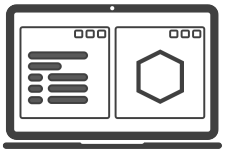


Introduction to Computational Chemistry
Handout Part 7

Eno Paenurk & Patrick Finkelstein & Felix Pultar

June 7, 2023

1 Visualizing MOs

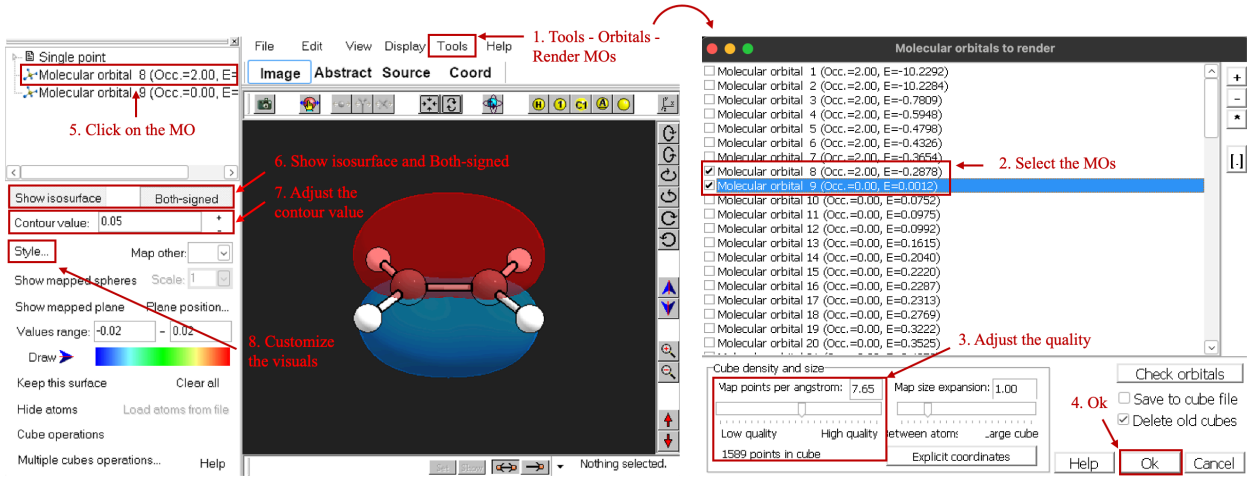
To directly render the MOs in Chemcraft or Avogadro, add the keywords `PrintBasis` and `PrintMOs` to your input file.

```
! BP86 def2-TZVP PrintBasis PrintMOs
# rest of the input
```

You can also extract the MOs from the `.gbw` file that is generated for any calculation.

1.1 Chemcraft

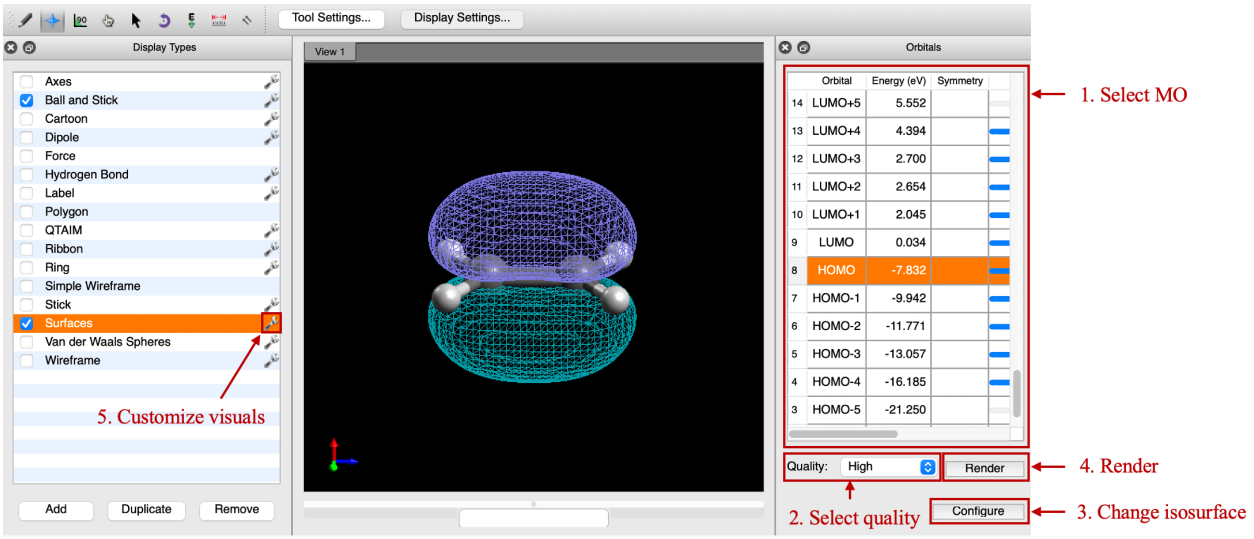
Click on *Tools*, select *Orbitals* and *Render MOs*. You now have a list of all MOs of your system, with their respective occupancy and energy (in eV). Click in the white boxes on the left to mark an MO to render. You can render as many as you like, it will just take more time. On the bottom you have additional options, such as the overall quality. Press `Ok` and you can now select the MOs you rendered in the left sidebar. Click on the the MO you want to visualize and select *Show isosurface* and *Both-signed*. You can use the *Contour value* to scale the isosurface by determining the cutoff.



To save the MO as a `.cube` file, click on *Save current cube to file* from the bottom left menu. If you have multiple MOs, you can save all of them to the same `.cube` file, click on *Multiple cubes operations* and *Save all cubes to files*. There are plenty of other options to play around with, so you can customize the visuals to what suit you best.

You can also show the MO energy diagram: From the top menu in Chemcraft select *Tools*, *Orbitals*, and *Show MOs energy diagram*. Occupied MOs are shown in red, empty MOs in yellow.

1.2 Avogadro (v1)



You should see the MO overview on the right; if you don't, then click on *Settings*, *Toolbars*, and *Orbitals* (Windows) or *Window*, *Toolbars*, and *Orbitals* (Mac). To view a rendered MO, simply click on it. If the MO wasn't rendered yet, click on it and then on *Render*. To change the quality or the isosurface value of the MO, click on the *Configure* button in the bottom right.

You can also change some other settings, like the render type (fill, points or lines) or the colors. Click on *Display settings* from the top bar and then on the little tool next to *Surfaces*.

1.3 Using `orca_plot`

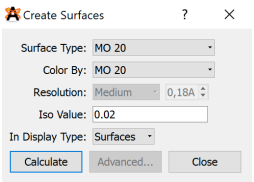
Plotting your MOs with `orca_plot` requires you to know in advance which MO numbers you are interested in. You can check which MOs are filled and which are empty in the output file. Once you know which MOs you want, you can use the `orca_plot` program on the `.gbw` file and render a cube file.

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

You will be prompted with an interactive menu that you can navigate by entering numbers. To generate a specific MO, you can follow the instructions given below.

- Select 1 (Enter type of plot) and then 1 (molecular orbitals)
- Select 2 (Enter no of orbital to plot) and enter the number of the MO that you wish to plot
- *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 have now generated a `.cube` file which contains the molecular orbital number in its name. You can open it in Chemcraft and use the tools/settings mentioned above, or you can use Avogadro, which will require an additional step. Once the file is opened in Avogadro, click on `Extensions` - `Create Surfaces`.



Change `Surface Type` and `Color By` to the MO number that you requested and click on `Calculate`.

2 Orbital Interactions

> In ORCA, this only works for RKS calculations. You need other software for open-shell analyses (e.g., ADF).

Firstly, you need to split the coordinates of the compound (AB) into two `.xyz` files – one for each fragment (`A.xyz` and `B.xyz`). For example, if you were studying water-borane interaction, you would start with the water-borane complex `.xyz` file, and split it into water fragment `.xyz` and borane fragment `.xyz`. Run single-point calculations on both fragment structures (do not optimize the geometries).

You will then have two wavefunction files (`A.gbw` and `B.gbw`). Next, combine them into one wavefunction of non-interacting fragments (`AB.gbw`):

```
orca_mergefrag A.gbw B.gbw AB.gbw
```

For the final calculation, we need to read in the combined non-interacting wavefunction. The input should look something like this:

```
# computational method keywords
! MOread # toggle .gbw reading
# resources

%moinp "AB.gbw" # read in the .gbw
%scf
 eda true # toggle energy decomposition analysis
end

*xyzfile 0 1 AB.xyz
```

The orbital interactions are listed in the following output section:

```
-------------------------------------------------------------
                     NOCV/ETS analysis
-------------------------------------------------------------

  negative eigen. (e)   positive eigen.(e)    DE_k (Kcal/mol)
```

where the third column contains the orbital interaction energies.

To visualize electron flow, you need to first generate `.cube` files for the NOCVs of interest – these are usually the ones corresponding to the highest interaction energies. For the first interaction energy as listed in the output, the corresponding donor and acceptor orbital are the first and the last NOCVs in `.nocv.gbw`, respectively. For the second interaction, it's the second orbital and second-to-last, etc.

Run `orca_plot` on the `.nocv.gbw` file:

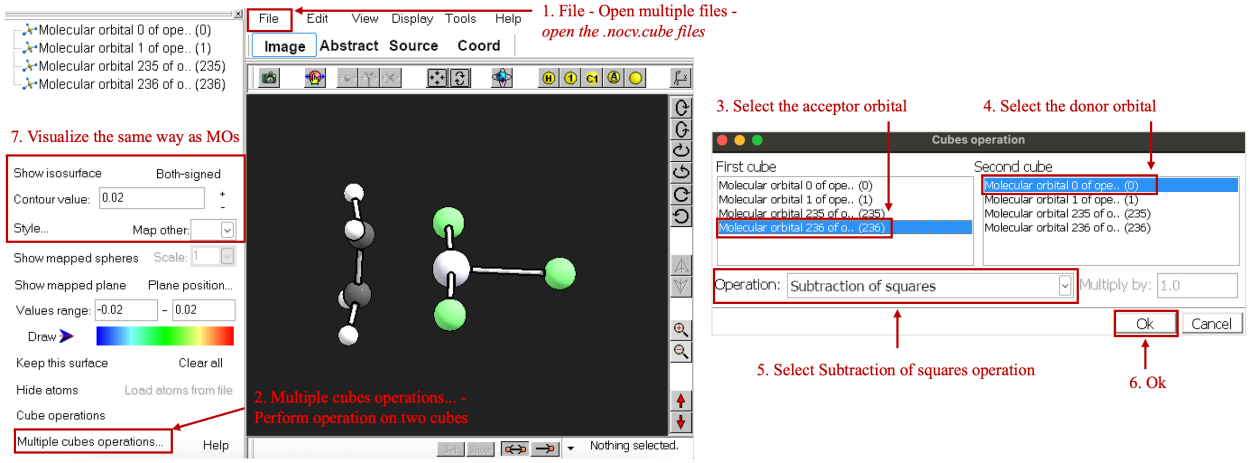
```
orca_plot AB.nocv.gbw -i
```

and identify the number of orbitals from the printed output:

```
===>>> Number of available orbitals : 237
```

So, for the first orbital interaction, you need orbital 0 (ORCA starts counting from 0) and 236 (which is the last one because we started from 0). For the second orbital interaction, it's orbitals 1 and 235, etc. Follow the procedure in Section 1.3 to generate the `.cube` files for the desired orbital pairs.

Finally, you need to subtract the final density from the initial density. We get the final and initial densities by squaring the acceptor and donor orbitals, respectively. This task can be performed with Chemcraft.



Open Chemcraft and open the NOCV pair `.cube` files you generated by *File - Open multiple files*. Now select in the lower right corner *Multiple cubes operations...* and *Perform operation on two cubes*. In this example, choose the first cube to be 236 (acceptor) and the second one 0 (donor). Now select from the *Operation* list *Subtraction of squares*. Click *Ok* to perform the operation.

You should now have a new item in the list – this is the *deformation density* that shows electron flow. Show its isosurface with both signs – the electron density changes that you see correspond to the first listed orbital interaction energy (look in *Style* to check which color corresponds to negative values and which positive).

3 Partial Charges

3.1 Mulliken and Löwdin

Mulliken and Löwdin (spelled `LOEWDIN` in the ouput) charges are printed after the SCF calculation by default. You should find these sections:

```
-----------------------
MULLIKEN ATOMIC CHARGES
-----------------------
```

and

```
-----------------------
LOEWDIN ATOMIC CHARGES
-----------------------
```

which contain the calculated atomic charges for all atoms.

3.2 ChElPG

You can request ChElPG (Charges from the Electrostatic Potential on a Grid) with specifying:

```
! CHELPG
```

in the input, and then looking for

```
CHELPG Charges
```

in the output. Alternatively, you can use another `ORCA` tool on an already existing `.gbw` file:

```
orca_chelpg dummy.gbw dummy.scfp -i
```

3.3 Hirshfeld

You can request Hirshfeld charges by adding the respective keyword in the input:

```
! Hirshfeld
```

and then looking for

```
------------------
HIRSHFELD ANALYSIS
------------------
```

in the output.

4 Electrostatic Potential Maps

The easiest option is partial-charges-based map visualization with Avogadro. You can open the an `ORCA` output file or just the `.xyz` file. In either case, you can generate the electrostatic potential on the van der Waals surface by selecting *Extensions* and *Create surfaces*. Then choosing *Surface Type* as *Van der Waals* and *Color By* as *Electrostatic potential*. You can also modify the resolution if you wish. When you're done, click *Calculate*. You should now see the map in the viewer.

If you opened the calculation output, then Avogadro used the Mulliken charges to calculate the electrostatic potential. If you opened the `.xyz` file, then it used some internal algorithm to predict the partial charges.

Note that the electrostatic potential map can only be visualized with the *Fill* rendering (this can be changed in the *Surfaces* settings).

5 Useful Links

- Some instructions for orbital analyses and visualization with `ORCA`:
  `https://sites.google.com/site/orcainputlibrary/orbital-and-density-analysis`
  `https://sites.google.com/site/orcainputlibrary/visualization-and-printing`
- A discussion about the interpretability of DFT (KS) orbitals:
  `http://dx.doi.org/10.1021/ja9826892`
- Some comparison studies of partial charges:
  `https://onlinelibrary.wiley.com/doi/full/10.1002/jcc.20157`
  `https://onlinelibrary.wiley.com/doi/10.1002/jcc.540141213`
  `https://www.frontiersin.org/articles/10.3389/fchem.2023.1152500`
- Tutorial for calculating Fukui functions (not mentioned, but can also be useful):
  `https://www.orcasoftware.de/tutorials_orca/react/FUKUI.html`