22.2.3: iii. Problems

Q1

Given the following orbital energies (in hartrees) for the N atom and the coupling elements between two like atoms (these coupling elements are the Fock matrix elements from standard ab-initio minimum-basis SCF calculations), calculate the molecular orbital energy levels and 1-electron wavefunctions. Draw the orbital correlation diagram for formation of the N_2 molecule. Indicate the symmetry of each atomic and molecular orbital. Designate each of the molecular orbitals as bonding, non-bonding, or antibonding.

$$N_{1s} = -15.31^*$$

$$N_{2s} = -0.86^*$$

$$N_{2p} = -0.48^*$$

$$N_2 \sigma_g \text{Fock matrix}^*$$

$$\begin{bmatrix} -6.52 & & \\ -6.22 & -7.06 & \\ 3.61 & 4.00 & -3.92 \end{bmatrix} \tag{22.2.3.1}$$

$$N_2 \pi_g \text{ For Matrix}^*$$

$$[0.28]$$

$$N_2 \sigma_u \text{ For Matrix}^*$$

$$\begin{bmatrix} 1.02 & & \\ -0.60 & -7.59 & \\ 0.02 & 7.42 & -8.53 \end{bmatrix} \tag{22.2.3.2}$$

$$N_2 \pi_u \text{ Fock matrix}^*$$

$$[-0.58]$$

*The Fock matrices (and orbital energies) were generated using standard STO3G minimum basis set SCF calculations. The Fock matrices are in the orthogonal basis formed from these orbitals.

Q2

Given the following valence orbital energies for the C atom and H_2 molecule draw the orbital correlation diagram for formation of the CH_2 molecule (via a C_{2v} insertion of C into H_2 resulting in bent CH_2). Designate the symmetry of each atomic and molecular orbital in both their highest point group symmetry and in that of the reaction path (C_{2v}).

$$C_{1s} = -10.91^* \qquad H_2 \sigma_g = -0.58^* \tag{22.2.3.3}$$

$$C_{2s} = -0.60^* \qquad H_2 \sigma_u = 0.67^* \tag{22.2.3.4}$$

$$C_{2p} = -0.33^* \tag{22.2.3.5}$$

*The orbital energies were generated using standard STO3G minimum basis set SCF calculations.

Q3

Using the empirical parameters given below for C and H (taken from Appendix F and "The HMO Model and its Applications" by E. Heilbronner and H. Bock, Wiley- Interscience, NY, 1976), apply the Hückel model to ethylene in order to determine the valence electronic structure of this system. Note that you will be obtaining the 1-electron energies and wavefunctions by solving the **secular equation** (as you **always** will when the energy is dependent upon a set of linear parameters like the MO coefficients in the LCAO- MO approach) using the definitions for the matrix elements found in Appendix F.

$$C\alpha_{2p\pi} = -11.4eV$$

$$C\alpha_{sp^2} = -14.7eV$$

$$H\alpha_s = -13.6eV$$

$$C - C\beta_{2p\pi-2\pi} = -1.2eV$$

$$C - C\beta_{sp^2-2p^2} = -5.0eV$$

$$C - H\beta_{sp^2-s} = -4.0eV$$

a. Determine the C=C (2π) 1-electron molecular orbital energies and wavefunctions. Calculate the $\pi \to \pi^*$ transition energy for ethylene within this model.
b. Determine the C-C (sp^2) 1-electron molecular orbital energies and wavefunctions.
c. Determine the C-H $(sp^2$-s) 1-electron molecular orbital energies and wavefunctions (note that appropriate choice of symmetry will reduce this 8x8 matrix down to 4 2x2 matrices; that is, you are encouraged to symmetry adapt the atomic orbitals before starting the Hückel calculation). Draw a qualitative orbital energy diagram using the HMO energies you have calculated.

Q4Q5

Using the empirical parameters given below for B and H (taken from Appendix F and "The HMO Model and its Applications" by E. Heilbronner and H. Bock, Wiley- Interscience, NY, 1976), apply the Hückel model to borane (BH_3) in order to determine the valence electronic structure of this system.

$$B\alpha_{2p\pi} = -8.5eV$$

$$B\alpha_{sp^2} = -10.7eV$$

$$H\alpha_s = -13.6eV$$

$$B - H\beta_{sp^2-s} = -3.5eV$$

Determine the symmetries of the resultant molecular orbitals in the D_{3h} point group. Draw a qualitative orbital energy diagram using the HMO energies you have calculated.

Q5

Qualitatively analyze the electronic structure (orbital energies and 1-electron wavefunctions) of PF_5. Analyze only the 3s and 3p electrons of P and the **one** 2p bonding electron of each F. Proceed with a D_{3h} analysis in the following manner:

a. Symmetry adapt the top and bottom F atomic orbitals.
b. Symmetry adapt the three (trigonal) F atomic orbitals.
c. Symmetry adapt the P 3s and 3p atomic orbitals.
d. Allow these three sets of D_{3h} orbitals to interact and draw the resultant orbital energy diagram. Symmetry label each of these molecular energy levels. Fill this energy diagram with 10 "valence" electrons.

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