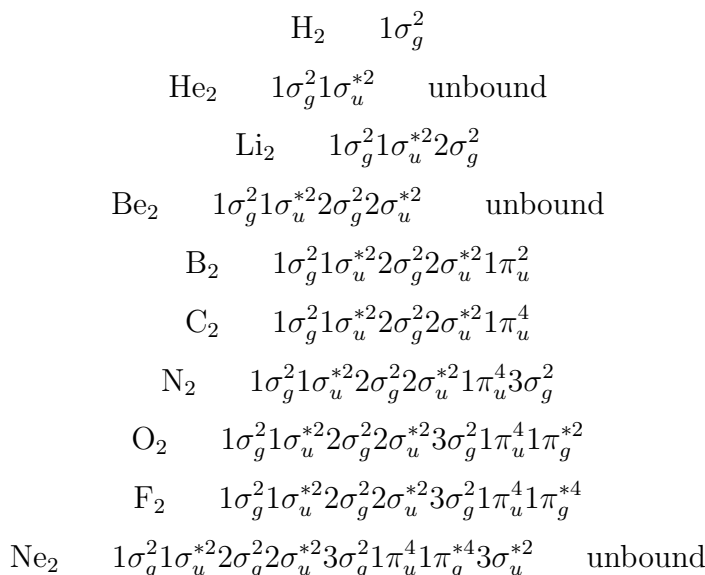


Chemistry 432
Problem Set 9
Spring 2020
Solutions

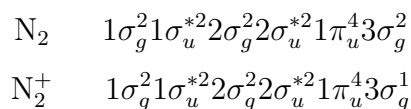
1. Give the electronic structures for all homonuclear diatomic molecules from H_2 to Ne_2 using molecular orbital theory. Which are predicted to be unbound?

Answer:

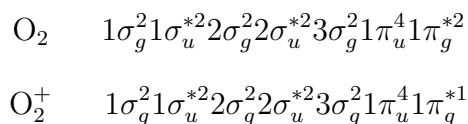


2. On the basis of molecular orbital theory, explain the following: The binding energy of N_2^+ is 6.35 eV and the binding energy of N_2 is 7.38 eV, whereas the binding energy of O_2^+ is 6.48 eV and the binding energy of O_2 is 5.08 eV.

Answer:



N_2^+ has 1 less bonding electron than N_2 , and N_2 is more strongly bound than N_2^+ .



O_2^+ has 1 less anti-bonding electron than O_2 , and O_2^+ is more strongly bound than O_2 .

3. Give the Born-Oppenheimer Hamiltonian operator for the Be₂ molecule. Use molecular orbital theory to compare the binding strengths of Be₂⁺, Be₂ and Be₂⁻ assuming the ordering of the molecular orbitals is the same for the ions as the ordering known to be correct for the neutral molecule.

Answer:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^8 \nabla_i^2 - \sum_{i=1}^8 \left(\frac{4e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_a|} + \frac{4e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_b|} \right) + \sum_{i < j}^8 \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \frac{16e^2}{4\pi\epsilon_0 |\vec{R}_a - \vec{R}_b|}$$

Be

$$\begin{array}{ll} \uparrow\downarrow & 2\sigma_u^* \\ \uparrow\downarrow & 2\sigma_g \\ \uparrow\downarrow & 1\sigma_u^* \\ \uparrow\downarrow & 1\sigma_g \end{array}$$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(4 - 4) = 0$$

Unbound

Be⁻

$$\begin{array}{ll} \uparrow & 1\pi_u \\ \uparrow\downarrow & 2\sigma_u^* \\ \uparrow\downarrow & 2\sigma_g \\ \uparrow\downarrow & 1\sigma_u^* \\ \uparrow\downarrow & 1\sigma_g \end{array}$$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(5 - 4) = \frac{1}{2}$$

Bound

Be⁺

$$\begin{array}{ll} \uparrow & 2\sigma_u^* \\ \uparrow\downarrow & 2\sigma_g \\ \uparrow\downarrow & 1\sigma_u^* \\ \uparrow\downarrow & 1\sigma_g \end{array}$$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(4 - 3) = \frac{1}{2}$$

Bound

4. Give the Born-Oppenheimer Hamiltonian operator for the C₂ molecule. Then use molecular orbital theory to determine the bond orders and relative binding strengths for the molecules C₂⁺, C₂ and C₂⁻.

Answer

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{12} \nabla_i^2 - \sum_{i=1}^{12} \frac{6e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{|\vec{r}_i - \vec{R}_b|} \right) + \frac{36e^2}{4\pi\epsilon_0 |\vec{R}_a - \vec{R}_b|} + \sum_{i < j}^{12} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

$$C_2^+ : \quad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^3$$

$$BO = \frac{1}{2}(7 - 4) = \frac{3}{2}$$

$$C_2 : \quad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4$$

$$BO = \frac{1}{2}(8 - 4) = 2$$

$$C_2^- : \quad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^1$$

$$BO = \frac{1}{2}(9 - 4) = \frac{5}{2}$$

$$BE_{C_2^-} > BE_{C_2} > BE_{C_2^+}$$

5. Give the Born-Oppenheimer Hamiltonian operator for the F_2 molecule. Use molecular orbital theory to compare the binding strengths of F_2^+ , F_2 and F_2^- assuming the ordering of the molecular orbitals is the same for the ions as the ordering known to be correct for the neutral molecule.

Answer:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{18} \nabla_i^2 - \sum_{i=1}^{18} \frac{9e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{|\vec{r}_i - \vec{R}_b|} \right) + \frac{81e^2}{4\pi\epsilon_0 |\vec{R}_a - \vec{R}_b|} + \frac{1}{2} \sum_{i \neq j}^{18} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

F_2

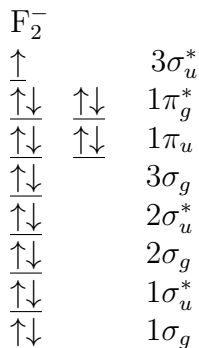
$$\begin{array}{ll} \uparrow\downarrow & \uparrow\downarrow & 1\pi_g^* \\ \uparrow\downarrow & \uparrow\downarrow & 1\pi_u \\ \uparrow\downarrow & & 3\sigma_g \\ \uparrow\downarrow & & 2\sigma_u^* \\ \uparrow\downarrow & & 2\sigma_g \\ \uparrow\downarrow & & 1\sigma_u^* \\ \uparrow\downarrow & & 1\sigma_g \end{array}$$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 8) = 1$$

F_2^+

$$\begin{array}{ll} \uparrow\downarrow & \uparrow & 1\pi_g^* \\ \uparrow\downarrow & \uparrow\downarrow & 1\pi_u \\ \uparrow\downarrow & & 3\sigma_g \\ \uparrow\downarrow & & 2\sigma_u^* \\ \uparrow\downarrow & & 2\sigma_g \\ \uparrow\downarrow & & 1\sigma_u^* \\ \uparrow\downarrow & & 1\sigma_g \end{array}$$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 7) = 3/2$$



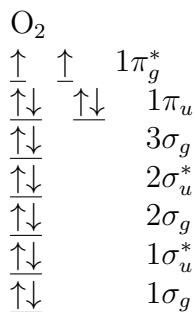
$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 9) = 1/2$$

Binding energy order is $\text{F}_2^+ > \text{F}_2 > \text{F}_2^-$

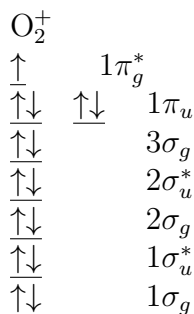
6. Give the Born-Oppenheimer Hamiltonian operator for the O_2 molecule. Then use molecular orbital theory to determine the bond orders and relative binding strengths for the molecules O_2^+ , O_2 and O_2^- .

Answer:

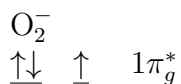
$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{16} \nabla_i^2 - \sum_{i=1}^{16} \frac{8e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{|\vec{r}_i - \vec{R}_b|} \right) + \frac{64e^2}{4\pi\epsilon_0 |\vec{R}_a - \vec{R}_b|} + \frac{1}{2} \sum_{i \neq j}^{16} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

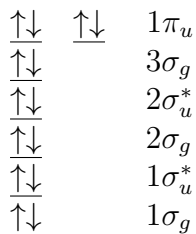


$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 6) = 2$$



$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 5) = 5/2$$





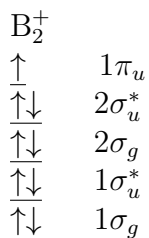
$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 7) = 3/2$$

Binding energy order is $O_2^+ > O_2 > O_2^-$

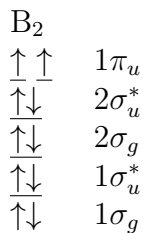
7. Give the Born-Oppenheimer Hamiltonian operator for the B_2^+ ion. Assuming the ordering of orbitals to be the same for neutral molecules as the ordering for ions, use molecular-orbital theory to compare the relative stabilities of B_2^+ , B_2 and B_2^- .

Answer:

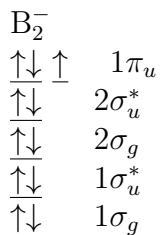
$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^9 \nabla_i^2 - \sum_{i=1}^9 \left(\frac{5e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_a|} + \frac{5e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_b|} \right) + \sum_{i < j}^9 \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \frac{25e^2}{4\pi\epsilon_0 |\vec{R}_a - \vec{R}_b|}$$



$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(5 - 4) = \frac{1}{2}$$



$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(6 - 4) = 1$$



$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(7 - 4) = \frac{3}{2}$$

Relative stability

$$B_2^+ < B_2 < B_2^-$$

8. The ungerade, antibonding molecular orbital of the H_2^+ molecule is given by

$$\psi_u = A[\phi_a - \phi_b]$$

with A the normalization and ϕ_a or ϕ_b the normalized 1s orbital centered respectively on nucleus a or b. Show that the expectation value of the Born-Oppenheimer Hamiltonian operator for the H_2^+ molecule with respect to ψ_u is given by

$$\langle \hat{H} \rangle = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

where

$$H_{aa} = \int \phi_a \hat{H} \phi_a d\tau, \quad H_{ab} = \int \phi_a \hat{H} \phi_b d\tau \quad \text{and} \quad S_{ab} = \int \phi_a \phi_b d\tau.$$

Answer:

First normalize

$$\begin{aligned} A^2 \int (\phi_a - \phi_b)^2 d\tau &= A^2 \left[\int \phi_a^2 d\tau + \int \phi_b^2 d\tau - 2 \int \phi_a \phi_b d\tau \right] \\ &= A^2 [2 - 2S_{ab}] = 1 \quad A = \frac{1}{\sqrt{2(1 - S_{ab})}} \\ \langle \hat{H} \rangle &= \frac{1}{2(1 - S_{ab})} \int (\phi_a - \phi_b) \hat{H} (\phi_a - \phi_b) d\tau \\ &= \frac{1}{2(1 - S_{ab})} \left[\int \phi_a \hat{H} \phi_a d\tau + \int \phi_b \hat{H} \phi_b d\tau - 2 \int \phi_a \hat{H} \phi_b d\tau \right] \\ &= \frac{1}{2(1 - S_{ab})} [H_{aa} + H_{bb} - 2H_{ab}] = \frac{1}{2(1 - S_{ab})} [H_{aa} + H_{aa} - 2H_{ab}] = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \end{aligned}$$

9. Consider the gas phase NH molecule, and let ϕ_H be the 1s-orbital wavefunction centered on the hydrogen atom and ϕ_N be the $2p_z$ -orbital wavefunction centered on the nitrogen atom. Noting that all wavefunctions for this system are real numbers, let the Coulomb integral for the hydrogen atom be given by

$$\alpha_H = \int \phi_H \hat{H} \phi_H d\tau,$$

the Coulomb integral for the nitrogen atom be given by

$$\alpha_N = \int \phi_N \hat{H} \phi_N d\tau,$$

the overlap integral be

$$S = \int \phi_H \phi_N d\tau$$

and the resonance integral be given by

$$\beta = \beta_{H,N} = \beta_{N,H} = \int \phi_H \hat{H} \phi_N d\tau.$$

Derive the secular equation for the molecular-orbital energies for NH in terms of S , α_H , α_N and β .

Answer

$$\begin{aligned} \langle E \rangle &= \frac{\int (c_H \phi_H + c_N \phi_N) \hat{H} (c_H \phi_H + c_N \phi_N) d\tau}{\int (c_H \phi_H + c_N \phi_N) (c_H \phi_H + c_N \phi_N) d\tau} \\ &= \frac{c_H^2 \alpha_H + c_N^2 \alpha_N + 2c_H c_N \beta}{c_H^2 + c_N^2 + 2S c_H c_N} \end{aligned}$$

or

$$\langle E \rangle (c_H^2 + c_N^2 + 2S c_H c_N) = c_H^2 \alpha_H + c_N^2 \alpha_N + 2c_H c_N \beta$$

Differentiating both sides with respect to c_H we obtain

$$2c_H \langle E \rangle + 2S c_N \langle E \rangle = 2c_H \alpha_H + 2c_N \beta$$

or

$$(\alpha_H - \langle E \rangle) c_H + (\beta - \langle E \rangle S) c_N = 0. \quad (1)$$

Next we differentiate with respect to c_N to obtain

$$2c_N \langle E \rangle + 2S c_H \langle E \rangle = 2c_N \alpha_N + 2c_H \beta$$

or

$$(\alpha_N - \langle E \rangle) c_N + (\beta - \langle E \rangle S) c_H = 0. \quad (2)$$

Equations (1) and (2) have non trivial solutions only if the secular determinant vanishes; i.e.

$$\begin{vmatrix} \alpha_H - \langle E \rangle & \beta - S \langle E \rangle \\ \beta - S \langle E \rangle & \alpha_N - \langle E \rangle \end{vmatrix} = 0$$

10. Consider the gas phase LiC molecule, and let ϕ_{Li} be the 2s-orbital wavefunction centered on the lithium atom and ϕ_C be the $2p_z$ -orbital wavefunction centered on the carbon atom. Noting that all wavefunctions for this system are real numbers, let the Coulomb integral for the lithium atom be given by

$$\alpha_{Li} = \int \phi_{Li} \hat{H} \phi_{Li} d\tau,$$

the Coulomb integral for the carbon atom be given by

$$\alpha_C = \int \phi_C \hat{H} \phi_C d\tau,$$

the overlap integral be

$$S = \int \phi_{Li} \phi_C d\tau$$

and the resonance integral be given by

$$\beta = \beta_{Li,C} = \beta_{C,Li} = \int \phi_{Li} \hat{H} \phi_C d\tau.$$

Using the expectation value of the Hamiltonian and the variational theorem, derive the secular equation for the molecular-orbital energies for LiC in terms of S , α_{Li} , α_C and β .

Answer:

$$\begin{aligned} \langle E \rangle &= \frac{\int (c_{Li} \phi_{Li} + c_C \phi_C) \hat{H} (c_{Li} \phi_{Li} + c_C \phi_C) d\tau}{\int (c_{Li} \phi_{Li} + c_C \phi_C) (c_{Li} \phi_{Li} + c_C \phi_C) d\tau} \geq E_0 \\ \langle E \rangle &= \frac{c_{Li}^2 \alpha_{Li} + c_C^2 \alpha_C + 2c_{Li} c_C \beta}{c_{Li}^2 + c_C^2 + 2S c_{Li} c_C} \end{aligned}$$

or

$$\langle E \rangle (c_{Li}^2 + c_C^2 + 2S c_{Li} c_C) = c_{Li}^2 \alpha_{Li} + c_C^2 \alpha_C + 2c_{Li} c_C \beta$$

Differentiating both sides with respect to c_{Li} we obtain

$$2c_{Li} \langle E \rangle + 2S c_C \langle E \rangle = 2c_{Li} \alpha_{Li} + 2c_C \beta$$

or

$$(\alpha_{Li} - \langle E \rangle) c_{Li} + (\beta - \langle E \rangle S) c_C = 0. \quad (3)$$

Next we differentiate with respect to c_C to obtain

$$2c_C \langle E \rangle + 2S c_{Li} \langle E \rangle = 2c_C \alpha_C + 2c_{Li} \beta$$

or

$$(\alpha_C - \langle E \rangle) c_C + (\beta - \langle E \rangle S) c_{Li} = 0. \quad (4)$$

Equations (1) and (2) have non trivial solutions only if the secular determinant vanishes; i.e.

$$\begin{vmatrix} \alpha_{Li} - \langle E \rangle & \beta - S \langle E \rangle \\ \beta - S \langle E \rangle & \alpha_C - \langle E \rangle \end{vmatrix} = 0$$

11. Recall that the anti-bonding, ungerade wavefunction of the H_2^+ molecule is given by

$$\psi_u = c_u(\phi_{1S_A} - \phi_{1S_B})$$

where ϕ_{1S_A} is the 1s, hydrogen atom orbital about center A, ϕ_{1S_B} is the 1s, hydrogen atom orbital about center B, and c_u is the normalization. Show that

$$c_u = \frac{1}{\sqrt{2(1 - S_{AB})}}$$

where S_{AB} is the overlap integral defined by

$$S_{AB} = \int \phi_{1s_A} \phi_{1s_B} d\tau.$$

Answer:

$$\begin{aligned} \int \psi_u^* \psi_u d\tau &= 1 \\ \int (c_u[\phi_{1S_A} - \phi_{1S_B}])^2 d\tau &= 1 \\ c_u^2 \left(\int \phi_{1S_A}^2 d\tau + \int \phi_{1S_B}^2 d\tau - 2 \int \phi_{1S_A} \phi_{1S_B} d\tau \right) \\ &= c_u^2(1 + 1 - 2S_{AB}) = c_u^2(2 - 2S_{AB}) = 1 \\ c_u &= \frac{1}{\sqrt{2(1 - S_{AB})}} \end{aligned}$$

12. Consider the gas-phase lithium dimer Li_2 . 1) Give the Born-Oppenheimer Hamiltonian operator for Li_2 . 2) Assuming a good representation for the ground-state wavefunction for Li_2 is

$$\psi = A[\phi_{2sa} + \phi_{2sb}],$$

where A is the normalization, ϕ_{2sa} is a 2s orbital centered on atom “a” and ϕ_{2sb} is a 2s orbital centered on atom “b.” Show that the expectation value of the Hamiltonian with respect to the approximate wavefunction ψ is given by

$$\langle \hat{H} \rangle = \frac{H_{aa} + H_{ab}}{1 + S}$$

where

$$H_{aa} = \int \phi_{2sa} \hat{H} \phi_{2sa} d\tau \quad H_{ab} = \int \phi_{2sa} \hat{H} \phi_{2sb} d\tau = \int \phi_{2sb} \hat{H} \phi_{2sa} d\tau$$

and the overlap integral is given by

$$S = \int \phi_{2sa} \phi_{2sb} d\tau.$$

Answer

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2m_e} \sum_{i=1}^6 \nabla_i^2 - \sum_{i=1}^6 \left(\frac{3e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_a|} + \frac{3e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_b|} \right) \\ & + \frac{1}{2} \sum_{i \neq j}^6 \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} + \frac{9e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|}\end{aligned}$$

Normalize

$$A^2 \int (\phi_{2a}^2 + \phi_{2b}^2 + 2\phi_{2a}\phi_{2b}) d\tau = A^2(1 + 1 + 2S) = 1$$

$$A = \frac{1}{\sqrt{2(1+S)}}$$

$$\begin{aligned}\langle \hat{H} \rangle &= \frac{1}{2(1+S)} \left(\int \phi_{2a} \hat{H} \phi_{2a} d\tau + \int \phi_{2b} \hat{H} \phi_{2b} d\tau + 2 \int \phi_{2a} \hat{H} \phi_{2b} d\tau \right) \\ &= \frac{1}{2(1+S)} (H_{aa} + H_{bb} + 2H_{ab}) = \frac{H_{aa} + H_{ab}}{1+S}\end{aligned}$$