



Max Planck Institute for Chemical Energy Conversion

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Mülheim an der Ruhr

Computational chemistry with ORCA

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Today's topics

9:00-12:00

General ORCA usage (Ragnar)

DFT and basis sets (Dimitrios)

Reactivity (Giovanni)

13:30-14:00 Tutorial on use of PC² cluster systems

14:00-18:00 ORCA Tutorial

The ORCA project



- A molecular quantum chemistry program written originally by Prof. Frank Neese.
- Developed at the Max Planck Institut für Kohlenforschung, Mülheim, Germany.
- **The binaries of ORCA are available free of charge** for academic users.

ORCA is a **flexible, efficient and easy-to-use** general purpose tool for quantum chemistry with specific emphasis on spectroscopic properties of open-shell molecules. It features a wide variety of standard quantum chemical methods ranging from semiempirical methods to DFT to single- and multireference correlated ab initio methods. It can also treat environmental and relativistic effects.

Due to the user-friendly style, ORCA is considered to be a helpful tool not only for computational chemists, but also for chemists, physicists and biologists that are interested in developing the full information content of their experimental data with help of calculations.

<https://orcaforum.cec.mpg.de>

The ORCA project

Hartree-Fock

RHF, UHF, ROHF
Direct, Semidirect, Conventional,
Approx: RI, RIJ-COSX, RI-JK
Converger: (K)DIIS, NR, SOSCF

Electron Correlation

MP2/RI-MP2
CCSD(T), QCISD(T), CEPA, CPF
(all with/without RI, Local)
MR-MP2, MR-MP3, MR-MP4(SD)
MR-CI, MR-ACPF, MR-AQCC
NEV-PT2, Extrapolation Schemes

Relativistic Methods

DKH, ZORA, IORA,
Picture Change Effects,
All electron basis sets,
Effective core potentials (ECPs)

Semiempirical

INDO/S, MNDO,
AM1, PM3, NDDO/1

Local Methods

DLPNO-MP2 (RF, UHF), CIM,
DLPNO-CCSD(T) (RHF, UHF),
DLPNO-MP2-F12
DLPNO-NEVPT2(-F12),
LPNO-CCSD-F12,
Mk-LPNO-MRCCSD(T)



Molecular Properties

Analytical Gradients (HF, DFT, MP2, TD-DFT), Geometries, Trans. States
Polarizabilities, Magnetizabilities,
Solvation Models (COSMO & C-PCM)
Analytical Hessian, IR, Raman and Resonance Spectra,
EPR-Parameters (g, A, D, J, Q), Mössbauer-Parameters ($\delta, \Delta E_Q$)
NMR (GIAOs), ABS, CD, MCD Spectra
Population Analysis, NBOs, Localization, Multipole Moments,
Energy Decomposition Schemes, Stability Analysis, FOD

Density Functional

LDA, GGA, Hybrid Functionals
Double hybrid functionals,
RI-Approx, RKS, UKS, ROKS,
HF-3c, PBEh-3c,
Range-Separated Functionals

Excited States

TD-DFT/CIS+gradients
MR-CI/DD-CI/SOR-CI, ROCIS,
sTDA/sTDDFT, EOM/STEOM CCSD

Multi-Reference

MR-CI/DD-CI/SOR-CI
CAS-SCF, ICE-CI, FIC-MRCI,
Mk-LPNO-MRCCSD(T), MREOM-CCSD

Availability and installations

- Binaries available for: Windows, Linux and Mac
- Installation programs (Windows, Mac) or compressed archive (Linux).
- OpenMPI parallelization.

Register at

<https://orcaforum.kofo.mpg.de>

sign-in and download binaries and the manual.

Downloads - Categories

Search download

CATEGORY / DESCRIPTION	FILE(S)	LATEST DOWNLOAD
ORCA 4.x End User License Agreement (EULA)	1	ORCA 4.x software EULA bugchucker Fri Feb 08, 2019 1:47 pm
ORCA 4.2.1	13	ORCA 4.2.1, Windows, 64bit, .zip Archive bugchucker Fri Dec 06, 2019 3:45 pm
ORCA 4.2.0	13	ORCA 4.2.0, Windows, 64bit, .zip Archive bugchucker Fri Aug 09, 2019 12:37 pm
ORCA 4.1.2	11	ORCA 4.1.2, Linux, x86-64, shared-version, .tar.zst Archive (OpenMPI 2.1.5) bugchucker Fri May 03, 2019 4:05 pm
ORCA 4.1.1	15	ORCA 4.1.1, Windows, 64bit, Installer Version bugchucker Fri Feb 15, 2019 10:36 am
ORCA 4.1.0	14	ORCA 4.1.0, Linux, x86-64, shared-version, .tar.zst Archive (OpenMPI 2.1.5) bugchucker Sun Dec 16, 2018 5:54 pm
ORCA Manuals	5	ORCA 4.2.1 Manual bugchucker Wed Oct 30, 2019 10:20 am
ORCA Jump-Start Guide	1	ORCA Jump-Start Guide bugchucker Wed Jan 23, 2019 10:09 am
CASSCF Tutorial	1	CASSCF Tutorial bugchucker Thu Nov 21, 2019 2:02 pm
Avogadro (ORCA enhanced version)	1	Avogadro, Windows Version bugchucker Tue Apr 02, 2019 12:36 pm

Help with setting up ORCA:

<https://sites.google.com/site/orcainputlibrary/setting-up-orca>

Setting up on a cluster for parallel execution

- OpenMPI parallelization. Use recommended version.
- Put ORCA directory in \$PATH and \$LD_LIBRARY_PATH
- Run parallel orca with full path : `/full/path/to/orca input.inp`

Use local scratch directory if available.

Make sure job-submission script *cd*'s to scratch-directory and runs ORCA from there. All tmp files will then be created there instead of being transferred constantly over network.

Help with setting up ORCA, example job-submission scripts etc.

<https://sites.google.com/site/orcainputlibrary/setting-up-orca>

How to do a basic ORCA calculation

- Use a command-line text editor (vim, emacs, nano) to create an inputfile named e.g. test.inp.
- Inputfile contains theory-level, job directives and usually coordinates.

! PBE def2-SVP opt

***xyz 0 1**

H 0.0 0.0 0.0

F 0.0 0.0 1.0

How to do a basic ORCA calculation

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- Inputfile contains theory-level, job directives and usually coordinates.

simple input-line

! PBE def2-SVP opt

theory basis set job-type

***xyz 0 1**

charge: 0

spin multiplicity: 1

coordinate block

H 0.0 0.0 0.0

Cartesian coordinates

F 0.0 0.0 1.0

in Å

A more complicated inputfile

simple input-line

! PBE def2-SVP def2/J opt Grid5 TightSCF Pa14

theory

auxbasis

DFT-grid

Convergence

basis set

job-type

setting

Number of

cores

%scf

maxiter 300

end

comment line

%basis

newgto H "def2-TZVPP" end

end

block-input

coordinate block

***xyz 0 1**

H 0.0 0.0 0.0

F 0.0 0.0 1.0 newgto "def2-QZVPP" end

An even more complicated inputfile

! MRCI+Q def2-TZVP Normalprint MOREAD Usesym

```
%moinp "orbitals.gbw"  
%pointcharges "pointcharges.pc"  
%casscf  
trafostep ri  
nel 5  
norb 4  
mult 2,4  
end  
  
%pal  
nprocs 12  
end  
  
%mrci  
Tsel 1e-8  
Tpre 1e-6  
Newblock 4 *  
  Nroots 10  
  Refs CAS(5,4) end  
End  
Newblock 2 *  
  Nroots 10  
  Refs CAS(5,4) end  
end  
end
```

Run the inputfile

- Directly:

orca test.inp > test.out

only for short test jobs

- Submitting job to job scheduler using a job-script:
sbatch orca_jobscript.sh test

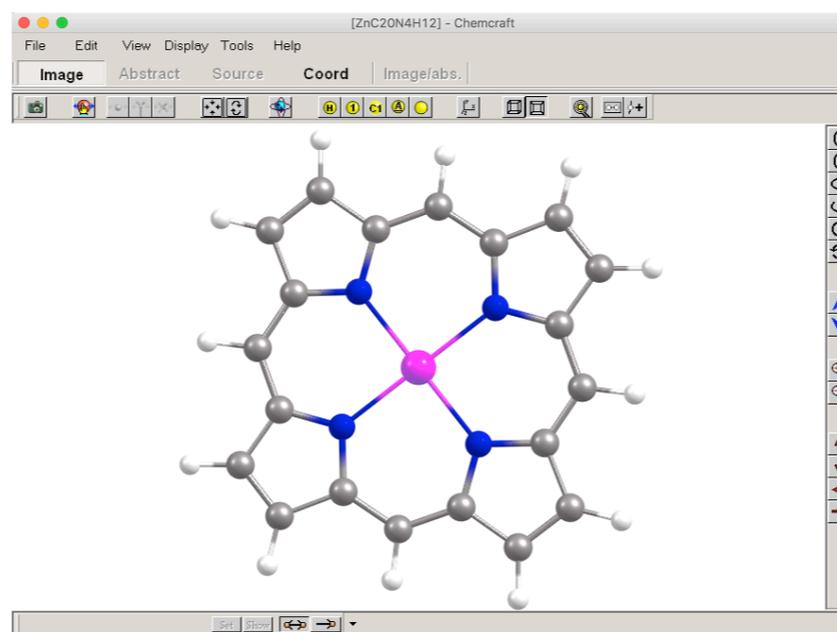
Ideally the job-submission script copies inputfile and other needed files to a local scratch directory, starts the job there, copies back the result files when job is done

Read the outputfile

- Open the outputfile using a command-line program:
less, vim, emacs
- Other outputfiles are also sometimes created:
 - GBW file: binary file containing geometry, basis, WF
 - XYZ file containing optimized geometry
 - Property file containing energy, geometry, properties
- Or open the outputfile using a GUI visualization program:
 - geometry optimizations
 - frequencies
 - orbitals

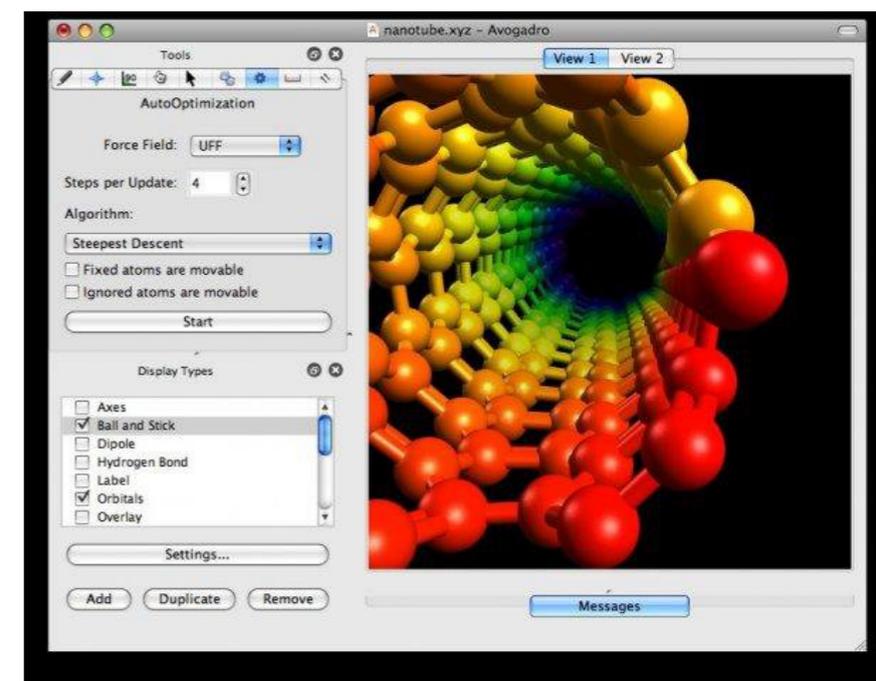
Visualization programs

- ORCA is completely command-line based.
- Useful visualization programs to use with ORCA:
 - Avogadro
 - Chemcraft
 - Molden
 - Chimera
 - VMD



Chemcraft

chemcraftprog.com
Commercial, 150-day trial



Avogadro

<http://avogadro.cc>
Free, open-source

Type of jobs

- **Single-point energy (on a single geometry):**
 - Hartree-Fock level: RHF or UHF
 - DFT level: RKS or UKS
 - post-HF level: MP2, CCSD(T)
 - multireference wavefunctions: CASSCF, NEVPT2, MRCI, MRCC
- **Molecular property job (single-point):**
 - NMR, EPR, Mössbauer properties
- **Geometry optimization: !Opt**
 - If method has gradient available
 - Find minimum or saddle-point (Opt-TS)
- **Frequency job: !Freq or !NumFreq**
 - Analytical or numerical Hessian available for DFT methods and MP2.
 - Confirm minimum or saddlepoint
 - Calculate thermodynamical corrections or get IR/Raman spectra
- **Excited state calculations**
 - Calculate UV-VIS, CD, XAS, XES, MCD, Resonance Raman spectra
 - Possible at TDDFT, CASSCF, NEVPT2, EOM-CCSD levels
- **Molecular dynamics (see talk by Martin Brehm)**
 - If method has gradient available

Output of Single Points

We first echo the input file and some references to the basis sets used. Then you get information on the job-type, the input coordinates in various formats and the basis set

```
*****  
* Single Point Calculation *  
*****
```

CARTESIAN COORDINATES (ANGSTROEM)

```
-----  
C      0.000000    0.000000    0.000000  
O      0.000000    0.000000    1.130000  
-----
```

BASIS SET INFORMATION

There are 2 groups of distinct atoms

```
Group  1 Type C  : 7s4p1d contracted to 3s2p1d pattern {511/31/1}  
Group  2 Type O  : 7s4p1d contracted to 3s2p1d pattern {511/31/1}
```

Next the one-electron integrals are calculated (and perhaps also the two-electron integrals if `conv` is requested for “conventional SCF”)

ORCA GTO INTEGRAL CALCULATION

BASIS SET STATISTICS AND STARTUP INFO

```
-----  
# of primitive gaussian shells      ... 24  
# of primitive gaussian functions   ... 48  
# of contracted shell                ... 12  
# of contracted basis functions     ... 28  
Highest angular momentum            ... 2  
Maximum contraction depth           ... 5  
Integral threshold                   Thresh ... 1.000e-010  
Primitive cut-off                    TCut   ... 3.000e-012  
-----
```

Next the SCF program is taking over and commences with giving all details about the SCF settings

SCF SETTINGS

Hamiltonian:

```
-----  
Density Functional      Method      .... DFT (GTOs)  
Exchange Functional    Exchange    .... B88  
  X-Alpha parameter    XAlpha     .... 0.666667  
  Becke's b parameter  XBeta      .... 0.004200  
Correlation Functional Correlation .... LYP  
LDA part of GGA corr.  LDAOpt     .... VWN-5  
Gradients option       PostSCFGGA .... off  
Hybrid DFT is turned on  
  Fraction HF Exchange  ScalHFX    .... 0.200000  
  Scaling of DF-GGA-X   ScalDFX    .... 0.720000  
  Scaling of DF-GGA-C   ScalDFC    .... 0.810000
```

General Settings:

```
Integral files          IntName     .... JOB-01  
Hartree-Fock type      HFTyp      .... RHF  
Total Charge           Charge      .... 0  
Multiplicity           Mult        .... 1  
Number of Electrons    NEL         .... 14  
Basis Dimension        Dim         .... 28  
Nuclear Repulsion      ENuc       .... 22.4778902655 Eh
```

Convergence Tolerance:

```
Energy Change          ToLE       .... 1.000e-008 Eh  
Max Density Change     TolMaxP    .... 1.000e-007  
RMS Density Change     TolRMSP    .... 1.000e-008  
DIIS Error             TolErr     .... 1.000e-007
```

Diagonalization of the overlap matrix:

```
Smallest eigenvalue    .... 1.911e-002  
Time for diagonalization ... 0.010 sec  
Time for construction of square roots ... 0.030 sec  
Total time needed      ... 0.040 sec
```

The integration grid is produced and the initial guess performed

```
-----  
DFT GRID GENERATION  
-----  
  
General Integration Accuracy   IntAcc   ...   4.010  
  
Total number of grid points    ...     5057  
  
-----  
INITIAL GUESS: MODEL POTENTIAL  
-----  
Loading Hartree-Fock densities  ... done  
....etc  
Now organizing SCF variables    ... done  
  
-----  
INITIAL GUESS DONE  
-----
```

Now we are ready to start the SCF iterations

```
-----  
SCF ITERATIONS  
-----  
  
*** Starting incremental Fock matrix formation ***  
***Turning on DIIS***  
  
-----  
!           ITERATION           0           !  
-----  
Total Energy      :   -112.951951547431 Eh  
Energy Change    :   -112.951951547431 Eh  
MAX-DP           :           0.674569966353  
RMS-DP           :           0.053899776162  
Actual Damping   :           0.0000  
Int. Num. El.    :   14.00002071 (UP=   7.00001035  
Exchange         :   -10.98287769  
Correlation      :   -0.58429246  
DIIS-Error       :           0.450135783168
```

Which hopefully eventually converge and:

```
*****  
*                               SUCCESS                               *  
*          SCF CONVERGED AFTER 11 CYCLES          *  
*****
```

The total energy and its components are printed

```
-----  
TOTAL SCF ENERGY  
-----  
  
Total Energy      :   -113.17273851 Eh   -3079.50944 eV  
  
Components:  
Nuclear Repulsion :           22.47789027 Eh   611.63913 eV  
Electronic Energy  :          -135.65062877 Eh -3691.14856 eV  
  
One Electron Energy:          -198.09397475 Eh -5390.27572 eV  
Two Electron Energy:           62.44334598 Eh   1699.12715 eV  
  
Virial components:  
Potential Energy  :          -225.62136955 Eh -6139.31540 eV  
Kinetic Energy    :           112.44863104 Eh   3059.80596 eV  
Virial Ratio      :                   2.00643945
```

Next you get the orbital energies printed:

```
-----  
ORBITAL ENERGIES  
-----  
  
NO   OCC      E (Eh)      E (eV)  
0   2.0000   -19.243280   -523.6231  
1   2.0000   -10.301611   -280.3141  
2   2.0000    -1.152619    -31.3636  
3   2.0000    -0.568518    -15.4698  
4   2.0000    -0.476766    -12.9731  
5   2.0000    -0.476766    -12.9731  
6   2.0000   -0.373742   -10.1698  
7   0.0000    -0.026298    -0.7156  
8   0.0000    -0.026298    -0.7156  
9   0.0000     0.221613     6.0303  
10  0.0000     0.400346    10.8937  
11  0.0000     0.457384    12.4458  
12  0.0000     0.457384    12.4458  
...
```

Now comes the "soft science" (e.g. population analysis of the SCF density matrix

```
*****
* MULLIKEN POPULATION ANALYSIS *
*****
```

MULLIKEN ATOMIC CHARGES

```
0 C : 0.016669
1 O : -0.016669
Sum of atomic charges: -0.000000
```

MULLIKEN REDUCED ORBITAL CHARGES

```
0 C s : 3.834569 s : 3.834569
    pz : 1.009723 p : 2.073008
    px : 0.531642
    py : 0.531642
    dz2 : 0.027088 d : 0.075754
    dxz : 0.024333
    dyz : 0.024333
    dx2y2 : 0.000000
    dxy : 0.000000
1 O s : 3.737862 s : 3.737862
    pz : 1.381818 p : 4.256855
    px : 1.437518
    py : 1.437518
    dz2 : 0.008940 d : 0.021953
    dxz : 0.006506
    dyz : 0.006506
    dx2y2 : 0.000000
    dxy : 0.000000
```

MULLIKEN OVERLAP CHARGES

```
B( 0-C , 1-O ) : 1.3340
```

The Löwdin analysis contains a detailed breakdown of the MOs in terms of angular momentum components of each atom. This helps a lot when you select the orbitals for plotting.

```
*****
* LOEWDIN POPULATION ANALYSIS *
*****
```

LOEWDIN ATOMIC CHARGES

```
0 C : -0.050462
1 O : 0.050462
```

etc.

LOEWDIN REDUCED ORBITAL POPULATIONS PER MO

THRESHOLD FOR PRINTING IS 0.1%

	0	1	2	3	4	5
ORB-EN	-19.24328	-10.30161	-1.15262	-0.56852	-0.47677	-0.47677
OCC	2.00000	2.00000	2.00000	2.00000	2.00000	2.00000
0 C s	0.0	99.5	18.6	11.5	0.0	0.0
0 C pz	0.1	0.0	16.7	4.8	0.0	0.0
0 C px	0.0	0.0	0.0	0.0	6.9	20.9
0 C py	0.0	0.0	0.0	0.0	20.9	6.9
0 C dz2	0.1	0.0	2.4	0.0	0.0	0.0
0 C dxz	0.0	0.0	0.0	0.0	0.5	1.5
0 C dyz	0.0	0.0	0.0	0.0	1.5	0.5
1 O s	99.8	0.1	54.7	20.8	0.0	0.0
1 O pz	0.0	0.4	7.3	62.3	0.0	0.0
1 O px	0.0	0.0	0.0	0.0	17.4	52.4
1 O py	0.0	0.0	0.0	0.0	52.4	17.4
1 O dz2	0.0	0.1	0.3	0.6	0.0	0.0
1 O dxz	0.0	0.0	0.0	0.0	0.1	0.3
1 O dyz	0.0	0.0	0.0	0.0	0.3	0.1
	6	7	8	9	10	11
	-0.37374	-0.02630	-0.02630	0.22161	0.40035	0.45738
	2.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0 C s	49.2	0.0	0.0	33.5	60.9	0.0
0 C pz	39.3	0.0	0.0	46.5	35.3	0.0
0 C px	0.0	15.2	54.7	0.0	0.0	15.5
0 C py	0.0	54.7	15.2	0.0	0.0	81.4
0 C dz2	0.8	0.0	0.0	7.8	1.2	0.0
0 C dxz	0.0	0.4	1.5	0.0	0.0	0.1
0 C dyz	0.0	1.5	0.4	0.0	0.0	0.3
1 O s	2.0	0.0	0.0	12.0	0.6	0.0
1 O pz	8.8	0.0	0.0	0.2	1.0	0.0
1 O px	0.0	5.9	21.2	0.0	0.0	0.3
1 O py	0.0	21.2	5.9	0.0	0.0	1.5
1 O dz2	0.0	0.0	0.0	0.0	0.9	0.0
1 O dxz	0.0	0.2	0.9	0.0	0.0	0.1
1 O dyz	0.0	0.9	0.2	0.0	0.0	0.7

Visualizing orbitals and densities

Using orca_plot

```
orca_plot filename.gbwn -i
```

ORCA creates a GBW binary file that contains information about the wavefunction and orbitals. By using the orca_plot program we can calculate isosurfaces for particular orbitals and print as e.g. Cube files. Cube files can be opened in several programs.

Print orbital information to ORCA output

```
! PBE def2-SVP printmos printbasis
```

Open outputfile in Chemcraft/Avogadro that creates the isosurfaces from the MO information.

Geometry optimizations

- Geometry optimizations are usually performed at the DFT level:
 - Availability of analytical gradients usually needed.
- Minimizes the energy by changing the coordinates.
- Use the ! `Opt` keyword in the inputfile to do an optimization
- ORCA uses a Quasi-Newton optimizer with BFGS update and uses redundant internal coordinates.

The optimization is considered converged when these criteria are fulfilled:

$\text{RMSG} < 1\text{E-}4 \text{ Eh/au}$

$\text{MaxG} < 3\text{E-}4 \text{ Eh/au}$

$\text{ToIE} < 5\text{E-}6 \text{ Eh}$

$\text{RMSD} < 2\text{E-}3 \text{ au}$

$\text{MaxD} < 4\text{E-}3 \text{ au}$

After calculating the SCF energy and the gradient of the energy, a relaxation is step is carried out: And a new geometry is proposed:

```

-----
ORCA GEOMETRY RELAXATION STEP
-----
Number of atoms          ....  4
Number of internal coordinates  ....  7
Current Energy           .... -114.317745134 Eh
Current gradient norm    ....  0.207887808 Eh/bohr
Maximum allowed component of the step  ....  0.300
Current trust radius     ....  0.300
Evaluating the initial hessian  .... (Almlloef) done
Projecting the Hessian     .... done
Forming the augmented Hessian  .... done
Diagonalizing the augmented Hessian  .... done
Last element of RFO vector  ....  0.957975075
Lowest eigenvalues of augmented Hessian:
-0.057174708  0.151693870  0.360949845  0.425465740  0.501166791
Length of the computed step  ....  0.299435193
The final length of the internal step  ....  0.299435193
Converting the step to cartesian space:
Transforming coordinates:
Iter  0:  RMS(Cart)=  0.0824560429  RMS(Int)=  0.1127292561
Iter  1:  RMS(Cart)=  0.0024951498  RMS(Int)=  0.0033197589
Iter  2:  RMS(Cart)=  0.0002432861  RMS(Int)=  0.0003067902
Iter  3:  RMS(Cart)=  0.0000185328  RMS(Int)=  0.0000231161
Iter  4:  RMS(Cart)=  0.0000012690  RMS(Int)=  0.0000015779
Iter  5:  RMS(Cart)=  0.0000000832  RMS(Int)=  0.0000001034
Iter  6:  RMS(Cart)=  0.0000000054  RMS(Int)=  0.0000000067
done
Storing new coordinates          .... Done

```

The status of the geometry convergence is printed:

```

-----|Geometry convergence|-----
Item          value          Tolerance  Converged
-----|-----|-----|-----
RMS gradient  0.07883145          0.00010000  NO
MAX gradient  0.14233649          0.00030000  NO
RMS step      0.11317586          0.00200000  NO
MAX step      0.18511086          0.00400000  NO
.....|-----|-----|-----
Max (Bonds)   0.0980          Max (Angles)  4.89
Max (Dihed)   0.00          Max (Improp)  0.00
-----|-----|-----|-----

```

The optimization has not yet converged - more geometry cycles are needed

```

-----
Redundant Internal Coordinates
(Angstroem and degrees)

Definition          Value    dE/dq    Step    New-Value
-----|-----|-----|-----|-----
1. B(O  1,C  0)          1.1500 -0.142336  0.0535  1.2035
2. B(H  2,C  0)          1.0000 -0.103355  0.0980  1.0980
3. B(H  3,C  0)          1.0000 -0.103355  0.0980  1.0980
4. A(H  2,C  0,O  1)      115.00 -0.017685  2.44   117.44
5. A(H  3,C  0,O  1)      115.00 -0.017685  2.44   117.44
6. A(H  3,C  0,H  2)      130.00  0.035370 -4.89   125.11
7. I(O  1,H  3,H  2,C  0)  0.00 -0.000000  0.00   0.00
-----|-----|-----|-----|-----

*****
*          GEOMETRY OPTIMIZATION CYCLE  2          *
*****

```

Then the next SCF is done and the next gradient calculated, a new geometry is proposed until (hopefully) finally:

```

*****HURRAY*****
***          THE OPTIMIZATION HAS CONVERGED          ***
*****

```

Following this statement one more energy calculation is performed in order to make sure that the energy and properties are really done at the stationary point of the PES.

Constraints and relaxed scans

- Specific atoms or internal coordinates can be frozen during the optimization.

Constraining bond (B) between atom 0 and atom 1.

```
! Opt
%geom
Constraints
{B 0 1 C}
end
```

- A relaxed scan where an internal coordinate is kept frozen and gradually changed while all other coordinates are minimized

```
! Opt
%geom Scan
B 0 1 = 1.0, 3.0, 12
end
end
```

Scanning bond (B) between atom 0 and atom 1 from 1.0 Å to 3.0 Å in 12 steps

Restarting calculations in ORCA

- If a geometry optimization failed to converge or crashed it is easiest to replace the coordinates of the inputfile with coordinates from the last step in the outputfile.
- Restarting a single-point energy calculation (or feed-in alternative guess orbitals):

```
! PBE def2-SVP def2/J
```

```
! MOREAD
```

```
%moinp "otherorbitals.gbwn"
```

Efficient DFT in ORCA: the RI approximation

- If one performs a regular non-hybrid DFT calculation, ORCA by default uses the resolution of identity (RI or RI-J) approximation, a.k.a. density fitting.
- The electron density is fit to an auxiliary basis set
- Speeds up the calculation of Coulomb integrals 10-100 times.
- Negligible errors in geometries and frequencies.
- Very small errors in absolute energies, error mostly cancels out in relative energies. Error depends on size of auxiliary basis set. Accurate general auxiliary basis sets available.

! PBE def2-SVP def2/J

orbital basis set

auxiliary basis set

Efficient hybrid DFT in ORCA: RI-JK and RIJCOSX

- If using a hybrid density functional (e.g. B3LYP, PBE0, TPSSh) i.e. method has HF exchange, ORCA by default makes no approximation to the present Coulomb and Exchange integrals.

RI-JK

Resolution of identity for Coulomb and Exchange integrals.

Not as efficient as RI-J. Requires different auxiliary basis sets.

! B3LYP RIJK def2-SVP def2/JK

RIJCOSX

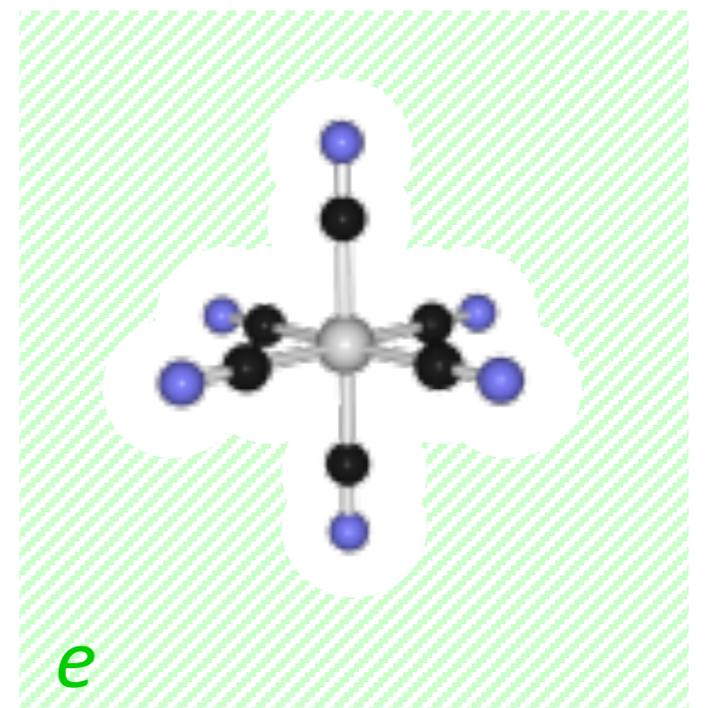
Resolution of identity for Coulomb (C) and Chain-of-sphere (COS) numeric integration for Exchange (X). Uses integration grid.

Very efficient, especially for large molecules. Slightly larger errors due to grid dependence, controlled by grid size.

! B3LYP RIJCOSX def2-SVP def2/J GridX4

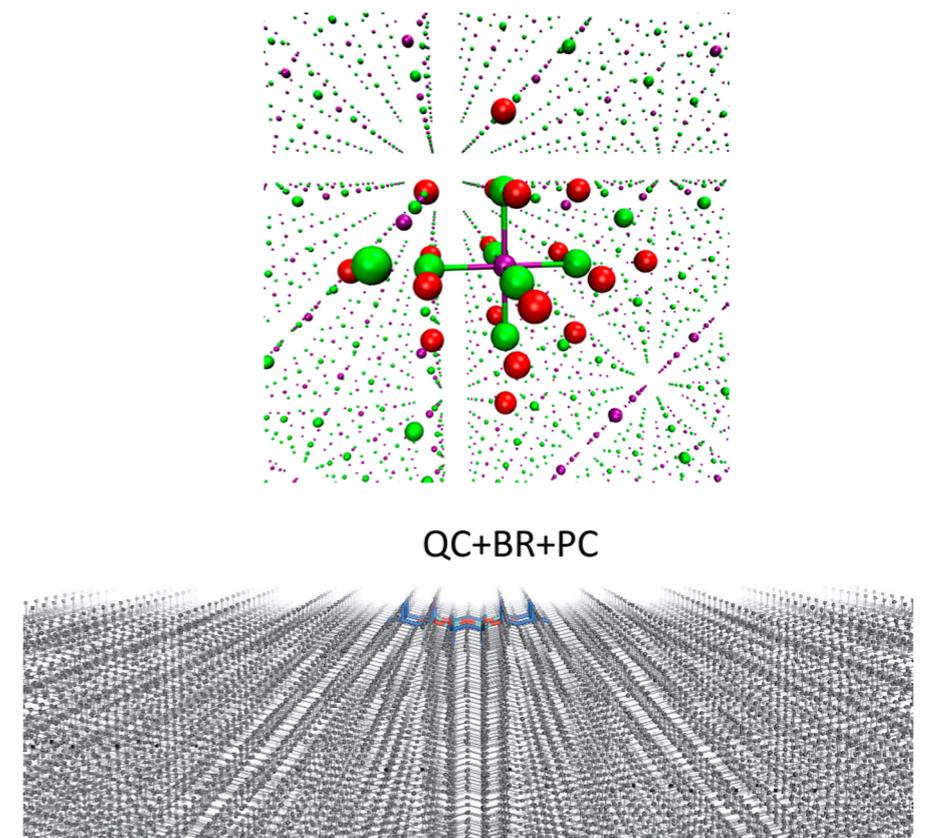
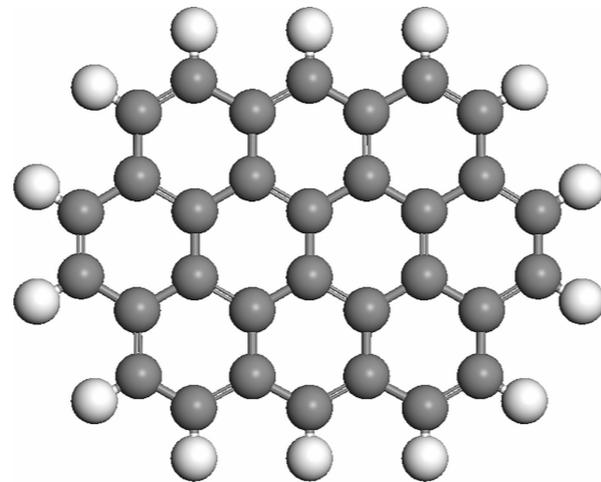
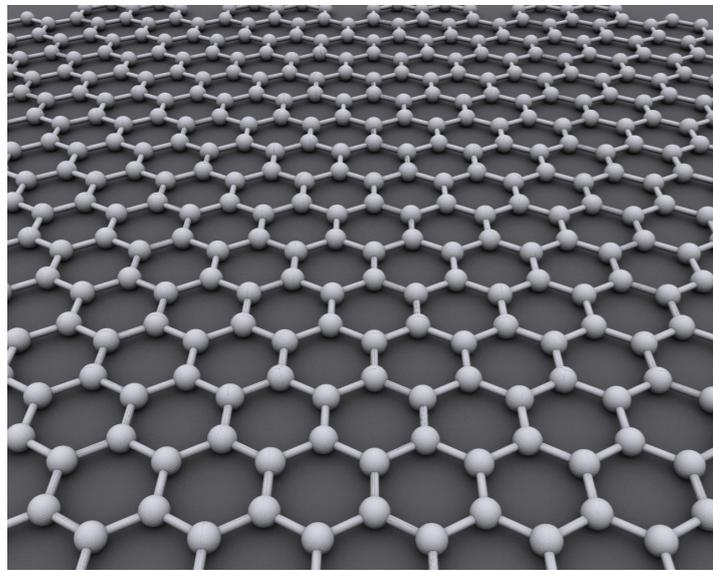
Solvation models in ORCA

- The vacuum approximation (i.e. modelling completely isolated molecules) will not always work when modelling molecular systems in solution.
- Especially for charged molecules, cations and especially anions, accounting for solvation effects becomes necessary.
- ORCA includes a polarizable continuum model that crudely accounts for solvation effects implicitly by calculating the interaction between a molecule inside a cavity of a polarizable continuum characterized by the dielectric constant of the solvent.
- Straightforward to use:
`! PBE def2-SVP CPCM(Water) Opt`
- Single-point energies, optimizations and frequencies are possible



What can I /can't I model with ORCA?

- ORCA is a molecular quantum chemistry code, using atom-centered basis functions.
- ORCA does not have periodic boundary conditions
- Modelling solids requires taking care of boundary effects



Disadvantages:

Truncation or boundary effects

Advantages:

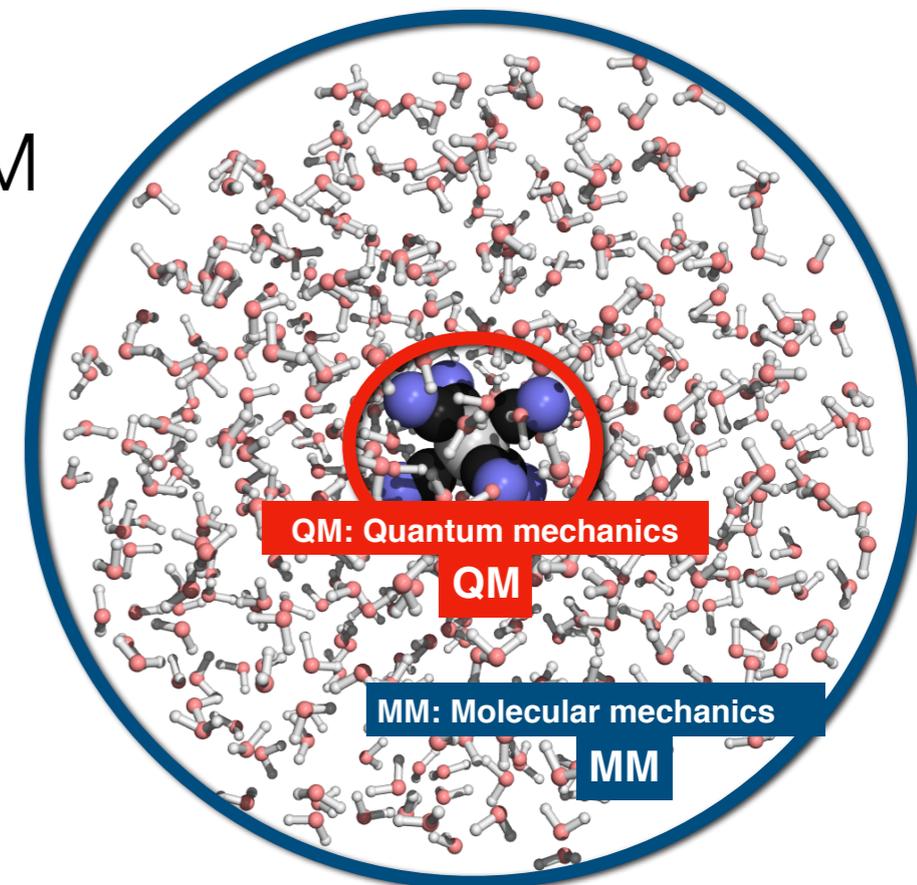
Going beyond DFT: WFT

QM/MM and ORCA

- Interfaces available to various popular QM/MM or MM codes:
 - Chemshell: <https://www.chemshell.org>
 - NAMD: <http://www.ks.uiuc.edu/Research/qmmm/>
 - GROMACS: <http://wwwuser.gwdg.de/~ggroenh/qmmm.html>
 - Cuby: <http://cuby4.molecular.cz>
 - pDynamo: <https://sites.google.com/site/pdynamowiki/>

ORCA QM/MM

- Latest ORCA version (4.2.1) has built-in QM/MM functionality.
- Currently supports the CHARMM protein forcefield.



Heavy elements and Relativistic approximations in ORCA

- The core electrons of heavy elements move faster than valence electrons
- Account for relativistic motion of electrons in heavy elements thus becomes vital.
- Two main ways of dealing with this:

All-electron (scalar) relativistic approach

- ZORA
 - DKH
- Necessary for core properties.
Requires special basis sets

Effective core (pseudopotential)

Good for energies, geometries.
Automatic assignment when using the Ahlrichs def2 basis set family

The Periodic Table

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

Molecular and spectroscopic properties in ORCA

- NMR Chemical shift calculations using a GIAO-DFT approach
- NMR J-coupling constants at the DFT level
- g-tensors: DFT level and CASSCF-NEVPT2 level
- hyperfine coupling tensors: DFT level and CCSD level
- Mössbauer isomer shifts and quadrupole couplings

- UV-VIS/CD/XAS absorption spectra using TDDFT or WFT.
- XES calculations using a 1-electron DFT model or WFT.
- Calculations of Resonance Raman and Nuclear Resonance Vibrational spectra
- RIXS spectra via a ROCIS WFT approach

Excited states in ORCA: TDDFT

- Time-dependent DFT (TDDFT) for the calculation of excited states.
With and without Tamm-Dancoff approximation

! PBE def2-SVP def2/J

**%tddft
nroots 10
end**

TD-DFT/TDA EXCITED STATES (SINGLET)

STATE 1: E= 0.364696 au 9.924 eV 80041.6 cm⁻¹
4a -> 5a : 0.999181 (c= -0.99959043)**

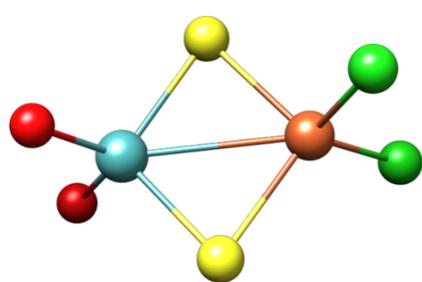
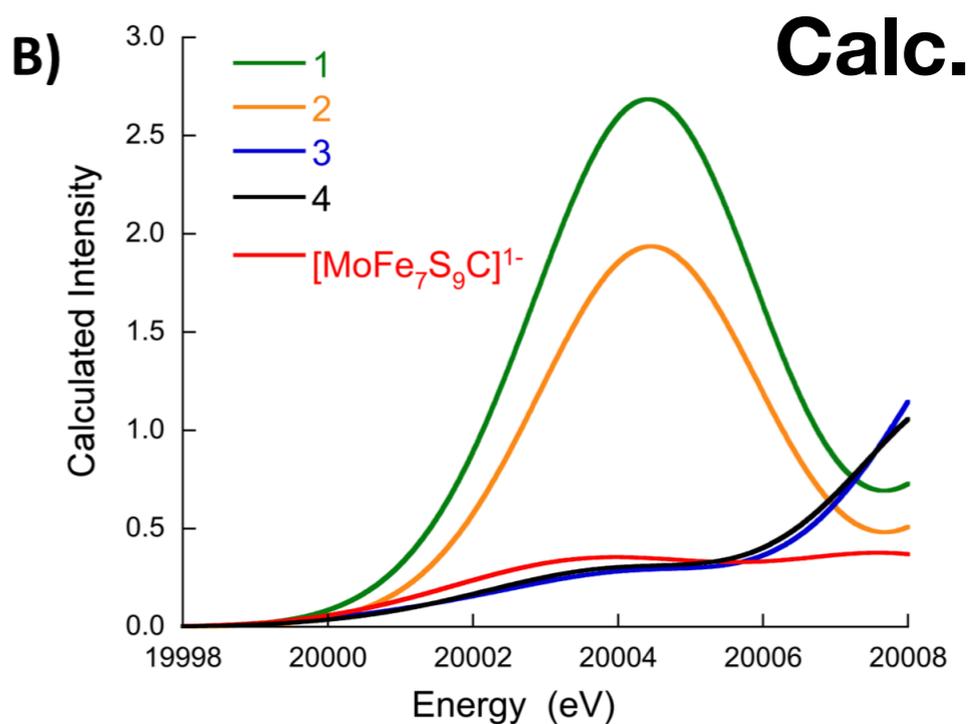
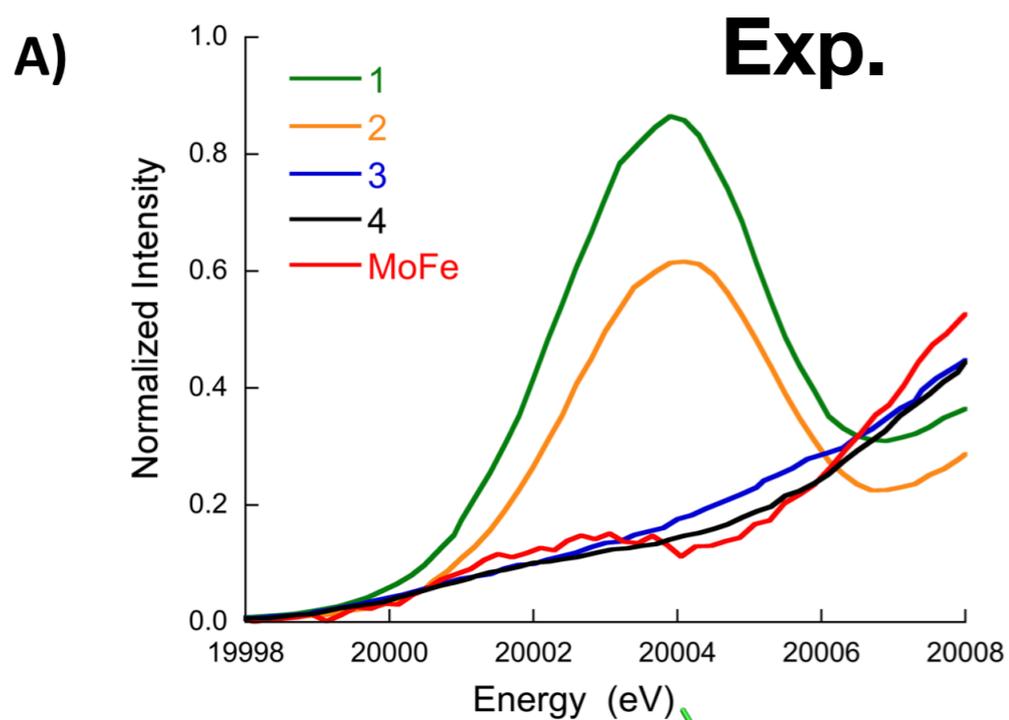
list of all states

Transition energy

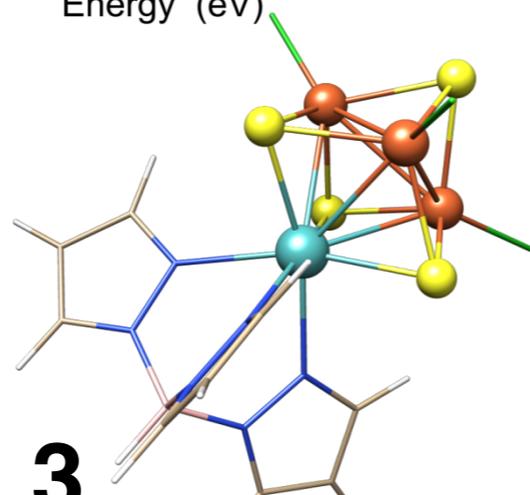
**Excitation described as an orbital excitation
from orbital 4a (HOMO) to 5a (LUMO)**

*Analysis of excited states:
difference density analysis, natural transition orbitals*

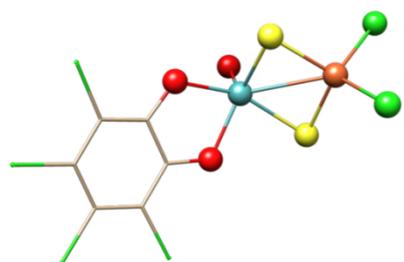
Example: TDDFT computations of molybdenum X-ray absorption spectra compared to experiment



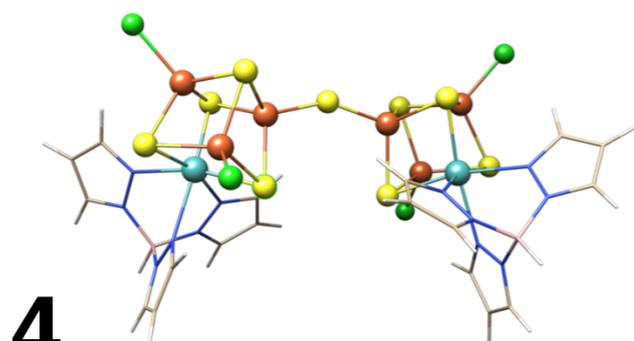
1



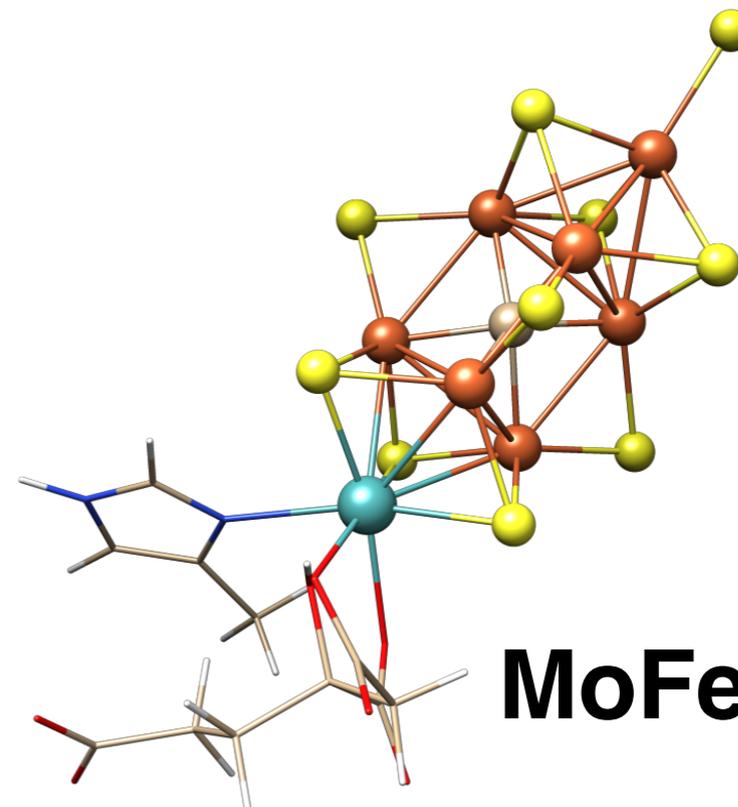
3



2



4



MoFe model

Multireference treatments

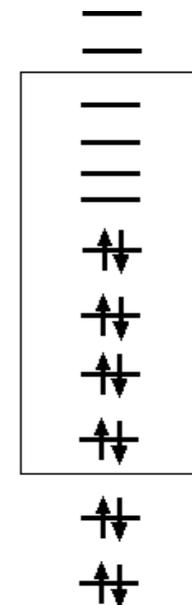
- ORCA has a state-of-the-art CASSCF module for multiconfigurational SCF.
- Dynamic correlation via NEVPT2, CASPT2, MRCI, MRCI+Q, MRCC, MREOM-CC.
- Large active space (50 orbitals) approximate CASSCF: DMRG and ICE-CI

! def2-TZVP MOREAD

```
%moinp "orbitals.gbwn"
```

Read-in carefully chosen active-space orbitals

active space



All excitations

```
%casscf
trafostep ri
nel 5
norb 4
mult 2,4
nroots 1,1
end
```

← Active space of 5 electrons in 4 orbitals CAS(5,4)

← Spin multiplicity of 2 and 4

← 1 root for mult2 and 1 root for mult4

=> State-averaged CASSCF calculations over 2 states.
Orbitals will be averaged over both states

ORCA Common Errors and Problems

- Sudden ORCA terminations:
Often due to insufficient memory or disk space. Rare with DFT, common problem with WFT calculations.
- Imaginary modes in a vibrational frequency calculation
Small frequencies: Numerical noise. Increase DFT grid or SCF/Opt thresholds
Large frequencies: Probable convergence to an n-th order saddlepoint.
- Molecule explodes during optimization: Problem with internal coords
- Energy increases during optimization: Noisy gradient (check grids)
- Strange energy or property:
possible convergence to an excited state or unstable solution
- ORCA result differs from **ProgramX** result:
 - Check functional definition (e.g. B3LYP has multiple definitions)
 - Check if basis set is the same.
 - Compare program defaults (e.g. Tamm-Dancoff approximation in TDDFT).
- SCF will not converge

VIBRATIONAL FREQUENCIES

```
-----  
0: 0.00 cm**-1  
1: 0.00 cm**-1  
2: 0.00 cm**-1  
3: 0.00 cm**-1  
4: 0.00 cm**-1  
5: 0.00 cm**-1  
6: -646.34 cm**-1 ***imaginary mode***  
7: -467.58 cm**-1 ***imaginary mode***  
8: -109.76 cm**-1 ***imaginary mode***  
9: 7.86 cm**-1
```

SCF convergence issues

- Check the basics
Are coordinates reasonable? Charge and spin multiplicity correct?
- If close to convergence, restart calculation, possibly increase MaxIter
- Try converging with a simpler method (small-basis HF or DFT) and read-in orbitals as better guess orbitals
- Change SCF algorithm or settings:
 - Turn off/on SOSCF (!SOSCF or !NOSOSCF)
 - Try KDIIS (!KDIIS)
 - Change the DIIS extrapolation settings (%scf DIISMaxEq 20 end)
 - Try adding damping or a levelshift. (%scf Shift Shift 0.1 ErrOff 0.1 end end)
 - Try Slowconv (!Slowconv)
 - Recalculate the Fock matrix more often (%scf directresetfreq 1 end)

<https://sites.google.com/site/orcainputlibrary/scf-convergence-issues>

SCF converged to something strange

- Any SCF calculation (DFT or HF) can converge to something not desirable.
 - excited state (i.e. a different occupation of orbitals)
 - saddlepoint in orbital space instead of a minimum
- Rare but happens in cases of high symmetry (e.g. atoms, diatomics, or other high-symmetry geometries, e.g. benzene and ferrocene).
- This problem can subsequently affect a post-HF calculation, e.g. MP2, coupled-cluster.

Example:

```
! B3LYP def2-TZVPP tightscf kdiis
*xyz 0 1
| 0.0 0.0 0.0
| 0.0 0.0 2.683
*
```

Will result in an SCF solution with an energy of -595.256765 hartree.

While nothing seemingly suspicious about this straightforward restricted DFT calculation, the energy is completely wrong.

SCF converged to something strange

Wrong energy

-595.256765 hartree

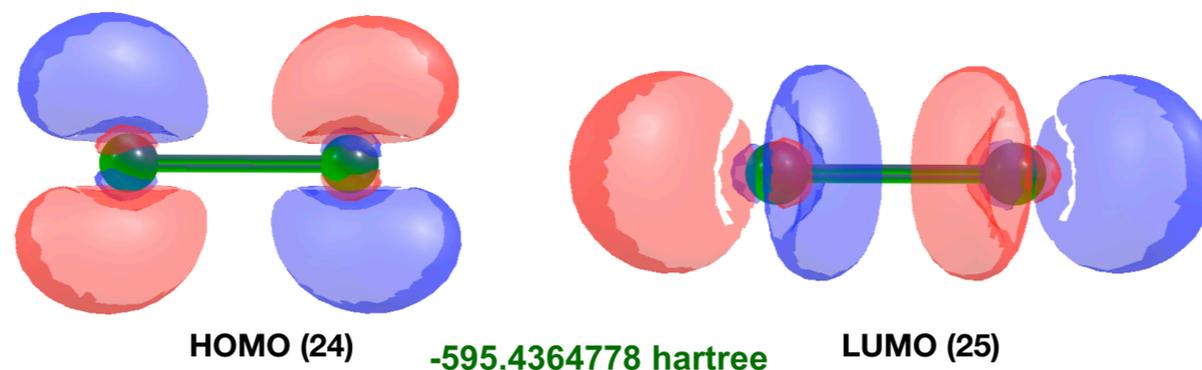
Difference of

112.8 kcal/mol or 4.9 eV

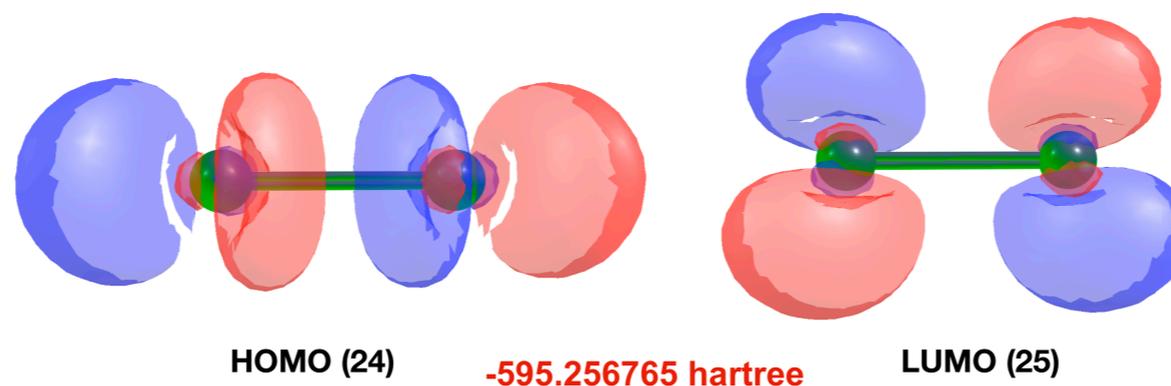
Correct energy

-595.4364778 hartree

Reason:



Swap orbitals:

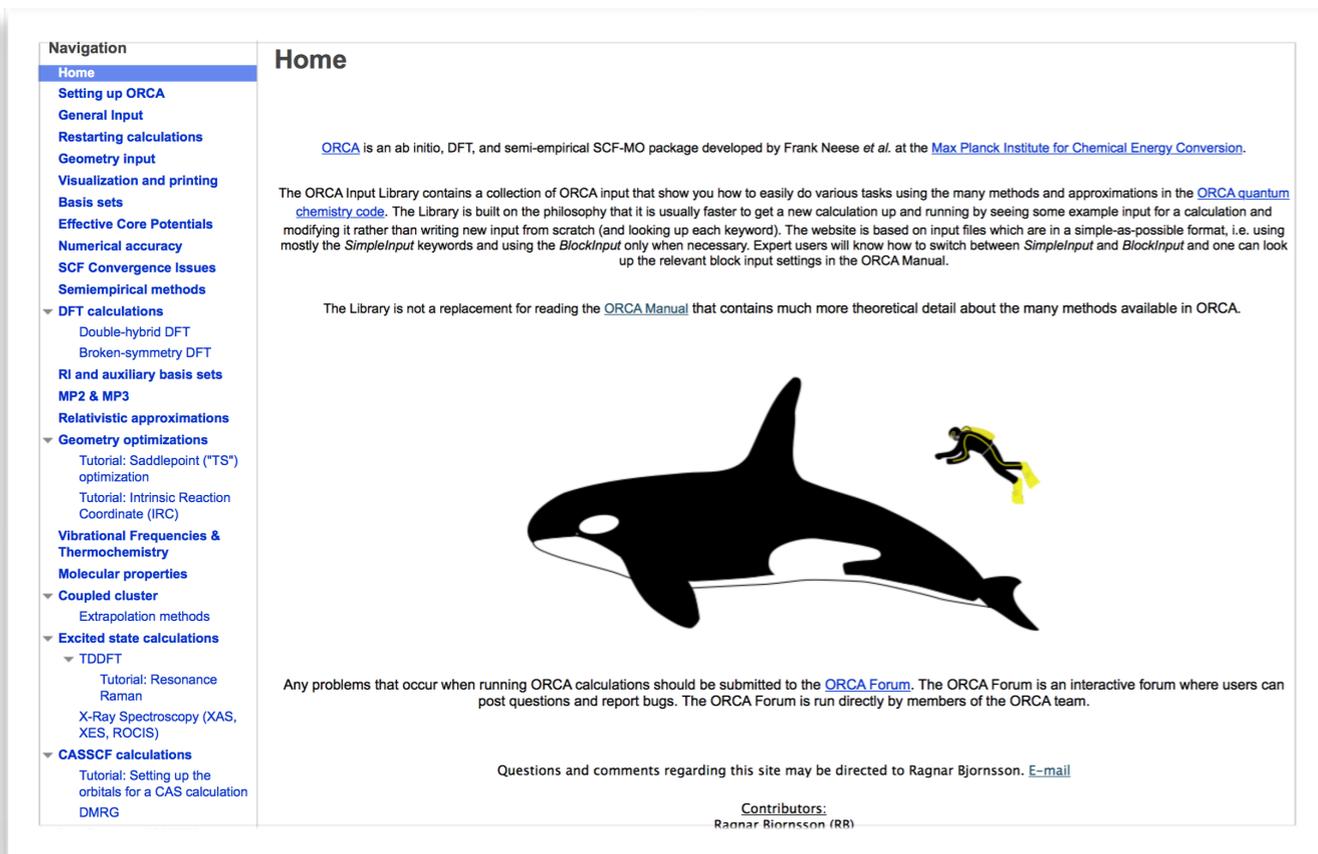


%scf
rotate {24,25,90,0,0} end
end

Stability analysis

%scf
Stabperform true
end

The ORCA Input Library

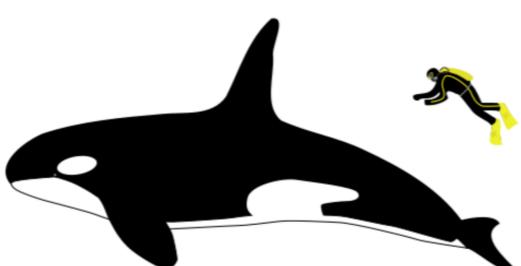


The screenshot shows the home page of the ORCA Input Library. On the left is a navigation menu with categories like 'Setting up ORCA', 'General Input', 'Restarting calculations', 'Geometry input', 'Visualization and printing', 'Basis sets', 'Effective Core Potentials', 'Numerical accuracy', 'SCF Convergence Issues', 'Semiempirical methods', 'DFT calculations', 'Geometry optimizations', 'Vibrational Frequencies & Thermochemistry', 'Molecular properties', 'Coupled cluster', 'Excited state calculations', and 'CASSCF calculations'. The main content area is titled 'Home' and contains the following text:

[ORCA](#) is an ab initio, DFT, and semi-empirical SCF-MO package developed by Frank Neese *et al.* at the [Max Planck Institute for Chemical Energy Conversion](#).

The ORCA Input Library contains a collection of ORCA input that show you how to easily do various tasks using the many methods and approximations in the [ORCA quantum chemistry code](#). The Library is built on the philosophy that it is usually faster to get a new calculation up and running by seeing some example input for a calculation and modifying it rather than writing new input from scratch (and looking up each keyword). The website is based on input files which are in a simple-as-possible format, i.e. using mostly the *SimpleInput* keywords and using the *BlockInput* only when necessary. Expert users will know how to switch between *SimpleInput* and *BlockInput* and one can look up the relevant block input settings in the ORCA Manual.

The Library is not a replacement for reading the [ORCA Manual](#) that contains much more theoretical detail about the many methods available in ORCA.



Any problems that occur when running ORCA calculations should be submitted to the [ORCA Forum](#). The ORCA Forum is an interactive forum where users can post questions and report bugs. The ORCA Forum is run directly by members of the ORCA team.

Questions and comments regarding this site may be directed to Ragnar Bjornsson. [E-mail](#)

Contributors:
Ragnar Bjornsson (RB)

A Wiki-like website for ORCA users.

Inputfile examples, tips & tricks, tutorials

<https://sites.google.com/site/orcainputlibrary>

Maintained by Ragnar Bjornsson

