Note Title 16-11-2016

Helium atom

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\text{ignore it!}}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

$$\psi(r_1, r_2) = \psi(r_1)\,\psi(r_2)$$

$$\hat{H}_1 \psi(r_1) = E_1 \psi(r_1)$$

$$\hat{H}_2 \psi(r_2) = E_2 \psi(r_2)$$

$$\hat{H}\psi(r_1, r_2) = \hat{H}\,\psi(r_1)\psi(r_2)$$

$$= (\hat{H}_1 + \hat{H}_2)\,\psi(r_1)\,\psi(r_2)$$

$$= \hat{H}_1 \psi(r_1)\psi(r_2) + \hat{H}_2 \psi(r_1)\psi(r_2)$$

$$= E_1 \psi(r_1)\,\psi(r_2) + E_2 \psi(r_1)\,\psi(r_2)$$

$$= (E_1 + E_2)\,\psi(r_1)\,\psi(r_2)$$

$$E = E_1 + E_2$$

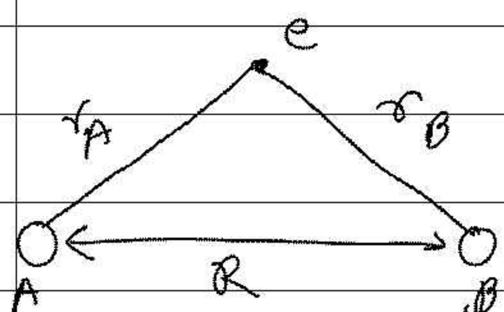
$$E_1 = -13.6\,\frac{Z^2}{n^2} = -13.6 \cdot \frac{2^2}{1^2} = \underline{-54.4\,\text{eV}}$$

$$E_2 = -54.4\,\text{eV}$$

$$E = E_1 + E_2 = \underline{-108.8\,\text{eV}}$$

$$E_{exp} = -79.0 \text{ eV}$$

Diatomic Molecules (H_2^+)



$$\hat{H} = -\frac{\hbar^2}{2m_{N_A}} \nabla_{N_A}^2 - \frac{\hbar^2}{2m_{N_B}} \nabla_{N_B}^2$$

$$- \frac{\hbar^2}{2m_e} \nabla_e^2$$

$$- \frac{Ze^2}{4\pi\varepsilon_0 r_A} - \frac{Ze^2}{4\pi\varepsilon_0 r_B}$$

$$+ \frac{e^2}{4\pi\varepsilon_0 R}$$

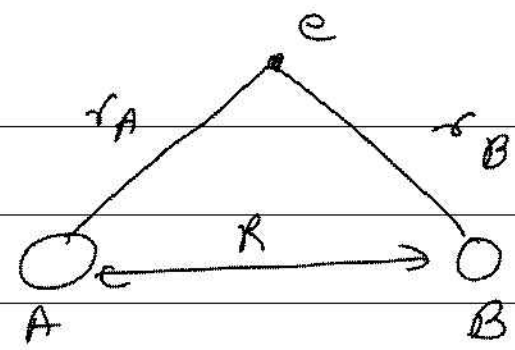
$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R}$$

$R \Rightarrow$ treated as a parameter

$\downarrow$

<u>parametric</u> dependence of electron wavefunction on nuclear coordinates

H_2^{+}



LCAO–MO approximation (treatment)

LCAO → Linear combination of atomic orbitals

MO → Molecular Orbital

$$\left.\begin{aligned}\psi_+ &= c_1\, 1s_A + c_2\, 1s_B \\ \psi_- &= c_1\, 1s_A - c_2\, 1s_B\end{aligned}\right\}\; c_1 = c_2$$

Normalisation constant

$$\psi_+ = N(1s_A + 1s_B)$$

$$\psi_- = N(1s_A - 1s_B)$$

find N

$$\int \psi_+^* \psi_+ \, d\tau = 1$$

$$N^2 \int (1s_A + 1s_B)(1s_A + 1s_B)\, d\tau = 1$$

$$N^2 \Big[\underbrace{\int 1s_A 1s_A d\tau}_{=1} + \underbrace{\int 1s_A 1s_B d\tau}_{=S} + \underbrace{\int 1s_B 1s_A d\tau}_{=S} + \underbrace{\int 1s_B 1s_B d\tau}_{=1} \Big] = 1$$

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

$S \Rightarrow$ overlap integral

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

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

$$|\psi_+|^2 = \frac{1}{2(1+S)} \left(1s_A + 1s_B \right)\left(1s_A + 1s_B \right)$$

$$= \frac{1}{2(1+S)} \left[1s_A^2 + 1s_B^2 + 2\, 1s_A 1s_B \right]$$