Lab 2:

Modeling Heats of Reaction

In this second computer exercise, you will calculate the combustion of the bipropellant used by SpaceX and compare its energy density to the world's most energetic molecule. The main purpose of this exercise is to familiarize yourself with accurate calculations of thermodynamics of reactions. You will also practice drawing a basic orbital interaction diagrams to rationalize the electronic structure of a molecule.

Methods:

In this exercise, the level of theory will be Density Functional Theory (DFT), using the B3LYP functional. We will use the Def2-SVP basis set, same as before.

For the optimizations, the input line in the orca input should be

! Grid4 B3LYP def2-svp opt freq

Modeling Combustion Reactions:

You will investigate the combustion of:

Methane and oxygen $\qquad$ $CH_4 + 2O_2 \rightarrow$

and

Nitryl cyanide $\qquad$ $NCNO_2 \rightarrow$

Assuming complete reaction to the lowest thermodynamic sinks, which molecules do you expect to form from methane oxidation and $NCNO_2$-decomposition? Before you do any calculations write out the stoichiometry above.

After that you have balanced the equations read the instructions for the program Avogadro below, and proceed with the orbital analysis of molecular oxygen. After that you have analyzed O_2, use Avogadro to create input files for all participating molecules in your reactions, and optimize each one. Make sure to include both the keywords *opt* and *freq*.

Instructions on how to use Avogadro:
This time we won't code the molecular structures by hand.
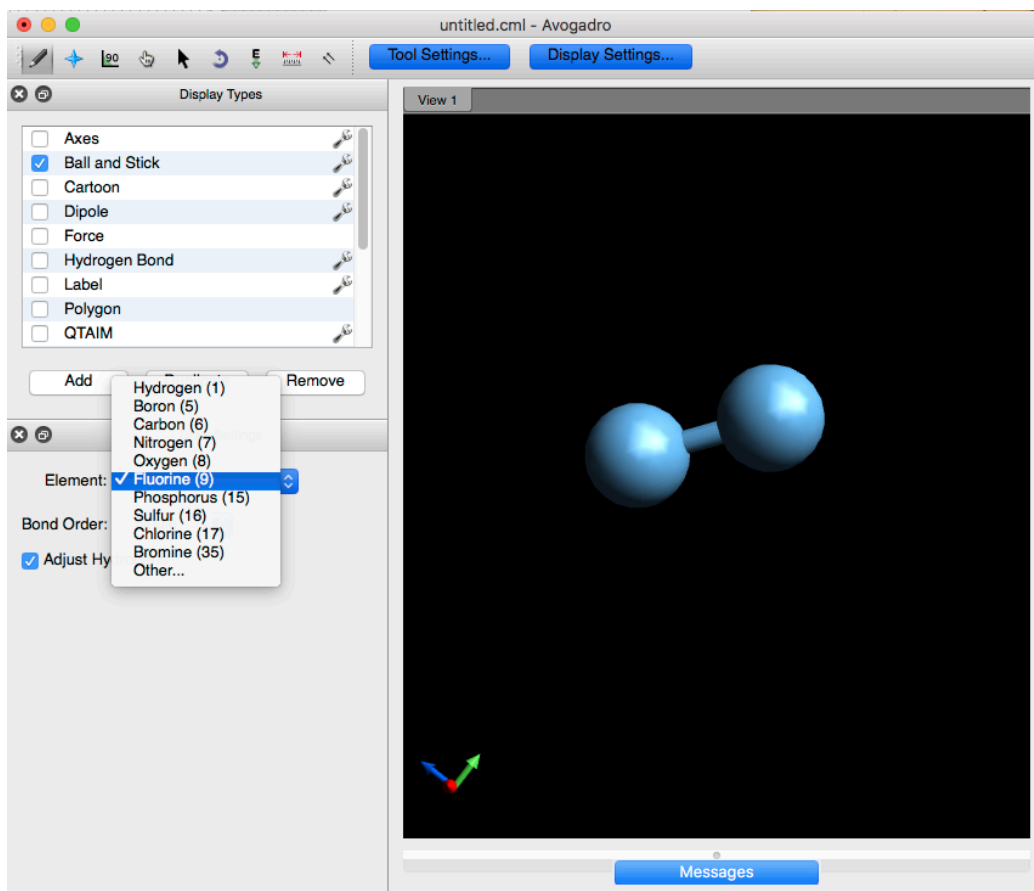
- Open Avogadro and select the draw tool from the toolbar

- Choose the element you want to build with from the *element* dropdown menu. Select *Adjust hydrogens* if you want the program to automatically bind hydrogens to your atom. Click in the view window to place your atom in your system.

- To indicate a bond between two atoms left click on one of the atoms and drag the mouse to its partner atom. To indicate a double or triple bond just left click on the bond.

- To remove an atom or bond, right click on the atom or bond.

- To change the element of an atom, select a different element from the element dropdown menu and left click on the atom you want to change.

- Choose the manipulation tool to drag atoms in a molecule or rotate or translate the molecule.

- When you have created a geometry that you are proud of select *Extensions* and then *Optimize geometry* to make a crude optimization of your structure using a built-in force field method.
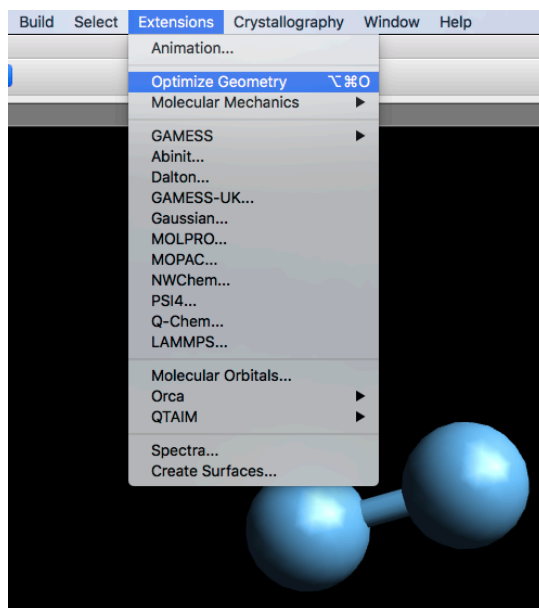
- To generate Orca input from Avogadro, go to *Extensions* and then *Orca -> Generate Orca input*
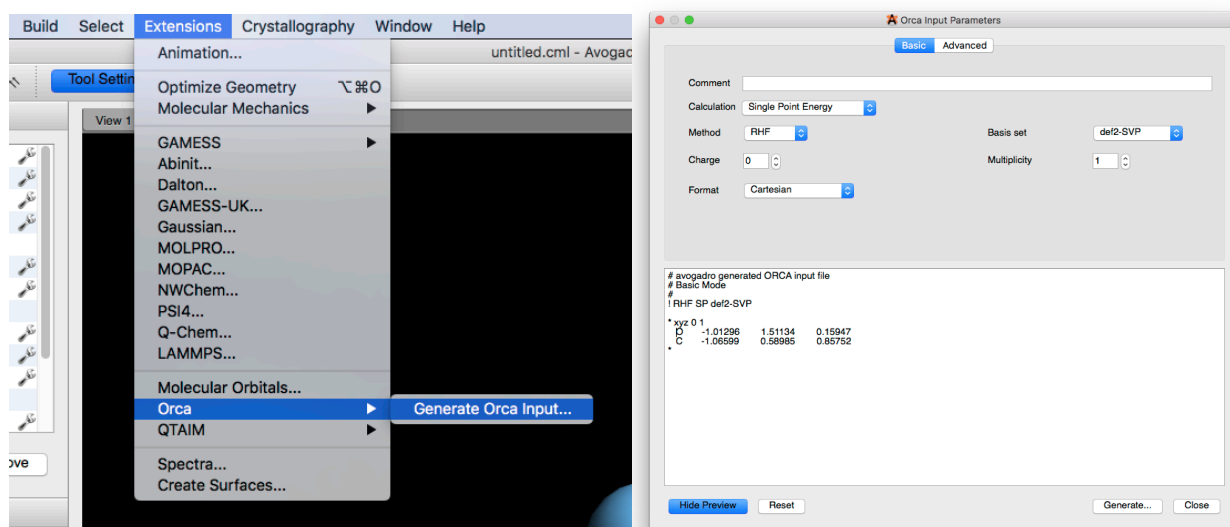
- From the popup window, you can now design your input file. In the calculation menu, you can choose the type of calculation you want to make, for example optimization or single point energy calculation. The geometry is per default in Cartesian coordinates. You can choose method (HF or DFT) and basis set from dropdown menus. If you do not find the method you want, you can edit the input file yourself by clicking on the preview. Charge and multiplicity can also be modified through dropdown menus or in the preview directly.

- Click on *Generate…* when you are finished modifying you input script. Save the file with the .txt extension in your working directory.

Orbital Analysis:

In the next section of this lab, oxygen is used as an oxidizing agent in a combustion of methane. Where does the energy come from?

First, ***without doing any calculations***, draw an orbital interaction diagram for O_2 and discuss which electronic structure you expect in the ground state. Sketch all valence orbital combinations and classify them with the correct labels (pointgroup $D_{\infty h} \rightarrow$ irreducible representations: σ_g, σ_u, π_g, π_u). Which orbitals are bonding and antibonding? Predict the multiplicity of O_2.

Secondly, calculate and compare the energy (*E*) of the triplet and singlet state of molecular oxygen, O_2. To visualize the molecular orbitals of the state with the lowest energy, perform a single point calculation on the optimized structure with the input:


```
! Grid4 B3LYP ROKS def2-svp
%output
print[P_basis] 2
print[P_mos] 1
end
…
```

Open the .out file in Avogadro to view the orbital shapes, their ordering and occupation. Does the calculation match your initial sketch of the MO diagram? What consequences do you think the electronic structure of oxygen have on its oxidizing strength, e.g. in a combustion reaction?

Thermal Corrections:

The *freq* keyword asks ORCA to perform a frequency analysis. This means calculating the second derivative of the energy expression with respect to the internal coordinates (also known as the Hessian). This is done analytically at the DFT level. The eigenvalues of the Hessian are force constants, which all need to be positive in a stationary state. Each force constant corresponds to a normal mode vibration, which can be visualized in Avogadro.

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

The frequencies of the optimized structure are listed under the last instance of the header "VIBRATIONAL FREQUENCIES" in the output file. If you see imaginary frequencies (written out as negative in the program output) it means that the structure is not a proper minimum. If so, modify the input and try the optimization again. If the molecule is flat or linear, Orca will not be able to calculate thermal corrections unless the molecule is completely symmetric. If you have issues, open the molecule in Avogadro and edit the coordinates of the

molecule so that the molecule is completely symmetric before optimizing and calculating frequencies.

The vibrational frequencies can be used to derive thermal and entropic corrections to the total energy. Search the output file for the following three energies, for each optimized structure:

```
FINAL SINGLE POINT ENERGY
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```
Total Enthalpy
```

```
Final Gibbs free enthalpy
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Calculate and discuss the reaction energy (ΔE), enthalpy (ΔH) and Gibbs energy (ΔG) for the two reactions, and discuss the effects of vibrational motion and entropy.

Energy Density:

Using your computed reaction enthalpies, ΔH, calculate the energy density for the two propellants in kcal/g and kcal/cm^3. The density of liquid methane, oxygen and nitryl cyanide are 0.424 ,1.14 and 1.24 g/cm^3, respectively. Discuss the implications for when you need to build a spaceship.

Energetic Extra Assignment 2:
(to be included in individual lab report for higher grades)

Nitryl cyanide, $NCNO_2$, holds promise as an exceptionally energetic future green propellant. However, its synthesis is very challenging due to poorly controlled side reactions that decompose the compound. In this extra assignment you will explore the electronic structure of $NCNO_2$ in search of ways to stabilize it. The stability of $NCNO_2$ is strongly related to the strength of the single bond between the CN group and the NO_2 group. Could we strengthen this bond, somehow?

$NCNO_2$ belongs to the point group C_{2v} and has ground state symmetry $^1A_1$. First, perform a single point calculation on the optimized structure with the input necessary to visualize the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). For this calculation use the same '%output' block as for O_2.

Secondly, use the character table provided in the lecture and determine the irreducible representations of the HOMO and LUMO molecular orbitals. For a correct assignment align the CN-group along the z-axis and the NO_2 group in the xz-plane.

Thirdly, sketch a Walsh diagram and *predict* how each of these molecular orbitals should change in energy as a function of the bond distance between the CN group and the NO_2 group. Note that you do not need to do any calculations in this step. Use this exercise to convince yourself which orbitals are bonding and antibonding with respect to the bond in question. Then discuss how you might change the bond strength by adding and subtracting an electron to the

molecule, forming a radical cation or a radical anion.

Finally, optimize the geometry of the two radicals of $NCNO_2$ and inspect the C-N bond distance between their CN and NO_2 groups. Knowing that bond strength correlates with bond distance, comment on what stability you predict for the three molecules (the neutral, the cation and the anion) with respect to dissociation into NO_2 and CN fragments.

Reminder: Criteria for higher (4 or 5) grades on individual lab report:

You do not need to present background theory on DFT or DFT functionals. But you do need to include a correct method description. Think of it this way: you are writing to another quantum chemist, who should be able to understand and reproduce what you have done. A quantum chemist who ideally should appreciate what you have found out. It is therefore very important to reflect and discuss your results.

Grade 4: A minimum of two out of three (2/3) energetic extra assignments performed and presented very well.

Grade 5: All energetic extra assignments performed and presented excellently.