## *Lab □Excited states (optimizations, crossings)*

Input files:
CASSCF.excited_state_optimization.acrolein
CASSCF.S-T_crossing.acrolein

## *Introduction*

In this lab we will study techniques for geometry optimizations of excited states and how to find crossings between states of different symmetry and/or spin multiplicity.

## Exercise 1: CASSCF.excited_state_optimization.acrolein

In this exercise we will, using the CASSCF module, optimize the second root of acrolein.

Look at the input and identify how we select that it is the second root which we want to optimize in the SA-CASSCF.

Run the job, identify the
a) geometry, and
b) the energy.

Try to do the optimization in which you optimize the coefficients with respect to the 2nd state only. Run the job! The CASSCF procedure does not converge. Discuss why!

Modify the input so that the RASSCF module will use the orbitals and the CI coefficients of the previous iteration. To what extent does this reduce the number of CASSCF iterations?

## Exercise 2: CASSCF.S-T_crossing.acrolein

In this example we will locate the minimum energy cross point (MECP) between a singlet and triplet state. The job formally looks like doing two different projects simultaneously. However, in the SlapAf module both run files will be used.

Look at the input and identify these features. Run the job, identify the structure and the energy of the two states!

The MECP is just one of many different points in the conical intersection manifold. We can map out the seem by combining the constraints for a conical intersection with other constraints.

Modify the optimization above with that the MECP should be the center of a hypersphere and make a optimization on the hypersphere surface still requiring that you are in the conical intersection manifold. Run the job for a few different radius. In difference to a MEP-search the center of origin of the hypersphere is fix and the radius in increased as we go for the next point. Discuss why! Modify the input so that you start from the previously converged structure while the original MECP is still the center of the hypersphere.

## Exercise 3:

Find the structure of ethene (get starting coordinates from Lab 2 exercise 9!) for which the ground state and the lowest triplet state have the same energy. Compare this structure and energy of that of the equilibrium structure of the lowest  triplet state.

Start by producing a good starting structure by twisting the ethene molecule using a constraint optimization!