

A TUTORIAL FOR COLUMBUS

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1. Before starting

1.1 Necessary programs

- COLUMBUS, the variable \$COLUMBUS should also be defined pointing to the program. (You need PERL 5.8 or higher to run the COLUMBUS input programs.)

In this tutorial we will also use the following auxiliary programs for visualization and further analysis of results:

- MOLDEN.
- GNUPLOT.
- MOLEKEL.
- MAPLE.

These programs are not necessary for running jobs and performing the basic analysis.

1.2 Notation

1. The Tutorial is divided in several sections with different jobs. Advanced jobs may make reference to basics jobs.
2. The basic instructions are sequentially numbered.

This kind of font indicates what is seen in the screen
and the command lines that you should write <ENTER> ! Comments come here

Important information related to Columbus but not necessarily connected to the current job comes in boxes like this. It is advisable to read the boxes, but you can follow the tutorial without them.

1.3 Preparing the jobs

3. Create a directory TUTORIAL. Inside tutorial, new subdirectories will be created for each job.

We suggest that you organize your jobs using the following structure of directories. This will make easier to copy the files between different jobs.

2. MCSCF single point calculation without symmetry

In this section we will prepare a complete input for single point calculation at MCSCF level. The system is methaniminium cation CH_2NH_2^+ , which will be calculated using a complete active space composed by four electrons in three orbitals [CASSCF(4,3)]. Three states will be included in the state average procedure (SA-3) and the 6-31G* basis set will be used. No symmetry will be used (C_1 point group).

This is a very basic job that will be the first step for most of the other advanced jobs.

2.1 Orbital occupation and DRT tables

Before starting any COLUMBUS input it is strongly advisable to write down the details of the orbital occupation and distinct row tables. This information will be used during the inputs and it is very useful to have them available.

You can download doc and pdf templates of these tables at

<http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable>

In the Appendix of this Tutorial you can also find a blank version of these Tables.

1. Fill out the occupation table according to Fig. 1.

System: CH_2NH_2^+

Point Group: C_1

N. Electrons: 16

Level: MRCI(4,3)/SA-3-CASSCF(4,3)

		IRREP <i>! Irreducible representation</i>						
		<u><i>a</i></u>						
SCF	DOCC	<u><i>8</i></u>		<i>! Doubly occupied in the SCF wavefunction</i>				
	OPSH	<u><i>0</i></u>		<i>! Singly occupied in the SCF wavefunction</i>				
MCSCF	DOCC	<u><i>6</i></u>		<i>! Doubly occupied orbitals in the MCSCF</i>				
	RAS	<u><i>0</i></u>		<i>! Restricted orbitals (only single excitation from them)</i>				
	CAS	<u><i>3</i></u>		<i>! Active orbitals (single and double excitations)</i>				
	AUX	<u><i>0</i></u>		<i>! Auxiliary orbitals (only single excitation into them)</i>				
MRCI	FC	<u><i>2</i></u>		<i>! Frozen core orbitals (the two 1s) in the MRCI</i>				
	FV	<u><i>0</i></u>		<i>! Frozen virtual orbitals</i>				
	DOCC	<u><i>4</i></u>		<i>! Reference doubly occupied orbitals</i>				
	ACT	<u><i>3</i></u>		<i>! Reference active orbitals</i>				
	AUX	<u><i>0</i></u>		<i>! Reference auxiliary orbitals</i>				
	INT	<u><i>7</i></u>		<i>! Internal (DOCC+ACT+AUX)</i>				

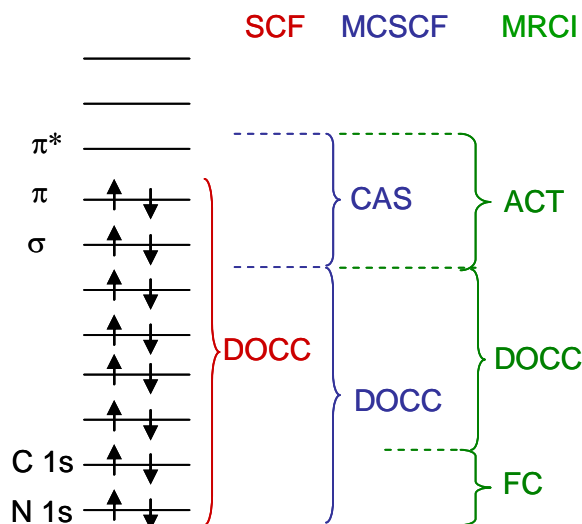


Fig. 1. Scheme of orbital occupation for MRCI(4,3) and CASSCF(4,3).

The orbital occupation should be done for each irreducible representation. In C_1 , there is only representation a . During the input, the representations are treated as numbers. These numbers are define in the next Table. (For example b_{2u} representation in D_{2h} symmetry has number 3).

	1	2	3	4	5	6	7	8
D_{2h}	a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u
D_2	a	b_2	b_1	b_3				
C_{2h}	a_g	b_u	a_u	b_g				
C_{2v}	a_1	b_1	b_2	a_2				
C_i	a_g	a_u						
C_s	a'	a''						
C_2	a	b						
C_1	a							

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
<u>1</u>	<u>1</u>	<u>16</u>	<u>A</u>
<u>2</u>	<u>1</u>	<u>16</u>	<u>A</u>
<u>3</u>	<u>1</u>	<u>16</u>	<u>A</u>

Number of distinct rows (DRTs): 1

To fill out this table, proceed writing one line for each desired state (in this job, three states). After that, just count the number of distinct rows. In this example, since all rows are the same, the number of distinct rows is 1.

2.2 Geometry file creation

3. In the TUTORIAL directory (see section 1.3) create a subdirectory called CNH4_CAS43_C1_SP:

```
> mkdir CNH4_CAS43_C1_SP
```

4. Move to this directory and create a file called cnh4.xyz containing the geometry in XYZ format:

6

N	0.051443	-0.125748	0.596619
C	0.067113	-0.025698	-0.683445
H	0.002169	0.695516	1.199263
H	0.087711	-1.030762	1.065358
H	0.027120	0.954772	-1.143351
H	0.120118	-0.922908	-1.288953

This initial geometry can be created by hand or with any molecular editor like MOLGEN. It is the simple xyz Cartesian format in Angstrom. The first line contains the number of atoms and it is followed by a blank line.

The hydrogen atoms must appear in the end of the file.

5. Convert geometry into COLUMBUS format.

```
> $COLUMBUS/xyz2col < cnh4.xyz <ENTER>
```

The COLUMBUS geometry file is called 'geom' and looks like

N	7.0	0.09721322	-0.23762938	1.12744696	14.00307401
C	6.0	0.12682524	-0.04856220	-1.29152439	12.00000000
H	1.0	0.00409882	1.31433528	2.26627952	1.00782504
H	1.0	0.16574983	-1.94785866	2.01323565	1.00782504
H	1.0	0.05124939	1.80425831	-2.16062112	1.00782504
H	1.0	0.22699021	-1.74404405	-2.43576913	1.00782504

The second column contains the atomic number, and the following three columns contain the x, y and z coordinates in atomic units. The last column contains the atomic mass.

COLUMBUS uses fixed format (1x,a2,2x,f5.1,4f14.8). Analogous file but with free format is also used in NEWTON-X.

The conversion back from COLUMBUS format to xyz can be done with the program geom2molden.

```
> $COLUMBUS/geom2molden geom
```

After running this program, the xyz-format geometry is written to file 'geom.molden'.

2.3 PREPINP step

6. Run:

```
> $COLUMBUS/prepinp <ENTER>
```

7. Enter information about symmetry and geometry file.

File inpcol exists. Do you want to overwritten it? y ! Press <ENTER> after the input

Enter the point group symmetry: c1 ! Only Abelian groups

Name of the file containing the cartesian coordinates of the unique atoms (COLUMBUS format): geom

Number of atoms = 6

8. Enter information about basis sets.

-- Set basis set --

Type the atomic symbol to select the basis set (eg, He): N ! basis sets for Nitrogen

...

```
30: NITROGEN      Pople 3-21g*
31: NITROGEN      Pople 3-21++g*
32: NITROGEN      Pople 6-31g
33: NITROGEN      Pople 6-31g* or 6-31g**
34: NITROGEN      Pople 6-31++g* or 6-31++g**
35: NITROGEN      Pople 6-311g* or 6-311g**
36: NITROGEN      Pople 6-311++g* or 6-311++g**
37: PAC-ECP basis; Pitzer group; cc-pvdz (4s4p1d)/[3s2p1d]/[2s2p1d]
38: Pseudo Basis: Stevens, Basch and Krauss, JCP 81, 6026 (1984).
(4s4p)/[2s2p]
0: Other library
```

Select the basis set for atom N: 33 ! 6-31G* was selected

...

Would you like to set the basis for other kind of atoms? (y/n) y

Type the atomic symbol to select the basis set (eg, He): C

...

Select the basis set for atom C: 30

...

Would you like to set the basis for other kind of atoms? (y/n) y

Type the atomic symbol to select the basis set (eg, He): H

...

Select the basis set for atom H: 27

Until now you've set the following basis sets:

```
N :: NITROGEN      Pople 6-31g* or 6-31g**
C :: CARBON        Pople 6-31g* or 6-31g**
H :: HYDROGEN      Pople 6-31g or 6-31g*
```

Would you like to set the basis for other kind of atoms? (y/n) n

Normal termination of prepinp. See result in inpcol.

You can enter the atoms in any order.

If you enter the wrong basis set for some atom type, just enter this atom again and the previous choice will be replaced.

Other basis sets not contained in the COLUMBUS library can be entered by selecting "0: Other library". In this case, PREPINP will ask the path to this library.

If different basis sets should be attributed to the same atom type, make the distinction in the geom file, by giving different symbols. For example H1, H2 for having hydrogen atoms with different basis sets. Remember that the format is A2.

Hint: Some programs like MOLDEN cannot recognize non-standard labels (H1, H2). Therefore, it may be helpful to rename to have names like (H, He). Of course, instead enter He basis set, the H basis set should be used by selecting "0: Other library".

The default address of the basis sets libraries in COLUMBUS is:

`$COLUMBUS/source/iargos/basis`

2.4 COLINP step: Integral input

9. Run:

```
> $COLUMBUS/colinp
```

```
->  1) Integral program input (for argos/dalton/turbocol)
    2) SCF input
    3) MCSCF input
    4) CI input
    5) Set up job control
    6) Exit the input facility
```

COLINP is the main input tool for COLUMBUS. The inputs for MCSCF and CI calculations are also made with it.

You can navigate through the menus with <up> and <down> arrows. To select the option, press <Enter>. You can also exit the program and return later on to resume the input.

To make the input, you should go through each option in the menu, in the sequence as they appear there (you will not be able to make the CI input before the MCSCF input, for example).

10. Select option 1) Integral program input.

```
...
Would you like to do an interactive input? <YES> n      ! Select "no".
```

If you select "yes", COLINP will ask to enter all information about geometry and basis sets again, atom per atom.

2.5 COLINP step: SCF input

11. Select option 2) SCF input.

```
->  1) Integral program input (for argos/dalton/turbocol)
    2) SCF input
    3) MCSCF input
    4) CI input
    5) Set up job control
    6) Exit the input facility
```

```
...
Do you want a closed shell calculation ? <YES> y ! If you just press
                                                    <ENTER>, the default
                                                    (yes) is assumed
```

Input the no. of doubly occupied orbitals for each irrep, DOCC:

```
8 <ENTER>
```

```

The orbital occupation is:          ! This information is in the Orbital
                                     occuparion table
                                     ! In representation a:
      a                             ! 8 double occupied orbitals
DOCC      8                         ! 0 open shell orbitals
OPSH      0

```

Is this correct? <YES> <ENTER>

Would you like to change the default program parameters? <NO> <ENTER>

Input a title: <Default SCF Title>

--> <ENTER>

2.6 COLINP step: MCSCF input

12. Select option 3) MCSCF input

```

      1) Integral program input (for argos/dalton/turbocol)
      2) SCF input
->    3) MCSCF input
      4) CI input
      5) Set up job control
      6) Exit the input facility

```

MCSCF WAVE FUNCTION DEFINITION

=====

...

Note: additional group restrictions available (see COLUMBUS documentation)

press return to continue <ENTER>

prepare input for no(0),CI(1) or MCSCF(2) analytical gradient 1

With this option it is possible to select whether the job is only a single point or the gradient should also be computed.

no (0) – for single point calculation

CI (1) – for jobs requiring gradient calculation with the CI gradient routine (for example, geometry optimization and non-adiabatic couplings at MRCI or state-averaged MCSCF).

MCSCF (2) – for jobs requiring gradient calculations using MCSCF gradient routine. Essentially geometry optimization with single state MCSCF.

In the current example, we select 1 because we are going to get gradients at MRCI level.

Note, however, that a single point calculation using option 0 is more computationally efficient than the same single point calculation using option 1.

Enter number of DRTS [1-8] 1 ! This information is in the DRT Table

number of electrons for DRT #1 16

multiplicity for DRT #1 1

spatial symmetry for DRT #1 1 ! Representation A (see Orbital occupation table)

excitation level (cas,ras)->aux 0 ! Allow 0 excitation into auxiliary

```

                                orbitals

excitation level ras->(cas,aux) 0 ! allow 0 excitation from the
                                restricted active orbitals

number of doubly occupied orbitals per irrep 6

number of CAS orbitals per irrep 3

Apply add. group restrictions for DRT 1 [y|n] n

Convergence
  1. Iterations                #iter [60 ]    #miter [30 ]    #ciiter [30 ]
  2. Thresholds                knorm [1.e-4 ] wnorm [1.e-4 ] DE [1.e-8 ]

  3. HMC-matrix                build explicitly [n]
                                diagonalize iteratively [y]
  4. Miscallenous              quadratic cnvg. [y] from #iter [5 ]

Resolution (NO)                RAS [NO ] CAS [NO ] AUX [NO ]
State-averaging
                                DRT 1: #states [3 ] weights[ 1,1,1
                                MCSCF transition moments [y]

                                FINISHED [y]

```

In this last panel, the only option that you should worry about is “#states” (number of state in the state average procedure). All others either are set to good default values or are automatically adjusted.

We also select y in “MCSCF transition moments” in order to have the oscillator strengths. The specific transitions that will be computed can be selected in the next panel.

```

                                transition moment selections

(Done with selections)
[ ] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
[x] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2 ! S0 → S1
[x] bra: DRT# 1 state# 1 ket: DRT# 1 state# 3 ! S0 → S2
[ ] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2
[ ] bra: DRT# 1 state# 2 ket: DRT# 1 state# 3
[ ] bra: DRT# 1 state# 3 ket: DRT# 1 state# 3

```

2.7 Running a MCSCF single point job

13. Select option 5) Set up job control

```

1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
4) CI input
-> 5) Set up job control
6) Exit the input facility

```

14. Select option 1) Job control for single point or gradient calculation

```

-> 1) Job control for single point or gradient calculation
2) Potential energy curve for one int. coordinate
3) Vibrational frequencies and force constants

```

4) Exit

15. Select option 1) Single point calculation

```
->  1) single point calculation
    2) geometry optimization
    3) saddle point calculation (local search - GDIIS)
    4) stationary point calculation (global search - RGF)
    5) nonadiabatic coupling (single point)
    6) optimization on the crossing seam (GDIIS)
    7) optimization on the crossing seam (POLYHES)
    8) Exit
```

16. Select the following options marked below and finish with “Done with selections”.

```
->  1) (Done with selections)
    2) [☒] SCF
    3) [☒] MCSCF
    4) [☒] transition moments for MCSCF
    5) [☐] standard MR-CISD with one DRT (ciudg)
    6) [☐] standard MR-CISD with several DRTs (ciudg)
    7) [☐] transition moments for MR-CISD
    8) [☐] <L> value calculation for MR-CISD
    9) [☐] parallel MR-CISD (pciudg)
   10) [☐] sequential version of pciudg (sciudg)
   11) [☐] one-electron properties for all methods
   12) [☒] convert MOs into molden format
   13) [☐] finite field calculation for all methods
```

17. In the next panels, select “Exit” until finishing COLINP execution.

The job control will instruct COLUMBUS to perform the SCF, the MCSCF and the transition moments calculations in sequence.

The SCF calculation is usually performed only at the first job, when we still do not have the molecular orbitals written to a file. When a good set of molecular orbitals is obtained, we should skip the SCF calculation.

18. Run Columbus.

```
> $COLUMBUS/runc -m 200000000 > runls &
```

“-m” command defines the memory allocated to COLUMBUS, in this case 200 million words (Mwords). The conversion is 1 GB = 134 Mwords.

2.8 Checking the results

19. Check the convergence of the MCSCF calculation in the LISTINGS/mcscfsm.sp file.

```
...
final mcscf convergence values:
iter=   7 emc= -94.1553285066 demc= 1.2233E-10 wnorm= 5.0301E-07 knorm= 3.8488E-08 apxde=
1.0167E-14      *converged*
```

20. The MCSCF energies are written in the same file LISTINGS/mcscfsm.sp file.

```
-----Individual total energies for all states:-----
DRT #1 state # 1 weight 0.333333 total energy=    -94.398532380
DRT #1 state # 2 weight 0.333333 total energy=    -94.053559794
DRT #1 state # 3 weight 0.333333 total energy=    -94.013893346
-----
```

21. The wavefunction information is written in LISTINGS/mcpcls.drt1.stateX.sp files. For the ground state for example, LISTINGS/mcpcls.drt1.state1.sp shows:

List of active orbitals:

7 a 8 a 9 a

csf	coeff	coeff**2	step(*)
1	0.9468051363	0.8964399661	330
2	0.3001655970	0.0900993856	312
3	-0.1145666379	0.0131255145	303
6	-0.0183066579	0.0003351337	033

The configuration state function (CSF) 1 is the dominant in the ground state with coefficient 0.9468. This CSF is characterized by the double occupation of the active orbitals 7 and 8, while orbital 9 is unoccupied.

In the GUGA approach the orbital occupation is defined as:

0 – unoccupied

1 – singly-occupied with spin α .

2 – singly-occupied with spin β .

22. The oscillator strengths and transition dipole moments are written to files LISTINGS/transls.FROMdrt1.stateXTOdrt1.stateY. For example, between the ground and the first excited state, one can read in LISTINGS/transls.FROMdrt1.state2TOdrt1.state1:

	State No. 1	State No. 2
Space symmetry:	A	A
Multiplicity:	1	1
No. of CSFs:	6	6
State energies:	-94.05355979	-94.39853238 a.u.
Transition energy:	-0.34497259 a.u.	
Transition energy:	-9.39 eV	
Transition frequency:	***** 1/sec	
Transition frequency:	***** cm-1	

Transition moment components:

x	y	z
-0.000002	-0.000004	0.000071 e*bohr

Tr.dipole length:	0.000071	e*bohr
Oscillator strength:	0.000000	
Einstein A coef.:	-4.4071E+00	1/sec
Einstein B coef.:	2.0340E+00	sec/g

23. The mscf, scf and natural orbitals are written to files MOCOEFS/mocoef_mc.sp, MOCOEFS/mocoef_scf.sp and MOCOEFS/nocoef_mc.sp respectively.

24. In directory MOLDEN, the molecular orbitals written in MOLDEN format are available.

```
> moldern MOLDEN/moldern_mo_mc.sp & ! 'moldern' is an alias to MOLDEN path
```

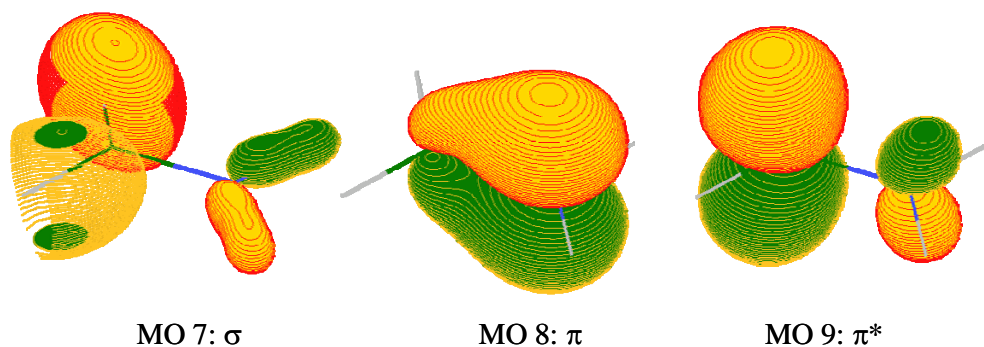


Fig. 2. Molecular orbitals visualized with Molden using contour value 0.1.

Usually, the active orbitals obtained in the first MCSCF calculation do not correspond to the active space that we have in mind.

When that happens, it is necessary to reorder the molecular orbital file and run the MCSCF calculation again.

COLUMBUS distribution contains an auxiliary program called `reordermo.x` to do this task.

In the current example, inspection of active orbitals (Fig. 2) shows that they correspond to the σ , π and π^ aimed. Therefore, no reordering is necessary.*

3. MRCI single point calculation without symmetry

In this section we will perform a single point calculation at MRCI level for methaniminium cation CH_2NH_2^+ . The reference space for the MRCI contains four electrons in three orbitals [MRCI(4,3)] (see Fig. 1). This calculation is done on the top of the SA-3-CASSCF(4,3) MCSCF calculation performed in section 2. The 6-31G* basis set will be used. No symmetry will be used (C_1 point group).

3.1 Basic input

1. In the TUTORIAL directory (see section 1.3) create a subdirectory called CNH4_MRCI43_C1_SP:

```
> mkdir CNH4_MRCI43_C1_SP
```

2. Move to this directory and repeat the geometry, SCF and MCSCF (sections 2.2 to 2.6).
Alternatively, just copy the input files from the MCSCF directory:

```
> cp ../CNH4_CAS43_C1_SP/* .
```

3. Copy the molecular orbital file generated in the MCSCF calculation.

```
> cp ../CNH4_CAS43_C1_SP/MOCOEFS/mocoef_mc.sp mocoef
```

In this job we will skip the SCF step. Therefore a molecular orbital file should be provided. The default name for this file is "mocoef".

3.2 COLINP step: MRCI input

```
> $COLUMBUS/colinp
```

```
1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
-> 4) CI input
5) Set up job control
6) Exit the input facility
```

It is strongly recommended to use the orbital occupation table during the input. Note that there is no way back in case of a mistake, i.e. the complete CI input has to be done again.

```
CI WAVE FUNCTION DEFINITION
```

```
...
```

```
press return to continue <enter>
```

```
1) Def. of CI wave function (data from MCSCF)
2) Def. of CI wave function for geom.opt (data from MCSCF)
-> 3) Def. of CI wave function - one-DRT case
4) Def. of CI wave function - one-DRT case (geom.opt.)
5) Definition of CI wave function - multiple-DRT case
6) Definition of CI wave function - multiple-DRT case (NAD coupl.)
7) Skip DRT input (old input files in the current directory)
```

Note that we could also have chosen option 1.

Ref.DOCC orbitals at the bottom (default)[0] or top [1]? (0|1) 0 <enter>

4. The orbital occupation and DRT information is defined in the following options:

Multiplicity: #electrons: Molec. symm.

```
count order (bottom to top): fc-docc-active-aux-extern-fv
irreps      a
# basis fcts 36
```

Enter the multiplicity 1 <enter> ! we want to calculate a singlet
Enter the number of electrons 16 <enter>
Enter the molec. spatial symmetry 1 <enter> ! Representation 'a' in C₁
number of frozen core orbitals per irrep 2 <enter>
number of frozen virt. orbitals per irrep 0 <enter>
number of internal(=docc+active+aux) orbitals per irrep 7 <enter>
ref doubly occ orbitals per irrep 4 <enter>
auxiliary internal orbitals per irrep 0 <enter>
Enter the excitation level (0,1,2) 2 <enter>
Generalized interacting space restrictions [y|n] y <enter> ! faster
Enter the allowed reference symmetries 1 <enter>

The options in "Enter the excitation level (0,1,2)" are:

0 – MCSCF

1 – MR-CIS

2 – MR- CISD

In several occasions, as for instance in the geometry optimization at state-average CASSCF level, the MCSCF calculation is defined also here, using excitation level 0.

5. The job summary should look like this now:

Ref.DOCC orbitals at the bottom (default)[0] or top [1]? (0|1) 0

Multiplicity:1 #electrons:16 Molec. symm.:a

```
count order (bottom to top): fc-docc-active-aux-extern-fv
irreps      a
# basis fcts 36
```

```
frozen core      2
frozen virt      0
internal         7
ref. docc.       4
ci active        3
ci auxiliary     0
external        27
```

exc.level:2 gen.space:y allowed ref. syms:1

6. Proceed with the input:

Apply additional group restrictions for DRT [y|n] n <enter>

Choose CI program: sequential ciudg [1]; parallel ciudg[2] 1 <enter>

7. The last panel will appear. The only thing which should be changed is NROOT from 1 to 3, the number of roots. By doing so, the last panel will look like this

```
Type of calculation:          CI [Y] AQCC [N] AQCC-LRT [N]
LRT shift:                  LRTSHIFT [0 ]
State(s) to be optimized    NROOT [3 ] ROOT TO FOLLOW [0]
Reference space diagonalization INCORE[Y] NITER [ ]
                             RTOL [1e-3,1e-3,1e-3, ]
Bk-procedure:               NITER [1 ] MINSUB [3 ] MAXSUB [8 ]
                             RTOL [1e-3,1e-3,1e-3, ]
CI/AQCC procedure:          NITER [60 ] MINSUB [5 ] MAXSUB [8 ]
                             RTOL [1e-3,1e-3,1e-3, ]
                             FINISHED [ ]
```

8. Move the cursor to FINISHED and press <enter>. The next panel allows the selection of transition moments. We select:

```
-> 1) (Done with selections)
    2) [ ] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
    3) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2 ! S0 → S1
    4) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 3 ! S0 → S2
    5) [ ] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2
    6) [ ] bra: DRT# 1 state# 2 ket: DRT# 1 state# 3
    7) [ ] bra: DRT# 1 state# 3 ket: DRT# 1 state# 3
```

3.3 Running a MRCI single point job

9. Enter the job control menu

```
    1) Integral program input (for argos/dalton/turbocol)
    2) SCF input
    3) MCSCF input
    4) CI input
-> 5) Set up job control
    6) Exit the input facility
```

10. Select a single point job:

```
-> 1) Job control for single point or gradient calculation
    2) Potential energy curve for one int. coordinate
    3) Vibrational frequencies and force constants
    4) Exit
```

11. If you have copied the files from your MCSCF calculation, COLUMBUS recognizes your old job control file and asks you whether to discard it or not. In this case type y <enter>.

12. Select single point calculation

```
-> 1) single point calculation
```

- 2) geometry optimization
- 3) saddle point calculation (local search - GDIIS)
- 4) stationary point calculation (global search - RGF)
- 5) nonadiabatic coupling (single point)
- 6) optimization on the crossing seam (GDIIS)
- 7) optimization on the crossing seam (POLYHES)
- 8) Exit

13. Choose the following options:

- ```
-> 1) (Done with selections)
 2) [] SCF
 3) [X] MCSCF
 4) [] transition moments for MCSCF
 5) [X] standard MR-CISD with one DRT (ciudg)
 6) [] standard MR-CISD with several DRTs (ciudg)
 7) [X] transition moments for MR-CISD
 8) [] <L> value calculation for MR-CISD
 9) [] parallel MR-CISD (pciudg)
 10) [] sequential version of pciudg (sciudg)
 11) [] one-electron properties for all methods
 12) [X] convert MOs into molden format
 13) [] finite field calculation for all methods
```

*Be careful to not to choose SCF and to have the right mocoef file in your directory.*

### 14. Exit the input facility.

### 15. Run Columbus.

```
> $COLUMBUS/runc -m 200000000 > runls &
```

## 3.4 Checking the results

### 16. Check the convergence of the MCSCF calculation in the LISTINGS/ciudgsm.sp file.

```
...
mr-sdci convergence criteria satisfied after XX iterations.
...
```

### 17. The MRCI energies are written in the same file LISTINGS/ ciudgsm.sp file.

```
final mr-sdci convergence information:
mr-sdci # 28 1 -94.6661949066 1.0772E-10 0.0000E+00 3.7264E-04 1.0000E-03
mr-sdci # 28 2 -94.3453200805 9.0450E-07 2.1115E-07 6.5044E-04 1.0000E-03
mr-sdci # 28 3 -94.3093367906 1.0570E-09 0.0000E+00 6.7046E-04 1.0000E-03
```

*After that summary, more detailed results collected root by root can be found like e.g. the Davidson and the Pople corrections.*

```
number of reference csfs (nref) is 6. root number (iroot) is 1.

eref = -94.398163755308 "relaxed" cnot**2 = 0.919592746017
eci = -94.666194906585 deltae = eci - eref = -0.268031151277
eci+dv1 = -94.687746555441 dv1 = (1-cnot**2)*deltae = -0.021551648856
eci+dv2 = -94.689630986251 dv2 = dv1 / cnot**2 = -0.023436079666
eci+dv3 = -94.691876533663 dv3 = dv1 / (2*cnot**2-1) = -0.025681627078
eci+pople = -94.686909114958 (12e- scaled deltae) = -0.288745359649

number of reference csfs (nref) is 6. root number (iroot) is 2.
```

```

eref = -94.053552141044 "relaxed" cnot**2 = 0.898537079403
eci = -94.345320080540 deltae = eci - eref = -0.291767939496
eci+dv1 = -94.374923707818 dv1 = (1-cnot**2)*deltae = -0.029603627278
eci+dv2 = -94.378266553152 dv2 = dv1 / cnot**2 = -0.032946472612
eci+dv3 = -94.382460448159 dv3 = dv1 / (2*cnot**2-1) = -0.037140367619
eci+pople = -94.374949340493 (12e- scaled deltae) = -0.321397199449

```

number of reference csfs (nref) is 6. root number (iroot) is 3.

```

eref = -94.011453695818 "relaxed" cnot**2 = 0.899008156050
eci = -94.309336790573 deltae = eci - eref = -0.297883094755
eci+dv1 = -94.339420553594 dv1 = (1-cnot**2)*deltae = -0.030083763021
eci+dv2 = -94.342800072100 dv2 = dv1 / cnot**2 = -0.033463281527
eci+dv3 = -94.347034971130 dv3 = dv1 / (2*cnot**2-1) = -0.037698180557
eci+pople = -94.339418866944 (12e- scaled deltae) = -0.327965171127

```

18. The wavefunction information for all states is written in LISTINGS/cipcls.drt1.sp file. For the ground state for example, the information can be found in the section labeled VECTOR # 1:

```

rmo(*) = 3 4 5 6 7 8 9

printing selected csfs in sorted order from cmin = 0.01000 to cmax =
1.00000

indcsf c c**2 v lab:rmo lab:rmo step(*)

1 -0.90693 0.82253 z* 3333330
2 -0.29722 0.08834 z* 3333312
3 0.09270 0.00859 z* 3333303

```

*The step vector uses the molecular orbitals in the order specified at rmo( \* ) .*

*The configuration state function (CSF) 1, characterized by the double occupation of the active orbitals 7 and 8 while orbital 9 is unoccupied (see Fig. 2), is the dominant one in the ground state with coefficient 0.90693. It can be written as  $\sigma^2\pi^2$  using only the orbitals of the CAS. The other contributions to the ground state are the  $\pi\pi^*$  CSF with a coefficient of -0.29722 and the  $\pi^{*2}$  CSF with a coefficient of 0.09270.*

19. The oscillator strengths and transition dipole moments are written to files LISTINGS/trncils.FROMdrt1.stateXTOdrt1.stateY. For example, between the ground and the first excited state, one can read in LISTINGS/trncils.FROMdrt1.state1TOdrt1.state2:

|                       | State No. 1       | State No. 2       |
|-----------------------|-------------------|-------------------|
| Space symmetry:       | A                 | A                 |
| No. of CSFs:          | 64477             | 64477             |
| State energies:       | -94.66619491      | -94.34532008 a.u. |
| Transition energy:    | 0.32087482 a.u.   |                   |
| Transition energy:    | 8.73 eV           |                   |
| Transition frequency: | 0.21113E+16 1/sec |                   |
| Transition frequency: | 0.70424E+05 cm-1  |                   |

Transition moment components:

|          | x        | y        | z         |        |
|----------|----------|----------|-----------|--------|
| electron | 0.000003 | 0.000012 | -0.000197 | e*bohr |

|                       |            |        |
|-----------------------|------------|--------|
| Tr.dipole length:     | 0.000197   | e*bohr |
| Oscillator strength : | 0.000000   |        |
| Einstein A coef.:     | 0.2745E+02 | 1/sec  |
| Einstein B coef.:     | 0.1574E+02 | sec/g  |

## 4. MRCI geometry optimization without symmetry

In this section we will optimize the geometry of the first singlet excited state at MRCI level. The system is methaniminium cation  $\text{CH}_2\text{NH}_2^+$ . The reference space for the MRCI contains four electrons in three orbitals [MRCI(4,3)] (see Fig. 1). This calculation is done on the top of the SA-3-CASSCF(4,3) MCSCF calculation performed in section 2. The 6-31G\* basis set will be used. No symmetry will be used ( $C_1$  point group).

### 4.1 Basic input

1. In the TUTORIAL directory (see section 1.3) create a subdirectory called CNH4\_MRCI43\_C1\_OPTS1:

```
> mkdir CNH4_MRCI43_C1_OPTS1
```

2. Move to this directory and repeat the geometry, SCF and MCSCF (sections 2.2 to 2.6).  
Alternatively, just copy the input files from the MCSCF directory:

```
> cp ../CNH4_MRCI43_C1_SP/* .
```

3. Copy the molecular orbital file generated in the MCSCF calculation.

```
> cp ../CNH4_CAS43_C1_SP/MOCOEFS/mocoef_mc.sp mocoef
```

*In this job we will skip the SCF step. Therefore a molecular orbital file should be provided. The default name for this file is "mocoef".*

*As usual, the optimization algorithm will keep the symmetry of the initial input even when the job is formally in  $C_1$ . Thus, if the initial structure is planar, the final optimized geometry will probably be planar unless the numerical errors are large enough to break the planarity themselves. If you do not want this kind of restriction, be sure that the initial geom file is truly non-symmetric.*

### 4.2 COLINP step: MRCI input

```
> $COLUMBUS/colinp
```

```
1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
-> 4) CI input
5) Set up job control
6) Exit the input facility
```

*It is strongly recommended to use the orbital occupation table during the input. Note that there is no way back in case of a mistake, i.e. the complete CI input has to be done again.*

```
CI WAVE FUNCTION DEFINITION
```

```
...
```

```
press return to continue <enter>
```

```
1) Def. of CI wave function (data from MCSCF)
2) Def. of CI wave function for geom.opt (data from MCSCF)
```

- 3) Def. of CI wave function - one-DRT case
- > 4) Def. of CI wave function - one-DRT case (geom.opt.)
- 5) Definition of CI wave function - multiple-DRT case
- 6) Definition of CI wave function - multiple-DRT case (NAD coupl.)
- 7) Skip DRT input (old input files in the current directory)

*Note that we could have chosen option 2.*

Ref.DOCC orbitals at the bottom (default)[0] or top [1]? (0|1) 0 <enter>

#### 4. The orbital occupation and DRT information is defined in the following options:

Multiplicity: #electrons: Molec. symm.

```
count order (bottom to top): fc-docc-active-aux-extern-fv
irreps a
basis fcts 36
```

```
Enter the multiplicity 1 <enter> ! we want to calculate singlet states
Enter the number of electrons 16 <enter>
Enter the molec. spatial symmetry 1 <enter> ! irrep a in C1
number of frozen core orbitals per irrep 2 <enter>
number of frozen virt. orbitals per irrep 0 <enter>
number of internal(=docc+active+aux) orbitals per irrep 7 <enter>
ref doubly occ orbitals per irrep 4 <enter>
auxiliary internal orbitals per irrep 0 <enter>
Enter the excitation level (0,1,2) 2 <enter>
Generalized interacting space restrictions [y|n] y <enter> ! faster
Enter the allowed reference symmetries 1 <enter>
```

#### 4. The job summary should look like this now:

Ref.DOCC orbitals at the bottom (default)[0] or top [1]? (0|1) 0

Multiplicity:1 #electrons:16 Molec. symm.:a

```
count order (bottom to top): fc-docc-active-aux-extern-fv
irreps a
basis fcts 36
```

```
frozen core 2
frozen virt 0
internal 7
ref. docc. 4
ci active 3
ci auxiliary 0
external 27
```

exc.level:2 gen.space:y allowed ref. syms:1

#### 5. Proceed with the input:

Apply additional group restrictions for DRT [y|n] n <enter>

Choose CI program: sequential ciudg [1]; parallel ciudg[2] 1 <enter>

6. The last panel will appear. The only thing which should be changed is NROOT from 1 to 2, the number of roots. By doing so, the last panel will look like this

```
Type of calculation: CI [Y] AQCC [N] AQCC-LRT [N]
LRT shift: LRTSHIFT [0]
State(s) to be optimized NROOT [2] ROOT TO FOLLOW [0]
Reference space diagonalization INCORE[Y] NITER []
 RTOL [1e-4,1e-4,]
Bk-procedure: NITER [1] MINSUB [2] MAXSUB [7]
 RTOL [1e-4,1e-4,]
CI/AQCC procedure: NITER [60] MINSUB [4] MAXSUB [7]
 RTOL [1e-4,1e-4,]

 FINISHED []
```

Move the cursor to FINISHED and press <enter>.

*In the case of geometry optimization, NROOT defines not only the number of CI roots but also which state will be optimized (the energy gradient will be calculated for state NROOT).*

7. Exit the input facility.

### 4.3 Running a MRCI geometry optimization job

8. Enter the job control menu

```
1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
4) CI input
-> 5) Set up job control
6) Exit the input facility
```

9. Select a gradient calculation job:

```
-> 1) Job control for single point or gradient calculation
2) Potential energy curve for one int. coordinate
3) Vibrational frequencies and force constants
4) Exit
```

10. If you have copied the files from your MCSCF calculation, COLUMBUS recognizes your old job control file and asks you whether to discard it or not. In this case type y <enter>.

11. Select geometry optimization

```
-> 1) single point calculation
2) geometry optimization
3) saddle point calculation (local search - GDIIS)
4) stationary point calculation (global search - RGF)
5) nonadiabatic coupling (single point)
6) optimization on the crossing seam (GDIIS)
7) optimization on the crossing seam (POLYHES)
8) Exit
```

Internal coordinates generated!

Press return to continue <enter>

Enter the number of optim. cycles: 10 <enter>

*Do not use a large number of maximum iteration cycles. The default number (10) is a good choice. The optimization algorithm works better if you restart the job after these cycles.*

## 12. Choose the following options:

- > 1) (Done with selections)  
2) [ ] mcscf gradient  
3) [X] ci gradient  
4) [ ] one electron properties  
5) [X] convert MOs into molden proprietary format  
6) [ ] fix one or more coordiante in optimization  
7) [ ] activate CI restart after 2-nd geomopt. iter.

Afterwards the program will ask for the starting orbitals:

starting orbitals from scf prior to mcscf? (y|n) n <enter>

*Be careful to choose no in “starting orbitals from scf prior to mcscf?”, otherwise Columbus will perform an initial SCF calculation and the desired mocoef file will not be used.*

*You can fix one or more internal coordinates during the geometry optimization. If you check the corresponding option, a panel asking the number of the internal coordinates that should be frozen will appear next. These numbers can be found in the intcfl file in the input directory. This file looks like:*

```
TEXAS
K STRE 1 2. 1.
K STRE 2 3. 1.
...
K0.5000000 1. TORS 12 5. 2. 1. 3.
 1. TORS 6. 2. 1. 3.
 1. TORS 5. 2. 1. 4.
 1. TORS 6. 2. 1. 4.
...
```

*The bond distance between the carbon atom (2.) and the nitrogen atom (1.) is coordinate 1.  
The linear combination of the four torsional angles is coordinate 12.*

## 13. Exit the input facility.

## 14. Run Columbus.

```
> $COLUMBUS/runc -m 200000000 > runls &
```

## 4.4 Checking the results

15. The convergence of the geometry optimization can be checked in the file LISTINGS/gdiisls.all.

Convergence of the geometry optimizations:

| criterion                  | required  | actual    | conv. |
|----------------------------|-----------|-----------|-------|
| Maximal coordinate change: | 0.0010000 | 0.0004280 | yes   |



|                          |           |           |     |
|--------------------------|-----------|-----------|-----|
| Coordinate rms value     | 0.0002000 | 0.0001273 | yes |
| Maximal gradient change: | 0.0010000 | 0.0004380 | yes |
| Gradient rms value       | 0.0002000 | 0.0001702 | yes |

\*\*\* Geometry optimization converged! \*\*\*

*The calculation will produce a set of geometries and their corresponding orbital files. The geometries are stored in the directory GEOMS whereas the orbital files are stored in the MOCOEFS directory.*

*The orbital files are also available in MOLDEN format stored in the directory MOLDEN. The ci natural orbitals for each state and the mcscf orbitals and natural orbitals of the  $i^{\text{th}}$  step are written to files `nocoef_ci.drt1.stateX.i`, `MOCOEFS/mocoef_mc.i`, and `MOCOEFS/nocoef_mc.sp` respectively. The optimized structure and its orbitals are stored also as “filename.min”.*

*Take note that the geom file in the main directory is updated every cycle and finally equals the geom.min file .*

16. Use molden to visualize the individual geometries of the optimization.

```
> molden MOLDEN/molden.all
```

17. Use the buttons Next or Movie to switch between them. The button “Geom. Conv.” opens a window showing additional information about the convergence.

## 5. MRCI single point non-adiabatic coupling vector calculation

In this section we will calculate the non-adiabatic coupling vectors at MRCI level for methaniminium cation  $\text{CH}_2\text{NH}_2^+$ . The reference space for the MRCI contains four electrons in three orbitals [MRCI(4,3)] (see Fig. 1). This calculation is done on the top of the SA-3-CASSCF(4,3) MCSCF calculation performed in section 2. The 6-31G\* basis set will be used. No symmetry will be used ( $C_1$  point group).

### 5.1 Basic input

1. In the TUTORIAL directory (see section 1.3) create a subdirectory called CNH4\_MRCI43\_C1\_NADSP:

```
> mkdir CNH4_MRCI43_C1_NADSP
```

2. Move to this directory and repeat the geometry, SCF and MCSCF (sections 2.2 to 2.6).  
Alternatively, just copy the input files from the MCSCF directory:

```
> cp ../CNH4_CAS43_C1_SP/* .
```

3. Copy the molecular orbital file generated in the MCSCF calculation.

```
> cp ../CNH4_CAS43_C1_SP/MOCOEFS/mocoef_mc.sp mocoef
```

*Again, we will skip the SCF step. Remember to copy “mocoef” file as it was done before.*

### 5.2 COLINP step: MRCI input

4. Remove *transmomin* file before running calculations.

```
> rm -f transmomin
```

... and run colinp

```
> $COLUMBUS/colinp
```

```
1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
-> 4) CI input
5) Set up job control
6) Exit the input facility
```

CI WAVE FUNCTION DEFINITION

...

press return to continue <enter>

```
1) Def. of CI wave function (data from MCSCF)
2) Def. of CI wave function for geom.opt (data from MCSCF)
3) Def. of CI wave function - one-DRT case
4) Def. of CI wave function - one-DRT case (geom.opt.)
5) Definition of CI wave function - multiple-DRT case
-> 6) Definition of CI wave function - multiple-DRT case (NAD coupl.)
7) Skip DRT input (old input files in the current directory)
```

*Generally rules are the same as for MRCI input so we will not repeat our comments;  
**Important:** the order of question is slightly changed for this type of input; so here we start...*

Ref.DOCC orbitals at the bottom (default)[0] or top [1]? (0|1) 0 <enter>

The orbital occupation and DRT information is defined in the following options:

```
=====
==== CIDRTMS input facility ==
==== Version 0.99 - 09/04/01 ==
=====
```

Enter number of DRTS [1-8] 1  
Spin-Orbit CI [y|n] n  
Enter the multiplicity (all DRTs) 1  
Enter the number of electrons (all DRTs) 16

*Note, that with input at the bottom of the screen you can see entered values, for example after this step you should see:*

Input shared by ALL DRTs:  
#DRTs:1 mult:1 #el:16 genspace: NO SOCI

Generalized interacting space restrictions [y|n] y

number of frozen core orbitals per irrep 2  
number of frozen virt. orbitals per irrep 0  
number of internal(=docc+active+aux) orbitals per irrep 7

*... a change ahead ...*

number of aux. orbitals per irrep 0

*...and here we see ...*

```
count order (bottom to top): fcore-docc-active-aux-extern-fvirt
irreps a
basis fcts 36
frozen core 2
frozen virt 0
internal 7
ci active 7
ci auxiliary 0
external 27
```

Input shared by ALL DRTs:  
#DRTs:1 mult:1 #el:16 genspace:y NO SOCI

press return to continue <ENTER>

*... and now we are going back to definitions ...*

DRT specific input

```
irreps a exc sym refsym
basis fcts 36
ci active 7
```

ref doubly occ orbitals per irrep for DRT #1 4

excitation level (0,1,2) 2

state symmetry (1 .. nsym) 1

allowed reference symmetries 1

Apply additional group restrictions for DRT 1 [y|n] n

5. The last panel will appear. We should change NROOT from 1 to 3, since for this example we will be interested in the NAD coupling between first (2) and the second excited state (3). After that we are almost done...

```
Type of calculation: CI [Y] AQCC [N] AQCC-LRT [N]
LRT shift: LRTSHIFT [0]
State(s) to be optimized NROOT [3] ROOT TO FOLLOW [0]
Reference space diagonalization INCORE[Y] NITER []
 RTOL [1e-4,1e-4,1e-4,]
Bk-procedure: NITER [1] MINSUB [3] MAXSUB [8]
 RTOL [1e-4,1e-4,1e-4,]
CI/AQCC procedure: NITER [90] MINSUB [5] MAXSUB [8]
 RTOL [1e-4,1e-4,1e-4,]
```

FINISHED [<ENTER>]

6. Next we do have to choose transition between states. We should mark these between states of our interest (in our example  $S_1$  to  $S_2$ ). Let's do so...

symmetric and antisymmetric transition moment selections

(for <L> calculation select all trasitions)

(for nonadiabatic coupling select only one trasitions)

```
1) (Done with selections)
2) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
3) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2
4) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 3
5) [] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2
-> 6) [X] bra: DRT# 1 state# 2 ket: DRT# 1 state# 3
7) [] bra: DRT# 1 state# 3 ket: DRT# 1 state# 3
```

*Header is not exactly telling the truth – for these single point calculations we can calculate ALL couplings ...but we don't need them now.*

## 7. ... and go back to the first point ...

```
-> 1) (Done with selections)
 2) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
 3) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2
 4) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 3
 5) [] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2
 6) [X] bra: DRT# 1 state# 2 ket: DRT# 1 state# 3
 7) [] bra: DRT# 1 state# 3 ket: DRT# 1 state# 3
```

<ENTER>

## 8. ... UFFFF, we are back to the main menu !!!

```
1) (Done with selections)
2) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
-> 3) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2
 4) [] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2
```

```
-> 1) (Done with selections)
 2) [] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
 3) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2
 4) [] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2
```

## 5.3 Running a single point non-adiabatic coupling vector calculation

### 9. Enter the job control menu

```
1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
4) CI input
-> 5) Set up job control
 6) Exit the input facility
```

### 10. Select nonadiabatic coupling (single point)

```
1) single point calculation
2) geometry optimization
3) saddle point calculation (local search - GDIIS)
4) stationary point calculation (global search - RGF)
-> 5) nonadiabatic coupling (single point)
 6) optimization on the crossing seam (GDIIS)
 7) optimization on the crossing seam (POLYHES)
 8) Exit
```

Internal coordinates are being generated.

Internal coordinates generated!

Press return to continue <ENTER>

Internal coordinate file exists, would you like to overwrite it? (y|n) n  
*! NO NEED FOR THAT*

### submenu 1.2.1: calculation of nonadiabatic coupling terms

- 1) DCI\*(E2-E1) term
- 2) DCSF term
- > 3) DCI+DCSF term ! Both terms should be selected

*The non-adiabatic coupling vector between electronic states I and J is defined at atom  $\alpha$  as:*

$$\mathbf{h}(J, I, \alpha) = \left\langle \Psi_J(\mathbf{r}, \mathbf{R}) \left| \frac{\partial \Psi_I(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_\alpha} \right| \right\rangle_{\mathbf{r}}$$

*where  $\mathbf{r}$  and  $\mathbf{R}$  stands for the electronic and nuclear coordinates respectively and the integration is performed over the electronic coordinates.*

*This formula splits in two terms:*

$$\mathbf{h}(J, I, \alpha) = D^{CI} + D^{CSF},$$

*where*

$$D^{CI} = \frac{1}{(E^I - E^J)} \left\langle C^J \left| \frac{\partial H}{\partial \mathbf{R}_\alpha} C^I \right| \right\rangle_{CSF} \quad \text{and}$$

$$D^{CSF} = \sum_{i,j} D_{i,j}^{JI} \left\langle \phi_i \left| \frac{\partial \phi_j}{\partial \mathbf{R}_\alpha} \right| \right\rangle.$$

*In these equations,  $C^K$  is the CI coefficient for state K and  $\phi_n$  is the configuration state function (CSF).*

Starting orbitals from scf prior to mcscf? (y|n) n  
 Orthogonalize g and h vectors before getting the phase? (y|n) y

Enter the energy threshold (eV):1 <ENTER>

11. And we are ready to run the job – see how the control.run file looks like. You should see:

```
niter = 1
slope
dethres = 1
nadcoupl
hermit
mcscf
ciudgav
ciudgmom
```

12. Run Columbus.

```
> $COLUMBUS/runc -m 200000000 > runls &
```

## 5.4 Checking the results

13. Check the convergence of the MCSCF calculation in the LISTINGS/ciudgsm.drt1.sp file.

```
...
mr-sdci convergence criteria satisfied after XX iterations.
...
```

14. The final results may be found in the GRADIENTS directory. The coupling terms in cartesian coordinates calculated between states 2 and 3 may be found in the file 'cartgrd.nad.drt1.state2.drt1.state3.sp.org':

```
1.364416E-06 2.440751E-05 4.265704E-04
3.962713E-06 -1.565968E-04 -5.777138E-04
-7.147144E-01 -3.451527E-02 -1.142651E-02
7.147225E-01 3.455307E-02 1.137612E-02
6.084168E-01 2.935855E-02 9.831089E-03
-6.084306E-01 -2.926358E-02 -9.623259E-03
```

15. The coupling terms in internal coordinates are located in the file 'intgrd.nad.drt1.state2.drt1.state3.sp'.

```
0.00302302
-0.00013260
-0.00013862
-0.00051124
-0.00127400
0.00015339
0.00066735
0.00009334
0.00038138
-0.00017425
0.00005698
9.87435264
```

16. The very nice summary of calculations is given in the file LISTINGS/slopels.drt1.state2.drt1.state3. We have there all results of our interest, additionally with description of the files in MAPLE and MOLDEN:

```
Gradient 1 (a.u.) ! gradient for S1
0.00034 0.00213 -0.02724
...

Gradient 2 (a.u.) ! gradient for S1
0.00358 0.02286 -0.29246
...

Nonadiabatic coupling vector (a.u.)
0.00000 0.00000 -0.00002
...

Sum gradient
0.00196 0.01249 -0.15985
...

Difference gradient
0.00162 0.01037 -0.13261
...

Orthogonalized g vector !!! This is our g vector
0.00162 0.01037 -0.13261
-0.00212 -0.01356 0.17347
-0.00029 0.00405 0.00551
0.00016 -0.00486 0.00482
-0.00052 0.01888 -0.02429
0.00114 -0.01488 -0.02691

Orthogonalized h vector ! and here it is our NAD coupling vector
0.00000 0.00000 -0.00003
```

```

0.00000 0.00000 0.00004
0.02572 0.00124 0.00041
-0.02572 -0.00124 -0.00041
-0.02189 -0.00105 -0.00036
0.02189 0.00105 0.00034

```

17. Here coming other information that may be useful for example when making visualization...

```

Norm and orthog. information:

g=(g2-g1)/2; s=(g2+g1)/2
g*h = 0.0000. Original value.
g*hort = 0.0000 . New g and h obtained via Yarkony orthogonaliz.

Frobenius norm of g, h and s vectors (hartree/a0):
|g| = 0.2235 |gort| = 0.2235
|h| = 0.0478 |hort| = 0.0478
|s| = 0.2052

Parameters analysis:

The linear adiabatic energies in the unscaled-orthogonal x-y space are:
Ea = sx*x+sy*y -/dgh*((x**2+y**2)/2+Delta_gh*(x**2-y**2)/2]**(1/2)
...

eV,Angstrom units:
Inclination: d_gh (eV/A) = 11.75
Cylindrical: Delta_gh = 0.91
Tilt g: s_x (eV/A) = 9.25
Tilt h: s_y (eV/A) = 0.01

sigma_x=s_x/d_gh; sigma_y=s_y/d_gh
Tilt g: sigma_x = 0.787
Tilt h: sigma_y = 0.001

```

*The two adiabatic surfaces around the conical intersection are written as:*

$$E_a = \sigma_x x + \sigma_y y \pm \delta_{gh} \left[ \frac{(x^2 + y^2)}{2} + \frac{\Delta_{gh}(x^2 - y^2)}{2} \right]^{1/2}.$$

*The parameters describe the pitch, inclination and ellipticity of the cone.*

```

MAPLE output

...

eV, Angstrom units ! see Fig. 3
dgh:= 11.75;
Delta:= 0.91;
sx:= 9.25;
sy:= 0.01;
Esup:=sx*x+sy*y+dgh*((x^2+y^2)/2+Delta*(x^2-y^2)/2)^(1/2);
Einfr:=sx*x+sy*y-dgh*((x^2+y^2)/2+Delta*(x^2-y^2)/2)^(1/2);

MOLDEN output !!! This is important for further visualization

Written to molden.nad (arbitrary value of freq.):
Vibration 1: g1
Vibration 2: g2
Vibration 3: s
Vibration 4: g (original)
Vibration 5: h (original)
Vibration 6: g (orthogonal)
Vibration 7: h (orthogonal)

```



Wrinting Molden with DE = -3.598324193599470E-002

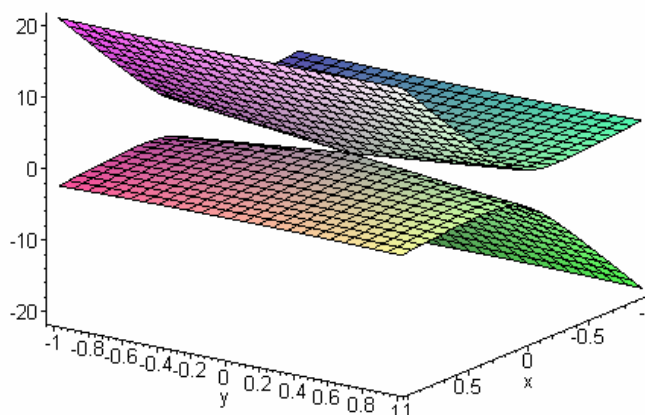


Fig. 3. Linear approximation of the  $S_1$  and  $S_2$  surfaces around de conical intersection plotted with MAPLE program.

---

18. To visualize the non-adiabatic coupling vectors we will use MOLEKEL program using the  
Vibration 5: h (original)

from the file located in MOLDEN/molden.nad.drt1.state2.drt1.state3:

```
> molekel -mldf MOLDEN/molden.nad.drt1.state2.drt1.state3
```

19. Then right click on the screen will give us menu from which we will choose Frequency.

20. In the “frequencies” window mark show arrows and click choose and in frequency selection click on 5 and accept. The NAD vector will be plotted on the screen as in the Fig. 4.

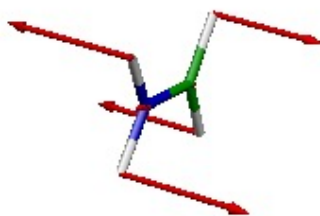


Fig. 4. Non-adiabatic coupling vector.

---

21. All other information like energies and molecular properties, etc. may be found in the usual places – see MRCI single point calculations.

## 6. MRCI conical intersection search

In this section we will optimize the conical intersection between states  $S_0$  and  $S_1$  at MRCI level for methaniminium cation  $\text{CH}_2\text{NH}_2^+$ . The reference space for the MRCI contains four electrons in three orbitals [MRCI(4,3)] (see Fig. 1). This calculation is done on the top of the SA-3-CASSCF(4,3) MCSCF calculation performed in section 2. The 6-31G\* basis set will be used. No symmetry will be used ( $C_1$  point group).

### 6.1 Basic input

1. In the TUTORIAL directory (see section 1.3) create a subdirectory called CNH4\_MRCI43\_C1\_MXS:

```
> mkdir CNH4_MRCI43_C1_MXS
```

2. Move to this directory and repeat the geometry, SCF and MCSCF (sections 2.2 to 2.6) and definition of CI wave function for multiple-DRT case (NAD coupl.) (settings for section 5.2). Alternatively, just copy the input files from the NADSP directory:

```
> cp ../CNH4_MRCI43_C1_NADSP/* .
```

3. Copy the molecular orbital file generated in the MCSCF calculation.

```
> cp ../CNH4_CAS43_C1_SP/MOCOEFS/mocoef_mc.sp mocoef
```

*Don't forget to copy "mocoef" file – without it calculations will not start. NOTE: If you copied input files from NADSP directory "mocoef" is already there...*

### 6.2 COLINP step: MRCI input

4. Run

```
> $COLUMBUS/colinp
```

```
1) Integral program input (for argos/dalton/turbocol)
2) SCF input
3) MCSCF input
4) CI input
-> 5) Set up job control
6) Exit the input facility
```

**IMPORTANT:** We can skip CI input step since we did it already for NAD coupling – otherwise YOU HAVE TO PERFORM "CI input" SETUP for "6) Definition of CI wave function - multiple-DRT case (NAD coupl.)" before setting up the job control, and when asked for transition **CHOOSE ONLY ONE CORRESPONDING MXS** – in our example it would be the same MXS between  $S_1$  and  $S_2$

5. Then we will choose following steps:

```
submenu 1: type of calculation
```

```
-> 1) Job control for single point or gradient calculation
```

- 2) Potential energy curve for one int. coordinate
- 3) Vibrational frequencies and force constants
- 4) Exit

6. If asked for discarding file select **y**

7. Select optimization on the crossing seam (GDIIS), and follow the input...

- 1) single point calculation
- 2) geometry optimization
- 3) saddle point calculation (local search - GDIIS)
- 4) stationary point calculation (global search - RGF)
- 5) nonadiabatic coupling (single point)
- > 6) optimization on the crossing seam (GDIIS)
- 7) optimization on the crossing seam (POLYHES)
- 8) Exit

Internal coordinate file exists, would you like to overwrite it? (y|n) **n**

[Enter the number of optim. cycles: **10**]

*The MXS search is an expensive type of calculation – better stay with smaller number and if necessary change it later, during the restart*

**<ENTER>**

Starting orbitals from scf prior to mcscf? (y|n) **n**

Orthogonalize g and h vectors before getting the phase? (y|n) **y**

[Enter the energy threshold (eV): **1**] **<ENTER>**

Fix one or more internal coordinates? (y|n) **n <ENTER>**

8. Leave input facility. We are **ALMOST** ready to run the job – see how the control.run file looks like. You should see:

```
niter = 10
cirestart
slope
dethres = 1
nadcoup1
hermit
mcscf
ciudgav
ciudgmom
gdiis
```

9. Manually remove line cirestart (if is there) and we are ready to go!

10. Run Columbus.

```
> $COLUMBUS/runc -m 200000000 > runls &
```

### 6.3 Checking the results

11. As in all cases we can see what is actually going on with our calculations by looking on standard output or in our case on the “*runls*” file where standard output was redirected. More information on the progress of the optimization of minimum on the crossing seam can be extracted from the LISTINGS/gdiisfl and LISTINGS/gdiisls.all files. COLUMBUS is also providing a graphical visualization of the convergence behavior of the calculation in the form of a MOLDEN file. The convergence informations are written in the file: MOLDEN/molden.all. To visualize ongoing optimization run molden:

```
> molden MOLDEN/molden.all &
```

12. A screen shot (here from the 7<sup>th</sup> step) would look like:

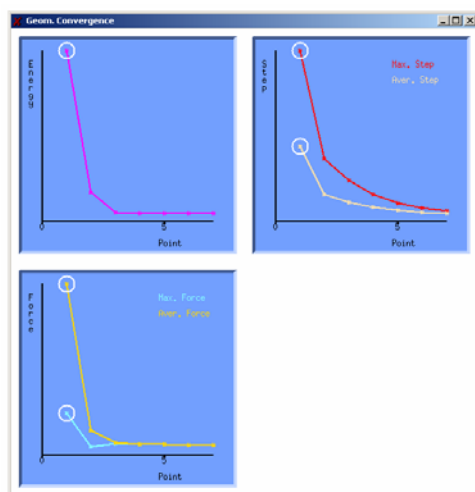


Fig. 5. MOLDEN output showing the MXS optimization steps. Upper-left panel: energy gap.  
Bottom panel:  $S_1$  and  $S_2$  energies.

*Unfortunately it is not possible to change the sub-window description by the MOLDEN input file (see Fig. 5). Therefore the comments in the sub-windows are not always corresponding to the displayed values. In the left upper sub-window the energy difference  $E(S_2)-E(S_1)$  is plotted. In the right upper sub-windows the maximal and average step size is plotted. In the left lower sub-window the total energies of the states  $S_2$  and  $S_1$  are plotted.*

*Remember that optimization of the MXS is quite an expensive process, thus try to start from the structure as close as possible to the result you think can be correct. Some general rules for possible localization of the MXS can be found in the literature. In the case of methaniminium cation conical intersection between states  $S_0$  and  $S_1$  – can be reached by 90 degree twist around CN bond – there it is much faster to get to the MXS when we would start from structure where hydrogens at the end are located in approximately perpendicular planes.*

*Additionally, in the case of such costly calculations it is always recommended to follow the process of optimization, and not to start with large number of the optimization cycles. After few steps we can see where the system is going and than if the number of steps was to small*

*eventually restart calculations copying last geometry (from GEOMS folder) and last molecular coefficient (from MOCOEFs folder) as a starting point.*

13. The convergence of the geometry optimization can be checked in the file LISTINGS/gdiisls.all

```

Maximal coordinate change: 0.0010000 0.0000435 yes
Coordinate rms value 0.0002000 0.0000214 yes
Maximal gradient change: 0.0010000 0.0512844 no
Gradient rms value 0.0002000 0.0167086 no
```

```
*** Geometry optimization converged! ***
```

14. Similar to the standard optimization all points during optimization and the optimized geometry (“geom.min”) in COLUMBUS format can be found in GEOMS directory.

*Existence of such a file is also one of the indications that optimization was successful.*

15. As in the previous case, it may be further useful to visualize NAD coupling vectors. For this please check section 5.4. When the optimization is finished, similar to previous cases all other information can be found in “usual” places; for example the energies for the optimized structure in “LISTINGS/ciudgsm.drt1.all”:

```
final mr-sdci convergence information:
mr-sdci # 43 1 -94.6357670741 2.8422E-14 0.0000E+00 4.4678E-05 1.0000E-04
mr-sdci # 43 2 -94.3542044966 6.1478E-09 1.2481E-08 9.8110E-05 1.0000E-04
mr-sdci # 43 3 -94.3542015923 2.6998E-10 0.0000E+00 3.7465E-05 1.0000E-04
```

16. Here we should see two crossing surfaces of our interest, having almost identical energy.

*One of the problems that you can run into performing analysis of MXS, is difficulties in identifying the character of the orbitals at this point. It is mostly due to the strong mixing between them especially when the geometry is quite distorted from the minima on the ground or excited states. In this case the best way to determine orbital character is to compare it with orbital of a known character in the point close to the MXS or if it is not possible on the starting point of the search.*

## Appendix: Orbital occupation and DRT tables

System:

Point Group:

N. Electrons:

Level:

|       |      | IRREP |  |  |  |  |  |  |  |
|-------|------|-------|--|--|--|--|--|--|--|
|       |      |       |  |  |  |  |  |  |  |
| SCF   | DOCC |       |  |  |  |  |  |  |  |
|       | OPSH |       |  |  |  |  |  |  |  |
| MCSCF | DOCC |       |  |  |  |  |  |  |  |
|       | RAS  |       |  |  |  |  |  |  |  |
|       | CAS  |       |  |  |  |  |  |  |  |
|       | AUX  |       |  |  |  |  |  |  |  |
| MRCI  | FC   |       |  |  |  |  |  |  |  |
|       | FV   |       |  |  |  |  |  |  |  |
|       |      | DOCC  |  |  |  |  |  |  |  |
|       |      | ACT   |  |  |  |  |  |  |  |
|       |      | AUX   |  |  |  |  |  |  |  |
|       |      | INT   |  |  |  |  |  |  |  |

| State | Multiplicity | N. electrons | Symmetry |
|-------|--------------|--------------|----------|
|-------|--------------|--------------|----------|

Number of distinct rows (DRTs):

|          | 1     | 2        | 3        | 4        | 5        | 6        | 7        | 8     |
|----------|-------|----------|----------|----------|----------|----------|----------|-------|
| $D_{2h}$ | $a_g$ | $b_{3u}$ | $b_{2u}$ | $b_{1g}$ | $b_{1u}$ | $b_{2g}$ | $b_{3g}$ | $a_u$ |
| $D_2$    | $a$   | $b_2$    | $b_1$    | $b_3$    |          |          |          |       |
| $C_{2h}$ | $a_g$ | $b_u$    | $a_u$    | $b_g$    |          |          |          |       |
| $C_{2v}$ | $a_1$ | $b_1$    | $b_2$    | $a_2$    |          |          |          |       |
| $C_i$    | $a_g$ | $a_u$    |          |          |          |          |          |       |
| $C_s$    | $a'$  | $a''$    |          |          |          |          |          |       |
| $C_2$    | $a$   | $b$      |          |          |          |          |          |       |
| $C_1$    | $a$   |          |          |          |          |          |          |       |