4.3: Computational Instructions

Start by creating a folder for exercise 5 on the local hard drive of your computer and name it Chair Equilibrium. Within this folder, create a subfolder for the axial conformer and a subfolder for the equatorial conformer. In the next few steps, we will place the input files for computation into these nested folders. A description of this file structure is shown in figure 2.

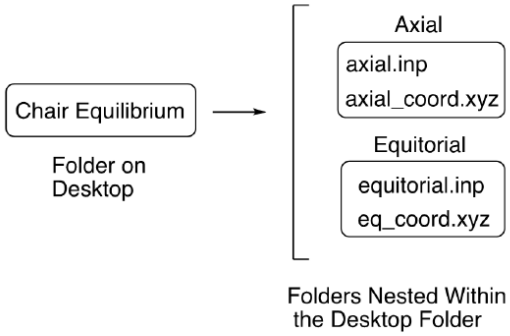

Figure 2: Example file structure for the cyclohexane chair computational exercise.

After you have created this set of nested folders, open Avogadro and draw the axial conformer of methylcyclohexane in the drawing window. The best way to accomplish this is to start by drawing cyclohexane (no specific orientation required) in Avogadro's drawing mode. After you have drawn a cyclohexane ring, optimize its geometry by clicking extensions → optimize geometry. This will form the cyclohexane ring into a chair. From here, go back into drawing mode by clicking the button shaped like a pencil and change one of the axial hydrogens into a methyl group (**Figure 3).** Save this file in the axial conformer folder that you created as axial_coord.xyz.

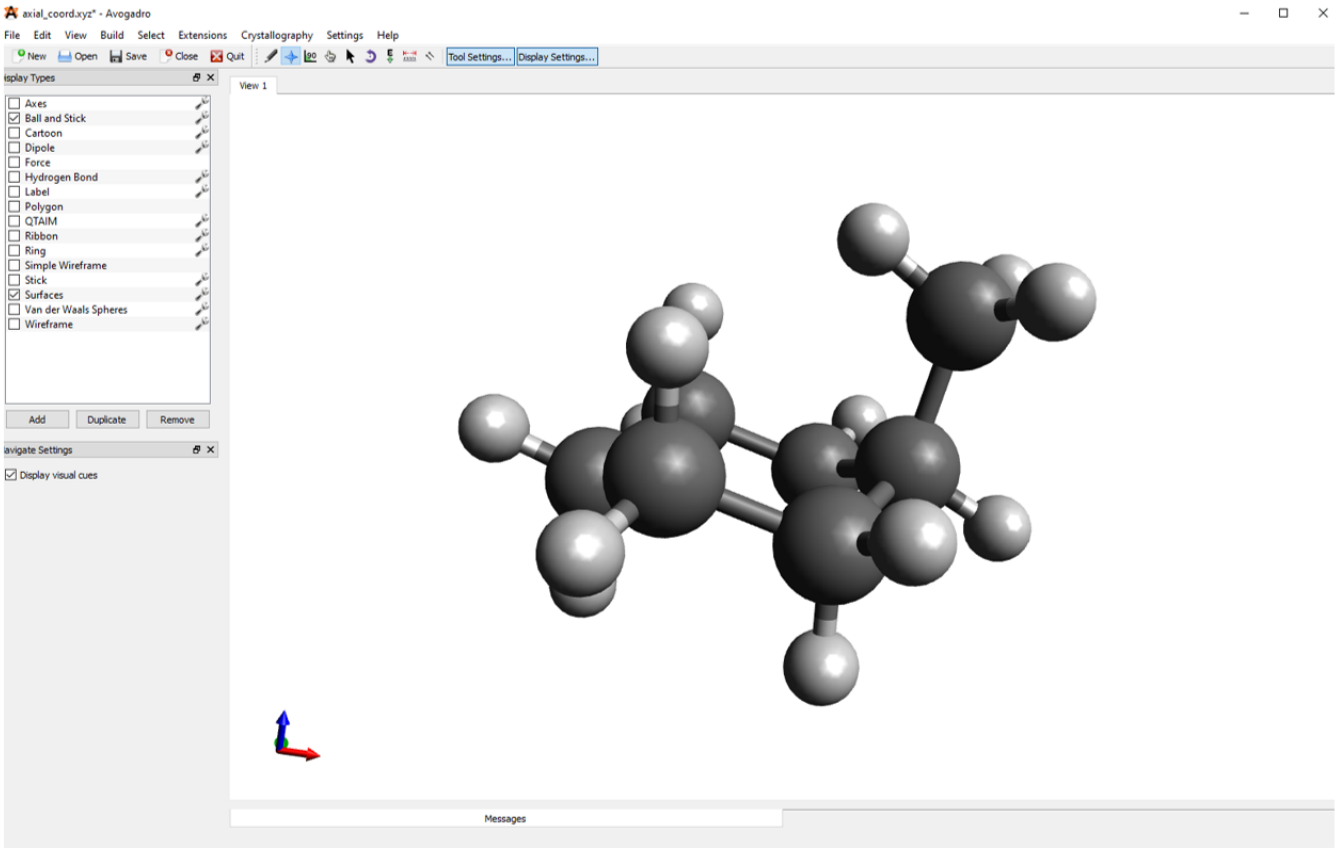

Figure 3. Drawing of the axial conformer of methyl cyclohexane

Next, you should download the template Orca input script and save it as axial.inp in the axial conformer folder that you have already saved the coordinate file. Open this file in notepad to modify it for use in determining the energy of the conformer. As

shown in Figure 4**,** you need to change the last line of the input script to match the coordinate file that you have created. You should change filename.xyz to the exact name of the coordinate file. Be sure to include the .xyz file descriptor at the end of the name.

```
# Axial methylcyclohexane energy
!B3LYP def2-SVP OPT FREQ

* xyzfile 0 1 filename.xyz
```

Figure 4. Generic conformer input script. You should change filename.xyz to the exact name of the coordinate file for the compound that you are calculating (axial_coord.xyz).

We can now run our calculation using Orca via the command line as we did in the previous exercise. Briefly, open the command prompt to your PC by right clicking on the start button and searching for command prompt. First, we need to tell the computer to look on the C drive and we do this by typing C: and hitting enter. Next, we need to tell the computer where the input script and the coordinates file are to run the calculation. We do this by typing cd (space) and pasting the file path. When you hit enter the computer will paste a new line indicating that the current directory has changed, as shown in Figure 5A. To find the file path of your input script, right click on the input script (axial.inp) and select properties. The file path will appear under location, and you can highlight and copy this file path (Figure 5B).

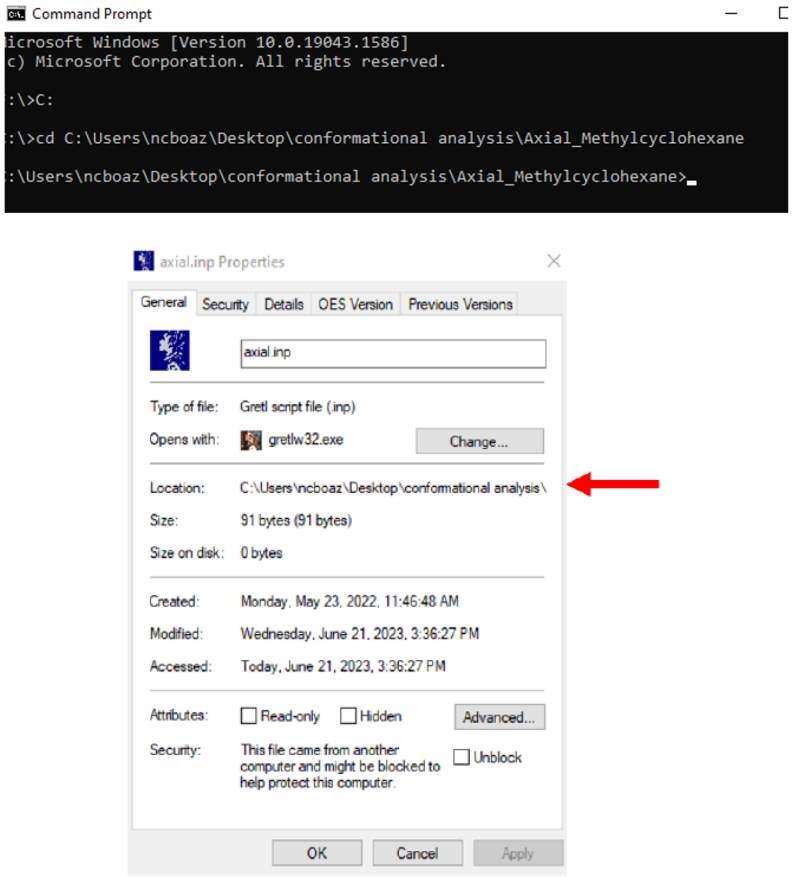

Figure 5A. (**Left**) Changing of the file path in the command prompt to match the location of our input script. **5B. (Right)** Locating the file path on the properties window of the input script (Red Arrow).

Next, we will run the calculation by typing orca axial.inp > axial.out and pressing enter. At first it may not appear like anything is happening, but the folder on your desktop labeled axial will quickly become populated with the output of your calculation. Depending upon the speed of your computer the calculation will take about 30-45 minutes, and upon completion the command prompt will print another line indicating that it is ready for the next command (Figure 6).

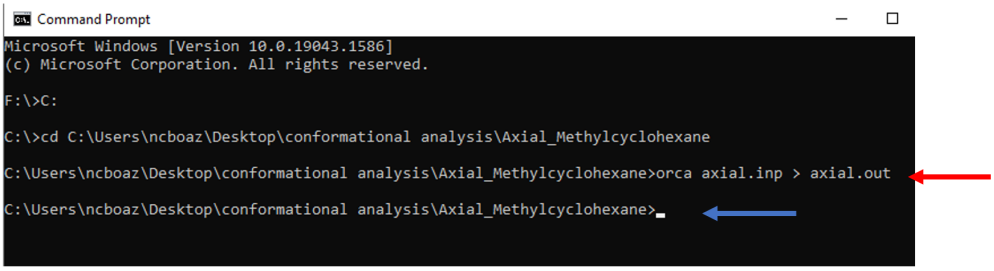

Figure 6. Running the calculation using the command line. The line indicated by the red arrow shows the computer that we want to use Orca to calculate the commands in axial.inp and that the results of this calculation should be placed in the output file axial.out. The line indicated by the blue arrow is the computer indicating that the calculation is complete, and the command prompt is ready for the next command.

After your Orca job has completed you can access the energy values by opening the output file (axial.out) in notepad. At the very end of the file (scroll to the bottom) will be the thermodynamic values that Orca calculated for the cyclohexane conformer as shown in Figure 7. The necessary value is adjacent to Final Gibbs free energy in the output file. Note that this value is given in Hartree (an energy unit). Your value of G may be very slightly different from the value below.

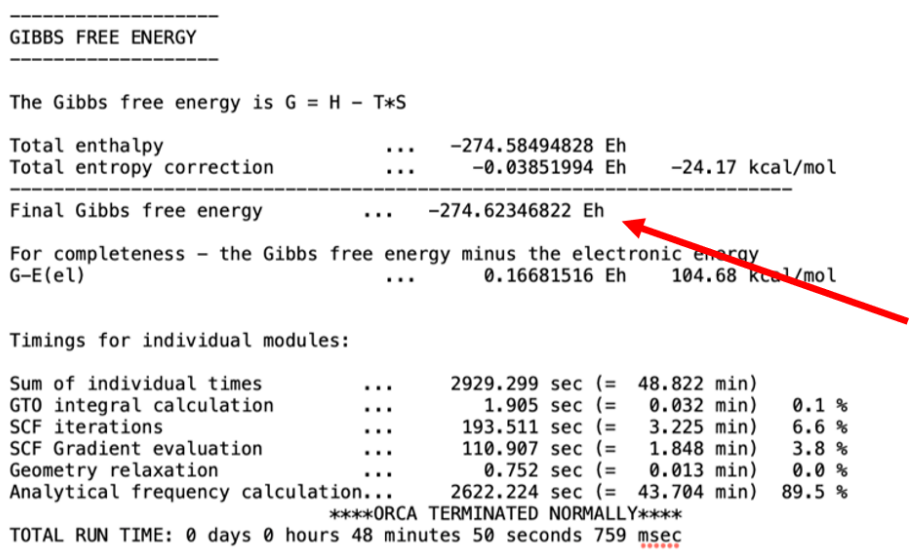

Figure 7. The output file for the axial conformer of methyl cyclohexane. The red arrow indicates where the Gibbs free energy value you should use.

At this point you have determined the energy of the axial conformer of methyl cyclohexane. To ascertain the difference in energy between the two conformers you will also need to determine the energy of the equatorial conformer of methyl cyclohexane. Using the method that you have determined the energy of the axial conformer as a guide, calculate the energy of the equatorial conformer of methyl cyclohexane. You can run both of the calculations at the same time by opening another command prompt window. After completing computational component of this exercise, please complete the questions at the end of this assignment.

References

1. Neese, F. The ORCA Program System. *WIREs Comput. Mol. Sci.* **2012**, *2* (1), 73–78. https://doi.org/10.1002/wcms.81.
2. Neese, F. Software Update: The ORCA Program System, Version 4.0. *WIREs Comput. Mol. Sci.* **2018**, *8* (1), e1327. https://doi.org/10.1002/wcms.1327.
3. Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA Quantum Chemistry Program Package. *J. Chem. Phys.* **2020**, *152* (22), 224108. https://doi.org/10.1063/5.0004608.
4. Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *J. Cheminformatics* **2012**, *4* (1), 17. https://doi.org/10.1186/1758-2946-4-17.
5. *Avogadro: An Open-Source Molecular Builder and Visualization Tool.*