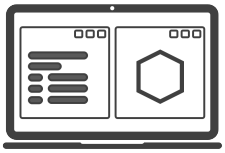

Introduction to Computational Chemistry
Handout Part 5

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In many cases, calculations on organometallic compounds can be executed as simply as on organic compounds. However, in some cases, the electronic structure of organometallic compounds can be tricker to get right. The usual suspects are:

- Relativistic "effects"
- Multireference character (strong electron correlation)
- DFT-related errors (especially for different spin states)

If you use the recommended def2 basis sets, then the main chemically relevant relativistic effects are taken care of by the effective core potentials without further effort from your side. For the other two cases, we list below some simple techniques to diagnose potential problems.

1 Stability Analysis

To check if the wavefunction is stable, add the block

```
%scf
STABPerform true
end
```

to the input file for a single point calculation. Make sure to not include `Miniprint` as a keyword, as the information will otherwise not be printed. The result can be seen in the "Stability Analysis" section of the output. To quickly access it, use the `grep` command.

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

2 Spin Contamination

For unrestricted Kohn-Sham (UKS) calculations, you get a spin contamination section in the output. To quickly access it, use the `grep` command.

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

The deviation between the expectation value and the ideal value should be as close to 0 as possible. If this is not the case you may have unphysical mixing of different spin states and you should seek help from your local computationalist.

3 FOD Analysis

To run a FOD analysis you only need the `FOD` keyword.

```
! FOD
%resources
*xyz file etc.
```

You can visualize the fractional orbital density as a `.cube` file, using the `orca_plot` tool. For an FOD calculation with the name `dummy` type

```
orca_plot dummy.gbw -i
```

and then navigate your way around the interactive menu.

- 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)

You can open the generated `.cube` file with either Chemcraft or Avogadro. Grimme suggests using an isovalue of $\sigma = 0.005$ e Bohr^{-3}.

4 Useful Links

- An example of a benchmark study, in this case of closed-shell metal organic reactions:
  J. Chem. Theory Comput. **2018**, *14*, 2596–2608.
  `https://pubs.acs.org/doi/10.1021/acs.jctc.7b01183`
- Chapter on spin-state energetics of transtion metal complexes:
  Adv. Inorg. Chem. **2019**, *73*, 221264.
  `https://www.sciencedirect.com/science/article/pii/S0898883818300370`
- Review on relativistic effects in chemistry:
  Annu. Rev. Phys. Chem. **2012**. *63*, 4564. `https://www.annualreviews.org/doi/full/10.1146/annurev-physchem-032511-143755`
- Chapter on relativistic effects in chemistry:
  Relativistic Effects in Chemistry. In Relativistic Quantum Chemistry **2014**, 605–630.
  `https://onlinelibrary.wiley.com/doi/10.1002/9783527667550.ch16`
- Discussion on the the accuracy of DFT with transition metals (a little bit outdated, but many points are still relevant):
  Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **2006**, *102*, 203–226.
  `https://pubs.rsc.org/en/content/articlelanding/2006/PC/b419105f`
- Input library section on SCF convergence issues
  `https://sites.google.com/site/orcainputlibrary/scf-convergence-issues`
- List of multireference diagnostics:
  J. Chem. Theory Comput. **2020**, *16*, 4373–4387.
  `https://pubs.acs.org/doi/abs/10.1021/acs.jctc.0c00358`
  See Section 2
- FOD analysis:
  `https://sites.google.com/site/orcainputlibrary/orbital-and-density-analysis/fod-analysis`
  ACIE **2015**, *54*, 12308–12313.
  `https://onlinelibrary.wiley.com/doi/full/10.1002/anie.201501887`
  Chem. Eur. J. **2017**, *23*, 6150–6164.
  `https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/chem.201604682`