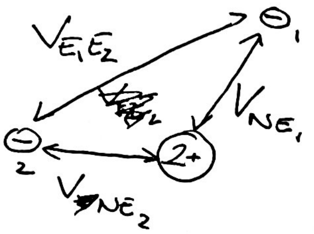
Diatomic Molecules

Ch-9

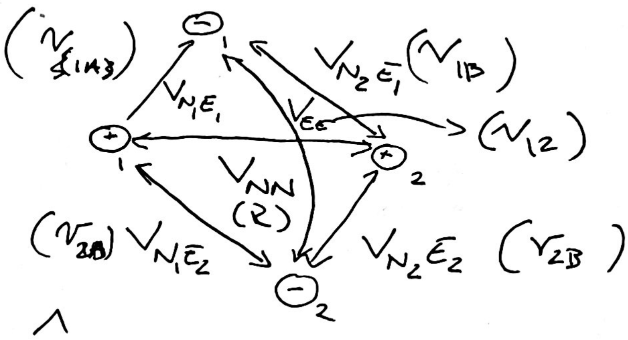
Helium Atom



$$\hat{H} = \underbrace{-\left(\frac{\nabla_1^2}{2} + \frac{\nabla_2^2}{2}\right) + \frac{1}{r_1} - \frac{1}{r_2}} + \frac{1}{r_{12}}$$

$\frac{1}{r_{12}} \to$ coupling

Hydrogen Molecule



$\hat{H} =$

Simplification: $H_2^{\oplus}$ molecule

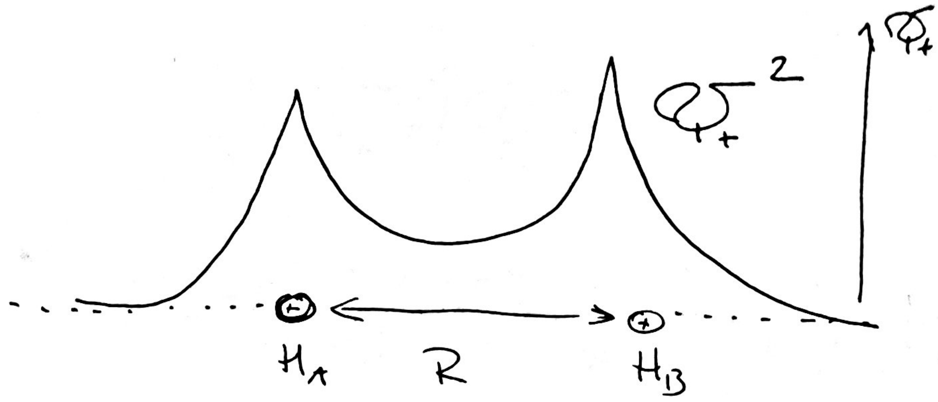
$\hat{H} =$

$$\hat{H}\Psi_j(r_A, r_B; \underbrace{R}) = \underbrace{E_j \Psi_j(r_A, r_B; R)}$$

$R \to$ parametric dependence on R.

Using known tools to solve the equation.

$$\Psi_+ = c_1 1s_A + c_2 1s_B$$
$$\Psi_- = c_1 1s_A - c_2 1s_B$$



Variational Principle

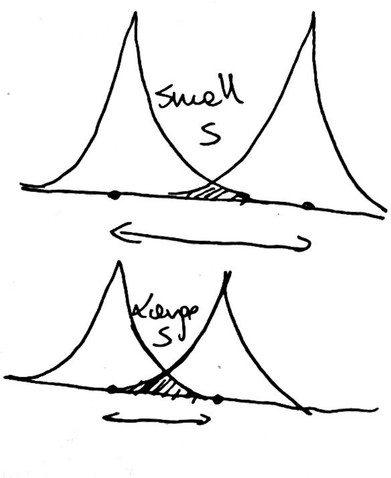
$$\hat{H}\Psi_+(\vec{r};R) = E_+\Psi_+(\vec{r};R) \quad / \ \Psi_+^* \cdot$$

$$E_+ = \frac{\int \Psi^* \hat{H} \Psi \, d\vec{r}}{\int \Psi^* \Psi \, d\vec{r}}$$

trial wavefunction is not normalized:

$$D = \int \Psi^* \Psi \, d\vec{r} = \int d\vec{r}\,(1s_A^* + 1s_B^*)(1s_A + 1s_B) =$$

$$= \int d\vec{r}\, 1s_A^* 1s_A + \int d\vec{r}\, 1s_A^* 1s_B + \int d\vec{r}\, 1s_B^* 1s_A + \int d\vec{r}\, 1s_B^* 1s_B^*$$



$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

P.S.3 look at elliptic

P.S.4 spherical coordin

$$D = \int \Psi^* \Psi \, d\vec{r} =$$

Normalized wavefunction $\Psi_+ =$

$$IN: \int d\vec{r}\, \Psi_+^* \hat{H} \Psi_- =$$

$$= \int d\vec{r} \left(1s_A^* + 1s_B^*\right)\left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right)\left(1s_A + 1s_B\right) =$$

$$= \int d\vec{r} \left(1s_A^* + 1s_B^*\right)\left(E_{1s} - \frac{1}{\underline{r_B}} + \frac{1}{R}\right) 1s_{\underline{A}}$$

$$+ \int d\vec{r} \left(1s_A^* + 1s_B^*\right)\left(E_{1s} - \frac{1}{\underline{r_A}} + \frac{1}{R}\right) 1s_{\underline{B}} \,.$$

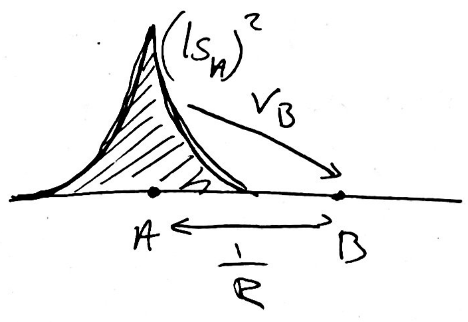
$$= 2E_{1s}(1+S) + \int d\vec{r}\, 1s_A^*\left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A + \int d\vec{r}\, 1s_B^*\left(-\frac{1}{r_A} + \frac{1}{R}\right) 1s_B$$

$$+ \int d\vec{r}\, 1s_B^*\left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A + \int d\vec{r}\, 1s_A^*\left(-\frac{1}{r_A} + \frac{1}{R}\right) 1s_B$$

Coulomb Integral

$$J = \int d\vec{r}\, 1s_A^*\left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A =$$

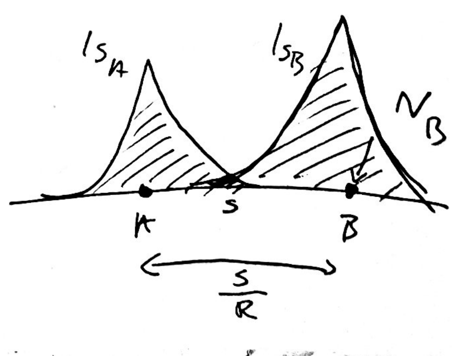
$$= -\int d\vec{r}\, \frac{1s_A^* 1s_A}{r_B} + \frac{1}{R}$$



Exchange Integral

$$K = \int d\vec{r}\, 1s_B^*\left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A =$$

$$= -\int d\vec{r}\, \frac{1s_B^* 1s_A}{r_B} + \frac{S}{R}$$



$$J = e^{-2R}\left(1+\frac{1}{R}\right) \qquad K = -e^{-R}(1+R) + \frac{S}{R}$$

$J > 0$

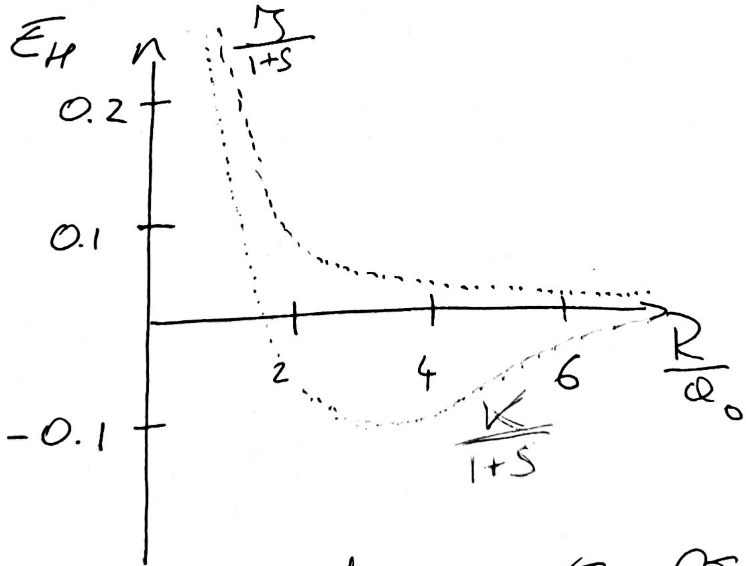
$N: \int \Psi_+^* \hat{H} \Psi \, d\vec{r} = 2E_{1s}(1+S) + 2J + 2K$

$D: \int \Psi_+^* \Psi_- \, d\vec{r} = 2 + 2S$

$$E_+ = \frac{N}{D} = E_{1s} + \frac{(J+K)}{1+S}$$

$$H + H^{\oplus} \rightarrow H_2^{\oplus}$$

$$\Delta E_+ = \underset{E_+}{E_{H_2^{\oplus}}} - \underset{E_{1s}}{E_H} - \underset{0}{E_{H^{\oplus}}} = \frac{J+K}{1+S} = \frac{J}{1+S} + \frac{K}{1+S}$$

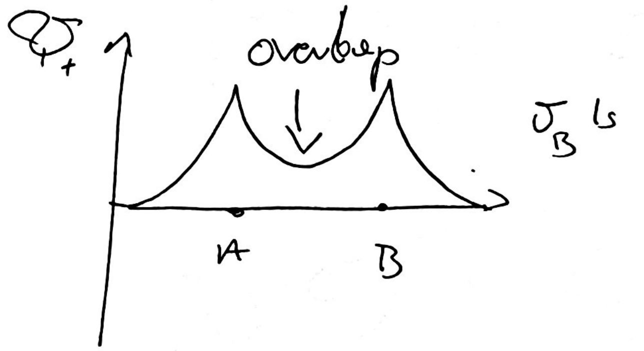


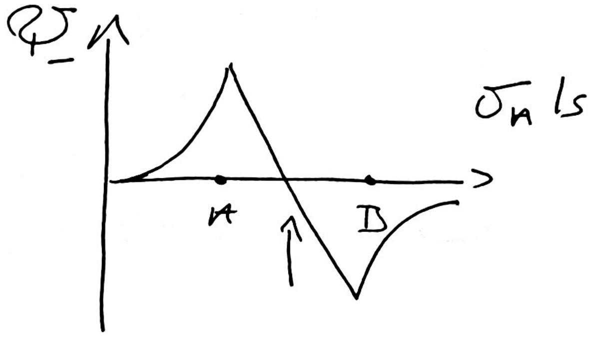
Calcs:
$E_B = 0.0648\,\text{He}$
$R = 2.5\,a_0$
Exp:
$E_B = 0.102\,\text{He}$
$R = 2.0\,a_0$

if we ~~ess~~ investigate $E_2 = \Psi_- = c_1\, 1s_A - c_2\, 1s_B$

$$E_- = \frac{J}{1+S} - \frac{K}{1+S}$$ (always positive)

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





Example ~~8~~ 8.2 / Variational Principle and Secular Determinant

$$\Psi = c_1\,1s_A + c_2\,1s_B \quad (\overset{\text{any}}{c_1, c_2})$$

$$\int \Psi^* \hat{H} \Psi\, d\vec{r} = E\int \Psi^* \Psi\, d\vec{r}$$

(Lecture 8.1 / Secular Determinant.

$$\begin{vmatrix} H_{AA} - S_{AA}E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

$$H_{AA} = \int d\vec{r}\, 1s_A^* \hat{H}\, 1s_A = \int d\vec{r}\, 1s_A^*\left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right) 1s_A = E_{1s} + J$$

$$H_{AB} = \int d\vec{r}\, 1s_A^* \hat{H}\, 1s_B = \int d\vec{r}\, 1s_A^*\left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right) 1s_B = E_{1s}S + K$$

$$\begin{vmatrix} E_{1s}+J-E & E_{1s}S+K-ES \\ E_{1s}S+K-ES & E_{1s}S+J-E \end{vmatrix} = 0$$

$$(E_{1s}+J-E)^2 - (E_{1s}S+K-ES)^2 = 0$$

$$(E_{1s}+J-E+E_{1s}S+K-ES)(E_{1s}+J-E-E_{1s}S+K+ES) = 0$$

$$(1+S)E = +E_{1s}(1+S)+J+K \qquad E(1-S) = E_{1s}(1-S)+J-K$$

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

$$\Delta E_{\pm} = \frac{J \pm K}{1 \pm S}$$

What about other orbitals?

$$\underbrace{\psi = c_1 1s_A + c_2 1s_B + c_3 2s_A + c_4 2s_B + c_5 2p_{zA} + c_6 2p_{zB}}_{}$$

6x6 Determinant → 6 roots

H_2 molecule:

(2-electron wavefunction)

$$\Psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \Psi_+\alpha(1) & \Psi_+\beta(1) \\ \Psi_+\alpha(2) & \Psi_+\beta(2) \end{vmatrix} =$$

$$= \frac{1}{\sqrt{2}} \underbrace{\Psi_+(1)\,\Psi_+(2)}\,\big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\big)$$

$$\frac{1}{2(1+S)}\big[1s_A(1) + 1s_B(1)\big]\big[1s_A(2) + 1s_B(2)\big] = \Psi_{MO}$$

(spatial part)

$\downarrow$

Linear Combination of Atomic Orbitals

~~MO~~ LCAO - MO