Using ORCA 4.2.1 on the Hoffman2 Cluster

Courtesy Martin Riu and the Houk Lab; please update or add to the document as new information becomes available!

Please Read: The goal of this SOP is to introduce the reader to submitting calculations to the Hoffman2 cluster using the ORCA quantum chemistry package. You can find more information on the Hoffman2 cluster using the following link: https://www.hoffman2.idre.ucla.edu/. Unlike Gaussian, ORCA has an excellent manual that will answer most of your questions. It also includes many examples that you can follow. Please create an ORCA Forum account (https://orcaforum.kofo.mpg.de/app.php/portal) and download the ORCA 4.2.1 manual (I also downloaded it onto the group computer). Note that there is no GUI for ORCA, so calculations are submitted using command line. If you are new to command line, refer to the following website: https://ubuntu.com/tutorials/command-line-for-beginners#1-overview.

Recommended Software

Avogadro

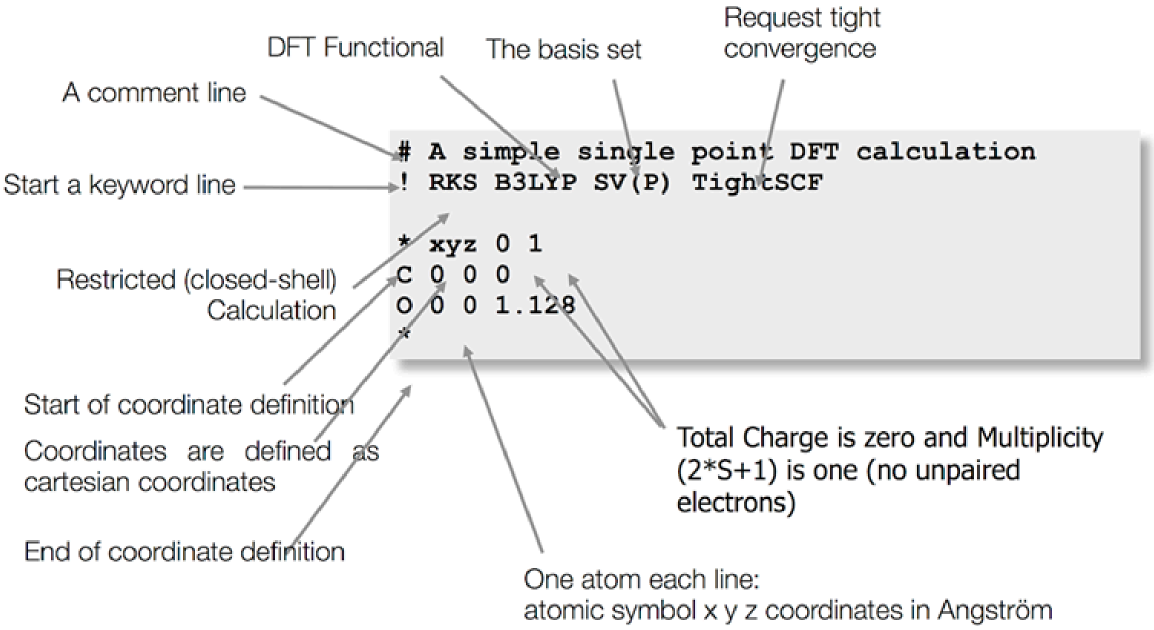
MobaXterm (refer to the Gaussian SOP)

The Input File

A sample job input file is shown below. Here, B3LYP is the method (DFT functional), def2-SVP the basis set and Opt is the jobtype (geometry optimization). Order of the keywords is not important. Cartesian coordinates (coordinates for water shown below) can be obtained using a molecular editing software, such as Avogadro. Generally, it's a good idea to optimize the molecular geometry using Grimme's GFN2-xTB software (see Tan's SOP). If you are unsure about what DFT functional or basis set you should use, read through some papers (computational section/supporting information) that run similar calculations.

```
 ! B3LYP def2-SVP Opt

  *xyz 0 1

O          -2.98023        -1.81780        0.01751

H          -1.99090        -1.78707        -0.01236

H          -3.26959        -1.13865        -0.64251

*
```

Input file guide:



```
# A simple single point DFT calculation
! RKS B3LYP SV(P) TightSCF

* xyz 0 1
C 0 0 0
O 0 0 1.128
*
```

For geometry optimization and frequency calculations, I use the following input file as a starting point. The functional and level of theory are sufficient for organic molecules and lighter d- and p-block elements. Always perform frequency calculations on optimized structures to ensure that it does exhibit any imaginary frequencies. If there are imaginary frequencies the structure is not at a local/global minimum (remember that an optimized transition state structure will exhibit a single imaginary frequency). The level of theory must be identical for the structure and frequencies or you will get imaginary frequencies or meaningless results.

```
 !B3LYP D3BJ def2-TZVP def2/J RIJCOSX TightSCF

!Grid6 FinalGrid7 GridX6 Opt NumFreq

%PAL nprocs 8 end

%MaxCore 2048

*xyz 0 1

[coordinates]

*
```

Submitting the Calculation

1. Create a folder containing your ORCA input file ‘job.inp’ and ‘ORCAsub.py’. ORCAsub.py, along with other helpful files, will be uploaded onto the group website under instrument SOPs.

2. Log into the Hoffman cluster using MobaXterm using your user ID and password. This will open up a terminal session and lefthand panel where you can navigate the cluster and drag and drop your files.

3. Transfer the folder into your directory on the Hoffman cluster using MobaXterm.

4. Run your calculation by entering the following command on terminal,

```
$ python2 ORCAsub.py job.inp
```

5. You can follow your calculation using the following command,

```
$ tail -f job.out
```

6. If your calculation terminated normally, you will see the following text at the end of ‘job.out’. It is recommended that you use the ‘vi’ text editor software to quickly navigate your files within terminal.

```
****ORCA TERMINATED NORMALLY****

TOTAL RUN TIME: 0 days 0 hours 20 minutes 44 seconds 619 msec
```

The default parameters of ORCAsub.py are 8 cores, 4GB per core, and 24 h runtime. If you would like to use, for example, 12 cores, 48 GB, and 48 h, with ORCA 4.1.1. Note that there is a 24 h calculation time limit set for our lab.

```
$ python2 ORCAsub.py -p 12 -t 48 -O 4.1.1 job.inp
```

If you are changing the number of cores used, make sure you also change the %PAL option accordingly (e.g. `%PAL nprocs 16 end` if you are using 16 cores).

Transition State Optimization and the Nudged Elastic Band Method

This method can be used to find the TS structure from the geometries of reactants and products. I normally use keyword zoom-neb-ts for these calculations. The obtained saddlepoint structure is often not well optimized, so I will often use the structure (or pre-optimized structure) as a starting geometry for a TS optimization (using the OptTS keyword) with an exact Hessian in ORCA. Prior to running the NEB calculation, I will run a preliminary optimization. In the calculation below, I'm investigating the dissociation a monodentate ligand from a metal complex. Here, I'm constraining the metal ligand bond distance to 3.7 Angstroms and optimizing the geometry. The output of this final will be used as our "final.xyz" file for the NEB calculation. You will probably end up applying a different constraint depending on the TS structure you're looking for. Read more here about constrained optimizations. Here I'm using r2SCAN-3c, which is referred to as a "swiss army knife" Read more about it here.

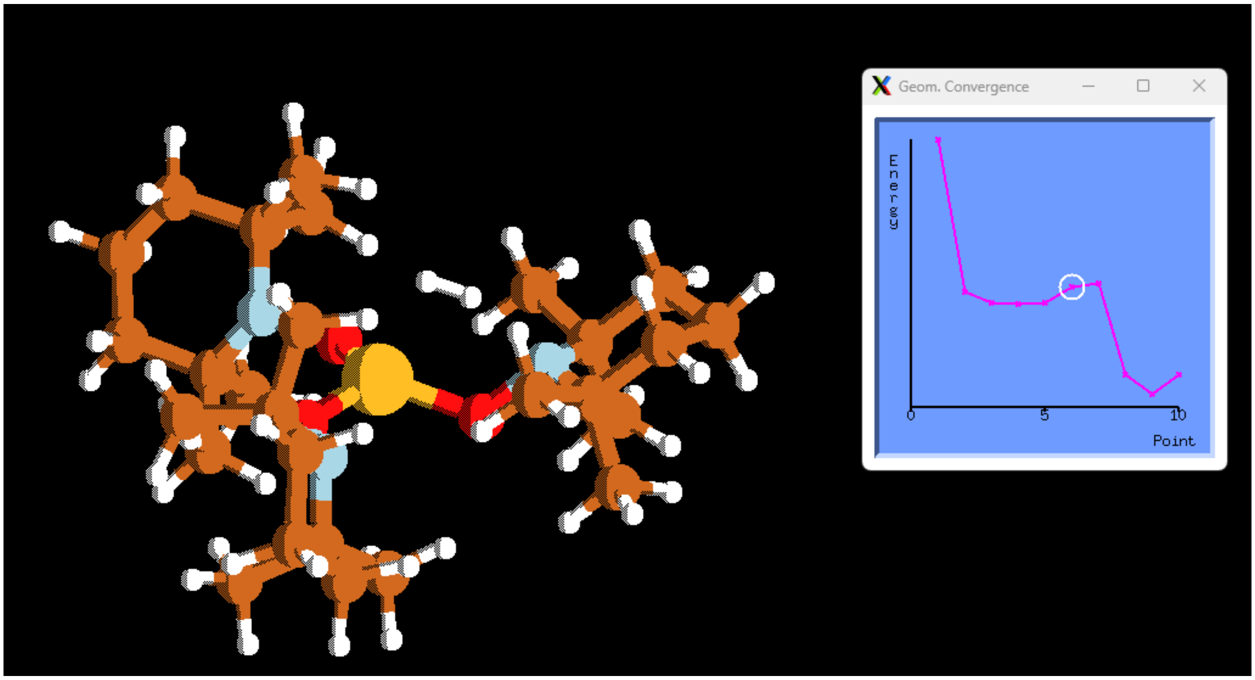
```
!r2SCAN-3c Opt

%pal nprocs 16 end

%maxcore 8000

%geom

    Constraints {B 7 129 C}

    end

end

*xyzfile 0 1 /u/home/m/mriu/model.xyz
```

Provided below is a sample input file for the "black box" NEB-TS method. Here I will be using 10 images to describe the PES (the more images you use, the more expensive the calculation will be). Read more here about the NEB method.

```
!ZOOM-NEB-TS

%PAL nprocs 16 end

%neb
```

```
    neb_end_xyzfile "/u/home/m/mriu/MYR-24-0016/Ga_TS/final.xyz"

    Nimages 10

end

*xyzfile 0 1 /u/home/m/mriu/MYR-24-0016/Ga_TS/starting.xyz
```

You can easily visualize the trajectory (job_MEP_trj.xyz) using Molden. An example is shown below.



Next, I will take the geometry of the model shown above and optimize it using the OptTS keyword. You will first have to run a hessian calculation on the model (if our calculations are restricted to 24 h).

```
!B3LYP D3BJ def2-TZVP def2/J RIJCOSX TightSCF NumFreq

%PAL nprocs 32 end

*xyzfile 0 1 /u/home/m/mriu/MYR-24-0016/Ga/Hessian/model.xyz
```

If you have unlimited cluster time, you can use the following input file instead. This calculation will run a frequency calculation on your pre-optimized structure and feed the results into an OptTS calculation. After the saddle point is optimized, a frequency calculation is run on the optimized structure. Click here to learn more.

```
!B3LYP D3BJ def2-TZVP def2/J RIJCOSX TightSCF OptTS NumFreq
```

```
%geom

Calc_hess true # Request an exact analytical Hessian in the first optimization step

end

%PAL nprocs 32 end

*xyzfile 0 1 /u/home/m/mriu/MYR-24-0016/Ga/Hessian/model.xyz
```

Above, an analytical Hessian is calculated; however, make sure it is compatible with the functional you're using. Alternatively, you can request a numerical Hessian instead (below). Generally, analytical Hessian are faster than numerical Hessian calculations, but they consume more memory.

```
!B3LYP D3BJ def2-TZVP def2/J RIJCOSX TightSCF OptTS NumFreq

%geom

Calc_Hess true # Request an exact Hessian in the first optimization step

NumHess true # Request the numerical exact Hessian (only one available for this method).

end

%PAL nprocs 32 end

*xyzfile 0 1 /u/home/m/mriu/MYR-24-0016/Ga/Hessian/model.xyz
```

Coming Soon…

DLPNO-CCSD(T)

LED

NMR Prediction

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