COLUMBUS
IN JOÃO PESSOA
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João Pessoa - Paraíba
ONDE O SOL NASCE PRIMEIRO!

A Quantum Chemistry Course on Multireference Methods, Energy Surfaces and Excited States

COLUMBUS

Tutorials

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Tutorial I. General Introduction

1. MCSCF single point calculation without symmetry

The system is the methaniminium cation $CH_2NH_2^+$, which will be calculated using a complete active space composed by four electrons in three orbitals [CASSCF(4,3)]. C_1 point group, three singlet states in the state averaging procedure (SA-3) and the 6-31G* basis set will be used.

A full version of the tutorial can be found at
https://www.univie.ac.at/columbus/docs_COL70/tutorial.pdf

1.1 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. You can download doc and pdf templates of these tables at http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable*

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

System: *$CH_2NH_2^+$*

Point Group: *C_1*

N. Electrons: *16*

Multiplicity:

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

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

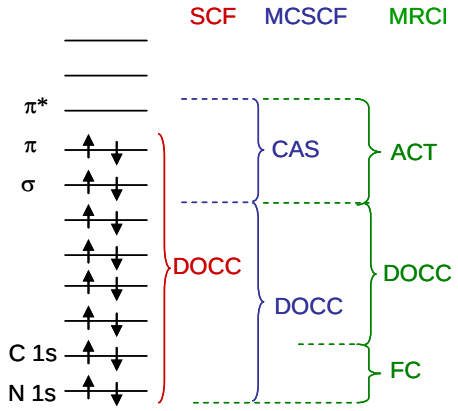


Fig. 1. Scheme of orbital occupation for MRCI(4,3) and CASSCF(4,3)

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	*1*	*16*	*A*
2	*1*	*16*	*A*
3	*1*	*16*	*A*
Number of distinct rows tables (DRTs):			*1*

1.2 Geometry file creation

3. Create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called CNH4_CAS43_C1_SP by mkdir command
4. Move to this directory and copy cnh4.xyz file from /home/aluno/cjp_2019/hans/CNH4_C1/INPUT/TUTORIAL directory which contains the geometry in XYZ format (in Angstrom)
5. Convert geometry into COLUMBUS format.

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

The COLUMBUS geometry file is called 'geom' and is in Bohr
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'.

1.3 Colinp integral input

6. Run and select

> $COLUMBUS/colinp

-> 1) Integral program input (for argos/dalton/turbocol/molcas)

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 simply pressing enter*

   -- Set basis set --

   27: HYDROGEN Pople 6-31g or 6-31g*

   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

   ...

   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.

10. Perform an automatic input of iargos.x.

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

1.4 Colinp step: SCF input

11. Select option 2) SCF input

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>

....

Is this correct? <YES><ENTER>

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

Input a title: <Default SCF Title>

--><ENTER>

1.5 Colinp step: MCSCF input

12. Select option 3) MCSCF input

MCSCF WAVE FUNCTION DEFINITION

==========

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

prepare input for no(0),CI(1), MCSCF(2), SA-MCSCF(3) analytical gradient1

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.

....

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 (cas,ras)->aux0 ! *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
....
State-averaging
DRT 1: #states [3] weights[1,1,1]
FINISHED [y]

1.6 Running a MCSCF single point job

13. Select option 5) Set up job control
14. Select option 1) Job control for single point or gradient calculation
15. Select option 1) Single point calculation
16. Select the following options marked below and finish with "Done with selections".

    -> 1) (Done with selections)

    2) [X] SCF

    3) [X] MCSCF

    13) [X] convert MOs into molden format

17. In the next panels, select "Exit" until finishing COLINP execution.
18. Run Columbus with the runc script and then analyze the results from LISTINGS/mcscfsm.sp and LISTINGS/mcpcls.drt1.stateX.sp files

    > nohup $COLUMBUS/runc -m 2000 > runls &

runc script runs COLUMBUS, relying on the control.run file. nohup is for keeping the calculation running, even after the terminal is closed. 2000Mb (2Gb) is the memory used, and the calculation steps are written in the runls file.

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 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
```

> molden MOLDEN/molden_mo_mc.sp & ! *'molden' is an alias to MOLDEN path*

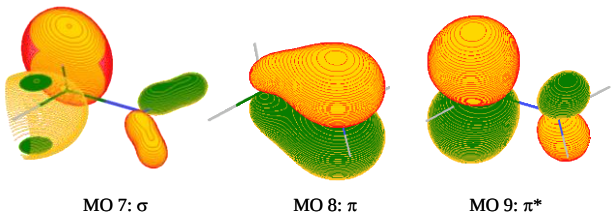


Fig. 2. Molecular orbitals visualized with Molden using contour value 0.1.

2. 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 top of the SA-3-CASSCF(4,3) MCSCF calculation performed in section 1. The 6-31G* basis set and no symmetry will be used.

2.1 Basic input

1. In the TUTORIAL directory create a subdirectory called CNH4_MRCI43_C1_SP
2. Move to this directory and 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".

2.2 Colinp step: MRCI input

> $COLUMBUS/colinp
-> 4) CI input
...
press return to continue<enter>
-> 2) Def. of CI wave function - one-DRT case
Do you want to compute gradients or non-adiabatic couplings? [y|n] n

4. The orbital occupation and DRT information is defined in the following options:
   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 C_1
   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. 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. In the last panel, the only thing which should be changed is NROOT from 1 to 3.

   State(s) to be optimized NROOT [3] ROOT TO FOLLOW [0]
   FINISHED [y]

7. 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 ! $S_0 \rightarrow S_1$
   4) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 3 ! $S_0 \rightarrow S_2$
   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

2.3 Running a MRCI single point job

8. Enter the job control menu and select

   -> 5) Set up job control

9. Select a single point job:

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

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 single point calculation

    -> 1) single point calculation

12. Choose the following options:

-> 1) (Done with selections)
   3) [X] MCSCF
   5) [X] MR-CISD (serial operation)
   13) [X] convert MOs into molden format

13. Exit the input facility.

14. Run Columbus with the SLURM script and analyze the results from LISTINGS/ciudgsm.sp and LISTINGS/cipcls.drt1.sp files.

    > nohup $COLUMBUS/runc -m 2000 > runls &

2.4 Checking the results

Check the convergence of the MR-CI calculation in the LISTINGS/ciudgsm.sp file.

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

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

3. 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 $CH_2NH_2^+$. 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 1. 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 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 1.2 to 1.5). 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

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
    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
        4) Skip DRT input (old input files in the current directory)
    Do you want to compute gradients or non-adiabatic couplings? [y|n] [ n]   y
```

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>

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

   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>.
```

8. Exit the input facility.

3.3 Running a MRCI geometry optimization 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 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
```

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 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>
```

13. Choose the following options:

```
    1) (Done with selections)
    2) [ ] mcscf gradient (single state)
    3) [ ] gradient for state averaged mcscf
->  4) [X] 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>

14. Exit the input facility.

15. Run Columbus.

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

3.4 Checking the results

16. 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.

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

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

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

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

Tutorial II. Hexatriene

1. MCSCF single point calculation using C_{2h} symmetry

The system is trans-1,3,5-hexatriene, C_6H_8, which will be calculated using a complete active space composed by six electrons in six orbitals [CASSCF(6,6)]. An auxiliary (Rydberg, 3s) orbital is also used. C_{2h} point group, three singlet states in the state averaging procedure (SA-3) and the 3-21G* + B2 extended diffuse basis sets will be used.

1.1 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. You can download doc and pdf templates of these tables at* http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable

1. Fill out the occupation table according toFig. 1:

System: *C_6H_8* Point Group: *C_{2h}*

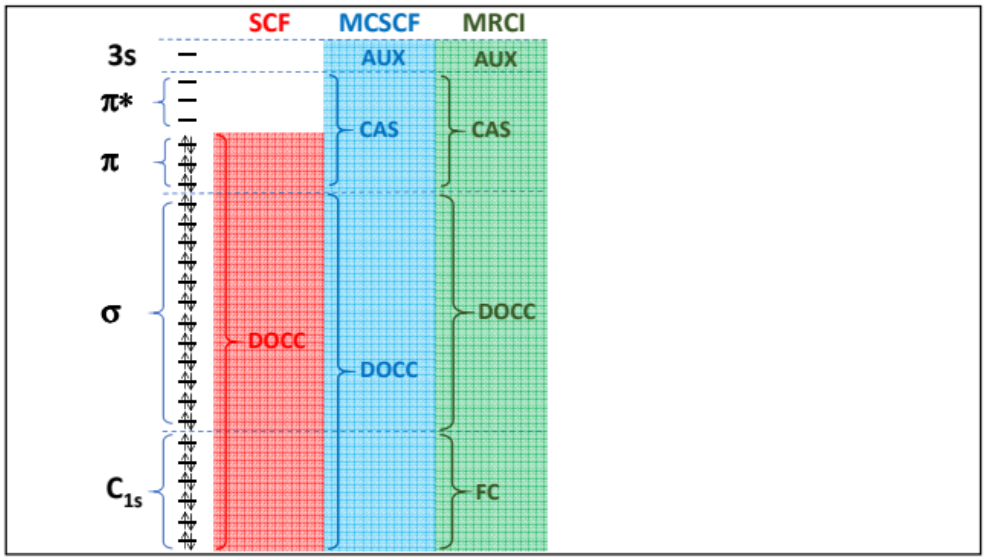
N. Electrons: *44* Multiplicity: *1*

Level: *MR-CISD(6,6)+AUX(3s)/SA-3-CASSCF(6,6)+ AUX(3s)*

						IRREP*! Irreducible representations*					
		a_g	***b_u***	***a_u***	***b_g***						
SCF	DOCC	*10*	*9*	*2*	*1*	*! Doubly occupied in the SCF wavefunction*					
	OPSH	*0*	*0*	*0*	*0*	*! Singly occupied in the SCF wavefunction*					
MCSCF	DOCC	*10*	*9*	*0*	*0*	*! Doubly occupied orbitals in the MCSCF*					
	RAS	*0*	*0*	*0*	*0*	*! Restricted orbitals (only a restricted number of excitations from them)*					
	CAS	*0*	*0*	*3*	*3*	*! Active orbitals (any kind of excitation); in this case only π orbitals*					
	AUX	*1*	*0*	*0*	*0*	*! Auxiliary orbitals (only restricted excitations into them):* ***look at the character Table !***					
MRCI	FC	*3*	*3*	*0*	*0*	*! Frozen core orbitals (the six 1s) in the MRCI;* ***They have the lowest energies at the RHF level!***					
	FV	*0*	*0*	*0*	*0*	*! Frozen virtual orbitals*					
	DOCC	*7*	*6*	*0*	*0*	*! Reference doubly occupied orbitals:* ***notice that FC + DOCC(CI) = DOCC (MCSCF)***					
	ACT	*0*	*0*	*3*	*3*	*! Reference active orbitals:= **MCSCF***					
	AUX	*1*	0	*0*	*0*	*! Reference auxiliary orbitals: = **MCSCF***					
	INT	*8*	*6*	*3*	*3*	*! Internal (DOCC+ACT+AUX)*					

Information concerning the basis set (from infofl file)

a_g	b_u	a_u	b_g
37	33	8	10



Scheme of orbital occupation for MRCI(6,6) + AUX(3s) and CASSCF(6,6) + AUX (3s).

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	1	44	A_g
2	1	44	B_u
3	1	44	A_u
Number of distinct rows tables (DRTs):			3

1.2 Geometry file creation

3. Create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called hexatriene_C2h_CAS66_AUX_3s_SP using mkdir command.
4. Move to this directory and copy geom file from /home/aluno/cjp_2019/silmar/hexatriene_C2h/INPUT/TUTORIAL/ directory which contains the geometry (symmetry unique) in COLUMBUS format (in Bohr)

The COLUMBUS geometry file is called 'geom' and is in Bohr
The conversion from COLUMBUS format to xyz can be done with the program geom2xyz.pl
> $COLUMBUS/geom2xyz.pl geom
After running this program, the xyz-format geometry (in Angstrom) is written to file 'geom.xyz'.

1.3 Colinp integral input

5. Run and select

   > $COLUMBUS/colinp

-> 1) Integral program input (for argos/dalton/turbocol/molcas)

6. Use the prepinp utility

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

7. Enter information about program, symmetry and geometry file.

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

   Enter the point group symmetry: c2h ! *Only Abelian groups*

   Name of the file containing the cartesian coordinates

   of the unique atoms (COLUMBUS format): geom

   Number of atoms = 8 ! *verify that the file was read in correctly*

   Sum formula: H4 X1 C3

8. 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)

   3-21g* !*you may enter "3-21g*" here or leave this empty and get the full list, simply pressing <ENTER>*

   -- Set basis set --
   25: HYDROGEN Pople 3-21g*

   Select the basis set for atom H:25! 3-*21G* was selected*
   ...
   Until now you've set the following basis sets:
   H :: HYDROGEN Pople 3-21g*

   1: B2 extended diffuse functions
   2: Universal Rydberg
   0: Other library
   Select the basis set for atom X:1
   ...
   Select the basis set for atom C:28! 3-*21G* was selected*
   ...
   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.

9. Perform an automatic input of iargos.x.

Would you like to do an interactive input? <NO>n! *Select "no"* and press *<ENTER>*

1.4 Colinp step: SCF input

10. Select option 2) SCF input

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:10 9 2 1 <ENTER>
....
Is this correct? <YES><ENTER>
Would you like to change the default program parameters? <NO><ENTER>
Input a title: <Default SCF Title>
--><ENTER>

1.5 Colinp step: MCSCF input

11. Select option 3) MCSCF input

MCSCF WAVE FUNCTION DEFINITION
==========
Freeze orbitals prior to MCSCF (no gradients available) [y|n]n
prepare input for no(0),CI(1), MCSCF(2), SA-MCSCF(3) analytical gradient1

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.

....

excitation level (cas,ras)->aux1 1 ! *Allow single excitations into auxiliary orbitals*
excitation level ras->(cas,aux) 0 ! *allow 0 excitation from the restricted active orbitals*

....
Apply add. group restrictions for DRT 1 [y|n]n
Apply add. group restrictions for DRT 2 [y|n]n
Apply add. group restrictions for DRT 3 [y|n]n
....
State-averaging
DRT 1: #states [1] weights[1]
DRT 2: #states [1] weights[1]
DRT 3: #states [1] weights[1]
FINISHED [y]

1.6 Running a MCSCF single point job

12. Select option 5) Set up job control
13. Select option 1) Job control for single point or gradient calculation
14. Select option 1) Single point calculation
15. Select the following options marked below and finish with "Done with selections".

    -> 1) (Done with selections)
    2) [X] SCF
    3) [X] MCSCF
    8) [X] one-electron properties for all methods
    13) [X] convert MOs into molden format

16. In the next panel select "second moment" and then "Done with selections".

    -> 1) (Done with selections)
    2) [ ] first moment
    3) [X] second moment
    4) [ ] third moment
    5) [ ] fourth moment

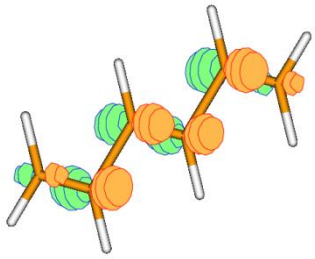
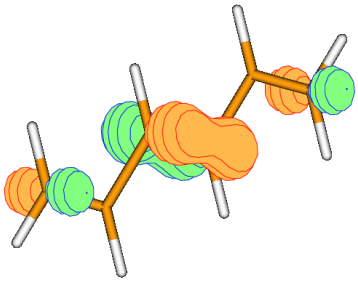
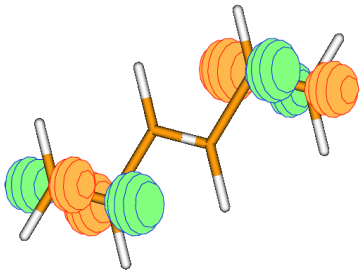
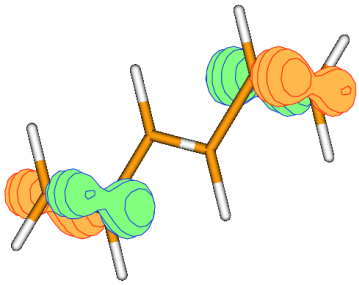
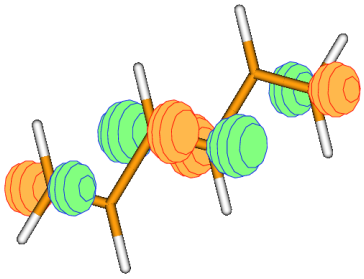
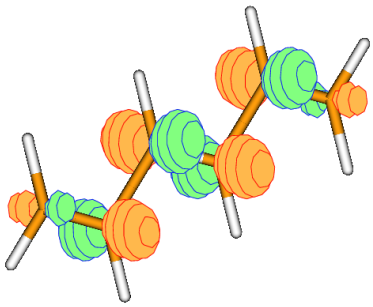
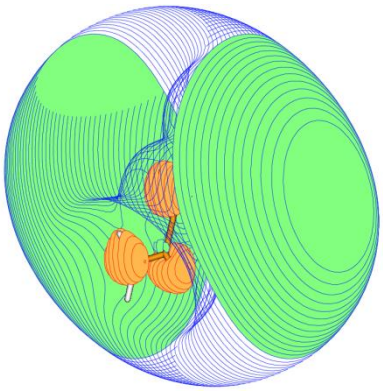
17. In the next panels, select "Exit" until finishing COLINP execution.
18. Run Columbus with the runc script and then analyze the results from LISTINGS/mcscfsm.sp, LISTINGS/mcpcls.drtX.state1.sp and LISTINGS/propls.mcscf.drtX.st01.sp files

    > nohup $COLUMBUS/runc -m 2000 > runls &

runc script runs COLUMBUS, relying on the control.run file. nohup is for keeping the calculation running, even after the terminal is closed. 2000Mb (2Gb) is the memory used, and the calculation steps are written in the runls file.

Try to identify the valence and Rydberg states and orbitals

> molden MOLDEN/molden_mo_mc.sp & ! *'molden' is an alias to MOLDEN path*

MO 71, π_1 ($1a_u$)	MO 72, π_2 ($2a_u$)	MO 73, π_3 ($3a_u$)
		
MO 79, π_1^* ($1b_g$)	MO 80, π_2^* ($2b_g$)	MO 81, π_3^* ($3b_g$)
		
MO 11, 3s ($11a_g$)		
		

Molecular orbitals visualized with Molden using contour values of 0.1 (valence) and 0.01 (3s).

2. MRCI single point calculation using C_{2h} symmetry

In this section we will perform a single point calculation at MRCI level for the trans hexatriene. The reference space for the MRCI contains six electrons in six orbitals, along with single excitations to the AUX(3s) orbital [MRCI(6,6) + AUX(3s)] (see 1.1). This calculation is done on top of the SA-3-CASSCF(6,6) + AUX(3s) MCSCF calculation performed in section 1. The 3-21G* + B2 extended diffuse basis sets and C_{2h} symmetry will be used. One separate calculation for each state (DRT) will be performed (see 1.1)

2.1 Basic input

1. In the TUTORIAL directory create a subdirectory called hexatriene_C2h_MRCI_SP
2. Move to this directory and create a directory called DRT1 ! For the 1^1Ag state
3. Move to this directory and copy the input files from the MCSCF directory:

   >cp ../../hexatriene_C2h_CAS66_AUX_3s_SP/* .

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

   >cp ../../hexatriene_C2h_CAS66_AUX_3s_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".

2.2 COLINP step: MRCI input

> $COLUMBUS/colinp
-> 4) CI input
...
press return to continue<enter>
-> 1) Def. of CI wave function - one-DRT case
Do you want to compute gradients or non-adiabatic couplings? [y|n] n

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

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

   ....

Do according to the DRT table.

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

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. In the last panel, NROOT should be chosen 1 for each DRT.

   State(s) to be optimized NROOT [1] ROOT TO FOLLOW [0]
   FINISHED [y]

8. Move the cursor to FINISHED and press <enter>. Do not select transition moments.

   -> 1) (Done with selections)

2.3 Running a MRCI single point job

9. Enter the job control menu and select

   -> 5) Set up job control

10. Select a single point job:

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

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

13. Choose the following options:

    -> 1) (Done with selections)

    3) [X] MCSCF
    5) [X] MR-CISD (serial operation)
    13) [X] convert MOs into molden format

14. Exit the input facility.

15. Run Columbus with the runc script and analyze the results from LISTINGS/ciudgsm.sp, LISTINGS/cipcls.drt1.sp and files.

    > nohup $COLUMBUS/runc -m 2000 > runls &

16. Repeat the whole procedure of MRCI calculation for DRT2 and DRT3, changing the allowed reference symmetries to 2 and 3, respectively.

    ! The MRCI calculation for DRT2 requires more iterations, so we should increase NITER to NITER = 30. Besides, it is better to run in another computer!

    ! You can run two MRCI calculations simultaneously (for DRT1 and DRT3)!

Tutorial III-1. Diatomic Molecules, O_2 Case.

1. MRCI single point calculation using D2h symmetry

The system is O_2 which will be calculated using a complete active space composed by whole valence, that is twelve electrons in eight orbitals [CASSCF(12,8)]. D_{2h} point group, one triplet state and the 6-31G* basis sets will be used.

> Before starting any COLUMBUS input, it is strongly advisable to write down the details of the orbital occupation and distinct row tables. You can download doc and pdf templates of these tables at: http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable

1.1 Orbital occupation and DRT tables

1 . Fill out the occupation table according toFig. 1:

System: O_2 Point Group: D_{2h}

N. Electrons: 16 Multiplicity: *3*

Level: *MR-CISD(12,8)/CASSCF(12,8)*

		IRREP							
		a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u
SCF	DOCC	3	1	1	0	2	0	0	0
	OPSH	0	0	0	0	0	1	1	0
MCSCF	DOCC	1	0	0	0	1	0	0	0
	RAS	0	0	0	0	0	0	0	0
	CAS	2	1	1	0	2	1	1	0
	AUX	0	0	0	0	0	0	0	0
MRCI	FC	1	0	0	0	1	0	0	0
	FV	0	0	0	0	0	0	0	0
	DOCC	0	0	0	0	0	0	0	0
	ACT	2	1	1	0	2	1	1	0
	AUX	0	0	0	0	0	0	0	0
	INT	2	1	1	0	2	1	1	0

Information concerning the basis set (from infofl file)

a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u
7	3	3	1	7	3	3	1

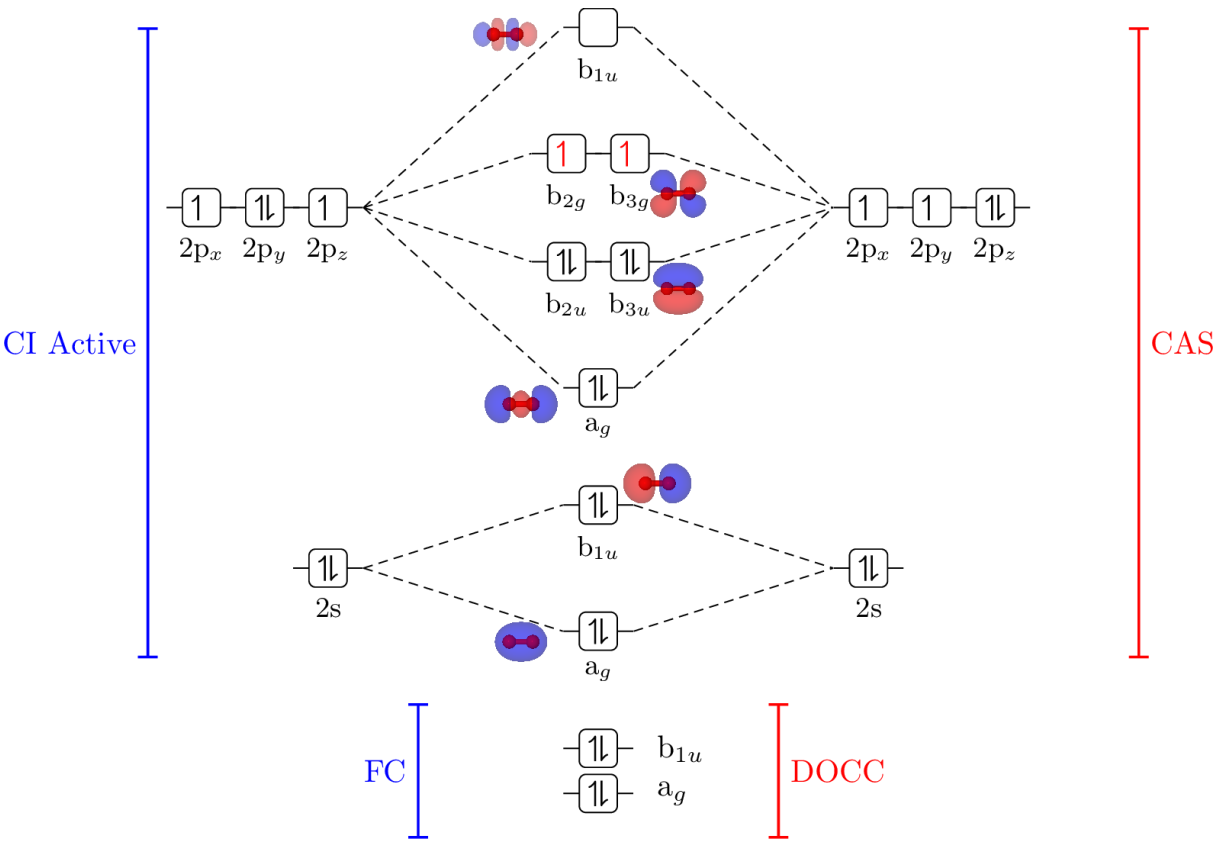


Figure 1 - Molecular orbitals diagram for the calculation.

2 . Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	3	16	B_{1g}
1	3	16	B_{1u}
Number of distinct rows tables (DRTs):			2

1.2 Geometry file creation

3. Create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called o2_d2h_cas128 using mkdir command.

4. Move to this directory and copy o2_d2h.xyz file from:

/home/aluno/cjp_2019/rene/o2_d2h/INPUT/TUTORIAL/

directory which contains the geometry (symmetry unique) in XYZ format.

5. Convert geometry into COLUMBUS format.

>$COLUMBUS/xyz2col.x < o2_d2h.xyz <ENTER>

The Columbus geometry file is called 'geom' and is in Bohr

```
The conversion from Columbus format to xyz can be done with the program
geom2xyz.pl
      > $COLUMBUS/geom2xyz.pl geom
After running this program, the xyz-format geometry (in Angstrom) is
written to file geom.xyz'.
```

1.3 Colinp integral input

6. Run and select

> $COLUMBUS/colinp

-> 1) Integral program input (for argos/dalton/turbocol/molcas)

7. Use the prepinp utility

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

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

Input for DALTON (1) or MOLCAS (2): 1
Enter the point group symmetry: d2h ! *Only Abelian groups*
Name of the file containing the cartesian coordinates of the unique atoms (COLUMBUS format): geom
Number of atoms = 1 ! *verify that the file was read in correctly*
Sum formula: O1

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)
6-31 ! *leave this empty and get the full list*

-- Set basis set --

34: OXYGEN Pople 6-31g* or 6-31g**

Select the basis set for atom O: 34 ! *6-31g* was selected*
...

Until now you've set the following basis sets:

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

1.4 Colinp step: SCF input

10. Select option 2) SCF input

Do you want a closed shell calculation ?<YES>n
Input the no. of doubly occupied orbitals for each irrep, DOCC:
3 1 1 0 2 0 0 0 <ENTER>

Input the no. of open shell orbitals for each irrep, OPSH:
0 0 0 0 0 1 1 0 <ENTER>

The orbital occupation is:

```
          ag b3u b2u b1g b1u b2g b3g  au
DOCC   3   1   1   0    2   0   0   0
OPSH   0   0   0   0    0   1   1   0
Is this correct? <YES><ENTER>

There are   2 open shell orbitals.
Would you like the high spin case? <YES><ENTER>

Would you like to change the default program parameters? <NO><ENTER>
Input a title: <Default SCF Title>
 --><ENTER>
```

1.5 Running just the Hartree-Fock Calculation and Storing it

11. Select option 5) Set up job control
12. Select option 1) Job control for single point or gradient calculation
13. Select option 1) Single point calculation
14. Select the following options marked below and finish.

```
-> 1) (Done with selections)

   2) [X] SCF

  13) [X] convert MOs into molden format
```

15. In the next panels, select "Exit" until finishing COLINP execution.
16. Run Columbus with the runc script

```
> nohup $COLUMBUS/runc -m 2000 > runls-ref &
```

and then analyze the results from files:

a) runls-ref;
b) LISTINGS/scfls.sp;

```
runc script runs COLUMBUS, relying on the control.run file. nohup is for
keeping the calculation running, even after the terminal is closed.
2000Mb (2Gb) is the memory used, and the calculation steps are written in
the runls file.
```

1.6 Colinp step: MCSCF calculation

17. Select option 3) MCSCF input

```
MCSCF WAVE FUNCTION DEFINITION

==============================

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 0
```

```
no (0) - for single point calculation
```

```
Enter number of DRTS [1-8] 2

number of electrons for DRT #1 (nucl. charge: 16) 16

multiplicity for DRT #1 3
```

spatial symmetry for DRT #1 4

excitation level (cas,ras)->aux 0

excitation level ras->(cas,aux) 0

number of electrons for DRT #1 (nucl. charge: 16) 16

multiplicity for DRT #2 3

spatial symmetry for DRT #2 5

excitation level (cas,ras)->aux 0

excitation level ras->(cas,aux) 0

number of doubly occupied orbitals per irrep 1 0 0 0 1 0 0 0

number of CAS orbitals per irrep 2 1 1 0 2 1 1 0

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

Apply add. group restrictions for DRT 2 [y|n] n

18. Considering one root of each state:

1. Iterations #iter [200]

State-averaging

DRT 1: #states [1] weights[1]
DRT 2: #states [1] weights[1]
transition moments / non-adiabatic couplings [N]

FINISHED [y] <ENTER>

1.7 Colinp Step: MRCI Input

19. Select option 4) CI input

20. Select option 2) Def. of CI wave function - multiple-DRT case (transition moments)

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

21. CIDRTMS input facility, input shared by all DRTs

Enter number of DRTS [1-8] 2

Spin-Orbit CI [y|n] n

Enter the multiplicity (all DRTs) 3

Enter the number of electrons (all DRTs)16

Generalized interacting space restrictions [y|n]} y

number of frozen core orbitals per irrep 1 0 0 0 1 0 0 0

number of frozen virtual orbitals per irrep 0 0 0 0 0 0 0 0

number of internal(=docc+active+aux) orbitals per irrep 2 1 1 0 2 1 1 0

number of aux. orbitals per irrep 0 0 0 0 0 0 0 0

<ENTER>

CIDRTMS input facility, DRT #1 specific input

ref doubly occ orbitals per irrep for DRT #1 0 0 0 0 0 0 0 0

excitation level (0,1,2) 2

state symmetry (1 .. nsym)} 4

allowed reference symmetries 4

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

22. CIDRTMS input facility, DRT #2 specific input

ref doubly occ orbitals per irrep for DRT #2 0 0 0 0 0 0 0 0

excitation level (0,1,2) 2

state symmetry (1 .. nsym)} 5

allowed reference symmetries 5

Apply additional group restrictions for DRT 2 [y|n] n

23. MRCI calculation options:

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

CIUDGIN INPUT MENU DRT# 1
...
NITER[80]
...
FINISHED [y] <ENTER>
CIUDGIN INPUT MENU DRT# 2
...
NITER[80]
...
FINISHED [y] <ENTER>

COLUMBUS INPUT FACILITY
symmetric and antisymmetric transition moment selections

1) (Done with selections)

2) [ ] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1

3) [ ] bra: DRT# 1 state# 1 ket: DRT# 2 state# 1

4) [ ] bra: DRT# 2 state# 1 ket: DRT# 2 state# 1

24. Select option 5) Set up job control
25. Select option 1) Job control for single point or gradient calculation and discard the contron file.
26. Select option 1) Single point calculation
27. Select the following options marked below

    1)(Done with selections)

    3) [X] MCSCF

    5) [X] MR-CISD (serial operation)

    13)[X] convert MOs into molden format

28. In the next panels, select "Exit" until finishing COLINP execution.

1.8 Running the calculation

29. Run Columbus with the runc script

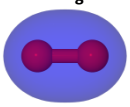
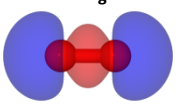
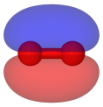
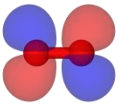
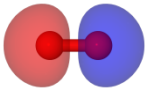
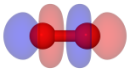
    > nohup $COLUMBUS/runc -m 2000 >> runls-ref &

and then analyze the results from:

a) runls;
b) LISTINGS/mcscfsm.sp;
c) LISTINGS/mcpcls.drtX.sp
d) LISTINGS/ciudgsm.drtX.sp
e) LISTINGS/cipcls.drtX.sp

1.9 Check the Orbitals

30. Later, using your favourite molecular viewer plot the orbitals from molden_mc.sp file.

$2a_g$ 	**$3a_g$** 	**$1b_{3u}$ or $1b_{2u}$** 
$1b_{3g}$ or $1b_{2g}$ 	**$2b_{1u}$** 	**$3b_{1u}$** 

2. MRCI Potential Energy Curve Calculation

2.1 Colinp Step: Potential Energy Curve Input

1. Select option 5) Set up job control
2. Select option 2) Potential energy curve for one int. coordinate

    Internal coordinates generated!
    Press return to continue
    <ENTER>
    Internal coordinate file exists, would you like to overwrite it? (y|n) y
    <ENTER>

3. Enter the curve parameters:

```
Potential energy curve calculation for one int.coord.:
( bond distances in Angstrom, angles in degree )
...
 int.coord. number [ 1 ]
 initial displacement [ -0.2 ]   final displacement [ 2.7 ]  !Relative to the current point
 number of displacements  [ 30 ] <ENTER>

                                                              ...
 Interval: 0.1 Ang! <ENTER>
```

4. In the next panels, select "Exit" until finishing COLINP execution.

2.2 Running The Calculations

5. All calculations were generated in the DISPLACEMENTS folder

```
> ls DISPLACEMENTS
```

6. There are some more control options in the DISPLACEMENTS/displfl file.
7. The calculation is performed with the $COLUMBUS/calc.pl script.
8. There are some desired behaviours for the calculation:

a) Use the orbitals from the current calculation as a guess for the first point
b) Use the orbitals from the previous point as a guess

This is reached using the -morestart option for the script

9. Copy the desired Molecular orbitals to start the calculation.

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

10. Run the calculation.

```
> $COLUMBUS/calc.pl -morestart -m 1000 -nproc 1 >> runls-surf &
```

```
calc.pl script runs COLUMBUS (with the appropriate options) in every
displacement created by colinp. This displacements are found in the
DISPLACEMENTS/displfl file.
```

11. The calculation may be tracked in the runsurfls and curve.log files .

```
> less -S +F runls-surf
> less curve.log.XXXXX
```

12. The results can be collected with the $COLUMBUS/curve.pl script. Create a file named curvein with the content:

```
msci    1    1      ! Multi State CI   STATE 1   DRT 1
msci    1    2      ! Multi State CI   STATE 1   DRT 2
```

and execute

```
> $COLUMBUS/curve.pl
```

```
curve.pl script collect the results in each folder in DISPLACEMENTS. At
least the desired method, # of states and the DRT # should be given, but
it can collect the c² for a particular DRT and a comment may be added.
```

2.3 Checking the Results

13. Create a folder CURVES with the mkdir command
14. Write the output from $COLUMBUS/curve.pl to a file named curve.out inside this folder and copy the runls-surf to this folder also.

    > $COLUMBUS/curve.pl >> CURVES/curve.out
    > cp runls-surf CURVES

15. Copy to CURVES a python script named get_results_o2.py from:
    /home/aluno/cjp_2019/rene/o2_d2h/INPUT/TUTORIAL/

    and enter the folder CURVES.

16. Execute the script

    python3 get_results_o2.py -h
    python3 get_results_o2.py -c curve.out -r runls-surf -d 30

17. Check the files
    a) drt1-state1.dat;
    b) drt1-state2.dat;
    c) tm.dat
18. There is also the plot for the curves in curves.png.

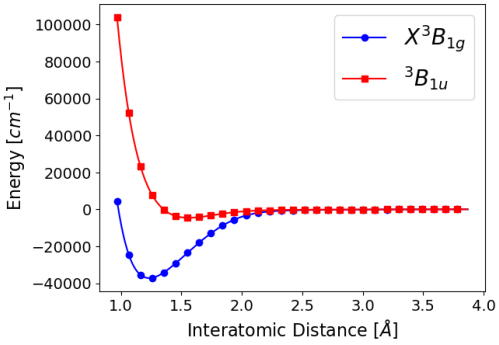


Figure 2 - Potential energy curves for the first and first root with B_{1g} and B_{1u} symmetries of the O_2 molecule. The energies were calculated with calculated with MRCI(12,8)/CAS(12,8).

19. From the created files drt1-state1.dat and drr2-state1.dat, collect the minimum value of the cubic spline interpolation (second line), and substract it from the last point (approximated as the dissociation limit). Also collect the minimum value position.

20. Compare these value with the values from **K. P. Huber, G. Herzberg,** *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules.*

State	Dissociation energy	Equilibrium distance
$^3\sum_g^-$	5.1 eV	~1.21 Å
$^3\sum_u^+$	0.7 eV	~1.52 Å

3. Useful Orbital Diagrams for the Calculations

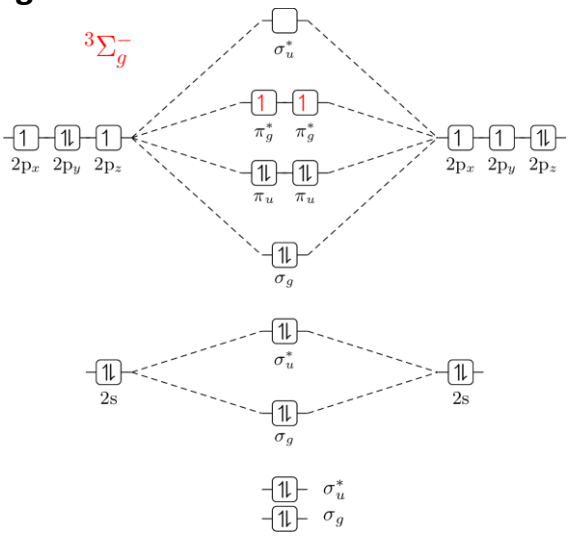


Figure 3 - Orbital diagram for the ground state ($^3\sum_g^-$) of the O_2 molecule in the $D_{\infty h}$ point group.

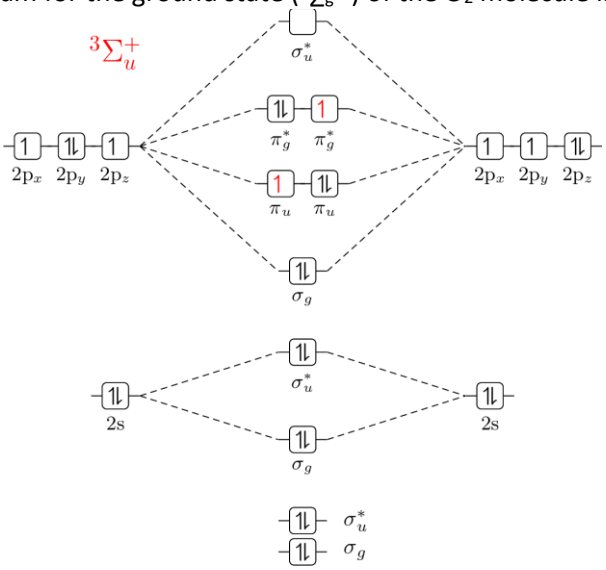


Figure 4 - Orbital diagram for the excited state ($^3\sum_u^+$) of the O_2 molecule in the $D_{\infty h}$ point group.

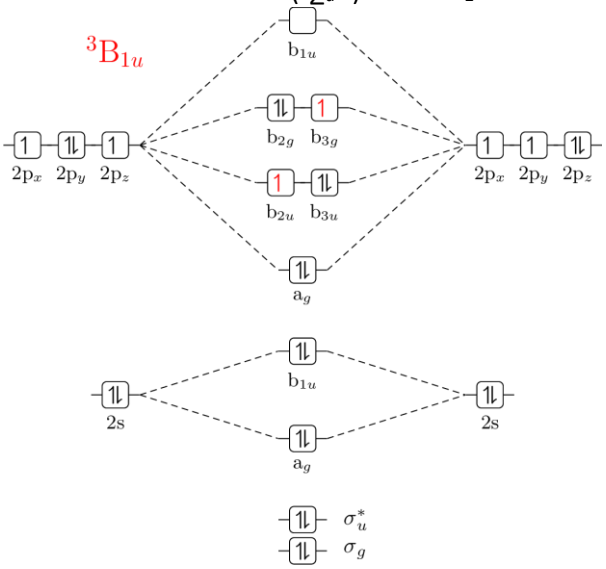


Figure 5 - Orbital diagram for the excited state ($^3B_{1u}$) of the O_2 molecule projected in the D_{2h} point group.

Tutorial III-2. Diatomic Molecules, CO Case.

1. MRCI single point calculation using C_{2v} symmetry

The system is CO which will be calculated using a complete active space composed by the whole valence, that is ten electrons in eight orbitals [CASSCF(10,8)]. C_{2v} point group, one triplet state and the 6-31G* basis sets will be used.

> Before starting any COLUMBUS input, it is strongly advisable to write down the details of the orbital occupation and distinct row tables. You can download doc and pdf templates of these tables at: http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable

1.1 Orbital occupation and DRT tables

1. Fill out the occupation table according toFig. 1:

System: CO

Point Group: C_{2v}

N. Electrons: 14

Multiplicity: 1

Level: MR-CISD(10,8)/CASSCF(10,8)

		IRREP							
		a_1	b_1	b_2	a_2				
SCF	DOCC	5	1	1	0				
	OPSH	0	0	0	0				
MCSCF	DOCC	2	0	0	0				
	RAS	0	0	0	0				
	CAS	4	2	2	0				
	AUX	0	0	0	0				
MRCI	FC	2	0	0	0				
	FV	0	0	0	0				
	DOCC	0	0	0	0				
	ACT	4	2	2	0				
	AUX	0	0	0	0				
	INT	4	2	2	0				

Information concerning the basis set (from infofl file)

a_1	b_1	b_2	a_2
14	6	6	2

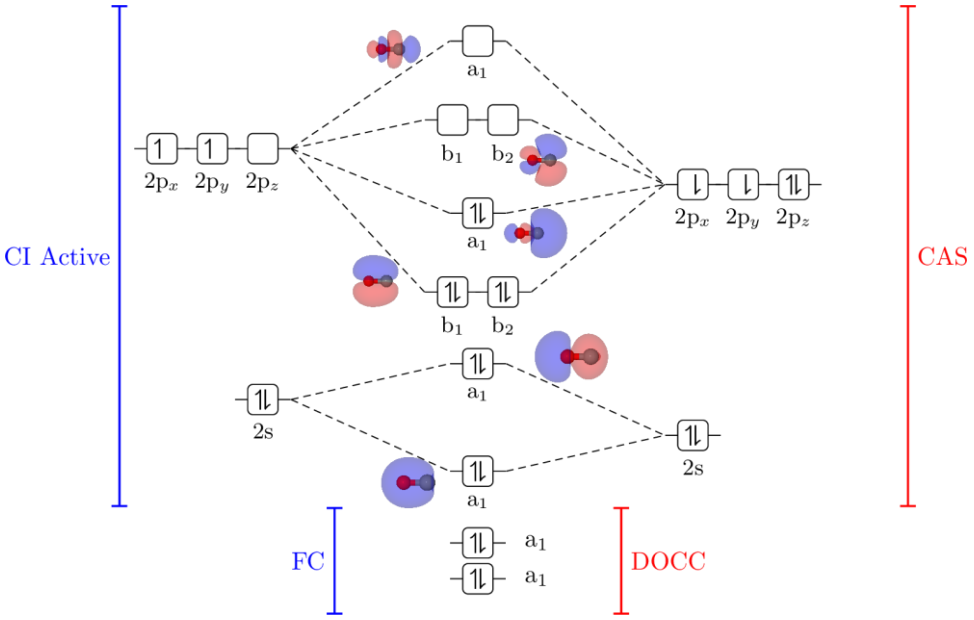


Figure 2 - Molecular orbitals diagram for the calculation.

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
2	1	14	A_1
Number of distinct rows tables (DRTs):			1

1.2 Geometry file creation

3. If it does not exist, create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called co_c2v_cas108 using mkdir command.

4. Move to this directory and copy co_c2v.xyz file from:

/home/aluno/cjp_2019/rene/co_c2v/INPUT/TUTORIAL/

directory which contains the geometry (symmetry unique) in XYZ format.

5. Convert geometry into COLUMBUS format.

>$COLUMBUS/xyz2col.x < co_c2v.xyz <ENTER>

The Columbus geometry file is called 'geom' and is in Bohr

```
The conversion from Columbus format to xyz can be done with the program
geom2xyz.pl
      > $COLUMBUS/geom2xyz.pl geom
After running this program, the xyz-format geometry (in Angstrom) is
written to file geom.xyz'.
```

6. Run and select

> $COLUMBUS/colinp

-> 1) Integral program input (for argos/dalton/turbocol/molcas)

7. Use the prepinp utility

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

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

Input for DALTON (1) or MOLCAS (2): 1
Enter the point group symmetry: c2v ! *Only Abelian groups*
Name of the file containing the cartesian coordinates of the unique atoms (COLUMBUS format): geom
Number of atoms = 2 ! *verify that the file was read in correctly*
Sum formula: O1 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)
6-31 ! *leave this empty and get the full list*
-- Set basis set --

34: OXYGEN Pople 6-31g* or 6-31g**

Select the basis set for atom O: 34 ! *6-31g* was selected*
...

-- Set basis set --

31: CARBON Pople 6-31g* or 6-31g**

Select the basis set for atom C: 31 ! *6-31g* was selected*
...

Until now you've set the following basis sets:

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

1.4 COLINP step: SCF input

10. Select option 2) SCF input

Do you want a closed shell calculation ?<YES>y
Input the no. of doubly occupied orbitals for each irrep, DOCC:
5 1 1 0 <ENTER>

The orbital occupation is:

	a1	b1	b2	a2
DOCC	5	1	1	0
OPSH	0	0	0	0

Is this correct? <YES><ENTER>

Would you like to change the default program parameters? <NO><ENTER>
Input a title: <Default SCF Title>
--><ENTER>

1.5 Running just the Hartree-Fock Calculation and Storing it

11. Select option 5) Set up job control
12. Select option 1) Job control for single point or gradient calculation
13. Select option 1) Single point calculation
14. Select the following options marked below and finish.

    1) (Done with selections)

    2) [X] SCF

    13) [X] convert MOs into molden format

15. In the next panels, select "Exit" until finishing COLINP execution.
16. Run Columbus with the runc script

```
> nohup $COLUMBUS/runc -m 2000 > runls-ref &
```

and then analyze the results from files:

a) runls;
b) LISTINGS/scfls.sp;

```
runc script runs COLUMBUS, relying on the control.run file. nohup is for
keeping the calculation running, even after the terminal is closed.
2000Mb (2Gb) is the memory used, and the calculation steps are written in
the runls file.
```

1.6 Colinp step: MCSCF calculation

18. Select option 3) MCSCF input

```
MCSCF WAVE FUNCTION DEFINITION
==============================
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 0
```

```
no (0) - for single point calculation
```

```
Enter number of DRTS [1-8] 1

number of electrons for DRT #1 (nucl. charge: 14) 14

multiplicity for DRT #1 1

spatial symmetry for DRT #1 1

excitation level (cas,ras)->aux 0

excitation level ras->(cas,aux)  0

number of doubly occupied orbitals per irrep    2 0 0 0

number of CAS orbitals per irrep    4 2 2 0


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

19. Considering two roots:

State-averaging

DRT 1: #states [2] weights[1,1]
transition moments / non-adiabatic couplings [Y]

FINISHED [y] <ENTER>

1.7 Colinp Step: MRCI Input

19. Select option 4) CI input

20. Select option 2) Def. of CI wave function - one-DRT case
Do you want to compute gradients or non-adiabatic couplings? [y|n] n

21. CIDRT input facility:

Spin-Orbit CI [y|n] n
Enter the multiplicity (all DRTs) 1
Enter the number of electrons 14
Enter the molec. spatial symmetry 1
number of frozen core orbitals per irrep 2 0 0 0
number of frozen virtual orbitals per irrep 0 0 0 0
number of internal(=docc+active+aux) orbitals per irrep 4 2 2 0
ref doubly occ orbitals per irrep for DRT #1 0 0 0 0
Auxiliary internal orbitals per irrep 0 0 0 0

excitation level (0,1,2) 2
Generalized interacting space restrictions [y|n]} y
Enter allowed reference symmetries 1
Apply additional group restrictions for DRT [y|n] n
<ENTER>

22. MRCI calculation options:

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

CIUDGIN INPUT MENU DRT# 1
...
NROOT [2]
CI/AQCC procedure: NITER [80]
...
FINISHED [y] <ENTER>

COLUMBUS INPUT FACILITY
symmetric and antisymmetric transition moment selections
1) (Done with selections)
2) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
3) [X] bra: DRT# 1 state# 1 ket: DRT# 1 state# 2
4) [X] bra: DRT# 1 state# 2 ket: DRT# 1 state# 2

23. Select option 5) Set up job control

24. Select option 1) Job control for single point or gradient calculation and discard the existing file.

25. Select option 1) Single point calculation

26. Select the following options marked below

1)(Done with selections)

3) [X] MCSCF

4) [X] transition moments for MCSCF

5) [X] MR-CISD (serial operation)

9) [X] transition moments for MR-CISD

13) [X] convert MOs into molden format

27. In the next panels, select "Exit" until finishing COLINP execution.

1.8 Running the calculation

28. Run Columbus with the runc script

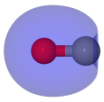
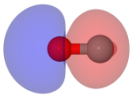
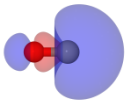
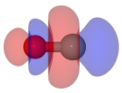
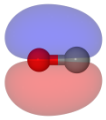
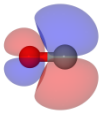
```
> nohup $COLUMBUS/runc -m 2000 >> runls-ref &
```

and then analyze the results from:

f) runls;
g) LISTINGS/mcscfsm.sp;
h) LISTINGS/mcpcls.drtX.sp
i) LISTINGS/ciudgsm.drtX.sp
j) LISTINGS/cipcls.drtX.sp

1.9 Check the Orbitals

29. Later, using your favourite molecular viewer plot the orbitals from molden_mc.sp file.

$3a_1$ 	**$4a_1$** 	**$5a_1$** 
$6a_1$ 	**$1b_1$ or $1b_2$** 	**$2b_1$ or $2b_2$** 

2. MRCI Potential Energy Curve Calculation

2.1 Colinp Step: Potential Energy Curve Input

1. Select option 5) Set up job control
2. Select option 2) Potential energy curve for one int. coordinate

```
                                    Internal coordinates generated!
                                    Press return to continue
                                    <ENTER>
Internal coordinate file exists, would you like to overwrite it? (y|n)y
<ENTER>
```

3. Enter the curve parameters:

Potential energy curve calculation for one int.coord.:
(bond distances in Angstrom, angles in degree)

...

int.coord. number [1]
initial displacement [-0.2] final displacement [3.0] !Relative to the current point
number of displacements [17] <ENTER>

...

Interval: 0.2 Ang! <ENTER>

4. In the next panels, select "Exit" until finishing COLINP execution.

2.2 Running The Calculations

5. All calculations were generated in the DISPLACEMENTS folder

> ls DISPLACEMENTS

6. There are some more control options in the DISPLACEMENTS/displfl file.
7. The calculation is performed with the $COLUMBUS/calc.pl script.
8 . There are some desired behaviours for the calculation:

c) Use the orbitals from the current calculation as a guess for the first point
d) Use the orbitals from the previous point as a guess

This is reached using the -morestart option for the script

9. Copy the desired Molecular orbitals to start the calculation.

> cp MOCOEFS/mocoef_mc.sp mocoef.start

10. Run the calculation.

> $COLUMBUS/calc.pl -morestart -m 1000 -nproc 1 >& runls-surf &

```
calc.pl script runs COLUMBUS (with the appropriate options) in every
displacement created by colinp. This displacements are found in the
DISPLACEMENTS/displfl file.
```

11. The calculation may be tracked in the runls-surf and curve.log.XXXX files .

> less -S +F runls-surf
> less curve.log.XXXXX

12. The results can be collected with the $COLUMBUS/curve.pl script. Create a file named curvein with the content:

```
ci    2    1       ! Method CI  STATES 2   DRT 1
```

and execute

> $COLUMBUS/curve.pl

```
curve.pl script collect the results in each folder in DISPLACEMENTS. At
least the desired method, # of states and the DRT # should be given, but
it can collect the c² for a particular DRT and a comment may be added.
```

2.3 Checking the Results

13. Create a folder CURVES with the mkdir command

14. Write the output from $COLUMBUS/curve.pl to a file named curve.out inside this folder and copy the runls-surf to this folder also.

> $COLUMBUS/curve.pl >> CURVES/curve.out

> cp runls-surf CURVES

15. Copy to CURVES a python3 script named get_results_co.py from:

/home/aluno/cjp_2019/rene/co_c2v/INPUT/TUTORIAL/

and enter the folder CURVES.

16. Execute the script

python3 get_results_co.py -h

python3 get_results_co.py -c curve.out -r runls-surf -d 17

17. Check the files

d) drt1-state1.dat;

e) drt1-state2.dat;

f) tm.dat

18. There is also the plot for the curves in curves.png.

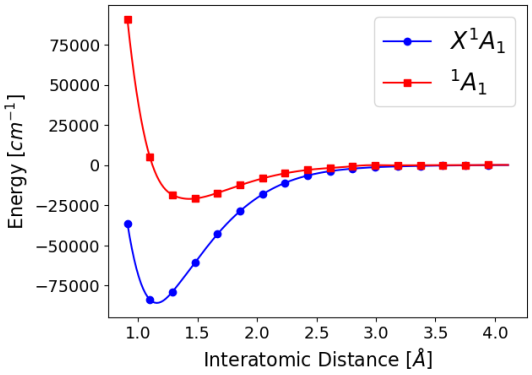


Figure 2 - Potential energy curves for the first and second roots with A_1 symmetry of the CO molecule. The energies were calculated with calculated with MRCI(10,8)/CAS(10,8).

19. From the created files drt1-state1.dat and drr2-state1.dat, collect the minimum value of the cubic spline interpolation (second line), and substract it from the last point (approximated as the dissociation limit). Also collect the minimum value position.

20 . Compare these value with the values from **K. P. Huber, G. Herzberg,** *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules.*

State	Dissociation energy	Equilibrium distance
$X^1\Sigma^+$	11.09 eV	~1.13 Å
$^1\Delta$	2.91 eV	~1.39 Å

3. Useful Orbital Diagrams for the Calculations

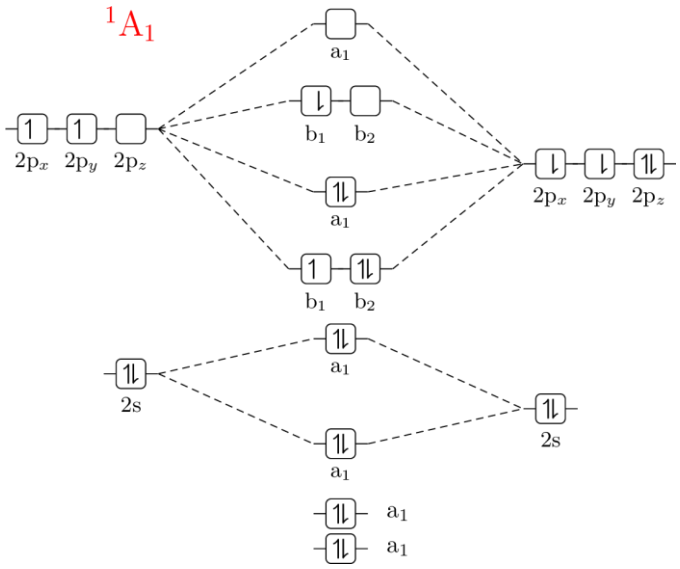


Figure 3 - Orbital diagram for the excited state ($^1A_1$) of the CO molecule projected in the C_{2v} point group.

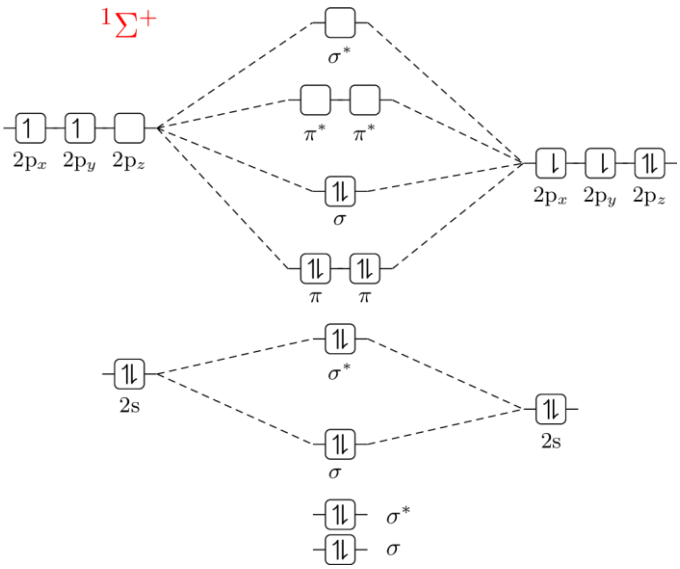


Figure 4 - Orbital diagram for the ground state ($^1\sum^+$) of the CO molecule in the $C_{\infty v}$ point group.

Tutorial III-3. Chloromethane

1. MCSCF single point calculation using C_s symmetry

The system is chloromethane, CH_3Cl, which will be calculated using a complete active space composed by six electrons in four orbitals [CASSCF(6,4)]. Three singlet states in the state averaging procedure (SA-3) and the 3-21G* basis sets will be used.

1.1 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. You can download doc and pdf templates of these tables at http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable*

1. Fill out the occupation table according toFig. 1:

System: *CH_3Cl* Point Group: *C_s*

N. Electrons: *26* Multiplicity: *1*

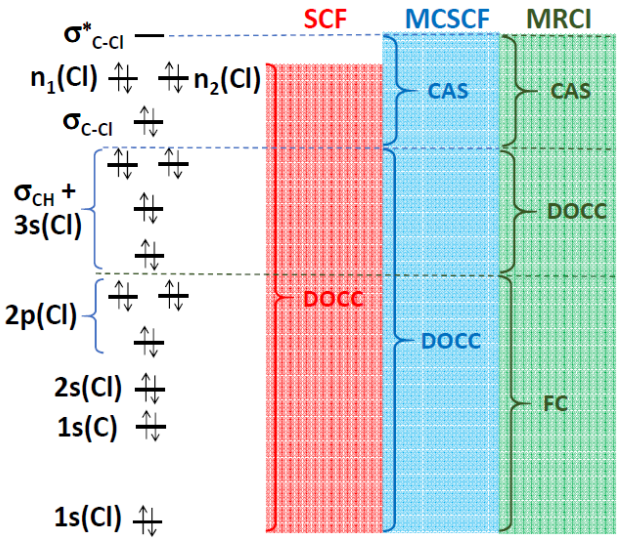
Level: *MR-CISD(6,4)/SA-3-CASSCF(6,4)*

IRREP*! Irreducible representations*

		a'	*a"*						
SCF	DOCC	*10*	*3*	*! Doubly occupied in the SCF wavefunction*					
	OPSH	*0*	*0*	*! Singly occupied in the SCF wavefunction*					
MCSCF	DOCC	*8*	*2*	*! Doubly occupied orbitals in the MCSCF*					
	RAS	*0*	*0*	*! Restricted orbitals (only a restricted number of excitations from them)*					
	CAS	*3*	*1*	*! Active orbitals (any kind of excitation); in this case the σ/σ^* and n(Cl) orbitals*					
MRCI	FC	*5*	*1*	*! Frozen core orbitals (six: C(1s) + Cl(1s,2s and 2p)) in the MRCI;* ***They have the lowest energies at the RHF level!***					
	FV	*0*	*0*	*! Frozen virtual orbitals*					
	DOCC	*3*	*1*	*! Reference doubly occupied orbitals:* ***notice that FC + DOCC(CI) = DOCC (MCSCF)***					
	ACT	*3*	*1*	*! Reference active orbitals:=* ***MCSCF***					
	INT	*6*	*2*	*! Internal (DOCC+ACT+AUX)*					

Information concerning the basis set (from infofl file)

a'	a"
24	9



Scheme of orbital occupation for MRCI(6,4) and CASSCF(6,4).

C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	−1	z, R_x, R_y	yz, xz

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	*1*	*26*	*A'*
2	*1*	*26*	*A''*
Number of distinct rows tables (DRTs):			*2*

1.2 Geometry file creation

3. Create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called chloromethane_Cs_CAS64_SP using mkdir command.

4. Move to this directory and copy geom file from /home/aluno/cjp_2019/silmar/CH3Cl_Cs/INPUT/TUTORIAL/ directory which contains the geometry (symmetry unique) in COLUMBUS format (in Bohr)

The COLUMBUS geometry file is called 'geom' and is in Bohr
The conversion from COLUMBUS *format to xyz can be done with the program geom2xyz.pl*
> $COLUMBUS/geom2xyz.pl geom
After running this program, the xyz-format geometry (in Angstrom) is written to file 'geom.xyz'.

1.3 Colinp integral input

5. Run and select
> $COLUMBUS/colinp
-> 1) Integral program input (for argos/dalton/turbocol/molcas)

6. Use the prepinp utility

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

7. Enter information about program, symmetry and geometry file.

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

   Enter the point group symmetry: cs ! *Only Abelian groups*

   Name of the file containing the cartesian coordinates

   of the unique atoms (COLUMBUS format): geom

   Number of atoms = 4 ! *verify that the file was read in correctly*

   Sum formula: Cl1 H2 C1

8. 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)

   3-21g*!*you may enter "3-21g*" here or leave this empty and get the full list, simply pressing <ENTER>*

   -- Set basis set --

   19: CHLORINE Pople 3-21g*

   Select the basis set for atom Cl:19! 3-*21G* was selected*

   ...

   Select the basis set for atom H:25! 3-*21G* was selected*

   ...

   Select the basis set for atom C:28! 3-*21G* was selected*

   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.

9. Perform an automatic input of iargos.x.

   Would you like to do an interactive input? <NO>n! *Select "no"* and press *<ENTER>*

1.4 Colinp step: SCF input

10. Select option 2) SCF input

    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:10 3 <ENTER>

    ....

    Is this correct? <YES><ENTER>

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

    Input a title: <Default SCF Title>

    --><ENTER>

1.5 COLINP step: MCSCF input

11. Select option 3) MCSCF input

```
MCSCF WAVE FUNCTION DEFINITION
==============================
Freeze orbitals prior to MCSCF (no gradients available) [y|n]n
prepare input for no(0),CI(1), MCSCF(2), SA-MCSCF(3) analytical gradient1
```

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.

```
....
excitation level (cas,ras)→aux 0        ! allow 0 excitation from the
active orbitals
excitation level ras->(cas,aux)  0      ! allow 0 excitation from the
        restricted active orbitals
....
Apply add. group restrictions for DRT 1 [y|n]n
Apply add. group restrictions for DRT 2 [y|n]n
....
State-averaging
                DRT 1: #states [2 ] weights[ 1,1          ]
                DRT 2: #states [1 ] weights[ 1            ]
            transition moments / non-adiabatic couplings [N]
                                FINISHED [y]
```

1.6 Running a MCSCF single point job

12. Select option 5) Set up job control
13. Select option 1) Job control for single point or gradient calculation
14. Select option 1) Single point calculation
15. Select the following options marked below and finish with “Done with selections”.

```
->  1) (Done with selections)
    2) [X] SCF
    3) [X] MCSCF
   13) [X] convert MOs into molden format
```

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

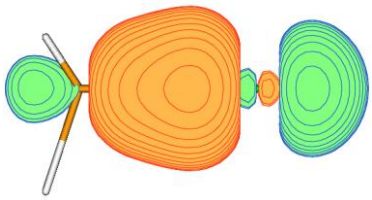
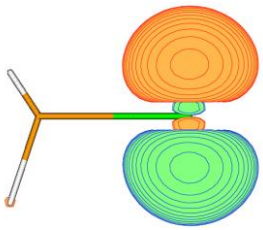
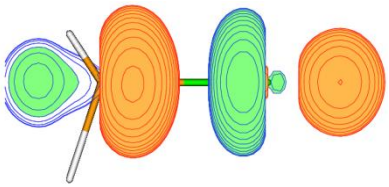
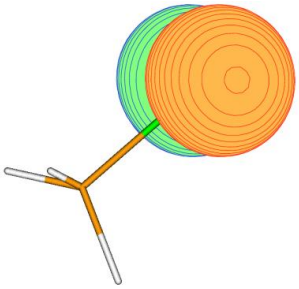
17. Run Columbus with the runc script and then analyze the results from LISTINGS/mcscfsm.sp, LISTINGS/mcpcls.drt1.state1.sp, LISTINGS/mcpcls.drt1.state2.sp and LISTINGS/mcpcls.drt2.state1.sp

    > nohup $COLUMBUS/runc -m 2000 > runls &

runc script runs COLUMBUS, relying on the control.run file. nohup is for keeping the calculation running, even after the terminal is closed. 2000Mb (2Gb) is the memory used, and the calculation steps are written in the runls file.

Try to identify the degenerate (^{1}E) state (nσ), as well as the σ, σ* and the two non–bonding orbitals, n(Cl).*

> molden MOLDEN/molden_mo_mc.sp & ! *'molden' is an alias to MOLDEN path*

MO 9, σ (9a')	MO 10, n_1 (10a')	MO 11, σ* (11a')
		
MO 27, n_2 (3a'')		
		

Molecular orbitals visualized with Molden using contour value of 0.1.

2. MRCI single point calculation using C_s symmetry

In this section we will perform a single point calculation at MRCI level for the chloromethane. The reference space for the MRCI contains six electrons in four orbitals (see 1.1). This calculation is done on top of the SA-3-CASSCF(6,4) calculation performed in section 1. The 3-21G* basis sets and C_s symmetry will be used. One separate calculation for each state (DRT) will be performed (see 1.1)

2.1 Basic input

1. In the TUTORIAL directory create a subdirectory called chloromethane_Cs_MRCI_SP
2. Move to this directory and create a directory called DRT1 ! For the ^{1}A' states
3. Move to this directory and copy the input files from the MCSCF directory:

   >cp ../../chloromethane_Cs_CAS64_SP/* .

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

   >cp ../../chloromethane_Cs_CAS64_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".

2.2 COLINP step: MRCI input

> $COLUMBUS/colinp

-> 4) CI input

...

press return to continue<enter>

-> 1) Def. of CI wave function - one-DRT case

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

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

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

   ....

Do according to the DRT table.

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

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. In the last panel, NROOT should be chosen 1 for each DRT.

   State(s) to be optimized NROOT [2] ROOT TO FOLLOW [0]

   ....

   FINISHED [y]

8. Move the cursor to FINISHED and press <enter>. Do not select transition moments.

   -> 1) (Done with selections)

2.3 Running a MRCI single point job

9. Enter the job control menu and select

   -> 5) Set up job control

10. Select a single point job:

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

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

13. Choose the following options:

-> 1) (Done with selections)

3) [X] MCSCF
5) [X] MR-CISD (serial operation)
13) [X] convert MOs into molden format

14. Exit the input facility.

15. Run Columbus with the runc script and analyze the results from LISTINGS/ciudgsm.sp, LISTINGS/cipcls.drt1.sp and files.

```
> nohup $COLUMBUS/runc -m 2000 > runls &
```

16. Repeat the whole procedure of MRCI calculation for DRT2, changing the allowed reference symmetries to 2 and making NROOT = 1.

Try to identify the degenerate (^{1}E) state (nσ)*

Tutorial IV. Symmetry Breaking in the Allyl Radical

1. Calculation using C_{2v} symmetry

The allyl radical will be calculated using the open shell SCF and CASSCF(3,3) methods and the cc-pVDZ basis. We use C_{2v} symmetry first, which enforces the equivalence of the two CC bonds. In the next step, only Cs symmetry of the molecular plane will be used.

Inputs available in /home/aluno/cjp_2019/hans/allyl_c2v/INPUT/

> Before starting any COLUMBUS input, it is strongly advisable to write down the details of the orbital occupation and distinct row tables. You can downlod doc and pdf templates of these tables at: http://www.univie.ac.at/columbus/documentation/utilities.html#orbocctable

1.1 Orbital occupation and DRT tables

1 . Fill out the occupation table according toFig. 1:

System: C_3H_5 Point Group: C_{2v}

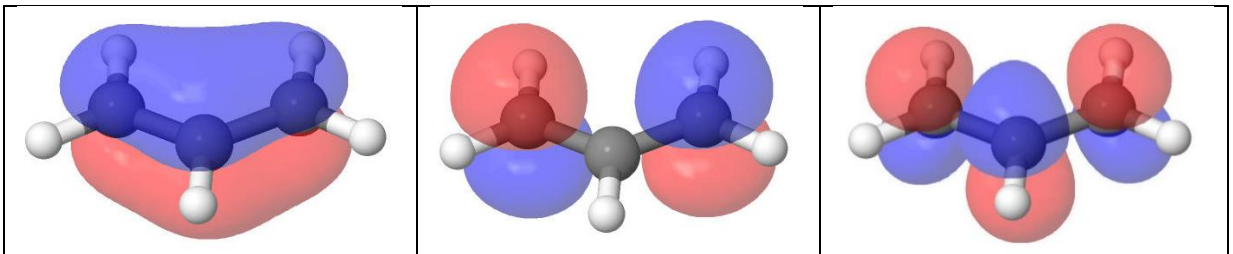
N. Electrons: 23 Multiplicity: 2

Level: SCF and CASSCF(3,3)

		IRREP							
		a_1	b_1	b_2	a_2				
SCF	DOCC	6	4	1					
	OPSH	0	0	0	1				
MCSCF	DOCC	6	4	0	0				
	RAS								
	CAS	0	0	2	1				
	AUX								

Information concerning the basis set (from infofl file)

a_1	b_1	b_2	a_2
28	22	10	7



$1b_2$	$1a_2$	$2b_2$

Figure 3 - Molecular π orbitals.

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	2	23	A_2
Number of distinct rows tables (DRTs):			1

1.2 Geometry file creation

3. If it does not exist, create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called **allyl_c2v** using mkdir command.

4. Move to this directory and copy allyl_opt.xyz file from:

/home/aluno/cjp_2019/hans/allyl_c2v/INPUT/TUTORIAL

directory which contains the geometry (symmetry unique) in XYZ format.

5. Convert geometry into COLUMBUS format.

>$COLUMBUS/xyz2col.x < allyl_opt.xyz <ENTER>

The Columbus geometry file is called 'geom' and is in Bohr

Create file of **unique** coordinates:

```
C   6.0   2.32548750   0.00000000  -0.31050027  12.00000000
C   6.0  -2.32548750   0.00000000  -0.31050027  12.00000000
H   1.0   0.00000000   0.00000000   2.95934083   1.00782504
H   1.0  -4.08521289   0.00000000   0.74288867   1.00782504
H   1.0  -2.45681407   0.00000000  -2.36101097   1.00782504
```

1.3 COLINP integral input

6. Run and select

> $COLUMBUS/colinp

-> 1) Integral program input (for argos/dalton/turbocol/molcas)

7. Use the prepinp utility

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

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

Input for DALTON (1) or MOLCAS (2): 1
Enter the point group symmetry: c2v ! *Only Abelian groups*
Name of the file containing the cartesian coordinates of the unique atoms (COLUMBUS format): geom
Number of atoms = 5 ! *verify that the file was read in correctly*
Sum formula: H3 C2

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)
cc-pv ! *leave this empty and get the full list*

-- Set basis set --

1: cc-pvdz (4s,1p)->[2s,1p]

Select the basis set for atom H: 1 ! *cc-pvdz was selected*

...

-- Set basis set --

1: cc-pvdz(9s,4p,1d)->[3s,2p,1d]

Select the basis set for atom C: 1 ! *cc-pvdz was selected*

...

Until now you've set the following basis sets:
H :: cc-pvdz (4s,1p)->[2s,1p]
C :: cc-pvdz(9s,4p,1d)->[3s,2p,1d]

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

1.4 COLINP step: SCF input

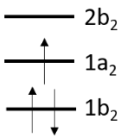
10 . Select option 2) SCF input

Do you want a closed shell calculation ?<YES>n
Input the no. of doubly occupied orbitals for each irrep, DOCC:
6 4 1 0 <ENTER>
Input the no. of open shell orbitals for each irrep, OPSH:
0 0 0 1 <ENTER>

The orbital occupation is:

	a1	b1	b2	a2
DOCC	6	4	1	0
OPSH	0	0	0	1

Is this correct? <YES><ENTER>



Occupied π orbitals: $1b_2$ (docc), $1a_2$ (open shell)

Would you like to change the default program parameters? <NO><ENTER>
Input a title: <Default SCF Title>
--><ENTER>

1.5 Running just the Hartree-Fock Calculation and Storing it

11. Select option 5) Set up job control
12. Select option 1) Job control for single point or gradient calculation
13. Select option 1) Single point calculation

14. Select the following options marked below and finish.

    1) (Done with selections)

    2) [X] SCF

    13) [X] convert MOs into molden format

15. In the next panels, select "Exit" until finishing COLINP execution.

16. Run Columbus with the runc script

    > nohup $COLUMBUS/runc -m 2000 > runls &

and then analyze the results from files:

a) runls;
b) LISTINGS/scfls.sp;

```
runc script runs COLUMBUS, relying on the control.run file. nohup is for
keeping the calculation running, even after the terminal is closed.
2000Mb (2Gb) is the memory used, and the calculation steps are written in
the runls file.
```

1.6 Colinp step: MCSCF calculation

17. Select option 3) MCSCF input

    MCSCF WAVE FUNCTION DEFINITION

    ==========

    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 0

```
no (0) – for single point calculation
```

    Enter number of DRTS [1-8] 1

    number of electrons for DRT #1 (nucl. charge: 23) 23

    multiplicity for DRT #1 2

    spatial symmetry for DRT #1 4

    excitation level (cas,ras)->aux 0

    excitation level ras->(cas,aux) 0

    number of doubly occupied orbitals per irrep 6 4 0 0

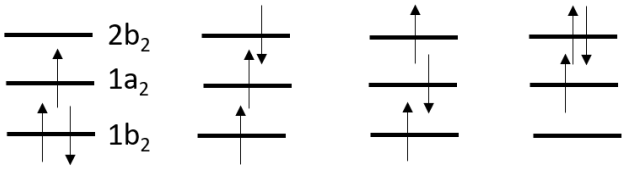
    number of CAS orbitals per irrep 0 0 2 1

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

    DRT1: #electrons:23 mult:2 sym:a2 exc:0 0

    count order (bottom to top): DOCC - RAS - CAS - AUX

irreps	a1	b1	b2	a2
# basis fcts	28	22	10	7
docc	6	4	0	0
cas	0	0	2	1



2. Calculations with C_s symmetry, Single Point

Inputs available in /home/aluno/cjp_2019/hans/allyl_cs/INPUT/

2.1 Orbital occupation and DRT tables

The symmetry plane is the molecular plane!

1. Fill out the occupation table according toFig. 1:

System: C_3H_5 Point Group: C_s

N. Electrons: 23 Multiplicity: 2

Level: SCF and CASSCF(3,3)

		IRREP							
		a	a"						
SCF	DOCC	10	1						
	OPSH	0	1						
MCSCF	DOCC	10	0						
	RAS								
	CAS	0	3						
	AUX								

Information concerning the basis set (from infofl file)

a'	a"
50	17

2. Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	2	23	A"
Number of distinct rows tables (DRTs):			1

2.2 Geometry file creation

3. If it does not exist, create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called **allyl_cs** using mkdir command.

4. Move to this directory and use the following geom file:

```
C   6.0   2.32548750  -0.31050027   0.00000000  12.00000000
C   6.0   0.00000000   0.89790429   0.00000000  12.00000000
C   6.0  -2.32548750  -0.31050027   0.00000000  12.00000000
H   1.0   0.00000000   2.95934083   0.00000000   1.00782504
H   1.0  -4.08521289   0.74288867   0.00000000   1.00782504
H   1.0  -2.45681407  -2.36101097   0.00000000   1.00782504
H   1.0   2.45681407  -2.36101097   0.00000000   1.00782504
H   1.0   4.08521289   0.74288867   0.00000000   1.00782504
```

Note the interchange of axis due to the symmetry definitions of the integral program Dalton

2.3 COLINP integral input

5. Run and select

```
> $COLUMBUS/colinp

->  1) Integral program input (for argos/dalton/turbocol/molcas)
```

6. Use the prepinp utility

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

7. Enter information about program, symmetry and geometry file.

```
Input for DALTON (1) or MOLCAS (2): 1
Enter the point group symmetry:  cs     ! Only Abelian groups
Name of the file containing the cartesian coordinates of the unique atoms (COLUMBUS format): geom
Number of atoms = 8                     ! verify that the file was read in correctly
Sum formula:     H5 C3
```

8. 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)
cc-pv ! leave this empty and get the full list
-- Set basis set --

 1:   cc-pvdz (4s,1p)->[2s,1p]

Select the basis set for atom H: 1 ! cc-pvdz was selected
...


-- Set basis set --

1:   cc-pvdz(9s,4p,1d)->[3s,2p,1d]

Select the basis set for atom C: 1 ! cc-pvdz was selected
...
```

Until now you've set the following basis sets:
H :: cc-pvdz (4s,1p)->[2s,1p]
C :: cc-pvdz(9s,4p,1d)->[3s,2p,1d]

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

2.4 COLINP step: SCF input

9. Select option 2) SCF input

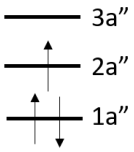
Do you want a closed shell calculation ?<YES>n
Input the no. of doubly occupied orbitals for each irrep, DOCC:
10 1 <ENTER>
Input the no. of open shell orbitals for each irrep, OPSH:
0 1 <ENTER>

The orbital occupation is:

	a'	a"
DOCC	10	1
OPSH	0	1

Is this correct? <YES><ENTER>

Occupied π orbitals: 1a" (docc), 2a" (open shell)



Would you like to change the default program parameters? <NO><ENTER>
Input a title: <Default SCF Title>
--><ENTER>

2.5 Running just the Hartree-Fock Calculation and Storing it

10. Select option 5) Set up job control
11. Select option 1) Job control for single point or gradient calculation
12. Select option 1) Single point calculation
13. Select the following options marked below and finish.

1) (Done with selections)

2) [X] SCF

13) [X] convert MOs into molden format

14. In the next panels, select "Exit" until finishing COLINP execution.
15. Run Columbus with the runc script

```
> nohup $COLUMBUS/runc -m 2000 > runls &
```

and then analyze the results from files:

a) runls;
b) LISTINGS/scfls.sp;

Compare SCF energy C_{2v} (-116.4544649900 a.u.) and C_s (-116.4544649900 a.u.). They are exactly the same.

2.6 Colinp step: MCSCF calculation

16. Select option 3) MCSCF input

MCSCF WAVE FUNCTION DEFINITION

==========

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 0

```
no (0) - for single point calculation
```

Enter number of DRTS [1-8] 1

number of electrons for DRT #1 (nucl. charge: 23) 23

multiplicity for DRT #1 2

spatial symmetry for DRT #1 2

excitation level (cas,ras)->aux 0

excitation level ras->(cas,aux) 0

number of doubly occupied orbitals per irrep 10 0

number of CAS orbitals per irrep 0 3

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

DRT1: #electrons:23 mult:2 sym:a2 exc:0 0

count order (bottom to top): DOCC - RAS - CAS - AUX

irreps	a'	a''
# basis fcts	50	17
docc	10	0
cas	0	3

Apply add. group restrictions for DRT 1 [y|n] n
Accept default values of mcscf parameters
FINISHED [X]
5) Set up job control
1) Job control for single point or gradient calculation
1) single point calculation

Compare CASSCF energies C_{2v} (-116.494272927 a.u.) and C_s (-116.494272927 a.u.). They are exactly the same.

3. Calculations with C_s symmetry, Geometry Optimization CASSCF(3,3)

Inputs available in /home/aluno/cjp_2019/hans/allyl_cs_broken/INPUT/

3.1 Geometry file creation

If it does not exist, create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called **allyl_cs_broken** using mkdir command.

1. Copy the all files from the directory allyl_cs to the new directory ally_cs_broken and go there. We will break the symmetry by changing the coordinates of one of the equivalent C atoms to

C 6.0 -2.**0**2548750 -0.31050027 0.00000000 12.00000000
Otherwise, we keep exactly the same orbital occupations as before. We only need to make part of the input again since we want to make a geometry optimization.

2. Move to this directory and use the following geom file (note the change marked in red):

C	6.0	2.32548750	-0.31050027	0.00000000	12.00000000
C	6.0	0.00000000	0.89790429	0.00000000	12.00000000
C	6.0	-2.**0**2548750	-0.31050027	0.00000000	12.00000000
H	1.0	0.00000000	2.95934083	0.00000000	1.00782504
H	1.0	-4.08521289	0.74288867	0.00000000	1.00782504
H	1.0	-2.45681407	-2.36101097	0.00000000	1.00782504
H	1.0	2.45681407	-2.36101097	0.00000000	1.00782504
H	1.0	4.08521289	0.74288867	0.00000000	1.00782504

Note the interchange of axis due to the symmetry definitions of the integral program Dalton

3.2 COLINP step: SCF input

3.3 Running just the Hartree-Fock Calculation and Storing it

3. Select option 5) Set up job control
4. Select option 1) Job control for single point or gradient calculation
5. Select option 1) Single point calculation
6. Select the following options marked below and finish.

    1) (Done with selections)

    2) [X] SCF

    13) [X] convert MOs into molden format

7. In the next panels, select “Exit” until finishing COLINP execution.
8. Run Columbus with the runc script

```
> nohup $COLUMBUS/runc -m 2000 > runls &
```

and then analyze the results from files:

a) runls;

b) LISTINGS/scfls.sp;

Compare SCF energy original C_s (-116.4544649900 a.u.) and displaced (-116.4288012560 a.u.). They are NOT the same anymore.

3.4 Colinp step: MCSCF calculation

9. Select option 3) MCSCF input

```
MCSCF WAVE FUNCTION DEFINITION

==============================

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 2
Skip DRT input (y|n) [ 1] y
FINISHED [X]
5) Set up job control
1) Job control for single point or gradient calculation
You have an existing job control file. Discard it? (y|n) y
2) geometry optimization with GDIIS
Internal coordinates generated!

            Press return to continue
|Enter the number of optim. cycles:10
2) [X] mcscf gradient (single state)
starting orbitals from scf prior to mcscf? (y|n) n

cp MOCOEFS/mocoef_mc.sp mocoef

run COLUMBUS

Note convergence from runls

-------------------- gdiis.x ------------------------

      value              converged
    -----------------------------------
    max-step=   0.0002612  yes
    rms-step=   0.0000761  yes
    max-force=  0.0005779  yes
    rms-force=  0.0001801  yes

 -----------------------------------------------------
```

Measure the two CC distances:

1st iteration: 1.387 Å and 1.248 Å; converged: both 1.392 Å. **The allyl is back to C_{2v} symmetry!**

4. Calculations with C_s symmetry, Geometry Optimization SCF

Inputs available in /home/aluno/cjp_2019/hans/allyl_cs_broken_scf/INPUT/

If it does not exist, create a directory TUTORIAL. In the TUTORIAL directory create a subdirectory called **allyl_cs_broken_scf** using mkdir command.

Follow all steps of the previous section. Change only the orbital occupation for CAS(3,3) to CAS(3,1) (=SCF)

		IRREP							
		a	a"						
SCF	DOCC	10	1						
	OPSH	0	1						
MCSCF	DOCC	10	1						
	RAS								
	CAS	0	**1**						
	AUX								

Note the change in the CAS occupation, marked in red.
Measure the two CC distances:
1st iteration: 1.387 Å and 1.248 Å; converged: 1.435 Å and 1.337 Å! Symmetry breaking

5. Calculations with C_s symmetry, Geometry Optimization with SCF for symmetric structure

Inputs available in:
/home/aluno/cjp_2019/hans/allyl_cs_symm_scf_broken_mos/INPUT/

We perform an SCF calculation at the symmetric structure of Sec. 2 in C_s symmetry using **symmetry broken** orbitals of the previous Sec. 4 as **starting orbitals**. If the symmetric orbital solution would be the minimum, the optimized orbitals should be symmetric. What is the result of the calculation?
Make a directory **allyl_cs_symm_scf_broken_mos.** Copy the files of allyl_cs_broken_scf into this directory and replace the geom file by

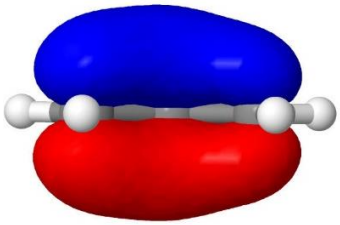
```
C    6.0    2.32548750   -0.31050027    0.00000000   12.00000000
C    6.0    0.00000000    0.89790429    0.00000000   12.00000000
C    6.0   -2.32548750   -0.31050027    0.00000000   12.00000000
H    1.0    0.00000000    2.95934083    0.00000000    1.00782504
H    1.0   -4.08521289    0.74288867    0.00000000    1.00782504
H    1.0   -2.45681407   -2.36101097    0.00000000    1.00782504
H    1.0    2.45681407   -2.36101097    0.00000000    1.00782504
H    1.0    4.08521289    0.74288867    0.00000000    1.00782504
```

Copy the mocoef file from allyl_cs_broken_scf/MOCOEFS/mocoef_mc.min to allyl_cs_symm_scf_broken_mos and change the name to mocoef. This file contains unsymmetric MOs since the come from an unsymmetric structure. Change the control.run file as:

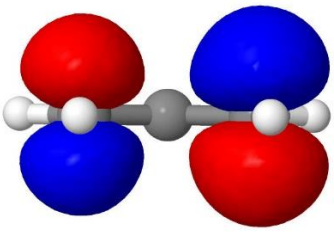
```
molden
hermit
mcscf
```

to perform a single point calculation and run the calculation.

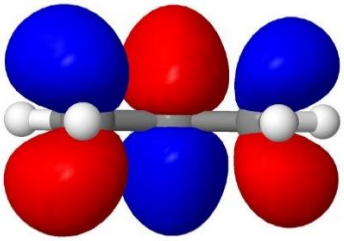
Compare the SCF energy at the C_{2v} symmetry (-116.4544649900 a.u.) with the energy at the **same geometry** with symmetry broken starting MOs (-116.454524940 a.u.). The enery is now **lower**. The three π orbitals are not symmetric.



1a”



2a”



3a”

The orbitals are symmetry broken!

6. Calculations with C_s symmetry, Geometry Optimization with CAS(3,4) and CAS(3,5)

Perform these calculations in analogy to CAS(3,3). Which CAS gives symmetry breaking and which not?