

Lab 6: Excited states (SA-CASSCF, CASSI, CASPT2)

Input files:

acrolein.xyz

CASSCF.excited.acrolein

CASSCF.excited_grid.acrolein

CASPT2.excited.acrolein

CASSI.excited.acrolein

Introduction

In this lab we will study the basic way to compute electronic excited states by using multiconfigurational wave functions and perturbation theory. Excitation energies and transition dipole moments will be obtained. Symmetry restrictions will not be used.

Exercise 1: CASSCF.excited.acrolein and CASSCF.excited_grid.acrolein

In this exercise we will carry out State-Averaged (SA) CASSCF calculations on the low-lying singlet states of acrolein, using the RASSCF module. One single set of molecular orbitals is used to compute all the states of a given spatial and spin symmetry. The obtained density matrix will be averaged between all the states, although each state will have its own set of optimized CI coefficients. Different weights can be considered for each of the states, although is a dangerous strategy. The use of a SA-CASSCF procedure has an enormous advantage, such as that all obtained states in a SA-CASSCF calculation are orthogonal to each other, avoiding unphysical state overlaps. In this case we will include four states of singlet character within the calculation. As no symmetry is invoked all the states belong by default to the first symmetry, including the ground state.

In order to define which states we are going to compute we should better have a rough understanding of the electronic structure of the acrolein molecule. Look at the input and identify how we select the main parameters of the calculation: inactive and active orbitals and electrons, and the number of roots.

Now run the job and check

- a) geometry
- b) RHF energy and orbital occupation
- c) CI coefficients for each one of the computed CASSCF states
- d) Natural occupation numbers for each state
- e) Nature of the molecular orbitals. You may use MOLDEN or GV, but do not forget to analyze the orbitals directly from the output
- f) Energies of the SA-CASSCF states
- g) SA-CASSCF properties: dipole moments, spatial extensions, population analysis

Why we perform SA-CASSCF calculations? Should not be better to compute each root independently from the others?

We have used as active the $\pi\pi^*$ structure of the molecule, two bonding and two antibonding π orbitals with four electrons plus the oxygen lone pair (n). Keyword **CiRoot** informs the program

that we want to compute a total of five states, the lowest five (at the CASSCF level), and that all them should have the same weight in the average procedure. Once analyzed we can observe that the calculation has provided, in this order, the ground state, two $n\pi^*$ states, and two final $\pi\pi^*$ states.

The nature of the orbitals and states can be analyzed graphically. In the **CASSCF.excited.acrolein** input, and although *MOLCAS* does it by default, we have included the **GRID_IT** input in order to emphasize the use of the **gv** interface. In any case, and also by default, *MOLCAS* generates in \$WorkDir a set of **MOLDEN** files named sequentially \$Project.rasscf.State_number.molden where the natural orbitals corresponding to the different states can be analyzed. When the CASSCF method is used, a proper analysis of the obtained orbitals and state configurations is compulsory.

Using the **CASSCF.excited_grid.acrolein** input generates five interface files, one per state, using the natural orbitals of the respective state. By plotting charge difference graphs from the ground to the excited state it is possible to view the transfer of the electronic charge upon excitation. Try for instance the command `molcas gv CASSCF.excited_grid.acrolein.M2Msi -a -1.0 CASSCF.excited_grid.acrolein.M2Msi2` to see the outcome for the second CASSCF root, etc.

Exercise 2: CASPT2.excited.acrolein

CASSCF wave functions are typically good enough, but this is not the case for electronic energies, and the dynamic correlation effects have to be included, in particular here with the CASPT2 method. Check the input for such calculations performed on top of the SA-CASSCF wave functions. Any difference with the previous one?

The CASPT2 program will perform a number of consecutive single-state (SS) CASPT2 calculations using the SA-CASSCF roots computed by the RASSCF module. At the end, a multi-state CASPT2 calculations will be added in which the four SS-CASPT2 roots will be allowed to interact.

Run the calculation and check:

- Are the SA-CASSCF results the same as in Exercise 1?
- CASPT2 output: check reference CASSCF energies and total SS-CASPT2 energies for each one of the roots
- CASPT2 output: analyze MS-CASPT2 results, energies, wave functions and interaction hamiltonian
- Do the SS-CASPT2 and MS-CASPT2 results differ? Why and how?

Exercise 3: CASSI.excited.acrolein

Apart from energies and state properties it is quite often necessary to compute state interaction properties such as transition dipole moments, Einstein coefficients, and many other. This can be achieved by using the RASSI module, a powerful program which can be used for many purposes.

Check the input. Observe the inclusion of the CASPT2 energies.

Run the calculation and check:

- Structure of the output: matrix elements, properties, and cartesian components
- Observe the states overlap and the energies used by the program
- Look for the desired transition dipole moments
- Analyze the final table: oscillator strengths and Einstein coefficients

To end this section we may prepare a table like that (ΔE in eV, energy difference with respect to S_0):

State label	State Nature	ΔE (CASSCF)	ΔE (CASPT2)	ΔE (MS-CASPT2)	f	μ (D)
S_0	ground state	-	-	-	-	x.xxx
S_1	$\pi-\pi^*$	x.xx	x.xx	x.xx	x.xxx	x.xxx
etc						

1 au (energy) = 27.21165 eV; 1 au (dipole) = 2.5417 D