X-ray Spectroscopy with ORCA

ORCA Practical Session

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Preface

Dear Participants of the CONEX Workshop 2021, welcome to the Core-level spectroscopy with quantum chemistry & hands-on: ORCA practical session!
Please find below the exercises that are aimed to help you to understand the basics of calculating Core-level spectroscopic properties and to use the ORCA program to perform these calculations and, what is more important, how to analyze its results.

ORCA is a fully parallelized, general-purpose quantum chemistry code that runs on all platforms (unix, windows, mac OS). It is based on atom centered Gaussian basis functions and can perform calculations on all elements of the periodic table (optionally with all-electron, scalar relativistic Hamiltonians or pseudopotentials). ORCA features extensive DFT capabilities (LDA, GGA, meta-GGA, hybrid, double-hybrid, range separated functionals) but is particularly powerful in the domain of wavefunction based ab initio methods (coupled-pair/coupled-cluster methods, multireference methods CASSCF/ NEVPT2/MRCI, MBPT). ORCA is an efficient code that, in conjunction with well-tested approximations (density fitting, chain-of-spheres), can be applied to systems with hundreds of atoms. Pair natural orbital (PNO) based local correlation treatments allow for correlated wavefunction calculations on large systems. Extended systems can be treated with QM/MM methods; solids and surfaces can be approached using cluster models with electrostatic embedding and capping ECPs. Geometry optimization/transition state searches using analytic gradient techniques are available and for Hartree-Fock and DFT methods analytic second derivatives are also available.
ORCA specializes on transition metals and the calculation of spectroscopic properties with an emphasis on many particle wavefunctions and wavefunction based ab initio methods. A broad range of spectroscopic parameters can be calculated with ORCA including all EPR parameters (g-tensor, hyperfine couplings, zero-field splittings, quadrupole couplings), some NMR properties (chemical shielding), Mössbauer parameters (isomer shift, quadrupole splitting), UV absorption spectra, absorption and fluorescence bandshapes using the independent mode displaced harmonic oscillator model, IR-, Raman- and resonance Raman spectra, magnetic circular dichroism spectra, X-ray absorption, X-ray emission spectra as well as RIXS spectra.

Relativistic effects can be treated with a number of approximations including the Douglas-Kroll-Hess (DKH) and 0th order regular approximation (ZORA) Hamiltonians. Picture change effects and finite nuclei can be taken into account. The treatment of spin-orbit coupling features and accurate spin-orbit meanfield approach that includes all two-electron terms and includes the important contributions form the spin-other-orbit interaction.

Valence or core excited states can be approached with a number of methods including configuration interaction singles (CIS, with doubles correction CIS(D)), time-dependent DFT with or without the Tamm-Dancoff approximation, MR-CI, MR-EOM, CASSCF/NEVPT2 and EOM-CCSD. A method specific to ORCA is the restricted open shell CI (ROCIS) approach. It is designed to provide a good balance between physical rigor and computational efficiency. It

provides many particle wavefunctions that have the correct multiplet structure (unlike TD-DFT or other particle/hole based approaches) and hence is a good basis for the treatment of spin-orbit effects using quasi-degenerate perturbation theory. It can be applied to systems with a few-hundred atoms and readily delivers a few hundred states. Hence, it is particularly useful for the calculation of core level spectra including L-edge XAS spectra. In order to account for dynamic electron correlation in a simple, average way, there is a parameterized version of the method (ROCIS/DFT) that introduces three universal scaling parameters that greatly improve the accuracy of the method in actual applications.

The ORCA hands-on tutorial is expected to familiarize the students with exercises material that involves:

1) Ground state calculations:
    Structure design
    Geometry Optimizations
    Electronic Structure Analysis
2) Excited state – Property calculations
    Metal and Ligand K-edge XAS spectra (TD-DFT)
    Metal L-edge XAS spectra (ROCIS/DFT, CASCI/NEVPT2/ MRCI)
    Metal L-edge XMCD spectra (MRCI)
    Mainline XES spectra (DFT, RASCI)

There are a few useful links:
Orca Manual: https://orcaforum.kofo.mpg.de/app.php/dlext/?view=detail&df_id=80
ORCA Forum:
https://orcaforum.kofo.mpg.de/index.php?sid=0d0e39bf0d1da37e88a8e84fcbce7dfc
ORCA Input Library: **https://sites.google.com/site/orcainputlibrary/**

We hope that you enjoy the experience of using quantum chemistry, and you continue to employ it in your science.

In the case you have questions or difficulties please don't hesitate to ask tutors at the session. If you have any questions concerning quantum chemical calculations in general or in particular to your problem you are welcome to contact users and developers via ORCA Forum (**https://orcaforum.kofo.mpg.de/index.php?sid=0d0e39bf0d1da37e88a8e84fcbce7dfc**)
Have fun!

Frank Neese, Dimitrios Manganas and the tutors of this workshop,
Anneke Dittmer, Tiago Leyser, Rami Shafei from MPI KoFo
and Sergio Jannuzzi and Derek Rice from MPI CEC

Additional Programs

This is a list of the programs that can be used to build models and visualize the results of the ORCA calculations. They are either free or have a free trial period.

Constructing molecules: Avogadro, Chemcraft, Molden
Plotting isosurfaces and structures: Avogadro, Chemcraft, Molden, VMD, Chimera

Proposed by the ORCA team

Avogadro (**https://orcaforum.kofo.mpg.de/app.php/dlext/?cat=7, http://avogadro.cc**)
free, works on Windows, Linux, OS X.

Other possibilities

USCF Chimera (**https://www.cgl.ucsf.edu/chimera/**)

Chemcraft (**http://www.chemcraftprog.com**)
180 day trial period and reduced freeware, works on Windows, Linux, and on Mac via the Wine app.

Molden (**http://www.cmbi.ru.nl/molden**)
free, works on Windows, Linux, OS X.

VMD (**http://www.ks.uiuc.edu/Research/vmd**)
free, works on Windows, Linux, OS X.

Energy Conversions and Constants

If not stated otherwise, ORCA uses atomic units. This means that the unit of energy is Hartree (E_h) and the unit of length is Bohr radius (a_0). The following conversion factors to other common units and constants might be useful:

1 E_h = 27.21138 eV = 2625.50 kJ mol^{-1} = 627.5095 kcal mol^{-1}
1 E_h / hc = 219474.6317 cm^{-1}
1 eV = 8065.54477 cm^{-1} = 23.0605 kcal mol^{-1}
1 cm^{-1} = 29979.2458 MHz

N_A = 6.0221415 10^{23} mol^{-1}
k_B = 1.38065 10^{-23} J K^{-1}
c = 2.99792458 10^8 m s^{-1}
h = 6.62607 10^{-34} J s

Command Line Tools (Linux, Mac)

pwd	prints the current working directory and its path
cd name	switches directory to name
ls	list all files in the current directory
mkdir name	creates and directory called name
rmdir name	deletes directory called name
cp file1 file2	copies file1 to file2
cp –r directory1 directory2	copy directories
rm file1	deletes file1
grep string1 file1	searches for string1 in document file1
ssh username@computer.com	login to remote computer

Command Line Tools Windows

To start the most basic Windows command line, you need to run the program cmd.exe. Alternatives exist, but are not covered here. Running cmd.exe can be done by pressing the "windows key" + "r" and entering "cmd" in the small window that opens. It may also be sensible to create a desktop shortcut to this program.

cd	prints the current working directory and its path
cd name	switches directory to name
dir	list all files in the current directory
md name	creates a directory called name
rd name	deletes empty directory called name
copy file1 file2	copies file1 to file2
del file1	deletes file1
find string1 file1	searches for string1 in document file1
type file1 | more	display text file file1 page by page. Press Enter to continue
cls	clear the screen
help	list commands. If argument is given, list help on that command
exit	close the window

Checks

ORCA runs on the CONEXS provided Cluster

Please Follow the CONEXS Organizers Instructions!

ORCA runs on a Personal Computer

For Linux/Mac:

Probably, you will need to include ORCA into the system PATH when you run calculation on your own computer. If ORCA is located in **/usr/bin/orca**, the command would be **export PATH=/usr/bin/orca:$PATH**. Thereafter, you can call ORCA in all the folders until you close the shell.

For Windows:

If ORCA does not work right away, the first thing to do is to check the PATH variable, which will tell the computer in which directories to look for programs, called through the command line. The command set PATH will display the current path. If the ORCA directory is not included, the command set **PATH=%PATH%;F:/directory1** will change the variable to include the directory "directory1" on drive F. Thereafter, you can call ORCA in all the folders until you close the window. If you have administrator rights on your machine, a permanent

solution is possible: **right-click My Computer → Properties → Advanced → Environment Variables. Do not forget the semicolon.**

ORCA requires a text file as input. There can be tremendous amount of output so pipe it (with >) into an output file: **orca myinput.inp > myinput.out &**

Minimal input requires some information about the basis, the method and details on the molecules (geometry, charge and multiplicity). Basis and methods can be specified with keywords in an exclamation line.

```
! B3LYP def2-SVP     # theoretical method
*xyz 0 1             # coordinates type, charge, multiplicity
```

The geometry can be specified in a block starting with asterisk (*). Allowed formats are Cartesian coordinates or internal coordinates. If not otherwise specified, ORCA assumes Angstrom as units of distance in the geometry block.

```
C 0 0 0
C 0 1.1 2.3
…
*
```

Comments start with a hash sign (#). This minimal type of input should be enough to get us started. More refined options and keywords are documented in the manual. An electronic copy of it should be found in the workshop's common directory.