Patna University

Chemical Bonding I

Dr Bina Rani
Univ. Prof. of Chemistry
Magadh Mahila College (P.U.)
Patna

M.Sc. 2nd Semester
Physical Chemistry

LCAO - Molecular Orbital Theory

The method of molecular orbital theory was developed in 1927-28 by Hund and Mulliken and in 1927 Lennard-Jones, In this approach, it is assumed that each electron in a molecule is described by a certain wavefunction ψ. This wavefunction describes the electron in the molecule and hence, it is called molecular orbital, the molecular orbital theory attempts to construct molecular orbitals in which the individuality of the atoms has disappeared completely, i.e molecular orbital are polycentric, whereas orbitals in valence bond theory are monocentric. Each of these orbitals represents a state at which the square of the molecular wavefunction (MO) is a measure of the probability of finding of electron at any point. Each molecular orbital is associated with a definite energy and the total energy of the molecule is the sum of energies of all the occupied molecular orbitals, The basic principles of the MO treatment are thus analogous to those used for atomic orbitals.

Now, the Problem is to construct resonable molecular orbitals for multi-electron molecular system, Just as the simple harmonic wave are combined when they are supposed to form another wavefunction, the molecular orbital may be obtained by taking Linear combination of atomic orbitals. This method is commonly known as Linear combination of Atomic orbitals. If ψ_a and ψ_b are the AO's of atom A and B respectively, then MO's (ψ) are written as

$$\psi_1 = c_a \psi_a(1) + c_b \psi_b(1) \quad -(1)$$

and $$\psi_2 = c_a \psi_a(2) + c_b \psi_b(2) \quad -(2)$$

where c^os are the arbitary constant chosen to give lowest energy value of Molecular orbital and electron 1 and 2 are placed either with AO's ψ_a or ψ_b. In general, if $\psi_1, \psi_2 \cdots \psi_n$ be the atomic orbitals on atom 1, 2, 3 ---, n respectively

According to the molecular orbital method, the combined wave function for the two is the Product of two wave functions ψ_1 and ψ_2

i.e $$\psi_{MO} = \psi_1 \psi_2 = [c_1 \psi_a(1) + c_2 \psi_b(1)] \; [c_1 \psi_b(2) + c_2 \psi_b(2)] \quad -(3)$$

or $$\psi_i = \sum_j^n c_j \psi_j \quad -(4)$$

Total molecula wave function can be then written as the product of all the molecular orbital i.e

$$\psi = \psi_1 \cdot \psi_2 \psi_3 \cdots \psi_n \quad -(5)$$