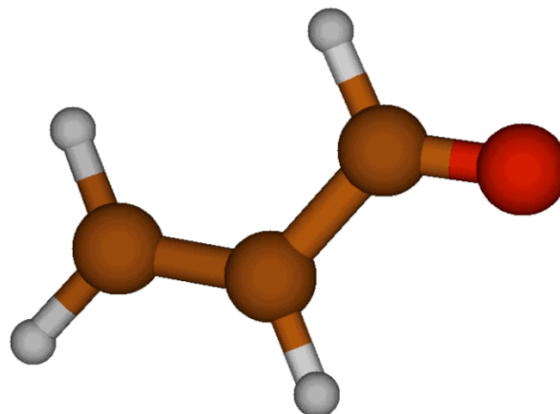


ACROLEIN:

The UV-VIS absorption spectrum of acrolein (2-propenal) shows two features as can be seen in the attached spectrum. The first peak is very weak, centered around 330 nm and ascribed to a $n \rightarrow \pi^*$ transition. The second peak is much intenser, centered at 200 nm and arises from $\pi \rightarrow \pi^*$ excitations. Let's see if we can confirm these assignments with DFT and/or a multiconfigurational approach.



Calculations:

1. Optimize the geometry of the molecule with DFT. Use the TPSS functional and the def2-SVP basis (see `acro.opt.inp`).
2. Perform a TD-DFT calculation with the same computational settings (see `acro.tddft.inp`)
3. Perform a CAS(6,5) calculation for the lowest five electronic states (see `acro.cas.inp`).
4. Include the dynamic electron correlation by means of a NEVPT2 calculation (see `acro.nevpt2.inp`)

Run the calculations with the following command:

```
> orca acro.???.inp > acro.???.out
```

where '???' stand for 'opt', 'tddft'; 'cas' and 'nevpt2', respectively. Don't forget to rename the `acro.opt.xyz` file to `acro.xyz` after the first calculation:

```
> mv acro.opt.xyz acro.xyz
```

Analysis:

1. Motivate why an active space with 6 electrons and 5 orbitals is the minimal reasonable active space to describe the low energy excitations of the molecule. Do not consult the outputs to answer this question, rely on your chemical knowledge!
2. Find the final geometry in the `acro.opt.out` file and write down the C-O and C-C distances. Do these make sense with respect to a simple reasoning in terms of Lewis structures?
3. Localize the transition energies and the oscillator strengths of the lowest transitions in the `acro.tddft.out` file. The lowest excitation is due to a replacement of an electron from orbital 14a into orbital 15a, that is the HOMO-LUMO transition:

```
STATE 1: E= 0.121694 au      3.311 eV    26708.7 cm**-1
14a -> 15a : 0.999190 (c= -0.99959489)
```

Identify the next three excited states by their main contribution.

4. The HOMO can be identified as the lone pair orbital on oxygen; the LUMO as a delocalized orbital of π^* character and the HOMO-1 as π orbital. Is the character of the transitions calculated with TDDFT in agreement with experiment? What about the transition energies and the relative oscillator strengths?
5. Locate the following parameters of the CASSCF calculation in the `acro.cas.out` file
 - Number of configurations:
 - orbitals doubly occupied in all configurations:
 - active orbitals:
 - active electrons:
 - total electrons:
6. After the list of orbital energies, Orca prints the multiconfigurational wave function for all the electronic states considered in the calculation (in this case 5 states, ROOT 0 for the ground state and ROOT 1-4 for the four excited states). Give the weight and the active orbital occupancies the five most important configurations of the wave function of the ground state. Orca uses the following way of representing a Slater determinant:

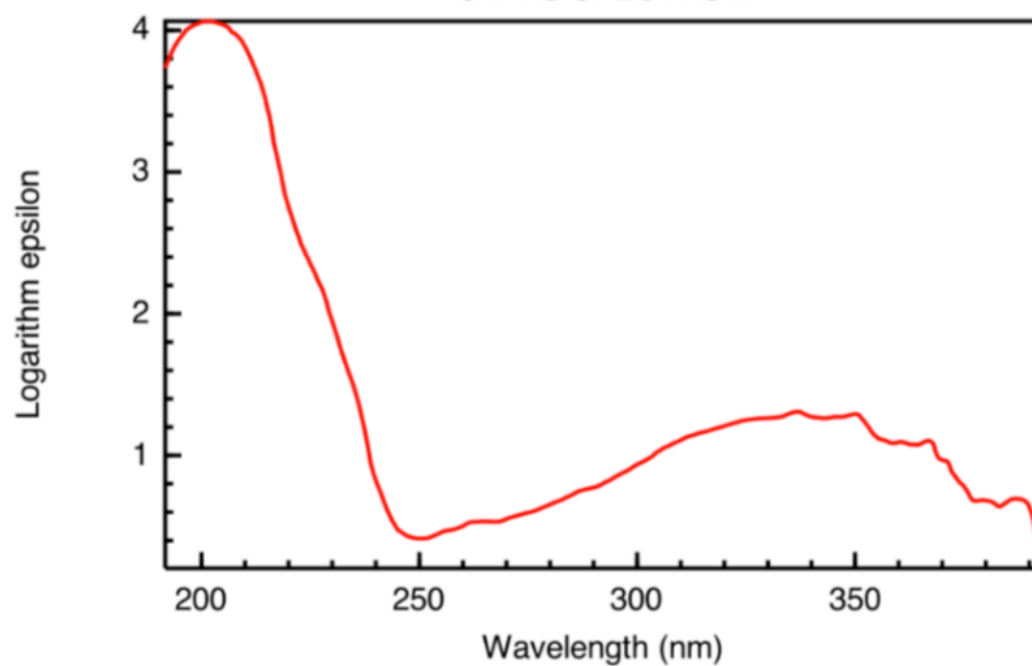

```
0.00767 [      8]: 02211
```

The first number is the weight of the configuration, the number in [] is the identifier, in this case we have configuration number 8. The last number is a list of active orbital occupations; '02211' means the first active orbital is not occupied in this configuration, active orbital 2 and 3 have two electrons and active orbitals 4 and 5 have each one electron.
7. Characterize the wave functions of the excited states in the same manner.
8. Make a table with the excitation energies and the oscillator strengths of the excited states calculated with CASSCF and NEVPT2 (see `acro.nevpt2.out`). Does the introduction of dynamic correlation improve the description of the excited states?
9. Generate an input for molden (a program to visualize the orbitals) by running the command


```
orca_2mkl acro.cas -molden
```

Open the `acro.cas.molden.input` file with molden and check the active orbitals. Are the orbitals as you expected? Why (not)?
10. Run orca with the `acro.cas_mod.inp` input file. Here, the first active orbital is exchanged with the last inactive one to obtain a more consistent active space. Are the CASSCF relative energies affected by this extension of the active space? And what about the NEVPT2 energies?
11. Try to come up with changes in the computational setup to improve the description of the excitation spectrum of acrolein.

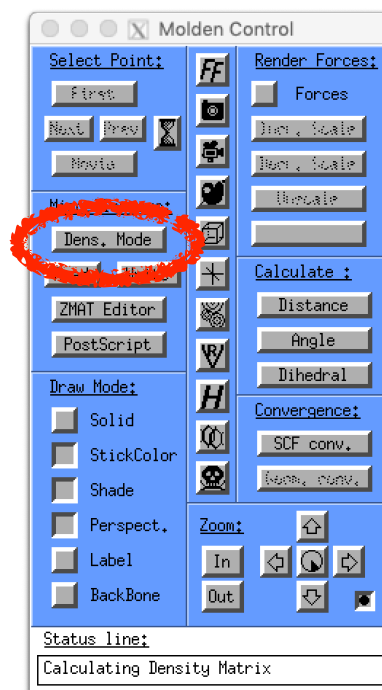
2-Propenal
UV/VIS SPECTRUM



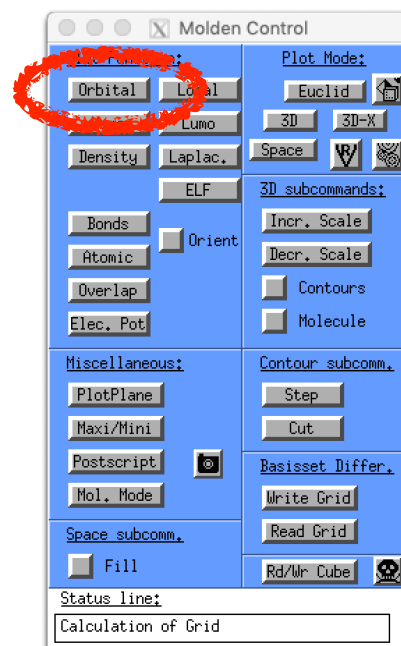
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

How to visualize orbitals with molden?

After opening molden (or gmolden) two windows pop-up: One with the molecule and a second (normally smaller) window with all type of buttons, called “Molden Control”.



Click on the “Dens. Mode” button. Both windows change their appearance and now click on the “Orbital” button in the “Molden Control” window. This will make a new window to pop-up with the header “Molden Orbital Select”



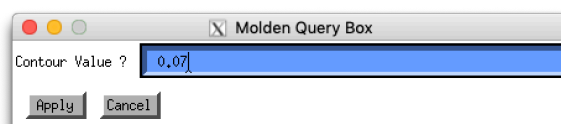
Scroll down the list until you find the first active orbital and click on it. Don't forget that orca starts counting at zero and molden at one. In the main window a raster representation of the orbital will appear that has to changed into a 3d isosurface representation.

The screenshot shows the 'Molden Orbital Select' window. It contains a table with the following data:

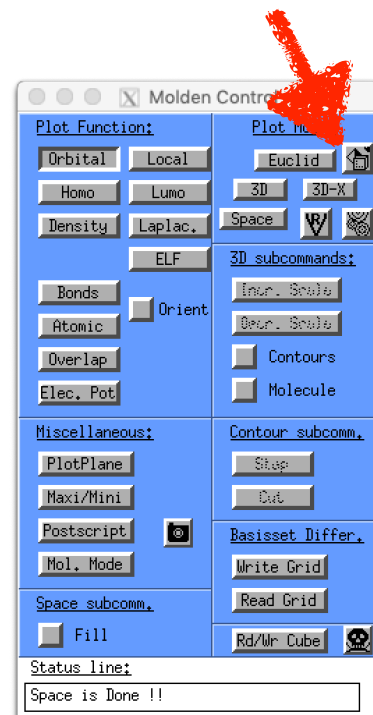
Nr.	Eigenvalue	Occupation
7	-0,868263	2,00
8	-0,763919	2,00
9	-0,665978	2,00
10	-0,638797	2,00
11	-0,602337	2,00
12	-0,557326	2,00
13	-0,542631	1,81
14	-0,356420	1,60
15	-0,345925	1,58
16	-0,027235	0,81
17	0,200915	0,20
18	0,191617	0,00
19	0,193950	0,00

Click on the “Space” in the “Molden Control” window.

A new small window pops up asking for a contour value. Type 0.07 and click “Apply”



If you are using gmolden (the OpenGL variant of molden) you might improve the representation by clicking on the upper right most button in the “Molden Control” window.



Visualize all the active orbitals (and maybe also some of the inactive and virtual orbitals) to get an idea of the active space and how it should possibly be improved.