Using Spartan to Calculate and Visualize Molecular Orbitals

There is more than one way to represent (and therefore recognize) a molecule. One could simply draw lines between atomic symbols. Or try to sketch the three-dimensional shape of the molecule. Or represent, somehow, the bulk of its atoms, a so-called space-filling model. Or estimate the electric field emanating from it. Or one (well, another molecule, that is) could ‘stroke’ the molecule. There are so many ways for us, or molecules to ‘see’ or ‘feel’ one another.

Roald Hoffmann

Molecular modeling can be used to provide accurate models for many aspects of molecules including molecular size and shape, bond lengths and angles, relative energies of structures, the distribution of electrons in molecular orbitals, charge distribution and vibrational modes of molecules. These molecular models result from the application of the physics and mathematics that describe the behavior of chemical systems.

In this exercise, you will investigate the distribution of electrons in molecules by calculating molecular orbitals for several molecules. While Spartan is a powerful program, it must be used with caution. The model you get out is only as good as the information that you provide to Spartan. Understanding the mechanics of the calculations done by Spartan is non-trivial (and not completely understood by your instructors). Before computational results are accepted as models that are described by reality, they need to be verified by experiment. In fact, empirical evidence helps chemists to develop better modeling programs; it’s an iterative process. Your instructors have selected problems that accurately reflect the world in which we live.

Computational Methods

When doing calculations about the chemical properties of molecules, you need to make physical assumptions about the molecules. There are several techniques used to calculate the properties of molecules; each has its advantages and disadvantages. Generically, methods fall into two class: classical (or Newtonian) mechanical methods and quantum mechanical methods.

- **Classical (Newtonian) Mechanical Models.** There are two main techniques that use classical mechanical models: molecular mechanics and molecular dynamics. From a classical perspective, a molecule is modeled as a collection of hard spheres (nuclei) that are connected by flexible springs (chemical bonds). Using classical models, electrons are not explicitly included. This severely limits the use of classical calculations because it means that they cannot accurately describe any properties associated with electrons and electron distribution. However, these methods are extremely powerful for doing conformational analysis (looking at bond lengths, angles, configurations) and the relative energies of conformational isomers because these models can be used for molecules containing upwards of 1,000 atoms. From a computational perspective, these calculations are also inexpensive.

- **Quantum Mechanical Models.** Quantum mechanical methods fall into two categories: semi-empirical methods and *ab initio* methods. Both techniques solve the Schrödinger equation for the molecule; they differ only in the approximations used. Because the electronic structure of the compound is calculated, quantum mechanical methods lead to a reasonable prediction of structure, thermochemical and electronic properties. In semi-empirical methods, experimental data is used to mathematically describe atoms. *Ab initio* methods (implemented with Hartree Fock Methods and Density Functional Theory) do not depend on empirical parameters. In these methods, appropriate mathematical forms that
describe the wavefunction of the atomic orbitals of different elements have been developed. These have been developed so that computationally generated molecular structures agree with experimental data. Semi-empirical methods are a bit less accurate but are computationally cheaper than \textit{ab initio} methods. Hartree-Fock methods (\textit{ab initio}) are best applied to organic compounds. Density Functional Models are relatively expensive but are particularly useful for high-quality structure, energy and property calculations, including calculations on transition-metal inorganic and organometallic compounds.

All of the methods described above are implemented in Spartan. The type of calculation can be chosen under \textbf{Select Calculation}.

\textbf{Calculating Molecular Orbitals Using Spartan}

MOs are very similar to the AOs that we use to describe an electron in an atom (1\textit{s}, 2\textit{s}, 2\textit{p}, etc.); they are different only because they describe electrons in molecules. Because MOs describe the location of electrons in molecules, quantum mechanical methods need to be used for calculation. For the inorganic molecules that we will be study, we will use semi-empirical methods with PM3 functions.

To calculate molecular orbitals with Spartan, you must first construct your molecule. If you have an ion, be sure to set the \textbf{Total Charge} (under \textbf{Setup Calculations}). For molecular orbital calculations of inorganic molecules, your best bet is to calculate \textbf{Equilibrium Geometry} with Hartree-Fock methods with the STO-3G basis set (see figure). If you are interested in the relative energy of your molecular orbitals, select \textbf{Orbitals & Energies} under \textbf{Print}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{setup_calculations.png}
\caption{Setup Calculations window in Spartan.}
\end{figure}

All orbital energies in Spartan are defined relative to the HOMO and the LUMO. The orbital that is lower in energy than the HOMO is HOMO\{-\}. Orbitals that are higher in energy than the LUMO are called LUMO\{+\}. Unfortunately, Spartan does not have a way of naming degenerate orbitals. For example, if your HOMO is a doubly degenerate set of orbitals, they may be named
HOMO and HOMO\(-\) in spite of the fact that they are degenerate and in reality the set compromises the HOMO. (In other words, you have to think; Spartan doesn't do everything for you.) If you are calculating MOs above the LUMO (LUMO\(+)\) or below the HOMO (HOMO\(-\)), you will have to select how far above the LUMO or below the HOMO the MO is. For example, if I wanted to calculate the MO directly below the HOMO (in terms of energy), I would select HOMO\(-\) 1. To get the most accurate picture of bonding in molecules, we will investigate all MOs that are constructed from valence orbitals whether they are filled or not.

Let's take a look at the dicarbide molecule, \(\text{C}_2\). (Before you draw this molecule in Spartan, draw the correct Lewis structure. It may not be what you think!) Carbon is in the second row and has 4 atomic orbitals associated with its valence electrons (2\(s\), 2\(p_x\), 2\(p_y\), 2\(p_z\)). Since there are two carbon atoms in dicarbide, there will be 8 atomic orbitals associated with the molecules. If there are 8 AOs going into the construction of the MOs, we need to make 8 MOs. (That conservation of orbital rule is funny that way!) Next, we need to figure out how many orbitals are below the HOMO. Dicarbide will have a total of 8 electrons since each carbon atom has four valence electrons. Assuming that all electrons are paired, there will be 2 electrons in the HOMO and three orbitals of lower energy than the HOMO will be needed to hold the other electrons. In other words, we'll need to generate HOMO, HOMO\(-1\), HOMO\(-2\), and HOMO\(-3\). At this point, we've used 4 MOs. There are four more. They will be LUMO, LUMO\(+1\), LUMO\(+2\), and LUMO\(+3\). Next we need to have Spartan set up these MOs.

To calculate MOs, select Setup Surfaces. An Add Surface window, similar to the one below, will appear.

![Add Surface](image)

You will need to change the Surface to reflect the MO that you would like to calculate. For example, if you want to calculate the HOMO, the box will appear as shown below.

![Add HOMO Surface](image)
You will find it easiest to begin with the highest energy orbital. In the case of dicarbide, this is LUMO\(^{(+)}\) 3. This is entered as \textbf{LUMO}\(^{(+)}\) and 3 for \textbf{Surface}.

\textbf{Resolution} can be left at medium. Changing the resolution will affect the precision to which Spartan calculates the surface of the MO. Visually, you will only notice changes for displaying the surface in mesh mode. Increasing the resolution will also increase calculation time.

You can select multiple surfaces to calculate. Once you have selected all surfaces to calculate, select \textbf{Submit Calculations}.

\textbf{Viewing MOs}

Once you’ve calculated your MOs, you can look at their appearance by selecting the appropriate MO in the surfaces list.

Let’s start with the lowest energy \(\sigma_g(2s)\). When you click on the box next to HOMO\(^{-3}\), the MO will appear on the molecule that you’ve constructed.
(If you take a close look at the bottom right hand corner of the box, you can see the symmetry of the molecule. Dih stands for $D_{\infty h}$.) This is exactly what we expect – a molecular orbital with no nodes and electron density distributed between the two atoms. The solid surface isn’t necessarily the best way to view the molecule because it’s hard to see atomic positions. The surface can also be viewed as a mesh grid, dots, or as a transparent surface. (The dots are amazingly hard to see on a printout.)

To select the surface of interest, click on the surface. A box should appear in the bottom right hand corner of your molecule window. Use the pull down menu to select the surface type.

Now that your surface is there, you can start interpreting the meaning behind your molecular orbitals!