

EXPERIMENT 10

Molecular Orbital Calculations and Their Interpretation

This experiment is assigned on page 633 of the textbook.

FOR THE INSTRUCTOR

This experiment was written for the Spring 2006 version of the PC Spartan Pro '04 molecular modeling program. If you have another modeling program, you will want to make adjustments to the assignment as written below. You may, of course, have to give introductory assignments for your students to become comfortable with your modeling program. Note that these are not discovery laboratories; they are intended to confirm principles after they have been covered in the text.

Although these calculations are suggested on page 633 of the textbook, they apply in different parts of Chapters 11 and 12. Exercise 10.I applies to homonuclear diatomic molecules, and students have the necessary background information by page 631. It is an assignment for groups of four students. Exercise 10.II applies to heteronuclear diatomic molecules and ions, and can be assigned after the completion of Section 11.4. It connects to Exercises 11.37 and 11.38. Exercise 10.III applies to polyatomic molecules, and therefore should be assigned after completion of Section 12.2. It is connected to Exercise 12.26, and is an assignment for groups of three students.

FOR THE STUDENTS

Part I. Homonuclear Diatomic Molecules

In this exercise the class will perform calculations at the Hartree-Fock (HF) level of theory, on the following set of homonuclear diatomic molecules with no unpaired electrons— H_2 , Li_2 , N_2 , and F_2 —in order to derive the MO's and their energy levels and pictorial representations for each of the molecules at the equilibrium bond distance. Optimize the geometry using the 6-31G** basis set. Each student will be assigned one molecule.

- A. Generate grid files for surface plot of the MO's (Output, Properties, and Surface menu); print out visual representations of the MO's that fall at energy levels between -25 and $+5$ eV; and print out the energy level of each MO.
- B. Give the irreducible representation symmetry label for each MO, including specifications as to whether any are core, bonding, antibonding, or nonbonding.
- C. Identify the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for your molecule.
- D. As a class, arrange the molecular orbitals of each molecule in order of increasing energy, and draw an energy-level diagram to scale on graph paper. Place the symmetry labels on each energy level.
- E. Compare the visual representations with those given in Figure 3.10 on page 108 of the text and describe how they correspond.
- F. Compare the visual representations with those given in Figure 11.6 on page 623 of the text. Decide if this molecule shows s - p hybridization. What is your evidence?
- G. If the photoelectron spectrum of this molecule is available (Figure 11.8 on page 629), tell how well the calculated energy levels of the molecule agree with the photoelectron spectrum. If the photoelectron spectrum of this molecule is not available, predict what it would look like between -25 and $+5$ eV.
- H. Comparing your results with those of your classmates, decide which of the four molecules appear to involve s - p hybridization and which do not.

Part II. Heteroatomic Diatomic Molecules and Ions

In this exercise the class will perform calculations at the Hartree-Fock (HF) level of theory, on the following set of heteroatomic diatomic molecules or ions with no unpaired electrons: N_2 (already done in Part I), CO , BF , NO^+ , and CN^- . The purposes of these calculations are to derive the MO's and their energy levels and pictorial representations for each of the molecules at the equilibrium bond distance, after optimizing the geometries using the 6-31G** basis set. Each student will be assigned one molecule or ion other than N_2 .

- A. Generate grid files for surface plot of the MO's (Output, Properties, and Surface menu); print out visual representations of the MO's that fall at energy levels between -25 and $+5$ eV; and print out the energy level of each MO.
- B. Give the irreducible representation symmetry label for each MO, including specifications as to whether it is core, bonding, antibonding, or nonbonding.

- C. Identify the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for your molecule or ion.
- D. As a class, arrange the molecular orbitals of each molecule or ion in order of increasing energy, and draw an energy-level diagram to scale on graph paper (in the manner of Figure 11.14 on page 639). Place the symmetry labels on each energy level.
- E. Compare the visual representations with those given in Figures 11.11 and 11.12a on pages 635 and 636 of the inorganic text for the same molecule or ion.
- F. Decide if this molecule or ion shows *s-p* hybridization. What is your evidence?
- G. If the photoelectron spectrum of your molecule or ion is available in Figure 11.12b on page 636, tell how well the calculated energy levels of the molecule agree with the photoelectron spectrum. If the photoelectron spectrum of this molecule is not available, predict what it would look like between -25 and $+5$ eV.
- H. Comparing your results with those of your classmates, decide which of the five molecules appear to involve *s-p* hybridization and which do not. Which of the five molecules or ions is the softest?

Part III. Type MO's of Polyalkenes and their Silicon and Tin Analogues

In this exercise each student is assigned a set of three molecules on which to compute and display the appropriate type of MO's. We will display and compare the π -type MO's of some alkenes of increasing chain length but based, not only on carbon atoms, but also on silicon and tin atoms. Probably the Hartree-Fock 6-31G* computations will give usable results, but if not, another type can be used. But each student should use the same computation type and basis set for all three of their molecules!

- A. Student A should construct, display, and print the π -type MO's of the all-*trans* conformations of the following molecules: $\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$.
- B. Student B should construct, display, and print the π -type MO's of the all-*trans* conformations of the following hypothetical silicon-based molecules: $\text{SiH}_2=\text{SiH}_2$, $\text{SiH}_2=\text{SiH}-\text{SiH}=\text{SiH}_2$, and $\text{SiH}_2=\text{SiH}-\text{SiH}=\text{SiH}-\text{SiH}=\text{SiH}_2$.
- C. Student C should construct, display, and print the π -type MO's of the all-*trans* conformations of the following hypothetical tin-based molecules: $\text{SnH}_2=\text{SnH}_2$, $\text{SnH}_2=\text{SnH}-\text{SnH}=\text{SnH}_2$, and $\text{SnH}_2=\text{SnH}-\text{SnH}=\text{SnH}-\text{SnH}=\text{SnH}_2$.
- D. Each student should locate, display, and print out each of the π -type MO's of each of their molecules. (Be sure to exclude MO's that are not of π type). Each MO should be labeled with (1) the molecule to which it applies; (2) the energy level of the MO; (3) identifications of the MO as a HOMO-2, etc.; and (4) by its irreducible representation.
- E. For Student A only, choose the ionization energies of the corresponding MO's from among these experimental values: 10.51 eV for ethylene; 11.87 eV and 9.03 eV for butadiene; 11.9 eV, 10.69 eV, and 8.29 eV for hexatriene. How well do your computed energy levels match up with the experimental values (which are from photoelectron spectra)?
- F. Each student should calculate the HOMO-LUMO separation for each compound. Then, using the relevant energy relationships, calculate the wavelength of each electronic absorption for the electron being promoted from the HOMO to the LUMO. Tell whether this band occurs in the UV, visible, or near-IR part of the spectrum.