

Experiment 9: Electronic Structure Calculations

Reading: Sections 9.4-9.8 in your textbook and this lab handout

Materials: Bring your textbook to lab

Ongoing Learning Goals:

- To use a scientific notebook as a primary record of procedures, data, observations, and example calculations
- To present your formal results through a laboratory report along with proper citations

Additional Learning Goals for Experiment 9:

- To explore the electronic and orbital structure of molecules and ions using more sophisticated functions of the computational program Spartan.

Introduction to Electron Surfaces

In Experiment 8 you calculated energies, geometries, and dipole moments for a series of molecules and ions. This week you will expand your computational exploration by looking at electronic structure, such as the distribution of electrons in a compound as well as the shape and energetics of the molecular orbitals.

Electron density plots tell you where the electrons are in a molecule. Electric potential surfaces tell you if the electron density is skewed from the distribution in isolated atoms. The electric potential is calculated by the energy of interaction between the molecule and an imaginary point charge. The point charge is a single positive charge and corresponds to the potential energy a H^+ ion would see. The point charge is moved around on the electron density surface, so the potential is mapped for a constant value of the electron density. As you generate these surfaces look at the distance from the nucleus of each atom to the surface. The greater this distance, or in other words the bigger the surface, the more electron density surrounds the atom. Also look at the size of the density surface along the internuclear axis between the two nuclei. This internuclear area is where electron density must build for a strong bond to form.

Part I: Electron potential density plots of the diatomic molecules H_2 , HF, and LiF

Build the molecules H_2 , HF, and LiF and compute the equilibrium geometry and at the default Hartree-Fock/3-21G level. Record the bond lengths, dipole, and molecule energies.

For each molecule, generate two electron potential density surfaces, one with a density setting (also called isovalue) of 0.004 and another with a density setting of 0.10. What you are doing by changing these settings is looking at electron density either farther away from the nuclei (what the molecule might look like from the “outside”) or closer in toward the nuclei (a better picture of the electron distribution in the bonds that hold the molecule together). A density of 0.004 is farther out, and a density of 0.10 is closer in. Details on generating these surfaces are provided in the Spartan Instructions – Surfaces handout. (Generate the electron potential density surface with different isovalues using the *more surfaces* option.)

Screen capture each surface that you generate (two for each molecule), and paste them into a word document for printing – make sure to be organized and clearly label each picture.

Part II: Electron density plots of the ions nitrate and acetate

As you did in Part I, generate electron density surfaces for the nitrate and acetate ions using density settings of 0.004 and 0.10. As you did in Part I, screen capture the surfaces that you generate. Is there anything different or unexpected about the different density views for these ions? Use measure tools to measure the bond distances and angles between oxygen and the central atom. What does this data tell you about the bond order?

Part III: Molecular Orbitals of the diatomic molecules H₂, O₂, and NO

Spartan makes it very easy to calculate and visualize the energies and shapes of molecular orbitals. For this experiment, you will calculate and visualize the molecular orbitals for H₂, O₂, and NO. For each calculation, you will visualize a series of molecular orbitals, record their energies and compare your findings to what you might expect from the information presented in class and in your textbook.

We recommend that you start with H₂. Molecular Orbitals can be viewed in the Display>Orbital Energies menu. Select the Mesh Style for the orbital to see the atoms and the orbital. The calculated molecular orbitals will be displayed in the window, along with the corresponding energies. Keep in mind that the orbital energies can tell you several things: the relative ordering/filling order of the orbitals, whether or not orbitals are degenerate (the same energy), and whether or not orbitals are in the same primary shell (different principle quantum shells have vastly different energies).

- For H₂, view and screen capture orbitals 1 and 2. Record the energies. As a “bonus”, feel free to take a look at orbital 3. From their appearance, what do you think these orbitals are?
- Note that both O₂ (in the lowest energy triplet state), and NO have unpaired electrons. Because of this, Spartan treats the orbitals a little differently. To simplify your “view” of the orbitals enter SCF = Restricted in the options box when you calculate the energy for O₂.
- For O₂, visualize orbitals 5-8, screen capture these orbitals and record their energies. Note whether each orbital looks like a σ , σ^* , π , or π^* orbital.
- For NO, visualize orbitals 7-9, screen capture these orbitals and record their energies. To simplify your “view” of the orbitals enter SCF = Restricted in the options box when you calculate the energy for NO (look at the a-orbitals). Note whether each orbital looks like a σ , σ^* , π , or π^* orbital.

What should you print out before leaving lab?

- Print out each surface/molecular orbital that you generated. Make sure everything is clearly labeled, and arrange and size the pictures so you can fit your images on as few pages as possible.

What should be in your laboratory notebook?

- The title for the experiment, name of your partner, and the date
- The results and sketches from all Parts I-III

Laboratory report: Use the **Report Form** for Experiment 9.

Literature Cited:

1. This exercise is based on: G. P. Shusterman, A. J. Shusterman, Teaching Chemistry with Electron Density Models, *J. Chem. Educ.* **1997**, *74*, 771.
2. P. Politzer, D. G. Truhlar, Eds., Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum: New York, 1981.

Short Primer: Interpreting Molecular Orbital Surfaces

Molecular orbital surfaces can be viewed to understand how atomic orbitals overlap to make molecular orbitals. To judge if an orbital is sigma (σ) or pi (π) type, you can consider the direction of overlap of the p orbitals on the two atoms. Sigma bonds are often stronger because the atomic p-orbitals point towards each other and have better overlap. When two atomic orbitals overlap, two molecular orbitals are formed. The lower energy molecular orbital is bonding and the higher energy orbital is anti-bonding. Bonding molecular orbitals increase the electron density between the two nuclei, while anti-bonding orbitals decrease the electron density between the two nuclei (a node forms at the overlap).

Molecular orbital surfaces are very useful for visualizing the difference between bonding and anti-bonding orbitals. Figure 1 shows the normal “cartoon” of a bonding and anti-bonding interaction of p-orbitals (left side), along with the corresponding calculated MO surfaces (right side). The trick to determining bonding or anti-bonding behavior is to look at the phases, or colors, of the orbitals in the overlap region. A change in sign of the orbital between the two nuclei (with formation of a node) signifies an anti-bonding orbital.

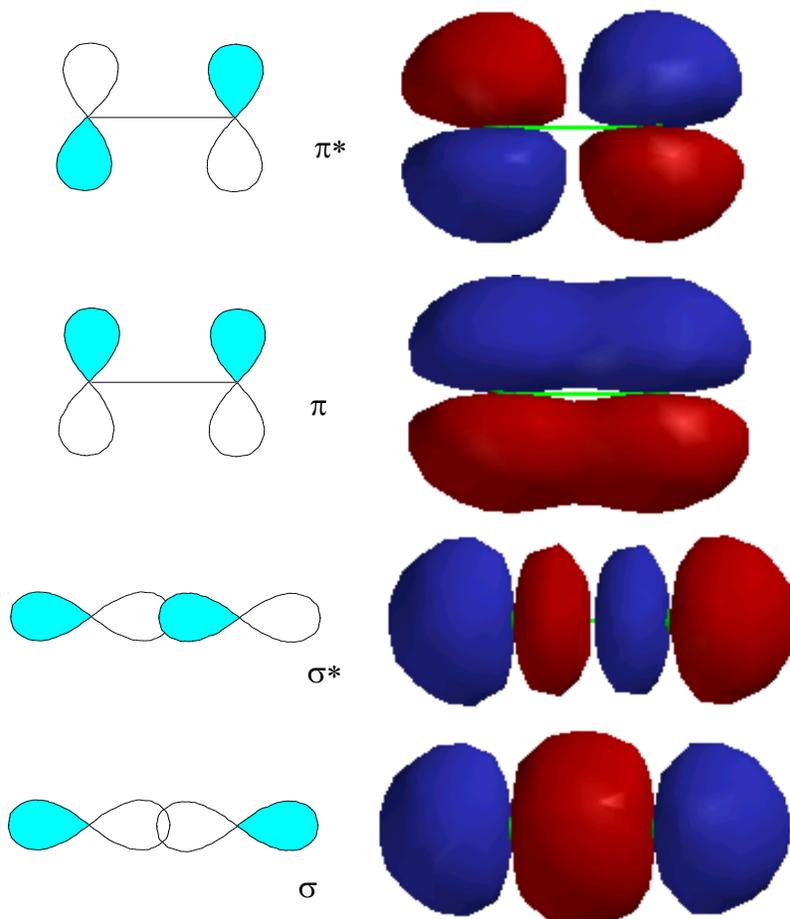


Figure 1: Bonding and anti-bonding orbitals