

Introduction to Quantum Chemistry Simulations with ORCA

HPRC Short Course Series

This tutorial is designed to get you started on setting up an ORCA calculation on vidi of Texas A&M High Performance Research Computing (HPRC) resources. ORCA runs completely from the command line, there is no native graphical user interface. In this tutorial, we will demonstrate how to use Avogadro (<https://avogadro.cc/>) and Molden (<http://www.cmbi.ru.nl/molden>) to build molecular geometries and visualize results. In the instructions, **bold** means to type what is in bold exactly as you see it, *italic* means to replace what is italicized with the appropriate text (ie *blank line* should be replaced with a blank line, *title* should be replaced with a descriptive title), `_` is a symbol that will be used to indicate that there should be a space in that location, text inside a box means a `button` to click, and `↵` is a symbol that will be used for the enter/return key.

To run an ORCA calculation, you must first create an input file. The input file should contain the keywords for the type of calculations (level of theory, basis sets, job type, etc.), the coordinates, charge, and spin multiplicity of the molecule being studied and to be performed.

I. Set up environments and run ORCA calculations

1. On your desktop, double click on the orca/h2/ folder, you should be able to see the h2.inp. Double click to open the file.
2. This is a sample ORCA input file.

```
! B3LYP OPT FREQ def2-SVP  
# This is just a comment.
```

```
%pal  
nprocs 2  
end
```

```
*gzmt 0 1  
H  
H 1 0.8  
*
```

Details about the input file lines:

(ORCA Input files are pretty much free-format. Blank lines are allowed, input is usually not case-sensitive. One can create comment lines by adding the "#" symbol to a line.)

! start a keyword line. In the Simple input syntax, keywords are added in any order to the line beginning with "!". Multiple "!" lines are also allowed.

B3LYP– use the B3LYP density functional for the calculation (method)

OPT – perform a geometry optimization

FREQ – perform an analytical frequency calculation (if opt and freq are both present, an optimization is performed 1st and then a frequency calculation on the optimized structure)

def2-SVP – use the def2-SVP basis set

Comment lines can be added if the line begins with a #.

% Start a block input. Advanced settings are often specified using the block input for different modules.

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pal – control of parallel jobs

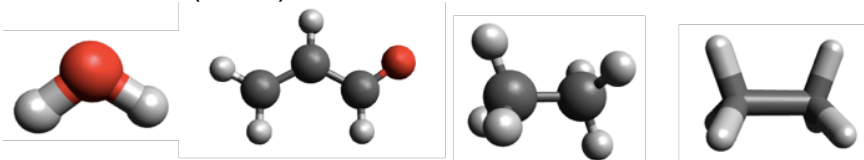
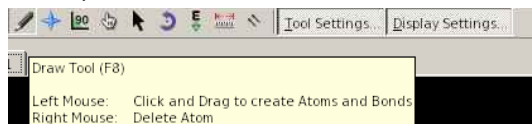
nprocs 2 – run the job with 2 cores in parallel

***gzmt** – Start of geometry input in the form of Gaussian Z-Matrices.

0_1 – charge and spin multiplicity of your molecule. Spin multiplicity = $2S+1$ where, S is the total electron spin of the molecule. If a molecule has 1 unpaired electron, $S=1/2$ and the spin multiplicity=2

***** – End of coordinate definition.

- Close the input file.
- Now that we can run the calculation with ORCA in command line. On your desktop, Right click at the background inside the h2 folder and choose open in terminal. To set up the environment, type: **module_load_sc/orca** at the prompt.
- Type: **\$ORCA_HOME/orca_h2.inp > h2.out**
- You can ignore the information print out in your terminal following the job submission. A large number of temporary files will appear in your h2/ directory (click reload in file browser). When the job is finished, no more lines should print out in your terminal and temporary files will disappear in h2/ folder. The running generally takes about 30 seconds. We will now look at the output file. In your file browser, double click to open the h2.out and scroll down to the bottom of the file. If you see the line "****ORCA TERMINATED NORMALLY****", this indicates you just successfully performed an ORCA calculation! (Don't forget to vote the poll in zoom.)
- Now it's your time to practice with Avogadro, a free and open source molecular editor. Type **avogadro&** in prompt (Click  to close Wine Mono Installer and Wine Gecko Installer if it pops up). Hover your mouse over the icons in the tool bar (see figure above) and get yourself familiar with the interface([user guide](#)). See if you can draw the following molecules. You do not have to finishing drawing these molecules as you can always download Avogadro on your own machine and practice later. Close Avogadro without saving and exit the terminal (**exit**) before the next session.



II. Geometry optimization and frequency calculation: A water molecule

- On your desktop, double click to open the orca/water directory. Right click to open the terminal and load the module (**module_load_sc/orca**). Open an Avogadro window (**avogadro&**) and draw a water molecule. Make sure you only have one water molecule in the view. Click **Extensions** ->Orca ->Generate Orca input. In the preview window, make changes manually so that your input looks similar to this. (Your coordinates may be different from mine.)

```
!BP86 def2-SVP opt freq  
!largeprint
```


```
%pal
```

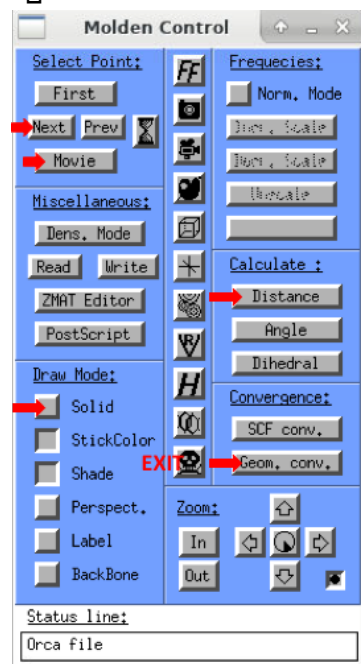
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```
nprocs 2
end
```

```
* xyz 0 1
O   -3.56626   1.77639   0.00000
H   -2.59626   1.77639   0.00000
H   -3.88959   1.36040  -0.81444
*
```

- Click **Generate** and find your home/*username*/Desktop/orca/water/ directory. Save the file as water.inp. Close Avogadro and discard changes.
- Submit the calculation using terminal
(**\$ORCA_HOME/orca_water.inp>water.out**↵).
- Wait for the job to finish (<1 minutes) and open water.out in file browser. You may need to reload  to see the output. Check if your job terminate normally. Close the output before move to the terminal.
- To visualize results with Molden, type in prompt: **molden_water.out**↵
- Change the draw mode by clicking **Solid**->Stick under Draw Mode. To change a perspective, left-click, hold, and drag to rotate the molecule.
- Click on the **Distance** button and then select the hydrogen atom and then the oxygen atom (You need to click at the very center of the atom or Molden does not respond). In the pop-up Calculate window, click the **monitor** button. You should see the bond distance appear in the window on the molecule.
- To visualize the change in the geometry that occurred during the geometry optimization, click on the **Geom. conv.** button. The Geom. Convergence window has a chart of energy vs. point, which shows how the energy of the molecule change as it was optimized and how many geometry optimization steps it took. Move the new window over such that you can see it and the molecule at the same time and then click on the **Next** button. You should see the geometry change. **NOTE:** Molden always starts by displaying the input structure (starting structure) and NOT the optimized structure. After you click the **Movie** button, molden will display the last geometry in the out file, which will be the optimized structure if the optimization finished normally. Close the Geom. Convergence window.
- Exit molden by clicking on the button with the **skull and cross-bones**.
- (Only for demonstration/Optional) Convert result into Molden file to visualize molecular orbitals. Type in prompt: **\$ORCA_HOME/orca_2mkl_water_-molden**↵ ; then **molden_water.molden.input**↵; In molden control panel, click **Dens. Mode**, **Orbital**, **Space**, change contour value to 0.2 and apply. You should be able to see plots of MOs. Switch back to **Mol. Mode** and exit molden.

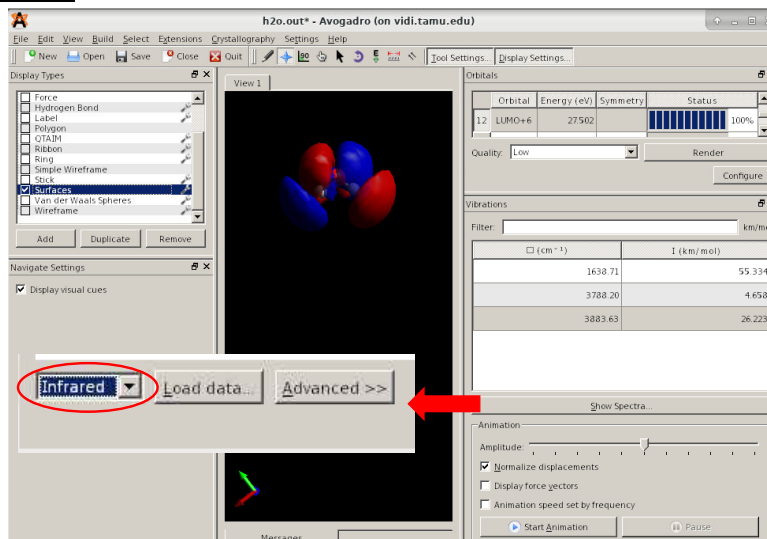



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18. Now we will use Avogadro to visualize the normal modes (vibrations). In the prompt, type: **avogadro_water.out**. You should be able to see a column on the right for vibrations. H₂O has 3 normal modes (3N-6). Select the first row of vibrational frequency and click **Start Animation** at the bottom. The molecule should start to vibrate. You may want to rotate the molecules to view it from a different perspective and examine the other two normal modes.

19. Stop the animation and click **Show Spectra**. A new window pops out. Change the box on the left corner to **Infrared**. You can change the background color by clicking **Advanced**. Under **Appearance** tab, choose **light**. Avogadro also allows you to adjust peak width, change scale factor, and export spectra to data/image files. Close the spectra.



20. In Avogadro, the top part of the column shows a table of molecular orbitals. You can close the vibration section to display more rows of MO. Scroll down to find HOMO and LUMO. Clicking in the row of an orbital with a full status bar  will create a quick low-quality rendition of the orbital. (**Configure** allows you to adjust the isosurface value for the orbital.) Now you can close Avogadro without saving and move to the terminal.

21. Extract the geometry optimization convergence criteria at each geometry step and after the frequency calculation by typing at the prompt: **grep -A17 'Geometry convergence' water.out**

The last set of lines is the convergence for the last step of geometry optimization. Did the geometry optimization reach convergence? You should be able to find this pattern in the output.

```
*****HURRAY*****
*** THE OPTIMIZATION HAS CONVERGED ***
*****
```

22. Extract the vibrational frequencies by typing at the prompt: **grep -A15_FREQUENCIES_ water.out**


The first six frequencies are 0 (ORCA counts from 0). You should have all real frequencies for a minimum (or 1 imaginary frequency labeled with a minus sign for a 1st order saddle point, i.e. transition state). If you have more than 1 imaginary mode then you have optimized to a higher order saddle point on the potential energy surface or the geometry optimization was not converged.

23. Extract pure electronic energy E, H^o and G^o by typing at the prompt (In ORCA, G = H - T*S is referred to as Gibbs free enthalpy, not energy):
grep 'Electronic_energy' water.out >> water.txt
grep 'Total_Enthalpy' water.out >> water.txt

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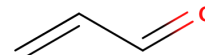
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```
grep 'Final_Gibbs_free_enthalpy' water.out >> water.txt
```

24. Reload the files , view the water.txt file and exit the terminal (type in prompt: **exit**). (Please take the poll in zoom and take a short break:)

III. Predict UV/Vis for propenal with TD-DFT calculations

25. Under the orca/propenal/ directory on your desktop, you should be able to find a file named propenal.xyz, which contains the optimized coordinates of propenal at the B3LYP/def2-SVP level of theory.



26. Right click to create a new document named td.inp in the propenal/ directory. Double click to open the file and copy/type the following contents to td.inp:
! B3LYP def2-SVP LARGEPRINT

```
%pal
nprocs 2
end
```

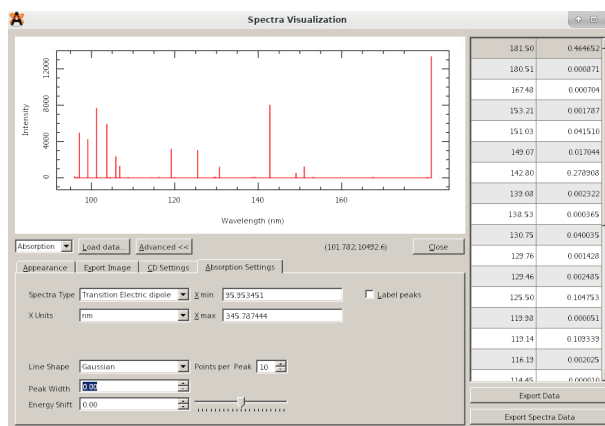
```
%TDDFT
NROOTS 30
END
```

```
*xyzfile 0 1 propenal.xyz
```

27. Right click to open a terminal under the propenal/ directory and load the orca module (**module_load_sc/orca**). Submit the td.inp to ORCA.

```
$ORCA_HOME/orca_td.inp > td.out
```

28. When the calculation finishes, open propenal_td.out with Avogadro (type in prompt: **avogadro td.out**) and check the spectra from menu **Extensions > Spectra**. Change to **Absorption** spectrum and adjust the range and peak width as you need. (These results usually does not match the experiment very well. It is much more prevalent that the predicted spectra is "shifted" by ± 0.1 to ± 0.5 eV and it is customary in the literature to fix that, if there is any reference, to correct systematic errors.)



29. To find the excitation information in the output file of the TD-DFT calculations, go to the file browser and double click to open **td.out**, use search tool to find **EXCITED**.
30. Below the energies (given in au, eV, and cm^{-1}), the contributions of each single excitation are printed, first with its relative contribution, followed by the eigenvector value.

```
STATE 1: E= 0.131767 au   3.586 eV  28919.5 cm**-1
14a -> 15a : 0.979239 (c= -0.98956485)
14a -> 16a : 0.018814 (c= -0.13716449)
```

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Excited State 1 composed of about 98% a HOMO to LUMO transition, from orbital 14 to orbital 15 (the "a" there means alpha orbital). Therefore, you could visualize MO 15 and 16 in Avogadro to determine their character and symmetry. (Note: ORCA counts orbital from 0 while Avogadro counts from 1)

31. Scroll down a few pages, you will be able to find the states and their respective vertical transition energies under the "ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS" section, together with the oscillator strength (fosc, proportional to the extinction coefficient) and transition dipole moments. From the calculation, we only get transition lines, not bands, as spectrum measured from experiment. (Please take the poll in zoom:)
32. (Optional) Find excited states with the relatively large oscillator strength, identify excitation(s) that has major contribution to the excited state, and visualize corresponding orbitals with Avogadro.
33. When finished, close Avogadro and exit the terminal. Click System from the menu listed on top of the screen to log out your account.