

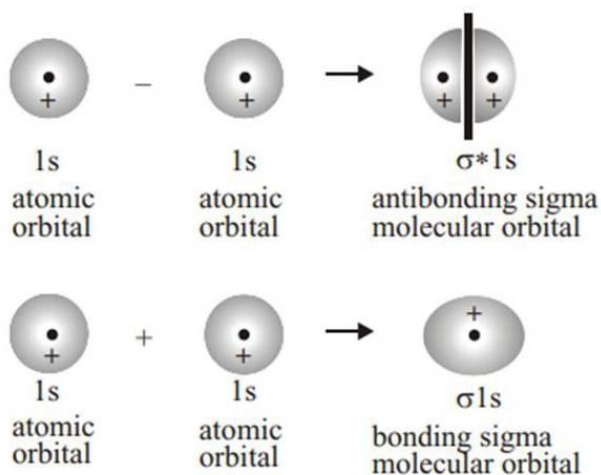
Molecular Orbital Theory (MOT)

VBT describes bond formation as a result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised.

MOT, developed by F.Hund and R.S.Mulliken in 1932, is based on the wave mechanical model of atom. In contrast to the localized bonding in VBT, the MOT visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals). These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not "belong" to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by **Linear Combination of Atomic Orbitals (LCAO)** approach in which, the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.
- The available electrons then fill these orbitals in the order of increasing energy as in the **Aufbau principle** used in the electron configurations of atoms.

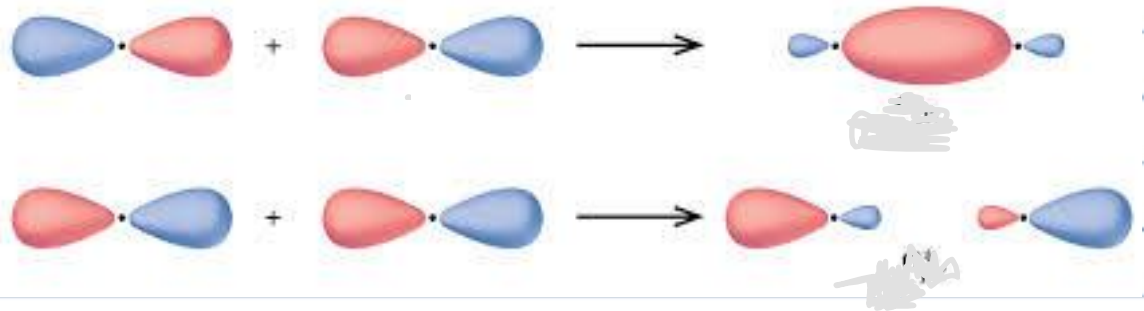
s - s Combination of Orbitals



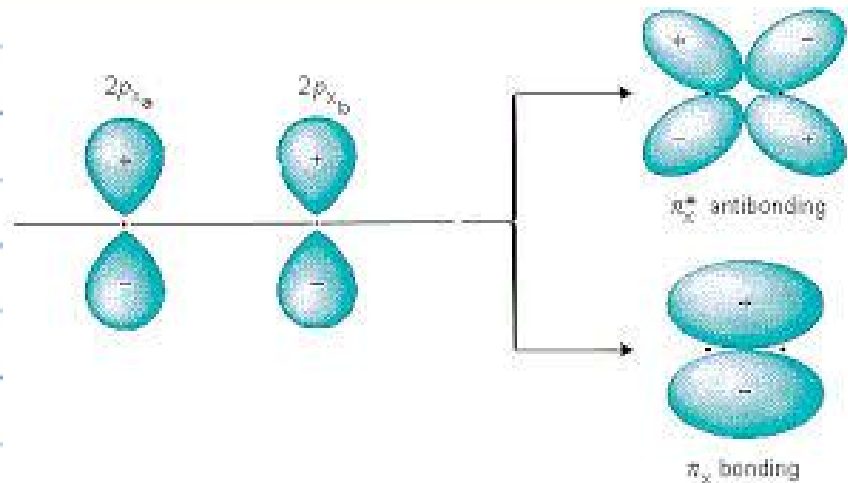
Molecular Orbital Theory (MOT)

$p - p$ Combination of Orbitals

As the two lobes of a p_z orbital are of opposite sign, the combination of two p_z orbitals, which have lobes pointing along the axis joining the nuclei, leads to σ -bonding as well as σ^* -antibonding orbitals.



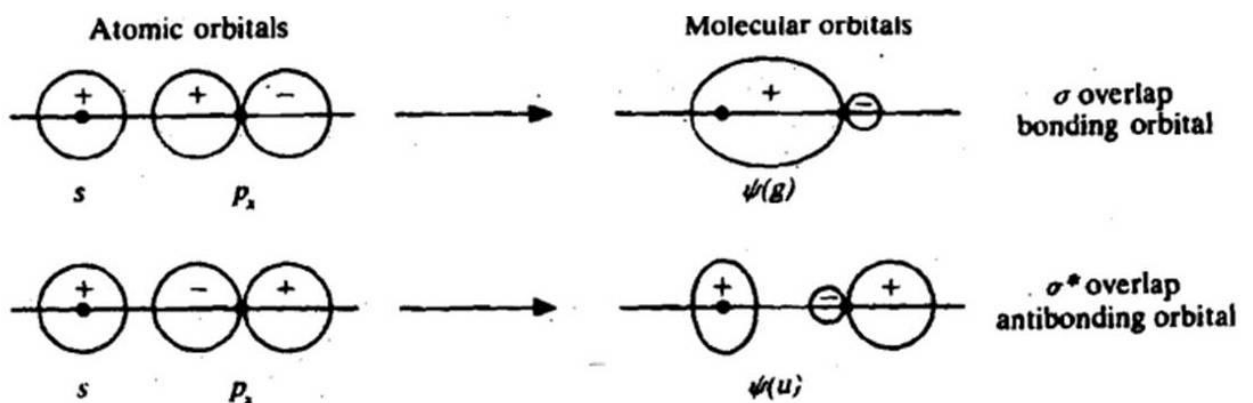
Lateral overlap of p_x and p_y orbitals will result in the π -bonding and π^* -antibonding molecular orbitals



Molecular Orbital Theory (MOT)

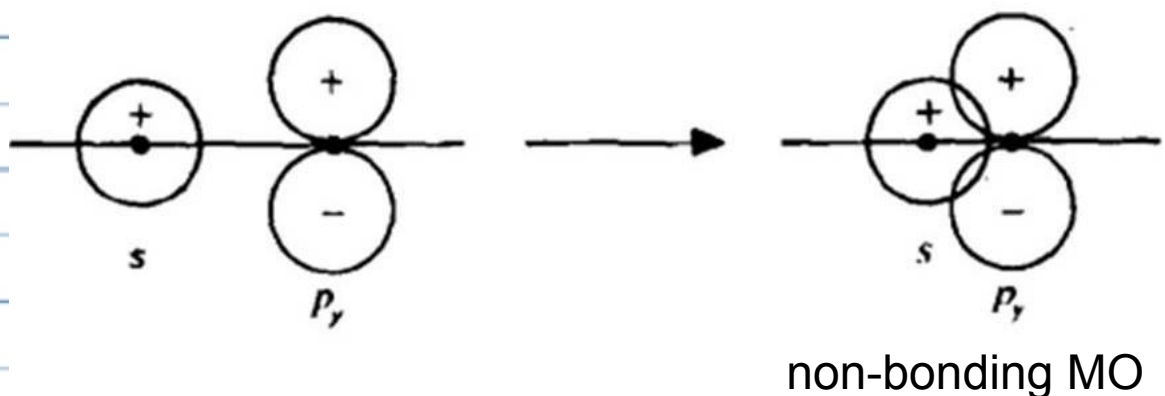
s - p Combination of Orbitals

Let us first consider the s - p, combination. When the lobes of s and p, orbitals have the same sign, the MO produced is bonding molecular orbital, whereas the antibonding molecular orbital results when the lobes are of opposite sign.



Upto this stage, we have learnt about two types of MOs viz. bonding and antibonding.

There is a third category called nonbonding molecular orbitals which can be understood when we consider the combination of an s-p_y or s-p_z atomic orbitals as shown



In this type, any stabilisation from overlapping of + and + parts of atomic orbitals is cancelled by the equal amount of overlapping between + and - parts of atomic orbitals. This evidently indicates that there is no net change in energy and hence no bonding occurs. Thus, this situation is called nonbonding combination of orbitals.

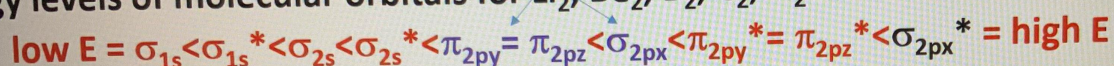
Molecular Orbital Theory (MOT)

Homonuclear diatomic molecules

The order of energy of molecular orbitals

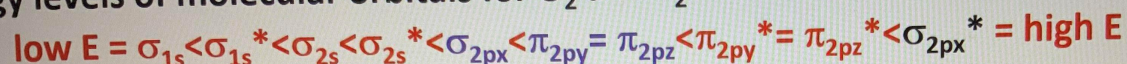
Rule 1: For total number of electrons less than or equal to 14

Energy levels of molecular orbitals for Li_2 , Be_2 , B_2 , C_2 , N_2 :



Rule 2: For total number of electrons more than 14

Energy levels of molecular orbitals for O_2 and F_2 :



Here, the energies of the π_{2py} and π_{2pz} orbitals are the same and hence they are called **degenerate orbitals**. Similarly, π_{2py}^* and π_{2pz}^* orbitals constitute another set of degenerate orbitals.

Bond Order

$$\text{Bond order (B.O.)} = \frac{1}{2}(n_b - n_a)$$

Where, n_b -number of electrons present in bonding MO

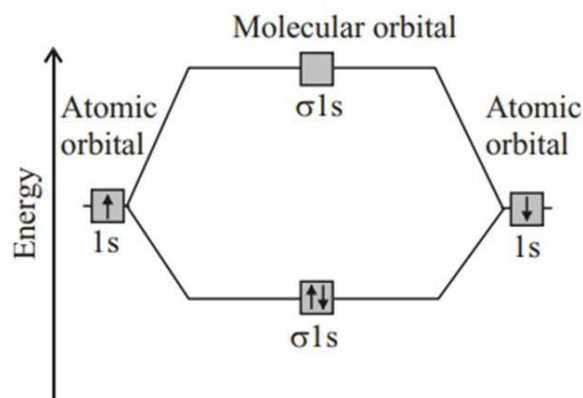
n_a -number of electrons present in bonding and antibonding MO

Molecular Orbital Theory (MOT)

Homonuclear diatomic molecules

H₂ molecule

The two hydrogen atoms have an electron each in their respective 1s orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wavefunction is obtained by addition of the two atomic wave functions whereas in the other the MO is obtained by subtraction of the atomic orbitals. The combination of the 1s orbitals on the two hydrogen atoms are shown below



There are a total of 2 electrons in a hydrogen molecule, according to Aufbau principle these are filled into σ_{1s} orbital. Since the σ_{1s} orbital is a bonding orbital, its getting filled leads to stability or the bond formation.

The MO configuration of hydrogen molecule is given as $(\sigma_{1s})^2$.

Bond order = $\frac{1}{2}(n_b - n_a) = \frac{1}{2}(2 - 0) = 1$, i.e., there is a single bond between two hydrogen atoms.

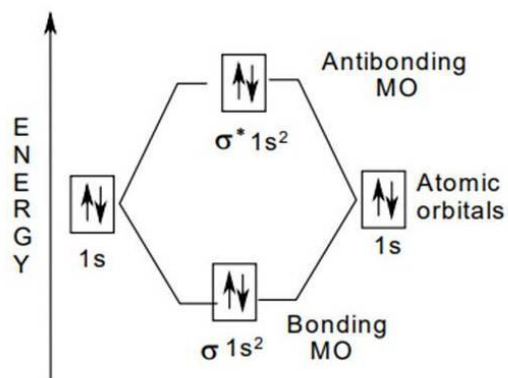
Molecular Orbital Theory (MOT)

Homonuclear diatomic molecules

He₂ molecule

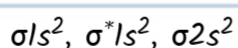
In case of He₂, also there will be linear combination of 1s orbitals leading to the formation of σ_{1s} and σ^*_{1s} orbitals. The four electrons would be distributed as per the MO electronic formation of σ_{1s} and σ^*_{1s} orbitals. The four electrons would be distributed as per the MO electronic configuration : $(\sigma_{1s})^2(\sigma^*_{1s})^2$

Bond order = $\frac{1}{2}(2-2) = 0$, that is there is no bond between two helium atoms. In other words He₂ molecule does not exist.



Li₂ and Be₂ molecules

Li₂ molecule-Each lithium atom has two electrons in its inner 1s orbital and one in the outer 2s orbital, making a total of six electrons in Li₂ which can be arranged as



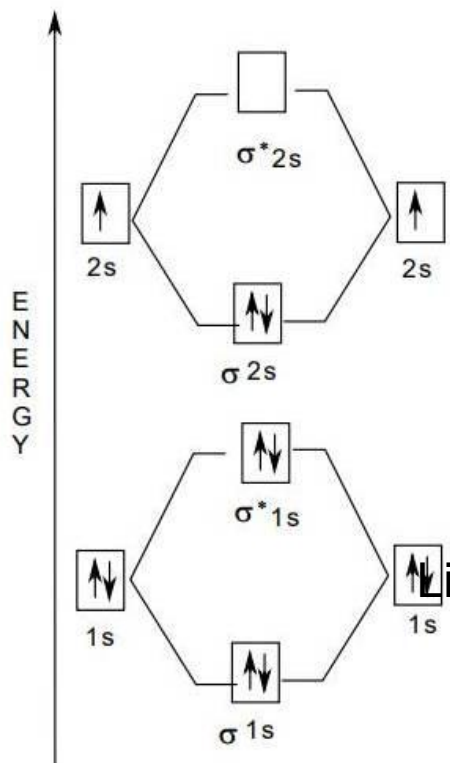
Bonding occurs due to the filling of σ_{2s} orbital and Li₂ has been found to exist in the vapour state.

Be₂ molecule-Combination of four electrons from each Be atom leads to eight electrons in Be₂ molecule which can be arranged as $\sigma_{1s}^2, \sigma^*_{1s}^2, \sigma_{2s}^2, \sigma^*_{2s}^2$. Again, the effect of bonding and antibonding 2s levels would cancel each other, so there is no net stabilisation and the molecule would not be expected to be stable.

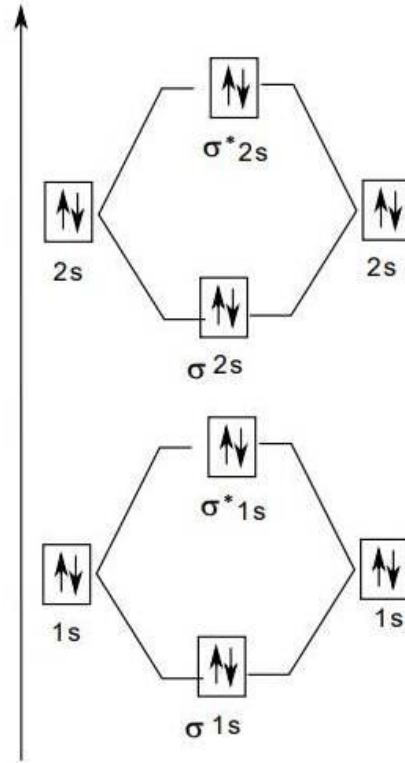
Molecular Orbital Theory (MOT)

Homonuclear diatomic molecules

Li_2 and Be_2 molecule



(a)



(b)

Molecular Orbital Theory (MOT)

Homonuclear diatomic molecules

N_2 molecule

In N_2 molecule, there are total 14 electrons arranged in the molecular orbital $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p_z^2$

Bond order : $\frac{1}{2} [n_b - n_a] = \frac{1}{2} [8 - 2] = \frac{1}{2} [6] = 3$; this means that in N_2 molecule, a triple bond exists between the two nitrogen atoms.

O_2 - Each oxygen atom has eight electrons, making a total of sixteen electrons for the molecule, which can occupy the molecular orbitals as $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1, \pi^* 2p_y^1$

Bond order : $\frac{1}{2} [n_b - n_a] = \frac{1}{2} [10 - 6] = \frac{1}{2} [4] = 2$; this means that in O_2 molecule, a double bond exists between the two oxygen atoms.

