



Introduction to Computational Chemistry

Exercises Part 5

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Goals:

- Calculating different spin states
- Performing stability analysis
- FOD analysis

Setting up calculations for organometallic compounds is often not harder than for organic compounds. However, the calculations can be more finicky and there are cases where plain old DFT won't be reliable. We will practice a few simple techniques to diagnose some of the common issues you may run into. For simplicity, we will neglect the organic part of organometallics and play with the notorious chromium dimer (Cr_2).¹

1 SCF issues

We will look at three ways to check for “warning signals” that the structure you provided cannot be reliably described by your method:

1. SCF convergence
2. Stability analysis
3. Spin contamination

The first potential “warning signal” is the SCF calculation not converging (that being said, non-convergence doesn't have to mean that there is a problem and some structures simply need more love to converge). In this case your output file will be terminated by:

```
*****
*                               *
*               ERROR           *
*   SCF NOT CONVERGED AFTER 125 CYCLES   *
*                               *
*****
```

In the Handout we have provided a link to the ORCA Input Library that offers some useful suggestions how to deal with convergence issues. Luckily, in the newest ORCA version, such issues are really exceedingly rare.

Unfortunately, even if the SCF calculation converges, it might still be possible that the calculation didn't converge to the correct (minimum energy) wavefunction. In this case, it is said that the wavefunction is not “stable”. You can ask ORCA to check the stability of the wavefunction by including the %scf block shown below.

¹To get an appreciation of the fame (or infamy) of Cr_2 , just check the title of this recent paper: <https://doi.org/10.1021/jacs.2c06357>.



```
! Keywords
%resources
%scf
STABPerform true
end
#rest of the input
```

If the wavefunction is stable, the output will have a section that reads

```
Stability Analysis indicates a stable HF/KS wave function.
```

If there is a problem, you will most likely get something similar to

```
Stability Analysis indicates an UNSTABLE HF/KS wave function with SEVERAL negative eigenvalues.
```

In this case, ORCA will restart the SCF calculation based on the stability analysis. This new solution may or may not converge (in the latter case, you should either consult the ORCA manual or your local computationalist).

To quickly access the result of the stability analysis from the terminal, use the `grep` command like last time.

```
grep "Stability Analysis indicates" dummy.out
```

Note: The stability analysis is not printed fully in the output file if you have requested `Miniprint` in the input file.

The third piece of information that can alert you to some potential problem is spin contamination. To check this, you can look for the section in the output where the expectation value of S^2 is compared to the ideal value of $S(S+1)$. If the deviation is larger than $\sim 10\%$, there is a problem. Note that ORCA prints a message that within DFT the calculation of $\langle S^2 \rangle$ has little theoretical justification; however, we can still use it as a warning sign.

Open the output file in a text editor and search for “UHF SPIN CONTAMINATION”.

You can again use the `grep` command:

```
grep "Expectation value of" -A 2 dummy.out
```

where the flag `-A 2` indicates that it should print the two subsequent lines as well.



2 Chromium dimer

Note: The following calculations are quite quick, so it is easier to go through this exercise by running the calculations in an interactive job, rather than submitting each calculation separately:

```
srun --pty bash      # for Euler
salloc               # for Grace
```

Once you've accessed a compute node interactively, you can run the calculations just as:

```
orca input.inp > output.out
```

The > symbol directs the output stream into the specified file (i.e., it won't be printed in the terminal). To have the output written into a file as well as the terminal, you can use the following command:

```
orca input.inp | tee output.out
```

where | is called a *pipe* that passes the output from the preceding command into the input of the following command – in this case **tee**, which acts as a “T-splitter” and writes into the file and the terminal.

If you're asking for more than 1 core in your input, you have to call **orca** with the full path to the executable (otherwise the calculation will crash right away). You can get the full path with

```
which orca
```

This prints the full path to **orca** in the terminal. You must use that path to run calculations with multiple cores:

```
/full/path/to/orca input.inp | tee output.out
```

For simplicity, we will compare just two spin multiplicities: singlet (open- and closed-shell) and quintet. The task is to calculate which spin state is more likely to be the ground state at the given bond length.

2.1 Simple calculation

The input for our calculations is fairly straightforward. We'll use the BP86 and PBE0 functionals with the def2-TZVP basis set.² Below is the input for the open-shell singlet calculation with BP86. For the closed-shell calculation remove the UKS keyword, and for the quintet calculation simply change the multiplicity from 1 to 5. For the sake of convenience, we have explicitly written the coordinates into the input file instead of a separate xyz file. Take care if you copy this from the PDF file, as it can introduce spaces in the text.

```
! UKS BP86 def2-TZVP
%pal nprocs 1 end
%maxcore 1024

*xyz 0 1
Cr 0 0 0
Cr 0 0 1.68
*
```

Run the aforementioned six calculations, and check the SCF convergence and spin contamination. Extract the FINAL SINGLE POINT ENERGY and assess which spin state is lower in energy. Compare the results from the UKS and RKS calculations.

2.2 Stability analysis

Let's now redo the same calculations but with the stability analysis option enabled. The open-shell singlet calculation input with BP86 is shown below.

²You may notice that we are not using the D3BJ correction that we recommended last week. As this correction would be the same in all our calculations, it would not change the relative spin state energies, and we can neglect it for simplicity.



```
! UKS BP86 def2-TZVP
%pal nprocs 1 end
%maxcore 1024

%scf
stabperform true
end

*xyz 0 1
Cr 0 0 0
Cr 0 0 1.68
*
```

Were the initial calculation results stable? Check again for spin contamination and extract the **FINAL SINGLE POINT ENERGY**. Which spin state would you predict to be lower in energy based on the new results?

Note: For RKS, ORCA will analyze the stability but will not perform an additional SCF calculation even if the solution is unstable. In these cases, the final energy is 0 with a warning.

2.3 FOD analysis

For the final check of our results, we will analyze the Fractional Occupation Density (FOD). It is a simple (but coarse) approach to diagnose multireference character. No other keywords are needed apart from FOD:

```
! FOD
%resources
*xyzfile 0 1 dummy.xyz
```

This will use the default setting, which are TPSS functional with def2-TZVP basis set. Additionally, electronic temperature is set to 5000 K, so that the electrons are “smeared” over the frontier molecular orbitals.

Below is the input for the quintet calculation.

```
! FOD
%pal nprocs 1 end
%maxcore 1024
*xyz 0 5
Cr 0 0 0
Cr 0 0 1.68
*
```

You can extract the `N_FOD` number either with a text editor or by using `grep`.

```
grep "N_FOD" fod.out
```

There unfortunately aren’t any standardized threshold values for `N_FOD` to tell you when you have a problem, but values above 1 are usually an ominous sign.

Further information can be gathered from FOD visualization. To this end, we must generate the FOD plot from the wavefunction. For all calculations, ORCA stores the wavefunction in the `.gbw` file (which is human non-readable, but ORCA-readable). We need to use the `orca_plot` tool, which is another useful ORCA utility. To use it, type

```
orca_plot filename.gbw -i
```

You will be prompted with an interactive menu that you can navigate by entering numbers:



```
Entering interactive generation of plots ...
...
...
  1 - Enter type of plot
  2 - Enter no of orbital to plot
  3 - Enter operator of orbital (0=alpha,1=beta)
  4 - Enter number of grid intervals
  5 - Select output file format
  6 - Plot CIS/TD-DFT difference densities
  7 - Plot CIS/TD-DFT transition densities
  8 - Set AO(=1) vs MO(=1) to plot

 10 - Generate the plot
 11 - exit this program
Enter a number:
```

Simply follow the steps below:

- Select 1 (Enter type of plot) and then 2 (electron density), press n and type `basename.scfp_fod` (substitute `basename` with the `basename` of your file)
- *Optional:* Select 4 (Enter number of grid intervals) and type a number, 60 is a good compromise. The higher the number, the better the quality, but also the more time and memory space it will require.
- Select 5 (Select output file format) and then 7 (3D Gaussian cube)
- Select 10 (Generate the plot) and wait for the plotting to finish
- Exit by selecting 11 (exit this program)

A `.cube` file will be generated, which you can visualize with Chemcraft or Avogadro.

With Chemcraft, you need to select *Show isosurface* from the bottom-left corner menu. You can use the *Contour value* to scale the isosurface by determining the cutoff. In his paper, Grimme suggests using an isovalue of $\sigma = 0.005 \text{ e Bohr}^{-3}$. For more information, check the original paper (*ACIE* **2015**, 54, 12308–12313).

Avogadro requires an additional step: once the file is opened in Avogadro, click on **Extensions - Create Surfaces**. Change **Surface Type** to **Cube data generated by ORCA**, choose the isovalue, and click on **Calculate**. Note that the default color may not be well visible - to make it visible, you have to open the “Display settings”, find “Surfaces” in the list, and click on the wrench icon that opens the visualization settings. There you can modify the colors and other visualization options.

Visualize the FOD plots for the singlet and quintet Cr_2 . The general guideline is that if your molecule “lights up” when you display the FOD plot, then you should start thinking about being concerned and looking into more multireference diagnostics (or just calling your computational friend). What’s the case for singlet and quintet Cr_2 ?



3 Final thoughts

We just used simple DFT calculations on a very hard problem, and expectedly we ran into several issues along the way. However, thanks to ORCA 5 having powerful SCF convergence algorithms, the simple calculations worked fine and we might've missed those issues had we not taken a closer look. For clarity, we have summarized our results in the table below:

Multiplicity	BP86		PBE0	
	E_{SCF}	$\Delta\langle S^2 \rangle$	E_{SCF}	$\Delta\langle S^2 \rangle$
without stability analysis				
1 (UKS)	-2089.202	0.00	-2088.304	0.00
1 (RKS)	-2089.202	-	-2088.304	-
5	-2089.105	0.01	-2088.334	0.01
with stability analysis				
1 (UKS)	-2089.221	1.70	-2088.414	3.00
5	-2089.152	0.01	-2088.334	0.01

The main take-aways from our results are:

- Without stability analysis, the two different types of functionals (BP86 and PBE0) give opposing answers for which spin state is lower in energy. That should usually prompt a more careful investigation.
- The UKS and RKS energies for the singlet are identical, which is usually the case for singlet states.
- The initial (open-shell) singlet and quintet calculations converged fine and have no significant spin contamination. Without knowing the conflicting functional dependency from the previous point, this result in itself could be interpreted as the calculations being fine. However, stability analysis flagged almost all the calculations as having converged to an unstable solution (except PBE0 quintet).
- The results from the second SCF after the stability analysis agree that the singlet is lower in energy, but at the same time, the singlet has large spin contamination.³ Note that you should check the stability of the second SCF solution, too. In the simplest approach, you can just call `orca` on the same input again and it will automatically start the calculation from the previous wavefunction (`.gbw`).
- Finally, we analyzed the two spin states with FOD. In both cases, we got large `N_FOD` values (> 1) and significant densities. This indicates that both states might have multireference character and further investigation is warranted. Note that so far there had been no other indication that the quintet had any problems. Also note that significant multireference character means that you should expect the DFT results to be numerically (more) unreliable.

As usual, we had you go through some of the worst case scenarios that you are not likely to meet in your day-to-day calculations (unless covalent metal-metal bonds and multiple spin states are your bread and butter). The skills from this exercise should help you flag problematic calculations, so that you'll know when to call your computational friend.

³If you looked more carefully around the output, you might've noticed from population analyses that the opposite spins had localized onto different Cr atoms – in computational lingo, these are broken symmetry solutions, which have their own special place in analyzing complicated organometallic complexes.