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 programs Gaussian/GaussView

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, occupancy, 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 density plots of the diatomic molecules H_2, HF, and LiF

Build the molecules H_2, HF, and LiF. For each, either load your .chk (checkpoint) file from Experiment 8 or optimize the geometry at the default HF/3-21G level. *Note that you must use the .chk file, not the .log file*. For LiF, record the bond length, charge distribution, and dipole moment in your notebook (you recorded this information for the other molecules in Experiment 8).

For each molecule, generate two electron 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.

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.

Drawing Electron Density Surfaces:

Electron density surfaces can be drawn by bringing up the Surfaces/Contours window from the pull-down menu Results → Surfaces/Contours. Once the window is open:

a) Under the "Cube Actions" menu select "New Cube"
b) Choose Type: "Total Density" and then accept the defaults
c) Make sure the "density" level is set properly to either 0.004 or 0.10 (or feel free to try other density settings just to see what happens!)
d) Under the "Surface Actions" menu select "New Mapped Surface"
e) Choose Type: "ESP" and then accept the defaults (ESP = electrostatic surface potential). Your suface should appear over your molecule. The colors should correspond to the charge density (red = most negative, blue = most positive).
f) To change the appearance of the surface, go to View → Display Format. When the window appears, select the Surface tab and then toggle between Format: Mesh/Solid/Transparent. Feel free to play around with the other view parameters and sliders to see what they do to the molecule's appearance.
g) You can also change the charge range by typing in different numbers on the left and right of the "rainbow" at the top of the window that shows your graphed molecular surface.
h) If you want to generate a different surface for the same molecule, go back to the Surfaces/Contours window. First select Surface Actions: "Hide Surface". Next, change your density level, and then select Surface Actions: "New Mapped Surface".

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 (you can load your existing .chk file or recalculate the a geometry optimization at the HF/3-21G level). 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?

Part III: Molecular Orbitals of the diatomic molecules H_2, O_2, and NO

Gausian/GaussView makes it very easy to calculate and visualize the energies, occupancies, and shapes of molecular orbitals. For this experiment, you will calculate and visualize the molecular orbitals for H_2, O_2, and NO. For each molecule, open an existing .chk file or run a geometry optimization at the default HF/3-21G level and then open your .chk file. For each calculation, you will visualize a series of molecular orbitals, record their energies and orbital occupancies, 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 H_2. Molecular Orbitals can be viewed by bringing up the Molecular Orbital Editor window from the pull-down menu Edit → MOs. The calculated molecular orbitals and occupancies will be displayed in the window, along with the corresponding energies (the energies are the blue numbers next to the orbital boxes, with units in hartrees). 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).

First select the Visualize tab. You can click on the orbitals that you want to view (they will become highlighted), and then push the "Update…" button (lower right). This tells the computer to calculate MO surfaces for all highlighted orbitals. Once this is complete (*be patient, depending on how many orbitals you selected, this can take over 1 minute*), those orbitals will have small grey boxes next to them. One orbital will be displayed, and that box will be red (selected). You can toggle between orbitals to view by simply clicking the grey boxes.

- For H_2, view and screen capture orbitals 1 and 2. Record the occupancies and energies. *As a "bonus", feel free to take a look at orbitals 3 and 4. From their appearance, what do you think these orbitals are?*

- Note that both O_2 (in the lowest energy triplet state), and NO have unpaired electrons. Because of this, Gaussian treats the orbitals a little differently. To simplify your "view" of the orbitals, you can go to the Calculation tab and select Wavefunction: "Restricted" [this will spin-pair each orbital that is able to spin-pair, rather than treating everything separately].

- For O_2, visualize orbitals 5-10. screen capture these orbitals and record their energies and occupancies. Note whether each orbital looks like a σ, $\sigma *$, π, or $\pi *$ orbital.

- For NO, visualize orbitals 7-9. screen capture these orbitals and record their energies and occupancies. Note whether each orbital looks like a σ, $\sigma *$, π, or $\pi *$ orbital.

- Make sure to File → Exit out of GaussView when you are finished

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 computer calculations in 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.
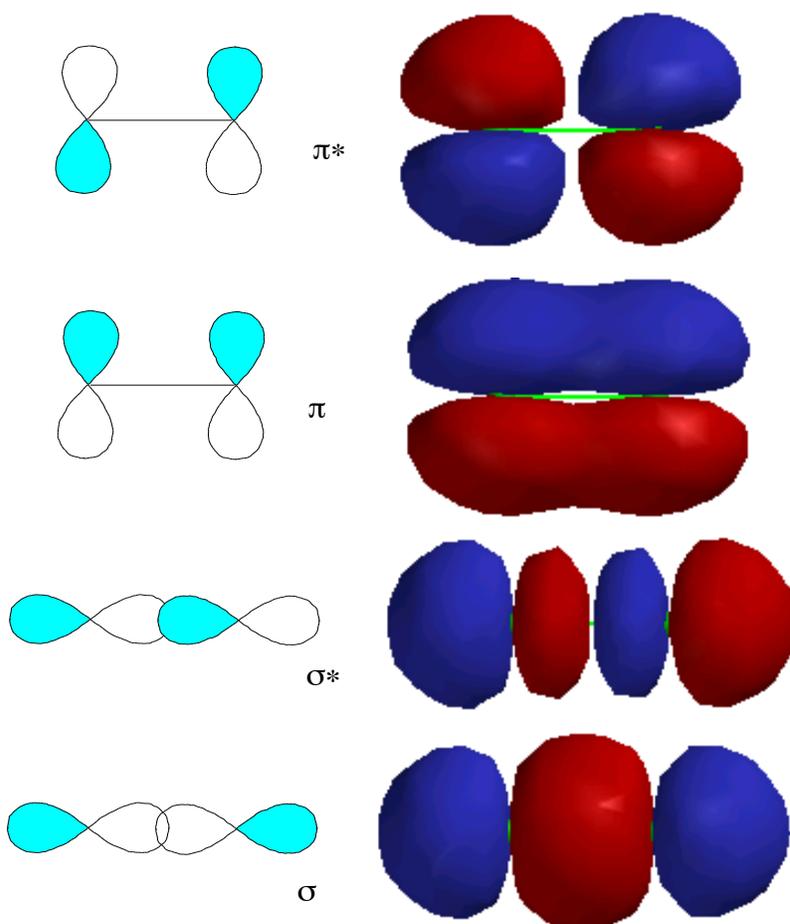
Figure 1: Bonding and anti-bonding orbitals