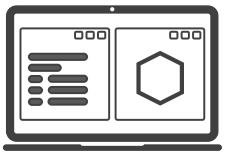

Introduction to Computational Chemistry
Handout Part 4

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1 Input file

The general structure of the ORCA input file is:

```
# Anything following a hash sign is ignored by ORCA
! Keywords1 # The keywords can appear all in one line
! Keywords2 # or on several lines
! keyWords3 # and they are case insensitive

%pal nprocs 2 end # This specifies the number of cores
%maxcore 1024 # This specifies memory per core in MB

*xyzfile 0 1 xyzfile.xyz # the charge, the multiplicity, and the xyz file
```

The xyz coordinates can also be directly listed in the input file (without the first two lines of the xyz file, i.e., only the coordinates):

```
! Keywords
%pal nprocs 2 end
%maxcore 1024

*xyz 0 1 # Note the change in the xyz keyword
<element symbol> X Y Z
<element symbol> X Y Z
...
* # the coordinates have to end with a *
```

The optimal number of processors (`nprocs`) and memory per core (`maxcore`) depend on the size of the system and the type of the calculation—the more you ask for, the faster the calculation is, but the longer it (usually) takes to start. For regular DFT single-point and optimization jobs for typical organic molecules (up to 50 atoms), 4–12 cores and 2048–4096 MB of memory are usually sufficient; for frequency calculations, the calculations may benefit from increased memory (e.g., up to 8192 MB).

In the following subsections we will show some examples for common calculations.

1.1 Geometry optimization and frequency calculation

```
! BP86 D3BJ def2-SVP Opt Freq
%pal nprocs 2 end
%maxcore 1024
*xyzfile 0 1 xyzfile.xyz
```

1.2 Transition state searches and confirmations

1.2.1 OptTS

```
! BP86 def2-SVP D3BJ optts freq
%pal nprocs 4 end
%maxcore 2048
*xyzfile 0 1 ts_initial.xyz
```

1.2.2 ScanTS

```
! Method ScanTS
% resources
%geom
  Scan # perform a scan
    B 0 1 = 3.0, 1.0, 10 # scan the distance between atoms 1 (0) and 2 (1) in 10 steps
  end
end
*xyzfile 0 1 reactant.xyz # xyz file of the reactant structure
```

1.2.3 NEB

```
! BP86 def2-svp d3bj neb-ts freq
%pal nprocs 4 end
%maxcore 2048
%neb
  NEB_END_XYZFile "product.xyz" # xyz file of the final structure
  PreOpt_Ends True # optimize the reactant and product before NEB (default: false)
  NImages 8 # number of structures along the trajectory (default: 8)
end
*xyzfile 0 1 start.xyz # xyz file of the reactant structure
```

As these calculations can take quite long, it might be worth using `xtb` for this.

1.2.4 IRC

```
! BP86 def2-svp d3bj IRC
%pal nprocs 4 end
%maxcore 2048
*xyzfile 0 1 ts.xyz # xyz file of the TS structure
```

1.3 Single point calculations

```
! B3LYP D3BJ def2-TZVP
%pal nprocs 2 end
%maxcore 1024

*xyzfile 0 1 xyzfile.xyz
```

1.4 Solvation

To use `cpcm` as the solvation model, simply add it as a keyword, with the solvent name in parentheses

```
! cpcm(solvent_name)
```

To use `smd` as the solvation model, call for `cpcm` as a keyword and add the following block. Note that you currently cannot use this in combination with an analytical frequency calculation, for this you have to change `freq` to `numfreq`.

```
%cpcm
 smd true
 SMDsolvent "solvent_name"
end
```

We have included a commented example input on GitHub. You can find more information on the available keywords in the ORCA manual.

2 Thermodynamics

Thermodynamical data can be quickly calculated from an existing Hessian file with the following input:

```
! PrintThermoChem
%geom
  InHessName "dummy.hess" # the .hess file from the frequency calculation
end
%freq
  Temp 283.15, 293.15, 303.15 # the temperature(s) for the thermochemistry calculations
end

*xyzfile 0 1 dummy.xyz # xyz of the structure
```

2.1 KIE

Thermodynamical data for different isotopes can be calculated as exemplifed:

```
! PrintThermoChem
%geom
  InHessName "h2.hess" # the .hess file from the frequency calculation of H2
end
%freq
  Temp 283.15 # the temperature(s) for the thermochemistry calculations
end

*xyz 0 1
H 0.0 0.0 0.0 # hydrogen (default)
H 0.0 0.0 0.7 M 2.00141 #  deuterium
*
```

By calculating $\Delta G^{\ddagger}$ with different isotopes, you can calculate the kinetic isotope effect of any element at any position. The KIE for H vs D can be calculated as:

$$\mathrm{KIE} = \mathrm{e}^{-(\Delta G^{\ddagger}_{H} - \Delta G^{\ddagger}_{D})/RT}$$

3 Energy units

The table below includes the main conversion factors used in computational chemistry. More conversion factors, and with higher numerical precision, can be found in the CRC Handbook (link in Section 6).

Unit	Hartree	eV	kcal/mol	kJ/mol
Hartree	1	27.211	627.509	2625.499
eV	3.675×10^{-2}	1	23.061	96.485
kcal/mol	1.594×10^{-3}	4.336×10^{-2}	1	4.184
kJ/mol	3.809×10^{-4}	1.036×10^{-2}	0.2390	1

4 Common errors

- Keyword typos – consult the manual
- Imaginary frequencies – tweak the calculation settings or consult an expert
- Calculation crashed because it exceeded maximum allowed memory (can be checked in the `.err` file) – ask for more memory
- Calculation crashed because the job ran out of time (can be checked in the `.err` file) – ask for more wall-time
- Geometry optimization reached the maximum number of iterations before converging – resubmit starting from the last geometry/increase the number of iterations (see ORCA 5.0.3 manual Section 9.24.1)

5 Generated files

`ORCA` generates several files as a result of a calculation. It also generates temporary files with a ".tmp" extension during the calculation that are removed after the calculation. If the calculation crashes, you may need to remove those files yourself by typing:

```
rm *.tmp
```

This will remove all files that end with ".tmp" in the current directory. Make sure you don't use this command in a directory where you have jobs running. For parallel calculations, processor-specific files are also sometimes kept. These include ".proc" in them, and they can be removed by:

```
rm *.proc*
```

Some files are only generated for specific job types. A list of possible files for the job types considered in this session is given below.

File	Description	Occurrence
`outfile`	contains information and results of the calculation	always
`basename.xyz`	optimized xyz coordinates	opt
`basename_trj.xyz`	trajectory of the optimization	opt
`basename.gbw`	the wavefunction	always
`basename.opt`	numerical information about the optimization	opt
`basename.engrad`	the energy gradient of the optimized structure	opt
`basename.cpcm`	surface information for the solvent model	cpcm
`basename.smd.out`	information for the SMD solvent model	smd
`basename.hess`	the Hessian and vibrational spectrum information	freq
`basename_property.txt`	Values of some selected properties	always
`basename.prop`	Property file for further calculations	always

6 Useful links

- ORCA Forum:
  `https://orcaforum.kofo.mpg.de/app.php/portal`
- ORCA Manual (the Bible):
  `https://orcaforum.kofo.mpg.de/app.php/dlext/?view=detail&df_id=186`
- ORCA input library (can be outdated on some topics, is incomplete):
  `https://sites.google.com/site/orcainputlibrary/`
- Various ORCA tutorials (we recommend):
  `https://www.orcasoftware.de/tutorials/`
- ORCA User Meeting 2020 videos on various ORCA-related topics:
  `https://orcaforum.kofo.mpg.de/app.php/dlext/?cat=11`