Combination of Atomic Orbitals

(i) **Combinaltion of s-orbitals:** The combination of two similar 1*s* atomic orbitals gives rise to two molecular orbitals, σ1s and σ *1s. σ1s is the bonding molecular orbital, whereas σ *1s is the antibonding molecular orbital. Similarly, the combination of two 2s atomic orbitals will give rise to σ2s and σ*2s molecular orbitals. These will be of higher energy than σ1s and σ*1s molecular orbitals as they are formed from atomic orbitals of higher energy.

(ii) **Combination of p-orbitals :** The p-orbitals can combine either along the axis to give σ molecular orbitals or perpendicular to the axis to give π-molecular orbitals.

Combination of Atomic Orbitals

(a) Combination of p_x orbitals: The overlapping of two P_x orbitals along the axis results in the formation of a bonding σ_{px} and antibonding σ^*_{px} molecular orbitals. The orbitals with same sign produce bonding molecular orbitals, whereas the orbitals with unlike signs produce anti bonding molecular orbitals .

(b) Combination of p_y or p_z orbitals: The overlapping of two p_y or two p_z atomic orbitals takes place perpendicular to the molecular axis and, thus, results in the formation of bonding and antibonding π- molecu!ar orbitals.

Molecular Orbital Treatment for Homonuclear Diatomic Molecules

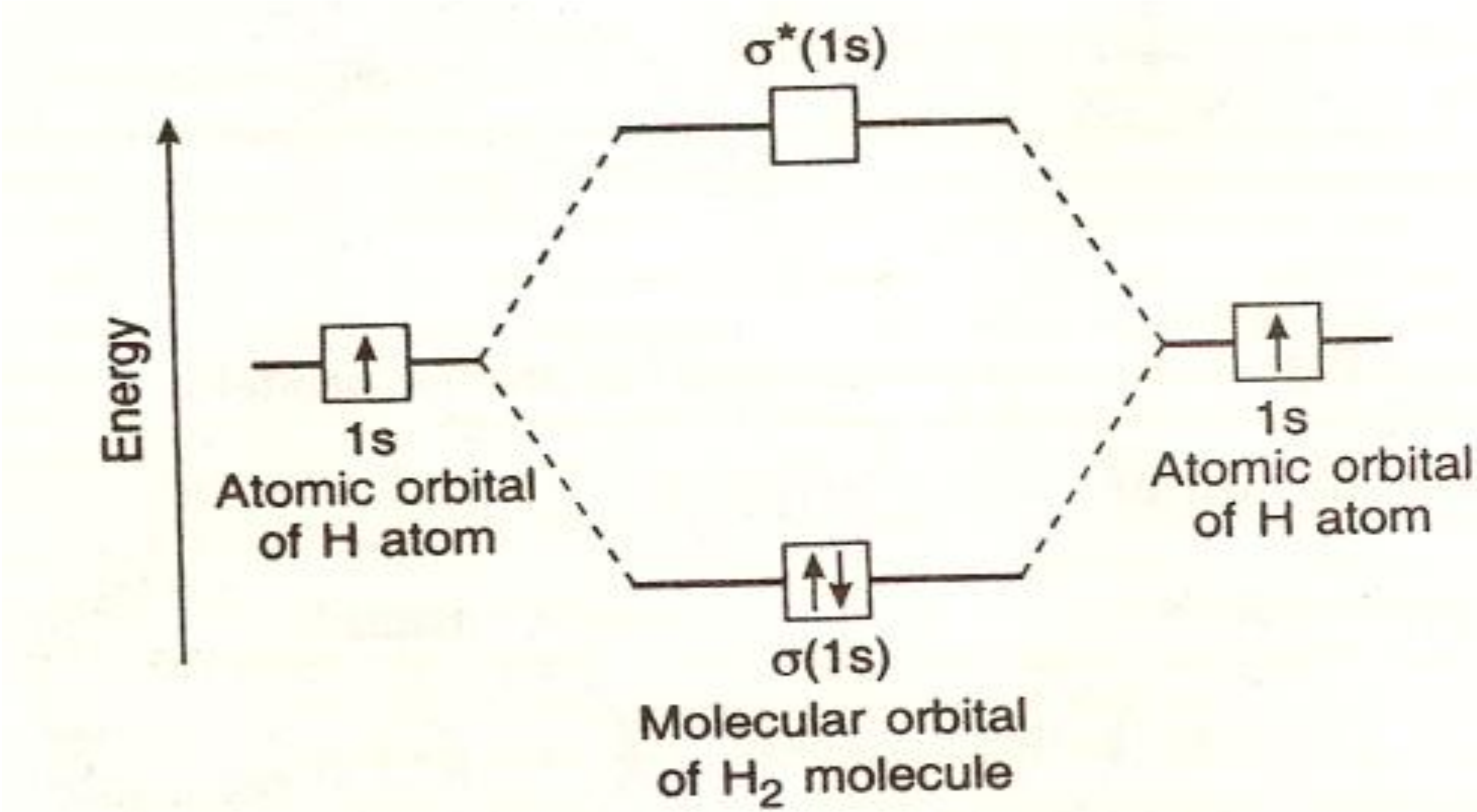
(1) Hydrogen molecule, H_2: Hydrogen molecule is formed from $1s^1$ atomic orbitals of two atoms. They give rise to two molecular orbitals σ(1s) and σ*(1s). Both these electron will be in σ(1s) bonding molecular orbital, but with opposite spin. The antibonding molecular orbital remains vacant. The electronic configuration of the molecule is $\sigma(1s^2)\ \sigma^*(1s^0)$.

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{[2-0]}{2} = 1.0$$

Since its B.O. is 1.0, so it exists and is stable.

Molecular Orbital Treatment for Homonuclear Diatomic Molecules

MO Diagram of H2 Molecule:



Molecular Orbital Treatment for Homonuclear Diatomic Molecules

(2) Lithium molecule Li_2: Lithium molecule is formed by the overlap between two lithium atoms each having the electronic configuration $1s^2 2s^1$. So, we have total of six electrons which have to be accomodated in 4 molecular orbitals, viz., σ1s, σ*1s, σ2s and σ*2s.

Hence, molecular orbital electronic configuration of Li_2 molecule

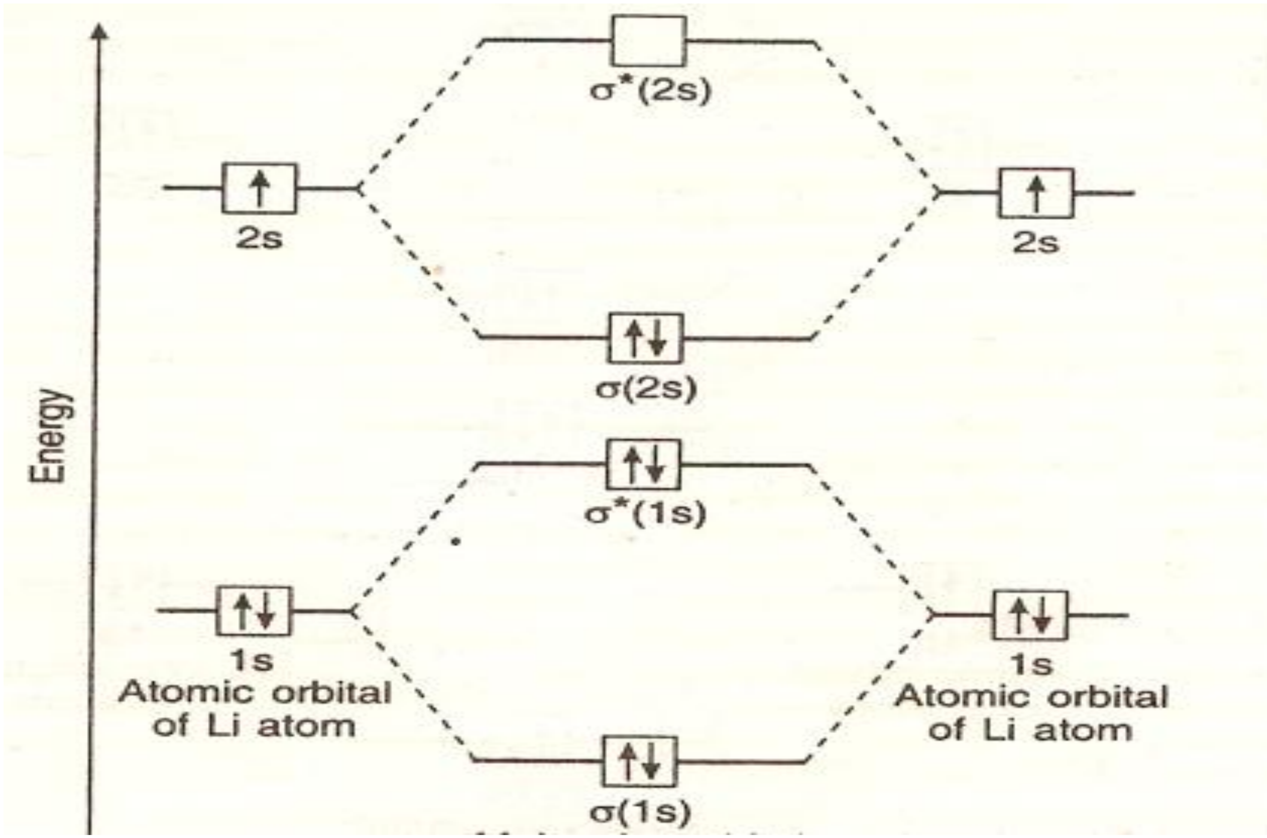
$$= \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2 = KK\ \sigma 2s^2$$

Since, the inner shell of filled σ1s and σ *1s molecular orbitals do not contribute to the bonding and is sometimes written as KK which means K-shell is completely filled.

Bond order = 1/2 (Nb - Na) = 1/2 (4 - 2) = 1/2 (2 - 0) = 1

Molecular Orbital Treatment for Homonuclear Diatomic Molecules

MO diagram of Li2 Molecule



Molecular Orbital Treatment for Homonuclear Diatomic Molecules

(3) Nitrogen Molecule, N_2 : A Nitrogen atom has 2+5=7 electrons. Thus, the N_2 molecule contains 14 electrons. These are arranged as

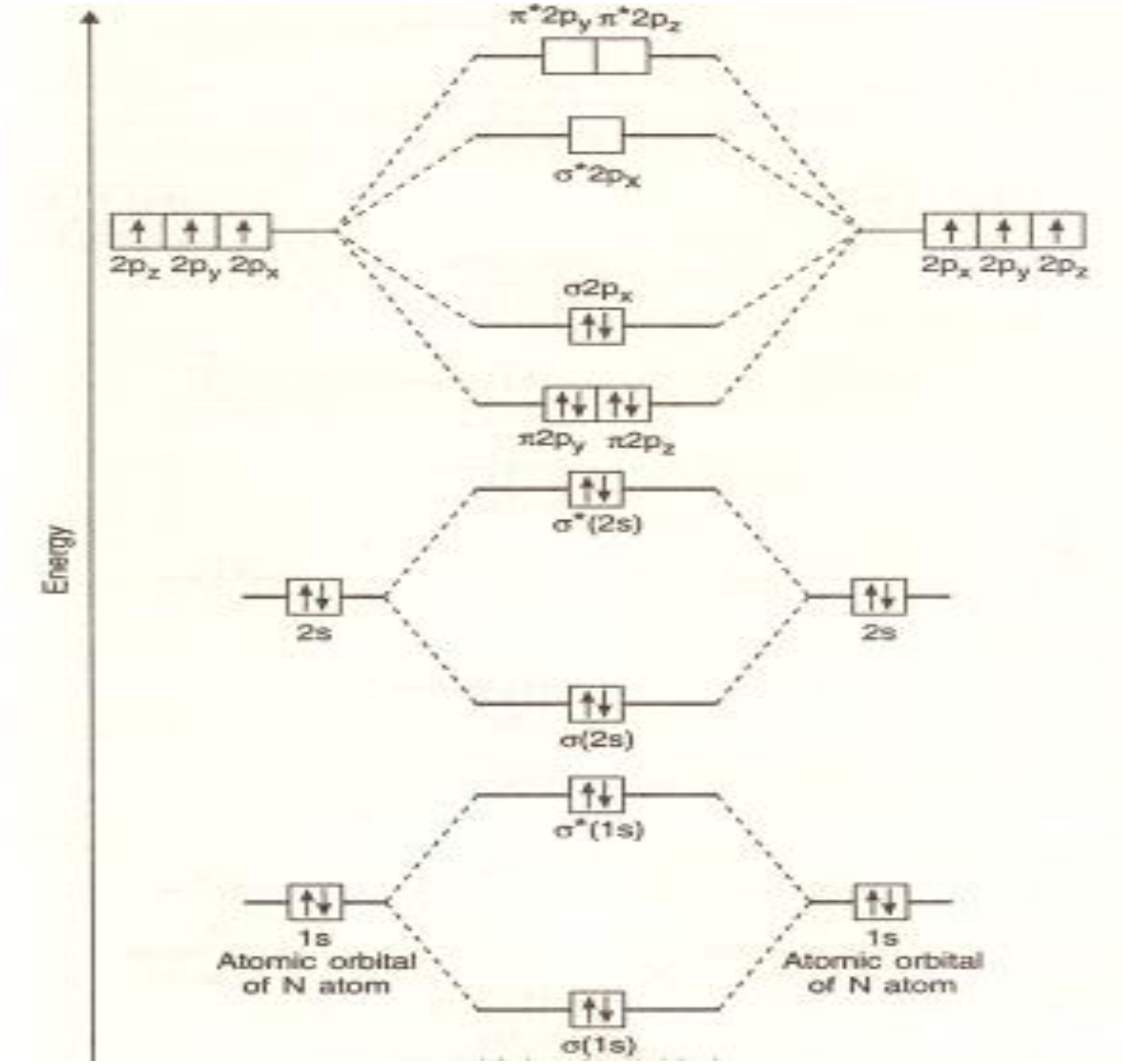
$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \sigma 2p_x^2 .$$

There are eight and two electrons in the bonding molecular orbital respectively.

Bond order of N_2 = ½ (8-2) =3

The N2 molecule is diamagnetic as it has no unpaired electron.

Molecular Orbital Treatment for Homonuclear Diatomic Molecules



Molecular Orbital Treatment for Homonuclear Diatomic Molecules

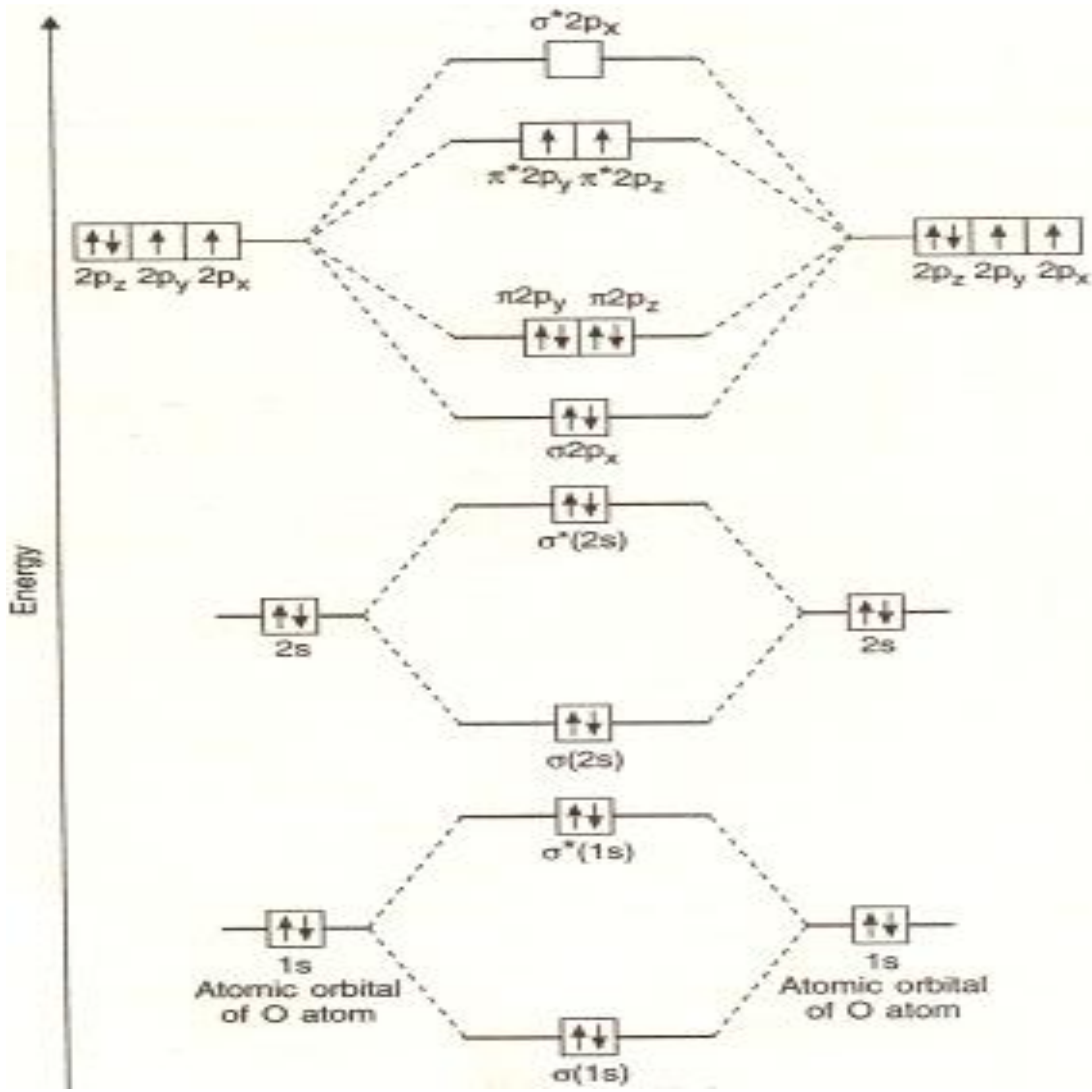
Oxygen molecule, O_2 : Each oxygen atom has 2+6=8 electrons. Thus O2 molecule contains a total of 16 electrons. These are arranged as

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{cases}$$

The presence of unpaired electrons in π^*2p_y and π^*2p_z give rise to paramagnetism.

B.O. of O2 = ½ (8-4) = 2

Molecular Orbital Treatment for Homonuclear Diatomic Molecules



Molecular Orbital Treatment for Homonuclear Diatomic Molecules

The electronic configuration, bond order and magenatic character of O_2^-, O_2^+ and O_2^{2-}

Species	Electronic configuration	Bond order	Magnetic behaviour
O_2^+	$kk\,\sigma 2s^2\sigma^*2s^2\sigma 2p_x^2 \begin{bmatrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{bmatrix}, \begin{bmatrix}\pi^*2p_y^1 \\ \pi^*2p_z^0\end{bmatrix}$	$\frac{(8-3)}{2} = 2.5$	Paramagnetic
O_2^-	$kk\sigma 2s^2\sigma^*2s^2\sigma 2p_x^2 \begin{bmatrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{bmatrix}, \begin{bmatrix}\pi^*2p_y^2 \\ \pi^*2p_z^1\end{bmatrix}$	$\frac{(8-5)}{2} = 1.5$	Paramagnetic
O_2^{2-}	$kk\sigma 2s^2\sigma^*2s^2\sigma 2p_x^2 \begin{bmatrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{bmatrix} \begin{bmatrix}\pi^*2p_y^2 \\ \pi^*2p_z^2\end{bmatrix}$	$\frac{(8-6)}{2} = 1$	Diamagnetic