Molecular Modeling with Spartan

In class we used the Valence-Shell Electron-Pair Repulsion (VSEPR) model to predict a molecule's or an ion's geometry by arranging its electron domains in a way that minimizes repulsion between pairs of electrons. We also explored the valence bond model and hybrid atomic orbitals as a way to consider how we might explain these geometries and explain some of the special properties of a double bond or a triple bond. While these approaches leave us with a general understanding of geometry and bonding, neither provides more quantitative information about the molecule or ion, such as bond lengths, bond angles, and bond energies. Molecular orbital theory, our last model of electronic structure, provides this information.

To provide a more detailed picture of bonding, we must use more computationally rigorous mathematical models. For example, we can use classical mechanics and Coulomb's law to maximize attractive interactions and to minimize repulsive interactions, and we can use quantum mechanics and the wave equation to calculate bond lengths and bond angles, and the energies of molecular orbitals. In this lab you will use the molecular modeling program Spartan to optimize the structure of some inorganic molecules and polyatomic ions, and evaluate the results of your calculations in light of the models described above.

Three Important Cautions

1. A computational lab changes what and how you record information in your lab notebook. Reproducing the result of a calculation requires that you begin with the same structure and that you use the same settings; it is essential, therefore, that you maintain a record of the structures and settings you use for each molecular or ion you are studying.
2. The computers in the Computational Chemistry Lab are configured to delete all locally saved files on each restart. If you wish to save your work you must use a USB drive or cloud storage.
3. Spartan occasionally becomes stuck during a computation. If this happen, you will need to reboot your computer and restart the calculation.

Pre-lab Assignment

Read through the lab handout paying particular attention to the instructions for using Spartan. We will review some features of the software using the ions PF_6^- and NO_3^- as examples, so come to lab having drawn their Lewis structures in your lab notebook and having predicted their geometry using VSEPR. We will review other features of the software using Li_2 as an example, so come to lab having drawn its complete molecular orbital diagram; see Figure 5.37 in your textbook for the molecular orbital diagrams for homonuclear (one type of atom) diatomic (two of which are bonded to each other) molecules (to make a molecule with the general formula X_2) for elements in the second row of the periodic table.

Procedure

Work with your assigned partner to complete the exercises described below. Pay particular attention to the questions included with each exercise as your answers to these questions will comprise your report. Each partner will prepare a separate report, so be sure that you record all work in your notebook.

Molecular Modeling Exercises

The molecular modeling exercises are divided into two sets, one that focuses on bond angles, bond lengths, and bond energies, and one that focuses on molecular orbitals.

Set I

Begin each of the following three exercises by drawing appropriate Lewis structures and using VSEPR to predict the geometry around the central atom. Be sure this information is recorded in your lab notebook. ***For these exercises, calculate the equilibrium geometry using the Semi-Empirical computational method with the PM3 basis set***.

Exercise 1

The species NH_4^+, NH_3, $N(CH_3)_3$, and H_2O have the same number of electron domains around the central atom (nitrogen or oxygen) but differ in the number of bonding domains and in the identity of the substituents (including lone-pairs of electrons) bound to the central atom. Use Spartan to optimize their structures. Measure the bond angles in each structure (place N or O in the middle) and organize them from largest-to-smallest in a table. What do your results imply about the relative size of a lone pair of electrons compared to –H and $–CH_3$? Explain your reasoning in 2–3 complete sentences.

Exercise 2

As we discussed in class, a trigonal bipyramidal geometry has two unique positions around the central atom: two axial positions and three equatorial positions. One consequence of this is that we can draw two structures for a molecule, such as SF_4, that has four bonding substituents and a single lone-pair of electrons, placing the lone-pair in either an axial position or an equatorial position. Use Spartan to optimize each structure; ***however, skip the step where you first minimize the energy using the minimization tool on the toolbar***. Identify the geometry that Spartan finds most stable and explain why this is the more stable structure in 2–3 complete sentences. As part of your answer, complete an analysis of the interactions at 90° as we did in class for AX_3 with two lone-pairs of electrons.

Exercise 3

Use Spartan to optimize the structure for NO_2^+, NO_2, and NO_2^-. Because NO_2 has an unpaired electron, when you set up your calculation you must let Spartan know that its ground electronic state is a doublet (this is just a fancy way of saying that NO_2 has an unpaired electron) rather than a singlet. Prepare a table that provides the O—N—O bond angles in each molecule, arranging them from smallest-to-largest. Propose a plausible explanation for your results in 2–3 sentences.

Set II

Begin each of the following two exercises by drawing the appropriate Lewis structures and, where there are more than two atoms, identifying the geometry around the central atom. Be sure this information is recorded in your lab notebook. ***For these exercises, calculate the equilibrium geometry using the Density Functional computational method with the WB97X-D 6-31G* basis set***.

Spartan identifies molecular orbitals by referencing them to the molecular orbital with the least negative energy that contains electrons (which we call the highest occupied molecular orbital, or HOMO) and the molecular orbital with the most negative energy that does not contain electrons (which we call the lowest unoccupied molecular orbital, or LUMO). Molecular orbitals with more negative energies than the HOMO are identified using the notation HOMO-1, HOMO-2, etc., and molecular orbitals with less negative energies than the LUMO are identified using the notation LUMO+1, LUMO+2, etc.

Exercise 4

Use Spartan to optimize the the diatomic molecules, Li_2, Be_2, C_2, N_2, and F_2. For each, complete the following:

- measure the bond length
- examine the valence shell molecular orbital energy levels and record their energies (in eV), and then assign each its appropriate designation from the following possibilities: σ_{2s}, σ^*_{2s}, σ_{2p}, σ^*_{2p}, π_{2p}, or π^*_{2p}. Note that if Spartan finds that two orbitals have the same energy—as it should for the π_{2p} orbitals since there are two of them—it will label them with two different labels even though they have the same energy. Spartan needs a unique label for each orbital so be observant as you interpret your data. It may help you to examine the orbital surfaces as their shape and presence or absence of nodes may help you identify an orbital as σ or π, or as bonding or anti-bonding.

Report the bond lengths for these diatomic molecules in a table from shortest-to-longest and, in 2–3 complete sentences, explain the trend in your results.

On a single graph, plot each molecule's molecular orbital diagram, creating a chart similar to Figure 5.37 in your textbook. Be sure you plot the energies to scale along the y-axis. In 2–3 complete sentences, compare your chart to that of Figure 5.37 in your textbook.

For F_2, examine the complete set of valence orbital surfaces, σ_{2s}, σ^*_{2s}, σ_{2p}, σ^*_{2p}, π_{2p}, or π^*_{2p}, making note of their shape and the presence of absence of nodes. Choose the option to view the surface as a mesh so that you see the atoms. In 3–5 complete sentences, describe the difference between a bonding molecular orbital and an anti-bonding molecular orbital, and the difference between a σ_{2p} and a π_{2p} molecular orbital. Illustrate your answer either by sketching each molecular orbital or by copying and pasting into a Word document the surface created by Spartan.

Exercise 5

Use Spartan to optimize the diatomic molecules, CO, CN^-, and NO^+, which are isoelectronic with N_2. Examine the valence shell molecular orbital energy levels and record their energies (in eV), and then assign each its appropriate designation from the following possibilities: σ_{2s}, σ^*_{2s}, σ_{2p}, σ^*_{2p}, π_{2p}, or π^*_{2p}.

On a single graph, plot the molecular orbital diagrams for CO, CN^-, NO^+, and N_2. Be sure you plot the energies to scale along the y-axis. In 3–5 complete sentences, discuss their similarities and differences.

For each of CO, CN^-, NO^+, and N_2, examine the shape of the σ_{2s} molecular orbital and in 3–5 sentences describe and explain any differences that you see. Illustrate your answer either by sketching each molecular orbital or by copying and pasting into a Word document the surface created by Spartan.