Molecular Orbital Theory (MOT)

Major Drawbacks in VBT:

1) VBT assume that each combining species will provide an unpaired electron of opposite spin to form a covalent bond but in case of co-ordinate covalent bond one species provide both electrons.

2) According to the VBT, in O_2 all electrons are paired, so it should be diamagnetic but O_2 is two electron paramagnetic species.

3) In VBT, N_2 contain a triple bond (N≡N) similar to acetylene (HC≡CH). In spite of similarity in bonding, N_2 is very much inert while acetylene is fairly active.

4) VBT can't explain the odd electron bond in a molecule like He_2^+, H_2^+ etc.

Molecular orbital theory (MOT):

- Molecular orbital theory was proposed and developed mainly by Mulliken, Lennard – Jones and Hückel.
- In this approach, the skeleton of the molecule with its nuclei in fixed position is first considered then develop molecular orbitals (MOs)
- The filling electrons to these MOs according to the aufbau principle, Hund's rule and Pauli's exclusion principle.
- The MOs are polycentric as it has more than one nucleus while the AOs are monocentric as it involves only one nucleus.
- The MOs are developing from the AOs according to the (i) Linear Combination of Atomic Orbitals (LCAO) method, (ii) United Atom method.

Important Aspect of LCAO-MOT:

(i) MOs are developed from the skeleton of the molecule containing the nuclei at the fixed position through LCAO method.

(ii) The number of MOs would be equal to the number of AOs involved.

(iii) For an effective combination of AOs they must satisfy the EOS conditions.

- Energy: The combining wave functions should have comparable energy.
- Overlap: The AOs representing the electron cloud must undergo overlap appreciably.
- Symmetry: The lobes of combining AOs must have same symmetry with respect to bond axis.

(iv) Depending upon the overlap integral (S_{AB}), MOs are classified as bonding MO ($S_{AB} > 0$), antibonding MO ($S_{AB} < 0$) and non bonding MO ($S_{AB} = 0$).

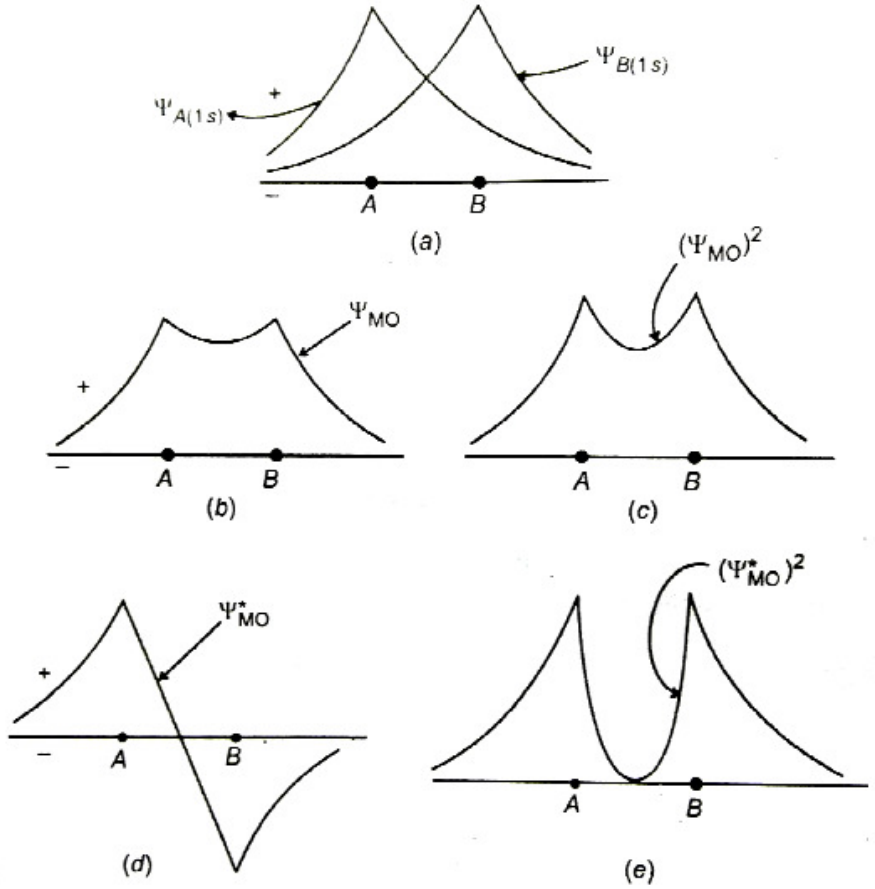
(v) After the construction of MOs, electrons are placed to these MOs according to the aufbau principle, Hund's rule and Pauli's exclusion principle.

(vi) The MOs are also defined by four quantum numbers as AOs. 'n' and 'l' are retained from the AOs and spin quantum number have same significance as in atoms. The magnetic quantum number of the MOs are representing by λ and have values λ = -l, -(l-1), ...,0, (l-1), l. (In diatomic molecule the axis containing the nuclei is taken reference axis.)

For $\lambda = 0$, orbitals are symmetrical around the reference axis and these are called σ-orbitals. $\lambda = \pm 1$, the orbitals are referred to as π-orbitals and $\lambda = \pm 2$, orbitals are termed as δ-orbitals.

(vii) Based on the symmetry they can be classified as gerade (g) and ungerade (u). The orbitals having centre of symmetry (C_i) are called gerade (g) and lacking of C_i are termed ungerade (u). s and d orbitals are represented by g while p and f orbitals are represented by u.

(viii) The bonding MOs concentrate the electron cloud between the nuclei to stabilize the system while the antibonding orbitals remove the electron cloud from the space between the nuclei to destabilize the system.



Quantitative representation: (a) wave function of H_A and H_B (b) Ψ_{MO} of H_2^+ (c) Probability of finding electron density in Ψ_{MO} of H_2^+ (d) Ψ^*_{MO} of H_2^+ (e) Probability of finding electron density in Ψ^*_{MO} of H_2^+

(ix) Approximately, the stabilization by the bonding molecular orbital (BMO) is balanced by the destabilization induced by the antibonding molecular orbital (ABMO). That's why the bond order is roughly calculated as,

$$\text{bond order} = \frac{\text{number of electron in BMO} - \text{number of electron in ABMO}}{2}$$

(x) In homonuclear diatomic molecules, both the atomic orbitals contribute equally in forming MO, but in heteronuclear diatomic molecules they contribute unequally.

(xi) The energy of each MOs can be calculated by solving the appropriate Schrödinger wave equation. For, homonuclear diatomic system energy of the MOs are as

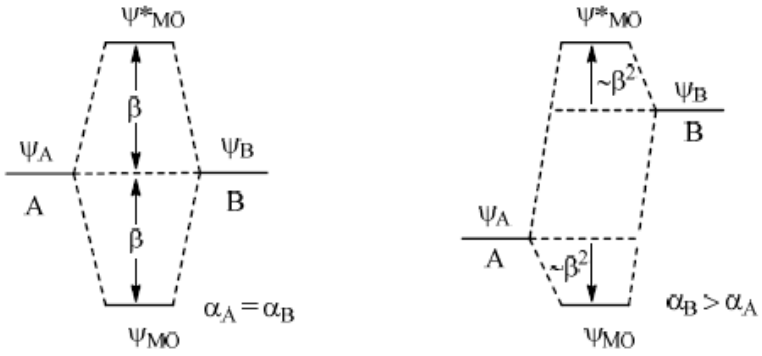
$$E_b = \alpha + \frac{\beta_{AB} - \alpha S_{AB}}{1 + S_{AB}} \qquad E_a = \alpha - \frac{\beta_{AB} - \alpha S_{AB}}{1 - S_{AB}}$$

For, heteronuclear diatomic system energy of the MOs are as

$$E_b = \alpha_A - \frac{(\beta_{AB} - \alpha_A S_{AB})^2}{\alpha_B - \alpha_A} \qquad E_a = \alpha_B + \frac{(\beta_{AB} - \alpha S_{AB})^2}{\alpha_B - \alpha_A}$$

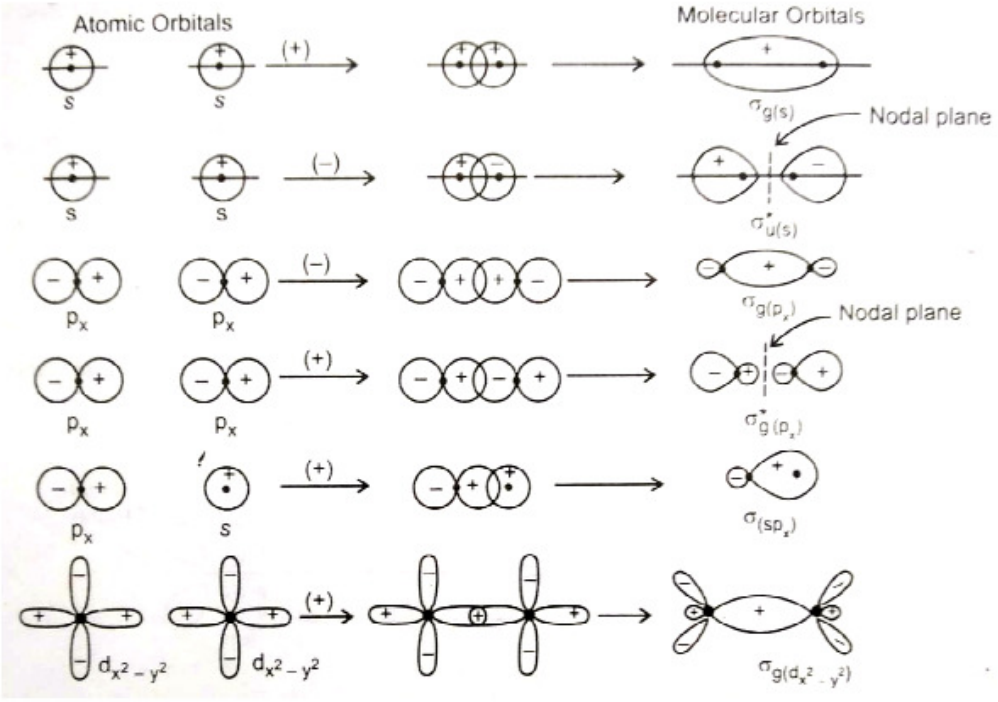
Where, α is Coulomb integral, β_{AB} is resonance integral and S_{AB} is overlapping integral.

(xii) All MOs are normalised. $\int (\Psi_{MO})^2 \, d\tau = 1$ or $\int (\Psi^*_{MO})^2 \, d\tau = 1$ and the corresponding bonding and antibonding MOs are mutually orthogonal i.e. $\int \Psi_{MO} \times \Psi^*_{MO} \, d\tau = 0$

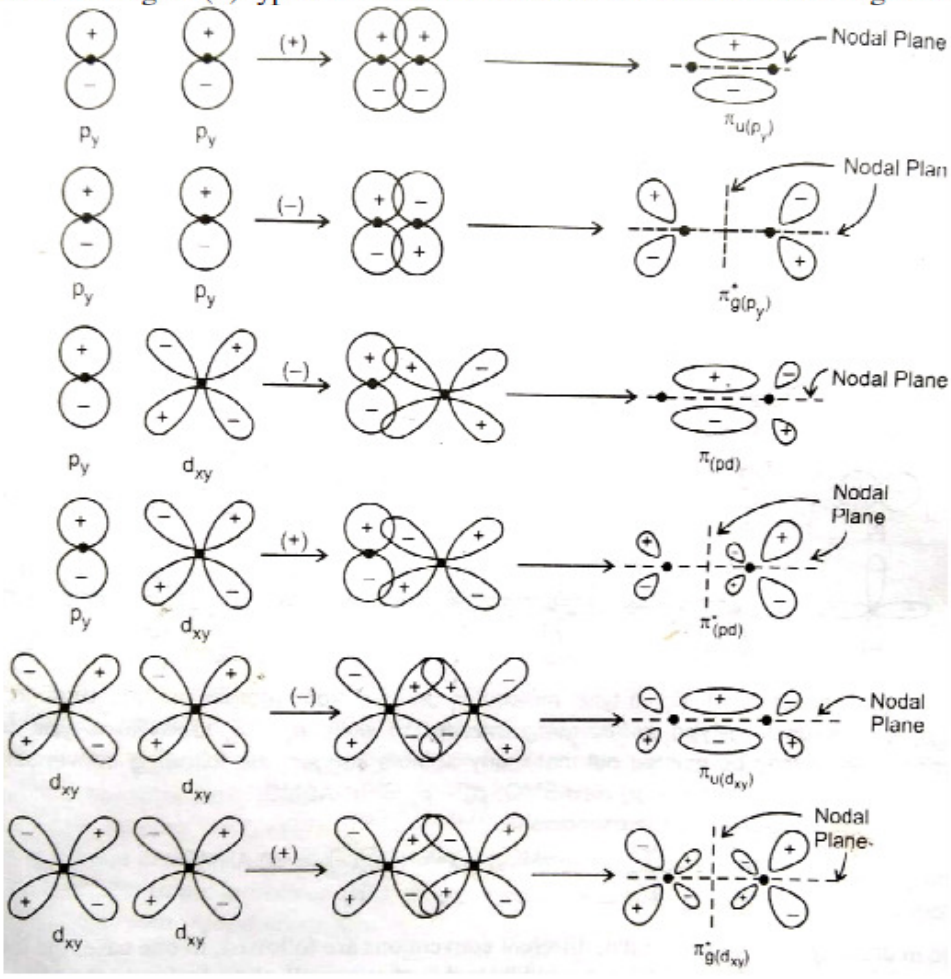


σ, π, δ and φ MOs : σ bond arises by the overlap of '1 lobe + 1 lobe', π bond arises by the overlap of '2 lobes + 2 lobes', δ bond arises by the overlap of '4 lobes + 4 lobes', φ bond arises by the overlap of '6 lobes + 6 lobes'. The s-orbital can only show σ-type interaction; p-orbital can show σ- and π-type interaction, d-orbital can show σ, π and δ-type interaction, f-orbital can show σ, π δ and φ-type interactions.

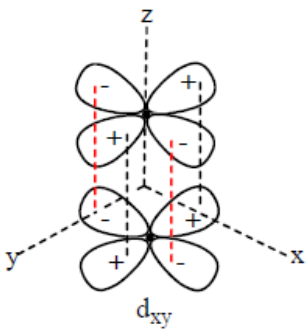
For the spherically symmetrical s-orbital, the (+) combination gives the sigma bonding molecular orbital (σ-BMO) while the (-) combination gives the sigma antibonding molecular orbital (σ-ABMO). The orbitals like p, d etc which are not spherically symmetrical, in the σ-type interaction, the (+) combination gives the σ-ABMO while the (-) combination gives the σ-BMO; for the π-type interaction the reverse is true.



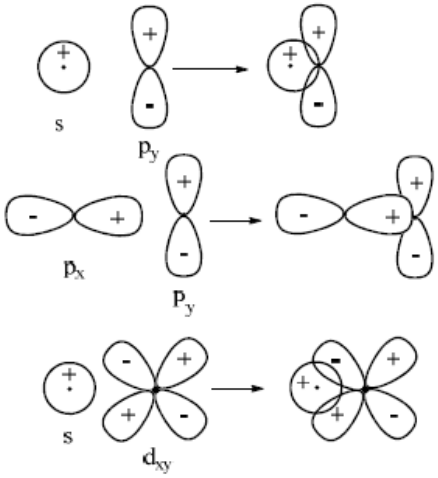
Formation of sigma (σ) type molecular orbitals from atomic orbitals through LCAO



Formation of pi (π) type molecular orbitals from atomic orbitals through LCAO



Schematic representation of δ-bonding

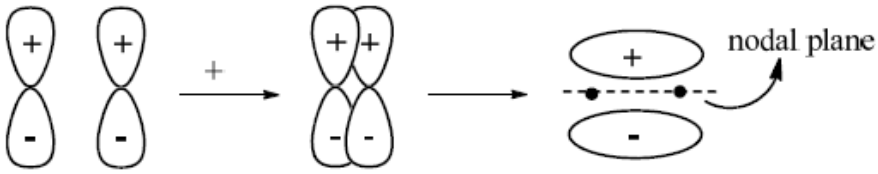


Schematic representation of non-bonding interaction

δ-Bonding: Two d orbital lying in parallel planes can overlap each other with all four lobes to produce a δ-bonding. The δ-Molecular orbital possesses two nodal planes containing the bond axis and nodal planes are mutually perpendicular. The δ-MOs can arise from the suitable d ± d, f ± f and d ± p_π^*-MO interaction. The magnetic quantum number (λ) of the δ-MOs is ±2.

σ-Bonding: End to end overlap of two lobes of two suitable orbital produce σ-bond. This bond is strong due to better overlap. σ-bond has cylindrical symmetry (C_∞) around the bond axis. It determines the direction of bond. σ-bonding electrons can't participate in delocalization. The magnetic quantum number (λ) of the σ-MOs is zero. σ-MOs, both σ and σ* have no nodal plane containing the internuclear axis.

π-Bonding: Side to side overlap of four lobes of two suitable orbital produce π-bond. This bond is weaker due to poor overlap. π-bond has no C_∞ symmetry so no rotation around bond axis is possible. It has no primary effect in determining the bond direction but it can shorten the bond length. π-bonding electrons being mobile can participate in delocalization. The magnetic quantum number (λ) of the π-MOs is ±1. π-MOs, both π and π* have nodal plane containing the internuclear axis.



Simple Molecular Orbital Diagram of Homonuclear Diatomic Molecule

❖ Here, no interaction between the MOs of same symmetry and no hybridization among the AOs participating in the formation of MOs are considered.

❖ The extent of splitting between the corresponding bonding and antibonding MOs depends on the extent of efficiency of overlapping. In sigma interaction, the better overlapping produces more splitting compared to that in the pi-interaction.

❖ X-axis is considered as bond axis. Therefore, $2p_x$ orbital produces σ-MOs while $2p_y$ and $2p_z$ orbitals produce two sets of π-MOs. The π-MOs are energetically degenerate but mutually perpendicular.

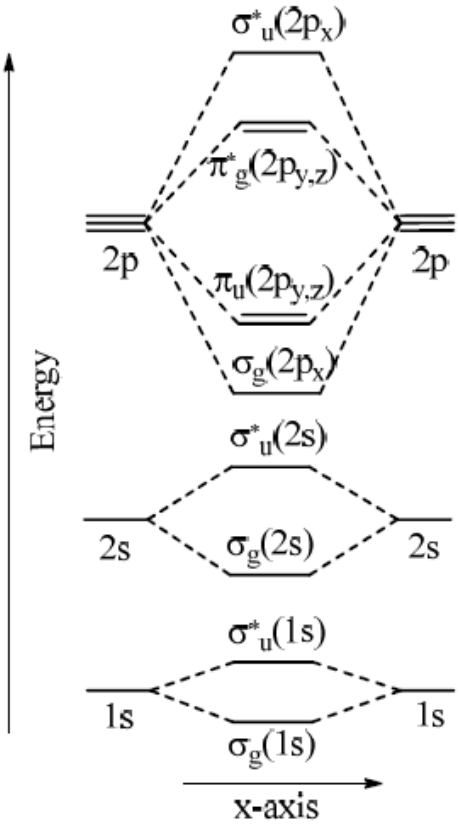
❖ In the MOs, electrons are placed according to the aufbau principal, Hund's rule and Pauli's exclusion principal.

❖ Highest occupied molecular orbital is denoted as HOMO and the lowest unoccupied molecular orbital is termed as LUMO. Both HOMO and LUMO are referred to as frontier molecular orbitals (FMOs). The singly occupied molecular orbital is called SUMO.

❖ Many author named the MOs as follows: $\sigma_g(1s) = 1\sigma_g$; $\sigma^*_u(1s) = 2\sigma^*_u$; $\sigma_g(2s) = 3\sigma_g$; $\sigma^*_u(2s) = 4\sigma^*_u$; $\sigma_g(2p) = 5\sigma_g$; $\pi_u(2p_{y,z}) = 1\pi_u$; $\pi^*_g(2p_{y,z}) = 2\pi^*_g$; $\sigma^*_u(2p_x) = 6\sigma^*_u$

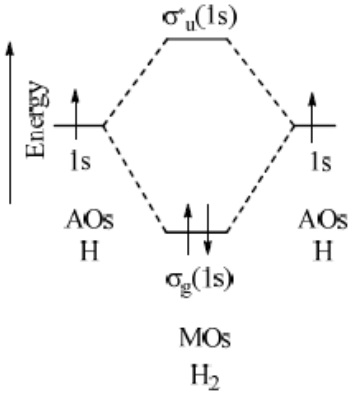
❖ The energy order of the MOs $1\sigma_g < 2\sigma^*_u < 3\sigma_g < 4\sigma^*_u < 5\sigma_g < 1\pi_u < 2\pi^*_g < 6\sigma^*_u$

Simple Molecular Orbital diagram

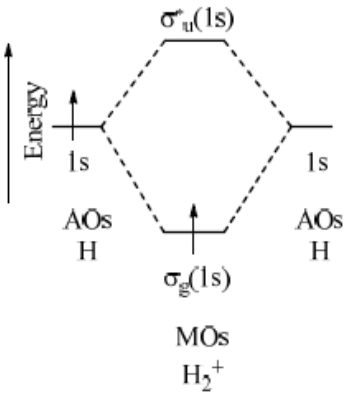


Molecular Orbital Picture of Homonuclear diatomic Molecule

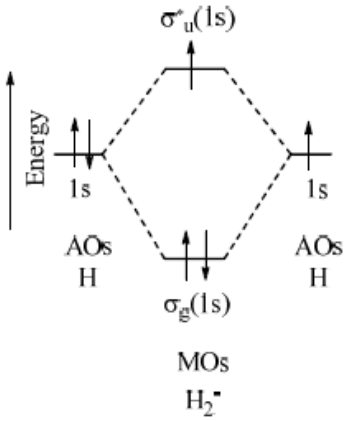
(i) H_2, H_2^+, H_2^-



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

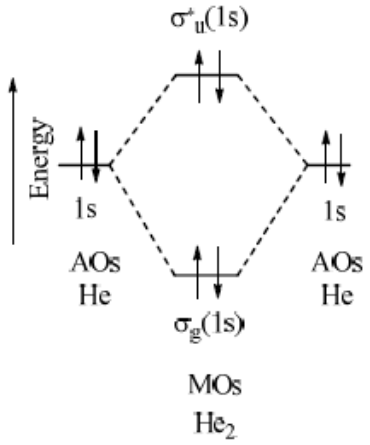


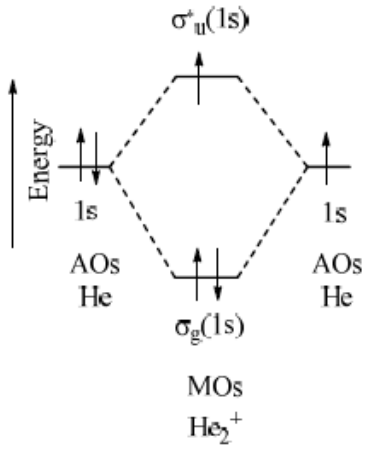
Bond order $= \frac{1-0}{2} = 0.5$



Bond order $= \frac{2-1}{2} = 0.5$

(ii) He_2 , He_2^+





Bond order $= \frac{2-2}{2} = 0$

Bond order $= \frac{2-1}{2} = 0.5$

- It is note that the bond order of H_2^+ and He_2^+ is 0.5, and their bond lengths are 105 and 108 pm respectively.
- Bond order of He_2 is zero. Because of this fact non existence of He_2. It is worth mentioning that actually the anti bonding orbital, $\sigma^*_{u(1s)}$ destabilises more than the stabilisation of bonding orbital, $\sigma_{g(1s)}$. If stabilisation of BMO and destabilisation of AMBO is equal then there would be a finite probability of existence of He_2 along with mono atomic He.

(iii) The simple model of MO can't explain the few properties of lighter element mainly lithium to nitrogen in which energy difference between the 2s and 2p orbital is smaller.

- Beryllium exists as a mono atomic species as gas phase. But, at very low temperature beryllium exist as diatomic molecule. But this model can't predict the fact.
- Experimentally B_2 is paramagnetic but simple MO diagram predicts it is diamagnetic.
- Experimentally C_2 is diamagnetic but simple MO diagram predicts it is paramagnetic.
- It shows existence of two pi-bonds along with a sigma bond as in acetylene. But, N_2 is inert unlike acetylene.
- Ionisation potential of N_2 established that the highest occupied orbital is a σ-orbital while this simple model predicts it is a π-orbital

Therefore some modification of simple MO is required to form MO.

Modification of Molecular Orbital Energy diagram

The modification can be attained in two possible ways:

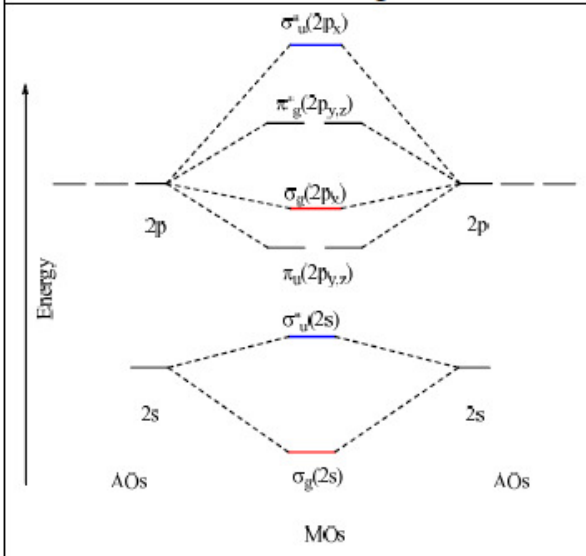
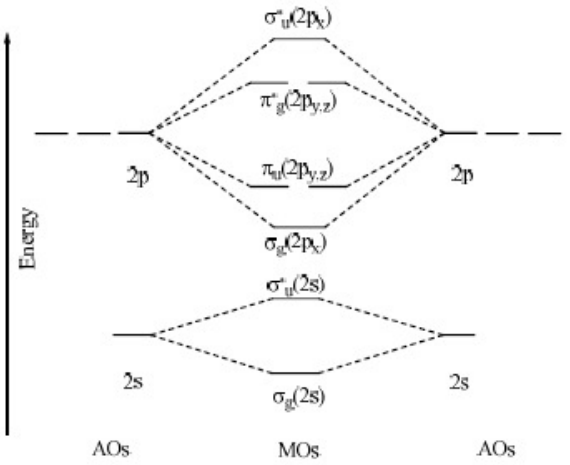
(i) Incorporation of symmetry interaction (i.e. noncrossing rule) among the molecular orbitals obtained in simple treatment. According to the quantum mechanics, two orbitals of the same symmetry mutually repel resulting the lower energy orbital become more stabilized and higher energy orbitals becomes more destabilized. If we considered the simple MO diagram, the pair $\sigma_{g(2s)}$ - $\sigma_{g(2px)}$ and $\sigma^*_{u(2s)} - \sigma^*_{u(2px)}$ interact to each other. As a result, the energy of $\sigma_{g(2s)}$ and $\sigma^*_{u(2s)}$ is lower down and the energy of $\sigma_{g(2px)}$ and $\sigma^*_{u(2px)}$ is increased. This type interaction becomes prominent when the energy difference of 2s and 2p orbital is smaller. As we go lithium to neon the energy difference of these two orbital increases as shown below.

2^{nd} period	Li	Be	B	C	N	O	F	Ne
$E_{2p} \sim E_{2s}$ (eV)	1.8	2.8	4.5	5.3	6.0	15.0	20.5	26.7
3^{rd} period	Na	Mg	Al	Si	P	S	Cl	Ar
$E_{3p} \sim E_{3s}$ (eV)	2.0	2.6	4.5	5.2	5.5	9.8	11.5	13.5

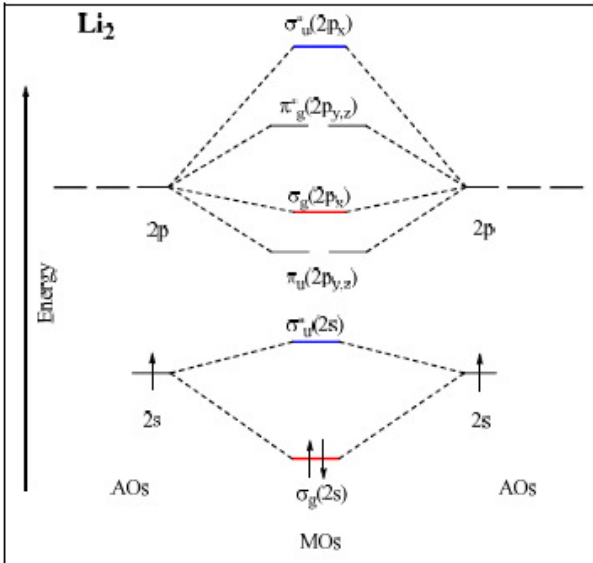
Therefore, this type of symmetry interaction is quite important for N_2 and lighter molecule. For highly electronegative atom like O and F, the 2s lie far below of 2p orbitals and do not interact significantly. In fact, simple MO diagram is quite appropriate for O_2 and F_2 molecule.

(ii) Participation of hybrid orbitals (mixing of s and p-orbitals) instead of pure atomic orbitals for generating the molecular orbitals.

Modified MO diagram for Li_2 to N_2

Modified MO diagram	Simple MO diagram
	

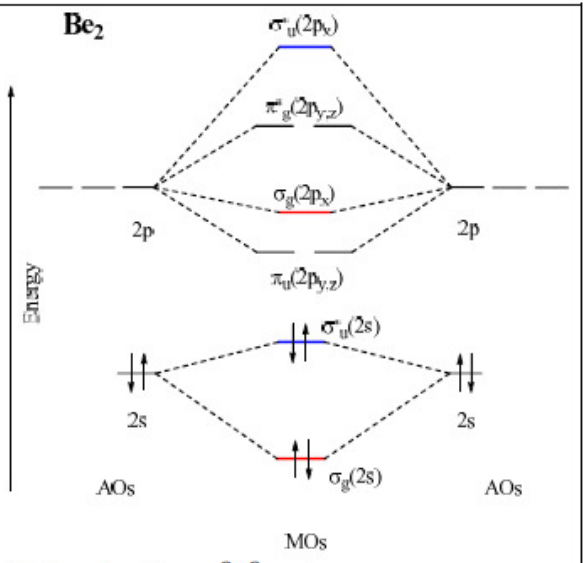
Li_2



(i) Bond order $= \frac{2-0}{2} = 1$

(ii) It exists as diatomic species in the gas phase.

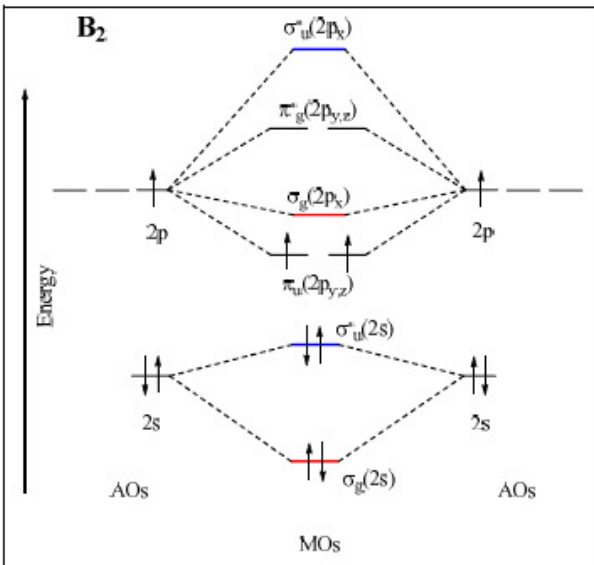
Be_2



(i) Bond order $= \frac{2-2}{2} = 0$

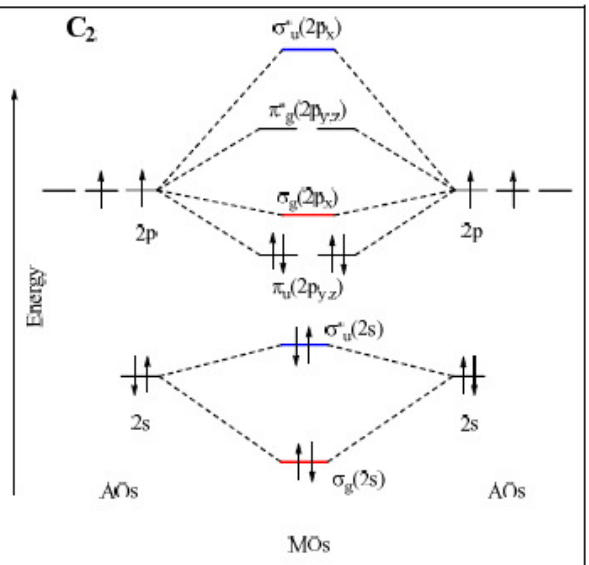
(ii) It exists as diatomic species in the gas phase.

(iii) MO diagram predicts the stabilization of BMO, $\sigma_{g(2s)}$, orbital is more compared to destabilization of AMBO, $\sigma^*_{u(2s)}$. This reveals its existence at low temperature.



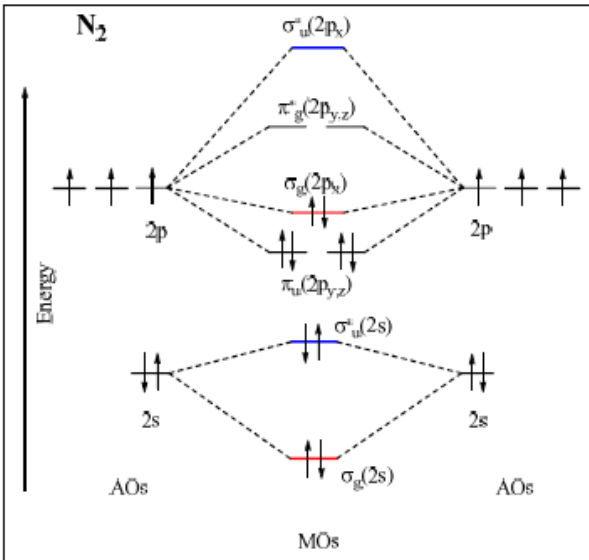
(i) Bond order $= \frac{4-2}{2} = 1$

(ii) It contains two unpaired electron. So it is paramagnetic.



(i) Bond order $= \frac{6-2}{2} = 2$

(ii) It is diamagnetic.



i) Bond order $= \frac{8-2}{2} = 3$

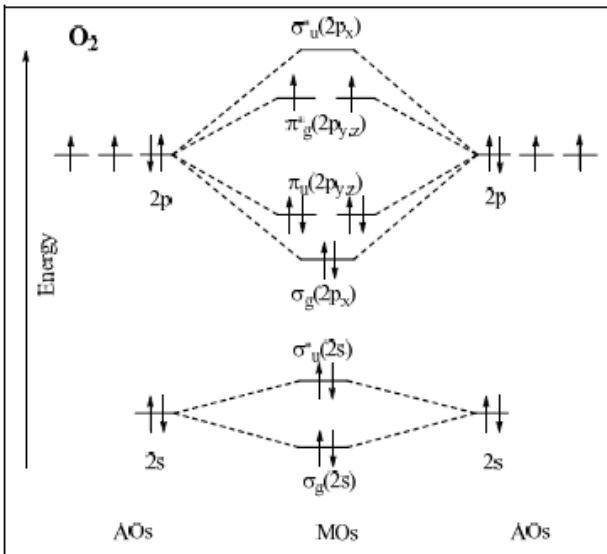
(ii) HOMO is $\sigma_{g(2px)}$. Therefore, ionisation energy is higher than the expected.

(iv) Since HOMO is $\sigma_{g(2px)}$, a sigma MO and LUMO is $\pi^{*}_{g(2py,z)}$. Thus, it is difficult to remove an electron from HOMO and acceptance of an electron in LUMO is also energetically unfavourable. That's why N_2 is inert.

(v) For the same reason N_2 can't acts as a good ligand.

Comparison of ionisation energy of atomic nitrogen and molecular nitrogen:

It is observed that the first ionisation energy of the atomic nitrogen is less than that of the molecular nitrogen. IE(N_2) = 1503 kJ mol^{-1} > IE(N) = 1402 kJ mol^{-1}. In case of N_2, the electron is to be removed from HOMO, a BMO (σ_g) which is comparatively more stable than the corresponding AO of atomic nitrogen. This is why, N_2 requires higher energy for ionisation.



(i) Bond order $= \frac{8-4}{2} = 2$

(ii) It shows existence of one pi-bond and a sigma bond.

(iii) It contains two unpaired electron so paramagnetic.

(iv) Ground state of O_2 is triplet instead of singlet (as expected from VBT). Actually triplet state is kinetically inert in most of the chemical reactions, but singlet O_2 is very much reactive. This is why singlet O_2 is toxic.

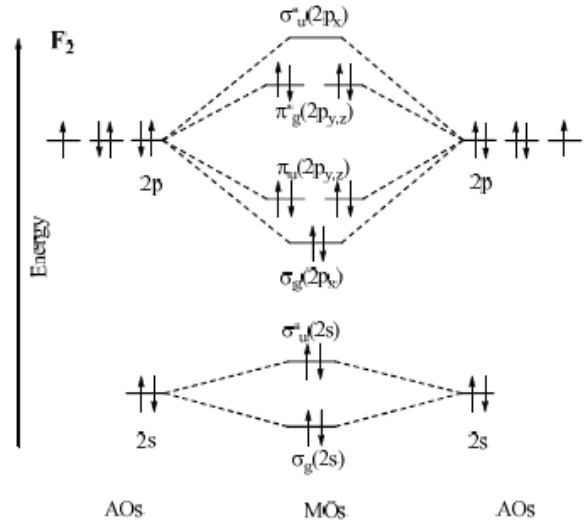
Comparison of ionisation energy of atomic oxygen and molecular oxygen:

It is observed that the first ionisation energy of the atomic oxygen is higher than that of the molecular oxygen. IE(O) = 1314 kJ mol^{-1} > IE(O_2) 1164 kJ mol^{-1}. In case of O_2, the electron is to be removed from HOMO (i.e. SOMO), an ABMO (π_g^*) which is destabilized compared to the outermost AO of oxygen atom. This is why, O_2 requires less energy for its ionisation.

Formation of superoxide (O_2^-), peroxide (O_2^{2-}), oxide (O^{2-}) and dioxygenyl cation (O_2^+):

MO diagram is predicting that the added electron to oxygen go to the π_g^*, an ABMO resulting decrease of bond order. If only one electron is added to O_2, it forms superoxide (O_2^-) having bond order 1.5. If two electrons are added to O_2, it forms peroxide (O_2^{2-}) having bond order one. If four electrons are added to O_2, it form O_2^{4-} having bond order zero. So it does not exist. Actually, due to zero bond order of O_2^{4-}, it breaks down to two oxide ions (O^{2-}).

On the other hand, on removing electrons from π_g^*, an AMBO, the number of antibonding electrons decreases and consequently, in O_2^+, bond order increases compared to that in O_2.



(i) Bond order $= \frac{8-6}{2} = 1$

(ii) It exists as di-atomic molecule. In fact, all halogens are exist as diatomic molecule

(iii) It is diamagnetic.

Colour of halogens (X_2): Explained from the MO diagram.

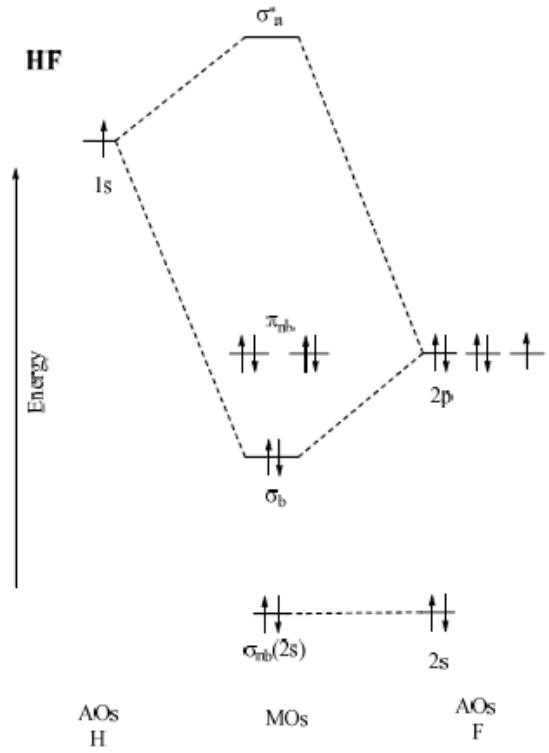
The electron of HOMO, $\pi^*_{g(np)}$, is excited to LUMO, $\sigma^*_{u(np)}$ by the absorption of visible light. The energy gap between these levels determines the colour of X_2. The observed colours are as follows: F_2 (pale yellow): $\pi^*_{g(2p)} \rightarrow \sigma^*_{u(2p)}$; Cl_2 (yellow): $\pi^*_{g(3p)} \rightarrow \sigma^*_{u(3p)}$

Br_2 (reddish brown): $\pi^*_{g(4p)} \rightarrow \sigma^*_{u(4p)}$; I_2 (violet): $\pi^*_{g(5p)} \rightarrow \sigma^*_{u(5p)}$

The energy gap between $\pi^*_{g(np)}$, HOMO and $\sigma^*_{u(np)}$, LUMO is decreased with the increase of the principal quantum number n. With the increase of n, the larger p-orbitals get more diffused and as a result, effectiveness in overlapping of AOs to form the MO decreases. Therefore, the energy difference between the BMO and ABMO is reduced. The sequence of increase of excitation energy is $F_2 > Cl_2 > Br_2 > I_2$. Gaseous F_2 absorb the highest energy light, violet and it appears pale yellow. Cl_2 absorb indigo light and appears yellow. Br_2 absorb lower energy bluish-green light and appears as reddish brown. I_2 absorb lowest energy light yellowish green and appears as violet.

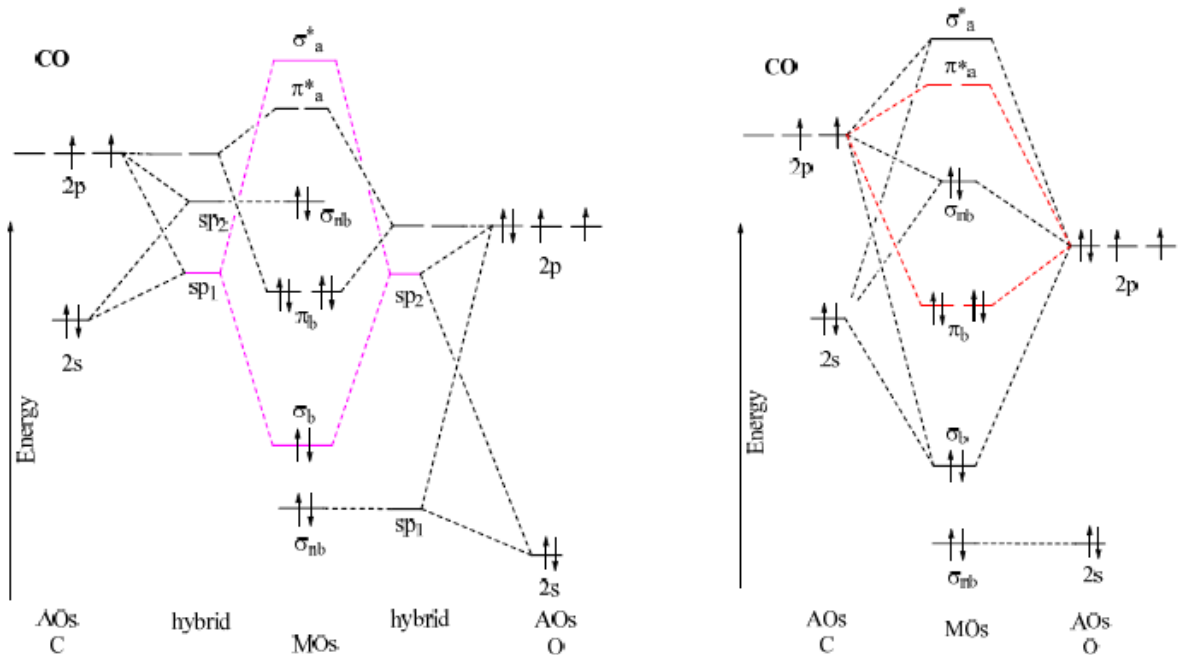
Though, this type of transition is forbidden because of the different spin states of ground state ($\pi_g^{*4}\sigma_u^{*0}$, singlet) and excited state ($\pi_g^{*3}\sigma_u^{*1}$, triplet). But with the decrease of energy gap probability of transition increases because of better spin-orbit coupling to mix the spin states and this is why colour intensity is increased from F_2 to I_2.

Molecular Orbital diagram of heteronuclear diatomic molecules



(i) Bond order $= \frac{2-0}{2} = 1$

(ii) All the occupied energy levels remain predominantly on the fluorine atom and it is expecting the HF molecule to be polar with a partial negative charge on fluorine atom.

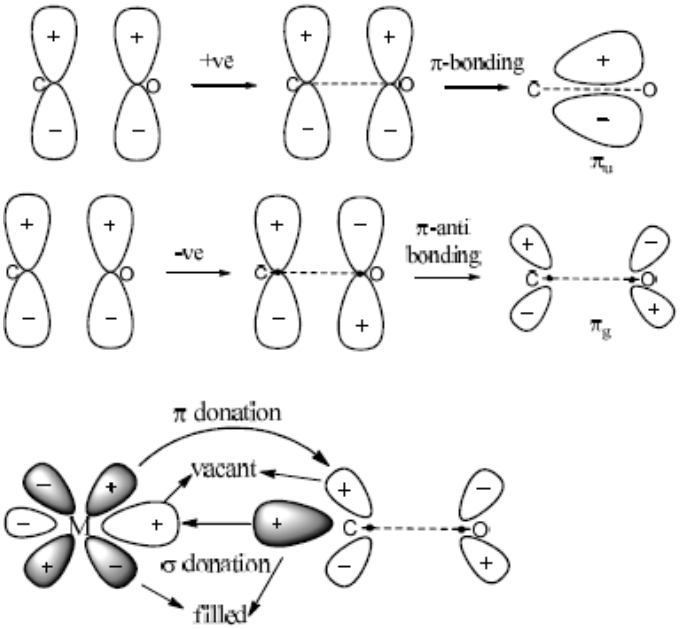


(i) Bond order $= \frac{6-0}{2} = 3$

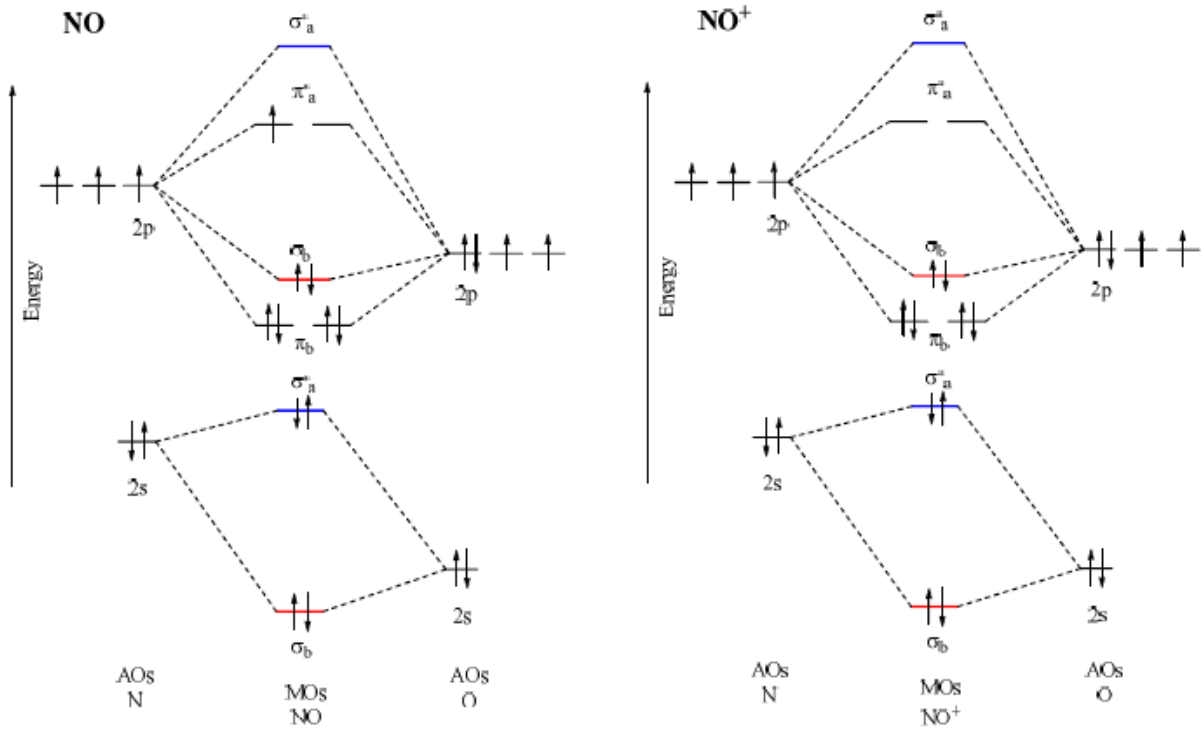
(ii) HOMO is σ_{nb} orbital and LUMO is π_a^* orbital.

(iii) Lower dipole moment of CO can be explained by MO diagram. HOMO is σ_{nb} orbital, which is mainly a $2p_x$ orbital of carbon. Therefore, in CO there is finite electron density on carbon due to presence of lone pair. This lone pair of electron on carbon predominates over the bond pair of electron localized towards oxygen due to higher electronegativity. This give rise to lower dipole moment and negative end of dipole lies on carbon.

(iv) CO binds the metal ion trough carbon rather than more electronegative oxygen. MO diagram of CO predicting that HOMO (σ_{nb}) and LUMO (π_a^*) both orbitals are enriching with carbon orbital (2p) character. During bond formation with the metal ion, CO donates electrons of σ_{nb} (HOMO) form an σ bond and it is reinforced by strong π-bond through accepting electron to vacant π_a^*(LUMO). Thus, CO acts as a good σ donor and π acceptor through its carbon end. So, in CO, carbon is ligating atom not the oxygen atom.


+ve
π-bonding
C
O
π_u
-ve
π-anti
bonding
π_g

π donation
vacant
M
C
O
σ donation
filled



(i) Bond order = $\frac{8-3}{2} = 2.5$

(ii) It is paramagnetic. The unpaired electron is present in the anti bonding orbital (π_a^*), which is delocalized over the whole molecule, though the π_a^* orbital possess more weightage of p-orbital of nitrogen. Since, the unpaired electron is not localized on a particular atom, it is reluctant to form dimer.

(iii) The HOMO (actually SOMO) is π_a^* whose energy is higher than that of AOs of nitrogen and oxygen. This is why, ionisation energy of NO is less than that of both nitrogen and oxygen. The first IP values (kJ mol^{-1}) of NO, N and O are: 894, 1402 and 1314 respectively. For this reason, NO readily lose this antibonding electron to form NO^+.

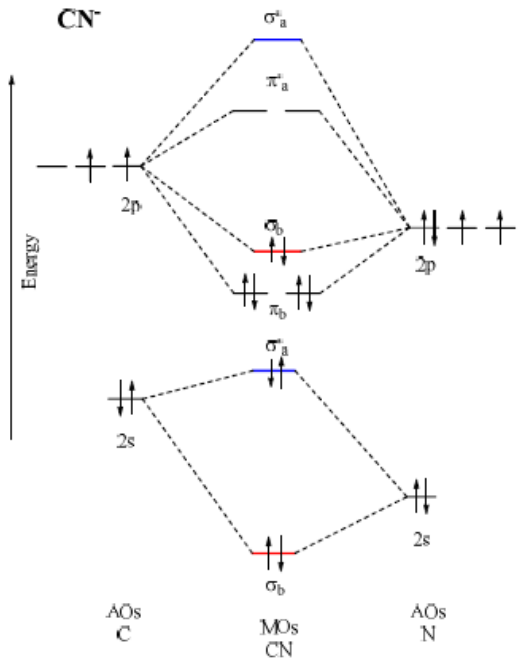
(iv) The bond order of NO^+ is $\frac{8-2}{2}$ =3. This is why, N-O bond length in NO^+ (106 pm) is shorter than that in NO (113 pm).

(v) Like, CO and CN-, NO+ can acts as π acid ligand.

(vi) HOMO is σ_b and LUMO is π_a^*.

(v) In NO^+, σ donation occur through σ_b (HOMO) orbital and π acceptance through vacant π_a^*(LUMO) orbital. Thus, NO^+ acts as a π-acid ligand. The positive charge on the ion will favour π acceptance but at the same time it will reduce the efficiency as an σ donation. The higher electronegativity of nitrogen compared to carbon will make NO^+ a stronger π acid ligand.

(vi) π acidity order is $NO^+ > CO > CN^-$ and σ donation order $CN^- > CO > NO^+$



(i) Bond order = $\frac{8-2}{2} = 3$

(ii) The CN^- is isoelectronic with CO, NO^+, N_2 (10 valence electrons).

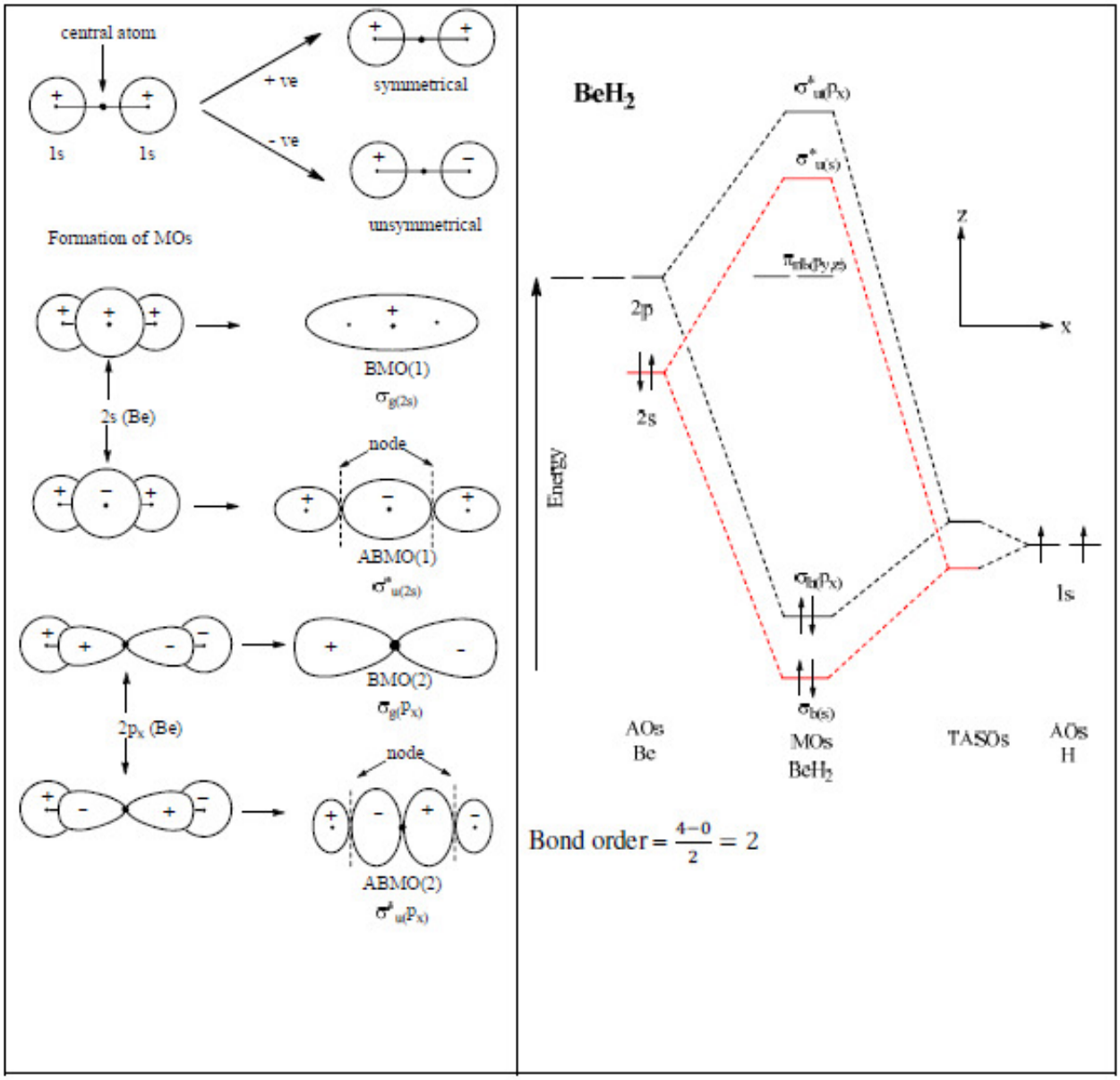
(iii) Like CO and NO^+, it acts as π-acid ligand.

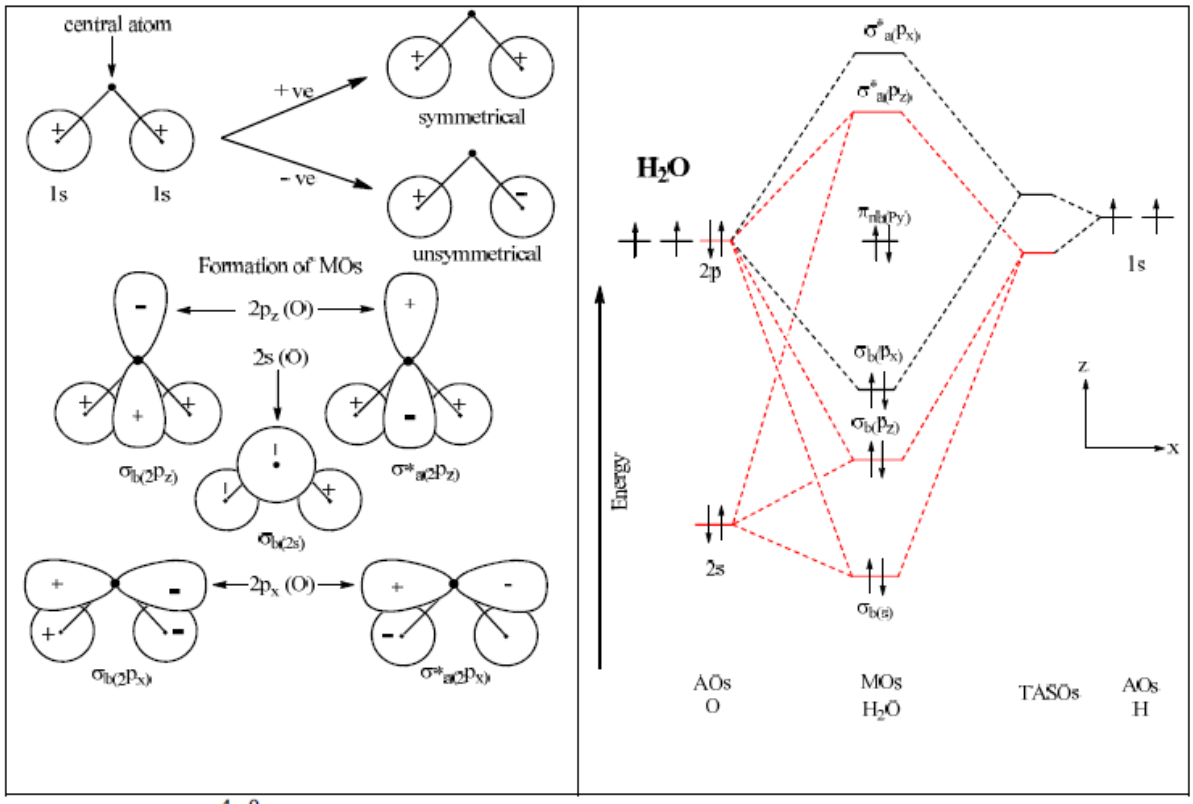
(iv) HOMO is σ_b and LUMO is π_a^*.

(v) CN^- donates electrons of σ_b (HOMO) to form an σ bond and takes back the electron by to vacant π_a^*(LUMO) to form π-bond. Thus, CN^- acts as a π-acid ligand. The negative charge on the ion will favour σ donation but at the same time it will reduce the efficiency as a π acceptor. The lower electronegativity of nitrogen compared to oxygen will make CN- a poorer π acid ligand.

Molecular Orbital diagram of heteronuclear triatomic molecules

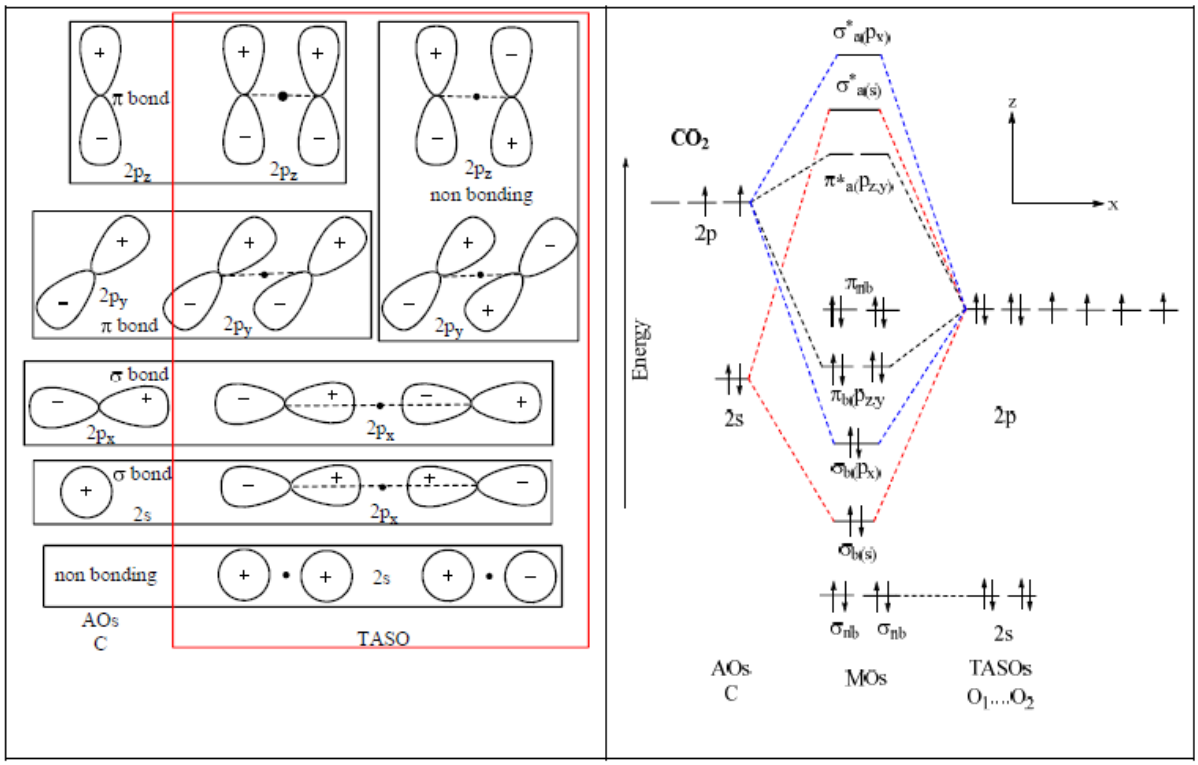
For triatomic molecules, it will first consider the formation of group orbital or symmetry adopted orbitals by linear combination of the atomic orbitals of terminal atoms. These group orbitals are described as ligand group orbitals (LGOs) or symmetry adapted linear combinations (SALCs) or terminal atom symmetry orbitals (TASOs). Then, these TASOs will combine with the suitable atomic orbitals of the central atom to generate the MOs.





(i) Bond order = $\frac{4-0}{2} = 2$

(ii) The lone pairs of oxygen are not equivalent. One is non-bonding, $\pi_{nb}(2p_y)$ and another is slightly bonding, $\sigma_b(s)$.



(i) Bond order = $\frac{8-0}{2} = 4$

(ii) The electron distribution indicates that out of total 16 valence electrons, 8 electrons occupy non-bonding MOs on oxygen and carbon. 4 electrons occupy two bonding σ MOs and 4 electrons occupy two π bonding MOs.

(iii) The 4σ-bonding electron and 4π-bonding electrons are responsible for carbon-oxygen double bond character.

(iv) Bond order of each C-O bond is 2 (1σ and 1π).

Metallic Bond

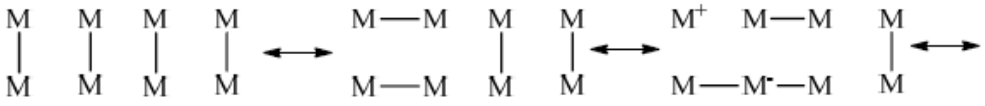
Metal are characterized by certain distinct features.

- Metals are hard and have high melting and boiling points that indicates strong cohesive force among the metal atoms.
- Metals are ductile and malleable that suggests the adjacent planes of metal atoms can easily glide over each other.
- Metals are good conductor of electricity.
- Metals are lustre and show photoelectric effect and thermionic emissions.
- The bonding between the metal atoms is strong and non-directional and non rigid.
- Metal atoms are bind together with large number of neighbouring atoms though a metal atom possesses only very few valence electrons.

All these properties can't be explained properly either by covalent or ionic model. Therefore, it is necessary separate bonding scheme for the metals.

(i) The valence bond theory:

The idea of classical 2c-2e covalent bond can be extrapolated in explaining the metallic bond. It suggests extensive resonance of electron pair and one electron bonds among all the nearest neighbouring atoms of a metal in an aggregate. For example, lithium, the electronic configuration ($1s^2 2s^1$), can form only one covalent bond. The interaction with the neighbouring atoms can be explain by typical 'canonical form' are shown below: the negative ion is formed by using sp hybrid orbital of the metal. Though somewhat successful but this theory can't explain the properties of metals properly.



M = Short period elements (He to Ne, Na to Ar).

Merit of Valence band theory:

i) Cohesive energy: In three dimensional crystals, due to formation of large number of canonical forms resonance energy will be high. This high resonance energy explains the high cohesive energy in metallic crystal.

ii) Electrical conductivity: Vacant valence orbitals of the metals are responsible for electrical conductivity. For example, in Li 2p levels are available for conducting electricity, in Gr-13 elements vacant np level can perform the same task.

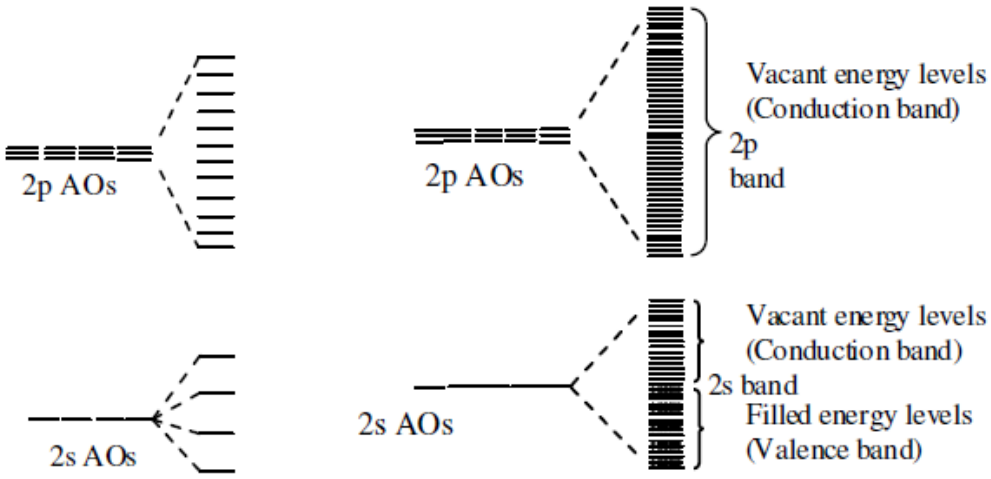
iii) Distribution of Metallic properties in the periodic table: Group 1, 2 and 13 elements are metals because of the presence of vacant metallic orbitals.

(ii) Band theory:

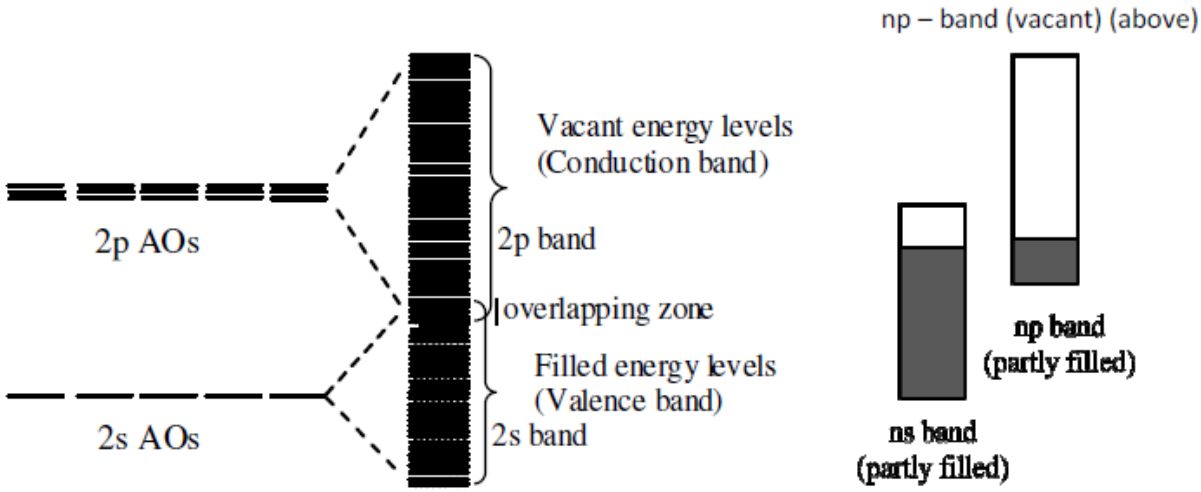
This theory provides the satisfactory explanation of metallic properties. Band theory is an extension of the molecular orbital theory for a large number of atoms. It suggests a large number (say n) of metal atoms, each offering one orbital for combination with others, there will be total 'n' new energy levels similar to 'n' MOs. These energy levels are actually multicentre MOs. This large number of energy levels will be closely space, one upon another, forming an energy band in which levels are quasi-continuous. The valence electrons from all the atoms will now enter these energy levels. The lowest energy levels are fully bonding in nature and the top most levels are fully anti bonding in nature, and the in-between levels are of intermediate character. A metal thus consists of energy bands formed by different combination of large number of atomic orbitals of three dimensional arrays of atoms.

The different valence orbitals produce different energy levels. These energy bands may be separated or overlapped depending upon the nature of the atoms. The energy gap between the two successive bands is called forbidden energy gap. When the highest energy level of lower energy band exceeds the energy of the lowest energy level of the next higher energy band overlapping occurs. In case of overlapping bands, before the completion of

electron filling in the lower energy band, the filling of the next higher overlapping bands start. Overlapping depends on band width which is controlled by the energy difference of the involved atomic orbitals and internuclear separation.



Combination of four Li atoms Combination of 'n' Li atoms



Merger of 2s and 2p band in beryllium overlapping of ns and np band

Band width: It is determined by the energy difference between the most bonding and antibonding combination of atomic orbitals. Efficient overlap of the orbitals gives a large band width while inefficient overlap gives a narrow band width.

Density of states (DOS) in an energy band: The number of energy levels (multicentred MOs) per unit energy increment gives the measure of density of states. It may be noted that a particular energy band is not uniformly packed i.e. DOS is not the same throughout the band. In three dimension, the centre of band is most heavily populated (DOS is maximum) while the edges (both top most and lowest level) are poorly populated (DOS is less).

Fermi level: The highest energy level occupied at 0 K is called Fermi level. But, generally working temperature is above 0 K, therefore a small fraction of the electrons from the level just below the Fermi level will promoted to the levels just above the Fermi Level.

Valence Band: The highest occupied band is called valence band. Elaborately one can say the energy band formed by the valence atomic orbitals.

Conduction band: The lowest vacant band is called conduction band. This band is responsible for the electrical conductivity. In presence of external electrical potential, electrons can jump to conduction band from valence band. In case of alkali metals, the incompletely filled valence band acts as a conduction band.

Insulator: The substances in which the energy gap between the highest filled valence band and the empty conduction band are so large that electron from the valence band can't go the conduction band under the ordinary electrical potential. That's why these substances can't carry electricity. Generally, the substances having forbidden energy gap (E_g) > 3 eV are referred to insulator. For diamond, E_g is ~ 5.5 eV.

Semiconductor: The solid substances that have electrical conductivity between that of an insulator and conductor are called semiconductors. In semi conductors, the forbidden energy gap is relatively small, lie in the range 2-3 eV. There are two types of semiconductors. (i) Intrinsic semiconductor and (ii) Extrinsic semiconductor.

(i) In intrinsic semiconductor, the energy gap between the filled band (Valence band) and next empty band (Conduction band) is so small that at higher temperature, the thermal energy

gained by the electron is sufficient to promote to the next empty band and shows conductivity. The electrons normally can't jump across this gap and so the substance behave as insulator as absolute zero.

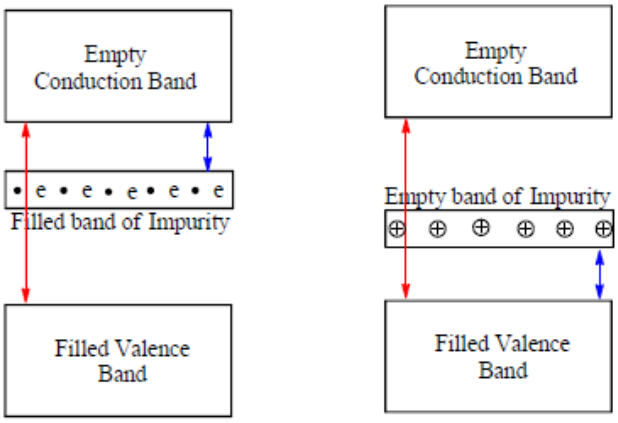
(ii) In extrinsic semiconductor, certain substances are introduced deliberately as impurities to reduce the gap between the filled band and next empty band. Extrinsic semiconductors are two types (i) n-type semiconductor (ii) p-type semiconductor.

(i) n-type semiconductor: The addition of arsenic or antimony (Group 15 elements) those have five valence electron to silicon or germanium produces an n-type semiconductor.

These impurities place a filled energy level just below the empty conduction band. Electrons from the impurities can be easily excited to the conduction band. Here the conductivity results from the flow of electrons and hence it is called a negative or n-type semiconductor.

(ii) p-type semiconductor: When gallium or indium (Group 13 elements) those have three valence electrons is added to silicon or germanium as impurities producing p-type semiconductor.

These impurities place an empty band just above the filled valence band of the metal. Now the passage of electrons from valence band of the metal to these empty bands results in a number of vacant sites on silicon and renders it positively charged. These vacant sites are called 'positive holes'. The adjacent electrons move to fill these positive holes, creating further positive holes behind them. Therefore, there is a migration of the positive holes and produces a positive or p-type semiconductor.



n-type p-type

Defects in Solids

Defects in solids mean imperfection of crystal lattice. Such defects may involve only in one or two lattice sites are called point defect. Alternation or displacements of a row of lattice sites are known as line defects. When an entire plane of lattice sites is imperfect are called plane defect.

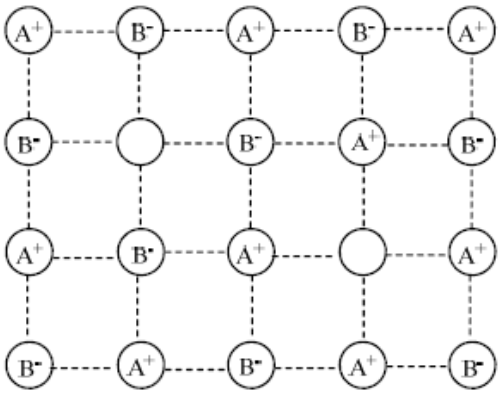
A point defect may result from a vacancy, that is, an atom is missing from its normal lattice site and occupies an interstitial space in the lattice. This is called intrinsic defects. When a foreign atom present in an interstitial position or in a regular lattice site then produce extrinsic defects. In ionic solids, such point defects involve ions rather than atoms.

Stoichiometric point defects:

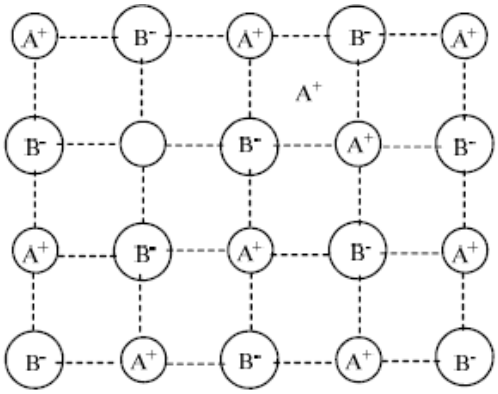
Point defects which do not alter the stoichiometry or composition of the crystal are two types (i) Schottky defect and (ii) Frenkel defect.

In **Schottky defects**, arises when a cation-anion pair is missing from its normal lattice sites creating a pair of holes or voids. Such defects thus maintain electrical neutrality and stoichiometry. But, the density of the solids may be slightly lowered when large numbers of defects are present. Generally, highly ionic compounds having high coordination numbers with cations and anions of comparable sizes show such defects. The crystal of NaCl, KCl, KBr, $CaCl_2$ etc. exhibit Schottky defects.

In **Frenkel defect**, an ion gets missing from its normal lattice point and occupies an interstitial position. Electrical neutrality and stoichiometry of the compound is not disturbed in this defect and also density of the solid remains unchanged. It occurs preferably in the compound having small cation and large anion to provide low coordination numbers to the ions or crystal with rather 'open' structure exhibits such defect. Examples are AgCl, AgBr, AgI, ZnS and CaF_2.



Schottky defect



Frenkel defect

A crystalline solid with a defective lattice site may conduct electricity to a small extent. An ion moves to the 'hole' from its own lattice site; a new 'hole' is thus created. In this way a 'hole' migrates across the crystal that is moving of charge in the opposite direction.

Non-Stoichiometric point defects:

Point defects which alter the stoichiometry or composition of the crystal are mainly two types (i) metal excess and (ii) metal deficiency. A third type of such defect may arise through substitution by impurities.

Metal excess may occur in two ways:

(i) An anion may be missing from its lattice site, an electron being present there to maintain electrical neutrality. These electrons in anion vacancies are called colour centre or F-centre (F stands for the German word 'Farbe' mean colour). Such type of defect is created when crystal of alkali metal halide is heating with alkali metal vapour. The metal atoms that deposited on the surface of the crystal diffuse inward and get ionized by the crystal energy. The metal ion occupies a normal cation site while the ionized electron occupies an anion vacancy. The resulting composition now becomes like $Na_{1+x}Cl$ where $x << 1$. Electrons so trapped in anion vacancies give rise to interesting colours. LiCl – pink, KCl – violet, KBr – blue green, NaCl – yellow.

(ii) An extra metal atom may be present in an interstitial position. An electron in some other interstitial position balances the charge. Zinc oxide exhibits such type of defect. When heated, the lattice loses oxygen ($O^{2-} - 2e \rightarrow \frac{1}{2}O_2$) reversibly resulting in a non stoichiometric phase like $Zn_{1+x}O$. The additional zinc ions go to interstitial position. The trap electron on the interstitial position can be excited by the absorption of visible light which imparts a yellow colour at hot condition. Similarly, CdO loses oxygen to form $Cd_{1+x}O$ on heating and the colour changes.

Metal deficiency may occur in two ways:

(i) A positive ion is absent from its lattice site. A doubly charge cation maintains the charge balance. This defect require variable valence of the metal. FeO, FeS, NiO are the examples to show this defect. When NiO (pale green) is heated at 1500 K with excess O_2, the colour turns black and oxide becomes an electrical semiconductor. Because of heating at higher temperature the partial oxidation of Ni^{2+} to Ni^{3+} and reduction of atmospheric oxygen to O^{2-} which gets incorporated to the crystal and thus composition of the oxide becomes $Ni_{1-x}O$ ($Ni_{0.97}O$) due to metal deficiency lattice defect. The deficiency of positive charge is now compensated by the presence of Ni^{3+} ion in other lattice site. Now, an electron from the neighbouring cations may jump to this Ni^{3+} ion and converting it to Ni^{2+} but at the same time creating a new Ni^{3+} ion at other lattice point. Thus, a positive hole is migrating through the crystal, making it a p-type semiconductor. A similar defect is known to occur in Cu_2S.

(ii) An extra negative ion occupies an interstitial place, and a doubly charge cation maintain the charge. It is very unlikely because of difficulty for anion generally have larger in size to occupy an interstitial position.

❖ Third type of non-stoichiometric defect occurs through substitution a cation of the lattice site by the foreign cation of comparable size. A Cd^{2+}, size comparable to Ag^+, can replace two Ag^+ ions from the crystal of AgCl. When Li_2O is dissolved in NiO, some Li^+ ions

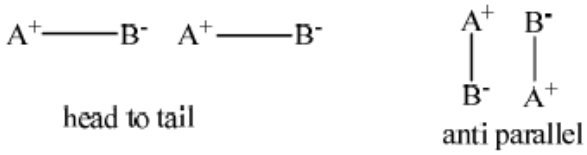
replace Ni^{2+} ion of the lattice. More Ni^{3+} ions are formed in the lattice to compensate the charge. Therefore, Li_2O doped NiO becomes a p-type semiconductor.

Weak Chemical Force

There is a net attractive force exists between the molecules of a gas. This force is mainly responsible for liquefaction and solidification of gases. The intermolecular force is also supported by the facts non-ideality of real gas, Joule-Thomson effect. This intermolecular force of attraction is commonly known as van der Waals force. Van der Waals force is also present in the liquid and solid states of many substances. Collectively all these forces have also been termed as London forces since the nature of such forces was first explained by Fritz London using wave mechanics.

Van der Waals forces are very weak in comparison to other chemical forces. For example, in solid ammonia its value is ~ 30 kJ mol^{-1} (energy of N-N covalent bond = 389 kJ mol^{-1}). These forces are non-directional. The strength of van der Waals forces increases as the size of molecule increases. Intermolecular forces may have a wide variety of origin depending upon the environment. These forces are related with the corresponding potential energy (E) terms. $F = \frac{dE}{dr}$, r = interacting distance. Mainly, three types of interaction among the covalent molecule are important.

(1) Dipole – dipole interaction (Keesom force): The dipoles with their opposite ends tend to oriented in two ways end to end (head to tail) and anti parallel arrangement.



The anti parallel arrangement is better for the molecules which are not too fat. Both arrangements can exist in liquid or solid only in situation when the attraction energy is larger than thermal energies. At higher temperature or in gas phase there will be a tendency for thermal motion to randomize the orientation of the dipoles and the energy of interaction will

be considerably reduced. For the head to tail arrangement, the energy of interaction of two dipole of different molecule may be expressed as

$$E_K = \frac{-2\mu_1\mu_2}{4\pi\varepsilon_0 r^3}$$

Where μ_1 and μ_2 are dipole moments of the interacting molecule, r is the distance between the centres of the interacting dipole. Dipole-dipole interaction is weaker than ion-dipole interaction and to fall off more rapidly with distance ($1/r^3$). Like ion-dipole forces, they are directional in the sense that there are certain preferred orientation and they are responsible for the association and structure of polar liquids.

❖ Comparison of boiling point of CF_4, NF_3 and OF_2: The boiling points and dipole moments of the corresponding compounds are CF_4 (-161 ºC, μ = 0 D); NF_3 (-129 ºC, μ = 0.234 D) and OF_2 (-145 ºC, μ = 0.3 D). Though the molar mass of CF_4 is higher than those of NF_3 and OF_2, the lower boiling point of CF_4 due its zero dipole moment results no dipole-dipole interaction for association of molecules. The dipole moment of NF_3 and OF_2 is comparable. The higher boiling point of NF_3 compared to OF_2 is due to its higher molecular mass.

It is noted that lower dipole moments of NF_3 and OF_2 arises because of the contribution of opposing lone pair moment to bond moment (μ of NH_3 = 1.47 D and μ of H_2O = 1.84 D).

❖ Boiling points of nitro alkanes: Nitro alkanes (RNO_2) possess high dipole moments and enjoy more intermolecular forces. This is why, nitro alkanes show higher boiling points compared to alkanes of comparable molecular mass.

(2) Dipole – induced dipole interaction (Debye force): If a charged particle, such as ion, is introduced into neighbourhood of an uncharged, non polar molecule (e.g., an atom of a noble gas), it will distort the electron cloud of the atom or molecule in the same way that a charged cation can distort the electron cloud of a large, soft anion (Fajans' rule). In a similar way, the

electric field of a dipole can induce another dipole in an uncharged, nonpolar (may be polar also) molecules. The polarization of the neutral species will depend upon its inherent polarizability (softness), α, and on the polarizing field afforded by the permanent dipole. The energy of such an interaction is given by

$$E_D = \frac{-\mu^2\alpha}{r^6}$$

Where μ_1 is the dipole moment of polarizing dipole and α is the distortion polarizability of the nonpolar molecule. This interaction is very weak since the polarizability of the most species is not large. Because of the interaction energy vary inversely with high power of r, it is effective only at very short distances. The energy of interaction is independent of temperature as it is arises due to distortion. This type of interaction is involved in the dissolution of ionic or polar compound in nonpolar solvents and also in the solubility of nonpolar molecule in polar solvents.

❖ Solubility of noble gas in water: The solubility of noble gases in water is fairly high and it increases with the increase of size of the inert gases. This is happen due to increased polarizability of the larger inert gases. Therefore noble gas hydrates becomes more stable as dipole-induced dipole interaction is higher in larger noble gas molecule.

(3) Instantaneous dipole – induced dipole interaction (London force): An intermolecular attraction force can exist even among the permanently nonpolar molecules through this type of interaction. This attractive force is described as London force and also referred to as dispersion force. Though time average electron distribution is symmetrical in nonpolar molecule but an instantaneous dipole will arise due to momentary imbalance in electron distribution. For example, in H_2, the accumulation of the two electrons on a particular nucleus produces a dipole moment in a particular direction, but the development of a dipole moment of same magnitude in the opposite direction due to accumulation of two electrons to the other

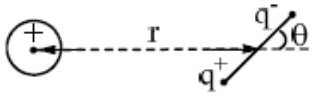
nucleus is also equally probable. Thus, each nonpolar molecule can be regarded as an instantaneous dipole which can induce a dipole in its neighbouring atoms or molecules to introduce an electrostatic interaction among the instantaneous dipoles. The energy of such interactions may be expressed as

$$E_L = \frac{-2\bar{\mu}\alpha}{r^6} \quad \text{or more conveniently } E_L = \frac{-3I\alpha^2}{4r^6}$$

Where α is the polarizability, $\bar{\mu}$ is mean instantaneous dipole moment and I is the ionisation energy of the species. This force is extremely short range in action (depending upon $1/r^6$) and weakest among the all attractive forces. As a result of the α^2 term, London force increases more rapidly with molecular weight or more properly with the molecular volume and polarizability of the species.

(4) Ion-dipole interaction: When placed in a electric field, a dipole will attempt to orient and become aligned with the field. If the field results from an ion, the dipole will orient itself so the attractive end (the end with charge opposite to that of the ion) will be directed toward the ion and the other, repulsive end directed away. In this sense, ion-dipole forces may be thought of as 'directional', though electrostatic forces are nondirectional. The potential energy of an ion-dipole interaction is given as

$$E_{min} = \frac{-Z^{\pm}\mu e}{4\pi r^2 \varepsilon_0}$$



$$E_{min} = \frac{-Z^{\pm}(\mu\cos\theta)e}{4\pi r^2 \varepsilon_0}$$

Where Z = numerical charge of the ion, μ = dipole moment of polar molecule, r = distance between the ion and centre of the dipole, ε_0 = permittivity of the free space. When $\theta = 0^o$ it gives maximum interaction and $\theta = 180^o$ it gives minimum attraction.

Ion–dipole interaction is similar to ion-ion interactions, except that it is more sensitive to the distance ($\propto 1/r^2$ instead of $1/r$) and tend to be somewhat weaker since the charges (q+, q-) comprising the dipole are usually less than the full electronic charge.

Such interactions are important in solvation and dissolution of ionic compounds in polar solvents. NaCl in water is hydrated as $Na(H_2O)_x^+$ and $Cl(H_2O)_y^-$. For the transition metal ions the ion-dipole interaction is so strong that it leads to discrete aqua and ammine complex in water or liquid ammonia solvent. In such cases, besides the simple electrostatic interaction, the covalent interaction plays an important role.

❖ **Effect of isotopic substitution on intermolecular attractive forces:** The boiling point of isotopes of hydrogen increases with the increase of molecular weight. H_2 (MW = 2; b.p. 20 K), D_2 (MW = 4; b.p. 23 K), T_2 (MW = 6; b.p. 25 K). Interestingly, the slightly lower boiling point of CD_4 than that of CH_4 probably due to the lower polarizability of CD_4.

Physical states of halogens and homologous series: Larger molecules are more polarisable so intermolecular attractive dispersion force will be higher. Because of this fact iodine is solid, bromine is liquid while chlorine and fluorine are gaseous at room temperature. Iodine being the largest halogen is the most polarisable one to have the highest dispersion force. Same trend also prevails among the inert gases. In a homologous series, the higher members show the higher melting and boiling points due to the larger polarizability of higher members.

Alkanes	Molecular mass	m.p. (K)	b.p. (K)	Alkanes	Molecular mass	m.p. (K)	b.p. (K)
CH_4	16	90.5	111.0	C_5H_{12}	72	143.0	309.1
C_2H_6	30	101.0	184.4	C_6H_{14}	86	179.0	342.0
C_3H_8	44	86.0	230.8	C_7H_{16}	100	182.5	371.5
C_4H_{10}	58	138.0	272.4	C_8H_{18}	114	216.2	400.0

❖ **Physical states of BX_3:** For the boron halides, BF_3 and BCl_3 are gaseous, BBr_3 is a volatile liquid while BI_3 is solid. It is due to the increasing trend of dispersion force as polarizability increases with the increase of the number of electrons in the molecules.

❖ **Boiling points of BF_3 vs. BMe_3, NF_3 vs. NMe_3:** Generally polarizability increases with the increase of molecular weight among the comparable species. As the London force increases with the increase of polarizability that's why boiling point of comparable species runs as $F_2<Cl_2<Br_2<I_2$; $He<Ne<Ar<Kr<Xe$; $CH_4<SiH_4<GeH_4<SnH_4<PbH_4$ and organic homologous compounds. But, molecular weight is not always good parameter to measure London force as polarizability largely depends on the chemical environment.

For example, the boiling point sequence is $BF_3 < BMe_3$, $NF_3 < NMe_3$. Though, molecular weights do not differ significantly but the substitution of nonpolarisable F by softer CH_3 will increase the polarizability of the methyl derivatives and hence have larger London force to increase boiling point. Similarly, fluorocarbons have unusually lower or equal boiling points compared to the corresponding hydrocarbon with much lower molecular weight because of tightly held electrons in the fluorine atoms have a low polarizability.

❖ **Solubility of $Me_4N^+Cl^-$ vs. $NH_4^+Cl^-$:** Though both are ionic compounds but the quaternary ammonium salt is more soluble in nonpolar solvents. In case of Me_4N^+, the charge is shielded by the hydrophobic groups and thus stabilized in nonpolar solvents through hydrophobic interaction (i.e. London force). No such stabilization is possible for $NH_4^+Cl^-$.

❖ **$SiCl_4$ vs. CCl_4:** Though $SiCl_4$ has higher molecular weight but shows lower boiling point than CCl_4. Because of the lower electronegativity of silicon than that of carbon, Cl atoms bear a higher negative charge in $SiCl_4$. Therefore, the negative charge density at the periphery of $SiCl_4$ is more than that of CCl_4 that results higher electrostatic repulsion among the $SiCl_4$ molecule than in CCl_4 molecules. At the same time, due to the $Si(d_\pi) \longleftarrow Cl(p_\pi)$ pi-bonding the nonbonding electron density on the periphery of $SiCl_4$ and positive charge on silicon is reduced which in turn decreases the polarizability of $SiCl_4$ molecule and also dispersion force. This type of pi-bonding is not possible in CCl_4.

❖ **Boiling point of isomeric hydrocarbons:** Branching of a hydrocarbon chain makes a molecule more compact and thereby reducing the surface area. The reduction of surface area reduces the dispersion force. This is why, branching in the alkyl chain reduces the boiling points among the isomeric organic compounds.

$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH(CH_3)CH_2CH_3$	$C(CH_3)_4$
(n-pentane, b.p. 36 °C)	(iso-pentane, b.p. 28 °C)	(neo-pentane, b.p. 9.5 °C)

In case of isomeric alcohols, branching reduces both the dispersion force and intermolecular H-bonding (due to steric hindrance) and consequently boiling point decreases.

$CH_3CH_2CH_2CH_2OH$	$(CH_3)_2CHCH_2OH$	$CH_3CH_2CH(OH)CH_3$	$C(CH_3)_3OH$
n-Butyl alcohol b.p. 118 °C	iso-Butyl alcohol b.p. 108 °C	sec-Butyl alcohol b.p. 100 °C	(tert-Butyl alcohol b.p. 83 °C)

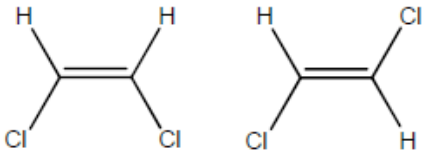
Branching of the hydrocarbon portion of the isomeric alcohols leads to decrease the relative volume. So the alcohols with more branching are more water soluble.

❖ **Magnitude of intermolecular attractive force in covalent lattice (solid state) depends on symmetry:** The symmetrical molecules have generally higher melting points. The symmetrical structures allow the close packing of the molecules in the crystal. It enhances the intermolecular attractive forces to increase the melting point. If the molecule is highly symmetrical, the melting point increases and consequently, such molecules very often sublime without melting. For example: SF_6, I_2, CO_2, camphor, $C_{20}H_{20}$(dodecahedron). The higher melting point of $C(CH_3)_4$ (-17 °C) compared to n-C_5H_{12} (-130 °C) due to the higher symmetry of $C(CH_3)_4$.

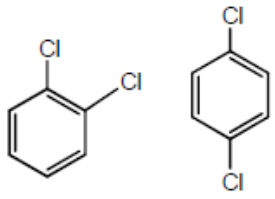
Therefore, the branching reduces intermolecular London forces in liquid phase while more symmetrical molecules (due to branching) experience the higher intermolecular attractive forces within the crystals due to the better packing.

❖ **Boiling point, melting point and solubility of *cis*- and *trans*-1,2-dichloroethane or *o*- and *p*-dichlorobenzene:** The *cis* or *o*-isomer is polar while the *trans* or *p*-isomer is nonpolar. The magnitude of intermolecular attractive force due to dipole-dipole interaction makes the boiling point of *cis/o*-isomer higher than that of *trans/p*-isomer. Whether, in terms of symmetry, the *trans/p*-isomer is more symmetrical than the *cis/o*-isomer. Consequently, the covalent lattice energy is higher for symmetrical *trans/p*-isomer due to its better packing in the crystals. Therefore, the *trans/p*-isomer shows the higher melting point and lower solubility in a given solvent. Thus the observations are;

boiling point: *cis/o-* > *trans/p-*; melting point: *cis/o-* < *trans/p-*; solubility: *cis/o-* > *trans/p-*

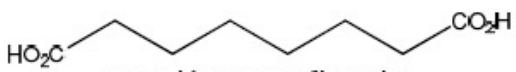


μ = 1.85 D μ ≈ 0.00 D



μ = 1.20 D μ ≈ 0.00 D

❖ **Melting point of dicarboxylic acids, HO_2C-$(CH_2)_n$-CO_2H:** It has been found that the melting point of dicarboxylic acid having an even number of C-atoms is higher than those of the acids having the odd number of carbon atoms lying immediately below or above it in the series. In zigzag orientation, the terminal -CO_2H groups lie on same side (*cis*-configuration) of the carbon chain for odd number of C-atoms chain while terminal -CO_2H groups lie opposite side (*trans*-configuration) for even chain. The *trans*-configuration is more symmetrical leading to close packing in the crystals. As a result, higher internuclear attractive force exists among the chains of even number of C-atoms. For this reason, the melting point of a dicarboxylic acid having an even number of C-atoms is always higher than the neighbouring dicarboxylic acids of odd number of C-atoms.



even acid, trans configuration
(more symmetrical)

odd acid, cis configuration
(less symmetrical)

❖ **Irregularity in melting point in a homologous series of alkanes:** In a homologous series, the intermolecular attractive London force increases with the increase of molecular mass but, for symmetrical molecules, the internuclear attractive force within the covalent lattice is higher due to the better crystal packing. For this reason, the melting point does not change smoothly in a homologous series but the boiling point increases regularly in a series. It is noted that the alkanes with even number of C-atoms show the relatively higher melting points. On moving from C_3 to C_4, the melting point increases by 52 K while C_4 to C_5, melting point increases only by 5.3 K.

Alkanes:	C_3H_8		C_4H_{10}		C_5H_{12}		C_6H_{14}		C_7H_{16}
m.p. (K):	86	52	138	5.3	143.3	35.7	179	3.5	182.5

Repulsive Force: As the molecules come closer, the van der Waals attractive forces ($\propto r^{-6}$) will gradually increase and become infinitely large at r = 0. At the same time, the repulsive force resulting from nucleus-nucleus repulsion (important in H_2 molecule) and more important, the repulsion between the inner or core electrons is also increased. Thus, the attractive and repulsive forces remain in equilibrium. At extremely short inter-atomic distances the inner electron clouds of the interacting atoms begin to overlap and Pauli repulsion becomes extremely large. The repulsive energy is given by:

$$E_{rep} = \frac{B}{r^n}$$

Where B is a constant for a particular type of interacting system and n, which depends on the electronic configuration, may have various values, comparatively large.

The repulsive potential is very much comparable with the Born repulsion. For ionic compound, n is called Born exponent ranging from 5 to 12. For covalent compound it is generally taken as 12.

Total interaction energy is given by:

$$E_{total} = E_{attractive} + E_{repulsive}$$
$$= \frac{-A}{r^6} + \frac{B}{r^n}$$

This interaction law is very often referred to as Lennard-Jones potential and sometimes also called as 6-12 function because it employs r^6 for attractive energy and r^{12} for repulsions.

Hydrogen Bond (H-Bond)

A hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms. Generally, an atom of hydrogen linked covalently to a strongly electronegative atom can establish an extra weak attachment to another electronegative atom. This secondary attachment is called a hydrogen bond.

❖ Hydrogen bonding represented as, $X^{\delta-}—H^{\delta+}\cdots Y$ where the hydrogen atom is covalently linked to X.

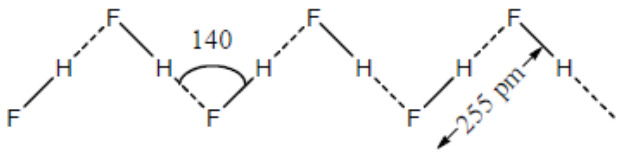
❖ X should be electronegative atoms, like F, O, N to polarise the $X^{\delta-}—H^{\delta+}$ bond.

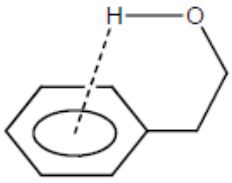
❖ Y should have lone pairs or polarisable electron cloud to show Lewis base property. Y may be an electronegative atom or simply π electron cloud moiety.

❖ H-bond may be linear or bent. Bifurcated and trifurcated H-bonds are also known.

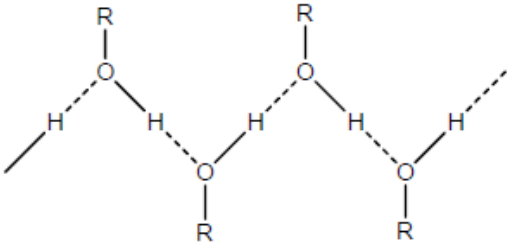
❖ Higher electronegativity of X results stronger of H-bonds. Thus, strength of H-bond increases from aliphatic alcohol to phenol, from NH_4^+ to substituted ammonium ions.

❖ Generally C—H bond would not participate in H-bonding. But, acetylinic hydrogen (i.e. ≡C—H), H—C≡N, H—CCl_3, RH_2C—H (R=CN, CH_3CO) participate in H-bonding.

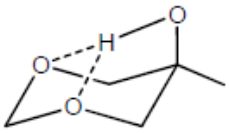


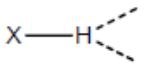


π–electron cloud involved in donation

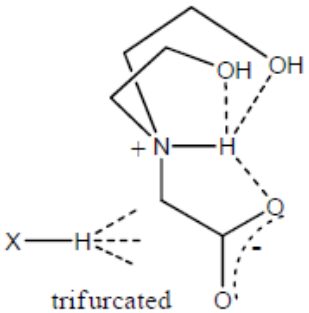


lone pair involved in donation





bifurcated



trifurcated

Types of Hydrogen bonding depending on the position of Y:

(1) Intermolecular H-bonding: X—H and Y comes from two different molecules.

Examples:

✓ In hydrides of highly electronegative elements such as HF, H_2O, NH_3, ROH etc.

✓ Hydrogen bonding in $KF{\cdot}HF$ leads to $K^+HF_2^-$ where HF_2^- is an H-bonded species. Other halogens (Cl, Br, I) can't form similar compound because of their lower electronegativity.

✓ Dimerization of carboxylic acid.

(2) Intramolecular H-bonding: X—H and Y comes from one single molecule that leading to a ring formation i.e. chelation. To favour this type of chelation, the ring should be planner and 5-6 membered. Example:

✓ Ortho-substituted aromatic compounds such as o-nitrophenol, salicyldehyde, o-chlorophenol, (Z)-picolinic oxime etc.

Symmetrical and unsymmetrical H-bonding:

In H-bonding, X—H$\cdots$Y where X and Y are the same chemical species e.g. HO—H$\cdots$O, N—H$\cdots$N, the H atom lies just midway of X and Y is leading to symmetrical H-bonding. In such cases H-bond energy is higher and X$\cdots$H$\cdots$Y bond length is relatively shorter. In unsymmetrical H-bonding X—H bond length is shorter than that of H$\cdots$Y bond. Examples:

✓ In potassium hydrogen phenyl acetate ($PhCH_2COOK{\cdot}PhCH_2COOH$), O$\cdots$H$\cdots$O length is 255 pm in which H is symmetrically placed.

✓ In HF_2^-, F$\cdots$H$\cdots$F length is 226 pm and bond energy is ~165 $kJmol^{-1}$ in which H is symmetrically placed. But, $(HF)_n$, exists in solid, liquid and even in vapour phase, F$\cdots$H$\cdots$F length is 255 pm and bond energy is ~30 $kJmol^{-1}$ in which H is unsymmetrically placed.

✓ In ice, each oxygen is tetrahedrally surrounded by four H atoms but the four O—H bonds are not identical. Two O—H bonds (~ 99 pm) are shorter than the others (~ 177 pm). Thus H is unsymmetrically placed.

✓ Unsymmetrical H-bond exists in crystal of orthoboric acid.

H-bond length and energy:

The H-bond is comparatively weaker and bond energy lies in the range 8-42 $kJmol^{-1}$ (typical covalent bond energy ranges from 100-400 $kJmol^{-1}$). The H-bond energy mainly depends on

✓ Dipole moment (μ_{X-H}) of the bond.

✓ Electronegativity of X atom.

✓ Donor property of Y which related with ΔI (difference of ionisation energy of Y and the noble gas atom of the same row).

✓ Internuclear distance between X and Y.

Few H-bond dissociation enthalpy ($kJmol^{-1}$)					
$HF\cdots F^-$	165	$HCl\cdots Me_2O$	30	$HCN\cdots HCN$	16
$H_3O^+\cdots H_2O$	151	$HF\cdots HF$	29	$SH_2\cdots SH_2$	7
$H_2O\cdots F^-$	98	$H_2O\cdots H_2O$	22		
$H_2O\cdots Cl^-$	55	$MeOH\cdots MeOH$	19		
$HF\cdots H_2O$	38	$NH_3\cdots NH_3$	17		

Unconventional H-bond:

The protonic hydrogen ($H^{\delta+}$) of O—H and N—H bonds may interact with the hydridic hydrogen ($H^{\delta-}$) of borohydrides and metal hydrides. In such cases the hydridic hydrogen act as Y. Such H-bonding may represented as $O^{\delta-}—H^{\delta+}\cdots H^{\delta-}—M^{\delta+}$; $N^{\delta-}—H^{\delta+}\cdots H^{\delta-}—B^{\delta+}$. Due to such type of H-bonding melting point of $H_3B\text{-}NH_3$ (104 ºC) adduct is much higher than the $CH_3\text{-}CH_3$ (-182 ºC).

Isotopic effect:

H-bond involving deuterium (D, heavier isotope of H) is stronger. Thus, O—H$^{\cdots}$O bond is weaker than O—D$^{\cdots}$O bond. In fact, boiling point of D_2O (heavy water) is higher than that of H_2O (normal water).

Effects of Intermolecular H-bonding on melting and boiling points:

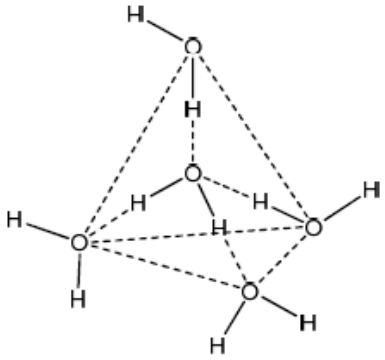
H-bonding influences several physical properties like melting and boiling temperature, dielectric constant, viscosity, solubility, miscibility with other solvents and even sensitivity to chromatographic separation.

Intermolecular association is leading to higher melting and boiling temperatures. Breaking of these H-bonds throughout the entire liquid or solid requires appreciable heat energy. This is the reason of relatively higher boiling and melting point of H-bonded species compared to similar compounds with little H-bonding.

Melting and boiling point of hydrides of Gr-15, Gr-16 and Gr-17 elements:

- ✓ For covalent compounds, melting and boiling points should rise gradually with increasing molecular weight owing to increasing London force. This is true for hydrides of Group-14 elements. But, in Groups 15, 16 and 17, the hydrides of first element in each group (which is most electronegative) have unusually higher boiling points than other group members. $NH_3 >> PH_3 < AsH_3 < SbH_3$; $H_2O >> H_2S < H_2Se < H_2Te$; $HF >> HCl < HBr < HI$
- ✓ Crystalline hydrogen fluoride consists of the polymer $(HF)_n$. It has a zigzag chain structure involving H-bonds. The H-bonding persists in liquid as well as in the vapour, even at its boiling point HF consists of species upto $(HF)_6$.
- ✓ Ice contains extensive hydrogen bonding. In ice, each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two H-atoms by covalent bond and the other two by longer H-bonds. When ice melts, some of these hydrogen bonds break, the water molecules can now come closer, hence the volume decreases on melting. The breaking of H-bonds

continues upto about 4 ºC and the contraction caused is greater than the thermal expansion. So, volume is decreases upto 4 ºC and then increases. Consequently, water has its highest density at 4 ºC.



Effect of alkylation: Boiling point of H_2O and its substituted compound:

Boiling point decreases on alkylation i.e. substitution of hydrogen by alkyl group. On substitution, the number of hydrogens which participate in H-bonding decreases and the boiling point decreases though the van der Waals force increases. The sequence of the boiling point is as follows H_2O (100 ºC) > CH_3OH (63 ºC) > CH_3OCH_3 (5 ºC).
Similarly, triethylamine shows lower boiling point (5 ºC) than dimethylamine (7 ºC), which is H-bonded. Similar result obtained on esterification of inorganic acids. Me_2SO_4 (188 ºC) < H_2SO_4 (decompose, 340 ºC); Me_3PO_4 (193 ºC) < H_3PO_4 (decompose, 212 ºC); Me_3BO_3 (65 ºC) < H_3BO_3 (decompose, 187 ºC); CH_3F (-78 ºC) < HF (20 ºC).

The dipole moment of C_2H_5F and HF are almost same but the boiling point of HF is much higher than that of C_2H_5F. In both compounds, the intermolecular attraction due to dipole-dipole interaction is more of les similar. But, association of HF molecule due to H-bond makes its boiling point higher.

Boiling point of RCO_2H and ROH:

The boiling points of carboxylic acids are higher than those of alcohols of comparable molecular weights. In $-CO_2H$ group, the –OH bond is more polarized because of the carbonyl group compared to –OH group of alcohols. This is why, the carboxylic acids are more strongly H-bonded than the alcohols, resulting higher boiling point.

Boiling points of alkyl derivatives of hydrides of Group 15 and 16 elements:

As hydrogens are substituted by the alkyl groups, the H-bonding interaction between the molecules are no longer exists. The van der Waals interaction force is now determining factor for boiling points of the compounds. As down the group, the molecular weight and hence polarizability of the alkylated hydrides increases the van der Waals force of interaction increases which reflects the increases of boiling point of such compounds down the group.

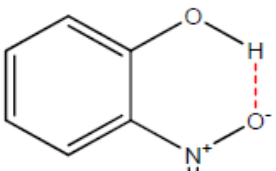
$Me_2Te \approx H_2O > Me_2Se > Me_2S > Me_2O$

$Me_3Sb \approx Me_3As > Me_3P > Me_3N > NH_3 > PH_3$

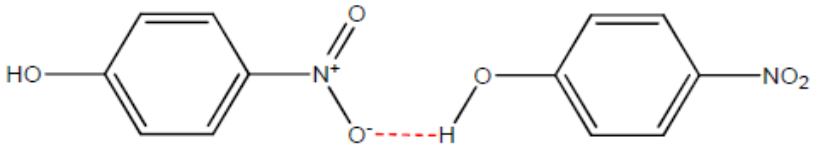
In the sequence of boiling point shows that boiling point of NH_3 is lower than that of Me_3N but H_2O has higher boiling point than Me_2O. Therefore, reverse trend is observed that reflects effect of H-bond in NH_3 is less important as in H_2O because of lower electronegativity of N.

Effects of intramolecular H-bonding on boiling and melting points:

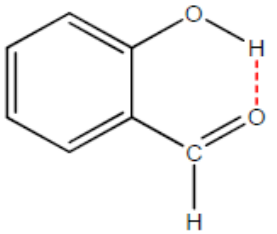
Boiling and melting points of o- and p-isomers of aromatic compounds: In case of o-isomers, no molecular association occurs because of absence of intermolecular H-bonding. Due to stronger nature of intramolecular H-bond over intermolecular H-bond, the o-isomeric compounds remains as monomer in the liquid state and only the weak van der Waals forces exists among the momomeric species. On the other hand, the p- and m-isomers undergo intermolecular H-bonding leading to an association to show relatively much higher boiling and melting points.



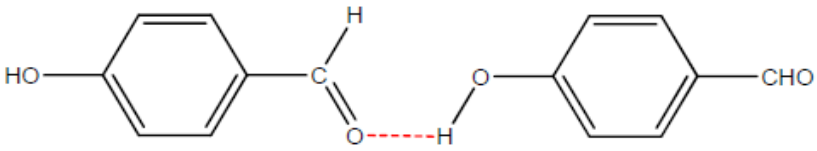
o-nitrophenol
b.p. 214 °C



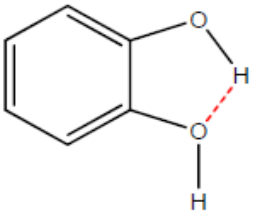
p-nitrophenol
b.p. 279 °C



o-hydroxybenzaldehyde
b.p. 196 °C

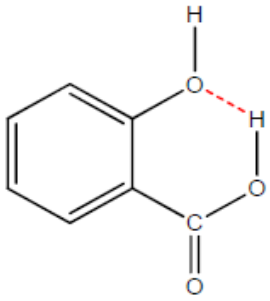


p-hydroxybezaldehyde
b.p. 310 °C



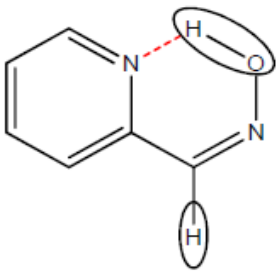
1,2-dihydroxybenzene
b.p. 245 °C

1,4-dihydroxybenzene
b.p. 286 °C

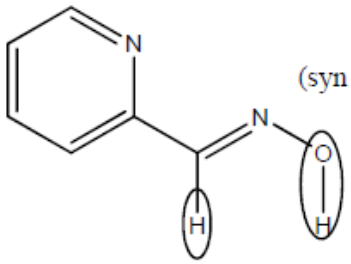


o-hydroxybenzoic acid
b.p. 158 °C

p-hydroxybenzoic acid
b.p. 214 °C



(anti form)



(syn form)

Theory of formation of H-bond:

(i) Electrostatic interaction: Since H-bonding occurs only with electronegative atoms, it was assumed that it involves mainly electrostatic interactions. An electronegative element X polarizes the X—H bond as $X^{\delta-}$—$H^{\delta+}$. This partially positive charged hydrogen may now give rise to ion-dipole or dipole-dipole interaction forming the H-bond. This electrostatic model fairly explains the experimental H-bond energy, dipole moment and also the linearity of H-bond as the primary requirement of maximum electrostatic interaction. The electrostatic model can explain the relative efficiency of H-bonding in the hydracids of halogens i.e. H-F

> H-Cl > H-Br > H-I. With the increase of electronegativity of X, the increased accumulation of positive charge on H facilitates the electrostatic interaction.

But, the simple electrostatic theory can't explain the marked increase of intensity of the stretching frequency $\nu_{X—H}$ after H-bond formation nor the lower intensity of bending vibration.

(ii) Valence bond approach: Formation of two covalent bonds (2c-2e) i.e. X—H—Y, requires the participation of 2s orbital which is not energetically forward and also all H-bonds would be symmetrical but it is not experimentally supported.

But, some covalent character may be assigned to the hydrogen bond in terms of covalent-ionic resonating structures of the types

$$X—H\bullet\bullet Y \longleftrightarrow \bar{X}\bullet\bullet H—\overset{+}{Y}$$

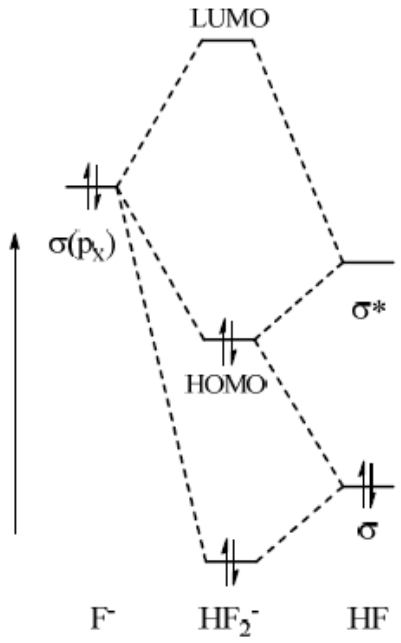
But, detailed calculations show that contribution of such covalent character is really small. But, such resonating structure is significant only for strong and short H-bonds like those in HF_2^- where H is symmetrically placed.

$$F—H\text{----}\bar{F} \longleftrightarrow \bar{F}\text{----}H—F$$

(iii) Molecular orbital approach:

MO diagram of HF_2^- (F—H—F^-) may be generalized for any hydrogen bonding of the type X—H----Y where XH replaces HF and Y replaces F^-. The species HF_2^- is the combination of HF and F^-. For simplicity we may consider only interacting orbitals i.e. σ and σ^* MOs of HF and p_x orbital of F^- (X-axis is considered as molecular axis). So, the resultant MOs is produced from the linear combination of these three orbitals. It leads to 3-centred MOs, (one bonding, one nonbonding and one antibonding) in which four electrons (bond pair of HF and lone pair of F^-) are accommodate in the bonding, and non-bonding MOs leading to 3-centred 4 electrons (3c-4e) bonding systems. It is seen that the electron pair from F^- now occupies stabilized non-bonding MO, which becomes HOMO. The antibonding MO becomes the

LUMO. The total energy of the resulting FHF^- species has a lower than the sum of the energies of HF and F^-.



The basic requirement for the stabilization of such 3c-4e bonding system is the high electronegativity of the terminal atoms. With the increase of electronegativity of X, the energies of both σ_{X-H} and σ^*_{X-H} will decrease. At the same time, X will polarise the X-H bond and σ_{X-H} orbital will be preferably concentrated on X and σ^*_{X-H} orbital will be preferably oriented on H. This will favour the H-bonding because of the better energy matching of p_x of Y with σ^*_{X-H} orbital and poorer energy matching σ_{X-H} orbital.

So it is seen that, if the HOMO of Y and the LUMO of HX have comparable energy, both occupied MO in X—H$^{\cdots}$Y will be lower in energy than either of the interacting orbitals (p_x of Y and σ^*_{X-H} orbital of HX) and the system become stabilized.

Again, if energy of the HOMO of Y lies far below that of the LUMO of XH, the HOMO in X—H$^{\cdots}$Y will be above of Y orbital (HOMO) and will not serve to stabilize the system.

Receptor-Guest Interactions

Receptor or Host: The molecule or molecular assembly which provides or creates a suitable cavity or site so that another molecule can sit there is called receptor.

Guest: The molecule which size and shape is properly matches with the dimension of the cavity can bind with the receptor is called guest.

Receptor – Guest are held together though non-covalent intermolecular forces. The attractive force operates efficiently when the receptor and guest molecules match both sterically and electronically so that they can recognise each other. This leads to molecular recognition. This is why, the chemistry of molecular recognition is also known as guest-host chemistry.

The non-covalent interactions are of different types, such as

i) Electrostatic interaction (ion-ion, ion-dipole, dipole-dipole)

ii) Dispersion force, hydrophobic interaction

iii) Hydrogen bonding interaction

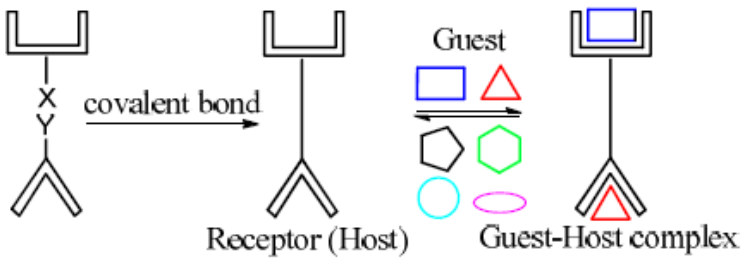
iv) π-π stacking

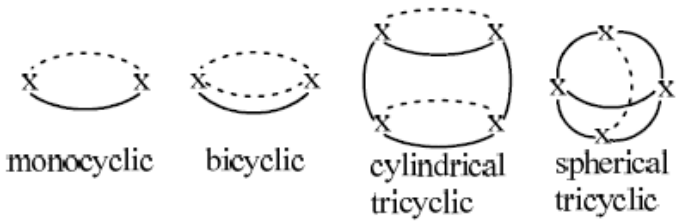
v) Hydrophilic-hydrophobic (solvatophobic) interaction.

Lock and Key principle:

In molecular assembly, the molecular component i.e. guest-host must maintain the proper complementary both electronically and sterically. This is why, the components can recognise each other through the interplay of supramolecular non-covalent forces. This leads to molecular recognition and forming supramolecules. The stability of supramolecular system depends on the degree of stereo-electronic fit among the components. Thus in such system the lock and key principle is followed. Because of this principle the selectivity is attained.

$$\text{Guest(G)} + \text{Host(H)} \rightleftharpoons \text{Guest-Host(G-H) complex (supramolecule)}$$





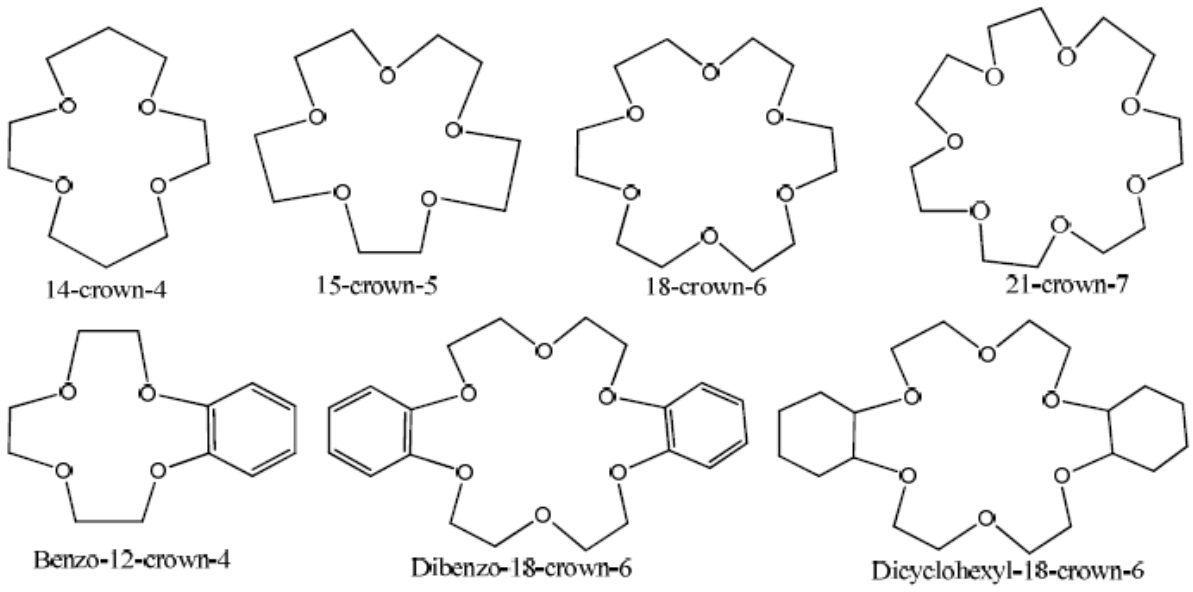
Macrocyclic receptors with cavity of different shape and size

Crown ether: Macrocyclic polyether is known as crown ether. Crown ether complexes are formed when the cation fit well into the cavity of the crown ethers.

Macrocyclic effect: The enhancement of the stability of the metal complex with macrocyclic ligands compared to those acyclic analogues is called macrocyclic effect. The stability of crown ether complex is 10^2-10^3 times greater than the open chain ligand.

Nomenclature and different types of Crown ether:

In naming of crown ethers, first consider the number of atoms in the ring and secondly, number of o-atom available for interaction.



Complex formation by crown ethers:

Crown ethers are selectively binds the alkali metal ions. Due to trapping of the cation within the cavity of crown ether the organic part of the ligand become puckered to give the crown arrangement. Such complexes are soluble in organic or nonpolar solvents because of the non-polar periphery. Thus, these ligands can acts as ionophores that carry ions through the biological lipid membrane. The poly ether can also accommodate the non-polar guest within the cavity in a hydrophilic medium.

The bonding interaction to trap the guest cation is basically electrostatic. The stability of such complexes depend several factors as given below:

i) Number of donor sites: Higher number of o-atoms in a plane resulting higher stability of the complex.

ii) Stereochemistry of the cavity: Stability of the complex is increased when the O-atoms are symmetrically placed and coordinated structure is free from steric strain, resulting requirement of less reorganization energy.

iii) Relative size of the ion and cavity size: A stable complex results when the metal ion fit well into the cavity resulting maximum electrostatic interaction.

iv) Basicity of the donor centre: With the increase of ligand basicity the stability of such complex increases. The O-atom bound to aliphatic carbon atom is more basic than the O-atom bound to the aromatic carbon atom. That's why, the dicyclohexyl-18-crown-6 forms a more stable complex with K^+ than dibenzo-18-crown-6.

v) Cation solvation: The less cation solvation, the more stable is the crown ether complex.

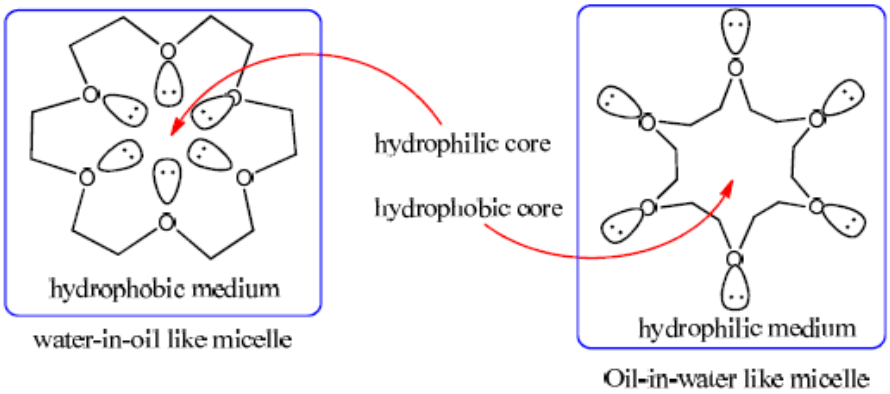
Cavity size of the crown ethers:

Crown ether; Diameter(ppm)	Metal ion
14-crown-4, (120-150)	Li^+(140), Na^+(190), Ca^{2+}(200), K^+(270), Ba^{2+}(270), Rb^+(300), Cs^+(330)
15-crown-5, (180-220)	
18-crown-6, (260-320)	
21-crown-7, (340-430)	

Therefore, crown-4 prefers Li^+, crown-5 prefers Na^+ and crown-6 prefers K^+ ion. The selective binding of such spherically charged cation is called spherical recognition. The selectivity sequence is as follows: Crown-6: $K^+ > Cs^+ > Na^+ > Li^+$; Crown-5: $Na^+ > K^+ > Cs^+ > Li^+$

Conformation change of crown ether:

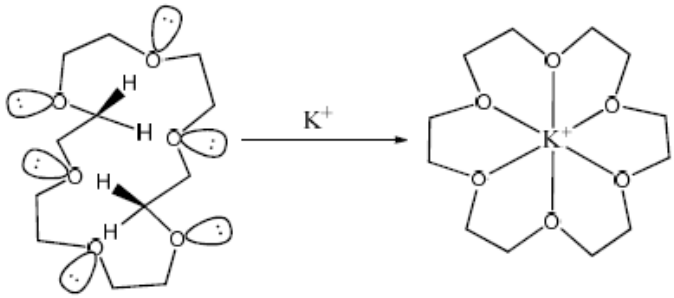
The crown ethers change their conformation during complexation. The energy requirement for such conformational change is called reorganisation energy. The higher value reorganisation energy results least affinity to form complex. The conformation adopted by crown ether depends on the nature of the solvents or medium. In a hydrophilic medium, the O-sites are projected outwards to produce a hydrophobic core in which organic molecule can be accommodated as guest. Again, in hydrophobic medium, $-CH_2$ groups are projected outwards and the O-sites are projected inwards producing a hydrophilic core.



water-in-oil like micelle

Oil-in-water like micelle

Different conformation of 18-crown-6 depending on the nature of medium

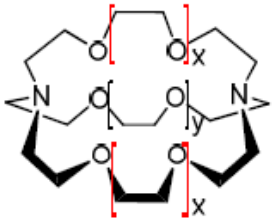


Conformational change of 18-crown-6 during complexation.

Cryptands: The Cryptands are macrobicyclic/tricyclic aminoether ligands having both N- and O-donor sites. Three dimensional Cryptands (bicyclic/tricyclic) are more preorganised than the monocyclic crown ethers for complexation. For this reason, the Cryptands form more stable complex than the crown ethers.

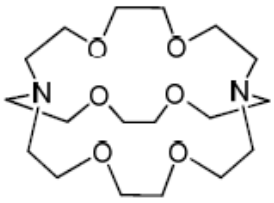
Nomenclature and different types of Cryptands:

Cryptands are named starting with the chain of highest number of o-donors.

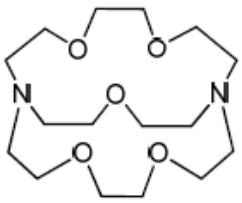


Crypt-[2,1,1] (x=0, y=1)

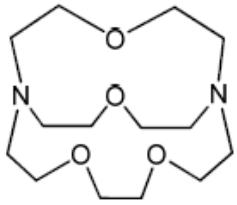
Crypt-[3,3,2] (x=2, y=1)



Crypt-[2,2,2]



Crypt-[2,2,1]



Crypt-[2,1,1]

Cavity size of the cryptands is increasing with the increase of the number of O-donor sites.

Crypt-[1,1,1] (100 pm) < Crypt-[2,1,1] (160 pm) < Crypt-[2,2,2] (280 pm) < Crypt-[3,2,2] (360 pm) < Crypt-[3,3,3] (480 pm)

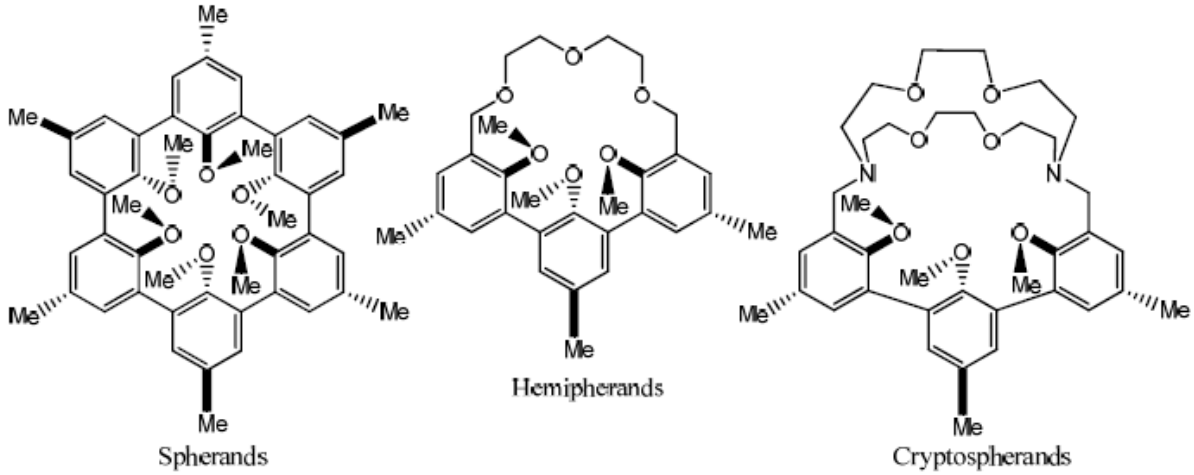
The metal complexes of cryptands are called cryptates. The bicyclic cryptands form 1:1 complex, where the bridgehead N-sites acts as the donor sites and the metal ion is positioned at the centre of the cage. All the N- and O- donor sites are more or less equidistance from the metal centre. Thus, in cryptates, the ligand possesses endo-endo conformation.

Similar to crown ether complex, the exterior part of the cryptate is hydrophobic while interior part is electron rich and hydrophilic. So, the cryptands can act as ionophores.

Spherands:

Fully preorganised macro monocyclic polyethers providing a spherical cavity in which six O-atoms are octahedrally positioned are called spherands. In spherands, the donor O-sites are present in the intra-anular substituents and are pointed towards the centre of the cavity. The mix structure of crown ether and spherands or cryptands and spherands produces the ligands like hemispherands, cryptopsherands etc.

Since, spherands are already structurally preorganised and the coordination sites are suitably projected towards the cavity for encapsulation of the metal ion, the spherands form much more stable complex than the crown ether.

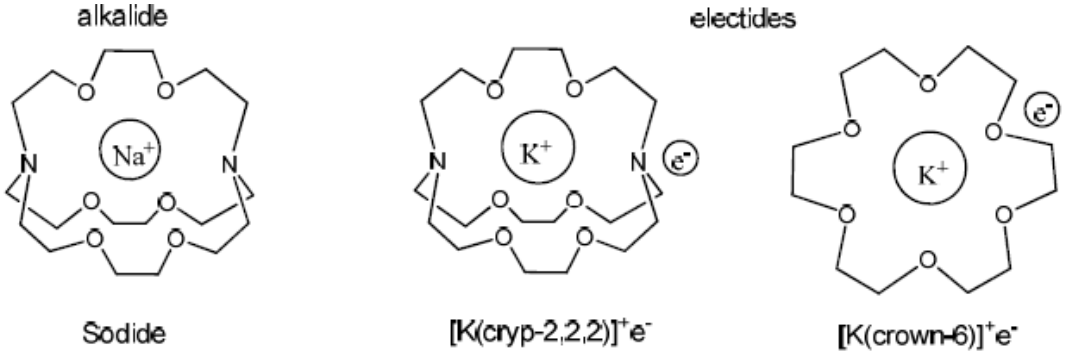


Application of Crown ethers and Cryptands:

i) Dissolution of alkali metal and formation of alkali metal anion alkalides:

Ether can't dissolve the alkali metal but the crown ethers or cryptands dissolute the alkali metals. $K + \text{crown-6} \xrightarrow{\text{THF solvent}} [K(\text{crown-6})]^+ + [e(\text{solvent 6})]^-$

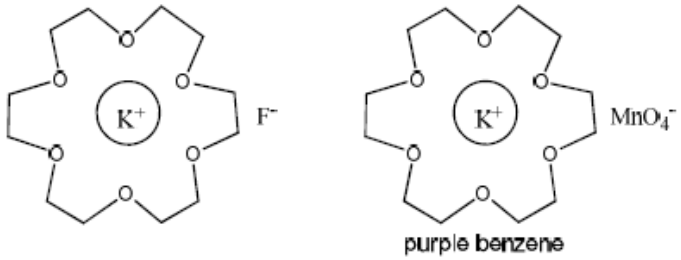
The alkali metal ion is stabilised in the cavity of the macrocycle and the released electron is solvated. Such complexes like $[K(\text{crown-6})]^+e^-$ are called electrides. The unusual compounds like $[Na(\text{crypt})]^+Na^-$ having sodide ion are stabilised by the shielding effect of the cryptand around the cation.



ii) Dissolution of salts in nonpolar solvents:

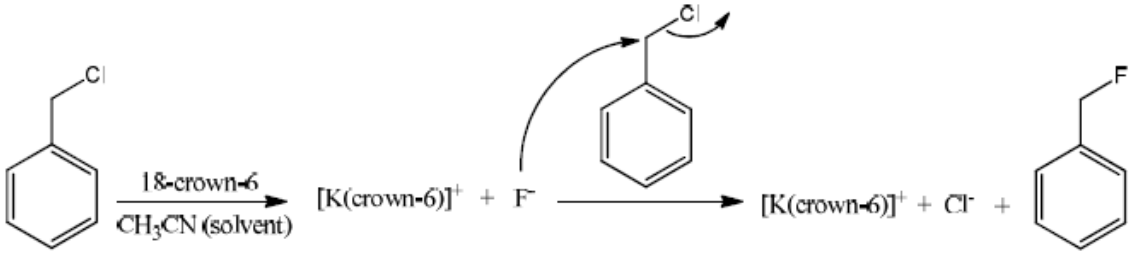
Crown ethers and cryptands can dissolute salts in organic solvents through encapsulation of the metal ion within the cavity.

$KF \xrightarrow{\text{Crown ether (benzene)}}$ solubilised; $KMnO_4 \xrightarrow{\text{crown ether (benzene)}}$ solubilised



iii) Phase transfer catalyst (PTC):

KF is an ionic compound does not dissolve in acetonitrile. But, in presence of 18-crown-6, KF is solubilised in acetonitrile and the unsolvated free F^- can acts as a powerful nucleophile.



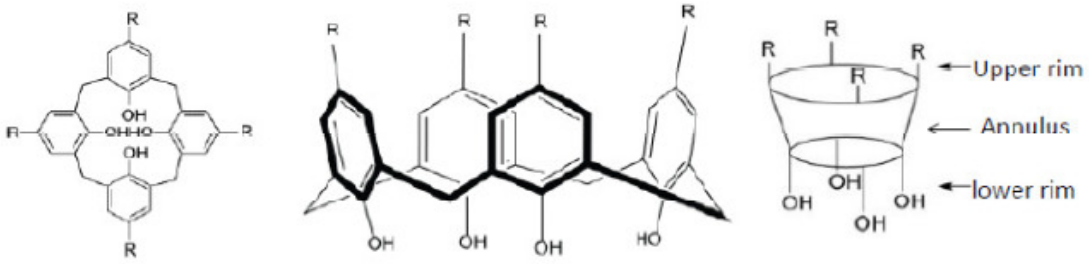
Similarly, $KMnO_4$ solubilised in benzene in presence of 18-crown-6 can acts as a powerful oxidizing agent due to unsolvated MnO_4^- in non-aqueous medium.

Ionophore: Ionophores are macromolecular antibiotic substance capable of inducing the passage of specific cations across the biological membranes. Due to their hydrophobic nature of their exterior surface, these substances, with their bound metal ion, can dissolve in and diffuse through non polar hydrocarbon layers in the membrane structure. Example:

i) Cyclic natural ionophore: Nonactin, valinomycin (selectively binds K^+)

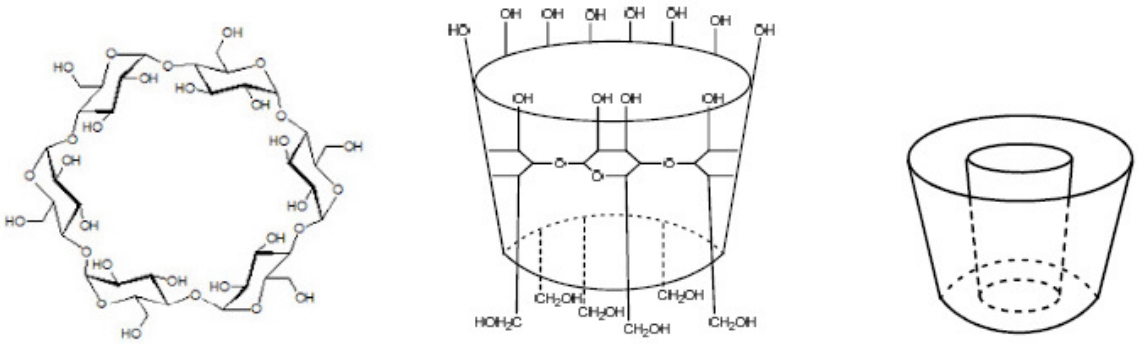
ii) Open chain ionophore: Monensin (selectively binds Na^+)

Calixarenes: Calixarenes is a macrocycle or cyclic oligomer obtained from condensation of a p-alkylphenols and an aldehyde. Calixarenes are characterised by a three-dimensional basket, cup or bucket shape having a wide upper rim, a narrow lower rim and a central annulus. In cup like structure, the hydrophilic Phenolic OH groups make legs or pedestals. Calixarenes can acts as receptor of both ionic and neutral guest species. It accommodates the sterically compatible organic molecules like xylene, anisole in hydrophobic cavity and cations in hydrophilic phenolic cavity.

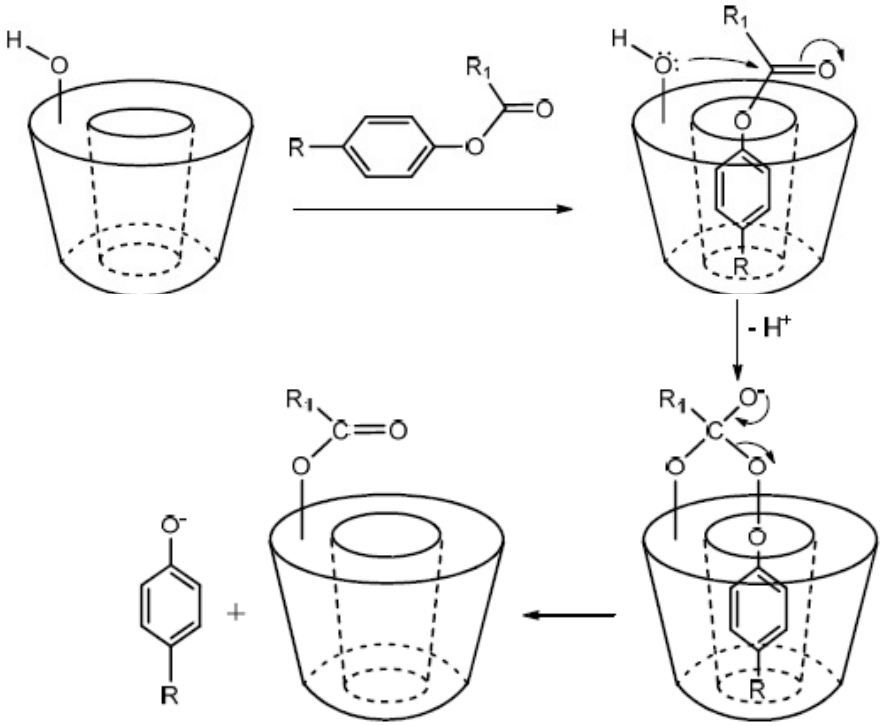


Representation of calix[4]arene where R= H, Me, t-Bu

Cyclodextrins: Cyclodextrins are also cyclic oligomers generally polysaccharides obtained from starch when treated with a particular enzyme of Bacillus macerans. They can produce beaker like hydrophobic cavities with both ends open. The cavity size depends on the degree of polymerisation. The cavity provides one rim with secondary OH-groups while the other rim is with primary OH groups. The hydrophobic interior cavity can acts as a receptor for different sterically fit non-polar guest molecule. They can also catalyse different types of cleavage reaction by using secondary OH groups present at the entrance of the cavity.



Schematic representation of structure and shape of α-cyclodextrin



Cyclodextrin catalysed hydrolysis of aryl ester.

Halogen Bond

The term "halogen bond", which suggests an inter- and intramolecular interactions involving a halogen atom in a molecular entity. Because of relatively high electronegativity, halogen atoms can behave as electron-rich (nucleophilic) sites and form net attractive interactions with electron-poor (electrophilic) partners. A halogen atom functioning as hydrogen bond acceptor is a typical example of such interactions as observed in case hydrogen bond formation ($R^{\delta-}$—$H^{\delta+}$----Y where Y is halogen). Halogen atoms can also function as electron-poor (electrophilic) sites and attractively interact with electron-rich (nucleophilic) sites and may be represent as $R^{\delta-}$—$X^{\delta+}$----Y where X is halogen. The two sets of interactions differ for their electronic features and several other characteristics, e.g., their directionality relative to the covalent bond(s) formed by the halogen atom. The latter set of non covalent interactions described above is termed as "halogen bond".

Definition: A halogen bond (XB) occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.

A typical halogen bond is denoted by the three dots in R–X···Y. R–X is the halogen bond donor, X is any halogen atom with an electrophilic (electron-poor) region, and R is a group covalently bound to X. Y is the halogen bond acceptor and is typically a molecular entity possessing at least one nucleophilic (electron rich) region.

Some common halogen bond donors and acceptors are itemized below.

R–X	Y
i) dihalogen molecule (e.g., I_2, Br_2, ICl, ClF)	i) lone pair possessing atom (e.g., N atom of a pyridine or an amine, O atom of a carbonyl group)
ii) haloalkane (e.g., CBr_4, CHI_3, $C_nF_{2n+1}I$)	ii) π system (e.g., double or triple bonds, arene moiety)
iii) haloarene or haloheteroarene (e.g., iodobenzene, halopyridinium and haloimidazolium cations)	iii) anion (e.g., halide anion, oxyanion)
iv) 1-haloalkyne (e.g., diiodoacetylene)	
v) halonium ion (e.g., diphenyliodonium or bromonium derivatives)	
vi) haloimide (e.g., *N*-bromo- or *N*-iodosuccinimide)	

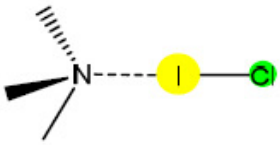
Features of Halogen bond (XB): In a typical halogen-bonded complex R–X···Y:

- Halogen bonds are strong, specific, and directional interactions that give rise to well-defined structures. Halogen bond strengths range from 5–180 kJ/mol.
- The inter-atomic distance between X and the appropriate nucleophilic atom of Y tends to be less than the sum of the van der Waals radii.
- The length of the R–X covalent bond usually increases relative to the non-halogen bonded R–X.
- The angle R–X···Y tends to be close to 180°, i.e., the halogen bond acceptor Y approaches X along the extension of the R–X bond.
- The halogen bond strength decreases as the electronegativity of X increases, and the electron withdrawing ability of R decreases. So, halogen bond formation ability run as follows I > Br > Cl > F.

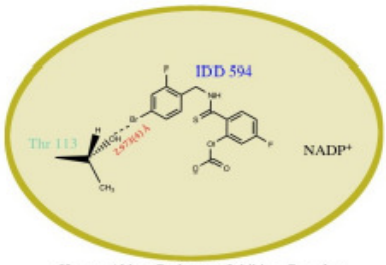
- The forces involved in the formation of the halogen bond are primarily electrostatic, but polarization, charge transfer, and dispersion contributions all play an important role. The relative roles of the different forces may vary from one case to the other.

Examples:

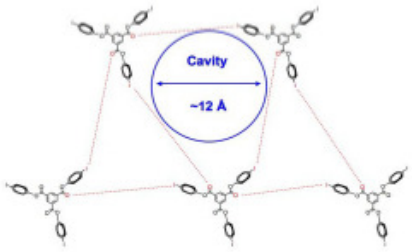
a) XB in complex between iodine monochloride and trimethylamine.



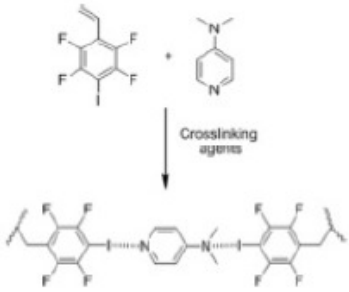
b) XB in biological macromolecules:



Human Aldose Reductase-Inhibitor Complex



c) XB in polymer obtained from 2,3,5,6-tetrafluoro-4-iodostyrene and 4-(dimethylamino) pyridine



d) Bromination of alkenes evidencing the formation of halogen-bonded adducts of the type X···π.