

## Lab 2 Solvent models

Input files:

acrolein.xyz

CASPT2.excited\_solvent.acrolein

### Introduction

In this lab we will study the inclusion of the effects of solvation in MOLCAS in different situations, both for absorption and emission processes, using the PCM approach. Symmetry restrictions will not be used.

### Exercise 1: CASPT2.excited\_solvent.acrolein

In this exercise we will apply the effect of an aqueous environment to the low-lying absorption and emission process in the previously studied acrolein molecule.

In order to properly compare results with and without solvent effects, let's start by copying the CASPT2.excited\_solvent.acrolein file with a new name (CASPT2.excited\_nosolvent.acrolein) and modify it in order to take away the solvent effects. Run both calculations and compare energies, wave functions, and properties.

Notice that the solvated calculations are made in two steps. First the reaction field in the ground (initial) state has to be computed. This is because solvation in electronic excited states is a non equilibrium situation in with the electronic polarization effects (fast part of the reaction field) have to be treated apart (they supposedly change during the excitation process) from the orientational (slow part) effects. The slow fraction of the reaction field is maintained from the initial state and therefore a previous calculation is required.

From the practical point of view the input is simple. First, the proper reaction-field input is included in **SEWARD**, then a **RASSCF** and **CASPT2** run of the ground state, with keyword **RFPErt** in **CASPT2**, and after that another SA-CASSCF calculation of two roots to get the wave function of the excited state. Keyword **NONEquilibrium** tells the program to extract the slow part of the reaction field from the previous calculation of the ground state (specifically from the *RUNFILE* file, which may be stored for other calculations) while the fast part is freshly computed. Also, as it is a SA-CASSCF calculation (if not, this is not required) keyword **RFRoot** is introduced to specify for which of the computed roots the reaction field is generated.

How would you design a calculation in two steps:

- Compute in one directory the solvated ground state.
- Compute the solvated excited state in a different directory including in the directory the proper previous files.

Notice that we have selected the fifth CASSCF root as excited state because it has the largest dipole moment among the computed states and then the observed effect will be larger (even if the excitation energy is exceedingly high for this state and level of calculation. You can now perform new calculations by changing the roots. The solvent effects will be smaller then.

The previous runs allow us to check the effect of the solvent on the vertical absorption. Could we design a calculation to study the effect of the solvent on the vertical emission (for the 2nd root)?

*Note:* As geometry for seaward you should use that obtained in the previous lab (CASSCF.excited\_state\_optimization.acrolein), because it corresponds to the minimum in the excited state.

Design a table as the one below.

State label	State Nature	Gas phase			Water		
		$\Delta E$ (CAS)	$\Delta E$ (CASPT2)	$\mu$ (D)	$\Delta E$ (CAS)	$\Delta E$ (CASPT2)	$\mu$ (D)
Vertical absorption							
S <sub>0</sub>	ground state	-	-	x.xxx	-	-	x.xxx
S <sub>1</sub>	n- $\pi^*$	x.xx	x.xx	x.xxx	x.xx	x.xx	x.xxx
S <sub>2</sub>	n- $\pi^*$	x.xx	x.xx	x.xxx	x.xx	x.xx	x.xxx
S <sub>3</sub>	$\pi$ - $\pi^*$	x.xx	x.xx	x.xxx	x.xx	x.xx	x.xxx
S <sub>4</sub>	$\pi$ - $\pi^*$	x.xx	x.xx	x.xxx	x.xx	x.xx	x.xxx
Vertical emission (fluorescence)							
S <sub>0</sub>	ground state	-	-	x.xxx	-	-	x.xxx
S <sub>1</sub>	n- $\pi^*$	x.xx	x.xx	x.xxx	x.xx	x.xx	x.xxx

1 au (energy) = 27.21165 eV

1 au (dipole) = 2.5417 D