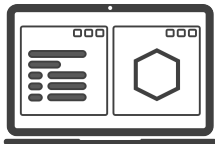


Introduction to Computational Chemistry

Part 5: Organometallics

Eno Paenurk & Patrick Finkelstein & Felix Pultar



24.05.2023



- Part 1: Takeoff
- Part 2: Reaction pathways from scratch
- Part 3: Preparing structures
- Part 4: Density Functional Theory
- **Part 5: Organometallics**
- Part 6: Spectroscopy
- Part 7: Chemical concepts

What you should know from Part 4



- Run simple DFT jobs with ORCA
- Read relevant data from the output



DFT with transition metals:

- Relativistic effects
- Unrestricted calculations
- Simple diagnostics



Good news

Many times the same inputs used in Part 4 work fine

Bad news

You may not notice when they don't

Usual suspects:

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



Relativistic quantum mechanics is necessary for describing the electronic structure of heavy elements (starting from 4th or 5th period, depending on who you ask).

Note

Relativistic QM is not only important for metals, but any heavy elements.

Relativistic “effects” in chemistry:

- s and p orbitals contract
- d and f orbitals expand
- spin-orbit coupling

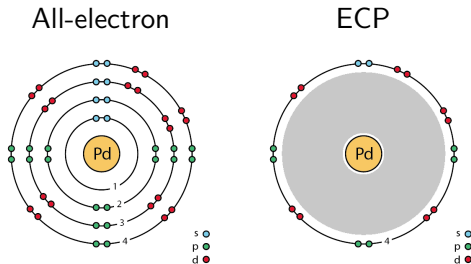
Effective core potentials



We would like to use the non-relativistic equations (simpler), but still account for some of the relativistic effects.

Common trick:

- Replace inner (core) electrons with a function that represents the relativistic effects (effective core potential – ECP)
- Calculate explicitly only the valence electrons
- Profit





Good news

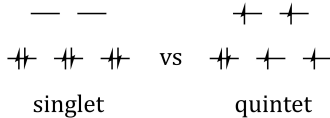
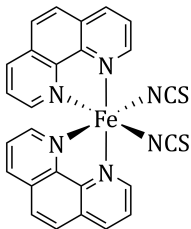
In ORCA, the def2 basis set is defined for all elements (except the 7th period) automatically with SDD ECPs, starting from the 5th period.

Features:

- Partially account for relativistic effects
- Are somewhat cheaper than all-electron calculations

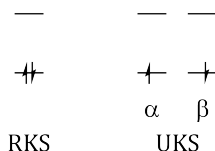
Caveats:

- Accuracy depends on parametrization, so use only recommended basis set and ECP combinations (e.g., def2 and SDD)
- You need explicit treatment of relativistic quantum mechanics if:
 - You want “more rigorously accurate” energies
 - Spin-orbit coupling is important
 - You are calculating spectroscopy that depends on inner electrons





DFT calculations of open-shell systems are usually done within the so-called unrestricted Kohn-Sham (UKS) formalism.



ORCA recognizes open-shell from multiplicity and switches to unrestricted itself, but we recommend explicitly adding the keyword:

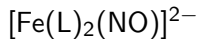
! UKS



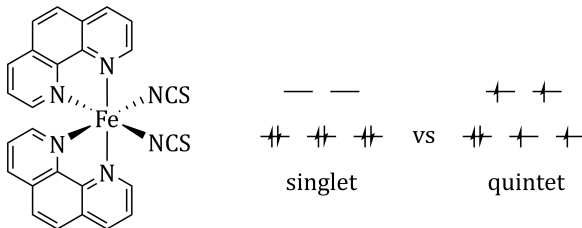
Caveat: UKS calculations can lead to “spin contamination” – unphysical mixing of different spin states.

Check the UHF SPIN CONTAMINATION section in the ORCA output – the deviation between expectation value of $\langle S^2 \rangle$ and the ideal value should be close to zero (up to 10% deviation is tolerable).

A bad example (with PBE0/def2-TZVP):



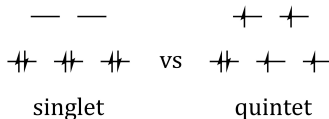
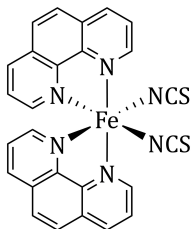
Expectation value of $\langle S^2 \rangle$: 4.322605
Ideal value $S(S+1)$ for $S=1.5$: 3.750000
Deviation	: 0.572605



“Good error cancellation is what computational chemists usually live off.”

-Frank Neese

- Same-spin and different-spin interactions are treated differently
→ They also have different accuracy
- Different spin states have different number of same-spin and different-spin interactions
→ Errors don't cancel!



Functional/TZVP	ΔE (kJ/mol)
BP86	66.0
B3LYP($c_3 = 0.00$)	82.6
B3LYP($c_3 = 0.13$)	5.5
B3LYP($c_3 = 0.15$)	-6.1
B3LYP	-33.4

Reiher, M. *Inorg. Chem.* **2002**, 41, 6928.

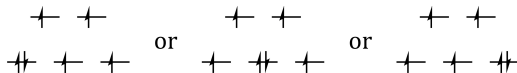
Take-home messages:

- Test several functionals
- Read benchmark studies



Multireference character can occur when the system has (partially filled) near-degenerate frontier orbitals (often the case with transition metals).

In such cases, the usual orbital picture becomes ambiguous, e.g.:



Conventional DFT methods either break down (SCF does not converge) or give unreasonable results (wavefunctions).

Take care if you are dealing with:

- “Strongly covalent” M-L bonds
- Redox non-innocent ligands
- Open-shell complexes

How to identify multireference character?



- SCF does not converge/behaves erratically/converges to a wrong solution
- Large spin contamination
- Possibly problematic electronic structure (intuition)
- Fractional Orbital Density (FOD) calculation
- Many, many more diagnostics...
See the useful links in the Handout

There is generally no easy answer to this question. If you suspect multireference character, consult your local computationalist.



In some hard cases, the SCF procedure can converge to a wrong solution (i.e., not the minimum energy wavefunction).

To check if the solution is “stable” under perturbations, use the scf module:

```
%scf
  StabPerform True # perform stability analysis
end
```

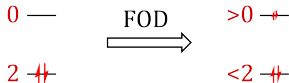
ORCA reports the result in the SCF STABILITY ANALYSIS RESULT section of the output:

Root	Eigenvalue (au)
0	-0.092704
1	0.112370
2	0.169101



Idea: apply finite temperature to the electrons, remove the integer electron occupation constraint, and see how many electrons are “smeared”. It should identify close-lying filled-unfilled orbitals (plausible multireference character).

occupation:



Simple keyword option in ORCA:

! FOD

The calculation will:

- tell you the (fractional) number of electrons that were smeared
- give you 3D data to visualize where these electrons are

Grimme, S.; Hansen, A. *ACIE* **2015**, 54, 12308.

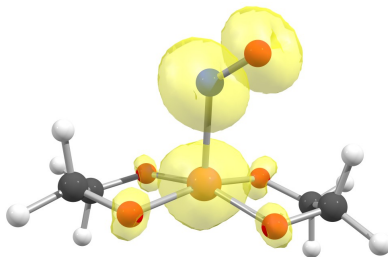
FOD – our bad example



Number of smeared electrons:

$$N_{\text{FOD}} = 1.88$$

3D visualization of the density (at $0.005 \text{ e Bohr}^{-3}$):





- For many closed-shell and high-spin organometallics, regular DFT often works fine
 - But the accuracy/reliability is often lower than for simple organics
- Most chemically relevant relativistic effects can be treated with ECPs
 - Use the def2 basis sets with SDD to have a balanced description of (almost) the whole periodic table
- Test different types of functionals: GGA (BP86) and hybrid (PBE0)
 - If results differ substantially, you probably have a problem
 - If they don't... you might still have a problem
- Monitor spin contamination in UKS calculations
- Use FOD calculations as a simple test for multireference character
 - Ask your computational friend for further assistance



