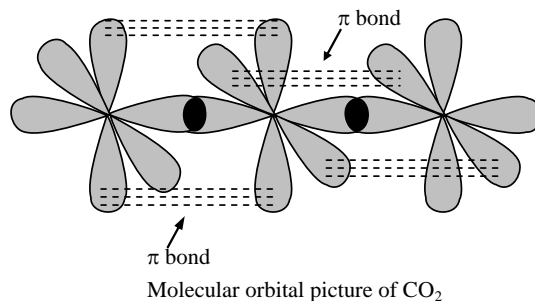


These two  $sp$  hybrid orbitals of  $\text{Be}$  overlap axially with the  $1s^1$  orbitals of 2  $\text{H}$  atoms to form 2 sigma bonds with linear in shape and bond angle  $180^\circ$



$\text{CO}_2$  Molecule ( $\text{O} = \text{C} = \text{O}$ ) : Here  $\text{C}$  has two  $sp$  hybrid orbitals & two unhybridised  $p$  orbitals. It shows linear in shape with  $180^\circ$  bond angle.





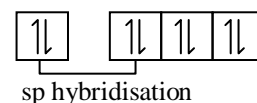
Bond length between C-

O bond is reduced due to the presence of  $\pi$  bond.

$C\equiv C$  [ $H-C_A \equiv C_B-H$ ] Here each C atom contains two sp hybrid orbitals & two unhybridised p orbitals



C atom accepts four electrons from H & C



- sp hybrid orbital of each C overlaps to give sigma bond C - C.
- The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bonds between C - H.
- The two unhybridised p orbitals of each C atom ( $p_y$  and  $p_x$ ) overlap laterally or sideways to form two pi ( $\pi$ ) bonds.

Therefore in  $H-C_A \equiv C_B-H$

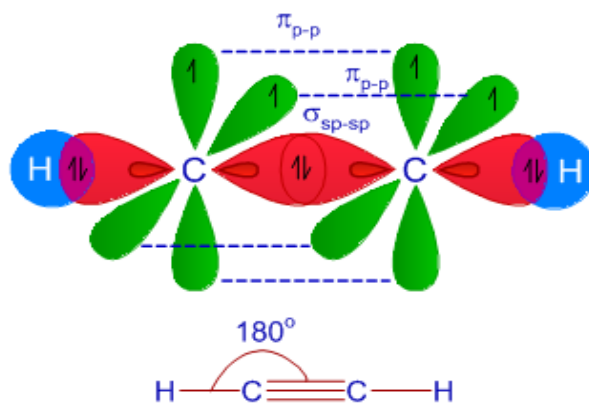
sigma bond between  $C_A - C_B$  is formed sp - sp overlapping

sigma bond between  $C_A - H$  is formed sp - s overlapping

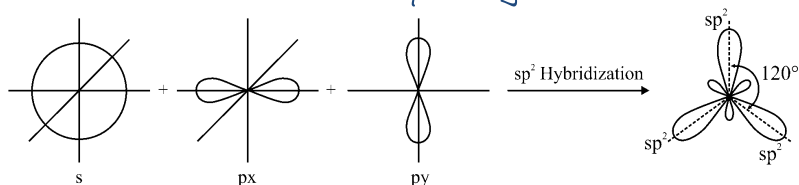
sigma bond between  $C_B - H$  is formed sp - s overlapping

pi bond between  $C_A - C_B$  is formed :  $p_y-p_y, p_x-p_x$  overlapping

- Each C atom forms two sigma bonds but in  $C_2H_2$  3 sigma bonds
- Each C atom forms two  $\pi$  bonds. Total  $\pi$  bonds in  $C_2H_2$  are two
- Total number of bonds in acetylene are :  $3\sigma + 2\pi$  bond = 5 bonds



- sp<sup>2</sup> Hybridisation: is intermixing of one s and two p orbitals to give 3 sp<sup>2</sup> hybrid orbitals is called sp<sup>2</sup> hybridisation.

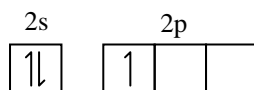


3 sp<sup>2</sup>-hybrid orbitals lie in the same plane, directed towards corners of equilateral triangle with 120° bond angle between them. sp<sup>2</sup> hybrid orbitals shows 33.3% of s-character, 66.7% of p-character.

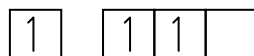
### Example: - BF<sub>3</sub>

In BF<sub>3</sub> molecule the central atom is B electronic configuration is in

B (ground state)

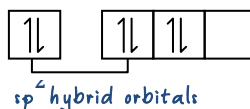


B (excited state)

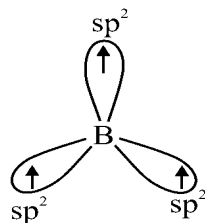


B atom accepts 3 electrons

From 3 F atom ∴ in BF<sub>3</sub>



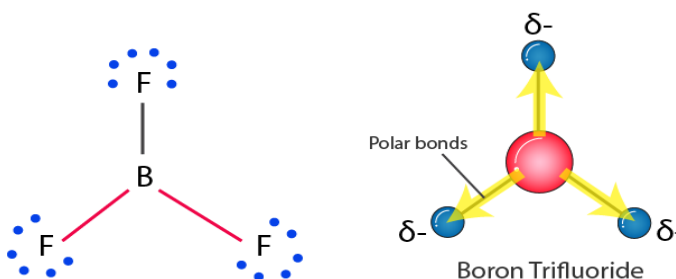
One S orbital and two P orbitals of B atom intermix to form 3 sp<sup>2</sup> hybrid orbitals. These 3 hybrid orbitals orient in space in a planar triangular manner with bond angle 120°



These three hybrid orbitals overlap axially with  $2p_z$  orbitals of 3F atoms to form 3 sigma bonds

### Hybridization of $BF_3$

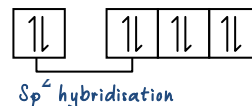
BYJU'S  
The Learning App



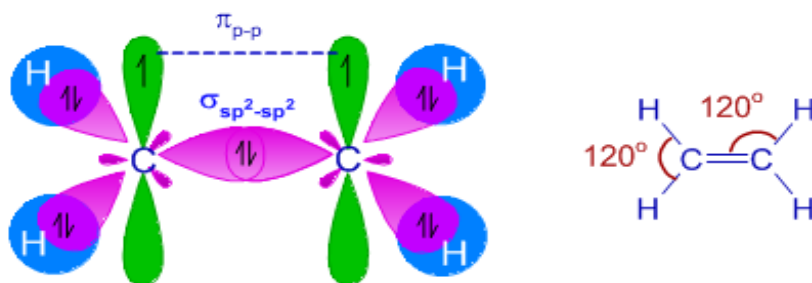
**Ethylene ( $C_2H_4$ )**. Here each C atom contains three  $sp^2$  hybrid orbitals & one unhybridised p orbitals arranged in trigonal manner with bond angle  $120^\circ$



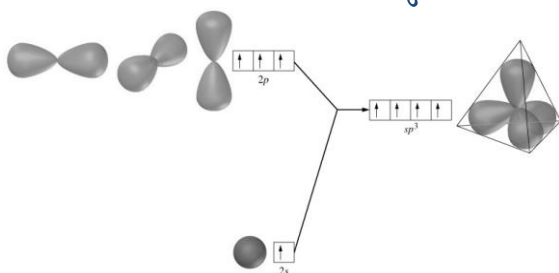
$C$  atom accepts four electrons from H & C



- $sp^2$  hybrid orbital of each C overlaps to give sigma bond C - C.
- The remaining two  $sp^2$  hybrid orbital of each C atom overlaps with s-orbital of two H atoms, forming 2 sigma bonds between C - H.
- The one unhybridised p orbital of each C atom ( $p_x$ ) overlap laterally or sideways to form one pi( $\pi$ ) bonds.
- Each C atom forms 3 sigma bonds but in  $C_2H_4$  5 sigma bonds
- Each C atom forms one  $\pi$  bond. Total  $\pi$  bonds in  $C_2H_2$  are two
- Total number of bonds in ethene are :  $5\sigma + 1\pi$  bond = 6 bonds



- sp<sup>3</sup> Hybridisation**: is intermixing of one s and 3 p orbitals to form 4 sp<sup>3</sup> hybrid orbitals is called sp<sup>3</sup> hybridisation. Formed hybrid orbitals oriented in **tetrahedral manner** with angle between them is 109° 28'. sp<sup>3</sup> hybrid orbital shows 50% of s and 50% of p characters.

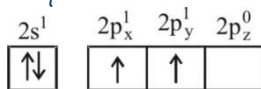


### Example: CH<sub>4</sub> (methane)

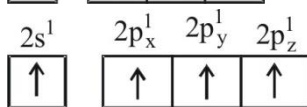
In CH<sub>4</sub>, the central atom is C. Electronic configuration of



C (ground state)

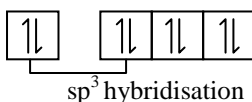


C (excited state)



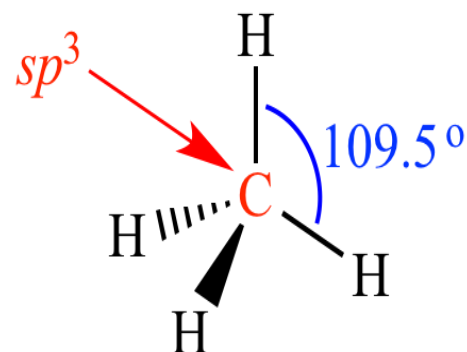
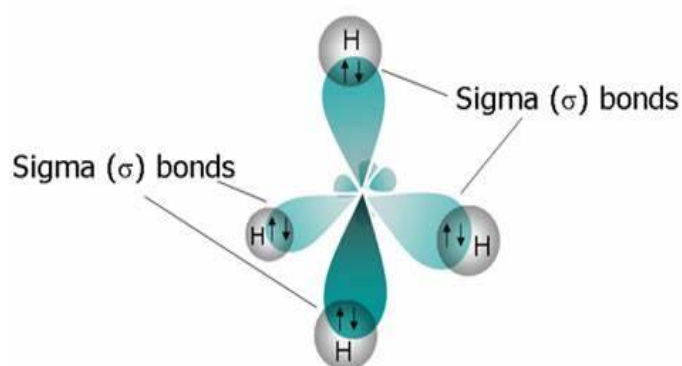
C atom share four electrons

with 4 hydrogen atoms



- One 's' orbital and three p orbitals of C intermix to form 4 sp<sup>3</sup> hybrid orbitals. The hybrid orbitals orient in space tetrahedrally with bond angle 109° 28'.

- These 4  $sp^3$  hybrid orbitals overlap with  $1s$  orbitals of four H atom to form 4 sigma bonds



### Note:

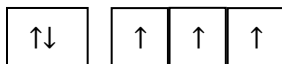
- In organic compounds, wherever C forms 4 sigma and zero pi bonds, it is  $sp^3$  hybridised.
- When C forms 1  $\pi$  bond, it is  $sp^2$  hybridized.
- When C forms 2  $\pi$  bonds, it is  $sp$  hybridised.

Find the hybridization of all c atoms in the following

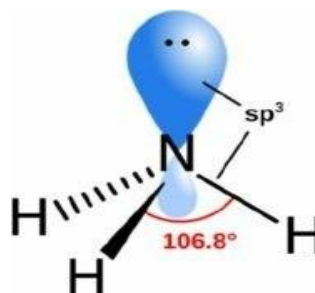
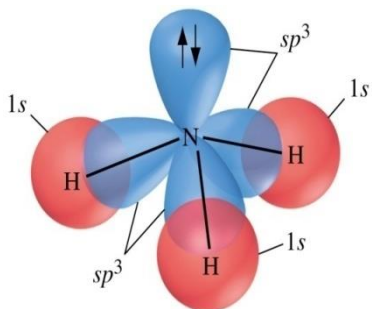
- $CH_2 = CH - CH_2 - CH_3$   
 $sp^2 \quad sp^2 \quad sp^3 \quad sp^3$
- $CCl_4$  - All carbon atoms shows  $sp^3$
- $CH_2 = C = CH_2$   
 $sp^2 \quad sp \quad sp^2$
- $CH_2 = CH - CH = CH_2$   
 $sp^2 \quad sp^2 \quad sp^2 \quad sp^2$

Ammonia (NH<sub>3</sub>) molecule In NH<sub>3</sub> the central atom is N.

$$\text{It's G.E.C} = 2s^2 2p^3$$



- One fully filled s and three half filled p orbitals intermix to form 4 sp<sup>3</sup> hybrid orbitals
- After hybridization Nitrogen with 5 valence electrons has 3 unpaired e<sup>-</sup> in 3 sp<sup>3</sup> hybrid orbitals and a lone pair in the fourth one.
- The three H s - orbitals each are having an unpaired electron overlap with the 3 sp<sup>3</sup> hybrid orbitals of N-atom. Thus 3 N — H electron pair bonds are formed
- Due to the presence of lone pair, the bond angle decreases to 107° due to lp - bp and bp - bp interactions and shows pyramidal shape.

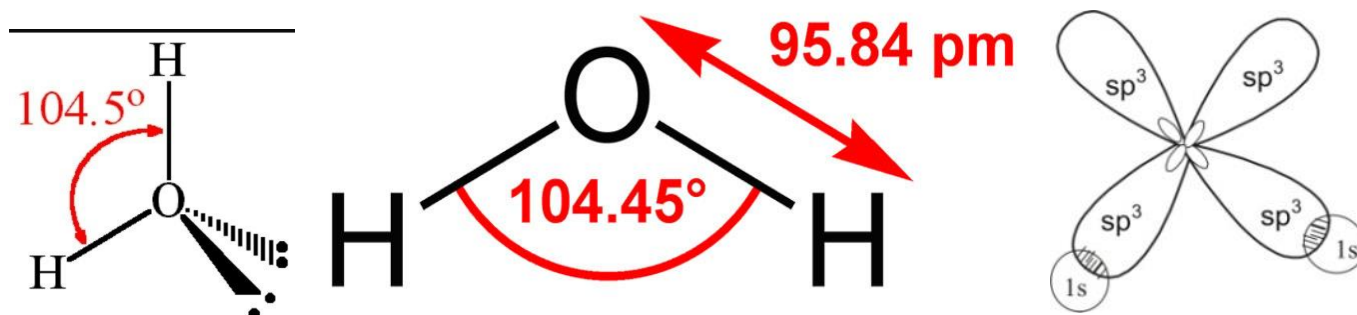


• H<sub>2</sub>O molecule: In H<sub>2</sub>O the central atom is O.

$$\text{Its G.E.C is } 2s^2 2p_x^2 2p_y^1 2p_z^1$$

- One s and three p orbitals intermix to form 4 sp<sup>3</sup> hybrid orbitals Oxygen with 6 valence electrons has 2 unpaired e<sup>-</sup> in two sp<sup>3</sup> hybrid orbital and two lone pair in remaining two.

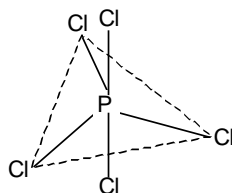
- The two  $1s$  orbitals of H each are having an unpaired  $e^-$  overlap with  $sp^3$  hybrid orbitals of Oxygen atom. Thus two O-H sigma bonds are formed.
- Due to the presence of two lps, the shape is distorted to **angular or bent-V** shape and bond angle is decreased from  $109^\circ 28'$  to  $104^\circ 30'$



•  $sp^3d$  Hybridisation :

- Here one s orb three p and one d orbital are mixed to give **five** new hybrid orbitals which are equivalent in shape and energy called as  $sp^3d$  hybrid orbitals.
- Out of these five orbitals, three hybrid orbitals are at  $120^\circ$  angle present on the plane and two hybrid orbitals are perpendicular to the plane, shape of molecule becomes is **trigonal bipyramidal**.

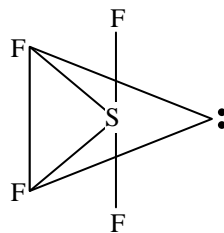
(a) Five sigma and zero lp electron : trigonal bipyramidal  
 $PF_5$ ,  $PCl_5$ ,  $PBr_5$ ,  $PI_5$ ,  $AsF_5$ ,  $AsCl_5$ ,  $SbCl_5$ ,  $SbF_5$  etc.



(b) Four sigma bonds and one lone pair of electron :

$SF_4$ ,  $SeF_4$ ,  $TeF_4$ ,  $PoF_4$ ,  $PF_4^-$ ,  $SbF_4^-$ ,  $SCl_4$ ,  $SeCl_4$ ,  $TeCl_4$  etc.

The shape of all above examples will be irregular tetrahedron.



Structure of  $SF_4$

(c) Three sigma bonds & two lone pair of electrons -  $ClF_3$ ,  $BrF_3$ ,  $IF_3$ ,

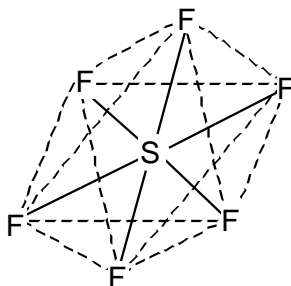
$BrCl_3$ ,  $ICl_3$  etc. The shape of all above compounds is 'T' shape

(d) Two sigma bonds & three lone pair of electrons :  $ICl_2^-$ ,  $I_3^-$ ,  $Br_3^-$ ,  $ClF_2^-$ ,  $IF_2^-$ ,  $BrF_2^-$ ,  $XeF_2^-$ ,  $I_3^-$ ,  $Br_3^-$  shows linear shape.

•  $sp^3d^2$  Hybridisation :

- one s-orbitals, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as  $sp^3d^2$  hybrid orbitals.
- The shape of molecule obtained from above six hybrid orbitals will be symmetrical **octahedral**.
- The angle between all hybrid orbitals will be  $90^\circ$ .

Example :  $SF_6$ ,  $AlF_6^{2-}$ ,  $PF_6^-$ ,  $ICl_5$ ,  $XeF_4$ ,  $XeOF_4$ ,  $ICl_4^-$ ,





Shape of molecules or ions involving hybridization with bond pair electrons

Hybridization	Bond angle	Shape of molecules	Example
$sp$	$180^\circ$	Linear	$\text{BeF}_2, \text{BeCl}_2, \text{CO}_2, \text{CS}_2, \text{HgCl}_2, \text{MgCl}_2, \text{C}_2\text{H}_2$
$sp^2$	$120^\circ$	Trigonal Coplanar	$\text{BF}_3, \text{BCl}_3, \text{BH}_3, \text{AlCl}_3, \text{SO}_2, \text{SO}_3, \text{C}_2\text{H}_4, \text{NO}_3^-, \text{CO}_3^{2-}$
$sp^3$	$109^\circ 28'$	Tetrahedral	$\text{SiCl}_4, \text{CH}_4, \text{SnCl}_4, \text{SO}_4^{2-}, \text{ClO}_4^-$
$sp^3d$	$120^\circ, 90^\circ$	Trigonal bipyramid	$\text{PCl}_5, \text{PF}_5, \text{SbCl}_5$
$sp^3d^2$	$90^\circ$	Octahedral	$\text{SF}_6, \text{SnCl}_6^{2-}, \text{PF}_6^-, \text{SeF}_6$
$sp^3d^3$	$90^\circ, 72^\circ$	Pentagonal bipyramid	$\text{IF}_7$
$dsp^2$	$90^\circ$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}, [\text{PtCl}_4]^{2-},$

Geometry of molecules or ions involving hybridization with lone pair of electrons

Hybridization	No. of lone pair of electrons	Bond angle	Shape of molecule	Examples
$sp^2$	1	$< 120^\circ$	Angular or V shape	$\text{SnCl}_2, \text{SO}_2, \text{NO}_2^-$
$sp^3$	1	$< 109^\circ 28'$	Pyramidal	$\text{NH}_3, \text{PH}_3, \text{PCl}_3, \text{AsH}_3, \text{ClO}_3^-$
$sp^3$	2	$< 109^\circ 28'$	V Shaped	$\text{H}_2, \text{H}_2\text{S}, \text{I}_3^+$
$sp^3d$	3	$180^\circ$	Linear	$\text{XeF}_2, \text{I}_3^-$
$sp^3d$	2	$180^\circ, 90^\circ$	T shape	$\text{ICl}_3, \text{ClF}_3$
$sp^3d$	1	$186^\circ, 116^\circ$	See saw	$\text{SF}_4, \text{TeCl}_4$
$sp^3d^2$	2	$90^\circ$	Square planar	$\text{XeF}_4$
$sp^3d^2$	1	$90^\circ, 180^\circ$	Square pyramidal	$\text{IF}_5, \text{XeOF}_4$
$sp^3d^3$	1	$72^\circ \& 90^\circ$	Pentagonal pyramid	$\text{XeF}_6$

Method of predicting the Hybrid state of the central atom

Simple Molecule	Polyatomic Anion	Poyatomic Cation
$X = \frac{1}{2}[V + G]$	$X = \frac{1}{2}[V + G + a]$	$X = \frac{1}{2}[V + G - c]$

Hybridisation or  $X = \frac{1}{2}$  [Total number of valence  $e^-$  in the central atom + total number of monovalent atoms - charge on cation + charge on anion]

In the above formulae,

$V$  = No, of monovalent atoms or groups attached to the central atom

$G$  = No, of outer shell electrons in ground state of the central atom

$a$  = Magnitude of charge on anion

$c$  = Magnitude of charge on cation

X	2	3	4	5	6	7
Hybrid state	sp	sp <sup>2</sup>	Sp <sup>3</sup>	sp <sup>3</sup> d	sp <sup>3</sup> d <sup>2</sup>	sp <sup>3</sup> d <sup>3</sup>

Calculate the value of X and decide the hybrid state of central atom as follows

For Example:

<b>PF<sub>5</sub></b>	<b>COCl<sub>2</sub></b>	<b>NH<sub>4</sub><sup>+</sup></b>	<b>ClO<sub>4</sub><sup>-</sup></b>
$X = \frac{1}{2}[5 + 5]$	$X = \frac{1}{2}[2 + 4]$	$X = \frac{1}{2}[4 + 5 - 1]$	$X = \frac{1}{2}[0 + 7 + 1]$
= 5	= 3	= 4	= 4
Hybrid state of P is sp <sup>3</sup> d	Hybrid state of C is sp <sup>2</sup>	Hybrid state of N is sp <sup>3</sup>	Hybrid state of Cl is sp <sup>3</sup>
<b>NO<sub>3</sub><sup>-</sup></b>	<b>IF<sub>5</sub></b>	<b>CO<sub>2</sub></b>	<b>XeF<sub>4</sub></b>
$X = \frac{1}{2}[0 + 5 + 1]$	$X = \frac{1}{2}[5 + 7]$	$X = \frac{1}{2}[0 + 4]$	$X = \frac{1}{2}[4 + 8]$
= 3	= 6	= 2	= 6
sp <sup>2</sup>	sp <sup>3</sup> d <sup>2</sup>	sp	sp <sup>3</sup> d <sup>2</sup>
<b>PCl<sub>6</sub><sup>-</sup></b>	<b>PH<sub>3</sub></b>	<b>SF<sub>3</sub><sup>+</sup></b>	<b>SF<sub>4</sub></b>
$X = \frac{1}{2}[6 + 5 + 1]$	$X = \frac{1}{2}[3 + 5]$	$X = \frac{1}{2}[3 + 6 - 1]$	$X = \frac{1}{2}[4 + 6]$
= 6	= 4	= 4	= 5
Hybrid state	Hybrid state	Hybrid state	Hybrid state
sp <sup>3</sup> d <sup>2</sup>	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>3</sup> d

SESSION - 9**AIM**

- To introduce dipole moment.
- To introduce resonance

**DIPOLE MOMENT ( $\mu$ )**

A polar covalent molecule behaves like a dipole. degree of polarity of a bond or molecule is expressed in dipole moment.

The product of magnitude of negative or positive charge ( $e$ ) on either atom and the distance between them is called dipole moment

Mathematically,

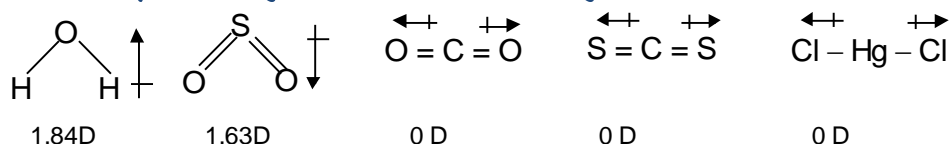
$$\mu = \text{electric charge} \times \text{bond length} = q \times d.$$

Special Unit of dipole moment is **Debye ( $\text{D}$ )**.

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

$$\text{or } 1 \text{ D} = 3.335 \times 10^{-30} \text{ coulomb meter (SI unit)}$$

- Dipole moment is a vector quantity and is indicated by an arrow having a symbol ( $\rightarrow$ ) pointing towards the negative end.



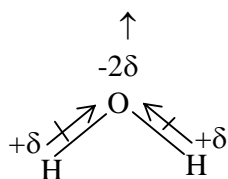
- Greater the dipole moment, greater is the polarity of the bond.
- In case of polar diatomic molecules there is one polar bond so, dipole moment of molecule = dipole moment of the polar bond.

$$\mu_{\text{bond}} = \mu_{\text{molecule}}$$

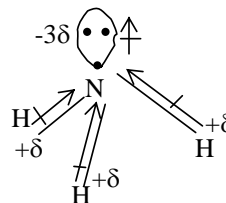
- In case of polyatomic molecules, there are more than one polar bonds, so,  $\mu$  = Resultant dipole moment of all individual polar bonds.

Resultant dipole moment may be calculated by the vectorial addition of the bond moments, as  $\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

e.g. (i) Dipole moment of water is  $1.84\text{D}$ , which is equal to the resultant dipole moment of two O-H bonds.



$$\mu = 1.84 \text{ D}$$



$$\mu = 1.49 \text{ D}$$

Dipole moment of unsymmetrical molecules.

e.g. (ii) Dipole moment of Ammonia is  $1.49\text{D}$ , which is equal to the resultant of dipole moments of three N-H bonds.

- The molecule having zero resultant dipole moment are said to be **non polar molecules** like  $\text{CO}_2$ ,  $\text{BeCl}_2$ ,  $\text{BeF}_2$ ,  $\text{CS}_2$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{CH}_4$ ,  $\text{CCl}_4$  having zero dipole moment but contain polar bond.

The molecules having certain dipole moments are said to be polar molecules like  $\text{H}_2\text{O}$  ( $\mu = 1.84\text{D}$ ),  $\text{NH}_3$  ( $\mu = 1.40\text{D}$ ),  $\text{NF}_3$  ( $0.24\text{D}$ )  $\text{CH}_3\text{Cl}$  ( $1.86\text{D}$ ),  $\text{CHCl}_3$ ,  $\text{PCl}_3$ ,  $\text{SO}_2$  etc.

Molecule has zero dipole moment under the following conditions:

(a) If it has  $sp$  hybridisation (linear geometry) because  $\mu_1 = \mu_2$  and  $\alpha = 180^\circ$

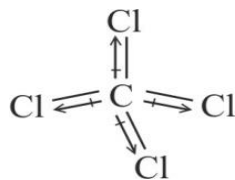
e.g.,  $\text{CO}_2$ ,  $\text{BeCl}_2$ ,  $\text{HgF}_2$  etc  $\text{O} \equiv \text{C} \equiv \text{O}$

(b) If it has  $sp^2$  hybridization (trigonal planar geometry) and the atomic number of the central atom is less than 21:

e.g.,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{SO}_3$  etc.  $\text{F} \leftarrow \text{B} \begin{matrix} \nearrow \text{F} \\ \dots \\ \searrow \text{F} \end{matrix}$

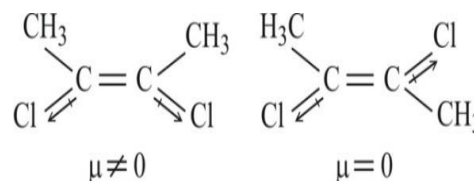
(c) Molecules which have symmetrical tetrahedral structure:

e.g.,  $\text{CCl}_4$ ,  $\text{CH}_4$ ,  $\text{SiCl}_4$  etc



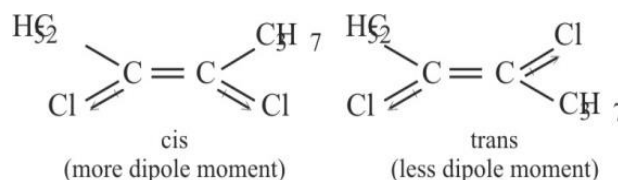
(d) If it is a Trans isomer:

e.g., Trans 1, 2, dichloro butene - 2



If there are 3 different groups around the double bond, then both cis and trans isomers show dipole moment but  $\mu_{\text{trans}} < \mu_{\text{cis}}$

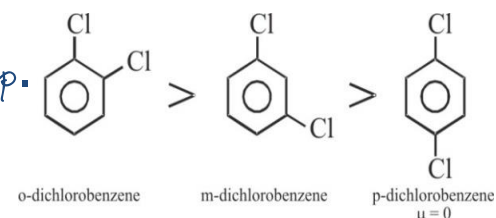
e.g., 3, 4 dichloro heptene - 3



(e) A para isomer has no dipole moment.

e.g., p-dichloro benzene.

Dipole moment follows the order  $o > m > p$ .



### Applications of Dipole moment

Dipole moment used to predict

(a) Geometry of the molecule

If  $\mu = 0$  compound is non polar and symmetrical

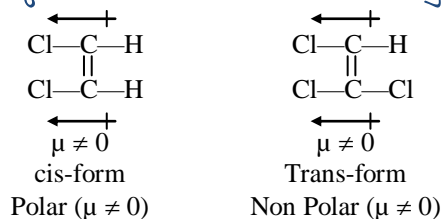
e.g.  $\text{CO}_2$ ,  $\text{BF}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_4$ ,  $\text{BeF}_2$  etc.

If  $\mu \neq 0$  compound will be polar and unsymmetrical.

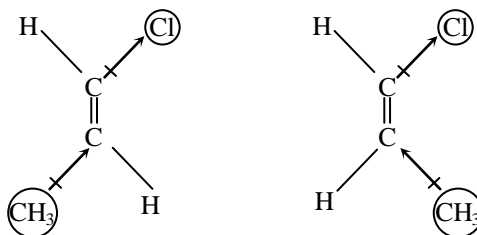
$\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{Cl}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  etc.

(b) cis or trans form of a geometrical isomer.

- Dipole moment of cis isomers is normally higher than trans isomers



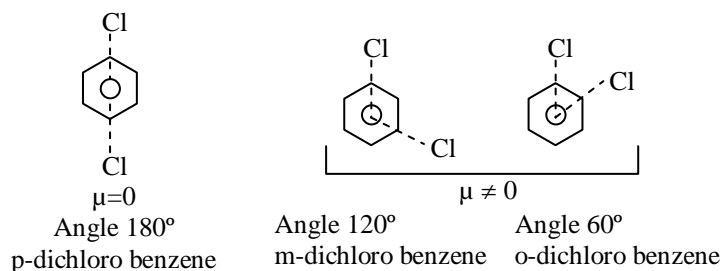
- If two groups have opposite inductive effect than trans-isomer will have greater dipole moment



### (c) Orientation in benzene derivatives or to locate position of substituents in aromatic compounds.

$$\mu \propto \frac{1}{\text{Bond angle}}$$

- If same substituents are present in the symmetrical position of benzene ring compounds will be zero



- As angle between substituents decrease value of  $\mu$  increase

### (d) % ionic character of a bond.

$$\text{Percent ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \times 100$$

$$\% \text{Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoretical value of } \mu} \times 100$$

e.g. Experimental dipole moment for HCl = 1.03

Suppose charge on  $H^+$  or  $Cl^-$ ,  $q = 4.8 \times 10^{-10}$  esu

$$d = 1.27 \text{ \AA}$$

$$\therefore \text{theoretical value of } \mu = q \times d = 4.8 \times 10^{-10} \times 1.27 \times 10^{-8} \\ = 6.09 \text{ D}$$

Thus, % ionic character in H - Cl bond or HCl molecule =  $\frac{1.03}{6.09} \times 100 \approx 16.9$

### (e) Extent of polarity

Molecules having zero dipole moment ( $\mu_R$ ) are nonpolar molecules and those having  $\mu_R \neq 0$  are polar in nature.

e.g.,  $H_2$ ,  $N_2$ ,  $O_2$  etc are nonpolar ( $\mu=0$ ) and HF, HCl, HBr, HI, etc are polar molecules ( $\mu_R \neq 0$ ).

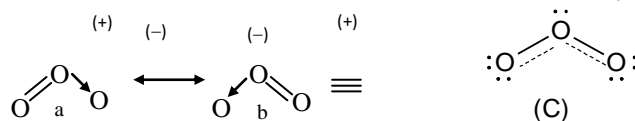
Thus, dipole moment can also be used to distinguish between polar and nonpolar molecules.

## RESONANCE

In certain molecules, a simple Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures.

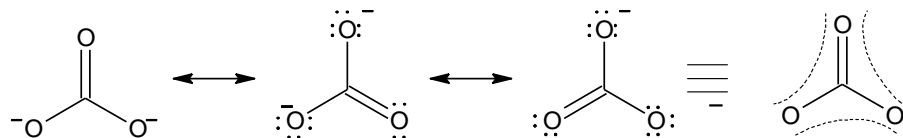
The actual structure is in between of all the contributing structures and is called **resonance hybrid**. The different individual structures are called **resonating structures** or **canonical forms**. This phenomenon is called **resonance**. In representing resonance, a double headed arrow ( $\longleftrightarrow$ ) is put between different contributing structures.

For example we can write two electronic structures of  $O_3$

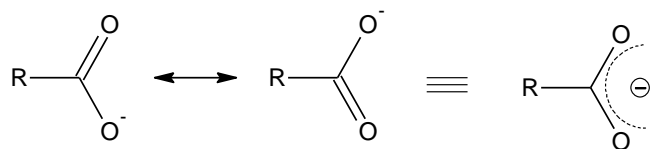


Structures (A) and (B) are called **resonating** or **canonical structures** and C is the **resonance hybrid**. This phenomenon is called **resonance**

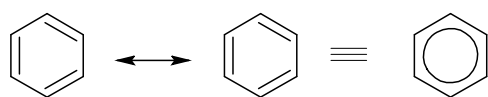
### Some other examples

(i)  $\text{CO}_3^{2-}$  ion

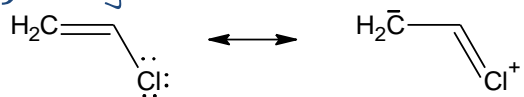
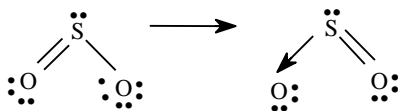
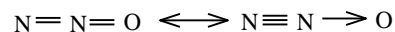
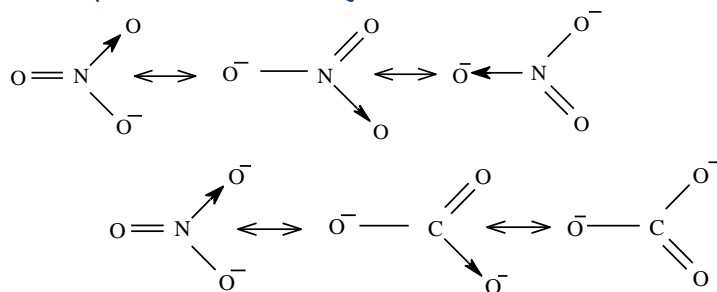
(ii) Carbon-oxygen bond lengths in carboxylate ion are equal due to resonance.



(iii) Benzene

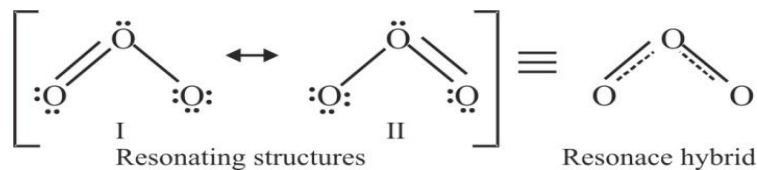


(iv) Vinyl Chloride

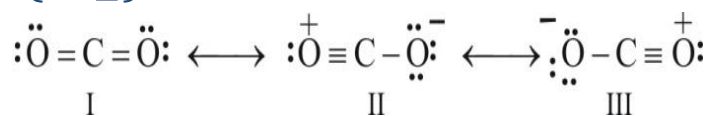
- Sulphur dioxide  $\text{SO}_2$ - Nitrous oxide (dinitrogen oxide),  $\text{N}_2\text{O}$ - Nitric oxide,  $\text{NO}$   $:\dot{\text{N}}=\ddot{\text{O}}:\rightarrow:\ddot{\text{N}}=\ddot{\text{O}}:$ - Nitrate ion,  $\text{NO}_3^-$  (planar, triangular)

$$\text{Bond Order} = \frac{\text{No. of bonds between the same two atoms in all the structures}}{\text{total no. of resonating structures}}$$

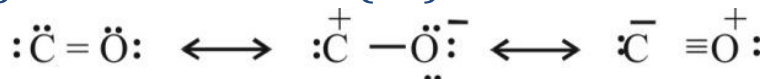


**Examples of Resonance:****(i) Ozone (O<sub>3</sub>)**

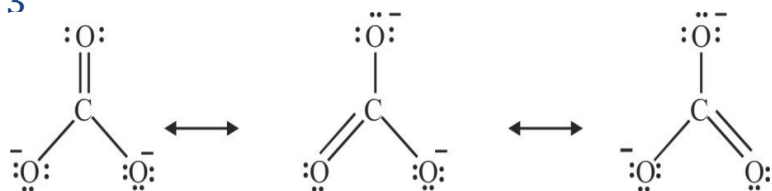
$$\text{Bond Order} = \frac{3}{2} = 1.5$$

**(ii) Carbon dioxide (CO<sub>2</sub>)**

$$\text{Bond Order} = \frac{6}{3} = 2$$

**(iii) Carbon monoxide (CO)**

$$\text{Bond Order} = \frac{6}{3} = 2$$

**(iv) Carbonate ion (CO<sub>3</sub><sup>2-</sup>)**

Resonance explain why all bonds are equivalent in length, energy.

**Resonance energy:** Difference in the energies of the canonical forms and resonance hybrid is called resonance stabilization energy.

The resonance hybrid is more stable than any of the resonating structure. Greater the resonance energy more will be the stability to species.

### Rules for writing Resonating Structures:

- (i) The various resonating structures differ in the position of electrons and not in the relative positions of atoms.
- (ii) All the contributing structures should have the same number of unpaired electrons.
- (iii) The various canonical structures shows same energy.
- (iv) Resonance structures in which the negative charge resides on electronegative atom and positive charge resides on electropositive atom in resonance hybrid
- (v) Resonance structures should be so written that unlike charges reside on adjacent atoms.
- (vi) Resonance structure with greater number of covalent bonds contributes more towards the resonance hybrid.

SESSION - 10

## AIM

1] To introduce bond parameters

2] To introduce formal charge

BOND PARAMETERS

■ Bond Length: The average distance between the nucleus of two bonded atoms is known as bond length, normally it is represented in Å or pm ( $10^{-10}$  cm) or Å<sup>0</sup> ( $10^{-8}$  cm).

- For the same atoms, bond length decreases with the multiplicity of bonds.

$$\text{Bond length} \propto \frac{1}{\text{Number of bond or bond order}}$$



- Bond length decreases with increase in s-character of the hybrid orbital used in bonding.



- Polar bonds are shorter than theoretical non-polar bonds.

Actual H-Cl distance < theoretical H-Cl distance.

- When the size of the atom increases, the bond length increases



■ Bond Energy or bond strength: It is amount of energy required to break one mole of the bonds to separate the bonded atoms in gaseous state.

Factors affecting bond energy:

- Size of the atoms: Larger the size of the bonded atoms, larger is the bond length and lesser is the bond energy.

$$\text{Bond energy} \propto \frac{1}{\text{Atomic size}}$$



- Multiplicity of bonds: For the bond between the same two atoms, bond energy increases with the multiplicity of the bond.

$$\text{Bond energy} \propto \text{Bond order}$$



- The energy required for homolytic cleavage is more than that required for heterolytic.

- Number of lone pairs of electrons:

Greater the number of lone pair of electrons present on the bonded atoms, greater is the repulsive interactions between them and smaller is the bond energy

- Bond Polarity :- Bond energy  $\propto$  polarity



- Hybridisation :- Bond energy  $\propto$  s-character in hybrid orbitals.



- Bond Angle :- The angle between any two adjacent bond is known as bond angle.

It is represented in degree ( $^{\circ}$ ), min ( $'$ ) and second ( $''$ )

Factors affecting the bond angle

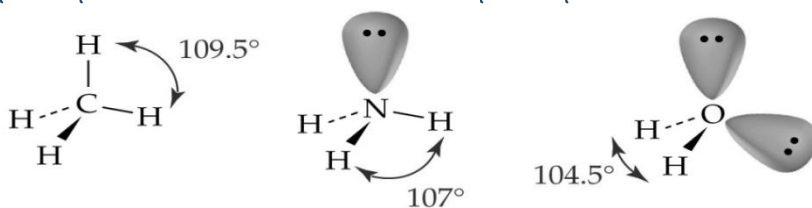
## Following factors can affect bond angle:

- Hybridisation of central atom: % of s character increases bond angle also increases



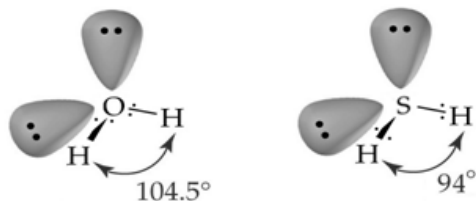
- Presence of lone pair: Then bond angle  $\propto \frac{1}{\text{No. of lone pair}}$

bcz lp-bp repulsion is more than bp-bp



- Electronegativity of central atom: Due to more electronegativity of central atom bond pair get shifted toward it and distance between them decrease thus further bp-bp repulsion increases.

- bond angle  $\propto$  electronegativity of central atom



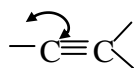
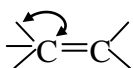
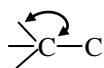
- Multiple bonds: Electron density for double bond is more than in single bond, so repulsion in double bond is more than single bond.

Bond angle  $\propto$  Number of bonds (Bond order)

109°

120°

180°



## FORMAL CHARGE

In a molecule, no charge on the molecule as a whole or in a polyatomic ion (e.g.,  $\text{CO}_3^{2-}$  or  $\text{NH}_4^+$  ion etc.) but charge present on the ion is the charge on the ion as a whole and not on the individual atoms,

Formal charge is the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis Structure. or

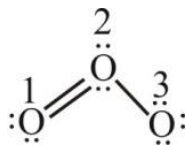
Individual charge possessed by an atom in a molecule.

Formal charge = Valence electrons of the atom - (Shared electrons of that atom + Unshared electrons of that atom).

Formal charge = Valence electrons of the atom - total number of lp electrons -  $\frac{1}{2}$  total number of bonded or shared electrons of that atom.

**Ex. 1]** Calculate formal charge on each O - atom of  $\text{O}_3$  molecule.

Sol: Lewis structure of  $\text{O}_3$  is:



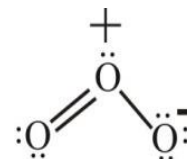
The atoms have been numbered as 1, 2 and 3.

$$\text{Formal charge on end O - atom numbered 1} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$\text{Formal charge on end O - atom numbered 2} = 6 - 2 - \frac{1}{2}(6) = +1$$

$$\text{Formal charge on end O - atom numbered 3} = 6 - 6 - \frac{1}{2}(2) = -1$$

Hence, we represent  $\text{O}_3$  along with formal charges as:



**Ex. 2]** Write the formal charges on atoms in (i) carbonate ion (ii) nitrite ion.

**Sol:** (i) Lewis structure of  $\text{CO}_3^{2-}$  ion is  $\left[ \begin{array}{c} \text{:O:} \\ || \\ \text{:}\ddot{\text{O}}-\text{C}-\ddot{\text{O}}\text{:} \end{array} \right]^{2-}$

Formal charge on C atom =  $4 - 0 - \frac{1}{2}(8) = 0$ , Formal charge on double bonded O atom

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

Formal charge on single bonded O atoms =  $6 - 6 - \frac{1}{2}(2) = -1$

(ii) Lewis structure of  $\text{NO}_2^-$  ion is  $\left[ \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ || \\ \text{:}\ddot{\text{N}}^+\text{:} \\ | \\ \text{:}\ddot{\text{O}}\text{:}^- \end{array} \right]$

Formal charge on N atom =  $5 - 2 - \frac{1}{2}(6) = 0$ ,

Formal charge on double bonded O atom =  $6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on single bonded O atom =  $6 - 6 - \frac{1}{2}(2) = -1$

## SESSION - 11

**AIM** To introduce hydrogen bonding

**HYDROGEN BONDING** is electrostatic force of attraction existing between covalently bonded H atom of one molecule and the electronegative atom of the other molecule.

This bond comes into existence when H atom is directly bonded to highly electronegative atom such as N, O or F.

### Properties and conditions of HYDROGEN BOND

- H should be covalently bonded with high electro-ve element like F, O, N.
- Atomic size of electro-ve element should be small.

Decreasing order of atomic size is  $N > O > F$

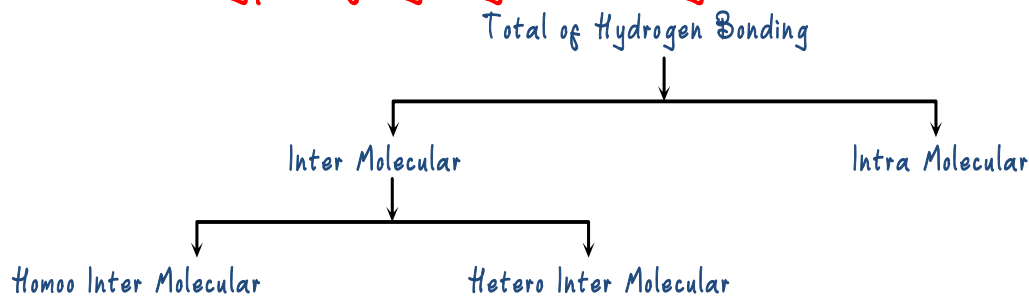
Strength of H-bond  $\propto$  Electronegativity of Z (element)  $\propto \frac{1}{\text{atomic size of Z}}$

- Hydrogen bonding occurs in HCN, due to  $(-C \equiv N)$  triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.



- A hydrogen bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms.
- Hydrogen bond is very weak compared to a covalent bond. The bond energy is in the range of 3-10 kcal/mole.
- Formation of H-bond does not involve sharing of electrons.

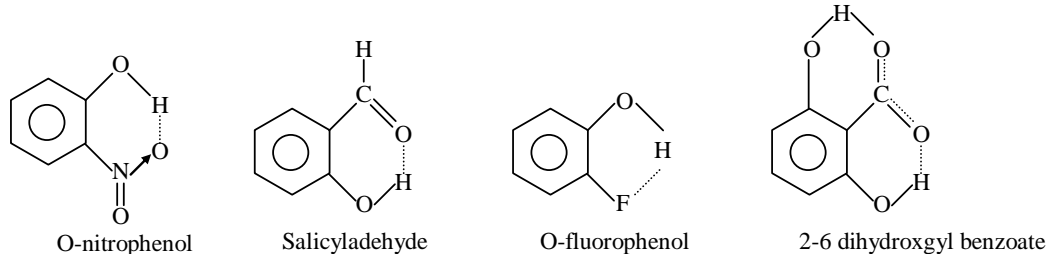
### Types of hydrogen bonding







b) Intra-molecular Hydrogen Bonding here H - bonding takes place when hydrogen and the electronegative atom are present in the same molecule.



### Conditions for formation of intramolecular hydrogen bonding:

- The ring formed should be planar
- Position of the interacting atoms should be such that there is minimum strain in ring formation.

e.g., Intramolecular H-bonding not possible in m- & p- isomers of nitrophenol.

### Effect of intramolecular H-bonding

- It decreases the boiling point of the compound.
- It increases the steam volatile nature of the compound.  
e.g., o-nitrophenol is steam volatile but p-nitrophenol is not.
- It increases the acid strength.  
e.g., salicylic acid is stronger than p- Hydroxybenzoic acid.

SESSION - 12

**AIM** To introduce MOT

MOLECULAR ORBITAL THEORY (MOT) put forward by Hund & Mulliken, to overcome the limitations of VBT (Valence bond theory) was unable to explain

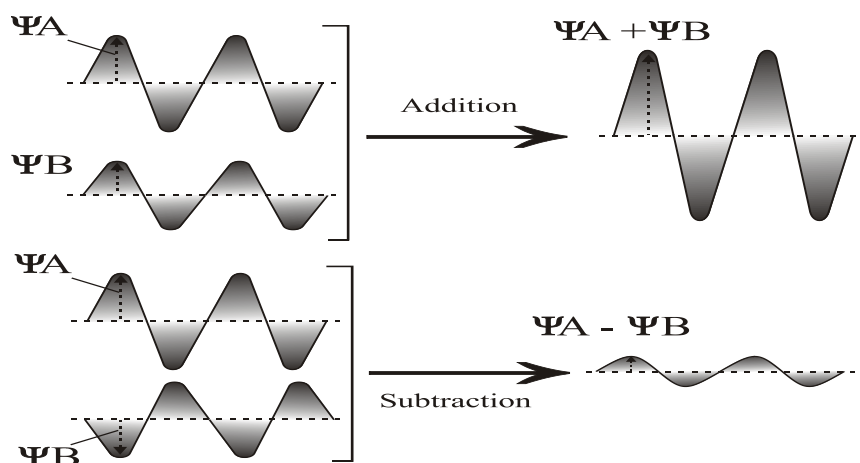
eg. Paramagnetic nature of  $O_2$  molecule, as per VBT ( $:O: :O:$ ) it should be diamagnetic.

According to this theory, all the atomic orbitals of the atoms participating in molecule formation. They all get mixed up to an equivalent number of new orbitals that belong to the molecule now. These are called **Molecular Orbitals**.

This theory is based on principle of

Linear combination of atomic orbitals (LCAO).

- Electron waves nothing but atomic orbitals have positive and negative phase. When waves are combined, they may interact either constructively or destructively.
- If two identical waves are added, they combine constructively to produce the wave with double the amplitude and same wavelength and form two new orbitals called 'bonding molecular orbital' (BMO)
- Conversely, if they are subtracted, they combine destructively to produce the wave with less or zero amplitude gives antibonding molecular orbital' (ABMO).



Suppose  $\psi_A$  and  $\psi_B$  represents the amplitude of electron waves of the 2 atomic orbitals of the atoms A and B respectively, then the situation may be represented as follows:

**Case I:** When the two waves are in phase (constructive interface), so that they add up and the amplitude of the new wave is:

$$\phi = \psi_A + \psi_B$$

The probability of electron density is given by the square of the amplitude, therefore, we have

$$\phi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

i.e.,  $\phi^2 > \psi_A^2 + \psi_B^2$

The molecular orbital formed by the additive effect or constructive interference of the atomic orbitals are called **BMO**.

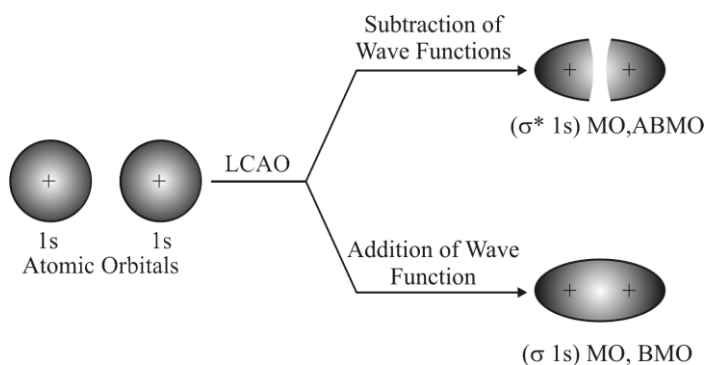
**Case II:** When the two waves are out of phase (destructive interface), the waves are subtracted from each other so that the amplitude of the new wave is:  $\phi = \psi_A - \psi_B$

The probability of electron density is given by the square of the amplitude, therefore, we have

$$\phi^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

i.e.  $\phi_1^2 < \psi_A^2 + \psi_B^2$

The molecular orbital formed by the subtractive effect of the atomic orbitals is called **ABMO**.



Combination of 1s atomic orbital of both atoms

Energy of  $\sigma$  MO is always less than the energy of the atomic orbitals. But energy of the  $\sigma^*$  MO is higher than the energy of atomic orbitals.

$\sigma$  In the  $\sigma$  MO, electron density in the internuclear region is high so the nuclei are shielded from each other and the between the nuclei are very small.

In  $\sigma^*$  MO, the electron density in the internuclear region is very low. As a result, the nuclei are directly exposed to each other i.e., there is very less shielding. Hence the repulsions between the nuclei are very large.

- Electrons present in  $\sigma$  MO contribute towards the stability of molecule where electrons present in  $\sigma^*$  MO destabilize the molecule
- Atomic orbitals participating in combination must have comparable energies.

**Ex:** For homogeneous diatomic molecule,  $1s$  atomic orbital of one atom can combine with  $1s$  atomic orbital of another atom or  $2s$  can combine with  $2s$  and  $2p$  with  $2p$  and so on.

- Combining atomic orbitals must have proper orientation.

i.e. same symmetry about the molecular axis.

**Ex:** Taking  $z$ -axis as the molecular axis,  $2p_z$  orbital of one atom can combine with  $2p_z$  of another atom but not with  $2p_x$  or  $2p_y$  orbitals because of their different symmetry.

- $\sigma$  MO's are represented as  $\sigma, \pi, \delta$  etc. While  $\sigma^*$  MO's are represented as  $\sigma^*, \pi^*, \delta^*$  etc.

Thus  $1s$  atomic orbitals of two atoms combine to form two MO's labeled as  $\sigma 1s$  ( $\sigma$  MO) and  $\sigma^* 1s$  ( $\sigma^*$  MO).

Similarly,  $2s$  atomic orbitals combine to form  $\sigma 2s$  and  $\sigma^* 2s$  of the  $2p$ -orbitals.

If  $z$ -axis is taken as molecular axis,

Combination of two  $2p_x$  or two  $2p_y$  atomic orbitals to form  $\pi(2p_x)$  and  $\pi^*(2p_x)$  or  $\pi(2p_y)$  and  $\pi^*(2p_y)$  molecular orbitals

- Filling of electrons in Molecular Orbitals occurs according to Aufbau principle, Pauli's exclusion principle and Hund's rule.
- The shape of the molecular orbitals depends upon the shapes of combining orbitals.

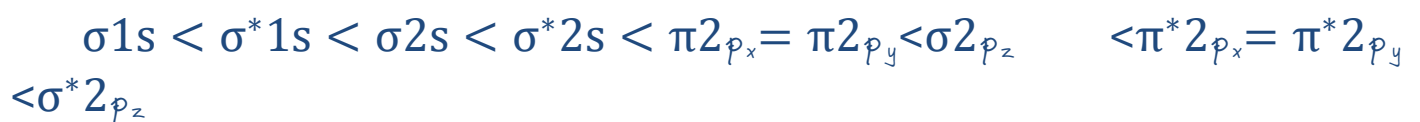
- The presence of one or more unpaired electrons in a molecule shows **paramagnetic nature**. Electronic configuration having all the electrons paired suggests its **diamagnetic nature**.

### Comparison of Bonding molecular orbital & Antibonding molecular orbital

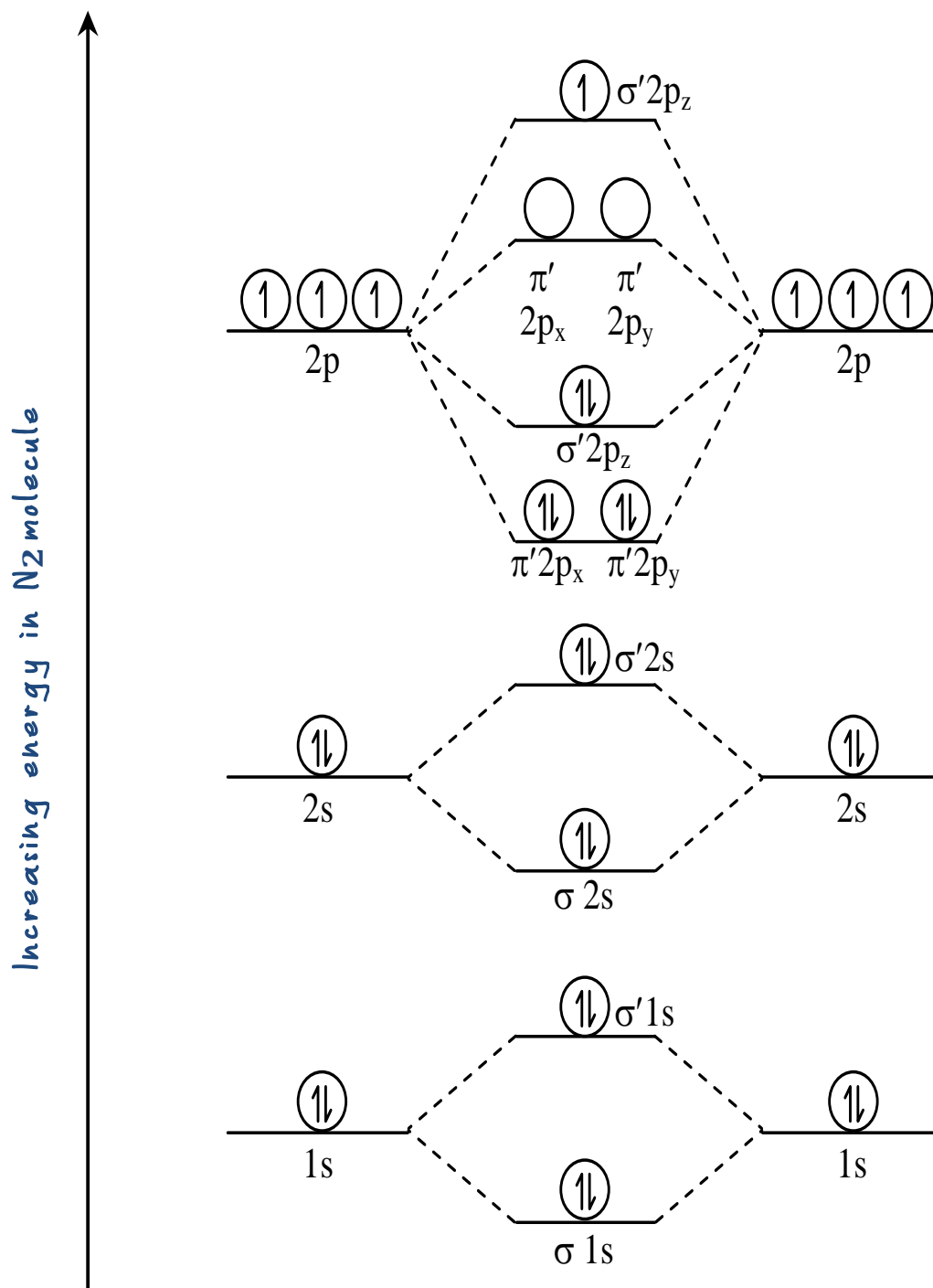
Bonding molecular orbital ( $\sigma MO$ )	Antibonding Molecular orbital
<ul style="list-style-type: none"> <li>- Bonding MO is the result of the linear combination of AO when their wave function are added <math>\Phi = \Psi_A + \Psi_B</math></li> <li>- It does not have node</li> <li>- Charge density increase between two nuclei resulting between two atoms</li> <li>- Energy of <math>\sigma MO</math> is less, hence stable</li> </ul>	<ul style="list-style-type: none"> <li>- <math>\sigma^* MO</math> is resulting of linear combination of AO when their wave function are subtracted <math>\Phi = \Psi_A - \Psi_B</math></li> <li>- It always have a node between two nuclei of bonded atom</li> <li>- Charge density decrease in between two nuclei, leads to repulsion between two atoms.</li> <li>- Energy of <math>\sigma^* MO</math> is high, hence unstable</li> </ul>

### Energy Level Diagram of molecular orbital :

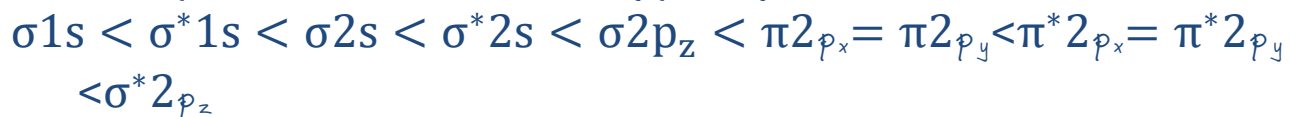
- For diatomic homonuclear molecules such as  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$ ,  $N_2$  is (where the energy difference between 2 s and 2 p-orbitals is large and hence they cannot interact)



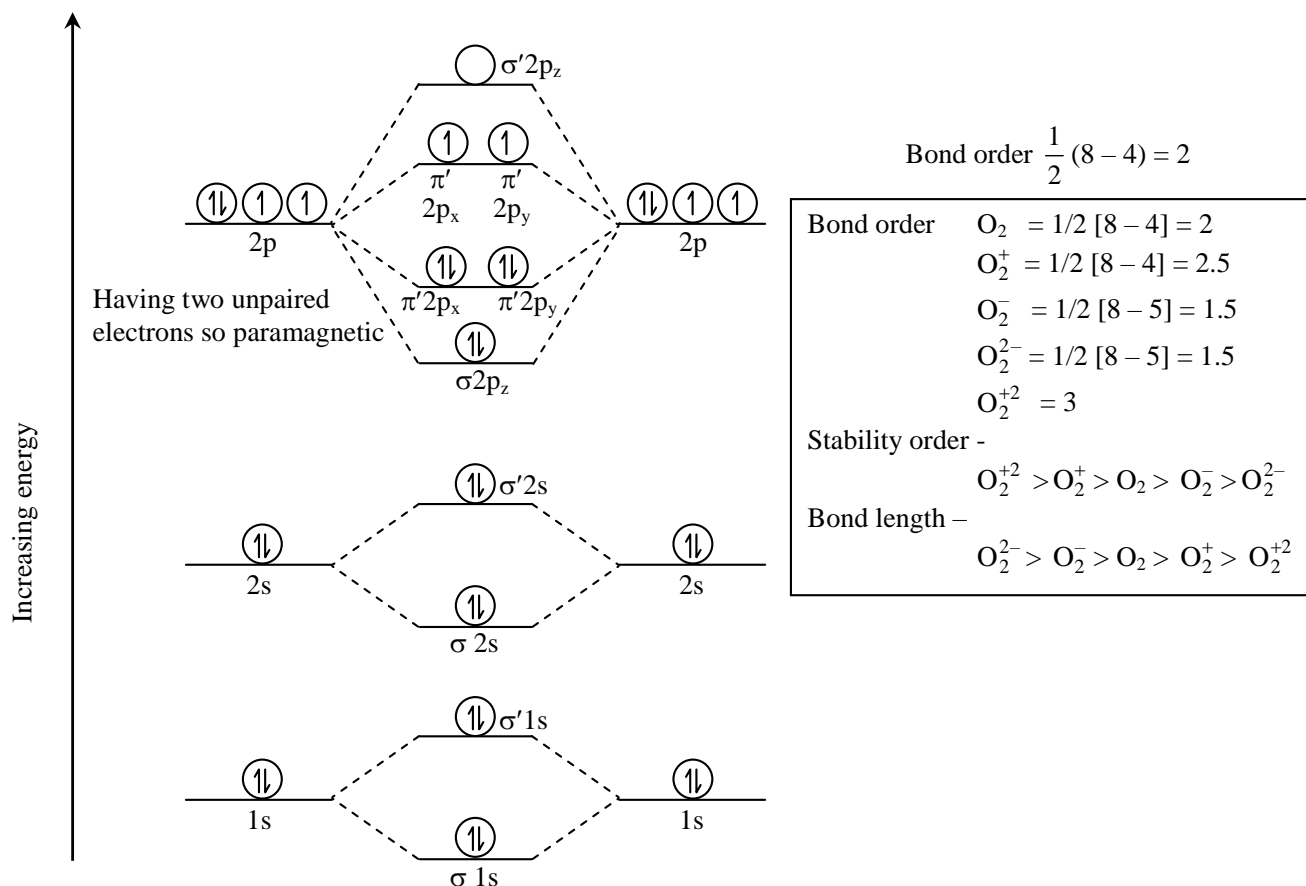
For N<sub>2</sub> type molecule



- For homogeneous diatomic molecules such as  $O_2$ ,  $F_2$ ,  $Ne_2$ , (where the difference in energies between  $2s$  and  $2p$ -orbitals is small and hence they can interact) the energy diagram is



For  $O_2$  type molecule-





INFORMATION FROM MO CONFIGURATIONS

(a) **Bond order (B.O.)** =  $\frac{1}{2} (N_b - N_a)$  or it is defined as half of the difference between the number of electrons present in the bonding and the antibonding orbitals.

Where  $N_b$  = no. of electrons in the bonding MO's

$N_a$  = no. of electrons in the antibonding MO's.

If bond order is more than zero, the molecule/ion exists, otherwise not.

- **Bond dissociation energy** - Higher the bond order, higher is the bond dissociation energy.

- **Stability** - Higher the bond order, greater is the bond stability.

If  $N_b > N_a$  the molecule is stable .bcz greater number of bonding orbitals are occupied than antibonding orbitals, resulting in a net force of attraction.

If  $N_b < N_a$ , the molecule is unstable. Bcz the antibonding influence is greater than the bonding influence, resulting in a net force of repulsion.

If  $N_b = N_a$ , the molecule is again unstable. Bcz the numbers of electrons are equal, the antibonding influence of the electrons in the antibonding molecular orbitals is greater than the bonding influence of the electrons in the bonding molecular orbitals.

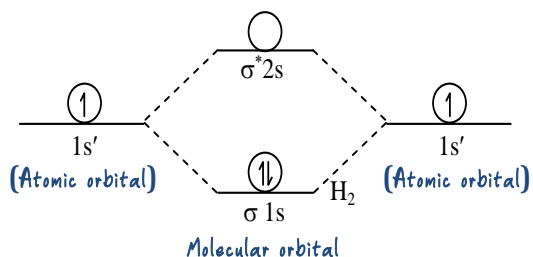
- **Bond length** - Higher the bond order, shorter is the bond length.

(b) **Magnetic properties**: Molecule/molecular ion are **paramagnetic** (atleast one electrons is unpaired) or **diamagnetic** (if all the electrons are paired).

Bonding in molecules :-**(I) H<sub>2</sub> molecule** - Having two H atoms with one electron (1s')

$$\text{M.O. configuration of H}_2 = (\sigma 1s)^2 (\sigma^* 1s)^0$$

$$\text{Bond order} = \frac{1}{2} [N_b - N_a] = \frac{1}{2} [2 - 0] = 1 \text{ i.e. single bond}$$

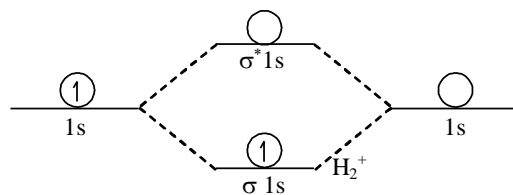
Having paired electron so **diamagnetic**.**(II) H<sub>2</sub><sup>+</sup> ion -**

$$\text{M.O. Configuration of H}_2^+ = (\sigma 1s)^1 (\sigma^* 1s)^0$$

One electron in bonding molecular orbital - **paramagnetic**

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

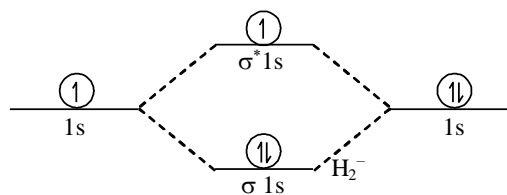
Less stable

**(III) H<sub>2</sub><sup>-</sup> anion -**

$$\text{M.O. configuration} - (\sigma 1s)^1 (\sigma^* 1s)^1$$

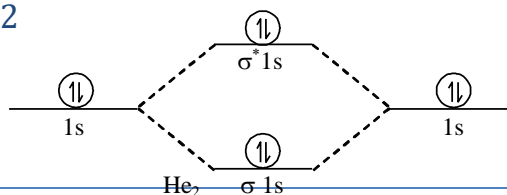
Paramagnetic

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

Stability is less than [H<sub>2</sub><sup>+</sup>] because H<sub>2</sub><sup>-</sup> contain **ABMO** electron**(IV) Helium molecule (He<sub>2</sub>) :**

$$\text{M.O. configuration} (\sigma\sigma 1s)^2 (\sigma\sigma\sigma 1s)^2$$

Diamagnetic



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

Bond order is zero shows no bond between He atoms. So  $\text{He}_2$  molecule does not exist

Stability ( $\text{He}_2$ ) Highly unstable molecule

(V)  $(\text{He}_2^+)$

$$\text{EC of He} = 1s^2, \text{He}^+ = 1s^1.$$

$$\text{MOC} = (\sigma 1s)^2 < (*1s)^1$$

$$\text{Bond order} = \frac{1}{2}$$

Nature – paramagnetic (stable).

(V) **Lithium molecule ( $\text{Li}_2$ )**: EC of Li –  $1s^2, 2s^1$

$$\text{MOC} = (\sigma 1s)^2 < (\sigma^* 1s)^2 < (\sigma 2s)^2, \text{Bond order} = 1$$

Nature = diamagnetic.

(VI) **Beryllium molecule ( $\text{Be}_2$ )** :  $\text{Be} - 1s^2, 2s^2$

$$\text{MOC} = (\sigma 1s)^2 < (\sigma^* 1s)^2 < (\sigma 2s)^2 < (\sigma^* 1s)^2$$

Bond order = 0, nature – diamagnetic (does not exist)

(VII) **Boron molecule ( $\text{B}_2$ )** :  $\text{B} - 1s^2 2s^2 2p^1$

$$\text{MOC} = (\sigma 1s)^2 < (\sigma^* 1s)^2 < (\sigma 2s)^2 < (\sigma^* 2s)^2 < (\pi 2p_x)^1 = (\pi 2p_y)^1$$

$\text{BO} = 1$ , Nature = paramagnetic

x) **Carbon molecule ( $\text{C}_2$ )** :  $6\text{C} - 1s^2 2s^2 2p^2$

$$\text{MOC} = (\sigma 1s)^2 < (\sigma^* 1s)^2 < (\sigma 2s)^2 < (\sigma^* 2s)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\sigma 2p_z)^0,$$

Bond order = 2, Nature = diamagnetic

xi) **Nitrogen molecule (N<sub>2</sub>):**

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

Nature — diamagnetic.

$$\text{BO} = 3,$$

Order of bond order of N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>-</sup>, N<sub>2</sub><sup>2-</sup> is N<sub>2</sub> > N<sub>2</sub><sup>+</sup> = N<sub>2</sub><sup>-</sup> > N<sub>2</sub><sup>2-</sup>

xii) **Oxygen molecule (O<sub>2</sub>) :** O — 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>

Molecular orbital energy level diagram for O<sub>2</sub>

$$\text{MOC} = \text{KK} < (\sigma 2s)^2 < (\sigma^* 2s)^2 < (\sigma 2p_z)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$$

$$\text{BO} = 2, \text{ Nature — paramagnetic}$$

Order of bond order of O<sub>2</sub>, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup> is O<sub>2</sub><sup>2+</sup> > O<sub>2</sub><sup>+</sup> > O<sub>2</sub> > O<sub>2</sub><sup>-</sup> > O<sub>2</sub><sup>2-</sup>

xii) **Fluorine molecule (F<sub>2</sub>) :** F — 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>

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

$$\text{BO} = 1, \text{ Nature diamagnetic (Stable, } \text{BDE} = 151 \text{ kJ mol}^{-1}\text{)}$$

xii) **Neon** molecular does not exist because Bond order is zero.

MO CONFIGURATIONS OF HETERONUCLEAR DIATOMIC SPECIES:

Molecule or ion	Molecular orbital Configuration	Bond order	unpaired Electrons	Magnetic character
CN(13e <sup>-</sup> )	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)\pi(2p_y)^2(\sigma 2p_z)^1$	$\frac{7-2}{2} = 2.5$	1	Paramagnetic
CN <sup>-</sup> (14e <sup>-</sup> )	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)(\pi 2p_y)^2\sigma(2p_z)^2$	= 3.0	Nil	Diamagnetic
NO (15e <sup>-</sup> )	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)\pi(2p_y)^2\sigma(2p_z)^2\pi^*(2p_x)$	$\frac{8-3}{2} = 2.5$	1	Paramagnetic
NO <sup>+</sup> (14e <sup>-</sup> )	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)\pi(2p_y)^2\sigma(2p_z)^2\pi^*(2p_x)$	$\frac{8-2}{2} = 3.0$	Nil	Diamagnetic
NO <sup>2+</sup> (13e <sup>-</sup> )	$KK\sigma(2s)^2\sigma^*(1s)^2\sigma(2p_z)\pi(2p_x)^2)\pi(2p_y)^1\pi^*(2p_x)$	$\frac{7-2}{2} = 2.5$	1	Paramagnetic
CO (14e <sup>-</sup> )	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)\pi(2p_y)^2\sigma(2p_z)^2$	$\frac{8-2}{2} = 3.0$	Nil	Diamagnetic