

The ORCA Quantum Chemistry Program

A Jump-Start Guide -

VERSION 2.7.0

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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.

General

- Provide an ASCII input file, e.g. MyJob.inp
- Make sure ORCA is visible in the system in your \$PATH variable
- 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

Input File

The input file has the general structure:

```
! Keywords
! moinp          (optional: tell the program to start from exis-)
                  (      ting orbitals)
%maxcore 1024    (optional: scratch array size in MB)
%moinp "MyInp.gbw" (optional: Input MOs to start from)
%base "MyBaseName" (optional: name of the generated scratch files)
                  (      e.g. MyJob - without the extension!)
$new_job
  (now you can add another job - as many as you want)
```

Keywords can be given in any order, don't need to be on one line and are not case sensitive.

The input molecular orbitals do not need to be in the same basis set as the calculation to be performed.

Coordinates

```
! Angs or Bohrs  (optional: default is Angström)
* xyz charge multiplicity
C 0.0  0.0  0.0
O 0.0  0.0  .128
*
Or
* xyzfile charge multiplicity MyCoordinateFile.xyz
```

You can also input internal coordinates or run series of structures from “multiple XYZ” files.

This is explained in the manual

Basis Sets

```
! BasisSet
BasisSet= SV(P), SVP, TZVP, TZVPP, QZVPP,
          def2-SVP, def2-TZVP, def2-TZVPP, def2-QZVPP
          cc-pVnZ, aug-cc-pVnZ, cc-pCVnZ, aug-cc-pCVnZ (n=D,T,Q,5,6)
          ano-pVnZ, saug-ano-pVnZ, aug-ano-pVnZ
          6-31G*, 6-31+G*, 6-31++G**, 6-311G**, 6-311G(2df,2pd),...
          pc-1, pc-2, pc-3
```

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

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 NewGTO H "cc-pVDZ" end
      GTOName "MyGTObasis.bas"
```

The format of the basis set input file is essentially that from the EMSL library for Gamess-US

Auxiliary Basis sets

Pure DFT calculations are done by default in the RI mode. For this an auxiliary basis set is necessary. It may be automatically chosen, but is better provided explicitly:

```
! AuxBasisSet
For Coulomb fitting in RI-DFT (GGA, meta-GGA functional)
AuxBasisSet= SV/J, SV/J(-f), TZV/J, QZVP/J,
             def2-SVP/J, def2-TZVP/J, def2-TZVPP/J, def2-QZVPP/J
For Correlation fitting (MP2 and Coupled Cluster)
AuxBasisSet= SV/C, TZV/C, QZVPP/C
             def2-SVP/C, def2-TZVP/C, def2-TZVPP/C, def2-QZVPP/C
             cc-pVnZ, aug-cc-pVnZ (n=D,T,Q,5,6)
For Coulomb and exchange fitting (HF and hybrid DFT)
AuxBasisSet= SV/JK, TZV/JK, QZVPP/JK
             def2-SVP/JK, def2-TZVP/JK, def2-TZVPP/JK, def2-QZVPP/JK
```

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

Density Functionals

```
! Functional GridX NoFinalGrid VDW
Functional=
  Local   : LSD, HFS   local and Hartree-Fock Slater
  GGA     : BP=BP86,PBE,PW91,OLYP,OPBE,BLYP,PWP
           GGAs in RI mode require an auxiliary basis set ('/J')
  Meta-GGA: TPSS
  Hybrid  : B3LYP=B3LYP/TM,B3LYP/G,PBE0,X3LYP,BHandHLYP,B3P,B3PW
           B3LYP/TM=consistent with TurboMole
           B3YP/G  =consistent with Gaussian
  Double-hybrid: RI-B2PLYP, RI-B2PLYP-D, RI-MPW2PLYP, RI-B2T-PYLP,
```

```

          RI-B2K-PYLP, RI-B2GP-PLYP
Double hybrids in RI mode require an auxiliary basis set ('/C')
GridX      = Grid1, Grid2, Grid3, Grid4, Grid5, Grid6, Grid7
NoFinalGrid= Do not use a larger grid for the final energy
Default is to use a combination of Grid2 (110 angular points) and
Grid4 (302 angular points)
VDW        = Empirical van der Waals correction of Stefan Grimme

```

There are many more functionals documented in the manual

Self-Consistent Field Calculations

```

! SCF-Keywords
SCF-Keywords= SP          (Single point calculation)
               NormalSCF  (Normal single point convergence criteria)
               TightSCF   (TightSCF 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)

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
! RI-JK
    Fully RI based treatment of Coulomb and exchange

```

The default is a combination of DIIS and SOSCF. The default is to run singlets closed shell and higher multiplicities spin unrestricted.

Solvation

```

! COSMO(solvent) or COSMO
COSMO alone uses an infinite dielectric
Solvent = Water,DMSO,DMF,CH3CN,Methanol,Ethanol,Acetone,Ammonia,
Pyridine,CH2CL2,DCM,THF,Chloroform,CCl4,Hexane

```

Möller-Plesset Theory

```

! MP2, RI-MP2, SCS-MP2, RI-SCS-MP2, MP3, RI-MP3, SCS-MP3, RI-SCS-MP3
%maxcore 2048

```

RI methods require an auxiliary correlation fitting basis set ('/C')!

Coupled Cluster Calculations

```

! Modifier-CC-Variant Extrapolate(m/n,basis)
%maxcore 2048

```

```

Modifer=  AO - Do 3- and 4-external terms in the AO basis
          MO - Do the full integral transformation (default)
          RI - Use the RI approximation (not recommended)
CC-Variant= QCISD,QCISD(T),CCSD,CCSD(T),CEPA/1,CPF,ACPF
Extrapolate= two point extrapolation of correlation energies
             m/n = cardinal number combinations (e.g. 2/3, 3/4)
             basis= cc, aug-cc, ano, aug-ano
ExtrapolateEC is a variant where only the lower basis Coupled
Cluster calculation is performed and the higher basis set
calculation is avoided through estimation at the MP2 level

```

Complete Active Space Self-Consistent Field

```

%casscf  Nel      2      (Number of active electrons)
        Norb     2      (Number of active orbitals)
        Mult    1,3     (list of multiplicities)
        NRroots 2,1     (number of roots for each multiplicity)
        Trafostep ri (or do not give for exact transformation)
        ShiftUp 1 ShiftDn 1 (Level shift for converger)
        end

```

Many other options are available. Also works together with RI-JK and RIJCOSX.

Multireference Perturbation Theory and Configuration Interaction

```
! MR-MP2 RI-MRMP2 MR-CI SORCI MR-ACPF MR-DDCI2 MR-DDCI3
```

This uses the preceding CASSCF as reference. Extensive additional functionality of the MRCI module is documented in the manual.

Scalar Relativity

```
! ZORA or DKH
```

If you use the Karlsruhe basis set, the program will automatically load relativistically recontracted variants of them. Other basis sets should be used in uncontracted form (Keywords ! Decontract and DecontractAux) or the results will be inconsistent!

Geometry Optimization

```

! OptMethod  TightOpt
TightOpt    = increases convergence criteria
OptMethod   = Opt      (Standard optimization in redundant internals)
              = Copt    (Optimization in Cartesian coordinates)
              = GDIISOpt (Optimization with GDIIS)
              = OptTS   (Transition state optimization)
              = ScanTS  (Scan a coordinate automatic TS opt)

```

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

Frequency Calculations

```
! NumFreq
```

Performs a numerical frequency calculation

Time-Dependent Density Functional Theory

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

Many other options to speed up TD-DFT calculations, (D) corrections to CIS and other subjects are discussed in the manual. The module works together with RIJCOSX but not with RI-JK. CIS gradients are available, TD-DFT will be in the future.

EPR and NMR Properties

```
%eprnmr gTensor 1      (calculates the electronic g-tensor)
        DTensor = SSandSO (spin-spin and spin-orbit)
              = SS        (only spin-spin)
              = SOC        (only spin-orbit)
        Nuclei = all N {aizo, adip, aorb, fgrad, rho, shift}
              (aizo = isotropic hyperfine interaction)
              (adip = dipolar hyperfine interaction)
              (aorb = spin-orbit hyperfine interaction)
              (fgrad = quadrupole interaction)
              (rho = electron density at the nucleus)
              (shift = chemical shielding tensor)
end
```

Many other options are available in this module.