

Chapter 8 Diatomic Molecules Homework Solutions

1. Please see the PowerPoint slides and class notes for answers to these qualitative questions.
2. HeH Hamiltonian: Three electrons (1, 2 and 3)

$$H = \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{2} \nabla_3^2 \right) + \left(-\frac{1}{r_{1H}} - \frac{2}{r_{1He}} - \frac{1}{r_{2H}} - \frac{2}{r_{2He}} - \frac{1}{r_{3H}} - \frac{2}{r_{3He}} \right) + \frac{1 \cdot 2}{R} + \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

3. The Antibonding Energy is: $\langle E_- \rangle = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$

One of the two linear Secular equations is: $(H_{aa} - \langle E \rangle)c_a + (H_{ab} - \langle E \rangle S_{ab})c_b = 0$

Let's plug the energy into the equation to determine a relation between c_a and c_b

$$\left(H_{aa} - \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \right) c_a + \left(H_{ab} - \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \cdot S_{ab} \right) c_b = 0$$

Multiply through by $1 - S_{ab}$

$$(H_{aa}(1 - S_{ab}) - (H_{aa} - H_{ab}))c_a + (H_{ab}(1 - S_{ab}) - (H_{aa} - H_{ab}) \cdot S_{ab})c_b = 0$$

Simplify terms

$$(-H_{aa}S_{ab} + H_{ab})c_a + (H_{ab} - H_{aa}S_{ab})c_b = 0$$

Divide through by $H_{ab} - H_{aa}S_{ab}$

$$\left(\frac{-H_{aa}S_{ab} + H_{ab}}{H_{ab} - H_{aa}S_{ab}} \right) c_a + c_b = 0$$

Therefore: $c_a + c_b = 0 \rightarrow c_b = -c_a$ and

$$\psi_- = c_a 1s_a + c_b 1s_b = c_a 1s_a - c_a 1s_b = c_a (1s_a - 1s_b) = N_- (1s_a - 1s_b)$$

$N_- = c_a$ is the normalization constant

Wavefunction Normalization

$$\begin{aligned}
 1 &= \langle \psi_- | \psi_- \rangle = \langle N_- (1s_a - 1s_b) | N_- (1s_a - 1s_b) \rangle \\
 &= N_-^2 [\langle 1s_a | 1s_a \rangle - \langle 1s_a | 1s_b \rangle - \langle 1s_b | 1s_a \rangle + \langle 1s_b | 1s_b \rangle] \\
 &= N_-^2 [1 - S_{ab} - S_{ab} + 1] = N_-^2 [2 - 2S_{ab}]
 \end{aligned}$$

$$\text{Therefore: } N_- = \frac{1}{\sqrt{2 - 2S_{ab}}} \text{ and } \psi = \frac{1}{\sqrt{2 - 2S_{ab}}} (1s_a - 1s_b)$$

4. $H_{aa} = -20 \text{ eV}$, $H_{bb} = -12 \text{ eV}$, $H_{ab} = -3 \text{ eV}$, $S_{ab} = 0$

(a) (i) The upper bound for the bonding orbital energy is $E_B \leq -20 \text{ eV}$. This is because the bonding MO must be lower in energy than the lower energy atomic orbital.

(ii) Because $H_{aa} < H_{bb}$, the **bonding** orbital would have a higher electron density around nucleus "a", and the **anti-bonding** orbital would have a higher electron density around nucleus "b". Hence $c_b > c_a$ in the **anti-bonding** orbital.

(b) The Secular Determinant is:

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0 \rightarrow \begin{vmatrix} -20 - \langle E \rangle & -3 \\ -3 & -12 - \langle E \rangle \end{vmatrix} = 0$$

Expanding the Secular Determinant, we get:

$$(-20 - \langle E \rangle)(-12 - \langle E \rangle) - (-3)(-3) = 0 \rightarrow \langle E \rangle^2 + 32\langle E \rangle + 231 = 0$$

$$\begin{aligned}
 \text{Therefore: } \langle E \rangle &= \frac{-32 \pm \sqrt{(32)^2 - 4(1)(231)}}{2} \\
 \langle E \rangle_B &= -21 \text{ eV and } \langle E \rangle_A = -11 \text{ eV}
 \end{aligned}$$

(c) (i) **Bonding Wavefunction**

$$(H_{aa} - \langle E \rangle_B)c_a + (H_{ab} - \langle E \rangle_B S_{ab})c_b = 0 \rightarrow (-20 - (-21))c_a + (-3 - 0)c_b = 0$$

$$\text{Therefore: } c_a - 3c_b = 0 \rightarrow c_b = +0.333 \cdot c_a \text{ and } \psi_B = N_B (1s_a + 0.333 \cdot 1s_b)$$

Normalization

$$\begin{aligned} 1 &= \langle \psi_B | \psi_B \rangle = \langle N_B (1s_a + 0.333 \cdot 1s_b) | N_B (1s_a + 0.333 \cdot 1s_b) \rangle \\ &= N_B^2 [\langle 1s_a | 1s_a \rangle + 0.333 \langle 1s_a | 1s_b \rangle + 0.333 \langle 1s_b | 1s_a \rangle + 0.111 \langle 1s_b | 1s_b \rangle] \\ &= N_B^2 [1 + 0.111] = 1.111 \cdot N_B^2 \rightarrow N_B = \frac{1}{\sqrt{1.111}} = 0.949 \end{aligned}$$

$$\psi_B = 0.949(1s_a + 0.333 \cdot 1s_b) = 0.949 \cdot 1s_a + 0.316 \cdot 1s_b$$

(ii) Antibonding Wavefunction

$$(H_{aa} - \langle E \rangle_A) c_a + (H_{ab} - \langle E \rangle_A S_{ab}) c_b = 0 \rightarrow (-20 - (-11)) c_a + (-3 - 0) c_b = 0$$

$$\text{Therefore: } -9c_a - 3c_b = 0 \rightarrow c_b = -3.00 \cdot c_a \text{ and } \psi_A = N_A(1s_a - 3.00 \cdot 1s_b)$$

Normalization

$$\begin{aligned} 1 &= \langle \psi_A | \psi_A \rangle = \langle N_A (1s_a - 3.00 \cdot 1s_b) | N_A (1s_a - 3.00 \cdot 1s_b) \rangle \\ &= N_A^2 [\langle 1s_a | 1s_a \rangle - 3.00 \langle 1s_a | 1s_b \rangle - 3.00 \langle 1s_b | 1s_a \rangle + 9.00 \langle 1s_b | 1s_b \rangle] \\ &= N_A^2 [1 + 9.00] = 10 \cdot N_A^2 \rightarrow N_A = \frac{1}{\sqrt{10}} = 0.316 \end{aligned}$$

$$\psi_A = 0.316(1s_a - 3.00 \cdot 1s_b) = 0.316 \cdot 1s_a - 0.948 \cdot 1s_b$$

(d) Fraction of electron density on atom a in ψ_B .

$$\psi_B = c_a 1s_a + c_b 1s_b = 0.949 \cdot 1s_a + 0.316 \cdot 1s_b$$

$$f_a = \frac{c_a^2}{c_a^2 + c_b^2} = \frac{(0.949)^2}{1} = 0.90 \quad \text{and} \quad f_b = \frac{c_b^2}{c_a^2 + c_b^2} = \frac{(0.316)^2}{1} = 0.10$$

Although not requested, let's perform the same calculation for ψ_A .

$$\psi_A = c_a \cdot 1s_a + c_b \cdot 1s_b = 0.316 \cdot 1s_a + 0.948 \cdot 1s_b$$

$$f_a = \frac{c_a^2}{c_a^2 + c_b^2} = \frac{(0.316)^2}{1} = 0.10 \quad \text{and} \quad f_b = \frac{c_b^2}{c_a^2 + c_b^2} = \frac{(0.948)^2}{1} = 0.90$$

5. CO: $6 + 8 = 14$ electrons

(a) CO Electron Configuration: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^2$

(b) CO^{2-} 16 electrons: e- config: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^2(\pi^* 2p)^2$
 CO^{2-} is a Triplet because there are two unpaired electrons

(c) Shortest bond length: Let's first determine bond orders

$$\text{CO: BO} = (1/2)[10-4] = 3$$

$$\text{CO}^+: \text{BO} = (1/2)[9-4] = 2.5$$

$$\text{CO}^{2+}: \text{BO} = (1/2)[10-5] = 2$$

The neutral molecule, CO, has the highest bond order, and therefore the shortest bond length

(d) Lowest vibrational frequency: Let's first determine bond orders

$$\text{CO: BO} = (1/2)[10-4] = 3$$

$$\text{CO}^-: \text{BO} = (1/2)[10-5] = 2.5$$

$$\text{CO}^{2-}: \text{BO} = (1/2)[10-6] = 2.0$$

The doubly charged anion, CO^{2-} , has the lowest bond order, and therefore the lowest vibrational frequency

6. N_2 : 14 electrons

(a) Let's do ground state configuration first:

$$\text{GS: } (\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$$

$$\text{BO} = (1/2)[10-4] = 3$$

$$\text{Lowest Excited State: } (\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^1(\pi_g^* 2p)^1$$

(b) The excited state bond order is: $\text{BO} = (1/2)[9-5] = 2$

(c) The N-N bond length will be longer in the excited state because the bond order is lower

7. H₂ Excited State: $(\sigma_g 1s)^1(\sigma_u^* 1s)^1$

$$\psi_I = N\psi_{Spat}\psi_{Spin} = N[\sigma_g 1s(1)\sigma_u^* 1s(2) + \sigma_u^* 1s(1)\sigma_g 1s(2)][\alpha_1\beta_2 - \beta_1\alpha_2]$$

Valid **antisymmetric** wavefunction

$$\psi_{II} = N\psi_{Spat}\psi_{Spin} = N[\sigma_g 1s(1)\sigma_u^* 1s(2)][\alpha_1\beta_2 - \beta_1\alpha_2]$$

Not valid because the spatial portion of the wavefunction is neither symmetric nor antisymmetric with respect to electron exchange.

$$\psi_{III} = N\psi_{Spat}\psi_{Spin} = N[\sigma_g 1s(1)\sigma_u^* 1s(2) - \sigma_u^* 1s(1)\sigma_g 1s(2)][\alpha_1\beta_2 - \beta_1\alpha_2]$$

Not valid because the total wavefunction is **symmetric** with respect to electron exchange

$$\psi_{IV} = N\psi_{Spat}\psi_{Spin} = N[\sigma_g 1s(1)\sigma_u^* 1s(2) - \sigma_u^* 1s(1)\sigma_g 1s(2)]\beta_1\beta_2$$

Valid **antisymmetric** wavefunction

8. $g_0 = 2$, $g_1 = 2$, $\tilde{\nu}_{e1} = 174 \text{ cm}^{-1}$, $T = 200^\circ\text{C} = 473 \text{ K}$

$$\Theta_{e1} = \frac{hc\tilde{\nu}_{e1}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(174 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 250.8 \text{ K} \approx 251 \text{ K}$$

Partition Function and Derivative

$$q^{elect} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} = 2 + 2e^{-\frac{251 \text{ K}}{473 \text{ K}}} = 2 + 1.18 = 3.18$$

$$\begin{aligned} \left(\frac{\partial \ln q^{elect}}{\partial T} \right)_{V,N} &= \frac{1}{q^{elect}} \frac{d \ln q^{elect}}{dT} = \frac{1}{g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}}} \frac{d}{dT} \left(g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} \right) \\ &= \frac{1}{g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}}} \left[g_1 e^{-\frac{\Theta_{e1}}{T}} \left(\frac{\Theta_{e1}}{T^2} \right) \right] = \frac{\Theta_{e1}}{T^2} \frac{g_1 e^{-\frac{\Theta_{e1}}{T}}}{g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}}} \end{aligned}$$

Internal Energy and Enthalpy

$$\begin{aligned}
 U^{elect} &= kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N} = kT^2 \left(\frac{\partial \ln (q^{elect})^N}{\partial T} \right)_{V,N} = NkT^2 \left(\frac{\partial \ln q^{elect}}{\partial T} \right)_{V,N} \\
 &= nN_a kT^2 \left(\frac{\partial \ln q^{elect}}{\partial T} \right)_{V,N} = nRT^2 \left(\frac{\partial \ln q^{elect}}{\partial T} \right)_{V,N} = nRT^2 \frac{\Theta_{e1}}{T^2} \frac{g_1 e^{-\frac{\Theta_{e1}}{T}}}{g_o + g_1 e^{-\frac{\Theta_{e1}}{T}}} \\
 &= nR\Theta_{e1} g_1 \frac{g_1 e^{-\frac{\Theta_{e1}}{T}}}{g_o + g_1 e^{-\frac{\Theta_{e1}}{T}}} \\
 U^{elect} &= nR\Theta_{e1} g_1 \frac{g_1 e^{-\frac{\Theta_{e1}}{T}}}{g_o + g_1 e^{-\frac{\Theta_{e1}}{T}}} = (2 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K})(251 \text{ K})(2) \frac{2e^{-\frac{251 \text{ K}}{473 \text{ K}}}}{2 + 2e^{-\frac{251 \text{ K}}{473 \text{ K}}}} \\
 &= 3090 \text{ J} = 3.09 \text{ kJ}
 \end{aligned}$$

$$H^{elect} = kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N} + kT \left(\frac{\partial \ln Q^{elect}}{\partial \ln V} \right)_{T,N} = kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N} = U^{elect} = 3.09 \text{ kJ}$$

The second term is 0 because Q^{elect} is independent of volume

Entropy

$$\begin{aligned}
 S^{elect} &= k \ln Q^{elect} + \frac{U^{elect}}{T} = k \ln (q^{elect})^N + \frac{U^{elect}}{T} = Nk \ln q^{elect} + \frac{U^{elect}}{T} \\
 &= nR \ln q^{elect} + \frac{U^{elect}}{T}
 \end{aligned}$$

Let's use the values of q^{elect} and U^{elect} from the earlier steps:

$$S^{elect} = (2 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K}) \ln(3.18) + \frac{3090 \text{ J}}{473 \text{ K}} = 19.23 \text{ J} / \text{K} + 6.53 \text{ J} / \text{K} \approx 25.8 \text{ J} / \text{K}$$

Gibbs Energy

$$\begin{aligned}
 G^{elect} &= -kT \ln Q^{elect} + kT \left(\frac{\partial \ln Q^{elect}}{\partial \ln V} \right)_{T,N} = -kT \ln \left(q^{elect} \right)^N + 0 = -nRT \ln q^{elect} \\
 &= -2 \text{ mol} (8.31 \text{ J} / \text{ mol} \cdot \text{ K}) (473 \text{ K}) \ln(3.18) = -9095 \text{ J} = -9.1 \text{ kJ}
 \end{aligned}$$