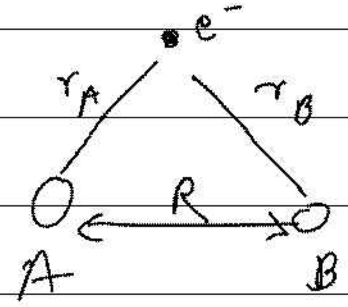
Note Title 16-11-2016

$H_2^{\oplus}$

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



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

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

E_+ :

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

$\int \psi_+^* \psi_+ d\tau \Leftarrow = 1$ because ψ_+ is already normalised

$$E_+ = \int \psi_+^* \hat{H} \psi_+ d\tau$$

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

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

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

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right] 1s_A = E_{1s}\, 1s_A$$

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

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

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

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

$= J \leftarrow$ coulomb integral

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

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

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

$$= E_{1s} \underbrace{\int 1s_A 1s_B \, d\tau}_{S} + \text{(the other term)}$$

$$\int 1s_A\left(-\frac{e^2}{4\pi\varepsilon_0 r_A}\right)1s_B\,d\tau + \int 1s_A \frac{e^2}{4\pi\varepsilon_0 R} 1s_B\,d\tau$$

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

$= K \Rightarrow$ Exchange integral

no classical analogue

→ reason why bond formation takes place

$$E_{1s}S + K \; ; \quad E_{1s} + J$$

$$2(E_{1s}+J) + 2(E_{1s}S + K)$$
$$= 2E_{1s}(1+S) + 2(J+K)$$

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

$$E_+ = E_{1s} + \frac{J+K}{1+S} \quad \text{(bonding orbital)}$$

$$E_- = E_{1s} - \frac{J-K}{1-S} \quad \text{(antibonding orbital)}$$