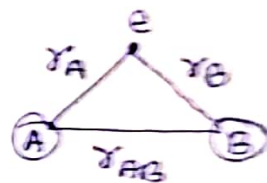**Q.** Write the Hamiltonian for (i) H_2^+ (ii) H_2 & (iii) H_2^-

(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.

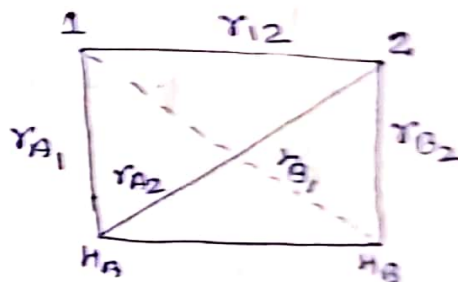$$\hat{H} = -\tfrac{1}{2}\nabla^2 + \left(\frac{1}{r_{AB}} - \frac{1}{r_A} - \frac{1}{r_B}\right)$$

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 -

$$\hat{H} = -\tfrac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \left(\frac{1}{r_{AB}} - \frac{1}{r_{A_1}} - \frac{1}{r_{A_2}} - \frac{1}{r_{B_1}} - \frac{1}{r_{B_2}} + \frac{1}{r_{12}}\right)$$

(iii) H_2^-

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

The Hamiltonian is —

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2 + \nabla_3^2\right) + \left(\frac{1}{r_{AB}} - \frac{1}{r_{A_1}} - \frac{1}{r_{A_2}} - \frac{1}{r_{A_3}} \right.$$
$$\left. - \frac{1}{r_{B_1}} - \frac{1}{r_{B_2}} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right).$$

* **LCMO - MO Wave function for H_2^+**

The wave function is written as:
$$\psi = a_1 \, 1s_A + a_2 \, 1s_B$$

Where, $1s_A$ & $1s_B$ are the atomic orbitals 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
$$\psi_1 = N_1\left(1s_A + 1s_B\right)$$
$$\psi_2 = N_2\left(1s_A - 1s_B\right)$$

where, N_1 & N_2 are normalised factors.
after calculating LCAO coefficients, we get the normalised MOs for H_2^+ as

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

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

where, 's' is the overlap integral.

Q. Prove that the BMO & ABMO for H_2 are orthogonal.

In the LCAO-MO approximation, the normalised MOs of H_2 are:

$$\psi_1 = \frac{1}{\sqrt{2(1+s)}} \left(1s_A + 1s_B \right) \qquad BMO$$

$$\psi_2 = \frac{1}{\sqrt{2(1-s)}} \left(1s_A - 1s_B \right) \qquad ABMO$$

for orthogonality,

$$\int \psi_1 \, \psi_2 \, d\tau = 0$$

i.e.

$$\int \frac{1}{\sqrt{2(1+s)}} \left(1s_A + 1s_B \right) \times \frac{1}{\sqrt{2(1-s)}} \left(1s_A - 1s_B \right) d\tau = 0$$

$$= \frac{1}{2(1-s^2)^{\frac{1}{2}}} \int \left(1s_A^2 - 1s_B^2 \right) d\tau$$

$$= \frac{1}{2(1-s^2)^{\frac{1}{2}}} \left[1 - 1 \right] d\tau = 0.$$

Proved

Q. Construct the normalised molecular orbital wave function for (i) H_2 (ii) H_2^- (iii) HeH.

In the LCAO-MO approximation, the total wave function of a molecule containing n-electrons is given by —

$$\psi_{MO} (1,2,3 \ldots n) = \psi_1(1) \cdot \psi_2(2) \cdot \psi_3(3) \cdots \psi_n(n)$$

If ψ_i's are molecular orbitals (MOs) and ψ_i's is written as linear combination of molecular orbitals (AOs), then

$$\psi_i = C_{ia} \phi_a(i) + C_{ib} \phi_b(i) + C_{ic} \phi_c(i) + \cdots$$

where, c's are the coefficient determined from the normalisation condition and its subscripts $a, b, c \ldots$ refer to its atoms in its molecule on which AO.s are centered.

(i) H_2 — There are two electrons $(1, 2)$

So, $\Psi_{MO}(1, 2) = \Psi_1(1) \cdot \Psi_2(2)$

$$\Psi_1 = c_1 \cdot 1s_a(1) + c_2 \cdot 1s_b(1)$$

$$\Psi_2 = c_3 \cdot 1s_a(2) + c_4(1s_b)(2)$$

(ii) H_2^- — There are three electrons $(1, 2, 3)$

$$\Psi_{MO}(1, 2, 3) = \Psi_1(1) \, \Psi_2(2) \, \Psi_3(3)$$

$$\Psi_1 = c_1 \, 1s_a(1) + c_2(1s_b)(1)$$

$$\Psi_2 = c_3(1s_a)(2) + c_4 \, 1s_b(2)$$

$$\Psi_3 = c_5(1s_a)(3) + c_6 \, 1s_b(3)$$

(iii) HCl —

1s-orbital of H-atom overlaps with $3p_z$-orbital of Cl atom.

$$\Psi_{MO} = \Psi_1 \cdot \Psi_2$$

$$\Psi_1 = c_1 \, \phi_{1s}(H)(1) + c_2 \, \phi_{3p}(Cl)(1)$$

$$\Psi_2 = c_1 \phi_{1s}H(2) + c_2 \, \phi_{3p}Cl(2)$$

$$\Psi_{HCl} = \Psi_1 \cdot \Psi_2 = c_1^2\big[\phi_{1s\,H}(1) \cdot \phi_{1s\,H}(2)\big] + c_2^2\big[(\phi_{3p\,Cl}(1) \, \phi_{3p\,Cl}(2)\big]$$

$$+ \, c_1 c_2 \big[\phi_{1s\,H}(1) \cdot \phi_{3p\,Cl}(2)\big] + c_1 c_2 \big[\phi_{1s\,H}(2) \cdot \phi_{3p\,Cl}(1)\big].$$

The first two terms represents the ionic terms Since, both the electrons are either on H-atom or cl-atoms while the last two represents Covalent terms. Since both electrons are on different atoms.

②. Given the following MOs

$$\Psi_1 = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2)$$

$$\Psi_2 = \frac{1}{\sqrt{3}} (\phi_1 + \phi_2 + \phi_3) \quad \&$$

$$\Psi_3 = \frac{1}{2} (\phi_1 - 2\phi_2 + \phi_3)$$

Where the ϕs are the orthonormal atomic orbitals, which of the them are normalised?

Sol⁵ for MOs to be normalised, the sum of the square of the coefficients of the AOs should be equal to one i.e.

$$\sum_{i=1}^{n} c_i^2 = 1$$

for, Ψ_1; $\left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1$

for Ψ_2; $\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{1}{\sqrt{3}}\right)^2 = 1$.

for. Ψ_3; $\left(\frac{1}{2}\right)^2 + (-1)^2 + \left(\frac{1}{2}\right)^2 \neq 1$.

Hence, Ψ_1 & Ψ_2 are normalised but Ψ_3 is not normalised.

Dr. A.K.Gutle
chemistry
L.S. College.