Multiconfigurational Quantum Chemistry
Acrolein homework

Anna Borisova

TCCM

2023

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!

Because the transitions involve molecular π molecular orbitals and the non-bonding orbital: These are generated by the 3 p_z atomic orbitals on the C atoms (singularly occupied, 3 electrons),1 p_z atomic orbital on the oxygen atom (singularly occupied, 1 electron) and the non-bonding orbital on the oxygen atom (double occupied, 2 electrons). This makes up for 5 orbitals and 6 electrons.

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?

$C = O = 1.21909\text{Å}$
$C - C(=O) = 1.47856\text{Å}$
$C = C = 1.34710\text{Å}$

Yes, this makes sense since double bonds are expected to be shorter than single bonds (and especially the C=O bond is stronger than the C=C bond, so the distance is even shorter).

3. Localize the transition energies and the oscillator strengths of the lowest transitions in the acro.tddft.out file. Identify the next three excited states by their main contribution.

Table 1: Detailed transition energies and oscillator strengths for various electronic excitations.

Excitation	Transition	Energy (eV)	Oscillator Strength
1st	$n \rightarrow \pi^*$	3.308	0.000 002 272
2nd	$n \rightarrow \pi^*$	6.345	0.001 215 606
3rd	$\pi \rightarrow \pi^*$	6.660	0.388 485 811
4th	$\pi \rightarrow \pi^*$	7.081	0.000 201 457

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?

The first excitation is represented by a weaker peak in the ultraviolet region (330 nm), and it has the lowest relative oscillator strength and energy since it is between HOMO and LUMO. The third excitation state is identified as a $\pi \to \pi^*$ transition and has the highest peak in the spectrum, as demonstrated by the table's highest oscillator strength value. So yes, these values are in agreement with experimental data, although for other excitations I have not found experimental data.

5. Locate the following parameters of the CASSCF calculation in the acro.cas.out file

Number of configurations: 45
Orbitals doubly occupied in all configurations: 12
Active orbitals: 5
Active electrons: 6
Total electrons: 30

6. Give the weight and the active orbital occupancies the five most important configurations of the wave function of the ground state.

Table 2: Weight and Active Orbital Occupancies of the Ground State Wave Function.

Weight	Active Orbital Occupancies
0.928 97	22200
0.027 53	21210
0.017 37	20211
0.015 58	20220
0.009 32	20202

7. Characterize the wave functions of the excited states in the same manner

Excited State 1		Excited State 2		Excited State 3		Excited State 4	
Weight	Occupancies	Weight	Occupancies	Weight	Occupancies	Weight	Occupancies
0.84559	22110	0.43976	22101	0.86241	21210	0.80207	12210
0.05347	21120	0.41499	21120	0.07557	20220	0.05592	12201
0.04493	21111	0.06794	21102	0.02225	22200	0.03192	11211
0.02411	22101	0.04057	21111	0.02167	20211	0.03142	22101
0.01275	20112	0.01663	20121	0.01029	21201	0.02495	21120
0.00683	20121	0.00845	22110	0.00368	20202	0.01761	22110
0.00383	12210	0.00459	11220	0.00265	22020	0.01553	21111

Table 3: Weight and Active Orbital Occupancies for Excited States 1-4

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?

Table 4: Comparison of CASSCF and NEVPT2 calculations for excited states

Excitation	λ_{CAS} (nm)	E_{CAS} (cm^{-1})	f_{CAS}	λ_{NEV} (nm)	E_{NEV} (cm^{-1})	f_{NEV}
1	338.4	29 553.2	0.000 014 483	332.2	30 104.1	0.000 014 753
2	176.1	56 799.4	0.000 780 512	183.2	54 583.7	0.509 931 308
3	147.2	67 936.7	0.634 677 193	179.0	55 862.3	0.000 767 635
4	133.6	74 872.0	0.000 172 145	150.6	66 383.7	0.000 152 629

The NEVPT2 calculations yield lower excitation energies compared to CASSCF, implying that dynamic electron correlation tends to stabilize the excited states. This stabilization is further indicated by the increased energies in the NEVPT2 results. Additionally, while the oscillator strengths remain fairly consistent for the 1st and 4th states across both methods, there's a notable change in the 2nd and 3rd states, particularly with a higher transition probability in the 2nd state for NEVPT2 and the 3rd for CASSCF. Dynamic correlation plays a crucial role in acrolein due to its conjugated π system and that is why NEVPT2 improved the description and aligns better with experimental data.

9. Generate an input for molden. Open the acro.cas.molden.input file with molden and check the active orbitals. Are the orbitals as you expected? Why (not)?

All of the orbitals in the table are partially occupied (from 0 to 2) and belong to the active space, consequently. The orbitals with lower orbital numbers have

occupation equal to 2, which makes sense — they are fully occupied and they belong to inactive space. The rest of the orbitals with an orbital number starting from 18 have an occupation equal to 0, and they are from virtual space. So yes, this is what was expected.

Orbital number	eigenvalue	occupation
13	−0.543 036	1.81
14	−0.356 371	1.60
15	−0.345 896	1.58
16	−0.026 974	0.80
17	0.200 649	0.20

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?

Table 5: Transition energies and oscillator strengths obtained using CASSCF and NEVPT2.

Excitation	λ_{CAS} (nm)	E_{CAS} (cm^{-1})	f_{CAS}	λ_{NEV} (nm)	E_{NEV} (cm^{-1})	f_{NEV}
1	330.6	30 243.8	0.000 002 505	316.1	31 631.1	0.000 000 262
2	176.4	56 693.6	0.000 449 294	184.2	54 280.4	0.613 434 045
3	163.0	61 349.4	0.004 833 639	169.7	58 937.9	0.000 467 080
4	134.7	74 215.1	0.838 721 079	151.7	65 926.0	0.005 194 218

Table 6: Delta of CASSCF and NEVPT2 calculations between 8th and 10th tasks

State	$\Delta\lambda_{CAS}$ (nm)	ΔE_{CAS} (cm^{-1})	Δf_{CAS}	$\Delta\lambda_{NEV}$ (nm)	ΔE_{NEV} (cm^{-1})	Δf_{NEV}
1	−7.8	690.6	−0.000 012	−16.1	1527.0	−0.000 014 5
2	0.3	−105.8	−0.000 331 2	1.0	−303.3	0.103 502 7
3	15.8	−6587.3	−0.629 843 6	−9.3	3075.6	−0.000 300 6
4	1.1	−656.9	0.838 548 9	1.1	−457.7	0.005 041 6

Adjusting the active space changes excited state energies and predicted transition probabilities. This means the updated active space provides better insights into acrolein aspects. Let's dive into details.

In CASSCF, expanding the active space raises the first excited state energy. Destabilisation of the excited state makes the transition less favourable. However, the fourth excited state shows a decrease in energy and a significant oscillator strength increase. This suggests a stronger and more likely transition,

indicating that the newly added orbital is crucial to accurately describing this transition.

In the third excited state, energy decreases even more, indicating greater stability. Despite remaining relatively high, the oscillator strength decreases, making it less likely than the fourth excited state transition.

Almost similar patterns appear in NVPT2. The first and third states have higher energy and lower oscillator strength, indicating fewer transitions. Conversely, the second and fourth states are more stable, making transitions easier.

11. Try to come up with changes in the computational setup to improve the description of the excitation spectrum of acrolein.

Table 7: Possibilities to Improve the Description of Acrolein's Excitation Spectrum

Possibility	Pros	Cons
Expand active space with more orbitals	Improved electronic transition description	Increased computational resources required
Evaluate different TDDFT functionals	Opportunity to find a better-suited functional	Requires testing and benchmarking for appropriateness
Explore other multiconfigurational methods (*e.g., RASSCF, DMRG, etc.*)	Potentially more accurate description	Higher computational cost, method-specific challenges
Use larger, flexible basis set	Enhanced accuracy in capturing transitions	Higher computational cost
Taking into account solution environment	Potential improvement in the accuracy of simulated spectra	Increased computational cost for solvent modeling