

## Chemistry : Chemical Bonding

### INTRODUCTION, KOSSEL AND LEWIS APPROACH TO CHEMICAL BONDING

- ❑ The force of attraction which holds the two atoms or ions together in a molecule is called as chemical bond.
- ❑ A chemical bond is atomic attraction which holds the two atoms together.
- ❑ Atoms of an elements have an unpaired electrons, thus they are highly unstable.
- ❑ To achieve more stability with minimum energy atoms can form chemical bond.
- ❑ Inert elements are stable due to the completeness of the octet. Hence every element try to complete octet and try to becomes stable like inert element.
- ❑ Inert elements in periodic table like He, Ne, Ar, Kr, Xe and Rn are stable. Their octet is complete.
- ❑ Remaining elements in periodic table are unstable they are try to becomes stable like inert elements. They have unpaired electrons, thus they can be form chemical bond.
- ❑ The chemical bonds are ionic, covalent, coordinate etc.
- **Chemical bond** : It is a force attraction by which two or more atoms or ions are hold together.  
i.e. Force which holds the atoms together in a molecule is called as chemical bond.
- ❑ Thus, to achieve the stability of the atom with minimum energy and to get configuration like inert elements, atoms of an elements combines together to form a chemical bond.
- **Kossel and Lewis approach to chemical bond.**
- ❑ Kossel and Lewis, proposed electronic theory of valence to explain chemical bond.
- ❑ Only unpaired or valence electrons in an atom take part in the bond formation.
- ❑ Atoms of an elements can gain, lose or shear electrons to complete their octet
- ❑ Thus atom have complete electronic configuration like inert elements.

- ❑ Atom must be contains unpaired electrons.
- **Octet rule** : In the formation of a chemical bond atoms of an element can gain lose or share electrons, so that it achieve the stable configuration like inert element.
- **Types of chemical bonds** :
- (i) **Ionic Bond or Electrovalent bond** : An electrostatic force of attraction between the oppositely charged ions called as ionic bond.
- ❑ It is bond formed due to transfer of an electron from one atom to another atom.
- ❑ e.g. NaCl, KCl, CaCl<sub>2</sub>, NaBr etc.
- ❑ Compounds of I and II group element like Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr and Ba with Cl, Br, F, O, N, S, P are ionic in the nature.
- ❑ In formation of ionic bond, energy release or required is called as crystal lattice enthalpy or energy.  
Energy required to separate one mole of solid ionic compound into gases components OR energy released to form one mole of ionic solid from their gases ions is called as crystal lattice energy.
- ❑ Crystal lattice enthalpy for NaCl is  $-788 \text{ kJ Mol}^{-1}$  or  $788 \text{ kJ Mol}^{-1}$  energy required to separate 1 mole NaCl into  $\text{Na}^+_{(g)}$  and  $\text{Cl}^-$  ions.
- ❑ Higher the charge on cation higher the lattice energy e.g.  $\text{AlCl}_3 > \text{BaCl}_2 > \text{NaCl}$ .
- ❑ As size of cation decreases, lattice energy increases.  $\text{LiF} > \text{NaF} > \text{KF}$
- ❑ If the difference in electronegativity of two atoms more than 1.7 strong covalent bond is formed.
- **Covalent bond**: A bond formed due to equal sharing of an electrons between two atoms is called as covalent bond.
- ❑ In mutual shearing of an electrons two atoms may have same or nearly same electronegativities value.
- ❑ Each bond forms one electron pair. Covalent bond may be single, double or triple.

❑ Energy released called as potential energy.

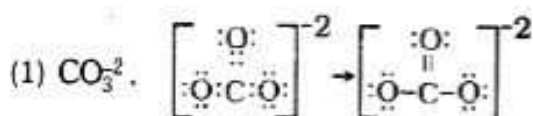
❑ e.g.  $H_2$ ,  $O_2$ ,  $N_2$ ,  $H_2O$ ,  $CCl_4$ ,  $HCl$  etc.

• **Lewis dot and dash structure:**

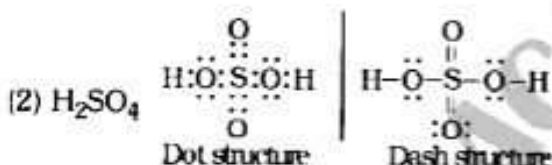
**Steps :**

- (1) Count and add total number of valence electrons of each atom in a molecule.
- (2) Subtract one electron for each positive charge and add one electron for each negative charge present on ion from total number of electrons.
- (3) Write skeletal structure of molecule in which least electronegative atom, is written of all element in central position.
- (4) Place one electron pair between each two atoms indicate forming single bonds. The remaining electron pair are used either multiple bonds as double bond or triple bonds or for lone pairs of electrons in molecule.

e.g.



Total electrons 22+(2negative) =24e <sup>-</sup>		Electron dot structure		Electron dash structure
--	--	---------------------------	--	----------------------------



Total no. of electrons = 32 e<sup>-</sup>

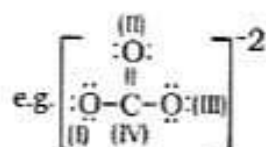
• **Formal charges:**

$$\left[ \begin{array}{c} \text{Formal charge on} \\ \text{an atom in a Lewis} \\ \text{structure} \end{array} \right] = \left[ \begin{array}{c} \text{Total number} \\ \text{of Valence} \\ \text{electrons in free atom} \end{array} \right] -$$

$$\left[ \begin{array}{c} \text{Total number of} \\ \text{non bonding or lone} \\ \text{pair electrons} \end{array} \right] - \frac{1}{2} \left[ \begin{array}{c} \text{Total number of bonding or} \\ \text{shared electrons} \end{array} \right]$$

Total number of non bonding or lone pair electrons

$$F.C = V.E. - N.E. - \frac{B.E.}{2}$$



$$(1) \text{ Formal charge on (I) oxygen} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

$$(2) \text{ Formal charge on (III) oxygen} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

$$(3) \text{ Formal charge on (II) oxygen} = 6 - 4 - 4 \times \frac{1}{2} = 0$$

$$(4) \text{ Formal charge on C atom} = 4 - 0 - 8 \times \frac{1}{2} = 0$$

• **Inadequacies of the octet rule OR Limitations of the octet rule**

- (1) **Incomplete octet molecules :** Molecules in which central atom have less than 8 electrons then they are stable.

e.g.  $BaCl_2$ ,  $BeF_2$ ,  $BH_3$ ,  $AlCl_3$ ,  $AlBr_3$  etc.

- (2) **Expanded octet molecules :** Molecules in which central atom have more than 8 electrons then they are stable.

e.g.  $PCl_5$ ,  $SF_6$ ,  $IF_7$ ,  $OsF_8$ ,  $H_2SO_4$  etc.

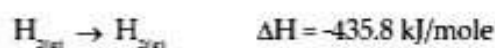
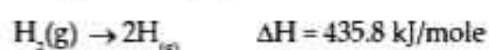
- (3) Octet rule cannot explain energy and reactivity of the molecule.
- (4) Geometry and shape of molecule cannot explain.
- (5) Odd electron species like NO (nitric oxide) and  $NO_2$  (nitrogen dioxide), N and oxygen does not satisfies octet rule, they have odd number of electrons in NO (9e<sup>-</sup>) and in  $NO_2$  (13 e<sup>-</sup>)

• **Bond parameters:**

- (1) **Bond energy or enthalpy**

❑ It is average amount of energy required in kJ/Mol to break a particular bond in a polyatomic molecule to form free gaseous atoms or radicals.

❑ For di-atomic molecules, bond formation energy may be positive or negative value. But bond dissociation energy is always positive value.



- For polyatomic molecules bond formation and bond dissociation energy have different values.



It is obtained as,

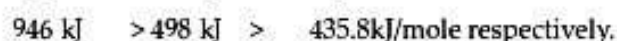


$$\text{Average bond energy} = \frac{502 + 427}{2}$$

$$= 464.5 \text{ kJ/mol}$$

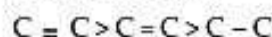
- Bond dissociation energy called as bond energy.
- Bond energy of triple bond > double bond > single bond.

e.g. Bond energy of



- As atomic size of overlapping atoms increases bond enthalpy decreases.

- Number of bonds between two atoms increases bond energy increases.



- Bond enthalpy  $839.9 \text{ kJ} > 614.7 \text{ kJ} > 348.4 \text{ kJ/mole}$

Average bond energy (kJ/Mol)

$$= \frac{\text{Total bond energy}}{\text{No. of bonds}}$$

- Average amount of energy required to break one mole of bond between two atoms in a gaseous state. For diatomic molecule

(-) Bond formation E = Bond dissociating E.

- For polyatomic molecules

Bond formation and bond dissociation E are possess different values. But bond dissociation energy is always endothermic reaction.

- Larger the atomic size, lesser the extent of overlapping thus lower the bond enthalpy.

$\text{C} - \text{C} < \text{C} = \text{C} < \text{C} \equiv \text{C}$  bond enthalpy values.

$$\text{Average bond} = \frac{\text{Total bond energy}}{\text{no of bonds}} \text{ kJ mol}^{-1}$$

- (2) **Bond length** : It is an equilibrium distance between nuclei of two bonded atoms in a molecule.

- For covalent bond covalent radius for inert atom Vander Waal's radius by which bond lengths is calculated.

- Bond length depends upon size of atoms, no. of bonds between two atoms.

- Bond length increases, size of atoms increases.

- Bond length decreases with the increase in the multiplicity of bonds.

- Bond length expressed in Pm or Å°.

- (3) **Bond angle** : Bond angle decides the geometry of the molecule.

Bond angle expressed in degree (°) minutes(') and seconds (").

e.g. bond angle between H-C-H is  $109^\circ 28'$

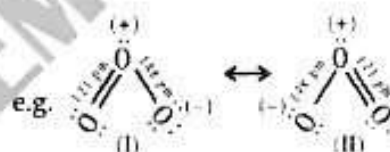
- (4) **Bond order** : Number of bonds between two atoms is called as bond order.

- Bond order increases bond enthalpy increases and bond length decreases.

- Stability of molecule can be determined by knowing the bond order.

- (5) **Resonance** : There are more than one possible arrangement of electrons in a molecule in lewis structure called as resonance.

The different structures are called canonical forms. Actual structure is combination of all canonical forms.



Canonical forms of  $\text{O}_3$  molecule.



(III) Resonance hybrid of  $\text{O}_3$  molecules.

- Resonance energy** : Difference in energy of a stable contributing structure and the resonating forms. It is called as resonance energy.

- Energy of resonance hybrid structure is less than it's any canonical form.

- Resonance stabilizes polyatomic molecule or ion.

- Resonating forms contributes overall bonding characters in a molecule.

- e.g. (III) Resonance hybrid of  $\text{O}_3$  have less energy than (I) and (II) canonical forms.

- Covalent character of ionic compounds**

- Many of the ionic compound possess partial ionic character.

- e.g. LiCl is ionic but highly soluble in organic solvent then water.  $\text{CuCl}_2$  is more covalent than ionic compounds.

□ Due to the polarization of an ion by cation, partial covalent character developed in a molecule.

□ Extent of polarizations in an ionic compound explain by Fajan's rule.

• **Fajan's rule :**

(1) The smaller the size of cation and larger the size of anion, greater the covalent character in ionic compound.

e.g.  $\text{Li}^+\text{Cl}^-$  is more covalent than  $\text{Na}^+\text{Cl}^-$ .

(2) Greater the charge on cation more the covalent character.

e.g.  $\text{Al}^{3+}(\text{Cl}^-)_3 > \text{Mg}^{2+}(\text{Cl}^-)_2 > \text{Na}^+\text{Cl}^-$

□ Outer electronic configuration of element  $s^2, p^6, d^{10}$  involvement have more covalent character than  $s^2, p^6$  configuration.

e.g.  $\text{Cu}^+\text{Cl}^-$  is more covalent than  $\text{Na}^+\text{Cl}^-$ .

$\text{Cu} + 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  involve (s, p, d) orbital but in  $\text{Na}^+ 1s^2 2s^2 2p^6$  involvement of s, p orbitals. Thus  $\text{CuCl}_2$  is more covalent than  $\text{NaCl}$ .

• **Ionic character of covalent compound**

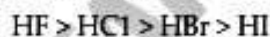
□ Covalent bond are formed by the same electronegative element or difference in electronegativity is zero called as a nonpolar covalent bond or compound, e.g.  $\text{H}_2, \text{Cl}_2, \text{F}_2, \text{N}_2, \text{I}_2, \text{Br}_2$  etc.

□ A covalent bond are formed between two different electronegative elements is called as polar covalent bond.

□ Then the sheared electron pair is shifted to the more electronegative element, thus it acquire partial negative charge and other element get partial positive charge.

□ It is polar covalent bond. Thus covalent molecules in two positive or negative poles are formed indicates ionic character.

□ Difference in electronegativity increases ionic or polar character increases.



e.g.  $\text{HF}, \text{HCl}, \text{HBr}, \text{O-H}$ , etc. are polar bonds.

• **Dipole moment : ( $\mu$ )**

□ It is a product of magnitude of two charges and, distance separated by two atoms.

$$\mu = Q \times r$$

□ It is expressed in Debye (D) or CM.

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

□ Dipole moment represented as  $\xrightarrow{\text{H}-\text{F}}$

□ Difference in electronegativity of two atom increases dipole moment increases.

e.g.  $\text{HF}$  have higher dipole moment than  $\text{HCl}$ .

□ Dipole moment of linear molecules like  $\text{BeF}_2, \text{CO}_2$  is zero.

□  $\text{BF}_3$  have zero dipole moment.

□  $\text{NH}_3$  and  $\text{NF}_3$  have pyramidal geometry but dipole moment of  $\text{NH}_3$  is higher than  $\text{NF}_3$  molecule. Dipole moment decides the geometry of the molecule.

• **Valence bond theory (VBT)**

VBT explain the formation of a covalent bond. According to VBT.

1) In the covalent bond formation, half filled atomic orbital of one atom overlaps with half filled atomic orbital of another atom.

2) Each overlapping atomic orbitals must contains an unpaired electron with opposite spin.

3) Overlapping orbitals at an atom should have same or nearly same energy.

4) During overlapping spin of electron neutralize, electrons are paired.

5) A stable bond is formed with minimum potential energy and minimum bond distance between two atoms.

6) Strength of covalent bond depends upon extent of overlapping, but complete merging of two atom is not possible.

7) Covalent bond have a particular direction with particular geometry.

8) The number of unpaired electrons in atom is equal to no. of covalent bond formed.

9) Covalent molecule have definite geometry. Overlapping atomic orbitals are oriented in the given space such that they have minimum repulsion and maximum symmetry.

• **Nature of interacting forces**

When two atoms closed to each other to form a bond. These types of forces are exists.

i) Repulsive force between nuclei and two atoms.

ii) Repulsive force between valence electron of two atoms.

iii) Attractive force between nuclei of first and electron of second atom vice versa.

□ When attractive forces are dominate then repulsive force, then stable bond is formed.

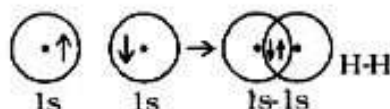
□ Formation of  $\text{H}_2$  molecule explain by VBT. RE for  $\text{H}_2$  molecule is  $-436 \text{ kJ/mol}$  and bond distance between  $\text{H}-\text{H}$  is  $0.74 \text{ \AA}$ . It is explained by RE. cure.



- **Overlap of atomic orbitals:**

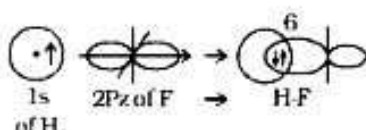
By using s and p, orbitals there are three types of overlaps.

- (1) **s-s overlap** : e.g.  $H_{2(g)}$  Half filled 1s orbital of H atom overlaps with half filled 1s atomic orbital of another H atom with opposite spin.

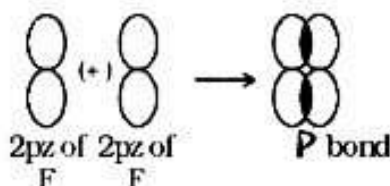


- (2) **s-p overlaps** : e.g. HCl, HF, HBr, HI.

Half filled S, orbital of H overlaps with half filled '2p<sub>z</sub>' orbital of another atom.



- (3) **p-p overlaps** : e.g.  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $O_2$ ,  $N_2$  etc. Half filled p orbital of one atom overlaps with Half filled 'p' orbital of another atom.



- **Limitation of valence bond theory:**

- (1) VBT can not explain correct valency of Be, B C etc.

□  $Be$   $1s^2 2s^2$  no unpaired electrons, but actually Be forms divalent compounds ( $Be$   $1s^2 2s^1 2p_x^1$ ) like  $BeF_2$ ,  $BeH_2$  etc.

□  $B$   $1s^2 2s^2 2p_x^1$  is monovalent but it forms trivalent compounds like  $BCl_3$ ,  $BF_3$ ,  $BH_3$ , etc.

□ ( $B$   $1s^2 2s^1 2p_x^1 2p_y^1$ )

□  $C$   $1s^2 2s^2 2p_x^1 2p_y^1$  it forms tetravalent compounds like  $CH_4$ ,  $CCl_4$  etc. ( $C$   $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ )

- (2) VBT can not explain correct geometry and bond angle, similarly bond equivalence. To explain these facts, hybridization its is important.

- **Hybridizations:**

□ Mixing and recasting of the atomic orbitals of a atom to form equal number of new hybrid orbitals with equal energy, same geometry and definite orientation.

□ Steps involved in hybridizations

- (1) **Formation of the excited state:**

It is not a necessary condition of hybridizations. It required number of unpaired electrons are not present in ground state, one or more electrons promoted to nearest empty orbitals.

- (2) **Mixing and recasting of atomic orbitals:**

It is important step in hybridization. Atomic orbitals of a atom are mixed together and reconstructed such that, newly formed hybrid orbitals have equal energy, same geometry and definite orientations.

- (3) **Reorientation of atomic orbitals:**

Hybrid orbitals are reoriented with minimum repulsion and maximum symmetry.

- (4) Orbitals of a one atom used for hybridisation.

- (5) Orbitals used for Hybridisation should have same or nearly same energy.

□ The structure of any molecule can be predicted on the basis of hybridisation.

$$H = \frac{1}{2} [V + M + A - C]$$

V = no. of valence electron in atom.

M = no. of monovalent atoms bonded.

A = Charge on anion

C = Charge on cation

Value of H	2	3	4	5	6	7
Hybridisation	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>

□ Hybridisation can be calculated as

- (1)  $ClF_3$

$$H = \frac{1}{2} (7 + 3 + 0 - 0) = \frac{1}{2} \times 10 = 5$$

5 hybrid orbitals  $\rightarrow$  sp<sup>3</sup> d hybridisation

- (2)  $SO_2$

$$H = \frac{1}{2} (6 + 0 + 0 - 0) = 3 \rightarrow sp^2 \text{ hybridisation}$$

- (3)  $COCl_2$

$$H = \frac{1}{2} (4 + 2 + 0 - 0) = 3 \rightarrow sp^2 \text{ hybridisation}$$

- (4)  $SO_4^{2-}$

$$H = \frac{1}{2} (6 + 0 + 0 - 0) = 4 sp^3 \text{ hybridisation}$$

(5) For complex ions like  $[\text{CO}(\text{NH}_3)_6]^{+2}$ ,  $[\text{PtF}_6]^{-2}$ ,  $[\text{Ni}(\text{NH}_3)_4\text{Cl}_2]$  hybridisation is calculated by counting ligands in the coordination sphere.

□ Depending upon the number of lone pair and bond pairs of electrons, molecules are represented as  $\text{AB}_2\text{E}$ ;

Where - A → Central atom B → Bonded atoms C → Lone pair of electrons

Molecule Type	No. of Lone pairs	No. of bonding pair	Bond angle	Geometry	Examples
$\text{AB}_2\text{E}$	1	2	$119^\circ.3'$	bent	$\text{SO}_2, \text{O}_3$
$\text{AB}_3\text{E}$	1	3	$107^\circ.18'$	Trigonal / Pyramidal	$\text{NH}_3, \text{PCl}_3$
$\text{AB}_2\text{E}_2$	2	2	$104^\circ.5'$	Bent/angular	$\text{H}_2\text{O}$ , of $\text{H}_2\text{S}$ , $\text{SCl}_2$ etc
$\text{AB}_4\text{E}$	1	4	-	See saw	$\text{SF}_4$
$\text{AB}_3\text{E}_2$	2	3	$86.02^\circ$	T-shape	$\text{ClF}_3, \text{BrF}_3, \text{ICl}_3$ etc.
$\text{AB}_5\text{E}$	1	5	-	Square Pyramid	$\text{BrF}_5, \text{IF}_5$
$\text{AB}_4\text{E}_2$	2	4	-	Square Planer	$\text{XeF}_4$
$\text{CH}_4$	$\text{Sp}^3$	4	-	$109^\circ.28'$	Tetrahedral
$\text{NH}_3$	$\text{sp}^3$	3	1	$107^\circ.18'$	Pyramidal distorted (Tetrahedral)
$\text{H}_2\text{O}$	$\text{sp}^3$	2	2	$104^\circ.35'$	Inverted V shaped (Tetrahedral distorted)
$\text{C}_2\text{H}_4$	$\text{SP}^2$	3	-	$120^\circ$	Trigonal 4C-H( $\sigma$ )bonds 1 C=H( $\pi$ )
$\text{BF}_3$	$\text{sp}^2$	3	-	$120^\circ$	Trigonal planer
$\text{C}_2\text{H}_2$	$\text{sp}$	2	-	$180^\circ$	Linear, diagonal 2C-H( $\sigma$ )bonds 2C=H( $\pi$ )bonds
$\text{BeF}_2$	$\text{sp}$	2	-	$180^\circ$	Linear
$\text{PCl}_5, \text{bF}_5$	$\text{sp}^3\text{d}$	5	-	$90^\circ$ and $120^\circ$	trigonalbipyramidal
$\text{AsF}_5, \text{SF}_6$	$\text{Sp}^3\text{d}^2$	6	-	$90^\circ$	Octahedral
$\text{TeF}_6, \text{SeF}_6$					

### 1 Characteristics of hybridisation

- (1) Atomic orbitals of the same atom can take part in hybridisation, they have same or nearly same energy.
- (2) Number atomic orbitals used for hybridisation equal to number of hybrid orbitals formed.
- (3) Hybrid orbitals formed strong covalent bond then pure atomic orbitals.
- (4) Hybrid orbitals arranged with minimum repulsion and maximum symmetry with definite bond angle.
- (5) Orbitals used for the hybridization of a one atom:
- (6) Hybrid orbitals can form sigma ( $\sigma$ ) and ( $\pi$ ) bonds. ,  $\text{AB}_3\text{F}$ ,  $\text{AB}_2\text{E}_2$  etc. With definite bond angle. It have definite geometry.

Sigma ( $\sigma$ ) bond	Pi ( $\pi$ ) bond
1. The bond formed by axial overlapping of atomic orbitals	1. The bond formed by lateral overlapping of atomic orbitals.
2. Electron density deposited at the centre of two nuclei.	2. Electron density distributed above and below the plane of geometry.
3. It is a strong bond.	3. It is a weak bond.
4. It involves s and p.	4. It involves only p orbital
5. More amount of energy released or required	5. Less amount of energy released or required.
6. It have a particular direction	6. It have no any direction

### Valence shell electron pair repulsion theory (VSEPR)

- ☐ Electron pair arrange with minimum repulsion between them.
- ☐ Molecule acquired minimum energy and maximum stability.
- ☐ Lone pair of electron useful to determine geometry of molecule.
- (4) Repulsion force in bond pair (B.P) and lone pair (L.R) in order as  $L-P-LP > LP-BP > BP-BP$

#### • $NH_3$ molecule :

- ☐ It is an example of  $sp^3$  hybridisation.
- ☐ Out of 4  $sp^3$  hybrid orbitals one lone pair and three bond pair orbitals.

Repulsion between  $BP-LP > BP-BP$  orbitals

- ☐ Due to effect of one L.P bond angle in ammonia decreases  $109^\circ.28'$  to  $107^\circ.18'$ .
- ☐ Geometry of a  $NH_3$  molecule changes tetrahedral to the pyramidal.
- ☐ Lone pair is present at the top of the pyramid and Bond pair are the bottom of the pyramid.

#### • $H_2O$ molecule :

- ☐ It is an example of  $sp^3$  hybridisation of oxygen, atom. 4,  $sp^3$  hybrid orbitals, 2 are lone pair and 2 B.P orbitals.
- ☐ Due to effect two L.P bond angle decrease  $109^\circ.28'$  to  $107^\circ.35'$ .
- ☐ Repulsion between  $LP-LP > LP-BP > BP-BP$
- ☐ Geometry of molecule is inverted V shaped i.e. distorted tetrahedral.
- ☐ Similar type examples as  $ClF_3$ ,  $BrF_3$ ,  $SbF_3$ ,  $PX_3$  etc.
- ☐  $ClF_3$  T shaped  $\rightarrow$  trigonal bipyramidal geometry ( $sp^3d$  hybridisation)
- ☐  $BrF_3 \rightarrow$  Regular octahedron geometry ( $sp^3d^2$  hybridisation)

- ☐  $IF_5 \rightarrow$  Pentagonal bipyramidal geometry ( $sp^3d^2$  hybridisation)

#### • Limitations of V.B.X:

- (i) VBT cannot explain formation of co-ordinate bond. In sheared electron pair from one of the element.
- (ii)  $O_2$  molecule expected to diamagnetic in nature but actually is paramagnetic it is unexplained.
- (iii) Bonding in electron deficient molecules in which central atom have less than eight electron e.g.  $B_2H_6$  unexplained.

#### • Molecular orbital theory (MOT):

- ☐ It is given by Hund and Mulliken
- ☐ The electrons in a molecule are present in the various molecular orbitals.
- ☐ Atomic orbitals with same or comparable energy and proper symmetry combines to form molecular orbitals.  
e.g.  $2s$  orbital combines with  $2p_z$  orbital but not with  $2p_x$  or  $2p_y$  because symmetry is not same.
- ☐ Molecular orbitals are influenced by more than one nuclei, i.e. they are polycentric.
- ☐ Number of combining atomic orbitals equal to number of molecular orbitals formed.
- ☐ Bonding M.O. have more energy and stability as compared to anti-bonding M.O.
- ☐ The M.O. gives electron probability distribution around a group of nuclei in a molecule.
- ☐ M.O. follows Aufbau principle, Pauli's exclusion principle and Hund's rule.
- ☐ Linear combination of atomic orbitals (LCAO) gives bonding M.O. and anti-bonding M.O. addition or subtraction of wave functions.
- ☐ Only two electrons occupy each M.O. and they have opposite spins that is their spins are paired.

- ❑ The increasing order of energy of various M.O. for  $O_2$  and  $F_2$  are  
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \sigma 2p_y, \pi 2p_z < \pi^* 2p_x = \pi^* 2p_y < \pi^* 2p_z$

- ❑ For the molecules  $Li_2, Be_2, B_2, C_2, N_2$ , increasing order of energies of various M.O. is

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

- ❑ Energy of  $\sigma 2p_x$  M.O. is higher than  $\pi 2p_x$  and  $\pi 2p_y$  M.O.

• **Factors for M.O.**

(1) **Stability of molecule**

If  $N_b$  = no. of electrons present in bonding  $N_a$  = no. of electrons in anti-bonding molecular orbitals.

then if

$N_b > N_a$  Stable molecule

$N_b < N_a$  unstable molecule

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

If Bond order positive  $\rightarrow$  stable molecule

Bond order zero or negative  $\rightarrow$  unstable molecule If Bond order 1,2,3 indicates single, double, triple bond.

(3) **Bond length** : Bond length increases bond order decreases.

(4) **Magnetic nature** : If molecule contains paired electrons or no unpaired electrons it is diamagnetic. If molecule contains unpaired electrons it is paramagnetic in nature.

(5) Formation of a molecule when bond order greater than zero.

(6) Higher the bond order higher bond dissociation energy.

Molecule	Bond order	Magnetic nature
$H_2$	1	diamagnetic
$He_2$	0	diamagnetic
$Li_2$	1	diamagnetic
$Be_2$	0	diamagnetic
$F_2$	1	diamagnetic
$C_2$	2	diamagnetic
$N_2$	3	diamagnetic
$B_2$	1	paramagnetic
$O_2$	2	paramagnetic

Species	Bond order	Species	Bond order
$H_2^+$	0.5	CN	2.5
$H_2^-$	0.5	$CN^-$	3.0
$N_2^+$	2.5	$CN^+$	2.0
$N_2^-$	2.5	NO	2.5
$O_2^+$	2.5	$NO^+$	3.0
$O_2^-$	1.5	CO	3.0
$O_2^{2-}$	1.0		
Ne	0.0		

- Atomic orbitals are monocentric, but M.O. are polycentric

- Order of bond lengths

$$O_2^{2+} > O_2^+ > O_2 > O_2^-, N_2^{2+} > N_2^+ = N_2^- > N_2$$

- Stability and bond dissociation energies are

(1)  $O_2^{2+} > O_2^+ > O_2 > O_2^-$

(2)  $N_2 > N_2^+ = N_2^- > N_2^{2-}$