

# **A TUTORIAL FOR COLUMBUS**

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[www.univie.ac.at/columbus/tutorial](http://www.univie.ac.at/columbus/tutorial)

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## Table of contents

Table of contents .....	3
1. Before starting .....	4
1.1 Necessary programs .....	4
1.2 Notation.....	4
1.3 Preparing the jobs .....	4
2. MCSCF single point calculation without symmetry .....	5
2.1 Orbital occupation and DRT tables.....	5
2.2 Geometry file creation .....	7
2.3 COLINP integral input .....	7
2.4 COLINP step: SCF input.....	9
2.5 COLINP step: MCSCF input .....	10
2.6 Running a MCSCF single point job.....	11
2.7 Checking the results .....	12
3. MRCI single point calculation without symmetry .....	14
3.1 Basic input .....	14
3.2 COLINP step: MRCI input.....	14
3.3 Running a MRCI single point job.....	16
3.4 Checking the results .....	17
4. MRCI geometry optimization without symmetry .....	20
4.1 Basic input .....	20
4.2 COLINP step: MRCI input.....	20
4.3 Running a MRCI geometry optimization job .....	22
4.4 Checking the results .....	24
5. MRCI single point non-adiabatic coupling vector calculation.....	25
5.1 Basic input .....	25
5.2 COLINP step: MRCI input.....	25
5.3 Running a single point non-adiabatic coupling vector calculation .....	27
5.4 Checking the results .....	29
6. MRCI conical intersection search .....	33
6.1 Basic input .....	33
6.2 COLINP step: MRCI input.....	33
6.3 Checking the results .....	34
7. Contact .....	36
Appendix: Orbital occupation and DRT tables .....	37

## 1. Before starting

### 1.1 Necessary programs

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

In this tutorial we will 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 analyses.

### 1.2 Notation

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

This kind of font indicates what is seen on 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 it 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 a single point calculation at MCSCF level. The system is the methaniminium cation  $\text{CH}_2\text{NH}_2^+$ , 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 averaging 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:  $\text{CH}_2\text{NH}_2^+$

Point Group:  $C_1$

N. Electrons: 16

Level:  $\text{MRCI}(4,3)/\text{SA-3-CASSCF}(4,3)$

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

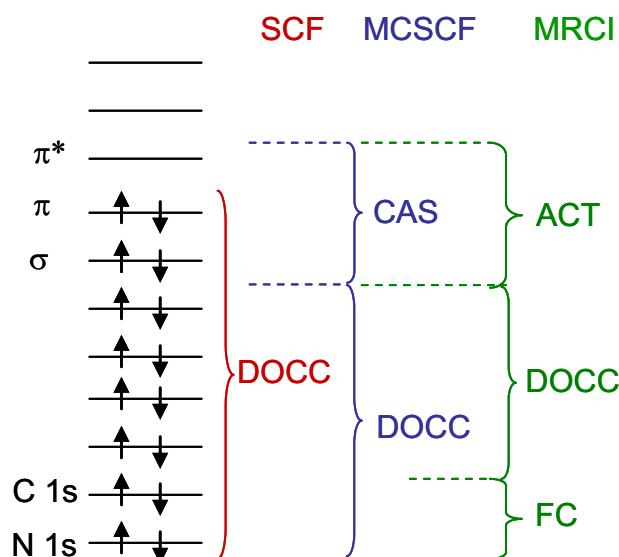


Fig. 1. Scheme of orbital occupation for MRCI(4,3) and CASSCF(4,3).

*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 defined 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 tables (DRTs): 1

*To fill out this table, proceed writing one line for each desired state (in this job, three states). Distinct row tables (DRTs) are the basic collection of data in the GUGA formalism. More than one DRT are only needed if you want to perform state averaging between states of a*

*different symmetry or a different number of electrons. In a usual  $C_1$  calculation, the number of DRTs 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 should appear at the end of the file.*

5. Convert geometry into COLUMBUS format.

```
> $COLUMBUS/xyz2col.x < 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 geom2xyz.*

```
> $COLUMBUS/geom2xyz geom
```

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

## 2.3 COLINP integral input

6. Run:

```
> $COLUMBUS/colinp
```

- > 1) Integral program input (for argos/dalton/turbocol/molcas)
- 2) SCF input
- 3) MCSCF input
- 4) CI input
- 5) Set up job control
- 6) Utilities
- 7) 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).

## 7. Use the prepinp utility

Run the preparation program (prepinp)? (y|n) y ! Press <ENTER> after the input

## 8. Enter information about program, symmetry and geometry file.

Input for DALTON (1) or MOLCAS (2): 1

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 ! verify that the file was read in correctly  
Sum formula: H4 N1 C1

## 9. Enter information about basis sets.

Show only basis sets containing the following string:  
(e.g. 6-31g, cc-pv - leave empty to show all basis sets)  
6-31g ! you may enter "6-31g" here or leave this empty and get the full list

-- Set basis set --

27: HYDROGEN Pople 6-31g or 6-31g\*  
28: HYDROGEN Pople 6-31g\*\*  
0: Other library

Select the basis set for atom H: 27 ! 6-31G\* was selected

...

Select the basis set for atom N: 34

...

Select the basis set for atom C: 31

...

Until now you've set the following basis sets:

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

Reorder geom file for geometry optimization and orbital print out? (y)  
y ! per default the geometry should be reordered to put the hydrogens



at the back of the file

Normal termination of prepinp. See result in inpcol.

*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`

## 10. Perform an automatic input of iargos.x .

...

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

*If you select "yes", COLINP will ask to enter all information about geometry and basis sets again, atom per atom. In the case of ANO basis sets it is currently necessary to perform the whole interactive iargos.x input. But you may use the file inpcol (as created in the previous step) as a template.*

## 2.4 COLINP step: SCF input

### 11. Select option 2) SCF input.

```
Integral program input (for argos/dalton/turbocol/molcas)
-> 2) SCF input
    3) MCSCF input
    4) CI input
    5) Set up job control
    6) Utilities
    7) 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:
DOCC      a      8                ! 8 double occupied orbitals
OPSH      0                ! 0 open shell orbitals
```

Is this correct? <YES> <ENTER>

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

Input a title: <Default SCF Title>

--> <ENTER>

## 2.5 COLINP step: MCSCF input

### 12. Select option 3) MCSCF input

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

MCSCF WAVE FUNCTION DEFINITION  
=====

(for an explanation see the COLUMBUS documentation and tutorial)

Freeze orbitals prior to MCSCF (no gradients available) [y|n] n

prepare input for no(0),CI(1), MCSCF(2), SA-MCSCF(3) 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, i.e. geometry optimization and non-adiabatic couplings at MRCI level.*

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

*SA-MCSCF (3) – for jobs requiring gradient calculation at the state averaged MCSCF level.*

*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 may be 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 (nucl. charge: 17) 16  
! nuclear charge: 17, 16 electrons -> net charge +1

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 [100]    #miter [50 ]   #ciiter [50 ]
  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 ]
                        ... only with wnorm < [1.e-3 ]

Resolution (NO)        RAS [NO ] CAS [NO ] AUX [NO ]
State-averaging
                        DRT 1: #states [3 ] weights[ 1,1,1 ]
                        transition moments / non-adiabatic couplings [n]

                        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. During the input procedure a keystroke file makmcky is produced. Try to run the MCSCF input again and you will see that the program provides your last input as default.*

## 2.6 Running a MCSCF single point job

### 13. Select option 5) Set up job control

```

  1) Integral program input (for argos/dalton/turbocol/molcas)
  2) SCF input
  3) MCSCF input
  4) CI input
-> 5) Set up job control
  6) Utilities
  7) 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 with GDIIS
  3) geometry optimization with SLAPAF
  4) saddle point calculation (local search - GDIIS)
  5) stationary point calculation (global search - RGF)
  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) [X] SCF
- 3) [X] MCSCF
- 4) [ ] transition moments for MCSCF
- 5) [ ] MR-CISD (serial operation)
- 6) [ ] MR-CISD (parallel operation)
- 7) [ ] SO-CI coupled to non-rel. CI
- 8) [ ] one-electron properties for all methods
- 9) [ ] transition moments for MR-CISD
- 10) [ ] single point gradient
- 11) [ ] nonadiabatic couplings (and/or gradients)
- 12) [ ] <L> value calculation for MR-CISD
- 13) [X] convert MOs into molden format
- 14) [ ] get starting MOs from a higher symmetry
- 15) [ ] finite field calculation for all methods
- 16) [ ] include point charges
- 17) [ ] extended MOLCAS interface

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

*The job control will instruct COLUMBUS to perform the SCF and the MCSCF 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 1700 > runls
```

*“-m” command defines the memory allocated to COLUMBUS, in this case 1700 MB.*

## 2.7 Checking the results

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

```
...
final mcscf convergence values:
  10   -94.1553285066  1.421E-14  4.772E-07  1.282E-08  3.936E-15  T  *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 wt 0.333 total energy=      -94.398532383, rel. (eV)=   0.000000
DRT #1 state # 2 wt 0.333 total energy=      -94.053559786, rel. (eV)=   9.387186
DRT #1 state # 3 wt 0.333 total energy=      -94.013893351, rel. (eV)=  10.466565
-----
```

*! The vertical excitation energies (9.39 eV and 10.47 eV) are in the last column.*

21. The wavefunction information is written in LISTINGS/mcpcfs.drt1.stateX.sp files. For the ground state for example, LISTINGS/mcpcfs.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, spin multiplicity increased by 1*

*2 – singly-occupied, spin multiplicity decreased by 1*

*3 – doubly occupied.*

22. The mscf, scf and natural orbitals are written to files MOCOEFs/mocoef\_mc.sp, MOCOEFs/mocoef\_sc.f.sp and MOCOEFs/nocoef\_mc.sp respectively.

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

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

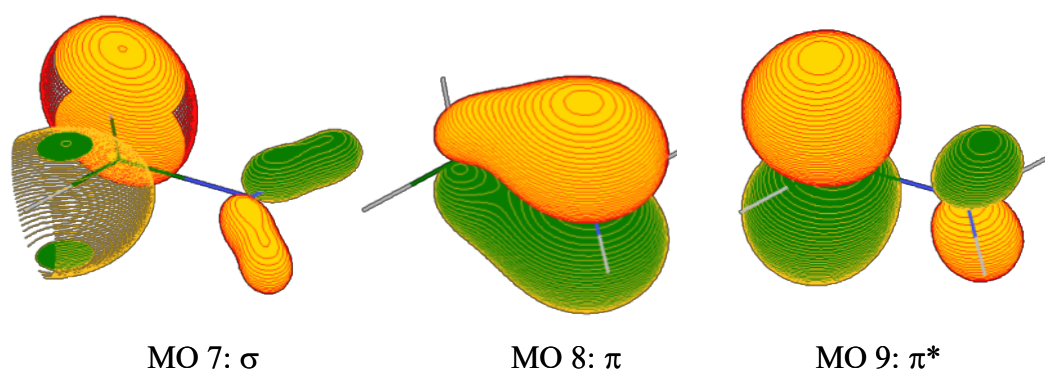


Fig. 2. Molecular orbitals visualized with Molden using contour value 0.1.

*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. This program may be accessed through the 7) Utilities option in `colinp`.*

*In the current example, inspection of active orbitals (Fig. 2) shows that they correspond to the  $\sigma$ ,  $\pi$  and  $\pi^*$  aimed at. 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  $\text{CH}_2\text{NH}_2^+$ . The reference space for the MRCI contains four electrons in three orbitals [MRCI(4,3)] (see Fig. 1). This calculation is done on 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 2.5).  
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) Utilities
7) 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. But a keystroke file cidrtplky is created to aid if the program is called a second time.*

```
CI WAVE FUNCTION DEFINITION
```

```
...
```

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

```
1) Def. of CI wave function - one-DRT case (data from MCSCF)
-> 2) Def. of CI wave function - one-DRT case
3) Def. of CI wave function - multiple-DRT case (transition moments)
4) Def. of CI wave function - independent multiple-DRTs (intersystem crossing)
5) Skip DRT input (old input files in the current directory)
```

Do you want to compute gradients or non-adiabatic couplings? [y|n] n

*Choosing y here would produce the same results. But single point MRCI calculations are faster if n is specified because that leads to a more efficient treatment of frozen orbitals.*

#### 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
Spin-Orbit CI [y|n]          n <enter>
```

```
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

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

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

```
count order (bottom to top): fc-docc-active-aux-extern-fv
irreps          a
# basis fcts    36
Enter the multiplicity 1
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/molcas)
2) SCF input
3) MCSCF input
4) CI input
-> 5) Set up job control
6) Utilities
7) 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] MR-CISD (serial operation)
    6) [ ] MR-CISD (parallel operation)
    7) [ ] SO-CI coupled to non-rel. CI
    8) [ ] one-electron properties for all methods
    9) [X] transition moments for MR-CISD
   10) [ ] single point gradient
   11) [ ] nonadiabatic couplings (and/or gradients)
   12) [ ] <L> value calculation for MR-CISD
   13) [X] convert MOs into molden format
   14) [ ] get starting MOs from a higher symmetry
   15) [ ] finite field calculation for all methods
   16) [ ] include point charges
   17) [ ] extended MOLCAS interface
```

*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 1700 > runls
```

### 3.4 Checking the results

#### 16. Check the convergence of the MR-CI 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.
c0**2 =  0.91959275  c**2 (all zwalks) =  0.92070333

eref      =  -94.398163757370  "relaxed" cnot**2      =  0.919592745530
eci       =  -94.666194906939  deltae = eci - eref    = -0.268031149569
eci+dv1   =  -94.687746555789  dv1 = (1-cnot**2)*deltae = -0.021551648849
eci+dv2   =  -94.689630986611  dv2 = dv1 / cnot**2    = -0.023436079671
eci+dv3   =  -94.691876534040  dv3 = dv1 / (2*cnot**2-1) = -0.025681627100
eci+pople =  -94.686909115325  ( 12e- scaled deltae ) = -0.288745357955
```

```

number of reference csfs (nref) is      6.  root number (iroot) is  2.
c0**2 =  0.89853684  c**2 (all zwalks) =  0.90961660

eref      =  -94.053552136190  "relaxed" cnot**2      =  0.898536837995
eci       =  -94.345320078822  deltae = eci - eref    = -0.291767942632
eci+dv1   =  -94.374923776853  dv1 = (1-cnot**2)*deltae = -0.029603698031
eci+dv2   =  -94.378266639029  dv2 = dv1 / cnot**2    = -0.032946560207
eci+dv3   =  -94.382460557704  dv3 = dv1 / (2*cnot**2-1) = -0.037140478883
eci+pople =  -94.374949423587  ( 12e- scaled deltae ) = -0.321397287398

number of reference csfs (nref) is      6.  root number (iroot) is  3.
c0**2 =  0.89900817  c**2 (all zwalks) =  0.90132415

eref      =  -94.011453700561  "relaxed" cnot**2      =  0.899008166094
eci       =  -94.309336791412  deltae = eci - eref    = -0.297883090851
eci+dv1   =  -94.339420551047  dv1 = (1-cnot**2)*deltae = -0.030083759635
eci+dv2   =  -94.342800068799  dv2 = dv1 / cnot**2    = -0.033463277386
eci+dv3   =  -94.347034966777  dv3 = dv1 / (2*cnot**2-1) = -0.037698175365
eci+pople =  -94.339418863807  ( 12e- scaled deltae ) = -0.327965163246

```

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 = 0.00000 to cmax = 1.00000

  indcsf      c      c**2    v  lab:rmo  lab:rmo  step(*)
-----
    1  0.90693  0.82252  z*
    2  0.29723  0.08834  z*
    3 -0.09270  0.00859  z*

```

*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 0.29723 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:

```

***   FINAL RESULTS   ***

                                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 the 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 MRCI(4,3) single-point calculation performed in section 3. 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 2.5).  
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
```

4. Remove the transmomin file from the last job

```
> rm transmomin
```

*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) Utilities
- 7) Exit the input facility

*If the file cidrtplky is present, colinp will provide you last input as default.*

```
CI WAVE FUNCTION DEFINITION
...
press return to continue <enter>
```

- 1) Def. of CI wave function - one-DRT case (data from MCSCF)
- > 2) Def. of CI wave function - one-DRT case
- 3) Def. of CI wave function - multiple-DRT case (transition moments)
- 4) Def. of CI wave function - independent multiple-DRTs (intersystem crossing)
- 5) Skip DRT input (old input files in the current directory)

Do you want to compute gradients or non-adiabatic couplings? [y|n] [ n] **y**

*The difference to last time is that we choose a wave function definition that allows for the inclusion of gradients and/or non-adiabatic couplings.*

#### 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

Spin-Orbit CI [y|n] [ n] <enter>

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>

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

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

count order (bottom to top): fc-docc-active-aux-extern-fv

irreps a

# basis fcts 36

Enter the multiplicity 1

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 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). Alternatively the gradient can be specified in `transmomin`.*

Select the following transition moment. For geometry optimizations at the MRCI level, this is the only allowable selection.

- > 1) (Done with selections)
- 2) [**X**] 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# 2 ket: DRT# 1 state# 2

### 4.3 Running a MRCI geometry optimization job

8. Enter the job control menu

- 1) Integral program input (for argos/dalton/turbocol/molcas)
- 2) SCF input
- 3) MCSCF input
- 4) CI input
- > 5) Set up job control
- 6) Utilities
- 7) 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 with GDIIS
- 3) geometry optimization with SLAPAF
- 4) saddle point calculation (local search - GDIIS)
- 5) stationary point calculation (global search - RGF)
- 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. It is usually better to check and restart optimizations that do not converge after a small number of cycles.*

## 12. Choose the following options:

- 1) (Done with selections)
- 2) [ ] mcscf gradient (single state)
- 3) [ ] gradient for state averaged mcscf
- > 4) [] ci gradient
- 5) [ ] one electron properties
- 6) [ ] convert MOs into molden proprietary format
- 7) [ ] fix one or more coordiante in optimization
- 8) [ ] 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 1700 > 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 | 0.0001124 | yes   |
| Coordinate rms value       | 0.0002000 | 0.0000396 | yes   |
| Maximal gradient change:   | 0.0010000 | 0.0002272 | yes   |
| Gradient rms value         | 0.0002000 | 0.0001041 | 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.*

*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 compute 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 MRCI(4,3) geometry optimization calculation performed in section 4 with the geom file and converged orbitals from the calculation in section 3. 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 2.5).

Alternatively, just copy the input files:

```
> cp ../CNH4_MRCI43_C1_OPTS1/* .
> cp ../CNH4_MRCI43_C1_SP/geom .
```

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

```
> cp ../CNH4_MRCI43_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/molcas)
    2) SCF input
    3) MCSCF input
->  4) CI input
    5) Set up job control
    6) Utilities
    7) Exit the input facility
```

```
CI WAVE FUNCTION DEFINITION
```

```
...
```

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

```
    1) Def. of CI wave function - one-DRT case (data from MCSCF)
    2) Def. of CI wave function - one-DRT case
    3) Def. of CI wave function - multiple-DRT case (transition moments)
    4) Def. of CI wave function - independent multiple-DRTs (intersystem crossing)
```

-> 5) Skip DRT input (old input files in the current directory)

*If the input from the geometry optimization is used, we can skip the DRT input.*

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

5. At the last panel 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

(select one or more transitions)

- ```
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
```

## 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>

cigrdin exists. Do you want to overwrite it? (y|n) **y**

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

### 8. Enter the job control menu

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

### 9. Select 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

You have an existing job control file. Discard it? (y|n) **y**

### 10. Select 1) single point calculation

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

### 11. Calculation of non-adiabatic couplings

- > 1) (Done with selections)
- 2) [ ] SCF
- 3) [X] MCSCF
- 4) [ ] transition moments for MCSCF
- 5) [X] MR-CISD (serial operation)
- 6) [ ] MR-CISD (parallel operation)
- 7) [ ] SO-CI coupled to non-rel. CI
- 8) [ ] one-electron properties for all methods
- 9) [ ] transition moments for MR-CISD
- 10) [ ] single point gradient

- 11) [X] nonadiabatic couplings (and/or gradients)
- 12) [ ] <L> value calculation for MR-CISD
- 13) [ ] convert MOs into molden format
- 14) [ ] get starting MOs from a higher symmetry
- 15) [ ] finite field calculation for all methods
- 16) [ ] include point charges
- 17) [ ] extended MOLCAS interface

## 12. Internal coordinates

Do you want to perform an analysis in internal coordinates? (y|n) y  
 Internal coordinate file exists, would you like to overwrite it? (y|n) y

Internal coordinates generated!  
 Press return to continue

## 13. Type of coupling

submenu 1.2.1: calculation of nonadiabatic coupling terms

- 1) DCI\*(E2-E1) term (interstate coupling)
- 2) DCSF term
- > 3) DCI+DCSF term (non-adiabatic coupling)

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

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

*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*

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

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

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

Perform intersection analysis (slope)? (y|n) y

Now exit the input facility.

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

```
niter = 1
hermit
```

```
mcsf
ciudg
slope
nadcoupl
```

## 15. Run Columbus.

```
> $COLUMBUS/runc -m 1700 > runls
```

### 5.4 Checking the results

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

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

## 17. 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:
```

```
1.344918E-06  2.412470E-05  4.317748E-04
4.018894E-06 -1.562551E-04 -5.830686E-04
-7.147146E-01 -3.451500E-02 -1.142632E-02
7.147229E-01  3.455281E-02  1.137631E-02
6.084143E-01  2.935967E-02  9.831065E-03
-6.084280E-01 -2.926442E-02 -9.623485E-03
```

## 18. 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
```

## 19. 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
...

Othogonalized 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

Othogonalized 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

```

20. 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*h_ort  =  0.0000 . New g and h obtained via Yarkony orthogonaliz.

Frobenius norm of g, h and s vectors (hartree/a0):
|g|      =  0.2235      |g_ort| =  0.2235
|h|      =  0.0478      |h_ort| =  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);
Einf:=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)
Writing Molden with DE = -3.598324193599470E-002

```

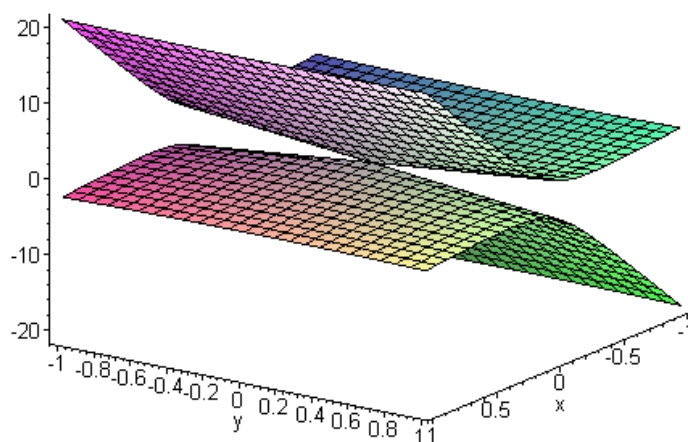


Fig. 3. Linear approximation of the  $S_1$  and  $S_2$  surfaces around de conical intersection plotted with MAPLE program.

21. 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
```

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

23. 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.

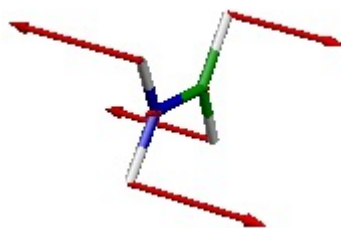


Fig. 4. Non-adiabatic coupling vector.

---

24. 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 2.5) and definition of CI wave function (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) Utilities
7) Exit the input facility
```

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 with GDIIS
- 3) geometry optimization with SLAPAF
- 4) saddle point calculation (local search - GDIIS)
- 5) stationary point calculation (global search - RGF)
- > 6) optimization on the crossing seam or ISC (GDIIS)
- 7) optimization on the crossing seam (POLYHES)
- 8) Exit

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

Internal coordinates generated!  
Press return to continue

```
[nadgdiis: 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  
 Coupling at the SA-MCSCF (1) or MR-CI (2) level? (1|2) 2  
 Optimize a conical intersection (1) or intersystem crossing (2) ? (1|2) 1  
 Activate CI restart after 2-nd geomopt. iter.? (y|n) n  
 Perform intersection analysis (slope)? (y|n) y  
 Fix one or more internal coordinates? (y|n) n <ENTER>

8. Leave input facility. See how the control.run file looks like. You should see:

```
niter = 10
slope
hermit
mcscf
ciudg
ciudgmom
nadcoupl
gdiis
```

9. Run Columbus.

```
> $COLUMBUS/runc -m 1700 > runls
```

### 6.3 Checking the results

10. 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 &
```

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

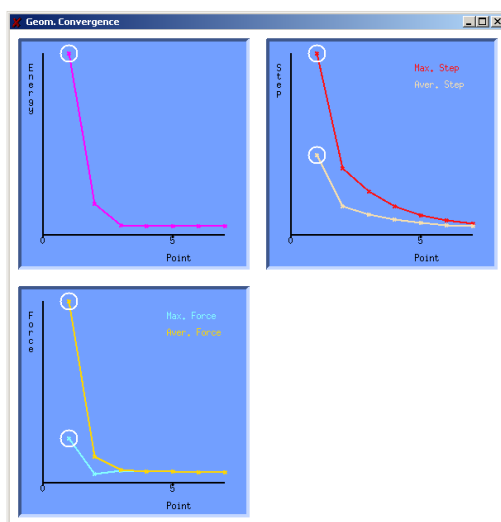


Fig. 5. MOLDEN output showing the MXS optimization steps. Upper-left panel: energy gap.  
Bottom panel:  $S_1$  and  $S_2$  energies.

*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.*

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

-----	-----	-----	-----
critereon	required	actual	conv.
Maximal coordinate change:	0.0010000	0.0000906	yes
Coordinate rms value	0.0002000	0.0000451	yes
Maximal gradient change:	0.0010000	0.0015474	no
Gradient rms value	0.0002000	0.0006613	no

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

13. 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.*

14. 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 # 41 1 -94.6357834488 3.9080E-13 0.0000E+00 4.5725E-05 1.0000E-04
mr-sdci # 41 2 -94.3542071794 8.0219E-09 3.2992E-09 8.1691E-05 1.0000E-04
mr-sdci # 41 3 -94.3541985763 5.2616E-11 0.0000E+00 6.8663E-05 1.0000E-04
```

15. 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.*

## 7. Contact

If you have any questions or comments about this tutorial, feel free to write me an email:

felix.plasser@univie.ac.at

## 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 row tables (DRTs):

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