

Lab 3: Energy point calculations for CASSCF/RASSCF and CASPT2/RASPT2

Coordinate files:

- phenyl_iodine.xyz (handed out separately)
- CH4.xyz
- ethene.xyz (extract from the text)

Input files:

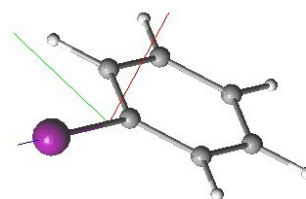
- Phenyl_iodine.input (handed out separately)
- CASSCF.energy.CH4.input
- RASSCF.energy.CH4.input
- CASPT2.energy.CH4.input
- CASPT2.energy.CH4plus.input

Introduction

In this lab we shall experience energy point calculations for the CASSCF, for the partially correlated RASSCF, and CASPT2 methods. We will first spend some time on a typical chemical problem in which we will select occupied, inactive and active orbitals. We shall then proceed with some examples where the focus is to find our way around in the output. We shall experience using the post processing utility GV to analyze the results from the calculations. This will be followed by a simple example in which we write an input from scratch. The structures of the molecule and ion are not equilibrium structures. Optimization will be the subject of a later lab.

Exercise 1: Active orbitals

The process of selecting active orbitals is the major difficulty in CASSCF calculations. In this exercise we will try using GSSORB and SCF orbitals as the starting orbitals for CASSCF. The GSSORB are the default starting orbitals, which are automatically generated by the SEWARD module (you actually only need to generate the one-electron integrals (keyword ONEONLY) for the GSSORB orbitals to be generated). The GSSORB orbitals tend to be localized. While the occupied SCF orbitals tend to be delocalized and the virtual SCF orbitals are not well defined. We will explore this difference.



The example here is for the phenyl iodine molecule. The molecule is placed in the YZ plane with the iodine-carbon bond in the z-direction. We will select an active space which would allow us to explore the dissociation of the iodine atom after a photo excitation within the π -system.

Task 1: Before we even start with the real calculations we will decide the selection of the inactive and active orbitals. We could do that by hand on a piece of paper. However, we will in this exercise use the GSSORB orbitals and GV to guide us. The first thing we need to do is to compute the number of valence orbitals. The input file phenyl_iodine.input has been rigged for that purpose. Here we will run only the GATEWAY module in combination with the explicit assignment of MOLCAS_PRINT=VERBOSE. Run the job with the command **molcas -f phenyl_iodone.input**. This will generate a detailed list of the symmetry adapted basis functions. View the log file with your favorite editor and add up the number of valence orbitals! Remember that the valence orbitals

for H, C, and I are 1s, 1s2s2p, and 1s2s2p3s3p4s3d4p5s4d5p, respectively (right answer: 30, 4, 18 and 10). Next compute the number of inactive orbitals! Clue: we trivially have the C 1s and I 1s2s2p3s3p4s3d4p5s4d inactive. Furthermore, we have all sigma orbitals, except for the C-I (i.e. 2px on carbon and 5px on iodine) are inactive. Finally we recognize that at infinite dissociation distance the 5px, 5py and 5pz of the iodine are degenerate, hence we keep them in the active space. This information is enough for us to find the inactive space (right answer: 22, 2, 12, and 5., this is split up as; the trivial core on C and I:

12, 2 5 5; sigma CH: 3 0 2 0; and sigma CC: 3 0 3 0). Make sure that you completely understand how to get all these numbers! At the same time we identify that the active space is generated from the 2px of the carbons, the 2pz and 5pz from the sigma C-I, and the 5px and 5py lone-pairs on the iodine (right answer: 2, 2, 1 and 5).

Task 2: Let us now look at the active orbitals as suggested by the GSSORB orbitals. Modify the input and make sure that the correct orbitals are generated by Grid_It (I have already done that for you, make sure that you understand the input). Run it! If you did everything alright you should after having cd:ed to phenyl_iodine/ and issued the command **molcas gv phenyl_iodin.grid** and pressed F3 see the following (see Illustration 1).

We identify the orbitals as: sigma C-I, sigma* C-I, pi, pi, y lone-pair, pi, pi, pi, and pi orbitals. Note that one of the lone-pairs of iodine mix with the conjugated system on the phenyl ring.

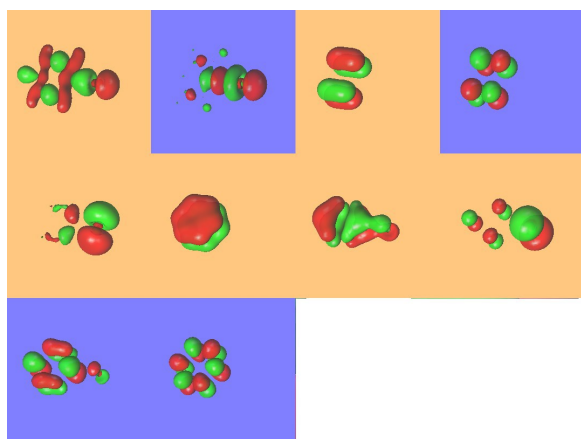


Illustration 2: GSSORB starting orbitals.

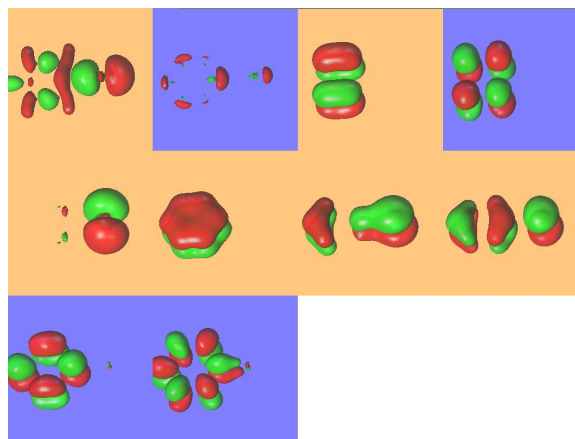


Illustration 1: SCF starting orbitals

Task 3: The next task is to run an SCF calculation and view the same set of orbitals. We have already the inactive orbitals and we need only to sort out which of the active orbitals are occupied at the SCF level of theory. The pi system contains 6 electrons, the lone-pair 4 electrons and the sigma C-I 2 electrons, hence we should have an additions 6 orbitals. From the orbital picture above we have that the following orbitals are double occupied at the SCF level of theory: 1, 3, 5, 6, 7 and 8, that is sigma C-I, pi. From this we deduce the occupied orbitals (right answer: 23, 3, 13, and 8). Use you favorite editor to activate the computation of two-electron integrals is Seward, inactivate the first Grid_it input and activate the SCF and the subsequent Grid_it input. Run the input, please. Then use GV to look at the corresponding SCF orbitals (see Illustration 2)! In particular, we note that in the place of the antibonding sigma C-I orbital we don't find what we anticipated.

This example is included to demonstrate the difficulty to get good starting vectors for the CASSCF or RASSCF procedure. We recommend that the you visually inspect the starting orbitals and the final CASSCF/RASSCF orbitals to make sure that you got what you anticipated. Remember that the CASSCF wave function has multiple solutions and that the starting orbitals are instrumental in helping you to find the correct solution for your particular choice of active space and active electrons. Some times DFT orbitals might be helpful. Sometimes particular CASSCF active spaces are only stable if a state average CASSCF (SA-CASSCF) approach is used. This is in particular the

case if in the ground state an orbital and its correlating partner is close to doubly occupied and empty. By including an Ciroot for which this is not the case will stabilize these orbitals presence in the active space.

Exercise 2: CASSCF

In this example we shall use the CASSCF wave function model applied to methane, in combination with a STO-3G basis set. The 1s orbital of the carbon atom will be inactive and all the valence orbitals will be in the active space. We shall compute the ground state first (a singlet).

Task 1: Look in the input (or see Illustration 3) and identify how we specified

- that the 1s orbital is doubly occupied (inactive),
- how the active orbitals are specified,
- how many electrons are used in the active space, and
- the spin.

Task 2: Run the job with the command **molcas -f CASSCF.energy.CH4.input!**

In the output identify (see Illustration 4 for the orbital section of the RASSCF module).

- the occupation numbers of the orbitals,
- the orbital energies (explain),
- the coefficient of the most important configuration state function (CSF),
- describe the second most important CSF,
- view the orbitals with GV (see Illustration 5) and identify the color coding for active and inactive orbitals. Why are there no virtual orbitals?

Task 3: Modify the input and make a calculation for the CH₄ cation (a doublet). What is the computed CH₄ ionization energy?

Illustration 4: Orbital output from the RASSCF module.

Illustration 5: CH₄ CASSCF orbitals

```
&GATEWAY
coord
CH4.xyz
basis
STO-3G
group
C1

&SEWARD

&RASSCF
Title
CH4 molecule
Spin
1
Nactel
8 0 0
Inactive
1
Ras2
8

&GRID_IT
All
Ascii
```

Illustration 3:
CASSCF.energy.
CH4.input

Molecular orbitals for symmetry species 1: a

Orbital	1	2	3	4	5	6	7	8	9
Energy	-11.0278	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Occ. No.	2.0000	1.9844	1.9766	1.9723	1.9672	0.0312	0.0266	0.0227	0.0190
1 C1 1s	-0.9933	0.2049	-0.0421	0.0367	-0.0302	-0.1008	0.1030	-0.1126	-0.1677
2 C1 2s	-0.0331	-0.6011	0.1364	-0.1234	0.1051	0.5710	-0.6068	0.6948	1.1004
3 C1 2px	-0.0005	-0.0666	0.2508	0.4615	-0.2064	-0.4329	0.5629	0.8052	0.1140
4 C1 2py	0.0003	0.0251	-0.0363	0.2503	0.5088	0.7751	0.7007	-0.0461	-0.0313
5 C1 2pz	-0.0008	-0.1625	-0.4949	0.1916	-0.1220	-0.3026	0.3540	-0.5607	0.8470
6 H2 1s	0.0084	-0.3230	-0.4144	0.1381	-0.0790	0.0247	-0.0688	0.2424	-1.2768
7 H3 1s	0.0078	-0.1797	0.4126	0.3059	-0.1096	0.0309	-0.1259	-1.1960	-0.2770
8 H4 1s	0.0073	-0.1096	0.1116	-0.4897	-0.2258	0.0519	1.1578	-0.1414	-0.1418
9 H5 1s	0.0068	-0.0694	0.0560	-0.1091	0.5503	-1.1168	0.0809	-0.0675	-0.0892

Illustration 4: Orbital output from the RASSCF module.

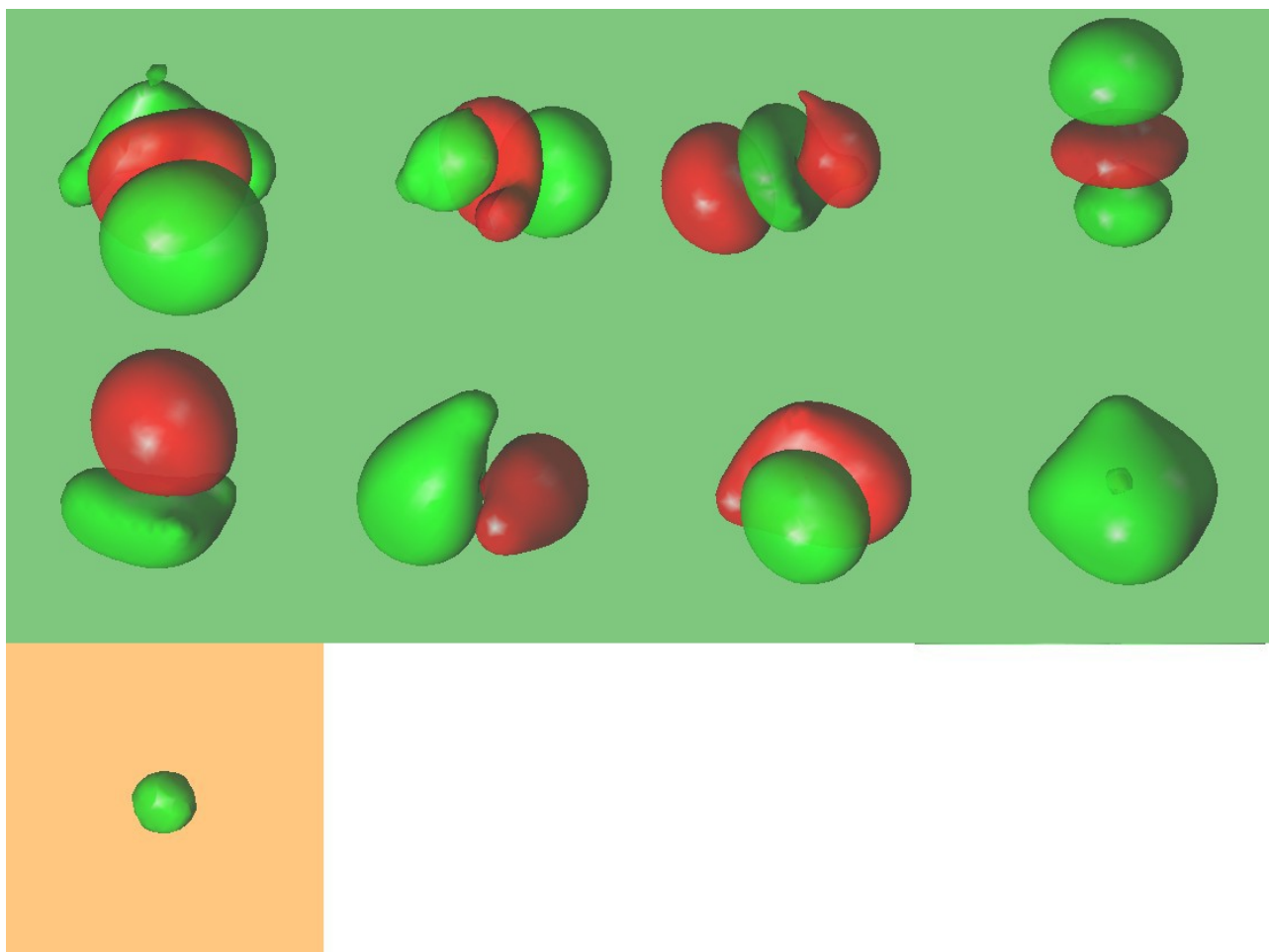


Illustration 5: Methane CASSCF orbitals.

Exercise 3: RASSCF

In this exercise we shall use the RASSCF model to reduce the number of CSFs in the calculation. The orbitals which in the CASSCF calculation were the closest to perfect double occupation are moved to the RAS1 space (space with limited number of holes) and the least occupied orbital of the RAS2 space are moved to the RAS3 space (see Illustration 6). Compare the inputs of exercises 2 and 3 and identify the difference.

Note: transformation to natural orbitals
has been made, which may change the order of the CSFs.

```
printout of CI-coefficients larger than 0.05 for root 1
energy=      -39.797180
conf/sym 11111111      Coeff Weight
      1  22220000      0.97531 0.95123
     18  22202000     -0.10528 0.01108
     60  22020200     -0.08115 0.00659
     93  20220020     -0.06061 0.00367
```

```
Natural orbitals and occupation numbers for root 1
sym 1:  1.984351  1.976645  1.972290  1.967240  0.031192  0.026621  0.022661  0.018999
```

Illustration 6: CSF and Occupation numbers from the CH₄ CASSCF calculation.

Task 1: Run the job (**molcas -f RASSCF.energy.CH4.input**) and identify the differences in

- occupation numbers,
- coefficients of the CSFs, and
- total energy between the CASSCF and RASSCF calculations.

Exercise 4: The ethene molecule

Task 1:Generate the input for a point energy calculation for ethene (see Illustration 7), for a) HF, b) DFT/B3LYP, and c) CASSCF in combination with a 6-31G** basis set.

Using the following xyz file:

```
6
Bohr
C 1.243000 0.000000 0.000000
C -1.243000 0.000000 0.000000
H 2.313000 1.731000 0.000000
H 2.313000 -1.731000 0.000000
H -2.313000 1.731000 0.000000
H -2.313000 -1.731000 0.000000
```

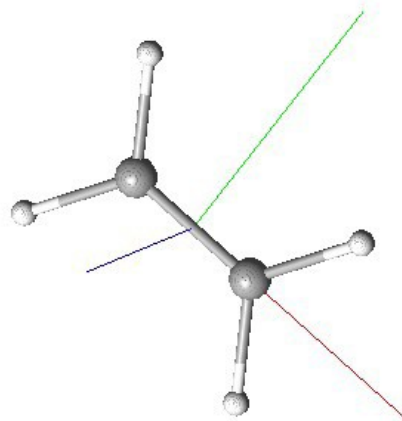


Illustration 7: The ethene molecule.

Task 2: Run and

- identify in the output which orbitals were the most important to correlate,
- identify the two most important CSFs, and
- compare SCF and DFT orbital energies of the HOMO and LUMO.

Create pictures of the HOMO and LUMO using the GV facility!

Exercise 5: CASPT2/RASPT2

The CASPT2 program accepts any general CASSCF/RASSCF type of reference states, i.e., radicals and excited states with arbitrary spin and electronic structure can be used in addition to closed-shell ground state electronic structures. The CASPT2 program uses a single CASSCF wave function, of arbitrary complexity, as the reference. The CASPT2 module can also do multi state calculations (MS-CASPT2), where several CASSCF wave functions (normally SA-CASSCF) are used simultaneously. The wave CASPT2 function is built from single and double excitations from the reference state.

Task 1:Run the job! In the CASPT2 output, find "Total number of CASPT2 parameters" (Trick question!). There are two numbers given. Try to explain the difference. Identify the "Reference energy", "Total Energy" and the "Reference weight" in the CASPT2 output (see Illustration 8).

```
Reference energy:          -39.7740740530
E2 (Non-variational):     -0.0164094188
E2 (Variational):        -0.0164094178
Total energy:            -39.7904834708
Residual norm:           0.0000003021
Reference weight:         0.99397
```

Illustration 8: Section of the output from the CASPT2 module.

Task 2 (If you have time): Modify the input to do a RASSCF/RASPT2 calculation!

Exercise 6: Methane cation (if you have time)

The CH_4^+ ion is a radical, since it has an unpaired electron. It can be computed by UHF or (unrestricted) DFT, but then all the alpha and beta orbitals will differ, and the resulting single determinant is then not a pure doublet, i.e. it breaks spin symmetry. This may be a serious disadvantage; sometimes it is, however, an advantage to have spin-polarized orbitals. If one wants a pure spin, there is in this and some other very simple cases a possibility to use the restricted open-shell HF (and DFT) method. Such programs are not included in MOLCAS, instead we use generally the CASSCF/RASSCF module which allows any general structure of the wave function. When spin, symmetry, number of active orbitals, etc., is such that the CI expansion is predetermined, so only orbitals remain to be optimized, the wave function is an open-shell HF wave function.

Task 1: Run the provided input. Identify that the CASSCF is a single determinant wave function (corresponds to a ROHF). Identify the reference weight and which are the important according to the CASPT2 analysis (see Illustration 9).

Report on small energy denominators, large coefficients, and large energy contributions.

The ACTIVE-MIX index denotes linear combinations which gives ON expansion functions and makes H_{00} diagonal within type.

DENOMINATOR: The $(H_{00} - E_0)$ value from the above-mentioned diagonal approximation.

RHS VALUE : Right-Hand Side of CASPT2 Eqs.

COEFFICIENT: Multiplies each of the above ON terms in the first-order wave function.

Thresholds used:

Denominators: 0.3000

Coefficients: 0.0250

Energy contributions: 0.0050

CASE	SYMM	ACTIVE-MIX	NON-ACTIVE	INDICES	DENOMINATOR	RHS VALUE	COEFFICIENT	CONTRIBUTION
AIVX	1	Mu1.0002	In1.002	Se1.006	1.94842015	0.05367987	-0.02752617	-0.00147760
BJAIP	1	Se1.008	In1.003	Se1.008 In1.003	2.47450445	0.08676857	-0.03508103	-0.00304393
BJAIP	1	Se1.009	In1.003	Se1.009 In1.003	2.61150566	0.09266482	-0.03549839	-0.00328945
BJAIP	1	Se1.008	In1.003	Se1.008 In1.004	2.45623591	0.06324070	-0.02577648	-0.00163012
BJAIP	1	Se1.007	In1.004	Se1.007 In1.004	2.32867597	0.11978295	-0.05152632	-0.00617197

Illustration 9: CASPT2 analysis of important external excitations.

Task 2: Take the information from **Task 1** and increase the active space to include the most important excitations of the CASPT2 already in the CASSCF wave function.