

Linear combination of trial wavefunction

Trial wavefunction

$$\phi = \sum_{n=1}^N c_n f_n = c_1 f_1 + c_2 f_2$$

Assume c 's and f 's are real (just to simplify things)

$$\begin{aligned} \int \phi \hat{H} \phi d\tau &= \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) d\tau \\ &= c_1^2 \int f_1 \hat{H} f_1 d\tau + c_1 c_2 \int f_1 \hat{H} f_2 d\tau + c_1 c_2 \int f_2 \hat{H} f_1 d\tau + c_2^2 \int f_2 \hat{H} f_2 d\tau \\ &= c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22} \end{aligned}$$

$$H_{ij} = \int f_i \hat{H} f_j d\tau = \int f_j \hat{H} f_i d\tau = H_{ji} \text{ (Hermitian)}$$

$$\int \phi^2 d\tau = c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22} \quad \text{where } S_{ij} = S_{ji} = \int f_i f_j d\tau$$

H_{ij} and S_{ij} are called the matrix elements.

Variational energy

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$E(c_1, c_2) \{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}\} = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

We need to minimize the energy w.r.t. c_1 and c_2

Differentiate w.r.t. c_1 and put $\frac{\partial E}{\partial c_1} = 0$

$$(2c_1 S_{11} + 2c_2 S_{12})E + \frac{\partial E}{\partial c_1} (c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = 2c_1 H_{11} + 2c_2 H_{12}$$

$$c_1 (H_{11} - ES_{11}) + c_2 (H_{12} - ES_{12}) = 0$$

Differentiate w.r.t. c_2 and put $\frac{\partial E}{\partial c_2} = 0$

$$c_1 (H_{12} - ES_{12}) + c_2 (H_{22} - ES_{22}) = 0$$

Secular equation, secular determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

The determinant must go to zero.

Born-Oppenheimer Approximation

H₂ molecule

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R}$$

Using the approximation

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R}$$

Using atomic units

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) + \frac{1}{r_{12}} + \frac{1}{R}$$

H₂⁺ Molecular Ion

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

Now there is only one electron. R is the internuclear separation that we can treat as a variable parameter. No interelectronic repulsions exist – exactly solvable problem.

Schrödinger equation

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

$\psi_j(r_A, r_B; R)$ are molecular orbitals that extend over both the nuclei

We can take an appropriate trial function – 1s orbital on atom A and 1s orbital on atom B. This is **Linear combination of Atomic Orbitals (LCAO)**

$$\psi_{\pm} = c_1 1s_A \pm c_2 1s_B$$

Both nuclei are identical => $c_1 = c_2 = c$. Use $c=1$ now. Normalize later.

The Overlap Integral

$$\hat{H}\psi_+(\mathbf{r}; R) = E_+\psi_+(\mathbf{r}; R)$$

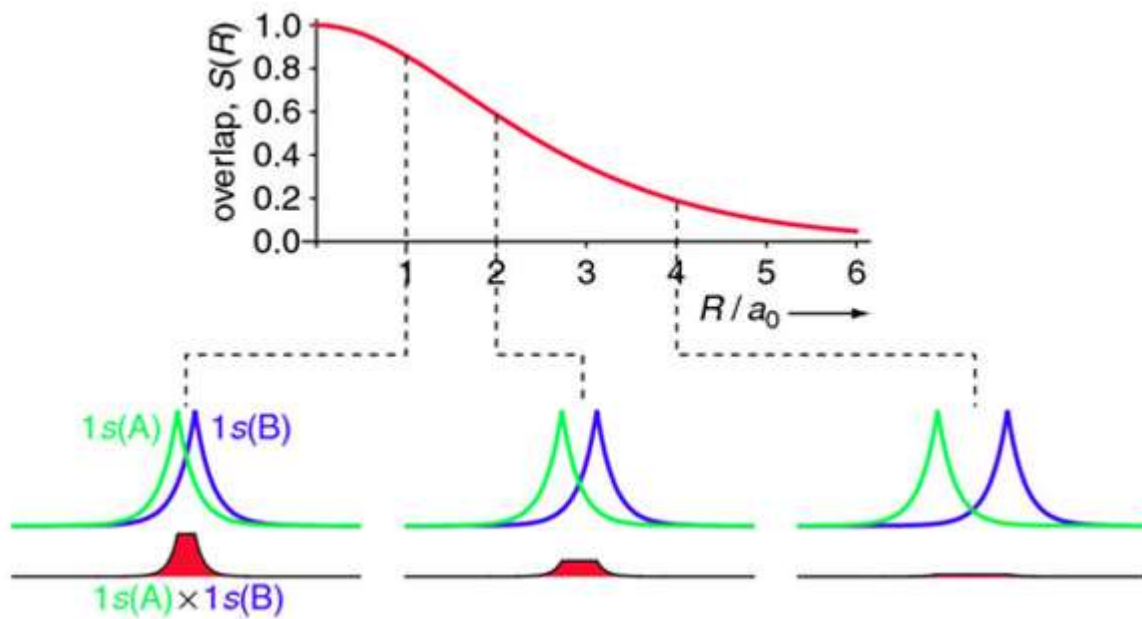
$$E_+ = \frac{\int d\mathbf{r} \psi_+^* \hat{H} \psi_+}{\int d\mathbf{r} \psi_+^* \psi_+}$$

The denominator $\int d\mathbf{r} \psi_+^* \psi_+$

$$\begin{aligned} \int d\mathbf{r} \psi_+^* \psi_+ &= \int d\mathbf{r} (1s_A^* + 1s_B^*)(1s_A + 1s_B) \\ &= \int d\mathbf{r} 1s_A^* 1s_A + \int d\mathbf{r} 1s_A^* 1s_B + \int d\mathbf{r} 1s_B^* 1s_A + \int d\mathbf{r} 1s_B^* 1s_B \end{aligned}$$

All real functions, so remove the *.

The first and the fourth terms are = 1 as these H-atom wavefunctions we took are normalized. 2nd and 3rd terms = $\int d\mathbf{r} 1s_A 1s_B = S$. This is called an **overlap integral**. S is a function of the internuclear separation, $S(R)$



Evaluate the integral $\int d\mathbf{r} 1s_A 1s_B$ to get

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

Denominator is then,

$$\int d\mathbf{r} (1s_A^* + 1s_B^*)(1s_A + 1s_B) = 2 + 2S(R)$$

This also gives the normalization constant for ψ_+ as $c = \frac{1}{\sqrt{2(1+S)}}$ and for ψ_- as $c = \frac{1}{\sqrt{2(1-S)}}$

The Numerator

$$\begin{aligned} \int d\mathbf{r} \psi_+^* \hat{H} \psi_+ &= \int d\mathbf{r} (1s_A^* + 1s_B^*) \hat{H} (1s_A + 1s_B) \\ &= \int d\mathbf{r} (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) (1s_A + 1s_B) \\ &= \int d\mathbf{r} (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A \\ &\quad + \int d\mathbf{r} (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B \end{aligned}$$

Solutions to the one-electron atomic S.E.

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A}\right)1s_A = E_{1s}1s_A \quad \text{and} \quad \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_B}\right)1s_B = E_{1s}1s_B \quad \text{where} \quad E_{1s} = -\frac{1}{2}E_H$$

Now we write the numerator as

$$\begin{aligned} \int d\mathbf{r} \psi_+^* \hat{H} \psi_+ &= \int d\mathbf{r} (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R}\right) 1s_A + \int d\mathbf{r} (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_A} + \frac{1}{R}\right) 1s_B \\ \int d\mathbf{r} \psi_+^* \hat{H} \psi_+ &= 2E_{1s}(1+S) + \int d\mathbf{r} 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A + \int d\mathbf{r} 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A \\ &\quad + \int d\mathbf{r} 1s_A^* \left(-\frac{1}{r_A} + \frac{1}{R}\right) 1s_B + \int d\mathbf{r} 1s_B^* \left(-\frac{1}{r_A} + \frac{1}{R}\right) 1s_B \end{aligned}$$

Coulomb integral, J : Charge density of the electron around nucleus A interacting with nucleus B + the internuclear repulsion. This is all Coulombic interaction! Remember R remains constant.

$$J = \int d\mathbf{r} 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A = \int \frac{d\mathbf{r} 1s_A^* 1s_A}{r_B} + \frac{1}{R} = e^{-2R} \left(1 + \frac{1}{R}\right) \text{ analytically}$$

Exchange integral, K : Quantum mechanical concept. Sharing of electrons.

$$K = \int d\mathbf{r} 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A = \int \frac{d\mathbf{r} 1s_B^* 1s_A}{r_B} + \frac{S}{R} = \frac{S}{R} - e^{-R}(1+R) \text{ analytically}$$

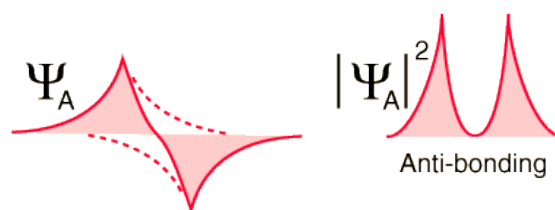
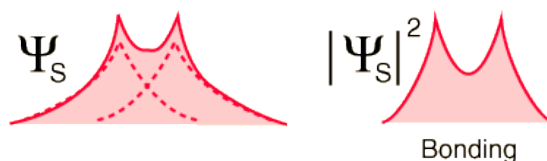
Finally, the numerator is

$$\int d\mathbf{r} \psi_+^* \hat{H} \psi_+ = 2E_{1s}(1+S) + 2J + 2K$$

$$\text{So, } E_+ = \frac{\int d\mathbf{r} \psi_+^* \hat{H} \psi_+}{\int d\mathbf{r} \psi_+^* \psi_+} = E_{1s} + \frac{J+K}{1+S}$$

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

$$\begin{aligned} \psi_- = c_1 1s_A - c_2 1s_B; \quad \Delta E_- = E_- - E_{1s} &= \frac{J-K}{1-S} \\ &= \frac{J}{1-S} - \frac{K}{1-S} \end{aligned}$$



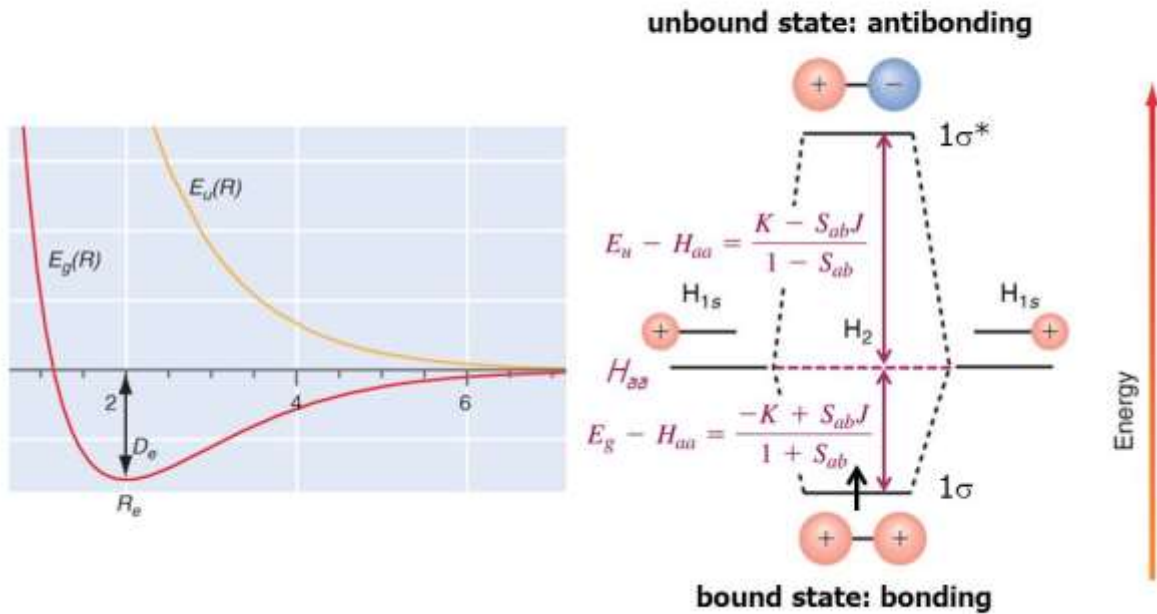
$$\psi_b = \psi_+ = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)$$

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

Theoretical: $E_{\text{binding}}(R = R_e) = 0.0648 E_h = 170 \text{ kJ. mol}^{-1}$, $R_e = 2.50 a_0 = 132 \text{ pm}$

Experimental: $E_{\text{binding}}(R = R_e) = 0.102 E_h = 268 \text{ kJ. mol}^{-1}$, $R_e = 2.00 a_0 = 106 \text{ pm}$

Molecular energy diagram for H₂⁺



Variational method for H₂⁺ molecular ion

$$\psi = c_1 1s_A + c_2 1s_B$$

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

Where,

$$H_{AA} = H_{BB} = \int dr 1s_A \hat{H} 1s_A = \int dr 1s_B \hat{H} 1s_B = E_{1s} + J$$

$$H_{AB} = \int dr 1s_A \hat{H} 1s_B = \int dr 1s_B \hat{H} 1s_A = E_{1s}S + K$$

$$S_{AA} = S_{BB} = \int dr 1s_A 1s_A = \int dr 1s_B 1s_B = 1$$

$$S_{AB} = \int dr 1s_A 1s_B = S$$

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

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

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

$$\psi_+ = c(1s_A + 1s_B); \quad \psi_- = c(1s_A - 1s_B)$$

We can include many more orbitals in our description

e.g.

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

This will give 6 energies and 6 MOs.

H₂ Molecular-Orbitals

$$\psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_b \alpha(1) & \psi_b \beta(1) \\ \psi_b \alpha(2) & \psi_b \beta(2) \end{vmatrix} = \psi_b(1)\psi_b(2) \left\{ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \right\}$$

Now put in two electrons into the bonding MO (ignoring spin)

$$\psi_{MO}(1,2) = \psi_b(1)\psi_b(2) = \frac{1}{2(1+S)} [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]$$

ψ_{MO} is a product of MOs which are LCAOs.

$$E_{MO} = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{MO}^*(1,2) \hat{H} \psi_{MO}(1,2)$$

Theoretical: $E_{binding}(R = R_e) = 0.0990 E_h = 260 \text{ kJ. mol}^{-1}$, $R_e = 1.61 a_0 = 85 \text{ pm}$

Experimental: $E_{binding}(R = R_e) = 0.174 E_h = 457 \text{ kJ. mol}^{-1}$, $R_e = 1.40 a_0 = 74.1 \text{ pm}$

Q. Why is He₂ unstable?