A DEEPER LOOK 4 The energy of the bonding molecular orbital of H_2^+

The goal is to calculate the energy of the σ orbital of the hydrogen molecule-ion, written as the linear combination $\psi_+ = N_+(\psi_A + \psi_B)$. In general, the energy is the expectation value of the hamiltonian operator. Therefore, the energy E_+ of ψ_+ is

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

with the hamiltonian given by eqn 9B.1 and $N_+ = 1/\{2(1+S)\}^{1/2}$. Begin by writing a general expression for E_+, and then refine it by recognizing that ψ_A and ψ_B are H1s atomic orbitals.

Step 1 *Write a general expression for the expectation value*

Begin by using eqn 9B.1 to write

$$\hat{H}\psi_+ = \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - j_0\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R} \right) \right\}\psi_+$$

$$= \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} - \frac{j_0}{r_{B1}} \right\}\psi_+ + \frac{j_0}{R}\psi_+$$

where $j_0 = e^2/4\pi\varepsilon_0$. Because the wavefunction is real, the expectation value of the hamiltonian is

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

$$= \overbrace{\int \psi_+ \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} - \frac{j_0}{r_{B1}} \right\}\psi_+ \, d\tau}^{\text{Evaluated in step 2}} + \overbrace{\int \psi_+ \left(\frac{j_0}{R} \right)\psi_+ \, d\tau}^{\text{Evaluated in step 3}}$$

Step 2 *Evaluate the first term*

With $\psi_+ = N_+(\psi_A + \psi_B)$, and after some algebra, the first term in the expression from Step 1 expands to

$$\int \psi_+ \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} - \frac{j_0}{r_{B1}} \right\}\psi_+ \, d\tau$$

$$= N_+^2 \int (\psi_A + \psi_B)\left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} - \frac{j_0}{r_{B1}} \right\}(\psi_A + \psi_B)\, d\tau$$

$$= N_+^2 \left\{ \overbrace{\int \psi_A \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} \right\}\psi_A \, d\tau}^{E_{1s}} - \overbrace{j_0 \int \frac{\psi_A^2}{r_{B1}}\, d\tau}^{j} \right.$$

$$\left. + \overbrace{\int \psi_A \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{B1}} \right\}\psi_B \, d\tau}^{E_{1s}S} - \overbrace{j_0 \int \frac{\psi_A \psi_B}{r_{A1}}\, d\tau}^{k} \right.$$

$$\left. + \overbrace{\int \psi_B \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} \right\}\psi_A \, d\tau}^{E_{1s}S} - \overbrace{j_0 \int \frac{\psi_B \psi_A}{r_{B1}}\, d\tau}^{k} \right.$$

$$\left. + \overbrace{\int \psi_B \left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{B1}} \right\}\psi_B \, d\tau}^{E_{1s}} - \overbrace{j_0 \int \frac{\psi_B^2}{r_{A1}}\, d\tau}^{j} \right\}$$

To see how the integrals give rise to the quantities in red, consider the following:

- The terms $-(\hbar^2/2m_e)\nabla_1^2 - j_0/r_{A1}$ and $-(\hbar^2/2m_e)\nabla_1^2 - j_0/r_{B1}$ have the form of the hamiltonian of a hydrogen atom (Topic 8A). Because in this case ψ_A and ψ_B are H1s orbitals centred on A and B, respectively, it follows that

$$\int \psi_A \overbrace{\left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} \right\}\psi_A}^{E_{1s}\psi_A} \, d\tau = E_{1s}\overbrace{\int \psi_A^2 d\tau}^{1} = E_{1s}$$

$$\int \psi_B \overbrace{\left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{B1}} \right\}\psi_B}^{E_{1s}\psi_B} \, d\tau = E_{1s}\overbrace{\int \psi_B^2 d\tau}^{1} = E_{1s}$$

$$\int \psi_A \overbrace{\left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{B1}} \right\}\psi_B}^{E_{1s}\psi_B} \, d\tau = E_{1s}\overbrace{\int \psi_A \psi_B d\tau}^{S}$$

$$\int \psi_B \overbrace{\left\{ -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{j_0}{r_{A1}} \right\}\psi_A}^{E_{1s}\psi_A} \, d\tau = E_{1s}\overbrace{\int \psi_B \psi_A d\tau}^{S}$$

where E_{1s} is the energy of the H1s orbital, and S is the overlap integral.

- Because the atoms are identical

$$j_0 \int \frac{\psi_A^2}{r_{B1}}\, d\tau = j_0 \int \frac{\psi_B^2}{r_{A1}}\, d\tau = j \quad \text{and}$$

$$j_0 \int \frac{\psi_A \psi_B}{r_{A1}}\, d\tau = j_0 \int \frac{\psi_B \psi_A}{r_{B1}}\, d\tau = k$$

Therefore, in terms of the parameters E_{1s}, S, j, and k, the first term simplifies to

$$\int \psi_+ \left\{ -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{j_0}{r_{A1}} - \frac{j_0}{r_{B1}} \right\} \psi_+ d\tau = 2N_+^2 \{ E_{1s}(1+S) - (j+k) \}$$

Step 3 *Evaluate the second term*

The second term in the expression from Step 1 is the contribution to the energy from the repulsion between nuclei. Because j_0/R is a constant and the wavefunction is normalized, that term simplifies to

$$\int \psi_+ \left(\frac{j_0}{R} \right) \psi_+ d\tau = \frac{j_0}{R} \overbrace{\int \psi_+^2 d\tau}^{1} = \frac{j_0}{R}$$

Step 4 *Combine the expressions from Steps 2 and 3*

Because H1s orbitals were used to arrive at the result in Step 2, write $E_+ = E_\sigma$, the energy of the σ molecular orbital and

$$E_\sigma = \overbrace{2N_+^2 \{ E_{1s}(1+S) - (j+k) \}}^{\text{From Step 2}} + \overbrace{\frac{j_0}{R}}^{\text{From Step 3}}$$

With $N_+ = 1/\{2(1+S)\}^{1/2}$, it follows that

$$E_\sigma = \overbrace{\frac{1}{(1+S)}}^{2N_+^2} \{ E_{1s}(1+S) - (j+k) \} + \frac{j_0}{R} = E_{1s} - \frac{j+k}{1+S} + \frac{j_0}{R}$$

as in eqn 9B.4.