Note Title 18-11-2016

The Chemical bond ($H_2^{\oplus}$)

bonding $\quad \psi_+ = \frac{1}{\sqrt{2(1+S)}} \left(1s_A + 1s_B \right) \quad \ldots \quad (1)$

antibonding $\quad \psi_- = \frac{1}{\sqrt{2(1-S)}} \left(1s_A - 1s_B \right) \quad \ldots \quad (2)$

$$E_+ = \frac{\int \psi_+^* \hat{H} \psi_+ \, d\tau}{\int \psi_+^* \psi_+ \, d\tau} \leftarrow = 1$$

(normalised)

$$E_+ = \int \psi_+^* \hat{H} \psi_+ \, d\tau \quad \ldots \quad (3)$$

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R}$$

$$\int \psi_+ \hat{H} \psi_+ \, d\tau$$

$$= \frac{1}{2(1+S)} \int (1s_A + 1s_B) \hat{H} (1s_A + 1s_B) \, d\tau$$

$$= \frac{1}{2(1+S)} \int (1s_A + 1s_B) \left[-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \right] (1s_A + 1s_B) \, d\tau$$

$$\int 1s_A \left[-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \right] 1s_A \, d\tau$$

$$= E_{1s} + J$$

$$\int 1s_A \underbrace{\left[-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} \right] 1s_A}_{\longrightarrow\ E_{1s} 1s_A} d\tau$$

$$= \int 1s_A \, E_{1s} \, 1s_A \, d\tau$$

$$= E_{1s} \int 1s_A 1s_A \, d\tau = \underline{\underline{E_{1s}}}$$

$$\int 1s_A \left[-\frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \right] 1s_A \, d\tau$$

$$= \int 1s_A \frac{-e^2}{4\pi\varepsilon_0 r_B} 1s_A \, d\tau + \int 1s_A \frac{e^2}{4\pi\varepsilon_0 R} 1s_A \, d\tau$$

$$= -\frac{e^2}{4\pi\varepsilon_0} \int \frac{1s_A 1s_A}{r_B} d\tau + \frac{e^2}{4\pi\varepsilon_0 R} \int 1s_A 1s_A \, d\tau$$

$$= -\frac{e^2}{4\pi\varepsilon_0} \int \frac{1s_A 1s_A}{r_B} d\tau + \frac{e^2}{4\pi\varepsilon_0 R}$$

$= J$ (Coulomb Integral)

$$\int 1s_A \left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \right] 1s_B \, dr$$

$$= E_{1s} S + K$$

$$\int 1s_A \underbrace{\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_B} \right] 1s_B}_{\longrightarrow\, E_{1s}\, 1s_B} \, dr$$

$$= \int 1s_A \, E_{1s} \, 1s_B \, dr$$

$$= E_{1s} \int 1s_A \, 1s_B \, dr = \underline{\underline{E_{1s} S}}$$

$$\int 1s_A \left[-\frac{e^2}{4\pi\varepsilon_0 r_A} + \frac{e^2}{4\pi\varepsilon_0 R} \right] 1s_B \, dr$$

$$= -\frac{e^2}{4\pi\varepsilon_0} \int \frac{1s_A \, 1s_B}{r_A} \, dr + \frac{e^2}{4\pi\varepsilon_0 R} \underbrace{\int 1s_A \, 1s_B \, dr}_{= S}$$

$= K$ [exchange integral]

$$E_+ = \left[2(E_{1s} + J) + 2(E_{1s} S + K) \right] \frac{1}{2(1+S)}$$

$$E_+ = \left[2E_{1s}(1+S) + 2(J+K) \right] \frac{1}{2(1+S)}$$

$$E_+ = E_{1s} + \frac{J+K}{1+S}$$ $\leftarrow$ <u>bonding orbital</u>

$$\Delta E = E_+ - E_{1s} = \frac{J+K}{1+S}$$

$$E_- = E_{1s} - \frac{J-K}{1-S}$$