

Molecular orbital

UNIT - I

1.1. MOLECULAR ORBITAL THEORY

Covalent Bond :

Covalent bond is a type of linkage in which two atoms combine with one another by sharing a pair of electrons in their outer shells so that the combining atoms to attain the nearest noble gas configuration in their valency shells. The electrons thus shared, contribute towards the stability of both the atoms.

To explain the concept of covalent bond we need theories to answer questions like why covalent bonds are formed, how the electrons are arranged in space in a molecule, how the sharing of electrons could takes place etc. One such theory is Molecular Orbital theory.

Basic concepts of Molecular Orbital Theory :

According to molecular orbital theory,

1. All the atomic orbitals of the atom, participating in molecule formation, get disturbed when the nuclei approach each other.
2. The atomic orbitals get mixed up to give equivalent number of new orbitals called **molecular orbitals**.
3. Just as each electron in a single atom can be represented a certain wave-function ψ , every electron in a molecule can be denoted by a similar wave function characteristic of a particular molecular orbital.
4. Like atomic orbital, a molecular orbital cannot accomodate more than a maximum of two electrons.
5. The two electrons should have opposite spins.
6. However there is a clear cut difference between atomic and molecular orbitals. An electron in the atomic orbital is influence by only one positive nucleus while an electron in the molecular orbital is under the combined influence of two or more nuclei.

Bonding and Anti Bonding Orbitals :

We have seen molecular orbitals are formed by combining the atomic orbitals of the bonded atoms. For this purpose we apply the principle of **Linear Combination of the Atomic Orbitals (LCAO)**. In a diatomic molecule the wave function for an electron in the field of two nuclei A and B will be given by two modes of combinations, symmetric and antisymmetric. So we have

$$\psi_s = \psi_A + \psi_B \quad (1)$$

$$\psi_a = \psi_A - \psi_B \quad (2)$$

The probability of finding an electron in the molecular orbital by LCAO according to equation (1) is greater than that in either of ψ_A or ψ_B . In other words the molecular orbital represented by ψ_s has a lower energy than ψ_A or ψ_B . This orbital therefore leads to the formation of a stable chemical bond. So this orbital is called **bonding orbital**.

The probability of finding an electron in the molecular orbital by LCAO according to equation (2) is less than that in either ψ_A or ψ_B . In other words the molecular orbital represented by ψ_a has higher energy than ψ_A and ψ_B . This orbital therefore cannot lead to the formation of a stable chemical bond. So this orbital is called **antibonding orbital**.

The formation of bonding molecular orbitals ψ_s and antibonding molecular orbitals ψ_a from two atomic orbitals ψ_A and ψ_B is given in the following figure 1.

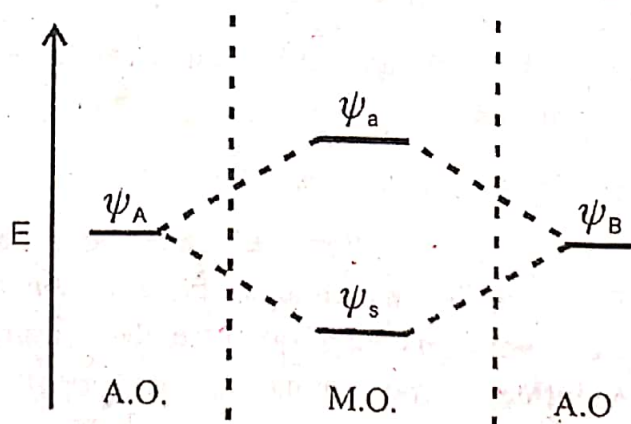


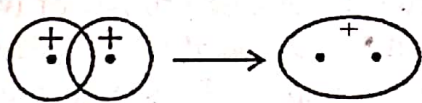
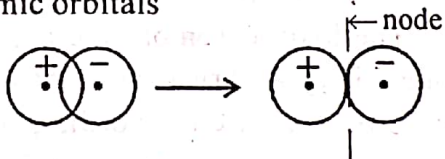
Figure - 1

Thus we find two atomic orbitals combine to give two molecular orbitals one of which is bonding and the other antibonding.

When the two atomic orbitals overlap in a linear fashion we get two MOs. They are termed as σ (bonding) and σ^* (antibonding). The overlapping atomic orbitals may be pure or hybridised. Thus we can have s-s, p-p, sp^3 -s, sp^2 -s, sp-s etc. overlaps. Each such overlap would give one σ and one σ^* orbital.

When the two atomic orbitals overlap in a side wise fashion we get two MOs. They are termed as π (bonding) and π^* (antibonding). We can have π - π overlap (lateral). This gives π and π^* orbitals.

Differences between bonding and anti bonding orbitals.

Bonding molecular orbital	Anti-bonding molecular orbital
1. Formed by the combination of electron wave of same sign i.e., by addition overlap of atomic orbitals	Formed by the combination of electron waves of opposite signs i.e., by the subtraction overlap of atomic orbitals
	
2. Possess lower energy than the atomic orbitals from which it is formed	Possess higher energy than the atomic orbitals from which it is formed.
3. The electron density in between the nuclei is high. So the attraction between the nuclei is high. This explains the formation of a bond between the atoms	The electron density in between the nuclei is low. So the repulsion between the nuclei is high. This explains the non formation of a bond between the atoms.

Bond order :

$$\text{Bond order} = \frac{1}{2} (N_b - N_a)$$

N_b = Number of electrons in bonding molecular orbitals.

N_a = Number of electrons in anti - bonding molecular orbitals.

Bond order gives the number of bonds in a molecule. When the bond order increase stability i.e., strength of the molecule also increase. Similarly

when the bond order increases bond length decreases.

Application of Molecular Orbital Theory

H_2 - Molecule

Let us consider the formation of hydrogen molecule according to molecular orbital theory. Two atomic orbitals, (1s), one from each hydrogen atom approach to form a molecule. The number of molecular orbitals formed from atomic orbitals is equal to the number of atomic orbitals. The molecular orbital which lowers the energy, brings about stability in the system and is responsible for bonding between the atoms. This type of molecular orbitals are therefore called **bonding molecular orbitals**. The bonding molecular orbitals of the type which is formed from 1s atomic orbitals are denoted as $\sigma(1s)$. The electron density in a bonding molecular orbital is more in the inter nuclear region than at the ends. The other type of molecular orbitals correspond to higher energy status. The electron density of such molecular orbitals is maximum at the ends. The electron density is almost zero in internuclear region. This is called the **antibonding molecular orbital** (denoted with an asterisk* mark).

The hydrogen molecule is formed from $1s^1$ atomic orbitals of two atoms. They give rise to two molecular orbitals $\sigma(1s)$ and $\sigma^*(1s)$. The two electrons are filled according to aufbau principle. Thus both these electrons go to the lower energy bonding molecular orbital and antibonding molecular orbital remains vacant.

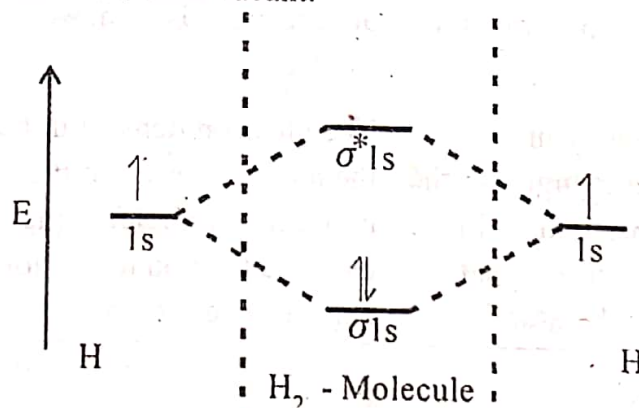


Figure - 2

Thus in hydrogen the bond order = $\frac{1}{2}$ (number of electrons in bonding orbitals - number of electrons in antibonding orbitals)

$$= \frac{1}{2}(2 - 0) = \frac{1}{2} \times 2 = 1.$$

That is, H_2 molecule is bonded by one bond as H-H

Its molecular orbital configurations is $\sigma(1s)^2 \sigma^*(1s)^0$.

The molecular orbital diagram of hydrogen molecule is given in figure-2.

He_2 - Molecule

Let us consider the possibility of combination of two helium atoms to form He_2 molecule. Each helium atom has two 1s electrons. Thus there are four electrons to be accommodated. The ($\sigma 1s$) molecular orbital will accommodate 2 electrons and ($\sigma^* 1s$) will accommodate 2 electrons as shown in the following figure - 3.

The MO configuration is $(\sigma 1s)^2; (\sigma^* 1s)^2$.

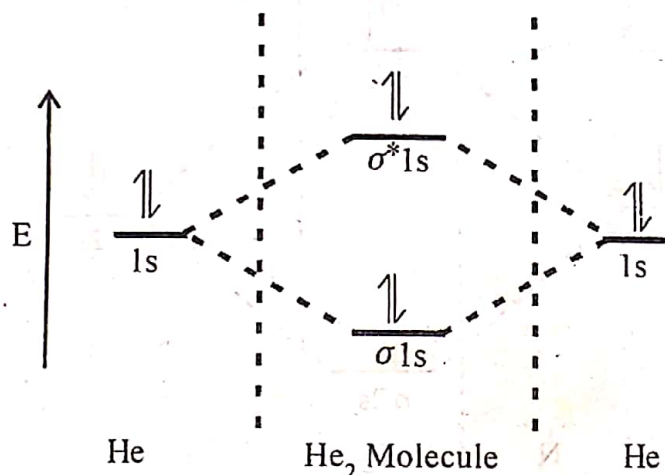


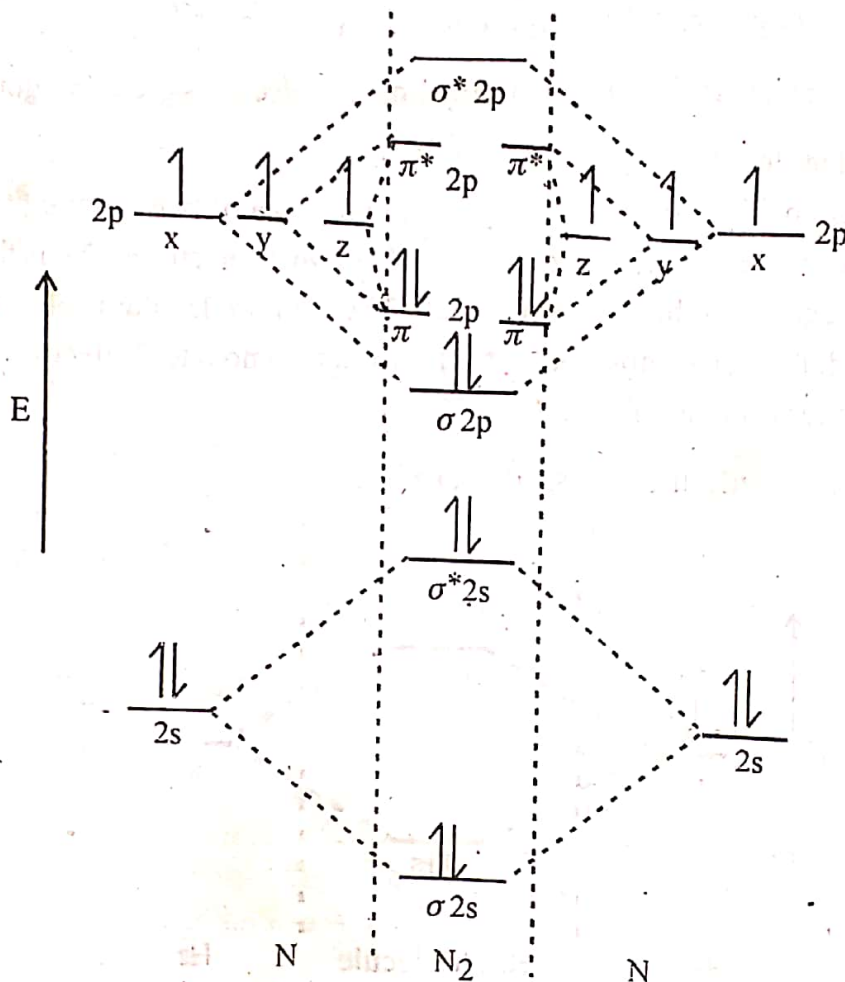
Figure - 3

There are two electrons in each of the bonding and antibonding orbitals. The number of bonds = $\frac{1}{2} (2 - 2) = 0$. That is, the bond order is zero. In other words, there can be no bond between two He atoms, i.e., He_2 - molecule cannot exist.

N_2 - Molecule

The electronic configuration of N is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Each atom contributes 5 valence electrons ($2+1+1+1$). The molecule would have eight molecular orbitals as shown in figure 4. Ten electrons are to be accommodated in them. Eight electrons go to the bonding molecular orbitals and two electrons go to antibonding molecular orbital. This gives

the number of bonds as $= \frac{1}{2} (8 - 2) = 3$. Thus N_2 molecule has a triple bond.



Nitrogen molecule

Figure - 4

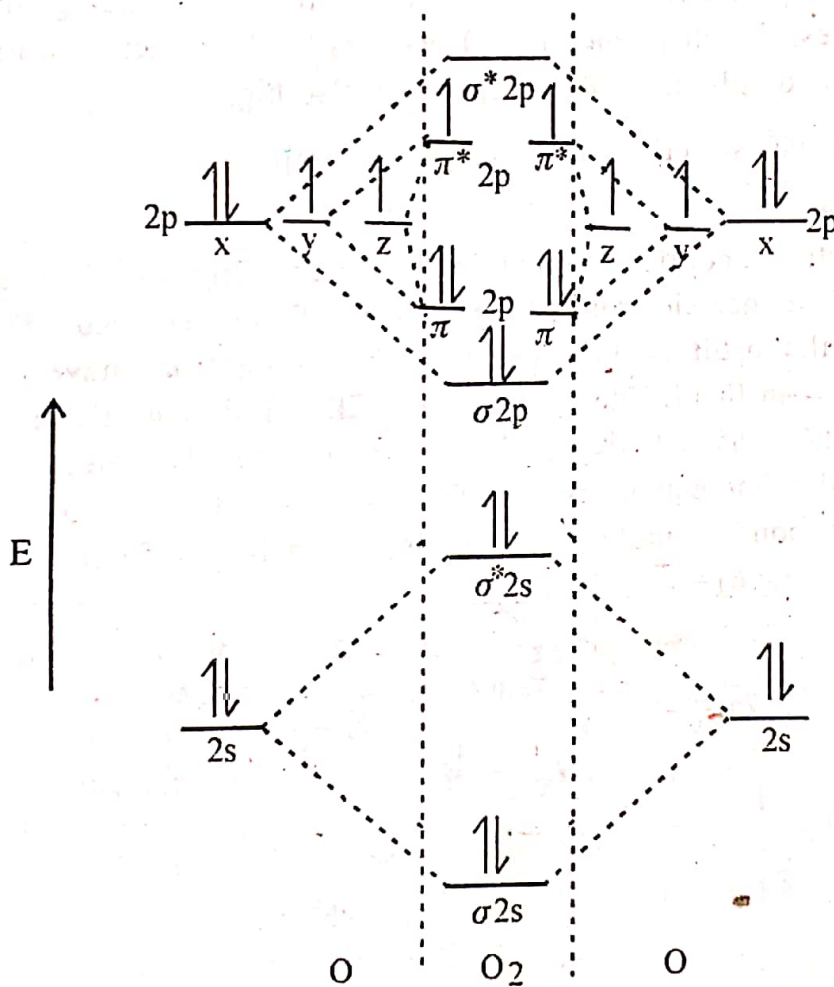
From the M.O. picture of N_2 the following become evident.

1. Bond order $= \frac{1}{2}$ (number of electrons in bonding orbitals - number of electrons in the antibonding orbitals). $= \frac{1}{2} (8 - 2) = 3$.
2. There are two electrons each in $\sigma 2s$ and $\sigma^* 2s$ orbitals. So these become nonbonding electrons. There are two electrons in ($\sigma 2p$) M.O. and four electrons in ($\pi 2p$) MOs. So there is one σ bond and two π bonds in nitrogen.
3. Since there are no unpaired electrons in the M.O. structures the molecule will be diamagnetic.

Thus the MO structure of nitrogen explains its properties.

O₂ - Molecule

The electronic configuration of O is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. Each atom contributes 6 valence electrons (2+2+1+1). The O₂ molecule would have eight molecular orbitals as shown in figure 5. Twelve (2x6) electrons are to be accommodated in them. The electrons are filled following the aufbau principle. 8 electrons go to the bonding molecular orbitals. 2 electrons go to the $\sigma^* 2s$ antibonding molecular orbitals. Two lone pair electrons go to each of the degenerate $\pi^* 2p_y$ and $\pi^* 2p_z$ antibonding molecular orbitals. The number of bonds in O₂ molecule = $\frac{1}{2}(8-4)=2$.



Oxygen molecule
Figure - 5.

From the MO picture of O₂ the following become evident

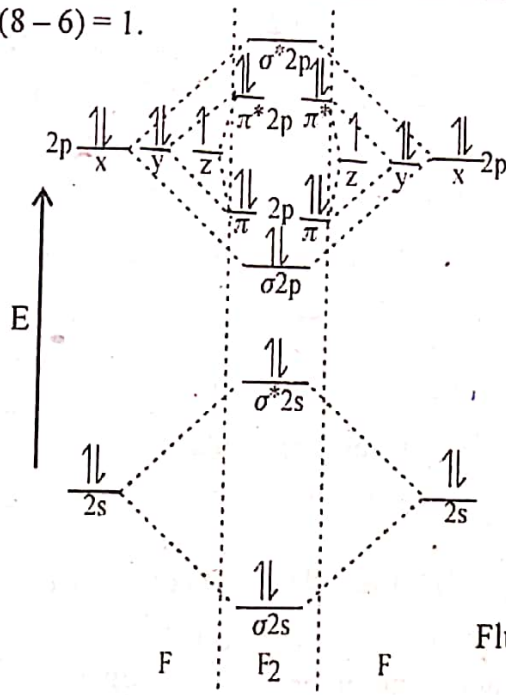
1. Bond order = $\frac{1}{2} [\text{number of electrons in bonding orbitals} - \text{number of electrons in the anti bonding orbitals}] = \frac{1}{2}(8 - 4) = 2$.

- Number of sigma bonds = $\frac{1}{2}$ [number of electrons in sigma orbitals - number of electrons in σ^* orbitals] = $\frac{1}{2}$ (4 - 2) = 1. i.e., There is one sigma bond.
- Number of π bonds = $\frac{1}{2}$ [number of electrons in π orbitals - number of electrons in π^* orbitals] = $\frac{1}{2}$ (4 - 2) = 1.
- Since there are two unpaired electrons in two degenerate ($2\pi^*$) orbitals O_2 molecule is paramagnetic.
- The difference between the number of bonding electrons and antibonding electrons determines the tightness of bonding, In O_2 molecules, this difference is 4. Hence its binding energy is more. Correspondingly dissociation energy is also high.

Thus the MO structure of O_2 explains its properties.

F_2 - Molecule

The electronic configuration of F is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. Each atom contributes 7 valence electrons (2+2+2+1). The F_2 molecule would have eight molecular orbitals. Fourteen (7 x 2=14) electrons have to be accommodated in them. The electrons are filled following the aufbau principle. 8 electrons go to the bonding molecular orbitals. 2 electrons to σ^*2s antibonding molecular orbitals. Two electrons go to each of π^*2p_y and π^*2p_z antibonding molecular orbitals. The number of bonds in F_2 molecule = $\frac{1}{2}$ (8 - 6) = 1.



From the M.O. picture of F_2 the following become evident.

1. Bond order = $\frac{1}{2}$ [Number of electrons in bonding orbitals - Number of electrons in antibonding orbitals] = $\frac{1}{2}(8 - 6) = 1$.
2. Number of σ bond = $\frac{1}{2}$ [Number of electrons in σ orbitals - Number of electrons in σ^* orbitals] = $\frac{1}{2}(4 - 2) = 1$.
i.e., There is one σ bond in F_2 molecule.
3. Number of π bonds = $\frac{1}{2}$ [Number of electrons in π orbitals - Number of electrons in π^* orbitals] = $\frac{1}{2}(4 - 4) = 0$. i.e., There is no π bond in F_2 molecule.
4. Since there is no unpaired electrons F_2 molecule is **diamagnetic**. Thus the M.O. structure of F_2 explains its properties.

UNIVERSITY QUESTIONS

1. What is a covalent bond ?
2. Write notes on molecular orbital theory.
3. What are the basic concepts of MO theory ?
4. How will you distinguish between bonding and anti bonding orbitals?
5. What is meant by bond order of a molecule?
6. Apply MO theory to describe the bonding in hydrogen molecule.
7. From the molecular orbital theory derive the bond order for He_2 .
8. He_2 Molecule does not exist. Why?
9. Draw the molecular orbital energy level diagram for N_2 molecule and the various orbitals. Calculate the bond order?
10. Explain the diamagnetism of nitrogen molecule on the basis of M.O. theory.
11. Write the molecular orbital structure of O_2 molecule.
12. Draw the molecular orbital energy diagram of oxygen molecule. Calculate the bond order.
13. What is the bond order of O_2 .
14. How many π bonds are there in O_2 molecule?
15. On the basis of M.O. theory explain the paramagnetic behaviour of the oxygen molecule.
16. Explain the MO structure of F_2 molecule.
17. With suitable examples explain σ , σ^* , π and π^* molecular orbitals.