Q. Determine the normalised ground-state molecular orbital wave function for H_2.

$$\psi_{MO}(1,2) = \psi_1 \psi_2$$

Where,

$$\psi_1 = C_1\, 1s_a(1) + C_2\, 1s_b(1)$$

$$\psi_2 = C_3\, 1s_a(2) + C_4\, 1s_b(2)$$

We have to determine the co-efficient c_1, c_2, c_3, c_4.

Let $c_1 = c_2 = c_3 = c_4 = C$.

So, $\psi_{MO}(1,2) = c^2 [1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)]$

for normalised molecular orbital wave function

$$\int \psi_{MO}^*(1,2)\, \psi_{MO}(1,2)\, d\tau = 1$$

but $\psi_{MO}^*(1,2) \cdot \psi_{MO}(1,2)\, d\tau = \langle \psi_1 | \psi_1 \rangle^2 = 1$.

$$\langle \psi_1 | \psi_1 \rangle = c^2 [\langle 1s_a(1) | 1s_a(1) \rangle + \langle 1s_b(1) | 1s_b(1) \rangle + \langle 1s_a(1) | 1s_b(1) \rangle + \langle 1s_b(1) | 1s_a(1) \rangle]$$

$$= c^2 [S_{aa} + S_{bb} + S_{ab} + S_{ba}]$$

Where, $S_{aa} = \langle 1s_a(1) | 1s_a(1) \rangle$

$S_{ab} = \langle 1s_a(1) | 1s_b(1) \rangle$ etc.

Where 'S' is called overlap integrals and determine the extent of overlap between the atomic orbitals.

By definition:

$$S_{aa} = S_{bb} = 1 \;\&\; S_{ab} = S_{ba} = S.$$

Hence, $\langle \psi_1 | \psi_1 \rangle = c^2(1+1+2S) = 2(1+S)c^2$

i.e. $2(1+S)c^2 = 1.$

$$c = \frac{1}{\sqrt{2(1+S)}}$$

Thus, $$\psi_1 = \frac{1}{\sqrt{2(1+S)}}\left[1S_a(1) + 1S_b(1)\right]$$

$$\psi_2 = \frac{1}{\sqrt{2(1-S)}}\left[1S_a(1) - 1S_b(1)\right]$$

Q. Given the following MOs

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$\psi_2 = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$$

$$\& \quad \psi_3 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$$

Where, ϕ_3 are the atomic orbitals which are orthonormal.

(i) Are ψ_1 & ψ_2 mutually orthogonal.

Soln for the given MOs to be orthogonal.—

$$\int \psi_1 \psi_2 \, d\tau \equiv \langle \psi_1 | \psi_2 \rangle = 0.$$

$$\langle \psi_1 | \psi_2 \rangle = \left\langle \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \middle| \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3) \right\rangle$$

$$= \frac{1}{\sqrt{6}}\Big[\langle \phi_1 | \phi_1 \rangle + 2\langle \phi_1 | \phi_2 \rangle + \langle \phi_1 | \phi_3 \rangle$$
$$+ \langle \phi_2 | \phi_2 \rangle + \langle \phi_2 | \phi_3 \rangle\Big]$$

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Since, given AOs are normalised

$$\langle \psi_1 | \psi_2 \rangle = \frac{1}{\sqrt{6}}(1+1) = \frac{2}{\sqrt{6}} \neq 0$$

[assuming overlap integrals $(\langle \phi_i | \phi_j \rangle = 0)$]

Hence, ψ_1 & ψ_2 are not orthogonal.

(ii) Is ψ_3 is normalised.

Soln

Given,

$$\psi_3 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$$

$$= \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(\phi_1 + \phi_2) - \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)\right]$$

$$= \left(\frac{1}{2} - \frac{1}{\sqrt{6}}\right)\phi_1 + \left(\frac{1}{2} - \frac{1}{\sqrt{6}}\right)\phi_2 - \frac{1}{\sqrt{6}}\phi_3$$

$$\sum_{i=1}^{3} c_i^2 = \left(\frac{1}{2} - \frac{1}{\sqrt{6}}\right)^2 + \left(\frac{1}{2} - \frac{1}{\sqrt{6}}\right)^2 + \left(-\frac{1}{\sqrt{6}}\right)^2$$

$$= 1 - \frac{2}{\sqrt{6}} \neq 1$$

So, ψ_3 is not normalised.

Dr. A.K. Gupta.
Chemistry.
L.S. College