ATOMS, MOLECULES & RESEARCH

QUANTUM MECHANICS - SPRING - WEEK 2

from the assigned HW sheet

① $$E = \frac{C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{BB}}{C_1^2 + 2C_1C_2 S_{AB} + C_2^2}$$

$$H_{AA} = H_{BB} \qquad S_{AB} = S$$

$$E = \frac{C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{AA}}{C_1^2 + 2C_1C_2 S + C_2^2}$$

$$E\left(C_1^2 + 2C_1C_2S + C_2^2\right) = C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{AA}$$

differentiate with respect to C_2

$$E\left(2C_1S + 2C_2\right) + \frac{\partial E}{\partial C_2}\left(C_1^2 + 2C_1C_2S + C_2^2\right) = 2C_1 H_{AB} + 2C_2 H_{AA}$$

$$\left(\frac{\partial E}{\partial C_2}\right) = \frac{2C_1 H_{AB} + 2C_2 H_{AA} - 2C_1SE - 2C_2E}{C_1^2 + 2C_1C_2S + C_2^2}$$

for the minimum ~~best~~ value of E, $\left(\frac{\partial E}{\partial C_2}\right) = 0$

This will provide the best value for C_2

$$\therefore\ 2C_1 H_{AB} + 2C_2 H_{AA} - 2C_1SE - 2C_2E = 0$$

$$2C_1\left(H_{AB} - SE\right) + 2C_2\left(H_{AA} - E\right) = 0$$

$$\Rightarrow \quad C_1 (H_{AB} - SE) + C_2 (H_{AA} - E) = 0 \quad - ②$$

② $$E_1 = \frac{H_{AA} + H_{AB}}{1+S} \qquad E_2 = \frac{H_{AA} - H_{AB}}{1-S}$$

Substitute E_1 into equation ①

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

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

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

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

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

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

Similarly substitute E_2 into equation ②

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

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

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

$$\Rightarrow \left(H_{AB} - SH_{AA}\right)(C_1 + C_2) = 0$$

$$\Rightarrow C_1 + C_2 = 0 \Rightarrow C_1 = -C_2$$

$$\therefore \underline{\underline{C_1 = \pm C_2}}$$

(3) $\psi = C_1 1S_A + C_2 1S_B$

If $C_1 = C_2$ then $\psi = C_1 1S_A + C_1 1S_B$

$$= C_1(1S_A + 1S_B)$$

ψ is normalized $\Rightarrow \int \psi^* \psi \, d\tau = 1$

$$\int C_1^*(1S_A^* + 1S_B^*) C_1(1S_A + 1S_B) = 1$$

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

$$C_1^2 \left[\underbrace{\int 1S_A^* 1S_A d\tau}_{=1} + \underbrace{\int 1S_A^* 1S_B d\tau}_{=S} + \underbrace{\int 1S_B^* 1S_A d\tau}_{=S} + \underbrace{\int 1S_B^* 1S_B d\tau}_{=1} \right] = 1$$

$$C_1^2 (2 + 2S) = 1 \Rightarrow 2C_1^2(1+S) = 1$$

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

$$\therefore \underline{\underline{C_2 = C_1 = \frac{1}{\sqrt{2(1+S)}}}}$$

4)

If $c_1 = -c_2$ then $\psi = c_1 1s_A - c_1 1s_B$

$= c_1 (1s_A - 1s_B)$

ψ is normalized $\Rightarrow \int \psi^* \psi \, d\tau = 1$

$\Rightarrow \int c_1^* (1s_A^* - 1s_B^*) \, c_1 (1s_A - 1s_B) d\tau = 1$

$$c_1^2 \left[\int \underbrace{1s_A^* 1s_A d\tau}_{=1} - \int \underbrace{1s_A^* 1s_B}_{=S} d\tau - \int \underbrace{1s_B^* 1s_A}_{=S} d\tau + \underbrace{\int 1s_B^* 1s_B d\tau}_{=1} \right] = 1$$

$c_1^2 (2 - 2S) = 1 \Rightarrow 2c_1^2 (1-S) = 1$

$$c_1^2 = \frac{1}{2(1-S)}$$

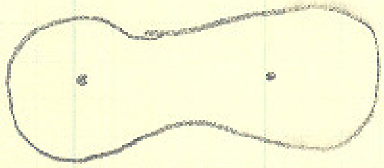
$$c_1 = \frac{1}{\sqrt{2(1-S)}} \quad \therefore \quad c_2 = -\frac{1}{\sqrt{2(1-S)}}$$

(4) $\psi = c_1 1s_A + c_2 1s_B$

If $c_1 = c_2$ $\quad \psi_1 = \dfrac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)$

If $c_1 = -c_2$ $\quad \psi_1 = c_1 1s_A - c_1 1s_B$

$$= \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B)$$

$\psi_1 =$ 

$\psi_2 =$