

# *Jump-Start Guide*

**ORCA 4.1**

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# The ORCA Quantum Chemistry Suite

## Jump-Start Guide

This document is intended to provide a “jump start” to the use of ORCA. It is not intended to replace the manual. There are many more options and features in the program that can be controlled by the user.

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## 1 General

1. Make sure ORCA is visible in the system in your \$PATH variable
2. Provide an ASCII input file, e.g. MyJob.inp
3. Run `orca MyJob.inp >& MyJob.out &`. This produces at least MyJob.out and MyJob.gbw. The latter contains a binary summary of geometry, basis sets and orbitals. It is necessary for restarting jobs or using one job as input for another job

## 2 Input File

The input file has the general structure:

```
# comments - write whatever you want
! Keywords          (control methods, basis sets, job type,...)
! moread            (optional: start from existing orbitals; also
                    requires %moinp, see next line)
%moinp "MyInp.gbw"  (optional: Input MOs to start from)
%maxcore 4096       (optional: scratch array size in MB)
%base "MyBaseName"  (optional: name of the generated scratch files)
* xyz Charge Mult   (required: coordinate type, charge, multiplicity)
C 1.23  16.481 -9.87 (Cartesian coordinates Angström or Bohr)
*                  (end of coordinate input)
$new_job
(now you can add another job - as many as you want)
```

Keywords can be given in any order, do not need to be on one line and they are not case sensitive. The input molecular orbitals do not need to be in the same basis set as the calculation to be performed and /or do not need to be calculated at the same geometry as given in the input file (but the atom types and their sequence must match).

## 3 Coordinates

```
! Angs or Bohrs      (optional: coordinate type, default = Angström)

* xyz charge multiplicity
C 0.0 0.0 0.0         (Cartesian coordinates for this atom)
O 0.0 0.0 1.128
*
```

or

```
* int charge multiplicity
AT NA NB NC  R A D    (AT= atom type H,C,N,O,...)
                      (NA= atom for distance NA-NB)
                      (NB= atom for angle- this atom-NA-NB)
                      (NC= dihedral angle- this atom-NA-NB-NC)
                      (R = actual distance (Angström or Bohr)
                      (A = Angle in degrees)
                      (D = dihedral angle in degree)
```

\*

or

```
*xyzfile charge multiplicity myCoordinateFile.xyz
```

charge is the total charge of the molecule and multiplicity is the spin multiplicity ( $=2S+1$  where  $S$  is the total spin of the desired state. NOTE – for non-closed shell systems, typically spin-unrestricted calculations are performed. These do NOT conserve the actual multiplicity. One obtains an eigenfunction of the z-component of the total spin operator, not of  $S^2$ !).<sup>1</sup>

You can also input and run a series of structures from “multiple XYZ” files (see manual).

## 4 Basis Sets

### **! BasisSet**

```
BasisSet= def2-SVP, def2-TZVP, def2-TZVPP, def2-QZVPP,  
          ma-def2-SVP, ma-def2-TZVP, ma-def2-TZVPP, ma-def2-QZVPP,  
          cc-pVnZ, aug-cc-pVnZ, cc-pCVnZ, aug-cc-pCVnZ (n= D,T,Q,5,6)
```

We recommend the ‘def2’ basis sets of the Karlsruhe group for most HF/DFT calculations.

By default, basis sets make use of ECPs. The def2 basis sets automatically load Stuttgart-Dresden effective core potentials for elements Rb-Rn.

Many other and specialized basis sets are documented in the manual. Basis sets can also be read from a file or manually input or they can be printed using (`! PrintBasis`) and modified basis sets can be input into the program using:

```
%basis      GTOName "MyGTObasis.bas" end
```

The format of the basis set input file is essentially that from the EMSL library for Gamess-US. ORCA will accept basis sets that are not normalized and will normalize them. Normalized basis sets are printed by ORCA using the `! PrintBasis` keyword. Individual basis sets for specific atoms or atom types can also be given in the input as described in the manual.

## 5 Auxiliary Basis sets

Methods that make use of the “RI” (‘resolution of the identity’ or density fitting) approximation require an auxiliary basis set. For example, pure DFT calculations are done by default in the RI mode. For this an auxiliary basis set is necessary.

### **! AuxBasisSet**

```
AuxBasisSet=def2/J, SARC/J
```

For Coulomb fitting in RI-DFT (GGA, meta-GGA functional). SARC/J is for scalar relativistic all electron calculations.

```
AuxBasisSet= def2-SVP/C, def2-TZVP/C, def2-TZVPP/C, def2-QZVPP/C, cc-pVnZ/C,  
aug-cc-pVnZ/C (n=D,T,Q,5,6)
```

For Correlation fitting (MP2 and Coupled Cluster)

---

<sup>1</sup> If you want to have a spin-eigenfunction for an open-shell system, you can resort to open-shell spin restricted calculations (for DFT only available for all unpaired spins aligned in parallel), or you proceed to a multiconfigurational wavefunction such as CASSCF.

AuxBasisSet= def2/JK, cc-pVnZ/JK, aug-cc-pVnZ/JK (n=T,Q,5)

For Coulomb and exchange fitting (HF and hybrid DFT)

If you do fitting for both, the SCF and a correlation calculation, you can provide two auxiliary basis sets.

### **! AutoAux**

Automatic construction of a general-purpose auxiliary basis for simultaneously fitting Coulomb, exchange and correlation calculations. This will be accurate, but will be larger than the optimized auxiliary basis sets. Safe choice in case of doubt or non-standard orbital bases.

## **6 Density Functionals**

### **! Functional GridN NoFinalGrid VDW**

Functional=

LDA : LSD, HFS, ...

GGA : BP=BP86, PBE, PW91, OLYP, OPBE, BLYP, PWP, ...

Note: LDAs/GGAs in RI mode require an auxiliary basis set ('J')

Meta-GGA : TPSS, revTPSS, M06L, ...

Hybrid : B3LYP, PBE0, X3LYP, BHandHLYP, B3P, B3PW, ...

Range-Sep. Hyb. : wB97, wB97X, CAM-B3LYP, LC-BLYP

Hybrid Meta-GGA : TPSSh, TPSS0, M06, M062X, ...

Double-Hybrid : RI-B2PLYP, RI-MPW2PLYP, RI-B2T-PYLP, RI-B2K-PYLP,  
RI-B2GP-PLYP

All also available without RI approximation. Double hybrids in RI mode require an auxiliary basis set ('C')

There are many more functionals documented in the manual.

GridN= Grid1, Grid2, ..., Grid7

NoFinalGrid= Do not use a larger grid for the final energy, alternatively use  
FinalGridN (N = 0-7)

The default is to use a combination of Grid2 (110 angular points) and Grid4 (302 angular points)

VDW=

D3BJ Grimme's atom-pairwise dispersion correction with Becke Johnson  
damping (recommended)

D3Zero atom-pairwise dispersion correction with zero damping

D2 Grimme's dispersion correction from 2006

## 7 Composite Methods for Optimization

**! HF-3c, PBEh-3c, B97-3c**

These are low-cost, composite methods from the Grimme group that are designed for optimization using a small basis, and corrections for dispersion, BSSE and basis set incompleteness.

## 8 Self-Consistent Field Calculations

**! SCF-Keywords**

```
SCF-Keywords=  SP                (Single point calculation)

                NormalSCF        (Normal SCF convergence criteria)
                TightSCF         (Tight SCF convergence criteria)
                VeryTightSCF     (Very Tight SCF convergence criteria)

                SlowConv          (Slow convergence expected)
                LShift            (Turn on level shifting)
                SOSCF             (Turn on approx. second order SCF)
                NRSCF             (Turn on Newton-Raphson SCF)
                DIIS              (Turn on DIIS)
                Direct            (Integral direct mode)
                Conv              (Integral conventional mode)

                RHF               (closed shell calculation)
                UHF               (spin unrestricted calculation)
                ROHF              (restricted open shell calculation; more
                                Input may be required)
```

The default is a combination of DIIS and SOSCF, unless transition metals are involved. The default is to run singlets closed shell and higher multiplicities spin unrestricted. The combination KDIIS SOSCF is often a good choice for rapid convergence but may not be as robust as the default for electronically difficult species.

### Powerful approximations

**! RI**

For non-hybrid DFT (automatically invoked. Turn Off=NoRI)

**! RIJCOSX**

Efficient approximation to HF and hybrid DFT. Does the Coulomb Term with RI and the exchange by seminumerical integration

Requires an auxiliary basis set ('/J') and an X-Grid for the seminumerical approximation to the exact exchange

GridXN = N = 1-9 (e.g. GridX6) Grids for the COSX approximation.

**! RI-JK**

Fully RI based treatment of Coulomb and exchange

Requires an auxiliary basis set ('/JK'). Will not scale well with system size!

## 9 Complete Active Space Self-Consistent Field Calculations

CASSCF calculations are not for the faint-hearted! They always require the user to look carefully at the orbitals and frequently require some manual adjustments to achieve self-consistent field convergence. Since the matter is complex, we have prepared a CASSCF tutorial in a separate document that walks the user through some typical calculations. The manual also provides a list of additional information

On the most elementary level, just use:

```
%casscf nel n      (number of electrons in the active space)
        norb m      (number of orbitals in the active space)
        nroots N    (number of states averaged over)
        nevpt2 true (calculate a second order correction for the
end                                dynamical correlation energy - easy!)
```

## 10 Solvation

**! CPCM(Solvent) or CPCM**

CPCM alone uses an infinite dielectric

Solvent = Water, Acetonitrile, Acetone, Ammonia, Ethanol, Methanol, CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, DMF, DMSO, Pyridine, THF, Chloroform, Hexane, Toluene

**!CPCM**

```
%cpcm smd true    # default false
        solvent "Name"
end
```

For the SMD solvation model there are at present 179 solvents in the library. If required, the user can manually specify the descriptors. For more information see manual.

## 11 Møller-Plesset Perturbation Theory

**! MP2, SCS-MP2, F12-MP2, RI-MP2, RI-SCS-MP2, F12-RI-MP2, DLPNO-MP2, F12-DLPNO-MP2, OO-RI-MP2, OO-RI-SCS-MP2, MP3, RI-MP3, SCS-MP3, RI-SCS-MP3**

```
%maxcore 2048    # higher maxcore required
```

RI methods require an auxiliary correlation fitting basis set ('C'). Additionally, the RIJCOSX or RI-JK methods can be used to accelerate the SCF calculation. A corresponding auxiliary basis set is required. Analytic gradients and Hessians are available for MP2 and RI-MP2.

## 12 Coupled Cluster Calculations

**! CC-Variant Extrapolate(n/m,bas)**

Extrapolate allows you to automatically extrapolate the result to the basis set limit using standard basis sets.

```
%maxcore 2048    # higher maxcore required
```

```
CC-Variant=CCSD, CCSD(T), QCISD, QCISD(T)
```



CCSD-F12, CCSD(T)-F12, QCISD-F12, QCISD(T)-F12

F12 methods require F12-specific basis sets ('F12' and 'F12/CABS')

CCSD-F12/RI, CCSD(T)-F12/RI, QCISD-F12/RI, QCISD(T)-F12/RI

Besides the F12-specific basis sets a regular auxiliary basis ('/C') must be provided. It is recommended to step one level up compared to the F12-basis (e.g. ! cc-pVDZ-F12 cc-pVDZ-F12-CABS cc-pVTZ/C)

CPF/1, NCPF/1, CEPA/1, NCEPA/1

DLPNO-CCSD, DLPNO-CCSD(T), DLPNO-QCISD, DLPNO-QCISD(T)

Local correlation methods. For DLPNO calculations an auxiliary basis ('/C') must be provided

Extrapolate(n/m,bas)=

n/m: cardinal number combinations, n,m = 2-5; n < m

Extrapolation of SCF and CC-Variant energies to the basis set limit. More extrapolation methods are described in the manual.

bas: cc, aug-cc, cc-core, ano, saug-ano, aug-ano, def2

Coupled cluster densities are available for closed and open shell systems (also in the DLPNO case), but coupled cluster gradients and Hessians are not available.

## 13 Relativity

**! RelMethod BasisSet AuxBasisSet**

RelMethod= ZORA, DKH, DKH2, ZORA/RI

BasisSet = ZORA-def2-XVP, DKH-def2-XVP, ma-ZORA-def2-XVP, ma-DKH-def2-XVP  
(where XVP stands for the whole range of def2 basis sets)

Adapted versions of the def2 basis sets. For elements H-Kr.

SARC-DKH-TZVPP, SARC-ZORA-TZVPP

For use with DKH2 and ZORA. For elements beyond Xe.

AuxBasisSet= SARC/J

More available basis sets are described in the manual. Spin-orbit coupling is treated by quasi-degenerate perturbation or linear-response theory in a variety of modules. What ORCA does not do are two- or four-component calculations with relativistic spinors (we simply don't like these methods).

## 14 Geometry Optimization

**! OptMethod TightOpt**

TightOpt= increases convergence criteria; default NormalOpt

OptMethod=	Opt	Standard optimization in redundant internals
	Copt	Optimization in Cartesian coordinates
	OptTS	Transition State optimization
	ScanTS	relaxed surface scan followed by automated TS opt

Many other options for constraint optimization, surface scans, minimum energy crossing point optimization, QM/MM optimizations etc. are documented in the manual.

## 15 Frequency Calculations

**! Freq**

Performs an analytic frequency calculation.

**! NumFreq**

Performs a numerical frequency calculation.

## 16 Parallel Runs

**! palN**

N= 2 - 8, 16, or use

**%pal nprocs N end** # N=any integer

Performs a parallel ORCA run using N cores. Installation of openmpi is required. PATH and LD\_LIBRARY\_PATH variables need to be set for openmpi.

## 17 Excited State Calculations

A number of ORCA modules calculate excited states. They all are capable of generating absorption and CD spectra at the various levels of theory. Only TD-DFT/CIS features analytic gradients.

### 17.1 Time dependent Density Functional Theory

```
%tddft NRoots 10      (number of roots to determine)
      MaxDim 100      (max. size of the expansion space)
      TDA true        (Tamm-Dancoff approximation used or not)
      Triplets true    (calc. triplets for closed shell references?)
      end
```

Note that this input is also valid to do CIS or RPA calculations in the Hartree-Fock framework. Many other options to speed up TD-DFT calculations, (D) corrections, analytic gradients and other topics are discussed in the manual. The module works together with RIJCOSX but not with RI-JK (but there are RI-JK like options).

### 17.2 Equation of Motion Coupled Cluster Theory

**! EOM-CCSD**

or

**%mdci doeom true end**

and the number of roots must be specified as well under

```
%mdci  NRoots 10          (number of roots to determine)
      NDav 20            (defines max. size of the exp. space as NDav*NRoots)
      DoRootwise true    (solve one root at a time, often more stable)
      CCSD2              (EOM with MP2 amplitudes, for RHF reference only)
      FollowCIS true     (follow CIS roots instead of energetic ordering)
      DoTDM true         (request transition properties)
end
```

along with other options. The EOM module is also capable of computing ionization energies, and it can handle RHF and UHF reference functions, the latter being more expensive. With a UHF reference, DOMO to virtual excitations must be handled with care since they are strongly spin contaminated. The COSX approximation is also available for certain terms, as described in the manual. Unlike in TDDFT, the transition properties require additional work, although a cheap approximation is printed at the end of the calculation.

For a cheaper but accurate option for computing excitation energies, the similarity transformed version of EOM (STEOM) can be invoked as

**! STEOM-CCSD**

or

```
%mdci dosteom true end
```

The keywords **NRoots**, **NDav** and **DoRootwise** function similarly as in the EOM case. A few of the STEOM specific keywords include

```
%mdci  DoTriplet true    (calculate triplet excited states)
      OThresh 0.001      (CIS cutoff for the occupied block)
      VThresh 0.001      (CIS cutoff for the virtual block)
end
```

The triplet option is only available for closed shell calculations. STEOM requires the selection of an active space to define the similarity transformation. While this is done automatically, the parameters can also be manually set, among them the most important ones are the occupied and virtual space CIS cutoff parameters described above. For closed shell calculations, both EOM and STEOM can be carried out in conjunction with DLPNO-CCSD calculations for the ground state, which are then back-transformed into the canonical basis, see the bt-PNO options in the manual.

### 17.3 Restricted open shell CIS (ROCIS) and ROCIS/DFT

```
%rocis NRoots 10          (number of roots to determine)
      MaxDim 100          (max. size of the expansion space)
end
```

Performs CIS calculations on top of a RHF or a high-spin ROHF reference function

**! B3LYP/BHLYP**

```
%rocis NRoots 10          (number of roots to determine)
      MaxDim 100          (max. size of the expansion space)
      DoDFTCIS true       (request the ROCIS/DFT calculation)
      DFTCIS_c = 0.20, 0.40, 0.30 (parameters for B3LYP functional)
end
```

Performs a ROCIS/DFT calculation.

In addition it is possible to treat relativistic effects or request spin-orbit coupling (SOC) treatment in the framework of the quasi-degenerate perturbation theory (QDPT). Many other options are available to speed-up the ROCIS calculations and to control the calculation output. Other topics are discussed in the manual.

### 17.4 N-Electron Valence Perturbation Theory (NEVPT2)

Strongly Contracted and Fully Internally Contracted NEVPT2 can easily be set up on top of any working CASSCF input adding the simple input keywords.

```
!NEVPT2, RI-NEVPT2           (strongly contracted)
!FIC-NEVPT2, DLPNO-NEVPT2   (fully internally contracted)
```

Refined settings (e.g. F12 correction, RI Approximation) are set in the %CASSCF block and the NEVPT sub-block – see the manual for details. A number of properties and spectra are accessible with NEVPT2. The CASSCF tutorial (downloadable from our website) covers many examples on the subject.

Note that the RI approximation is available for SC- and FIC-NEVPT2. The RI and DLPNO versions require auxiliary basis sets (/C or /JK) for the integral transformation. The approaches can be combined with **!RIJK** and **!RIJCOSX** for additional speed-up.

### 17.5 Multireference Configuration Interaction (MRCI)

A traditional (uncontracted) MRCI with a plethora of truncation options resides in the orca\_mrci module and allows the computation of various spectra and properties (SOC, SSC, MCD, g-Tensor, D-Tensor,...). Examples can be found in the CASSCF tutorial (downloadable from our website) and the manual. The minimal input requires a set of orbitals and a multiplicity block:

```
!MORead Allowrhf NoIter (reading arbitrary orbitals e.g. from CASSCF,HF)
%moinp "start.gbw"

%mrcki
  citype MRCI           (MRCI, SORCI, MRDDCI3, MRDDCI2, MRDDCI1,...)
  newblock M *          (multiplicity block, * can be replaced by IRREP)
    ref CAS(n,m) end    (reference WF, can also be RAS or a list of CFGs)
    NRoots N            (number of roots in the multiplicity/IRREP block)
  end
end
```

ORCA also features a fully internally contracted MRCI, which is implemented in the orca\_autoci module. The input mimics a standard CASSCF input mask. The reference wavefunction is restricted of the CAS-CI type.

```
!MORead CASSCF NoIter   (reading CASSCF orbitals)
%moinp "start.gbw"

%autoci
  citype FICMRCI        (FICMRCI, FICDDCI3, FICMRCEPA0)
  nel n                 (number of active electrons)
  norb m                (number of active orbitals)
  Mult M                (multiplicity)
  NRoots N              (number of roots in the multiplicity)
end
```

The contracted and uncontracted MRCI approaches can be combined with the RI approximation. In general, MRCI calculations are very resource demanding and thus should be carefully designed.

## 18 Spectroscopic and other Properties

### 18.1 Electric Moments and Polarizabilities

```
%elprop dipole true      (compute the dipole moment)
      quadrupole true    (compute the quadrupole moment)
      polar 1            (compute the polarizability using analytical
end                      derivatives)
```

This input block will yield the dipole moment vector (in a.u. and Debye) including some informations about rotational parameters, the quadrupole moment (as full tensor and diagonalized) and run a CP-SCF calculation to obtain the polarizability tensor (raw Cartesian and diagonalized). Note that the analytical derivative for the polarizability is only available at the HF and DFT level of theory. For other methods, the polarizability can be computed as finite differences.

```
%elprop polar 3          (compute the polarizability using fully numerical
      efield 1e-5         derivatives, efield is used in the finite difference
end                      scheme and should be experimented with)
```

For this purpose - like for all numerical derivative schemes – very tight SCF criteria (**VeryTightSCF**) are highly recommended. Polarizabilities with methods, for which analytical dipole moments are implemented (like MP2), a mixed analytical / numerical scheme is available. Use the same input as above but specify **polar 3** instead.

### 18.2 NMR Parameters

**! NMR**

Nuclear magnetic resonance chemical shielding constants are available for HF and DFT (excluding range-separated hybrid functionals) levels of theory, as well as for RI-MP2 and double-hybrid DFT functionals (with RI). TPSS and M06L are usually a good choice. Implicit solvation (CPCM) is also supported. It is recommended to use the pcSseg-*n* basis sets in combination with the def2/JK fitting basis (even for non-hybrid functionals). For RIJCOSX a larger grid should be used, e.g.

**! GridX6 NoFinalGridX**

```
%epnrmr GIAO_2el GIAO_2el_RIJCOSX end (also use RIJCOSX for GIAO integrals
                                         GIAO_2el_RIJK is default)
```

Remember to run the calculation on the reference molecule (e.g. TMS) with the same method and basis set. The chemical shift is then calculated as  $\delta_{\text{mol}} = \sigma_{\text{ref}} - \sigma_{\text{mol}}$ . Many more options are available and described in the manual

Indirect nuclear spin-spin coupling (*J*-coupling) constants are also available for HF and DFT:

```
%epnrmr Nuclei = all H {ssall, ist = 1 } (calculate J for all H nuclei
                                         assuming they are all 1H)

      SpinSpinRThresh 6.0 (couple nuclei up to 6 Angstroms apart)
end
```

### 18.3 EPR Parameters

The calculations of the EPR parameters (*g*-tensor, D-tensor, hyperfine coupling constant (HFC) etc.) can be calculated at HF, DFT and hybrid DFT level of theory. The calculations for these parameters can be invoked with the %eprnmr module in the input file.

```
%eprnmr

#calculation of g-tensors
gtensor 1
#calculation of D-tensor
dtensor so      spin-orbit part
          ss      spin-spin part
          ssandso both parts

#method for spin-orbit and spin-spin part
DSOC      cp      coupled-perturbed method (default)
DSS        uno      use of spin density from UNOs

#choice of gauge-origin
Ori        centerofelcharge      centre of the electric charge (default)
          n                      Number of the atom user defines as the origin
          x,y,z                  Origin of your choice

#method of solving CP-SCF equations
solver     pople      Pople solver (default)
          cg          conjugate gradient

#calculation of the hyperfine coupling constants
Nuclei = all types {FLAGS}

"all types" refers to the atom(s) of interest. For e.g., "all N {FLAGS}"
calculates HFC for all Nitrogen atoms or HFC parameters can also be
calculated for individual atoms of interest, for e.g. "Nuclei = 1, 3, 4
{FLAGS}". IMP NOTE: Counting of atoms starts from 1 in this section!

FLAGS: also (Calculates isotropic part of the hyperfine couplings)
          adip (Calculates dipolar term of the hyperfine coupling)

PrintLevel N      amount of output required by the user, default is 2

end
```

NOTE: The correct choice of DFT functional and basis-set is important when calculating these properties (especially using DFT or hybrid DFT methods), for e.g. hybrid DFT functionals (B3LYP, TPSSh, PBE0) give reliable results. At even higher cost, double hybrids like B2PLYP give even better results. Basis-sets, such as "EPR-II, EPR-III, IGLO-II and IGLO-III" add flexibility in the core region, thus performs well for the organic radicals.

In many instances, the calculation of EPR parameters on the basis of CASSCF/NEVPT2 wavefunctions is more reliable than DFT (in particular for transition metal complexes). For details please see the CASSCF tutorial and main manual.

## 18.4 Mößbauer Parameters

Requested through the EPRNMR module.

```
%epnmr
  nuclei = all Fe {fgrad, rho}      (rho: electron density at Fe nuclei)
                                   (fgrad: electric-field gradients and quadrupole splitting parameters)

  origin CenterOfMass
        CenterOfNucCharge
        CenterOfElCharge (default)
  PrintLevel n                     (controls the amount of output, default 2)
end
```

The use of core property basis CP(PPP) basis for iron is recommended for these calculations and this may be requested via

```
%basis NewGTO Fe CP(PPP) end
```

The output file should contain the following information:

Mößbauer quadrupole splitting parameter (proper coordinate system)  
 $e^{*2}qQ = \text{--- MHz} = \text{--- mm/s}$  (quadrupole splitting)  
 $\eta = \text{---}$  (asymmetry parameter  $0 \leq \eta \leq 1$ )  
 $\Delta E_Q = (1/2 \{e^{*2}qQ\} \sqrt{1 + 1/3 \eta^2}) = \text{--- MHz} = \text{--- mm/s}$   
 $\rho(0) = \text{----- a.u.}^{*-3}$  (electron density at the Fe nucleus)

Calculation of Mößbauer parameters at the DLPNO-CCSD level of theory may be requested via

```
! RHF DLPNO-CCSD (for S=0 systems)
```

```
! UHF/UKS DLPNO-CCSD (for S≠0 systems)
```

and requesting in addition

```
%mdci DenMat UnRelaxed end
```

## 18.5 Vibrational spectra (IR, Raman, resonance Raman, NRVS)

```
! Freq
```

Automatically performs an analytical calculation of the IR spectrum.

```
! NumFreq
```

Automatically performs a numerical calculation of the IR spectrum.

```
%elprop polar 1
end
```

Performs a Raman calculation, including activities and depolarization ratios.

*Raman/Polarizability calculations only work in combination with numfreq!*

For NRVS calculations: run the following utility programs on the hessian file (extension: .hess) after completion of the frequency calculation:

```
orca_vib MyJob.hess > MyJob.vib.out
orca_mapspc MyJob.vib.out NRVS
```

This produces a stick NRVs spectrum **MyJob.vib.out.stk** and a dressed NRVs spectrum **MyJob.vib.out.dat**. These ASCII files can subsequently be imported in any plotting program (e.g. Origin).

*NRVS calculations only work for iron containing systems.*

For Resonance Raman calculations a three-step procedure is required:

1. Optimize molecule and create hessian file

**! Opt Freq**

2. Calculate electronic spectrum, normal mode gradients and dimensionless nuclear displacements

**! NMGrad**

```
%cis nroots 10          (number of roots to determine)
      maxdim 100         (dimension of expansion space, maxdim*roots)
end

%rr
  HessName "mycalc.hess" (name of hessian file from step 1)
  ASAInput true           (create input for step 3)
  Tdnc 0.005             (cutoff threshold for dimensionless nuclear
                        displacements)
  States 1,2,3,4,5,6,7,8,9,10 (list of excited states for which numerical
                        gradients and displacements will be
                        calculated)
end
```

3. Calculate Resonance Raman spectrum

Inspect and analyze the calculated electronic spectrum and determine which calculated bands correspond to the experimentally observed bands. Shifts of up to 100 nm are not uncommon! Modify the newly created file **mycalc.asa.inp** to include the excitation energies in wavenumbers (e.g. 63500, 63800 and 64000  $\text{cm}^{-1}$ ) by adding

**RRSE 63500, 63800, 64000**

The excitation energies have to be chosen in order to mimic experimental excitation into one of the bands of the electronic spectrum. The energies are thus only identical to the energy of the laserlight in cases where perfect agreement between the experimental and calculated electronic spectrum is reached.

Also adjust linewidth parameters of the electronic transitions as well as the linewidth parameter of the Resonance Raman bands in the asa input file to match the experimentally observed linewidths. Then run

**orca\_asa mycalc.asa.inp > mycalc.asa.out**

to obtain files

**mycalc.asa.rrs.63500.stk**  
**mycalc.asa.rrs.63500.dat**

which contain the Resonance Raman spectra as a stick spectrum (.stk) and as a dressed spectrum (.dat).



## 18.6 Optical spectra

Ultraviolet and visible absorption spectroscopy (UV/vis), (electronic) circular dichroism spectroscopy (CD) and magnetic circular dichroism spectroscopy (MCD) are methods to probe electronically excited states of molecules.

ORCA provides a multitude of different methods by which electronically excited states are accessible, most notably TDDFT, CASSCF/NEVPT2, MRCI, ROCIS, as well as EOM-CC and STEOM-CC methods.

Transition dipole moments and rotational strengths (needed respectively for UV/Vis and CD spectra) are automatically printed at the end of every TDDFT, CASSCF, NEVPT2 and MRCI calculation. For EOM-CC and STEOM-CC methods, transition dipole moments are also automatically printed at the end of a calculation, but rotational strengths are currently not available. In ROCIS, transition dipole moments are automatically printed, but rotational strengths have to be explicitly requested by

```
%rocis
    docd true
    doquad true
end
```

MCD results can be generated by CASSCF (including NEVPT2), MRCI and ROCIS modules. The respective parts in the input file are (please refer to the dedicated sections of the different methods for information on other keywords)

```
%casscf
    rel
        dosoc true                (turn on spin-orbit coupling)
        mcd true                  (turn on MCD)
        B 43500                   (static magnetic field in Gauss)
        Temperature 299.0         (the experimental temperature)
    end
end

%mrci
    soc
        dosoc true
        mcd true
        B 43500
        Temperature 299.0
    end
end

%rocis
    soc true
    domcd true
    B 43500
    SOCTemp 299.0
end
```

## 18.7 Absorption Fluorescence and Phosphorescence Lifetimes and Bandshapes

Emission rates and spectra, as well as absorption spectra can be calculated if one has at least a ground state geometry and Hessian. First, optimize the ground state and get its Hessian using

```
! Opt Freq
```

Then call the ORCA\_ESD module using ABS or FLUOR and give the Hessian file name, as

```
! ESD (ABS) or ESD (FLUOR)
```

```
%tddft nroots      10
end
%esd   GS_Hessian "Basename.hess"
       states 1,2,3,4...
end
```

The spectrum will be saved on a Basename.spectrum file and the rates will be printed on the output.

You have to select one excited state method in order to compute the gradient and transition dipoles. ORCA\_ESD is currently optimal for TDDFT, but it also works with ROCIS, (ST)EOM and CASSCF (without analytic gradients).

It is necessary that the geometry on the second input is the same as in the .hess file. It can be obtained from Basename.xyz after optimization or copied from the .hess (in Bohrs then). To include vibronic coupling (Herzberg-Teller effect) in weakly allowed transition, set **DOHT TRUE** under **%ESD**.

If you want a higher quality spectra/rates, set **Hessflag AHAS**, with more methods discussed on the manual.

For phosphorescence, you have to also optimize the triplet using a UHF/UKS method and input both Hessians, as well as the energy difference (in wavenumbers!) between them on each geometry

```
! ESD (PHOSP)
```

```
%tddft      nroots      10
              doSOC      TRUE
end
%esd   GS_Hessian "Basename.hess"
       TS_Hessian "Basename_T.hess"
       delE      20000
states      1
end
```

In this case, you also have to set the flag for including SOC on each module.

OPTIONAL:

Resonant Raman spectra can also be computed by using the same module, the main difference is that you have to set a laser energy, as in

```
! ESD (RR)
```

```
%tddft nroots      10
end
%esd   GS_Hessian "Basename.hess"
       states 1,2,3,4...
       laserE      15000
end
```

## 18.8 X-Ray absorption and emission spectra

ORCA features several approaches to X-ray absorption and emission spectra.

TD-DFT can be used to calculate the pre-edge K-edge X-ray absorption spectra of transition metal complexes.

```
%tddft
  NRoots 80                (number of roots to determine)
  MaxDim 500               (max. size of the expansion space)
  OrbWin[0] = 0,0,-1,-1    (for an RKS reference function choose e.g.
```

```

                                excitations from the 1s orbital (0,0) to the
                                entire (-1,-1) acceptor space)
Doquad true                    (request for Quadrupole and magnetic dipole
                                contributions)
end

```

ROCIS or ROCIS/DFT can also be used to calculate X-ray absorption spectra. In fact these methods are especially designed to treat the metal L/M-edge problems in transition metal complexes.

```

%rocis
NRoots 80
SOC true                      (request for SOC treatment)
DoRI true                     (request for RI treatment)
PrintLevel 3                  (Control the amount of printing)
DoLowerMult true              (Invokes a CI calculation with S'=S-1)
DoHigherMult true             (Invokes a CI calculation with S'=S+1)
OrbWin = 6,8,0,2000           (request for excitations from the 2p orbital
                                (6,8) to an upper limit (default value is 2000)
                                (0,2000) acceptor space)
end

```

This approach can also be used to calculate resonant inelastic X-ray scattering (RIXS) and resonant X-ray emission (RXES) spectra while the X-ray absorption spectra of large molecules can be calculated by employing the PNO version of these methods (core PNO-ROCIS, core PNO-ROCIS/DFT). Further details are described in the manual

CASCI/NEVPT2 can also provide access to X-ray spectra. This is a multistep protocol and requires significant insight from the user. In a nutshell:

- 1) The orbitals from a previous SA-CASSCF valence electron calculation are used as input
- 2) The frozen core treatment is explicitly deactivated
- 3) The core orbitals in request are rotated into the active space
- 4) The CASCI/NEVPT2 problem is then solved in the space of singly core-excited electronic configurations using the previously optimized set of orbitals

```

!MORead

%moinp "MOs.gbw"

%method
    FrozenCore FC_NONE
end

%scf
    rotate {6,39,90} {7,40,90} {8,41,90} end
end

%casscf
    nel 11                    (number of electrons, core + valence)
    norb 8                    (number of orbitals, core + valence)
    mult 6,4                  (requested multiplicities)
    nroots 16,173             (requested roots to be determined for mults 6 and 4)
    nevpt2 true               (request the NRVPT2 calculation)
    maxiter 1                  (number of iterations, need to set to 1 for the
                                CASCI/NEVPT2 calculation)
end

```

This approach can also be used to calculate RIXS and RXES spectra. Further details are provided in the manual.

An alternative and far more simplistic approach to X-ray absorption, and X-ray emission intensities is provided by the one-electron approach based on the DFT orbitals and orbital energies.

#### **! UKS BP86**

```
%xes
      coreorbs 0,0      (range of core orbitals to be treated)
      orbop 0,1        (include spin-up and spin-down MOs)
end
```

This approach can also be used to calculate valence to core resonant X-ray emission spectra (VtC RXES). Further details are provided in the manual.

## **19 Analysis tools and interfaces**

### **19.1 Population analysis**

By default, the Mulliken Population Analysis, Loewdin Population Analysis and Mayer Population Analysis are automatically performed after SCF calculations. To turn off a certain population analysis, use keyword:

#### **! NoMulliken**

Turns off Mulliken population analysis

#### **! NoLoewdin**

Turns off Loewdin population analysis

#### **! NoMayer**

Turns off Mayer population analysis

To turn them on simply type “Mulliken”, “Loewdin” or “Mayer” in the input. Other useful keywords include:

#### **! Allpop**

Turns on all population analysis

#### **! NoPop**

Turns off all population analysis

### **19.2 Local energy decomposition (LED)**

The local energy decomposition is a way to analyze the DLPNO coupled cluster energy in physical terms (such as electrostatic interactions and dispersion energy). All that is required is that the calculation is a DLPNO-CCSD or DLPNO-CCSD(T) calculation and that the atoms are assigned to fragments as in the example below. The LED is requested by:

```

! LED
%mdci printlevel 3
end
* xyz 0 1
O(1) -0.03927172712553 -0.05314132591150 0.08218758558907
H(1) 0.93067536168966 -0.05970332184924 0.07804455467818
H(1) -0.28396499015190 0.88544835339923 0.07926277816645
O(2) -0.90315523402475 -1.18937566538863 2.59796265057253
H(2) -0.64227331879731 -0.83788044760509 1.72189785393425
H(2) -1.47240409159018 -1.94579659264477 2.39478357705952
*

```

Turns on the LED calculation (! LED) and prints additional information (printlevel 3). Each water in the dimer in this example is assigned to an own fragment in the geometry block.

### 19.3 *Ab initio ligand field theory (AILFT)*

The ab initio ligand field (AILFT) analysis can be requested by:

```

%casscf actorbs dorbs or forbs
end

```

This requires that the active orbitals are just the five metal based d-orbitals in case of d-block elements or just the seven f-orbitals in the f-block elements. Making sure that this happens is the user's responsibility. The calculation will automatically spit out the ligand field and Racah parameters that can then be further analyzed manually.

It is recommended to take reference of the "CASSCF-tutorial.pdf" in the ORCA forum.

### 19.4 *Natural Bond Orbital analysis*

**! NPA**

Turns on NPA analysis

**! NBO**

Turns on NBO analysis

In addition to using the HF density, one can use post-HF densities for NBO analysis

**! MP2 NBO**

```

%MP2 density relaxed
end

```

Turns on NBO analysis using the relaxed MP2 density.

The calculation will produce a .47 file for expert users that can be manipulated before running the NBO program standalone.

### 19.5 *Atoms in molecules analysis*

**! AIM**

Generate the .wfn file for topological analysis.

Alternatively one can use orca\_2aim reading a .gbw file to generate the .wfn file.

## 20 Visualization tools and interfaces

### (1) Visualize canonical orbitals:

Step1: Transform the .gbw file to “Molden” format by

```
orca_2mkl "filename" -molden
```

(note: no suffix following the “filename”)

Step2: Read in the generated file by any visualization tool, such as Avogadro.

Other type of orbitals stored in the .gbw format can be visualized in the same way. Just change the suffix to gbw. e.g. change the suffix of a localized orbital file:

```
mv filename.loc filename.gbw
```

### (2) Visualize densities:

Step1: Call the interactive program orca\_plot and follow the instructions.

```
orca_plot filename.gbw -i
```

Step2: Use any visualization tool to read the generated file, such as Chimera.

### (3) Visualize trajectories:

Step1: Perhaps the most convenient way is to use Molden to read the .trj file:

```
Molden filename.trj
```

### (4) Visualize vibrations:

Step1: Perhaps the most convenient way is to use Avogadro to read the output file:

```
Avogadro filename.out
```

### (5) Plot spectra:

The spectra can be created by using “orca\_mapspc” program:

```
orca_mapspc outputfile -(type of spectrum) -options
```

The type of spectra include:

<i>ABS</i>	<i>ABSV</i>	<i>ABSQ</i>	<i>CD</i>	<i>IR</i>	<i>Raman</i>
<i>NRVS</i>	<i>VDOS</i>	<i>MCD</i>	<i>SOCABS</i>	<i>XES</i>	<i>XESV</i>
<i>XESQ</i>	<i>XAS</i>	<i>XASV</i>	<i>XASQ</i>	<i>XESSOC</i>	<i>XASSOC</i>

The options include:

```
-o output file
```

-cm use  $\text{cm}^{-1}$  (default)  
 -eV use eV (default  $\text{cm}^{-1}$ )  
 -g use Gaussian lineshape default  
 -l use Lorentz lineshape  
 -x0 initial point of spectrum  
 -x1 final point of spectrum  
 -w line width  
 -kw coefficient for the line width calculated as  $\text{kw} \times \sqrt{\text{energy}}$   
 -n number of points

Example: Plot an IR spectrum in the region 300-4000  $\text{cm}^{-1}$ , using default broadening

```
orca_mapspc jobname.out IR -x0300 -x14000
```

More examples can be found in ORCA Input Library

## 21 ORCA File Types

ORCA generates a wide range of files, depending on the type of calculation used.

.gbw	contains information on <b>G</b> eometry, <b>B</b> asis and <b>W</b> avefunction (Orbitals). Can be used as initial guess in subsequent calculation. Can be used to plot MOs, electron density, ... with <code>orca_plot</code>
.loc	gbw type file, contains information localized orbitals (requested via <code>%loc</code> block)
.uno	gbw type file, contains information on unrestricted natural orbitals (requested by <code>!UNO</code> ).
.unso	gbw type file, contains information on unrestricted natural spin orbitals (requested by <code>!UNO</code> ).
.qro	gbw type file, contains information on quasi-restricted orbitals (requested by <code>!UNO</code> ).
.uco	gbw type file, contains information on unrestricted corresponding orbitals (requested by <code>!UCO</code> ).
.xyz	coordinate file, contains the optimized structure after a geometry optimization. If the optimization was not successful, it contains the geometry of the last step (requested by <code>!Opt</code> ). Can be visualized by standard molecular visualization programs.
.trj	trajectory of geometry optimization. Contains the entire trajectory of all steps for relaxed surface scans (requested by <code>!Opt %geom Scan ... end end</code> ).
.hess	contains Hessian matrix (frequency calculation). Can be used as input to <code>orca_vib</code> or <code>orca_pltvib</code> .
.00n.xyz	coordinate file of the nth optimized structure of a relaxed surface scan.
.00n.gbw	gbw file of the nth optimized structure of a relaxed surface scan.
.allxyz	coordinate file, contains all optimized structures of a relaxed surface scan. Can be used as xyzfile for SP calculations on all optimized structures of a scan.
.relaxscanscf.dat	data file, contains the SCF energy for all optimized structures of the surface scan
.relaxscanact.dat	data file, contains actual (SCF or post-HF) energy for all optimized structures of the surface scan
.nto	gbw type file containing information on natural transition orbitals in TDDFT calculations.
.scfp	contains the electron density matrix (requested by <code>!KeepDens</code> )
.scfr	contains the spin density matrix (requested by <code>!KeepDens</code> )