

UNIT I

LECTURE - 1

Molecular Orbital Theory (MOT)

- Molecular orbital theory was given by **Hund** and **Mulliken** in 1932.
The main ideas of this theory are:
- When two atomic orbitals combine or overlap, they lose their identity and form new orbitals. The new orbitals thus formed are called **molecular orbitals**.
- Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled just as atomic orbitals are the energy states of an atom in which the electrons of the atom are filled.
- In terms of probability distribution, a molecular orbital gives the electron probability distribution around a group of nuclei just as an atomic orbital gives the electron probability distribution around the single nucleus.
- Only those atomic orbital can combine to form molecular orbital which have comparable energies and proper orientation.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
- When two atomic orbitals combine, they form two new orbitals called bonding molecular orbital and antibonding molecular orbital.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- The bonding molecular orbitals are represented by σ , π etc, whereas the corresponding antibonding molecular orbitals are represented by σ^* , π^* etc. (Figure 1)
- The shapes of the molecular orbitals formed depend upon the type of combining atomic orbitals.
- The filling of molecular orbitals in a molecule takes place in accordance with **Aufbau principle**, **Pauli's exclusion principle** and **Hund's rule**.
- Electrons are filled in the increasing energy of the MO which is in order
- Bond order \propto Stability of molecule \propto Dissociation energy \propto (1/Bond Length).
- If all the electrons in a molecule are paired then the substance is a diamagnetic on the other hand if there are unpaired electrons in the molecule, then the substance is paramagnetic. More the number of unpaired electrons in the molecule greater are the paramagnetism of the substance.

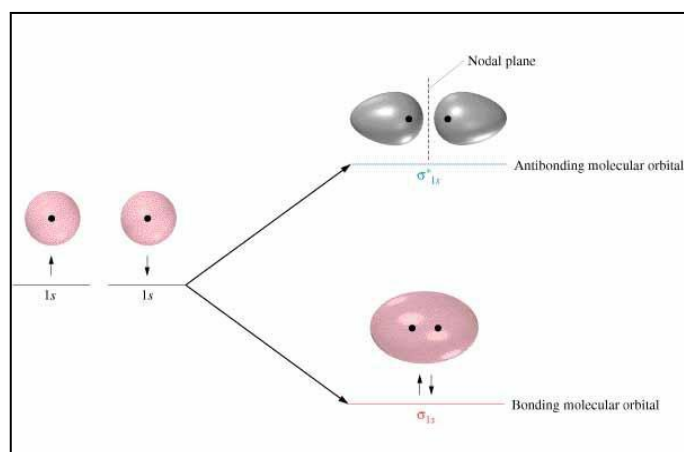


Figure 1

LECTURE- 2

Bond Order

In molecular orbital theory, we calculate bond orders by assuming that two electrons in a bonding molecular orbital contribute one net bond and that two electrons in an antibonding molecular orbital cancel the effect of one bond.

The stability of the molecule can be determined from the parameter called Bond Order. Bond order may be defined as half the difference between number of electrons in bonding molecular orbitals and number of electrons in antibonding molecular orbitals.

$$\text{BO} = \frac{N_b - N_a}{2}$$

Molecular orbital diagrams of Homodiatomic molecules

MO Diagrams for O₂ and N₂ as shown in Figure 2.

MO diagrams – Contains same number of MOs as the number of atomic orbitals. The more electronegative element is kept on the right - lower in energy. Homoatomic means “of the same atom”—such a molecule contains only one kind of atom. Examples include: H₂, N₂, O₂, F₂, P₄, S₈, Cl₂, Br₂, I₂.

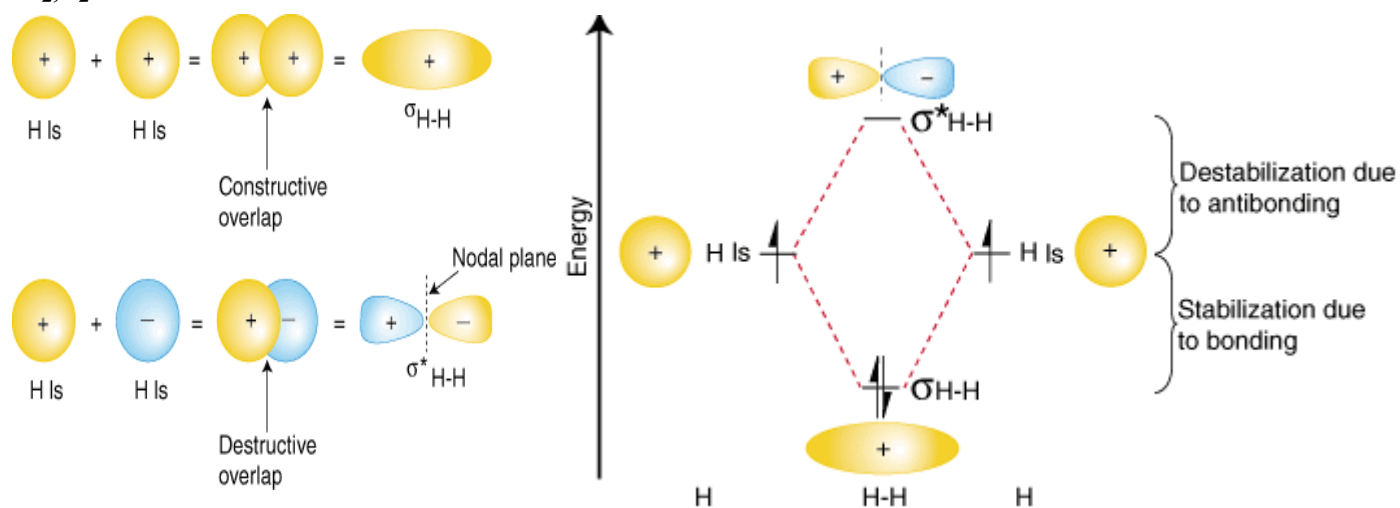


Figure 2: Two 1s Orbitals combine to form a bonding and an antibonding M.O

The orbitals of the separated atoms are written on either side of the diagram as horizontal lines at heights denoting their relative energies shown in Figure 2. The electrons in each atomic orbital are represented by arrows. In the middle of the diagram, the molecular orbitals of the molecule of interest are written. Dashed lines connect the parent atomic orbitals with the daughter molecular orbitals.