**CHEM 213: Inorganic Chemistry Laboratory, Spring 2014**

Prelab: *Computational Applications to Molecular Orbitals*

You should thoroughly review the discussion from lecture on generator functions and LGOs. You will be assigned to a group (Group A, Group B, etc.) and then your group will be performing calculations on the molecules we examined in class, NH3 and the molecule assigned below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Group A** | **Group B** | **Group C** | **Group D** | **Group E** |
| SiH4 | SH4 | CH4 | PH6- | PH4+ |

**Inorganic Chemistry Laboratory**

**Experiment:**

*Computational applications to molecular orbitals*

PURPOSE

To gain additional practice generating molecular orbital diagrams using generator functions and LGOs and to visualize the MOs that are generated using computational techniques.

INTRODUCTION

Group theory was introduced in class as a starting point for generating MO diagrams for large molecules. Previously, *Spartan ’10* was used to investigate the geometry of molecules. In this lab, *Spartan ’10* will be used to examine the MO diagrams of several molecules. In lecture, the focus was primarily on the possible interactions between the central atom in a molecule and the outer atoms. While relative energies of the molecular orbitals could be predicted, there was no way to estimate these values. *Spartan ’10* will estimate the energy levels for the MO diagram.

Calculations will be performed using Density Functional Theory (DFT). This is a mathematical treatment of the electron density distribution throughout a molecule. The Becke, 3-parameter, Lee-Yang-Parr (B3LYP) hybrid functionals will be employed as they tend to give more reasonable results in the calculations. Finally, the 6-31G\* basis set, which is an approximation of atomic orbitals, will be used to calculate the molecular orbitals.

EXPERIMENTAL

You will use the computer program *Spartan ‘10* to perform calculations on the molecules of interest in this lab. You will compare the results obtained from *Spartan ’10* to those you obtained using the methodology from class.

I. Using the program

1. Starting the program

The icon for *Spartan ’10* should be on the desktop.

That should get you going.

1. Drawing a structure

Under the file menu select new.

On the right side of the screen click on the inorganic button.

Click the long button underneath the picture of an atom (default is a tetrahedral C atom) and a periodic table will appear allowing you to change the atom.

Select the closest possible geometry.

Place the atom on the screen.

If you need to, the red 'star' towards the top of the screen is a delete button, just be sure to click the plus next to it when you need to add additional atoms.

Add the remainder of the atoms by putting them on the end of the bonds.

Remember to make these atoms terminal (upper left of the geometry section).

1. Calculations

Under the Setup menu select calculations.

Set the menus under calculate to Equilibrium

Geometry, Ground, Density Functional, B3LYP and 6-31G\* in Vacuum.

Start from the current geometry.

The subject to symmetry box should be selected.

Select print Orbitals & Energies.

Hit submit.

You will have to enter a name for the file and save it, but these will not be saved to the hard drive permanently.

If your initial structure was drastically wrong, you may have to do this step multiple times.

1. Analysis

Under the display menu is select orbital energies.

This will bring up an MO diagram for your molecule.

Click on any of the orbitals in your diagram and it will be displayed.

You can change the way the orbital is displayed with the menu in the bottom right corner that initially will say solid.

Record the energy for each orbital.

Record the symmetry of the molecule which can be found in the lower right corner.

Under the Options menu select Colors and change the background color to white.

Copy and paste pictures of each MO for use in your lab report.

1. Finishing up

Be sure to close each model when you are done or you can end up with a huge mess.

II. Data of interest

Perform calculations on the three molecules that were discussed in lecture. However, instead of PF5, perform the calculation on PH5. In class, we essentially treated the F atoms as contributing on orbital to bond to the P. In other words, we completely ignored any lone pair electrons on the F atoms. *Spartan ’10* does not ignore those electrons. While a calculation can be done on PF5, the results will include the 15 lone pairs on the F atoms. This will only serve to complicate the MO diagram and as such, we will simplify the calculation and use PH5. In addition to the molecules from class, you should perform a calculation on NH3 and the molecule assigned to your group. You will want to pay attention to the energies for the MO’s that are calculated as well as the general shapes of the MO’s.

REPORT

This lab does not require a formal report. Your group report should address the following points.

1. Using the methodology from lecture, derive MO diagrams for NH3 and the molecule assigned to your group.
2. Include pictures of MO’s for all of the molecules you did calculations on. Be sure to list the energy for each filled MO and the LUMO. Also include the point group of the molecule as determined by *Spartan ’10*.
3. Based on comparison between the computational results and your results from question (1) and those in class, provide the proper symmetry labels to all of the MO’s calculated by *Spartan ’10*. Be sure to say if the orbitals are bonding, non-bonding or anti-bonding. If there are any discrepancies between your rough MO diagram and the results from *Spartan ’10* be sure to point them out and account for them.
4. Compare the following sets of molecules and explain any similarities and differences. This will require you to meet with other groups. You only need to do the comparison if you did calculations on one of the members of a given pair.

CH4 with SiH4

SiH4 with SH4

CH4 with SH4

PH6- with PH4+

PH6- with PH5

PH4+ with PH5