## *Lab Excited states and symmetry*

Input files:
CASSCF.excited.tButadiene.1Ag
CASSCF.excited.tButadiene.1Bu

## *Introduction*

In this lab we will focus on the study of excited states using the symmetry properties of the wave functions.

## Exercise 1: CASSCF.excited.tButadiene.1Ag CASSCF.excited.tButadiene.1Bu

In this exercise we will carry out State-Averaged (SA) CASSCF calculations on three low-lying singlet states of $A_g$ symmetry in the trans-1,3-butadiene molecule, using the RASSCF module.

Run the calculation and check
a) In SEWARD: character table, full geometry, basis set, adapted basis functions
b) In SCF: check the ground state Hartree-Fock configuration. Read the orbital list and compare with the orbital scheme displayed below.
c) In RASSCF: understand the input and the obtained structure of states.

| | $a_g$ | $b_u$ | $b_g$ | $a_u$ |
|---|---|---|---|---|
| $(1s)_C$ | 2 | 2 | 0 | 0 |
| $(\sigma)_{CC}$ | 2 | 1 | 0 | 0 |
| $(\sigma)_{CH}$ | 3 | 3 | 0 | 0 |
| $(\pi)_{CC}$ | 0 | 0 | 1 | 1 |
| $(\pi^*)_{CC}$ | 0 | 0 | 1 | 1 |
| $(\sigma^*)_{CC}$ | 2 | 1 | 0 | 0 |
| $(\sigma^*)_{CH}$ | 3 | 3 | 0 | 0 |

Run also the calculation on two $^1B_u$ states and compute the transition dipole moments.

## Exercise 2: RASSCF.excited.tButadiene.1Ag

Change the previous input to run a true RASSCF calculation (singles and doubles excitations only) on the singlet Ag states including $\sigma$, $\sigma*$ and $\pi$, $\pi*$ space within the calculations.

## Exercise 3: CASSCF.excited.acrolein.pipi

### CASSCF.excited.acrolein.npi

Using your previous experience on acrolein design two different calculations to compute (just at the CASSCF level) the $\pi\pi^*$ and $n\pi^*$ states of the acrolein molecule within the $C_s$ symmetry.

## Exercise 4: more advanced calculations

The most complex type of calculations implies the study of high symmetry systems using low symmetries. Different cases such as homo- and heteronuclear diatomic molecules are carefully detailed in the examples section of the MOLCAS manual, for instance, how to calculate NiH ($C_{\infty v}$ computed as $C_{2v}$), $C_2$ or $Ni_2$ ($D_{\infty h}$ computed as $D_{2h}$). We will check and try to understand this type of calculations.