

UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

According to **Molecular Orbital Theory**,

Atomic orbitals of comparable energies combine to form equal no of molecular orbitals.

- Out of two molecular orbitals formed one is bonding molecular orbital (BMO) while other is antibonding molecular orbital (ABMO).
- BMO is formed by addition of atomic orbitals and lower in energy compared to AMO, which is formed due to subtraction of atomic orbitals.

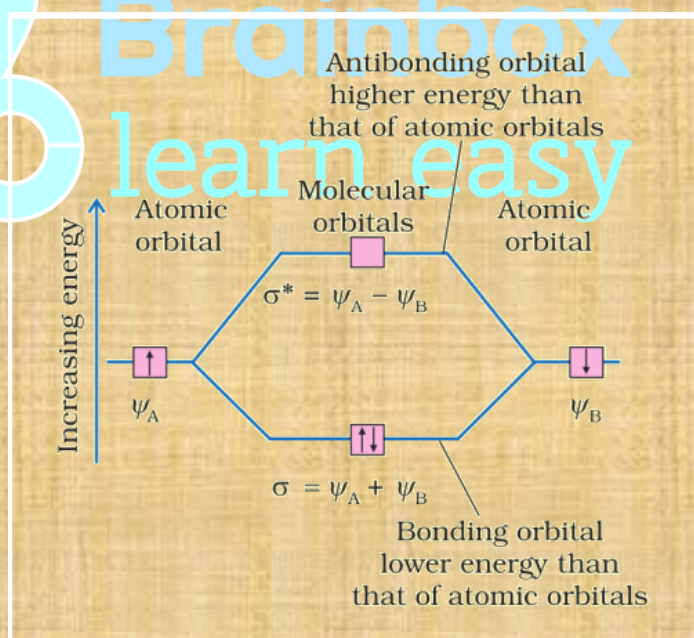


Fig. Formation of bonding (σ) and antibonding (σ^*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.

- The combining atomic orbitals must have same energy, same symmetry about molecular axis and maximum extent of overlapping.
- Energy level diagram for molecular orbitals.

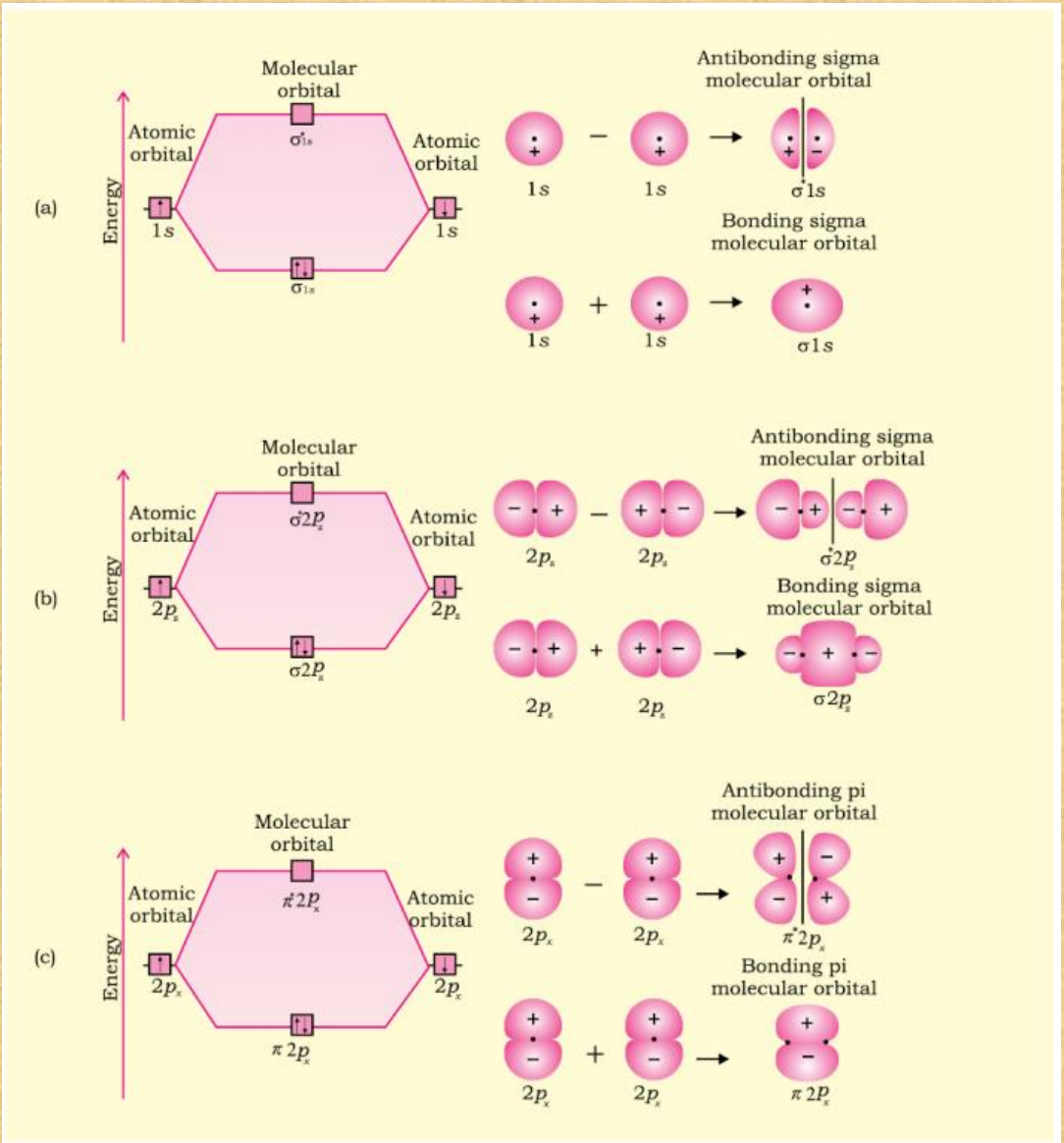


Fig. Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals

The increasing order of energies for various molecular orbitals is,

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

- The above sequence is applicable only for the molecules with 14 or more no of electrons.
- The molecules with no of electrons less than 14 sequence is given as,

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

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

Ex. In H_2 molecule, two is orbitals overlap to form two molecular orbitals $\sigma 1s$ & $\sigma^* 1s$.

The configuration $\sigma 1s^2 \Rightarrow \text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$

In O_2 molecule each atom has 8 electrons – total 16 electrons electronic configuration is,

$$\Rightarrow \text{Bond order} = \frac{10 - 6}{2} = 2$$

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

