

Chemistry Study Materials for Class 11 (NCERT Based Notes of Chapter- 04)

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CHEMICAL BONDING AND MOLECULAR STRUCTURE

Molecular Orbital Theory

This theory was developed by F. Hund and R.S Mulliken. The important postulates of this theory are:

- 1) In molecules, the electrons are present in some special type of orbitals called molecular orbitals (M.Os).
- 2) The atomic orbitals (A.Os) of comparable energy and proper symmetry combine to form molecular orbitals.
- 3) Atomic orbitals are monocentric, while molecular orbitals are polycentric. i.e. electrons present in atomic orbitals are attracted by only one nucleus. While the electrons present in molecular orbitals are attracted by more than one nucleus.
- 4) The number of molecular orbitals formed = the number of atomic orbitals combined. i.e. if 2 atomic orbitals combined, 2 molecular orbitals are formed. One is called bonding molecular orbital (BMO) and the other is called anti-bonding molecular orbitals (ABMO)
- 5) The BMO has lower energy and greater stability than the corresponding ABMO.
- 6) The molecular orbitals give the electron probability distribution around a group of nuclei.
- 7) The molecular orbitals are filled according to 3 rules – Aufbau principle, Pauli's exclusion principle and Hund's rule.

Formation of molecular orbitals

Linear Combination of Atomic Orbitals (LCAO) method

Molecular orbitals are formed by the combination of atomic orbitals by an approximate method known as Linear Combination of Atomic Orbitals (LCAO).

According to this theory, the combinations of atomic orbitals take place by addition and subtraction of wave functions of atomic orbitals. The M.O formed by the addition of A.Os is called the bonding molecular orbital (BMO) and by the subtraction of A.Os is called the anti-bonding molecular orbitals (ABMO).

The electron density in a BMO is located between the nuclei of the bonded atoms. So the repulsion between the nuclei is very low. Therefore a BMO always possess lower energy than the combining A.Os. While in the case of an ABMO, most of the electron density is located away from the space between the nuclei. There is a nodal plane between the nuclei and hence the repulsion between the nuclei is high. So an ABMO possess higher energy than the combining A.Os. ABMO is denoted by using an asteric (*) mark.

Conditions for the combination of atomic orbitals

The combination of A.Os to form M.Os takes place only if the following conditions are satisfied:

1. The combining A.Os must have the same or nearly the same energy.
2. The combining A.Os must have the same symmetry about the molecular axis.
3. The combining A.Os must overlap to the maximum extent.

Types of molecular orbitals

M.Os of diatomic molecules are designated as σ (sigma), π (Pi), δ (delta) etc. the sigma M.Os are symmetrical about the bond axis, while the pi M.Os are not symmetrical.

Linear combination of two 1s atomic orbitals produces two M.Os – a BMO σ_{1s} and an ABMO σ^*_{1s} .

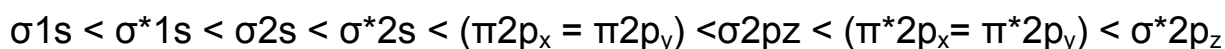
Similarly linear combination of two 2s atomic orbitals produces two M.Os – σ_{2s} and σ^*_{2s} .

If z-axis is taken as the inter nuclear axis, linear combination of two $2p_z$ orbitals produces two sigma M.Os σ_{2p_z} and $\sigma^*_{2p_z}$.

While the combination of $2p_x$ and $2p_y$ orbitals produce M.Os which are not symmetrical about the bond axis. So two $2p_x$ orbitals produces 2 sigma M.Os – π_{2p_x} and $\pi^*_{2p_x}$ and two $2p_y$ orbitals produce 2 M.Os – π_{2p_y} and $\pi^*_{2p_y}$.

Energies of various M.Os

The various M.Os are filled in the increasing order of their energies (Aufbau Principle). The increasing order of energy is:



For O_2 , F_2 and Ne_2 , the order is:



Bond Order

It is defined as *the half of the difference between the number of bonding electrons*

(N_b) and the number of anti-bonding electrons (N_a).

$$\text{Bond Order (B.O)} = \frac{1}{2}[N_b - N_a]$$

A molecule is stable only if the bond order is positive. (i.e. $N_b > N_a$).

a negative bond order (i.e. $N_b < N_a$ or $N_b = N_a$) means an unstable molecule.

For a single bond, B.O = 1, for a double bond B.O = 2 and so on. Bond order gives an approximate measure of the bond length.

In general, ***as the bond order increases, bond length decreases and bond enthalpy increases.***
