

→ Each MO can hold one or more electrons in accordance with Pauli's exclusion principle, Hund's rule etc.

Let us consider a homonuclear diatomic molecule AB. If ψ is the wave function of 10 MO obtained from two AOs of two atoms A and B having ψ_A and ψ_B respectively then -

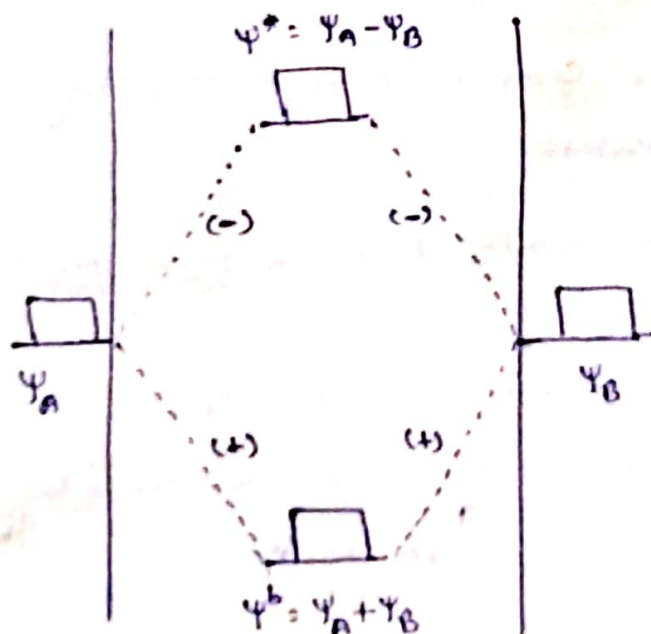
$$\psi = \psi_A \pm \psi_B$$

The linear combination of ψ_A and ψ_B gives two MO's i.e. ψ^b and ψ^* given as -

$$\psi^b = \psi_A + \psi_B$$

$$\text{and } \psi^* = \psi_A - \psi_B$$

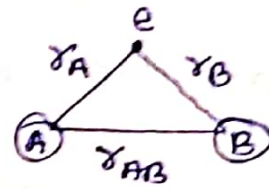
The energy level diagram is shown as -



Q Write the Hamiltonian for (i) H_2^+ (ii) H_2 & (iii) H_2^-

(i) H_2^+ :- H_2^+ has only one electron. Using SI units and Born-Oppenheimer approximation, Hamiltonian for H_2^+ may be written as (in atomic units), A & B are two nuclei.

$$\hat{H} = -\frac{1}{2} \nabla^2 + \left(\frac{1}{r_{AB}} - \frac{1}{r_A} - \frac{1}{r_B} \right)$$



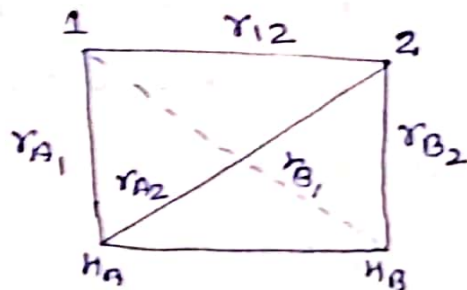
The 1st term represents kinetic energy operator of the single electron, $\frac{1}{r_A}$ & $\frac{1}{r_B}$ represent the Coulombic attraction of electron with nuclei A & B respectively and $\frac{1}{r_{AB}}$ represents Coulombic repulsion between two nuclei A & B.

(ii) H_2 :-

It contains two electrons 1 & 2 and two nuclei A & B

The Hamiltonian for H_2 molecule may be written as -

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \left(\frac{1}{r_{AB}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} \right)$$



(iii) H₂⁻

It contains three electrons 1, 2, 3 and two nuclei A & B.

The Hamiltonian is —

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + \left(\frac{1}{r_{AB}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{A3}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

* LCMO-MO Wave function for H₂⁺

The wave function is written as:

$$\psi = a_1 1s_A + a_2 1s_B$$

Where, 1s_A & 1s_B are the atomic orbitals ~~at~~ centered around, H-atoms A & B. These atomic orbitals are given as:

$$1s_A = \frac{1}{\sqrt{\pi}} e^{-r_A} \quad \& \quad 1s_B = \frac{1}{\sqrt{\pi}} e^{-r_B}$$

The MOs can be constructed as

$$\psi_1 = N_1 (1s_A + 1s_B)$$

$$\psi_2 = N_2 (1s_A - 1s_B)$$

Where, N₁ & N₂ are normalised factors.

After calculating LCAO coefficients, we get the normalised MOs for H₂⁺ as

$$\psi_+ \equiv \psi_1 = \frac{1}{\sqrt{2(1+s)}} (1s_A + 1s_B) \quad (\text{Bonding M.O.})$$

$$\& \quad \psi_- \equiv \psi_2 = \frac{1}{\sqrt{2(1-s)}} (1s_A - 1s_B) \quad (\text{Antibonding M.O.})$$

Where, 's' is the overlap integral.