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SEM-II

Physical Chemistry

Unit - V

Molecular
Orbital Theory

LCAO, Its
applications



Molecular Orbital Theory

→ This theory was developed by Hund, Mulliken, Hückel and others.

The main points of this theory are :-

(i) A molecule is considered as a group of nuclei and all the electrons are distributed around this group in different energy levels. The energy levels of the molecule are called molecular orbitals.

(ii) The atomic orbitals are monocentric while the molecular orbitals are polycentric.

(iii) Each molecular orbital in the molecule is described by a wave function called molecular orbital wave function.

(iv) Each molecular orbital is associated with definite amount of energy.

(v) In a molecule, $\psi^2 dr$ gives the probability of finding the electron in a volume element $\delta\tau$.

(vi) Only those atomic orbitals combine to form molecular orbitals which have comparable energies and same symmetry.

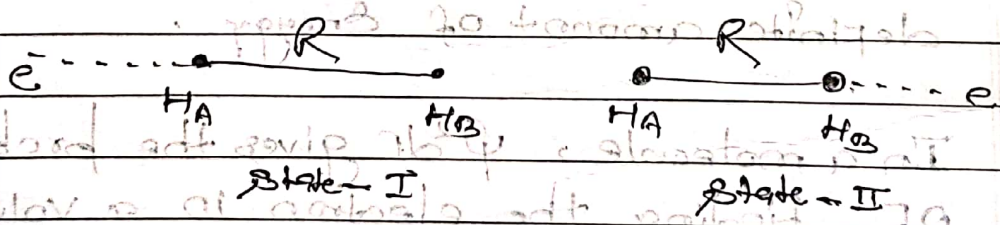
(vii) The filling of electrons into molecular orbitals follows the rule - Aufbau principle, Pauli exclusion principle, Hund's rule of maximum spin multiplicity.

LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

Application to H_2^+ ion

We can construct a molecular orbital wave function by LCAO approximation. To understand this method, let us consider the case of H_2^+ ion.

H_2^+ ion consists of two protons H_A and H_B separated by a distance R and only one electron. The electron is considered to be moving in a molecular orbital under the influence of both the nuclei.



When the electron is in the neighbourhood of A , it will behave as if it were moving in the atomic orbital of H_A and effect of nucleus of H_B will be negligible. Similarly, when the



∴ electron is in the neighbour of H_B , the influence of the nucleus of H_A or the electron is negligible.

In state - (1), the wave function of the electron will be ψ_A and in the second case; the wave function of the electron will be ψ_B . In between these two extremes, the electron may be under the influence of both the nuclei and may have characteristics of both wave function ψ_A and ψ_B , the wave function of such system called molecular orbital wave function (ψ_{MO}) is then obtained by linear combination of atomic orbital wave functions

$$\psi_{MO} = C_1\psi_A + C_2\psi_B \quad \text{--- (1)}$$

Where C_1 and C_2 are the coefficient of the wave functions ψ_A and ψ_B .

(ii) The coefficients C_1 and C_2 are found by variation method which give minimum value of energy. When variation method is applied, we get two values of energy represented by E^+ and E^- . The symbol E^+ represents the molecular orbital with energy lower than combining atomic orbitals (E_A or E_B). E^- represents the molecular orbital with energy higher than the combining atomic orbitals.

(4)



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The function ψ is acceptable only if it is normalized

$$\int \psi_{\text{MO}}^2 \delta\tau = 1$$

$$\text{or, } \int (C_1\psi_A + C_2\psi_B)^2 \delta\tau = 1$$

$$\text{or } \int C_1^2 \psi_A^2 \delta\tau + \int C_2^2 \psi_B^2 \delta\tau + \int 2C_1C_2\psi_A\psi_B \delta\tau = 1$$

As the atomic orbital wave functions are also normalized

$$\int \psi_A^2 \delta\tau = 1, \int \psi_B^2 \delta\tau = 1$$

$$\text{Hence, } C_1^2 + C_2^2 + 2C_1C_2 \int \psi_A\psi_B \delta\tau = 1 \quad \text{--- (i)}$$

If $\int \psi_A\psi_B \delta\tau$ is represented by 's'

called overlap integral b/w the orbitals ψ_A & ψ_B .

$$\therefore C_1^2 + C_2^2 + 2C_1C_2s = 1 \quad \text{--- (ii)}$$

- For Zero Overlap approximation

$$s = 0$$

$$\therefore C_1^2 + C_2^2 = 1 \quad \text{--- (iv)}$$

In case of H_2^+ , as both the atoms are same, there will be equal contribution by the atomic wave functions towards the molecular orbital wave function.

$$\therefore C_1^2 = C_2^2$$

From eqn (v), $C_1^2 = C_2^2 = \frac{1}{2}$

$$\therefore C_1 = \pm C_2 = \pm \frac{1}{\sqrt{2}}$$

Thus two sets of values are possible for C_1 and C_2

i.e., $C_1 = +\frac{1}{\sqrt{2}}, C_2 = +\frac{1}{\sqrt{2}}$

and $C_1 = +\frac{1}{\sqrt{2}}, C_2 = -\frac{1}{\sqrt{2}}$

Putting these values in eqn (i), we get

$$\psi_+(MO) = \frac{1}{\sqrt{2}} \psi_A + \frac{1}{\sqrt{2}} \psi_B = \frac{1}{\sqrt{2}} (\psi_A + \psi_B) \quad \text{--- (vi)}$$

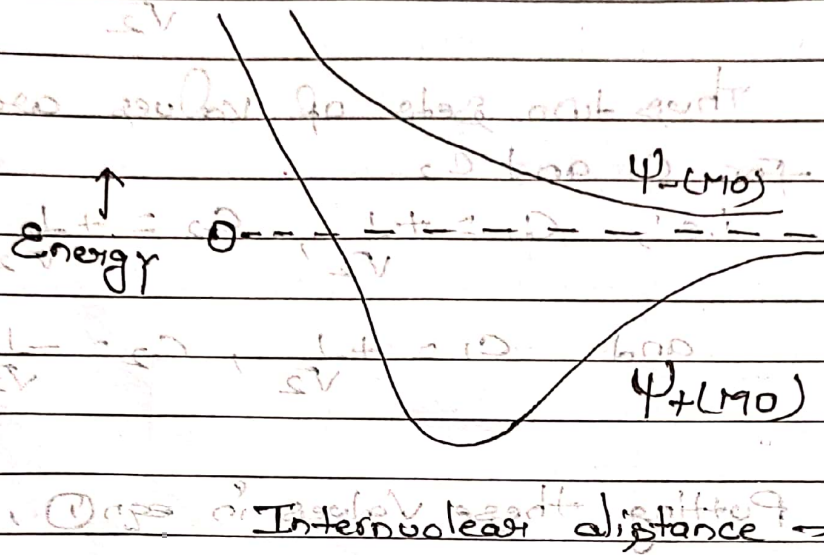
$$\psi_-(MO) = \frac{1}{\sqrt{2}} \psi_A - \frac{1}{\sqrt{2}} \psi_B = \frac{1}{\sqrt{2}} (\psi_A - \psi_B) \quad \text{--- (vii)}$$

The wave functions $\psi_+(MO)$ corresponds to the energy E^+ whereas $\psi_-(MO)$ corresponds to the energy E^- .

Egn (vi) and (vii) give the values of the wave function according to LCAO-MO treatment of H_2^+ ion. Using these wave functions, energies (E^+ and E^-) are calculated for different internuclear distances.

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A graph is then plotted between energy versus internuclear distance. The graph is shown in following figure -



ψ+(MO) is called bonding molecular Orbital (BMO) and ψ-(MO) is called anti-bonding molecular orbital (ABMO)

Application of LCAO to the Formation of H₂ molecule:

In the case of H₂ molecule, both the atomic orbitals are identical. Hence, their wave functions will contribute equally towards molecular orbital wave function. So the coefficients c₁ and c₂ can be ignored.

According to LCAO approximation, the



molecular orbital can be taken as the sum of the atomic orbital wave functions.

In H_2 molecule, there are two nuclei H_A and H_B . The two electrons may be written as 1 and 2. Let the atomic orbital wave functions of atoms H_A and H_B be ψ_A and ψ_B respectively.

Let us consider the first electron 1. As the electron is under the influence of both the nuclei. Then by LCAO approximation, the molecular orbital wave function for the electron 1 can be written as

$$\psi_1 = \psi_A(1) + \psi_B(1) \quad \text{--- (1)}$$

Similarly, as electron 2 is also under the influence of both the nuclei, so by LCAO approximation, the molecular orbital wave function of electron 2 can be written as

$$\psi_2 = \psi_A(2) + \psi_B(2) \quad \text{--- (2)}$$

Thus, total molecular orbital wave function will be given by

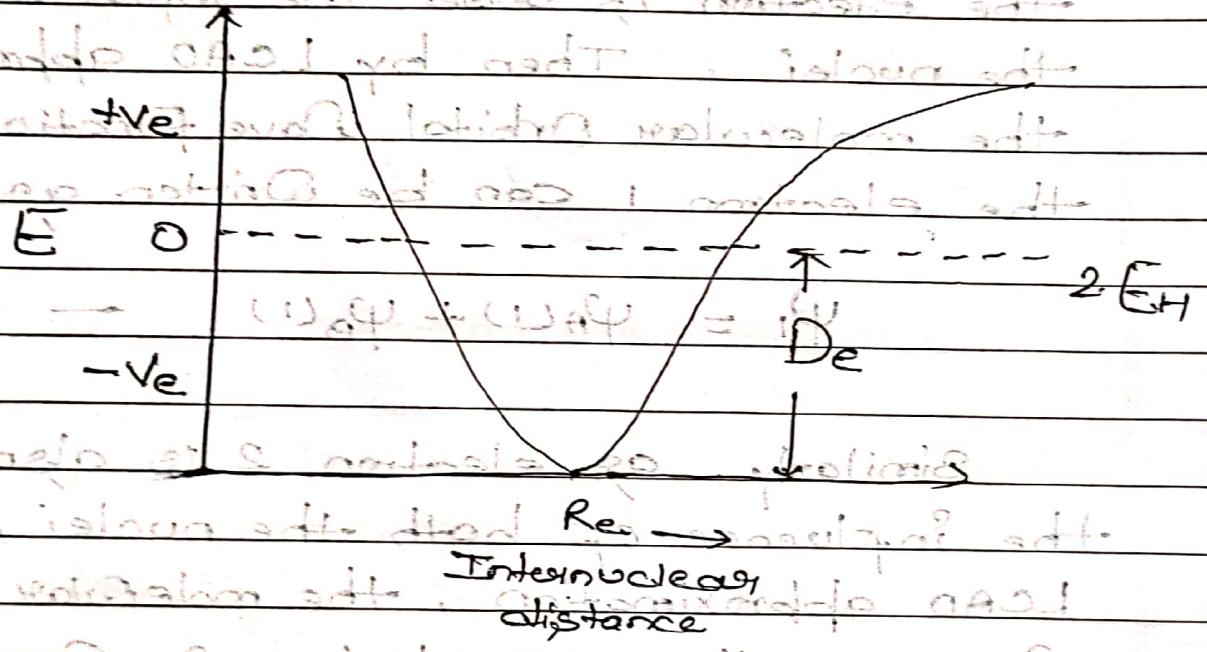
$$\psi_{MO} = \psi_1 \psi_2$$

$$= [\psi_A(1) + \psi_B(1)] [\psi_A(2) + \psi_B(2)]$$

--- (3)

(8) (F)

Using the molecular Orbital wave function given by equation (3), Energy is calculated for different internuclear distances and a graph is plotted between energy versus internuclear distance. The value corresponding to the minimum in the curve is calculated which is the bond dissociation energy.



(2) $(\psi_1)^2 + (\psi_2)^2 = 2\psi$