

(the absorption spectrum), the ratio between the MCD and absorption intensities, and the last three columns represent the “sticks” of the corresponding transitions.

Energy	C	D	C/D	C	D	E/D
24310.8	0.6673	980.2678	0.0006	0.0000	0.0000	0.0000
24340.1	0.8471	1174.3637	0.0007	-0.0001	0.0129	-0.0112
24369.5	1.0664	1408.5788	0.0007	0.0001	0.0281	0.0033
24398.8	1.3325	1690.5275	0.0007	0.0000	0.0000	0.0000
24428.1	1.6542	2029.0152	0.0008	0.0000	0.0000	0.0000
24457.4	2.0416	2434.1699	0.0008	0.0000	0.0332	0.0003

Now the MCD and the absorption spectra can be plotted with a suitable graphical program, for instance with the Origin program.

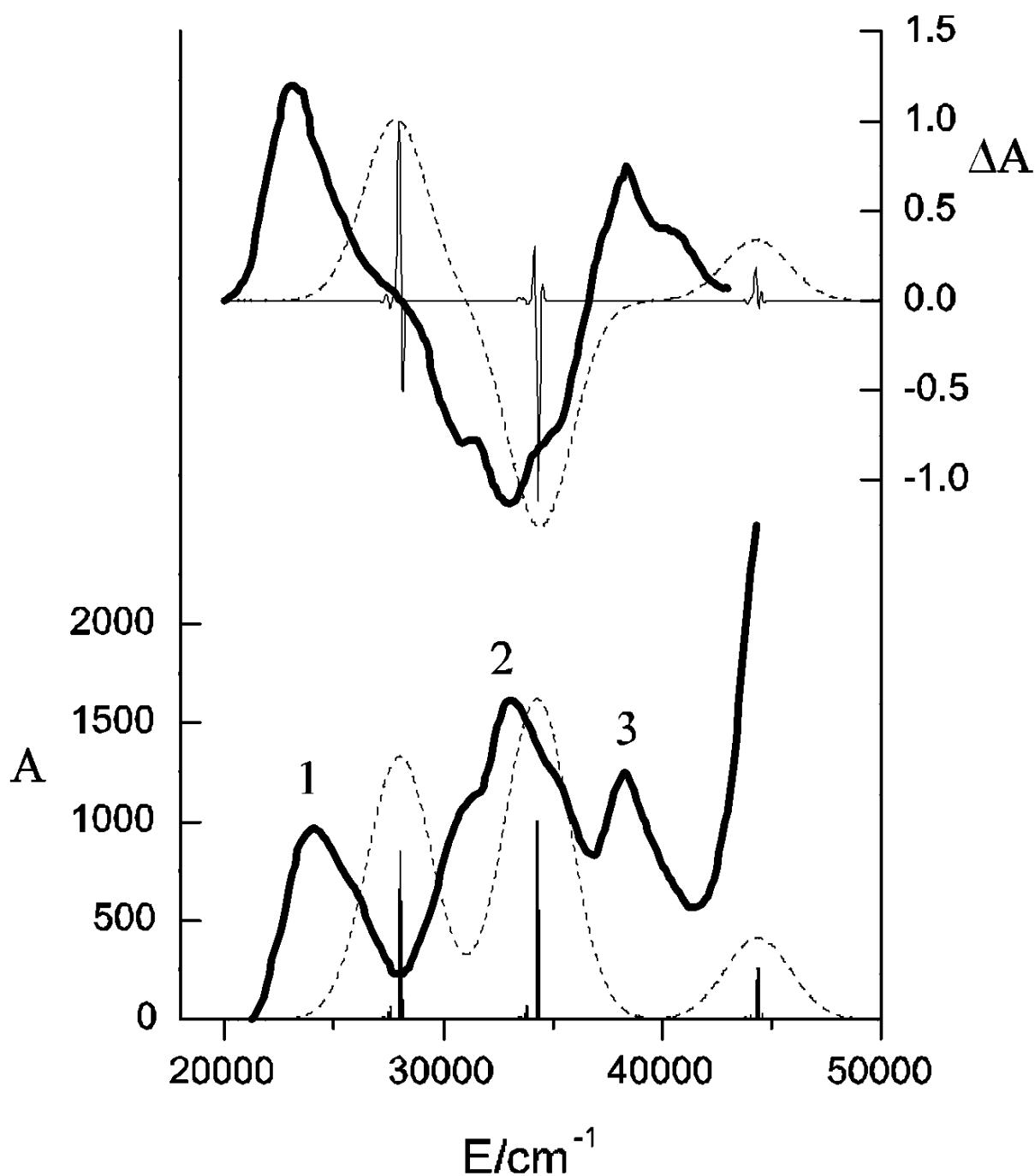


Fig. 3.47: Calculated MCD and absorption spectra of $[\text{Fe}(\text{CN})_6]^{3-}$ (dash lines) compared to experimental spectra (solid lines).

Addition of Magnetic Fields

The inclusion of the Zeeman contribution into the QDPT procedure allows to obtain the splittings of the magnetic levels in an external magnetic field. The switch for this calculation and the magnetic field strength are defined in the soc subblock of the mrci block. Optionally the wave function decomposition can be printed for `MagneticField_PrintLevel` larger 0. The latter employs the thresh `TPrint` to omit small contributions from the printing:

```
%mrci
soc
```

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```

DoSOC true          #
DoSSC true          #
MagneticField true  # default false
B 1,10,100,1000    # Strength of the magnetic field in Gauss.
                   # 4000 is the default value

# Optional printing of the wave function for each
# magnetic field settings
MagneticField_PrintLevel 0 # default (disabled)
TPrint               1e-3
end
end

```

Then, the output contains three sets of data of splittings of the magnetic levels with the magnetic field applied parallel to x, y, and z directions:

```

End B (Gauss)  Energy levels (cm-1) and populations for B || x

    1.0  -0.030  0.333  0.012  0.333  0.018  0.333
   10.0  -0.030  0.333  0.012  0.333  0.018  0.333
  100.0  -0.031  0.333  0.012  0.333  0.020  0.333
 1000.0  -0.102  0.333  0.012  0.333  0.091  0.333

B (Gauss)  Energy levels (cm-1) and populations for B || y

    1.0  -0.030  0.333  0.012  0.333  0.018  0.333
   10.0  -0.030  0.333  0.012  0.333  0.018  0.333
  100.0  -0.032  0.333  0.014  0.333  0.018  0.333
 1000.0  -0.105  0.334  0.018  0.333  0.087  0.333

B (Gauss)  Energy levels (cm-1) and populations for B || z

    1.0  -0.030  0.333  0.012  0.333  0.018  0.333
   10.0  -0.030  0.333  0.011  0.333  0.018  0.333
  100.0  -0.030  0.333  0.005  0.333  0.025  0.333
 1000.0  -0.079  0.333 -0.030  0.333  0.108  0.333

```

Here the number in a row represents the strength of the magnetic field (in Gauss), and the following pairs of numbers denote the energy of the magnetic level (in cm^{-1}) with its occupation number. This table can be readily plotted with any suitable graphical program.

Relativistic Picture Change in Douglas-Kroll-Hess SOC and Zeeman Operators

The DKH correction to the SOC operator is implemented in ORCA as a correction to the one-electron part of the SOMF operator. The DKH transformation is performed up to the second order, and the two-electron part in our implementation is left untransformed. However, the electronic density employed for evaluating the SOMF matrix elements is obtained from a scalar relativistic calculation. The inclusion of the DKH correction is controlled by the `picturechange` key in the `rel` block:

```

%rel method DKH          # relativistic method
  picturechange 2         # include the DKH correction to SOC
end

```

The “`picturechange`” key can be set to 0, 1, and 2 for no picture change, the first order, and the second order DKH transformations of the SOC operator.

With “`picturechange`” set to 1 or 2 the DKH correction are applied in the first order to the Zeeman operator. This correction has a visible effect on calculated g-tensors for molecules containing third-row and heavier atoms.

X-ray Spectroscopy

Likewise to the CASCI/NEVPT2 computational protocol presented in section *Core Excited Spectra: CAS-CI/RAS-CI XAS/RIXS* starting from ORCA 4.2 the MRCI module can be used to compute core excited spectra, namely X-ray absorption (XAS) and resonant inelastic scattering (RIXS) spectra.

As discussed in the case of CASCI/NEVPT2 protocol *Core Excited Spectra: CAS-CI/RAS-CI XAS/RIXS* a similar strategy is followed to compute XAS/RIXS spectra within the MRCI module. In principle the XAS/RIXS spectra calculations require two steps:

- In a first step one needs to optimize the valence active space orbitals in the framework of SA-CASSCF calculations, e.g. including valence excited states in the range between 6 to 15 eV.
- In a second step the relevant core orbitals are rotated into the active space and the MRCI problem is solved by saturating the excitation space with singly core-excited electronic configurations using the previously optimized sets of orbitals.
- The core orbitals are also included in the XASMOs definition. The use of this keyword is two fold. At first it effectively reduces the number of the generated configuration state functions (CSFs) to those that exclusively contain contributions from the defined core orbitals. In the case of RIXS also XES (see below) the specified XASMOs are used to define intermediate or core ionized states.

A representative input for the case of $\text{Fe}(\text{Cl})_4$ is provided below:

- In the first step one performs a SA-CASSCF calculation for the 5 and 15 quintet and triplet states ($\text{FeI-ICl}_4.\text{casscf.inp}$).

```
!cc-PWCVTZ-DK cc-pVTZ/C RIJCOSX SARC/J TightSCF DKH2

%rel
  FiniteNuc true
end

%basis
  newgto Cl "cc-pVTZ-DK" end
  newauxgto Cl "cc-pVTZ/C" end
end

%method FrozenCore FC_NONE
end

%casscf nel 6
  norb 5
  mult 5,3
  nroots 5,15
  switchstep nr
end

* xyz -2 5
Fe -17.84299991694815 -0.53096694321123 6.09104775508499
Cl -19.84288422845700 0.31089495619796 7.04101319789001
Cl -17.84298666758073 0.11868125024595 3.81067954087770
Cl -17.84301352218429 -2.87052442818457 6.45826391412877
Cl -15.84311566482982 0.31091516495189 7.04099559201853
*
```

- In a second step the core orbitals are rotated in the active space and the MRCI problem is solved by saturating the excitation space with all the quintet and triplet states that involve single excitations from the core orbitals ($\text{FeIICl}_4\text{-mrci.inp}$)

```
!MORRead CC-PWCVTZ-DK cc-pVTZ/C RIJCOSX SARC/J TightSCF DKH2

%moinp "FeIICl4-casscf.gbw"
```

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```

%rel
  FiniteNuc true
end

%method FrozenCore FC_NONE
end

%scf
  rotate { 6,42,90} { 7,43,90} { 8,44,90}  end
end

%basis
  newgto Cl "cc-pVTZ-DK" end
  newauxgto Cl "cc-pVTZ/C" end
end

%casscf
  nel      12
  norb     8
  mult     5,3
  nroots   34,195
  maxiter  1
  switchstep nr
end

%mrcki
  CItpe MRCI
  intmode fulltrafo
  XASMOs 42, 43, 44
  newblock 5 *
  nroots 34
  excitations cisd
  refs CAS(12,8)
  end
  end
  newblock 3 *
  nroots 195
  excitations cisd
  refs CAS(12,8)
  end
  end
  maxiter 100
  soc
  printlevel 3
  dosoc true
  end
end

* xyz -2 5
Fe -17.84299991694815      -0.53096694321123      6.09104775508499
Cl -19.84288422845700      0.31089495619796      7.04101319789001
Cl -17.84298666758073      0.11868125024595      3.81067954087770
Cl -17.84301352218429     -2.87052442818457      6.45826391412877
Cl -15.84311566482982      0.31091516495189      7.04099559201853
*

```

In a similar fashion Multireference Equation of Motion Couple Cluster MR-EOM-CC (see next section) can also be used to compute X-ray spectra. Further information can be found in reference[514]

As it is explicitly described in the respective ROCIS section RIXS spectra can be requested by the following keywords:

```
RIXS      true      # Request RIXS calculation (NoSOC)
RIXSSOC   true      # Request RIXS calculation (with SOC)
Elastic   true      # Request RIXS calculation (Elastic)
```

Please consult section *Resonant Inelastic Scattering Spectroscopy* for processing and analyzing the generated spectra

Likewise to TDDFT (*Excited States via RPA, CIS, TD-DFT and SF-TDA*) ROCIS (*Excited States with Restricted Open-shell CIS - ROCIS*) and CASSCF (*Core Excited Spectra: CAS-CI/RAS-CI XAS/RIXS*) the computed transition densities also in the presence of SOC can be taken beyond the dipole approximation by using the *OPS tool* for details.

1. by performing a multipolar expansion
2. by computing the full semiclassical transition moments

The whole set of spectroscopy tables can be requested with the following commands:

```
%mrci
  DoDipoleLength      true
  DoDipoleVelocity    true
  DecomposeFosc       true
  DoFullSemiclassical true
end
```

More details can be found in TDDFT (*Excited States via RPA, CIS, TD-DFT and SF-TDA*) ROCIS (*Excited States with Restricted Open-shell CIS - ROCIS*) and CASSCF (*Core Excited Spectra: CAS-CI/RAS-CI XAS/RIXS*) sections.

Starting from ORCA 4.2 the previously reported RASCI-XES protocol reference[515], which can compute K_β Main-line XES spectra, can be processed entirely within the ORCA modules. In ORCA 5.0 a similar protocol (CASCI-XES) exist in the CASSCF module (*Core Excited Spectra: CAS-CI/RAS-CI XAS/RIXS*)

- Like above or in the CASCI/NEVPT2 case in a first step one needs to optimize the valence active space orbitals in the framework of SA-CASSCF calculations, e.g. including valence excited states in the range between 6 to 15 eV for the N electron system.
- In a second step the metal 1s and 3p orbitals are rotated in the active space and the 1s MO is defined in the XASMOs list
- Computes the XES spectrum in the RASCI framework for the N-1 electron system in the presence of SOC if the XESSOC keyword for all the states that are dominated by 3p-1s electron decays.

A representative input sequence for the case of $\text{Fe}(\text{Cl})_6$ is provided bellow:

As described in reference[515] at first for a CAS(5,5) the excitation space is saturated by the sextet as well as the 24 quartet and the 75 doublet states which are optimized in the SA-CASSCF fashion.

```
X2c x2c-TZVPall x2c/J def2-TZVP/C

%scf
  MaxDisk 40000
end

%casscf
  nel 5
  norb 5
  mult 6,4,2
  nroots 1,24,75
  shiftup 0.5
  shiftdn 0.5
  trafostep RI
  maxiter 150
end
```

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```
*xyz -3 6
Fe      0.0000      0.0000      0.000000
Cl      2.478       0.0000      0.000
Cl     -2.478       0.0000      0.000
Cl      0.000005     2.478      0.00000
Cl      0.000005    -2.478     -0.0000
Cl     -0.000      -0.000      2.478
Cl      0.000      -0.0000     -2.478
*
```

In following the 1s and 3p Fe based MOs are rotated in the active space and the XES spectra are computed for the $[\text{Fe}(\text{Cl})_6]^+$ system for the 4 septet and 81 quintet states.

```
! X2c x2c-TZVPall x2c/J def2-TZVP/C MORead AllowRHF
! NormalPrint
! NoLoewdin NoMulliken

%moinp "fecl6_casscf.gbw"

%scf
  MaxDisk 40000
end

%scf
  #Rotate the 1s and 3p orbitals below the SOMOs by using the rotate option
  rotate {0,59,90} {36,60,90} {37,61,90} {38,62,90} end
end

%casscf
  nel 5
  norb 5
  mult 6,4
  nroots 1,24
  shiftup 0.5
  shiftdn 0.5
  trafostep exact
  maxiter 1
end

%mrcki citype mrcki
  UseIVOs false
  Etol 1e-8
  IntMode fulltrafo
  PrintLevel 3
  newblock 7 *
    excitations none
    nroots 4
    refs ras(12:4 1/5/0 0) end
  end
  newblock 5 *
    excitations none
    nroots 81
    refs ras(12:4 1/5/0 0) end
  end
  XASMOS 59
  soc
  dosoc true
```

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```

xessoc true
end
end

*xyz -2 7
Fe      0.0000      0.0000      0.000000
Cl      2.478       0.0000      0.000
Cl     -2.478       0.0000      0.000
Cl      0.000005     2.478      0.00000
Cl      0.000005    -2.478     -0.0000
Cl     -0.000      -0.000      2.478
Cl      0.000      -0.0000     -2.478
*
```

As a result the X-ray emission spectrum is calculated and the intensities are computed on the basis of the transition electric dipole moments

SOC CORRECTED EMISSION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS							
Transition	Energy	Energy	Wavelength	fosc(D2)	D2	DX	
DY	DZ	(eV)	(cm-1)	(nm)	(au**2)	(au)	
(au)	(au)						
426-7.0A -> 420-5.0A	7083.210737	57129953.4	0.2	0.000000203	0.00000		
0.00002	0.00002	0.00002					
427-7.0A -> 420-5.0A	7083.210737	57129953.4	0.2	0.000003409	0.00000		
0.00003	0.00014	0.00000					
426-7.0A -> 419-5.0A	7083.210739	57129953.4	0.2	0.000000626	0.00000		
0.00004	0.00004	0.00002					
427-7.0A -> 419-5.0A	7083.210739	57129953.4	0.2	0.000000169	0.00000		
0.00000	0.00001	0.00003					
426-7.0A -> 418-5.0A	7083.210756	57129953.5	0.2	0.000000867	0.00000		
0.00003	0.00006	0.00002					
427-7.0A -> 418-5.0A	7083.210756	57129953.5	0.2	0.000000228	0.00000		
0.00000	0.00000	0.00004					
426-7.0A -> 417-5.0A	7083.210911	57129954.8	0.2	0.000000824	0.00000		
0.00001	0.00003	0.00006					
427-7.0A -> 417-5.0A	7083.210911	57129954.8	0.2	0.000001296	0.00000		
0.00008	0.00004	0.00000					
426-7.0A -> 416-5.0A	7083.211098	57129956.3	0.2	0.000000159	0.00000		
0.00000	0.00002	0.00002					
...							
428-5.0A -> 0-5.0A	7159.092436	57741980.6	0.2	0.000000000	0.00000	0.	
0.00000	0.00000	0.00000					
430-5.0A -> 0-5.0A	7159.092436	57741980.6	0.2	0.000000000	0.00000	0.	
0.00000	0.00000	0.00000					
429-5.0A -> 0-5.0A	7159.092436	57741980.6	0.2	0.000000000	0.00000	0.	
0.00000	0.00000	0.00000					
431-5.0A -> 0-5.0A	7159.092436	57741980.6	0.2	0.000000000	0.00000	0.	
0.00000	0.00000	0.00000					
432-5.0A -> 0-5.0A	7159.092436	57741980.6	0.2	0.000000000	0.00000	0.	
0.00000	0.00000	0.00000					

The resulted XES spectrum can be visualized by processing the above output file with the `orca_mapspc`


```
orca_mapspc fecl6_xes.out XESSOC -x07000 -x17200 -w4.0 -eV -n10000
```

Note

It is in general not recommended to compute rasci XES spectra on the basis of mrci module.

- In fact K_α : Fe $2p \rightarrow$ Fe $1s$ and K_α : Fe $2p \rightarrow$ Fe $1s$ (Mainline XES) spectra are extreme state demanding and require a large number of relativistic transition densities to be generated which brings a lot of stress to the mrci module.
- A more direct and computationally efficient alternative is provided by the rasci xes protocol via the %casscf module as described in *Core Excited Spectra: CAS-CI/RAS-CI XES*. This in principle provides suitable protocols for the computation of all X-ray emission
- K_α : Fe $2p \rightarrow$ Fe $1s$
- $K_{\beta_{1,3}}$: Fe $3p \rightarrow$ Fe $1s$ (Mainline XES)
- $K_{\beta_{2,5}} / K_{\beta'}$: (Cl $2p +$ Fe $3d$) \rightarrow Fe $1s$ (VtC-XES)

as well the respective resonant XES (RIXS) spectra.

- We also recall that within the limits of their applicability XES and RIXS spectra can also be computed on the basis of Static Ground State DFT (SGS-DFT), see discussion in *Static Ground State DFT (SGS-DFT)* and ROCIS family of methods, see discussion in *Resonant Inelastic Scattering Spectroscopy*.
- A general discussion regarding X-ray spectroscopy experiments and how to approach them on the basis of modern computational spectroscopy methodologies is provided in reference [458]

Hence by processing the above spectra one obtains the exact similar spectrum as presented in Fig. 3.23

3.19.15 Keywords

Caution

The MRCI program is considered legacy.

Simple input keywords for the MRCI module are given in Table 3.52. Note that if these are used, all information about reference spaces, number of roots etc. is taken from the CASSCF module that is assumed to be run in advance. In general, these calculations are of the individually selecting type and are very time consuming. Very many flags can be set and modified for these methods and in general using these methods requires expert users! See the variables Tsel, Tpre and Tnat that define the individual selection process. All of these methods can be used with RI integrals by using RI-<Method> etc. However, then the calculations become even more time consuming since integrals are made one- by one on the fly. Non-RI calculations will be pretty much limited to about 200-300 orbitals included in the CI. A reasonably complete list of %mrci block keywords and their meaning follows below.

Table 3.52: Simple input keywords for the MRCI module.

Keyword	Description
MRCI	Initiates a multireference configuration interaction calculation with single and double excitations
MRCI+Q	Same with multireference Davidson correction for unlinked quadruples
MRACPF	Average coupled-pair functional
MRAQCC	Average quadratic coupled-cluster
MRDDCI1	Difference dedicated CI with one degree of freedom
MRDDCI2	Same with two degrees of freedom
MRDDCI3	Same with three degrees of freedom
MRDDCI<n>+Q	MRDDCI with Davidson correction (n = 1-3)
SORCI	Spectroscopy oriented CI

```

%rci
# -----
# Orbital selection
# NOTE: The orbitals are used as supplied. Thus, the ORDER of
# orbitals is critical. Say you have
#   nact   electrons in the active space
#   nint   electrons in the internal space
#   nfrozen electrons
# * The first nfrozen/2 orbitals will not be included in the CI
# * The next nint/2 orbitals will be doubly occupied in all
#   references
# * the nact electrons are distributed over the, say, nact
#   orbitals according to the active space definitions.
# The remaining orbitals are external.
# IT IS YOUR RESPONSIBILITY THAT THE ORBITAL ORDERING MAKES
# SENSE!
# A sensible two-step procedure is:
# * generate some orbitals and LOOK AT THEM. Decide which ones
#   to include in the CI.
# * re-read these orbitals with ! MOREad NoIter. Perhaps use
#   the "rotate" feature to reorder the MOs
#   Then jump right into the CI which is defined in this se-
#   cond job
#
# NOTE: the MRCI module respects the %method FrozenCore settings
# -----
Loc  0,0,0
    # Localize orbitals in the internal (first flag), active
    # (second flag) and external space (third flag).
UseIVOs  false
    # Use improved virtual orbitals in the CI
# orbital energy window for the frozencore option FC_EWIN
EWIN -40,1000
# alternative MO definition
MORanges  First_internal, Last_Internal, First_active, Last_Active, First-
↪Virtual, Last_virtual
XASMOs  x1,x2,x3,...   # List of XAS donor MOs (see above)

# -----
# Method selection
# -----
CITYPE  MRCI          # Multireference CI (default)
        MRDDCI1       # Difference dedicated CI 1-degree of freedom
        MRDDCI2       # Difference dedicated CI 2-degrees of freedom
        MRDDCI3       # Difference dedicated CI 3-degrees of freedom
        MRACPF        # Average coupled-pair functional
        MRACPF2       # Modified version of ACPF
        MRACPF2a      # A slightly modified version of ACPF-2a
        MRAQCC        # Average quadratic coupled-cluster
        MRCEPA_R      # Multireference CEPA due to Ruttink
        MRCEPA_0      # CEPA-0 approximation
        SORCI         # Spectroscopy oriented CI
        SORCP         # Spectroscopy oriented couplet pair approx.
        MRMP2         # Multireference Moeller-Plesset at second order
        MRMP3         # Multireference Moeller-Plesset at third order
        MRMP4         # Multireference Moeller-Plesset at fourth order
                        # but keeping only singles and doubles relative to
                        # the reference configurations.

# -----
# Selection thresholds
# -----

```

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```

Tsel      1e-6  # Selection threshold for inclusion in the CI based
               # 2nd order MP perturbation theory <0|H|I>/DE(MP)
Tpre      1e-4  # Selection of configurations in the reference space
               # after the initial diagonalization of the reference
               # space only configurations with a weight large>Tpre
               # to any root are included
AllSingles false
               # include ALL SINGLES in the CI. Default is now TRUE!!!

# perturbative estimate of the effect of the rejected configurations
EunselOpt  0    # no correction
           1    # based on the overlap with the 0th order wavefunction
           2    # calculation with the relaxed reference space
               # coefficients. This is the most accurate and only
               # slightly more expensive

# For CITYPE=MRCI,MRDDCI and SORCI the approximate correction for
# higher excitations
DavidsonOpt Davidson1 # default
            Davidson2 # modified version
            Siegbahn  # Siegbahn's approximation
            Pople     # Pople's approximation

# For MRACPF,MRACPF2,MRAQCC and SORCP
NelCorr    0
  # Number of electrons used for computing the average coupled-
  # pair correction.
  # =0 : set equal to ALL electrons in the CI
  # =-1: set equal to all ACTIVE SPACE electrons
  # =-2: set equal to ACTIVE SPACE electrons IF inactive doubles
  #      are excluded (as in MRDDCI)
  # >0 : set equal to user defined input value
LinearResponse false
  # Use ground state correlation energy to compute the shift for
  # higher roots (not recommended)

# -----
# Natural Orbital Iterations
# -----
NatOrbIters  0 # default
  # number of average natural orbital iterations
Tnat         1e-4
  # cutoff of natural orbitals. NOs with an occupation number less
  # than Tnat will not be included in the next iteration
  # Also, orbitals with occupation number closer than Tnat to 2.0
  # will be frozen in the next iteration
Tnat2        -1
  # if chosen >0 then Tnat2 is the threshold for freezing the
  # almost doubly occupied orbitals. Otherwise it is set equal
  # to Tnat

# -----
# Additional flags and algorithmic
# details
# -----
PrintLevel   2  # default. Values between 1 and 4 are possible

DoDDCIMP2    false
  # for DDCI calculations: if set to true the program computes
  # a MP2 like correction for the effect of inactive double
  # excitations which are not explicitly included in the CI. This

```

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```

# is necessary if you compare molecules at different geometries
# or compute potential energy surfaces.
# -----
# The SORCP model
# -----
CITYPE_in  # First step CITYPE
CITYPE_fi  # Second step CITYPE
Exc_in     # First step excitation scheme
Exc_fi     # Second step excitation scheme
Tsel_in    # First step Tsel
Tsel_fi    # Second step Tsel
Tpre_in    # First step Tsel
Tpre_fi    # Second step Tpre

# Thus, the SORCI model corresponds to CITYPE=SORCP with
# CITYPE_in MRCI  CITYPE_fi MRCI
# Exc_in      DDCI2 Cexc_fi   DDCI3
# Tsel_in     1e-5  Tsel_fi   1e-5
# Tpre_in     1e-2  Tpre_fi   1e-2

# -----
# Multireference perturbation theory
# -----
MRPT_b  0.02  # Intruder state avoidance PT after Hirao (default 0.0)
#           # with this flag individual intruders are shifted away to
#           # to some extent from the reference space
MRPT_shift 0.3 # Level shift introduced by Roos which shifts the entire
#           # excited manifold away in order to avoid intruder states.
#           # A correction is applied afterwards but results do depend
#           # on this (arbitrary) value to some extent.
H0Opt    projected # use an off-diagonal definition of H0
         Diagonal  # use a diagonal definition of H0 (much faster but maybe
#           # a little less reliable
Partitioning MP    # Moeller plesset partitioning
              EN    # Epstein-Nesbet partitioning (not recommended)
              RE    # Fink's partitioning
Fopt     Standard  # Standard definition of MR Fock operators
         G3        # uses Anderson's g3 correction also used in CASPT2
UsePartialTrafo true/false # speedups MRMP2

#-----
# restrict reference configurations
#-----
RejectInvalidRefs true # by default reference CSFs are restricted
#           #to target spin and spatial symmetry

# =====
# Definitions of blocks of the CI Matrix
# =====
NewBlock 2 *      # generate a Block with doublet(=2) multiplicity
Nroots  1         # number of roots to be generated
Excitations cis   # CI with single excitations
         cid     # CI with double excitations
         cisd    # CI with single and double excitations
         ddci1   # DDCI list with one degree of freedom
         ddci2   # DDCI list with two degrees of freedom
         ddci3   # DDCI list with three degrees of freedom
Flags[_class_] 0 or 1
#           # Turn excitation classes on or off individually
#           # ``s`` stands for any SOMO, ``i``, ``j`` for internal orbitals.

```

→and

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```

# ``a'','b' for external orbitals
# Singles _class_ = ss, sa, is, ia
# Doubles _class_ = ijss, ijsa, ijab,
#                   isss, issa, isab,
#                   ssss, sssa, ssab
# ``Flags' takes priority over ``Excitations''. In fact
->``Excitations''
# does nothing but to set ``Flags''. So, you can use
->``Excitations''
# to provide initial values for ``Flags' and then modify them
# with subsequent ``Flags' assignments

refs
#
# First choice - complete active space
#
CAS(nel,norb) # CAS-CI reference with nel electrons in
              # Norb orbitals
#
# Second choice - restricted active space
#
RAS(nel: m1 h/ m2 / m3 p)
      # RAS-reference with nel electrons
      # m1= number orbitals in RAS-1
      # h = max. number of holes in RAS-1
      # m2= number of orbitals in RAS-2 (any number of
      #       electrons or holes)
      # m3= number of orbitals in RAS-3
      # p = max. number of particles in RAS-3
#
# Third choice - individually defined configurations
#
\{ 2 0 1 0\}
\{ 1 1 1 0\}
etc.
# define as many configurations as you want. Doubly occupied MOs
# singly occupied MOs and empty MOs. Important notes:
# a) the number of electrons must be the same in all references
# b) the number of orbitals is determined from the number of
#     definitions. Thus, in the example above we have three
->active
#     electrons and four active orbitals despite the fact that
->the
#     highest orbital is not occupied in any reference.
# The program determines the internal, active and external
->spaces
#     automatically from the number of active electrons and orbitals
end
end
# there can be as many blocks as you want!!!

# -----
# Density matrix generation flags
# First Key= State densities <I|D|I>
# =0: none
# =1: Ground state only (lowest root of all blocks; Electron only)
# =2: Ground state only (Electron and spin density)
# =3: Lowest root from each block (Electron density)
# =4: Lowest root from each block (Electron and spin density)
# =5: All states (Electron density)
# =6: All states (Electron and spin density)
# Second Key= Transition densities <I|D|J>

```

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```

#      needed for all transition intensities, g-tensor etc
#      =0: none
#      =1: from the ground state into all excited states (el)
#      =2: from the ground state into all excited states (el+spin)
#      =3: from all lowest states into all excited states (el)
#      =4: from all lowest states into all excited states (el+spin)
#      =5: all state pairs (el)
#      =6: all state pairs (el+spin)
# Note that for perturbation theory the density is computed as
# an expectation value over the first (second) order wavefunction.
# which is renormalized for this purpose
# -----
Densities 1,1

# -----
# Complete printing of the wavefunction
# -----
PrintWF      1      # CFG based printing (default)
              det    # Determinant based wavefunction printing
TPrintWF     3e-3   # Threshold for the printing of the CFGs/Dets

# -----
# Algorithm for the solver
# -----
Solver      Diag    # Davidson like solver
            DIIS    # DIIS like solver
            # both solvers have their pros and cons. The DIIS may converge
            # better or use less time since it only recomputes the vectors that
            # have not yet converged; The DIIS may be less sensitive to root flipping
            # effects but occasionally it converges poorly and states of the same
            # symmetry are occasionally a little problematic
            # For perturbation theory DIIS is always used.
# For both solvers
MaxIter      100    # the maximum number of iterations
Etol         1e-6   # convergence tolerance for energies in Eh
Rtol         1e-6   # convergence tolerance for residual

# For Solver=Diag (Davidson solver)
Otol         1e-16  # Orthogonality threshold for Schmidt process
NGuessMat    512    # Dimension of the guess matrix 512x512
                # be used to compute the initial guess of the actual MRCI_
↪ calculation
NGuessMatRefCI 512 # Dimension of the guess matrix
                # for the reference CI

MaxDim        3     # Davidson expansion space = MaxDim * NRoots
# For the Solver=DIIS. Particularly recommended for anything else but
# straightforward CI and also for calculations in direct2 mode!
MaxDIIS       5     # Maximum number of old vectors to be used in DIIS
RelaxRefs     true  # Relax reference space coefficients in the CI or
                # freeze them to their zeroth order values
LevelShift    0.4   # Level Shift for stabilizing the DIIS procedure

# -----
# RI Approximation
# -----
IntMode      RITrafo #Use RI integrals
              FullTrafo #No RI (default)

# -----
# Integral storage, memory and files

```

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```

# -----
FourIndexInts false (default)
                True
    # Store ALL four index integrals over Mos in main memory
    # only possible for relatively small systems, perhaps up
    # to 150-200 MOs included in the CI
MaxMemInt      256
    # Maximum amount of core memory devoted to the storage of
    # integrals. If NOT all three index integrals fit into main
    # memory the program fails
MaxMemVec      16
    # Maximum amount of memory used for section of the trial and
    # sigma vectors. This is not a particularly critical variable
KeepFiles      false
    # Keep integrals and CI program input file (.mrciinp). Then
    # you can manually edit the .mrciinp file which is a standard
    # ASCII file and run the MRCI program directly. The only thing
    # you cannot change is the orbital window.
end

```

3.20 Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC)

The Multireference Equation of Motion Coupled-Cluster (MR-EOM-CC) methodology [516, 517, 518, 519, 520, 521] has been implemented in ORCA. The strength of the MR-EOM-CC methodology lies in its ability to calculate many excited states from a single state-averaged CASSCF solution, for which only a single set of amplitudes needs to be solved and the final transformed Hamiltonian is diagonalized over a small manifold of excited states only through an uncontracted MRCI problem. Hence, a given MR-EOM-CC calculation involves three steps, performed by three separate modules in ORCA :

1. a state-averaged CASSCF calculation (CASSCF module),
2. the solution of amplitude equations and the calculation of the elements of the similarity transformed Hamiltonians (MDCI module),
3. and the uncontracted MRCI diagonalization of the final similarity transformed Hamiltonian (MRCI module).

The current implementation allows for MR-EOM-TIT[†]-h-v, MR-EOM-TIT[†]ISXD-h-v and MR-EOM-TIT[†]ISXD|U-h-v calculations. A more detailed description of these methods and the available input parameters will be given in Sec. Section 3.20.4. We also note that the theoretical details underlying these methods can be found in Ref. [521]. In Sec. Section 3.20.4, we will discuss a strategy for the selection of the state-averaged CAS and other steps for setting up an MR-EOM-CC calculation in more detail. Furthermore, we will discuss how spin-orbit coupling effects can be included in MR-EOM-CC calculations, a projection scheme to aid with convergence difficulties in the iteration of the T amplitude equations, an orbital selection scheme to reduce the size of the inactive core and virtual subspaces in the calculation of excitation energies and a strategy for obtaining nearly size-consistent results in MR-EOM-CC. The purpose of this section is simply to provide a simple example which illustrates the most basic usage of the MR-EOM-CC implementation in ORCA.

3.20.1 A Simple MR-EOM-CC Calculation

Let us consider an MR-EOM-T \ddagger |SXD|U-h-v calculation on formaldehyde. An MR-EOM-T \ddagger |SXD|U-h-v calculation is specified via the MR-EOM keyword along with the specification of a state-averaged CASSCF calculation (i.e. CASSCF(nel, norb) calculation with the number of roots of each multiplicity to be included in the state-averaging for the reference state) and the number of desired roots in each multiplicity block for the final MRCI diagonalization. We note that the CASSCF module is described in section [Section 3.13](#) and that a description of the MRCI module is given in section [Section 3.19](#). Here, we have a state-averaged CAS(6,4) calculation, comprised of 3 singlets and 3 triplets and we request 6 singlet roots and 6 triplet roots in our final MRCI diagonalization (i.e. the roots to be computed in the MR-EOM-T \ddagger |SXD|U-h-v calculation):

```
!MR-EOM def2-TZVP VeryTightSCF

%casscf # reference state
  nel 6
  norb 4
  mult 1,3
  nroots 3,3
end

%mdci
  STol 1e-7
end

%mrcki # final roots
  newblock 1 *
    nroots 6
    refs cas(6,4) end
  end
  newblock 3 *
    nroots 6
    refs cas(6,4) end
  end
end

* xyz 0 1
H      0.000000      0.934473     -0.588078
H      0.000000     -0.934473     -0.588078
C      0.000000      0.000000      0.000000
O      0.000000      0.000000      1.221104
*
```

One can alternatively perform an MR-EOM-T \ddagger -h-v or MR-EOM-T \ddagger |SXD-h-v calculation by replacing the MR-EOM keyword, in the first line of the input above, by MR-EOM-T|Td or MR-EOM-T|Td|SXD, respectively. Namely, replacing the first line of the input above with

```
!MR-EOM-T|Td def2-TZVP VeryTightSCF
```

runs the MR-EOM-T \ddagger -h-v calculation, while

```
!MR-EOM-T|Td|SXD def2-TZVP VeryTightSCF
```

runs the MR-EOM-T \ddagger |SXD-h-v calculation.

The final MRCI diagonalization manifold includes 2h1p, 1h1p, 2h, 1h and 1p excitations in MR-EOM-T \ddagger -h-v calculations, 2h, 1p and 1h excitations in MR-EOM-T \ddagger |SXD-h-v calculations and 1h and 1p excitations in MR-EOM-T \ddagger |SXD|U-h-v calculations. Note that in the %mdci block, we have set the convergence tolerance (STol) for the residual equations for the amplitudes to 10^{-7} , as this default value is overwritten with the usage of the TightSCF, VeryTightSCF, etc. keywords. It is always important to inspect the values of the largest T , S (here, we use S to denote the entire set of S , X and D amplitudes) and U amplitudes. If there are amplitudes that are large (absolute values > 0.15), the calculated results should be regarded with suspicion. For the above calculation, we obtain:

LARGEST T AMPLITUDES

8-> 13	8-> 13	0.060331
4-> 17	4-> 17	0.029905
8-> 9	8-> 9	0.028160
8-> 16	8-> 16	0.027266
6-> 20	6-> 20	0.025885
8-> 21	8-> 21	0.025308
4-> 16	4-> 16	0.024803
8-> 12	8-> 12	0.023915
5-> 18	5-> 18	0.023553
8-> 23	8-> 23	0.023384
3-> 16	3-> 16	0.023182
7-> 19	7-> 19	0.023043
8-> 13	4-> 11	0.022010
3-> 19	3-> 19	0.021987
8-> 16	8-> 9	0.021230
8-> 9	8-> 16	0.021230

for the T amplitudes,

LARGEST S AMPLITUDES

4-> 8	8-> 11	0.074048
3-> 8	8-> 9	0.064886
4-> 5	5-> 11	0.045479
3-> 8	8-> 16	0.042657
4-> 7	7-> 11	0.042598
4-> 5	5-> 17	0.042076
4-> 5	8-> 11	0.039958
4-> 8	8-> 17	0.037532
3-> 5	8-> 9	0.035907
4-> 7	7-> 17	0.035767
2-> 6	6-> 19	0.034148
3-> 5	5-> 10	0.033339
2-> 6	6-> 10	0.032691
4-> 6	6-> 11	0.032181
8-> 8	3-> 16	0.031775
2-> 7	7-> 22	0.031238

for the S amplitudes, and

LARGEST U AMPLITUDES

3-> 8	3-> 8	0.026128
3-> 8	3-> 5	0.007683
2-> 8	2-> 8	0.006182
3-> 8	2-> 5	0.006154
2-> 8	3-> 5	0.004954
3-> 5	3-> 5	0.004677
4-> 8	4-> 8	0.003989
3-> 8	2-> 8	0.002040
2-> 8	3-> 8	0.002040
2-> 8	2-> 5	0.001818
4-> 8	4-> 5	0.001173
2-> 5	2-> 5	0.001107
4-> 5	4-> 5	0.000714
3-> 7	3-> 7	0.000607
3-> 6	3-> 6	0.000521

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```
2-> 5 3-> 5 0.000365
```

for the U amplitudes. Hence, one can see that there are no unusually large amplitudes for this calculation. **We note that there can be convergence issues with the T amplitude iterations and that in such cases, the flag:**

```
DoSingularPT true
```

should be added to the %mdci block. The convergence issues are caused by the presence of nearly singular T_2 amplitudes and setting the DoSingularPT flag to true activates a procedure which projects out the offending amplitudes (in each iteration) and replaces them by suitable perturbative amplitudes. For more information, see the examples in section [Section 3.20.4](#).

After the computation of the amplitudes and the elements of the similarity transformed Hamiltonians, within the MDCI module, the calculation enters the MRCI module. For a complete, step by step description of the output of an MRCI calculation, we refer the reader to the example described in section [Section 3.19.4](#). Let us first focus on the results for the singlet states (CI-BLOCK 1). Following the convergence of the Davidson diagonalization (default) or DIIS procedure, the following results of the MRCI calculation for the singlet states are printed:

```
-----
CI-RESULTS
-----
```

```
The threshold for printing is 0.30 percent
```

```
The weights of configurations will be printed. The weights are summed over
all CSFs that belong to a given configuration before printing
```

```
STATE 0: Energy= -114.321368425 Eh RefWeight= 0.9781 0.00 eV 0.0 cm**-1
0.0137 : h---h---[0222]
0.0756 : h---h---[1221]
0.8879 : h---h---[2220]
STATE 1: Energy= -114.176866027 Eh RefWeight= 0.9765 3.93 eV 31714.6 cm**-1
0.0039 : h---h---[1122]
0.9726 : h---h---[2121]
0.0071 : h---h 4[1222]
0.0085 : h---h 4[2221]
STATE 2: Energy= -113.988050555 Eh RefWeight= 0.9774 9.07 eV 73154.8 cm**-1
0.0044 : h---h---[1212]
0.9730 : h---h---[2211]
0.0063 : h---h 3[1222]
0.0041 : h---h 3[2221]
STATE 3: Energy= -113.963862283 Eh RefWeight= 0.8810 9.73 eV 78463.5 cm**-1
0.7459 : h---h---[1221]
0.0807 : h---h---[2022]
0.0533 : h---h---[2220]
0.0228 : h---h 4[2122]
0.0034 : h---h---[1220]p13
0.0072 : h---h---[1220]p18
0.0236 : h---h---[2120]p11
0.0148 : h---h---[2120]p14
0.0069 : h---h---[2120]p17
0.0056 : h---h---[2120]p20
0.0098 : h---h---[2210]p19
STATE 4: Energy= -113.931144468 Eh RefWeight= 0.0003 10.62 eV 85644.3 cm**-1
0.0045 : h---h---[0122]p9
0.0089 : h---h---[1121]p9
0.9333 : h---h---[2120]p9
0.0243 : h---h---[2120]p10
0.0080 : h---h---[2120]p12
0.0113 : h---h---[2120]p16
STATE 5: Energy= -113.929056780 Eh RefWeight= 0.6857 10.68 eV 86102.5 cm**-1
0.0061 : h---h---[0222]
```

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```

0.0918 : h---h---[1221]
0.5784 : h---h---[2022]
0.0048 : h---h---[2202]
0.0047 : h---h---[2220]
0.2905 : h---h 4[2122]
0.0045 : h---h---[2021]p13

```

For each state, the total energy is given in E_h ; the weight of the reference configurations (RefWeight) in the given state is provided, and the energy differences from the lowest lying state are given in eV and cm^{-1} . Also, in each case, the weights and a description of the configurations which contribute most strongly to the given state are also provided. See section [Section 3.19.4](#) for a discussion of the notation that is used for the description of the various configurations. To avoid confusion, we note that in the literature concerning the MR-EOM methodology [517, 518, 519, 520, 521, 522, 523], the term “%active” is used to denote the reference weight multiplied by 100%. In general, RefWeight should be > 0.9 , such that the states are dominated by reference space configurations. This criterion is satisfied for the first three states and the reference weight of the fourth state is sufficiently close to 0.9. **However, the reference weights of the two higher lying states (especially state 4) are too small and these states should be discarded as the resulting energies will be inaccurate (i.e. states with significant contributions from configurations outside the reference space cannot be treated accurately) .**

In the case of the triplet states (CI-BLOCK 2), we obtain the following results:

```

-----
CI-RESULTS
-----

```

The threshold for printing is 0.30 percent

The weights of configurations will be printed. The weights are summed over all CSFs that belong to a given configuration before printing

```

STATE 0: Energy= -114.190840989 Eh RefWeight= 0.9693 0.00 eV 0.0 cm**-1
0.9691 : h---h---[2121]
0.0079 : h---h 4[1222]
0.0115 : h---h 4[2221]
STATE 1: Energy= -114.106733017 Eh RefWeight= 0.9941 2.29 eV 18459.6 cm**-1
0.9941 : h---h---[1221]
STATE 2: Energy= -114.015150051 Eh RefWeight= 0.9787 4.78 eV 38559.7 cm**-1
0.9786 : h---h---[2211]
0.0050 : h---h 3[1222]
STATE 3: Energy= -113.939299674 Eh RefWeight= 0.0006 6.84 eV 55206.9 cm**-1
0.0044 : h---h---[0122]p9
0.0084 : h---h---[1121]p9
0.9419 : h---h---[2120]p9
0.0131 : h---h---[2120]p10
0.0043 : h---h---[2120]p12
0.0173 : h---h---[2120]p16
STATE 4: Energy= -113.925571130 Eh RefWeight= 0.4017 7.22 eV 58220.0 cm**-1
0.3863 : h---h---[1122]
0.0154 : h---h---[2121]
0.1722 : h---h 4[1222]
0.4098 : h---h 4[2221]
0.0045 : h---h---[2120]p13
STATE 5: Energy= -113.910479339 Eh RefWeight= 0.0009 7.63 eV 61532.3 cm**-1
0.0088 : h---h---[0122]p10
0.0030 : h---h---[1121]p10
0.0120 : h---h---[2120]p9
0.9408 : h---h---[2120]p10
0.0106 : h---h---[2120]p16
0.0112 : h---h---[2120]p19

```

Here, we see that the first three states have reference weights which are > 0.9 , while the reference weights of the final three states are well below that threshold. Hence, the latter three states should be discarded from any meaningful

analysis.

Following the printing of the CI results for the final CI block, the states are ordered according to increasing energy and the vertical transition energies are printed:

----- TRANSITION ENERGIES -----

The lowest energy is -114.321368425 Eh

State	Mult	Irrep	Root	Block	mEh	eV	1/cm
0	1	-1	0	0	0.000	0.000	0.0
1	3	-1	0	1	130.527	3.552	28647.5
2	1	-1	1	0	144.502	3.932	31714.6
3	3	-1	1	1	214.635	5.841	47107.0
4	3	-1	2	1	306.218	8.333	67207.2
5	1	-1	2	0	333.318	9.070	73154.8
6	1	-1	3	0	357.506	9.728	78463.5
7	3	-1	3	1	382.069	10.397	83854.4
8	1	-1	4	0	390.224	10.619	85644.3
9	1	-1	5	0	392.312	10.675	86102.5
10	3	-1	4	1	395.797	10.770	86867.5
11	3	-1	5	1	410.889	11.181	90179.7

Furthermore, following the generation of the (approximate) densities, the absorption and CD spectra are printed:

===== MR-EOM-CC Non Relativistic Properties =====

----- ->----- ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS -----

Transition		Energy	Energy	Wavelength	fosc(D2)	D2	DX	
DY	DZ	(eV)	(cm-1)	(nm)		(au**2)	(au)	
(au)	(au)							
0-1A -> 1-1A		3.932110	31714.6	315.3	0.000000000	0.00000	-0.00000	-
0.00000	0.00000							
0-1A -> 2-1A		9.070040	73154.8	136.7	0.002137450	0.00962	0.09808	-
0.00000	-0.00000							
0-1A -> 3-1A		9.728237	78463.5	127.4	0.157495738	0.66081	-0.00000	-
0.00000	-0.81290							
0-1A -> 4-1A		10.618534	85644.3	116.8	0.025353906	0.09746	-0.00000	-
0.31218	-0.00000							
0-1A -> 5-1A		10.675343	86102.5	116.1	0.024673667	0.09434	-0.00000	-
0.00000	0.30715							

----- ->----- CD SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS -----

Transition		Energy	Energy	Wavelength	R	MX	MY	
MZ		(eV)	(cm-1)	(nm)	(1e40*cgs)	(au)	(au)	
(au)								

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