

Introduction to Computational Chemistry

Exercises Part 7

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Goals:

- Extracting HOMO and LUMO
- Visualizing orbitals
- Calculating orbital interactions
- Extracting partial charges
- Visualizing electrostatic potential maps

1 Extracting HOMO/LUMO and Visualizing Orbitals

We'll start simple by studying ethylene. Generate initial coordinates for ethylene, optimize the structure with BP86-D3BJ/def2-SVP, and run a single-point calculation with PBE0/def2-TZVP.¹

1.1 HOMO/LUMO

To find the HOMO and LUMO numbers and energies, you can look for **ORBITAL ENERGIES** section in the output:

----- ORBITAL ENERGIES -----

NO	OCC	E (Eh)	E (eV)
...			
X	2.0000	-0.287834	-7.8324
Y	0.0000	0.001228	0.0334
...			

where **X** is the HOMO number and **Y** the LUMO number.

Note that when you run UKS calculations, then the **ORBITAL ENERGIES** section is split into spin up and spin down orbitals, and each orbital has an occupation of 1 or 0. For anything except singlet multiplicity, the spin up and spin down HOMO and LUMO will be different.

For closed-shell cases, you can calculate the HOMO/LUMO numbers by dividing the number of electrons in your system by 2 for the LUMO and then subtracting 1 for the HOMO (the counting starts from 0).

¹We want the single-point calculation for orbitals, and the dispersion correction doesn't affect orbitals, so we can skip it.



To quickly check the number of electrons, use

```
grep "Number of Electrons" ethylene.out
```

1.2 Orbital visualization

In the following sections, we'll show you two ways for rendering the molecular orbitals (MOs) from single-point calculations. Option 1 (Section 1.2.1) will allow you to quickly access any MO but comes at the cost of larger file sizes. Option 2 (Section 1.2.2) uses the `orca_plot` tool and requires you to choose which MOs to render.

1.2.1 Option 1 – large output files

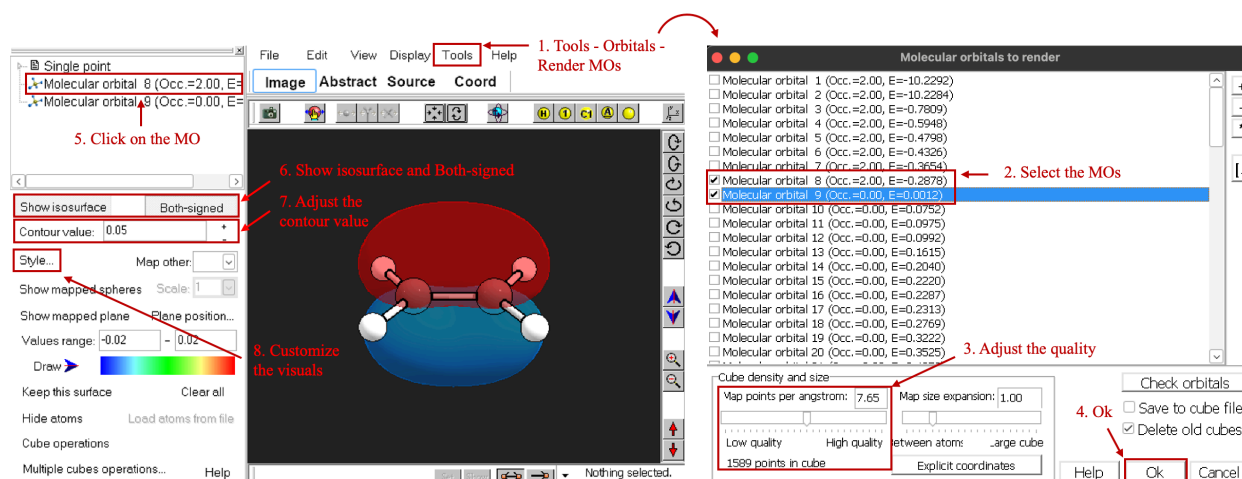
Add `PrintBasis` and `PrintMOs` to the keyword line. This will allow you to easily render the MOs directly from the output file. However, adding the `print` keywords comes at a cost – your output file will now be significantly larger.

```
! PBE0 def2-TZVP PrintBasis PrintMOs
%pal nprocs 1 end
%maxcore 1024
*xyzfile 0 1 ethylene_ini.xyz
```

Once the calculations are finished, you can open them in either Chemcraft or Avogadro.

Chemcraft

Open the `.out` file. 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). We are usually interested in the HOMO/LUMO region. 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. A good starting point is somewhere in the middle. Press **Ok** and you can now select the MOs you rendered in the left sidebar. Click on the MO you want to visualize – you will see nothing so far. For this you need to select *Show isosurface* from the bottom menu as well as *Both-signed*. You can use the *Contour value* to scale the isosurface by determining the cutoff – 0.02 to 0.06 is typically a good range.



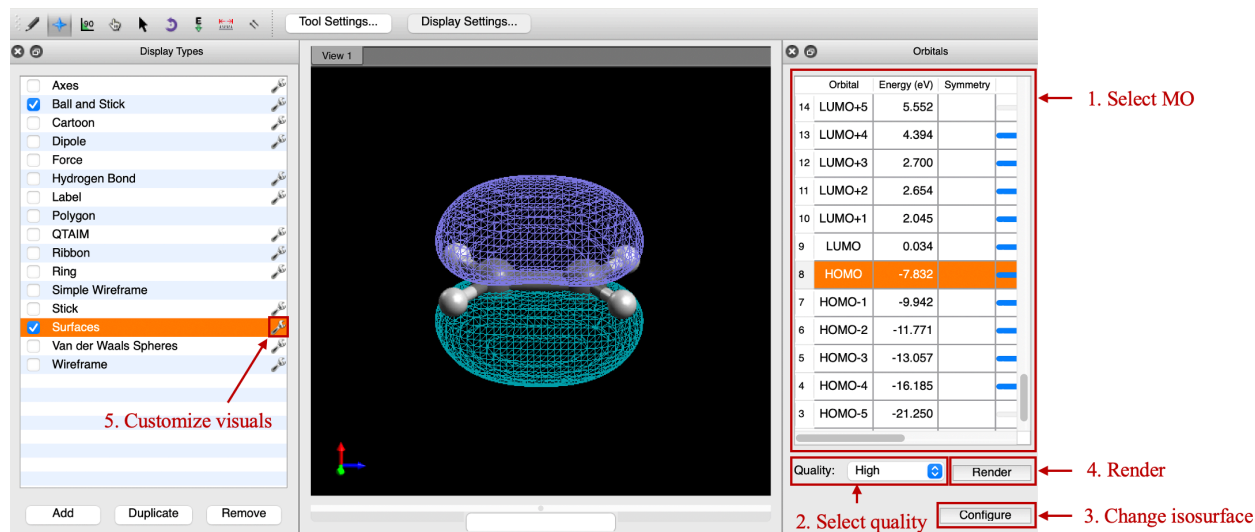
To save the MO as a `.cube` file, click on *Save current cube to file* from the bottom left menu. This enables you to look at this specific MO at a later time. If you have multiple MOs, you can save all of them to the same `.cube` file, simply click on *Multiple cubes operations* and *Save all cubes to files*.

There are plenty of other options to play around with, so you can customize the visuals to what suit you best.



Apart from rendering the MOs, you can also show the MO energy diagram: From the top menu in Chemcraft select *Tools*, *Orbitals*, and *Show MOs energy diagram*. This can be useful to get a quick picture of the orbital energy spacing. Occupied MOs are shown in red, empty MOs in yellow.

Avogadro



Open the `.out` file. You will already 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). By default, Avogadro pre-renders 10 MOs around the HOMO and LUMO, which you can tell by the green status bar. You can change the default settings by clicking on *Configure* on the bottom of the orbital sidebar. 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*. This will allow some modifications of the default settings.

1.2.2 Option 2 – .cube files

An alternative way to get to your orbitals is using the `orca_plot` tool and the `.gbw` file that you get after running a single-point calculation.

For all calculations, the wavefunction is stored in the `.gbw` file, albeit in a human non-readable format. Plotting your MOs with `orca_plot` requires you to know in advance which MO numbers you are interested in. We found out the HOMO and LUMO numbers in Section 1.1. We can use the `orca_plot` program interactively on the `.gbw` file to render `.cube` files of the MOs:

```
orca_plot ethylene.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 A0(=1) vs MO(=1) to plot

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

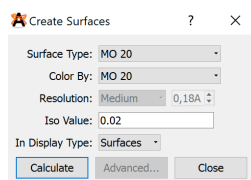


To generate a specific MO, you can follow the instructions given below.

- 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. When generating `.cube` files of several orbitals in one go, you do not need to set the filetype and grid size each time, but only need to do the 2 – #MO – 10 sequence.

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

Be prepared, this task is more involved than usually (but also very satisfying if you like thinking about chemistry in terms of orbital interactions).

Now that we have identified ethylene frontier orbitals, let's see how they interact with an organometallic complex. We'll look into one of the earliest alkene complexes – Zeise's salt, or specifically the anion $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ – and we'll try to recover the Dewar–Chatt–Duncanson binding picture. Generate the initial structure, and optimize it with BP86-D3BJ/def2-SVP.

2.1 Interaction Calculation

To calculate the orbital interactions with the ETS-NOCV (Extended Transition State - Natural Orbitals for Chemical Valence) scheme, we need to do two steps:

1. Calculate the fragment wavefunctions and combine them
2. Calculate the wavefunction of the compound starting from the combined wavefunction

It might sound complicated, but ORCA is going to help us get there quite easily.

2.1.1 Fragment Calculations

Firstly, we need to split the optimized coordinates into two `.xyz` files – one for each fragment. The structures should be the same as in the final complex, so it's best you extract the individual fragments from the optimized `.xyz` file. You can either use Chemcraft/Avogadro to delete the unwanted part of the compound and copy the coordinates of the remaining fragment, or work on the text file directly. In this case it is easy to distinguish the two fragments in the text file directly, because the ethylene fragment has all the C and H



atoms, and the $[\text{PtCl}_3]^-$ fragment has the Pt and Cl atoms. Make two new .xyz files: `ethylene_frag.xyz` and `ptcl3_frag.xyz`. Run PBE0/def2-TZVP single-point calculations on both fragment structures.

You should now have two wavefunction files (.gbw). You can use another nifty ORCA tool to combine them into one wavefunction of non-interacting fragments:

```
orca_mergefrag ethylene_frag.gbw ptcl3_frag.gbw zeise_frags.gbw
```

This merges the two fragment wavefunctions into `zeise_frags.gbw`, which we use to start the final single-point calculation.

2.1.2 Combined calculation

For the final calculation, we need to read in the combined non-interacting wavefunction. The calculation then “relaxes” this wavefunction by allowing the fragments to interact, and calculates the orbital interaction from the wavefunction changes. The input should look something like this:

```
! pbe0 def2-tzvp
! M0read # toggle .gbw reading
%pal nprocs 2 end
%maxcore 2048

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

*xyzfile -1 1 zeise_opt.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. We will look next how to visualize the respective orbitals and electron density changes.

2.2 Deformation Density Visualization

2.2.1 Preparing the Orbitals

The calculation with `eda true` produced a new wavefunction file `basename.nocv.gbw`. This contains the Natural Orbitals for Chemical Valence that we will use to calculate and visualize electron flow.

We first want to 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. As this can be a bit confusing, we’ll walk you through this case. Let’s start by running `orca_plot` on the .nocv.gbw file:

```
orca_plot zeise_eda.nocv.gbw -i
```

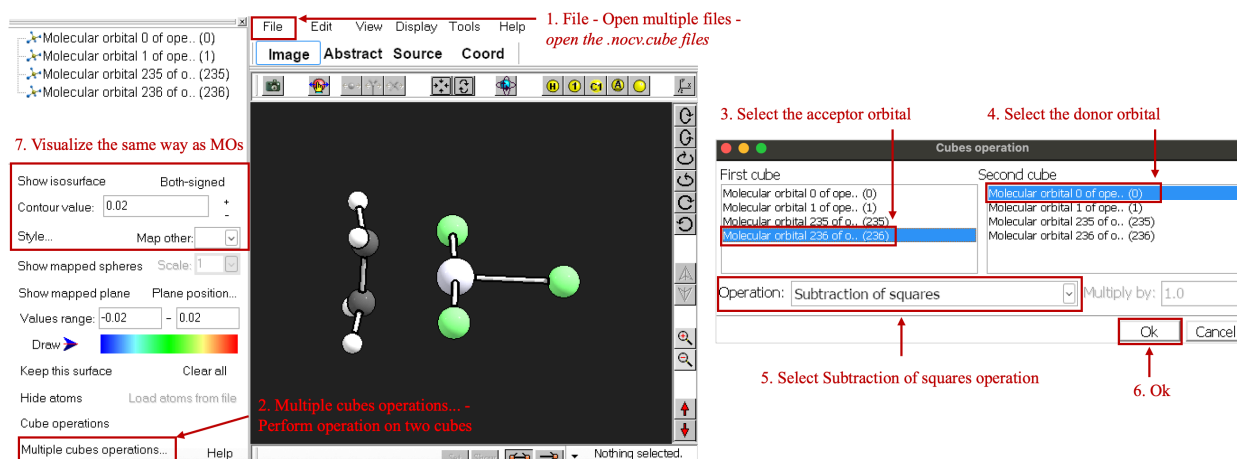
If you look carefully, you should see that it prints:

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

So, for the first orbital interaction, we want orbital 0 (ORCA starts counting from 0) and 236 (which is the last one because we started from 0). For the second orbital interaction, we want orbitals 1 and 235. Follow the procedure in Section 1.2.2 to generate the .cube files for orbitals 0, 1, 235, and 236.

2.2.2 Visualizing Deformation Density

We now want to visualize the changes in electron density to characterize the electron flow corresponding to the energy values given in the output. Conceptually, we are going to subtract the final density from the initial density. We get the final and initial densities by squaring the acceptor and donor orbitals, respectively (density is the wavefunction squared). This task can be easily performed with Chemcraft.



Open Chemcraft and open the four NOCV .cube files you generated by *File - Open multiple files*. Now select in the lower left corner *Multiple cubes operations...* and *Perform operation on two cubes*. Let's start with the first orbital interaction (NOCVs 0 and 236). Choose the first cube to be 236 (acceptor) and the second one 0 (donor). Now select from the *Operation* list *Subtraction of squares* – this will square our wavefunction and perform a subtraction, which is exactly what we wanted. 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).

Do the same analysis for the second interaction (orbitals 235 and 1). Do you get the Dewar–Chatt–Duncanson picture?

3 Partial Charges

Occasionally, it can be useful to study the partial charges and the electrostatic potential of your molecules, e.g., for predicting non-covalent binding motifs.

3.1 Mulliken and Löwdin

Mulliken and Löwdin (spelled LOEWDIN in the output) charges are printed after the SCF calculation by default. Have a look at the output file from before, either in an external text editor or in *vim*, for which there is a neat command.

Typing `/dummy` in *vim* (make sure you are not in *insert* mode) will search for the occurrence of “dummy” in the file. Pressing **Enter** will allow you to navigate through all occurrences with either **n** (for next) or **N** for the previous one.

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.

Generate coordinates for benzene; no need to optimize with DFT, **xtb** is just fine for our analysis. Calculate the four types of partial charges for these compounds with your method of choice and compare the numbers (they should be quite similar for this simple symmetric compound).

4 Electrostatic Potential Maps

Electrostatic potential maps are often utilized as visual aids in the field of supramolecular chemistry. Simple binding motifs can be predicted from the partial-charges-based surfaces that we will generate here, but for more complicated interactions (like halogen or chalcogen bonding), you would need to generate electrostatic potential maps from the calculated electron density (which is doable but more involved).

Let's investigate the electrostatic potential map for benzene to predict the binding site of an alkali metal cation (so-called cation- π interaction). You can open the output file from the previous section 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).