ATOMS, MOLECULES & REACTIONS - I

QUANTUM MECHANICS HW - WEEK 7

From the worksheet

(1) $$C_1 [H_{AA} - \langle E \rangle] + C_2 [H_{AB} - S\langle E \rangle] = 0 \quad \text{---(1)}$$

Substitute $\langle E \rangle = E_1 = \dfrac{H_{AA} + H_{AB}}{1+S}$ into (1)

$$C_1 \left[H_{AA} - \frac{H_{AA} + H_{AB}}{1+S} \right] + C_2 \left[H_{AB} - S\left(\frac{H_{AA} + H_{AB}}{1+S} \right) \right] = 0$$

$$C_1 \left[\frac{H_{AA}(1+S) - H_{AA} - H_{AB}}{(1+S)} \right] + C_2 \left[\frac{H_{AB}(1+S) - S H_{AA} - S H_{AB}}{(1+S)} \right] = 0$$

$$C_1 [H_{AA} + S H_{AA} - H_{AA} - H_{AB}] + C_2 [H_{AB} + S H_{AB} - S H_{AA} - S H_{AB}] = 0$$

$$H_{AA}(S C_1 - S C_2) + H_{AB}(C_2 - C_1) = 0$$

$$S H_{AA}(C_1 - C_2) - H_{AB}(C_1 - C_2) = 0$$

$$(C_1 - C_2)[S H_{AA} - H_{AB}] = 0$$

$$\Rightarrow C_1 - C_2 = 0 \quad \Rightarrow \quad \underline{C_1 = C_2}$$

Substitute $\langle E \rangle = E_2 = \dfrac{H_{AA} - H_{AB}}{1-S}$ into (2)

$$C_1\left[H_{AB} - S\left(\frac{H_{AA}-H_{AB}}{1-S}\right)\right] + C_2\left[H_{BB} - \left(\frac{H_{AA}-H_{AB}}{1-S}\right)\right] = 0$$

$$C_1\left[\frac{H_{AB}(1-S) - S H_{AA} + S H_{AB}}{(1-S)}\right] + C_2\left[\frac{H_{BB}(1-S) - H_{AA} + H_{AB}}{(1-S)}\right] = 0$$

$$C_1\left[H_{AB} - \cancel{S H_{AB}} - S H_{AA} + \cancel{S H_{AB}}\right] + C_2\left[\cancel{H_{BB}} - S H_{BB} - \cancel{H_{AA}} + H_{AB}\right] = 0$$

$$H_{AB}(C_1 + C_2) - S H_{AA}(C_1 + C_2) = 0 \qquad \text{since } H_{AA} = H_{BB}$$

$$(C_1 + C_2)(H_{AB} - S H_{AA}) = 0$$

$$\Rightarrow \quad C_1 + C_2 = 0 \quad \Rightarrow \quad \underline{\underline{C_1 = -C_2}}$$

(2) Let $C_1 = C_2 \qquad \psi = C_1 1S_A + C_2 1S_B = C_1(1S_A + 1S_B)$

$$\int \psi^* \psi \, d\tau = 1$$

$$C_1^2 \int (1S_A^* + 1S_B^*)(1S_A + 1S_B)\, d\tau = 1$$

$$C_1^2 \left[\int 1S_A^* \, 1S_A \, d\tau + \int 1S_A^* \, 1S_B \, d\tau + \int 1S_B^* \, 1S_A \, d\tau + \int 1S_B^* \, 1S_B \, d\tau \right] = 1$$

$$C_1^2\left[\,1 + S + S + 1\,\right] = 1$$

$$C_1^2 = \frac{1}{2+2S} = \frac{1}{2(1+S)}$$

$$C_1 = \frac{1}{\sqrt{2(1+S)}}$$

Let $C_1 = -C_2$ $\quad \psi = C_2(1s_A - 1s_B)$

$$\int \psi^* \psi \, d\tau = 1$$

$$\int C_2^2 (1s_A^* - 1s_B^*)(1s_A - 1s_B)\, d\tau = 1$$

$$C_2^2\left[\int 1s_A^* 1s_A d\tau - \int 1s_A^* 1s_B d\tau - \int 1s_B^* 1s_A d\tau + \int 1s_B^* 1s_B d\tau\right] = 1$$

$$C_2^2\left[\,1 - S - S + 1\,\right] = 1$$

$$C_2^2 = \frac{1}{2(1-S)} \qquad C_2 = \frac{1}{\sqrt{2(1-S)}}$$

Term symbols for diatomic molecules & ions are given in Table 11.1