# ADVANCED CHEMISTRY - 2008

## QUANTUM MECHANICS - SPRING - WEEK 3

### From the worksheet

(1) Substitute $E_1$ in equation (1)

$$C_1\left[H_{AA} - E_1\right] + C_2\left[H_{AB} - E_1 S\right] = 0$$

$$C_1 H_{AA} - E_1 C_1 + C_2 H_{AB} - E_1 C_2 S = 0$$

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

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

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

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

$$C_1 = \frac{-C_2\left(H_{AB} - SH_{AA}\right)}{\left(SH_{AA} - H_{AB}\right)} = \frac{C_2\,\cancel{\left(SH_{AA} - H_{AB}\right)}}{\cancel{\left(SH_{AA} - H_{AB}\right)}}$$

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

Substitute $E_2$ in equation ②

$$C_1\left[H_{AB}-E_2 S\right]+C_2\left[H_{BB}-E_2\right]=0$$

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

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

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

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

$$C_1=-C_2\frac{\cancel{\left(-SH_{BB}+H_{AB}\right)}}{\cancel{\left(H_{AB}-SH_{AA}\right)}}$$

since $H_{AA}=H_{BB}$

$$C_1=-C_2$$

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

(2) $\psi_{H_2^+} = C_1\, 1s_A + C_2\, 1s_B$

when $C_1 = C_2$ $\quad \psi_{H_2^+} = C_1 (1s_A + 1s_B)$

$$\int \psi^*_{H_2^+}\, \psi_{H_2^+}\, d\tau = 1 \quad \text{(normalization requirement)}$$

$$\int C_1^* (1s_A^* + 1s_B^*)\, C_1 (1s_A + 1s_B)\, d\tau = 1$$

$$C_1^* C_1 \int (1s_A^*\, 1s_A + 1s_A^*\, 1s_B + 1s_B^*\, 1s_A + 1s_B^*\, 1s_B)\, d\tau = 1$$

$$C_1^2 \Big[ \underbrace{\int 1s_A^*\, 1s_A\, d\tau}_{=1} + \underbrace{\int 1s_B^*\, 1s_B\, d\tau}_{=1} + 2 \int 1s_A^*\, 1s_B\, d\tau \Big] = 1$$

since $1s_A$ and $1s_B$ are normalized

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

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

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

Similarly when $C_1 = -C_2$

$$\psi_{H_2^+} = C_1 1S_A - C_1 1S_B = C_1 (1S_A - 1S_B)$$

$$\int \psi^*_{H_2^*} \psi_{H_2^+} d\tau = 1$$

$$\int C_1^* (1S_A^* - 1S_B^*) C_1 (1S_A - 1S_B) d\tau = 1$$

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

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

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

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

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