Introduction to Computational Chemistry

Part 7: Chemical concepts

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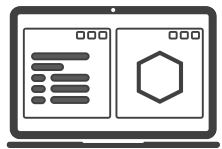

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Webinar overview

- 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

Goals accomplished so far

- Obtaining reaction profiles with `autodE`
- Obtaining good starting structures
  - from SMILES
  - from a guess
  - refining with `xtb`
- Running DFT jobs with `ORCA`
  - Minima – intermediates
  - Saddle-points – transition states
  - Transition metals
  - Spectroscopy: IR, NMR, UV/Vis
- Reading relevant data from the output
  - Energies
  - Thermochemistry
- Visualizing the results
  - 3D structures/trajectories
  - Vibrations

Goals today

- Extract information about the HOMO/LUMO
- Visualize molecular orbitals
- Calculate and visualize orbital interactions
- Calculate partial charges
- Visualize electrostatic potential maps

Orbitals

Remember that orbitals are not observables, but:

"Whatever makes you inspired to do new experiments, it's fine."

-Frank Neese

Orbital occupations and energies are listed after the SCF calculation:

```
----------------
ORBITAL ENERGIES
----------------

  NO   OCC          E(Eh)            E(eV)
...
   6   2.0000      -0.324924         -8.8416   <- HOMO
   7   0.0000      -0.077083         -2.0975   <- LUMO
...
```

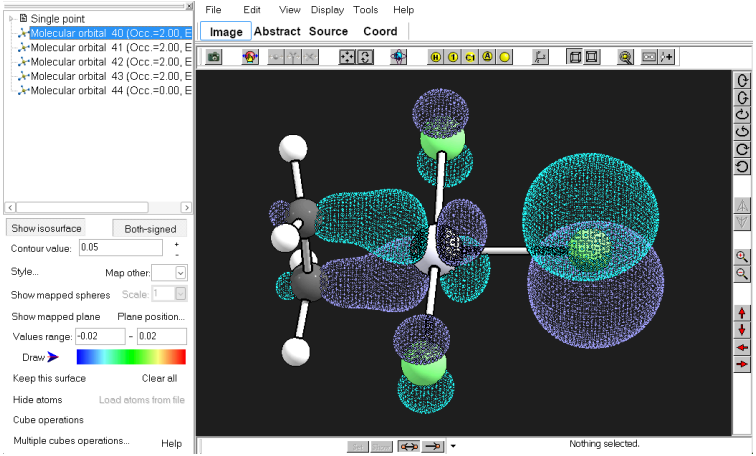
Orbital visualization

To visualize the orbitals, you can either:

- generate `.cube` files of orbitals with `orca_plot`
  (one `.cube` file per orbital)
- request extra printout to the output:
  `! Printbasis PrintMOs`
  (recommended only for single points)

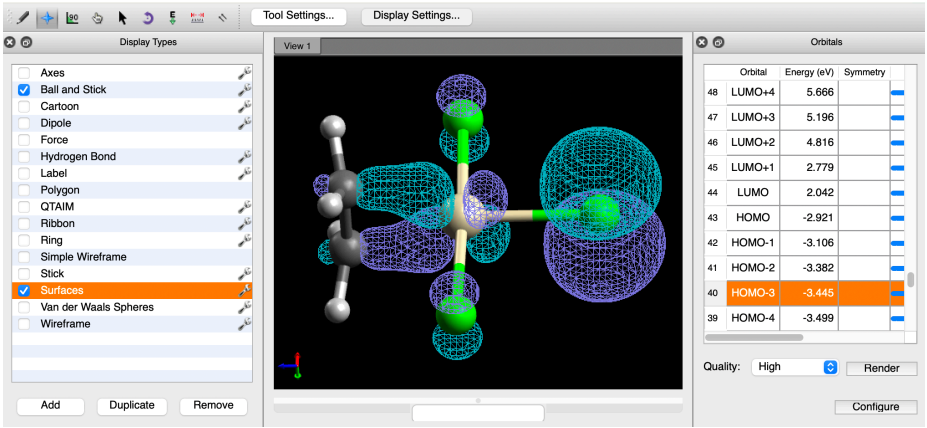
Orbital visualization

The `.cube` or the output file can be opened by Chemcraft ...



Orbital visualization

... and Avogadro.



Orbital visualization

How big is the orbital?

You need to choose the contour value (or isovalue) when visualizing 3D functions like orbitals. Usually values between 0.02 and 0.06 ($e/Bohr^3$) give reasonable results.

There is more than one flavor

We show how to plot "canonical" molecular orbitals. There are various transformation schemes that can produce "more intuitive" orbitals.

Orbital interactions

If we want more insight into the orbital interactions between different parts of the molecule, we can perform energy decomposition analysis techniques.

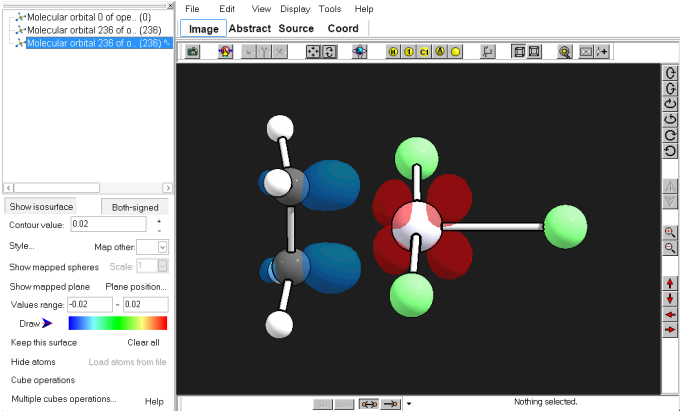
In ORCA, we can use the ETS-NOCV* workflow:

1. Run SP calculations on the two interacting fragments
2. Combine the wavefunctions of the fragments
3. Run SP calculation of the combined fragments starting from the combined wavefunction
4. Read the orbital interaction energies from the output
5. Visualize the respective orbitals and the electron density flow (so-called deformation density)

*Extended Transition State - Natural Orbitals of Chemical Valence

Orbital interactions

The NOCV `.cube` files can be opened by Chemcraft to calculate the *deformation density*.



2nd strongest orbital interaction (30% of total interaction energy)

Red – electron density depletion
Blue – electron density accumulation

Partial charges

There are a lot of methods for calculating partial charges

Partial charges in `ORCA`:

Method	**Approach**	**How to invoke**	**Comment**
Mulliken and Löwdin (`LOEWDIN`) population analyses	Dissect the wavefunction	printed by default	basis set dependent, not very reliable
ChElPG (Charges from the Electrostatic Potential on a Grid)	Fit charges to electrostatic potential	`! CHELPG`	stable, but not always great for large molecules
Hirshfeld population analysis	Dissect the electron density	`! Hirshfeld`	stable, but typically too low

Partial charges

Showcase: CO_2 (showing C)

	B3LYP/def2-		BP86/def2-	
Method	SVP	TZVP	SVP	TZVP
Mulliken	0.26	0.37	0.21	0.31
Löwdin	0.13	-0.41	0.09	-0.45
ChElPG	0.74	0.71	0.69	0.66
Hirshfeld	0.36	0.35	0.33	0.32

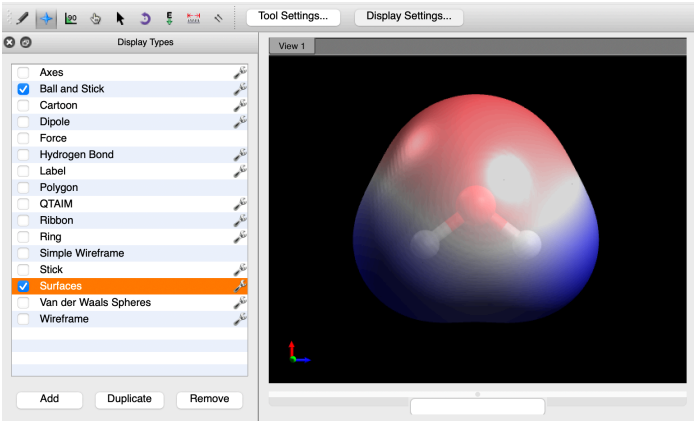
- ChElPG and Hirshfeld preferred over Mulliken and Löwdin
- Look into different options if good partial charges are crucial for your study

Note

Partial charges are not oxidation states. If you want to calculate oxidation states, talk to your local computationalist.

Electrostatic potential map

The electostatic potential (calculated from Mulliken charges) can be mapped onto the electron density or van der Waals surface in Avogadro.



Summary

There are a lot of ways to chemically interpret and analyze your calculations – we barely scratched the surface.

We covered:

- Orbital analyses
  - Visualization
  - Orbital interaction calculations
- Electrostatics
  - Partial charges
  - Electrostatic potential maps from partial charges

You may further find interesting:

- Formal oxidation states
- Spin density
- Energy decomposition analyses
- Localized orbitals
- Electrostatic potential maps from electron density

Live-Demo

Exercises