

**MPI for Chemical Energy Conversion**

Mülheim an der Ruhr, Germany



# **X-ray Spectra with ORCA**

**Computer Exercises**

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## Preface

Dear Participants of the EWinS 2016 (**Winter School on core level spectroscopies**), 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 approximation 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 from 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, CASSCF/NEVPT2 and EOM-CCSD. A method specific to ORCA is the restricted open shell CI (ROCI) 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 8 hours Orca hands-on tutorial is expected to familiarize the students with exercises material that involves:

- 1) Ground state calculations:
  - Structure design
  - Geometry Optimizations
- 2) Excited state – Property calculations
  - Metal and Ligand K-edge XAS spectra (TD-DFT)
  - Metal L-edge XAS spectra (ROCIS/DFT)
  - Valence to Core XES spectra (DFT, RASCI)

There are a few useful links:

ORCA Manual (<http://www.cec.mpg.de/forum/OrcaManual.pdf>)

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 (<http://cec.mpg.de/forum>)

Have fun!

Frank Neese, Serena DeBeer and the tutors of this workshop,  
Dimitrios Manganas, Benjamin Van Kuiken, George Gutsail.

## 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 (<http://cec.mpg.de/forum>, <http://avogadro.cc>)

free, works on Windows, Linux, OS X.

Other possibilities

USCF Chimera (<http://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:

$$1 E_h = 27.21138 \text{ eV} = 2625.50 \text{ kJ mol}^{-1} = 627.5095 \text{ kcal mol}^{-1}$$

$$1 E_h / hc = 219474.6317 \text{ cm}^{-1}$$

$$1 \text{ eV} = 8065.54477 \text{ cm}^{-1} = 23.0605 \text{ kcal mol}^{-1}$$

$$1 \text{ cm}^{-1} = 29979.2458 \text{ MHz}$$

$$N_A = 6.0221415 \cdot 10^{23} \text{ mol}^{-1}$$

$$k_B = 1.38065 \cdot 10^{-23} \text{ J K}^{-1}$$

$$c = 2.99792458 \cdot 10^8 \text{ m s}^{-1}$$

$$h = 6.62607 \cdot 10^{-34} \text{ J s}$$

## Command Line Tools (Linux, Mac)

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

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

## Checks

### 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.



## Exercise 1: Electronic Structure of Iron Chlorides

### A) Overview

Calculation of spectroscopic properties by quantum chemical methods always requires one to properly set up the chemical system. One must build a molecular model, optimize its geometry, and analyze its geometric and electronic structure to verify. During this process important choices must be made regarding the choice of methods and basis sets. In this exercise, you will use quantum chemistry to predict the geometric structure and vibrational frequencies of iron chloride complexes. After you have computed structural properties you will examine the Mulliken/Löwdin population analysis to identify the important molecular orbitals (i.e. the Fe d orbitals). Finally, you will use a molecular viewer to plot selected molecular orbitals

### B) Model Construction, Geometry Optimization, and Vibrational Frequencies

Use a molecular editor of your choice (or a bit of trigonometry) to prepare the tetrahedral  $[\text{FeCl}_4]^{3-}$  anion and save this as a .xyz file. The .xyz file format is a simple plain text coordinate file, and it has the advantage of being compatible with most molecular editors and viewers. The .xyz for water is given with the following syntax:

```
3
O  x1 y1 z1
H  x2 y2 z2
H  x3 y3 z3
```

The coordinates should be in the units of angstrom. It is important to construct a realistic geometry. Starting with a poor geometry can result lead to convergence problems in both the SCF and geometry optimization. After constructing the model for  $[\text{FeCl}_4]^{1-}$ , repeat the process building a structure for octahedral  $[\text{FeCl}_6]^{3-}$ .

The next step is to use ORCA to optimize the geometry of these models. All ORCA inputs require that you choose a computational method and basis set. For these exercises we will use density functional theory (DFT). DFT typically gives reasonable geometric structures of transition metal complexes at a modest computational cost. When investigating large molecules involving transition metals, DFT is usually the only reasonable choice An example input is given below:

```
! UKS BP86 def2-TZVP def2-TZV/J Opt
```

```
* xyzfile -1 6 fecl4.xyz
```

Notes on input:

- **UKS:** This specifies that the calculation should be carried out as an unrestricted Kohn-Sham type. This is also the default wave function for an open shell molecule.
- **BP86:** This is the exchange--correlation functional for the calculations. It is comprised of the Becke exchange functional from 1988 and the Perdew correlation functional from 1986. These functionals are constructed at the level of the generalized gradient approximation (GGA)
- **Basis Sets:** The suggested input uses a triple- $\zeta$  basis set (def2-TZVP) which is large enough for most situations. Additionally, the auxiliary basis set (def2-TZV/J) is specified. This is used to speed up the calculation of 2-electron integrals.
- **Opt:** This keyword specifies that the job is a geometry optimization.
- **Molecule Specification:** This section of the input specifies that the geometry should be read from the file fecl4.xyz, and it indicates that this molecule has a charge of -1 and a multiplicity of 6.

Now perform the geometry optimization on  $[\text{FeCl}_4]^{1-}$ . When the calculation finishes, check to see if it finished properly. Open the output file with a text editor of your choice. The end of the output file should read “**ORCA TERMINATED NORMALLY**”. Did the geometry optimization converge? Search for the word “**HURRAY**”? How many iterations were required for the geometry optimization? Next, you should use a viewer to look the optimized structure found in [jobname].xyz. Does the optimized structure conform to what you expected? Repeat the optimization for  $[\text{FeCl}_6]^{3-}$ .

The next task will be to analyze the computed structure to determine test the geometry has been optimized to a minimum on its potential energy surface. The standard procedure for determining whether an optimization has found a minimum is to calculate the second derivatives (Hessian) of the wave function with respect to the position of the atoms. These second derivatives are related to the vibrational frequencies, so a frequency calculation is performed. This is a straightforward calculation. It can easily be carried out by replacing **! Opt** in the optimization input by the directive **! Freq** and by using the optimized geometry.

When the frequency calculations finish make sure that your calculation has completed and search for “**VIBRATIONAL FREQUENCIES**” in the output file. How many modes are there? Is this what you expect? Do you have any negative frequencies? If you are interested in the IR intensities, you can scroll down to “**IR SPECTRUM**”. Sometimes it can happen that you have

an appropriate geometry, but you find that there are modes with imaginary (negative) frequencies. This can often be due to numerical issues that can be resolved by increasing tolerances on your calculations. You can try some combination of the following keywords to re-optimize the geometry and re-compute the frequencies:

```
! TightOpt # Request high Geometry Optimization Convergence
! TightSCF # Request high SCF convergence
! Grid4 NoFinalGrid # Use a dense integration grid for the calculation DFT exchange and correlation
```

In many cases it is useful to visualize the vibrational normal modes to assign spectra. For this purpose open the output file in Avogadro. The each normal mode is listed on the right, and the mode can be visualized by selecting a mode and pressing the “Start Animation” button.

### *C) Population and Orbital Analysis*

In order to perform and interpret the calculated X-ray spectra, some knowledge of the ground state wave function is required. For this purpose run an additional single point calculation that includes the directive **! LargePrint**. This will print the orbitals, basis set, and additional population analysis. Typically one should be careful using this option because it can create very large output files (especially in the case of optimizations).

For X-ray spectra it is typical that you need to identify specific core orbitals. The easiest way to identify orbitals of interests is to look at the population analysis of the SCF wave function. First, the use of the **! LargePrint** keyword will generate both Löwdin and Mulliken population analyses. ORCA includes a useful form population analysis listed called “reduced orbital populations”, which are a percentage of the contribution of each basis function type to each MO. This makes identifying the character of each MO much simpler. Let’s start by identifying core orbitals of interest. In the upcoming exercises, you will be looking at Fe and Cl K-edges and Fe L-edges. Begin by searching the output for “**REDUCED ORBITAL POPULATIONS**”. This should find the Löwdin reduced orbital populations per MO. Can you identify the Fe and Cl 1s orbitals in  $[\text{FeCl}_4]^{1-}$  and  $[\text{FeCl}_6]^{3-}$ ? What do you notice about the Cl 1s orbitals? Given your knowledge of X-ray spectroscopy, do the orbital energies make sense to you?

While core orbitals are typically easy to identify, figuring out the character of valence orbitals can be significantly more difficult. For both complexes, what is the character of the highest occupied MO? Now try to find the Fe 3d orbitals. For valence orbitals there are often many different contributions to a particular orbital, and it is useful to visualize the MOs with a molecular viewer. For this purpose we recommend the use of Avogadro. When **! LargePrint** is used, opening the output files with Avogadro gives direct access to the MOs. Plot the occupied

3d orbitals. Remember ORCA is always 0 indexed, but Avogadro starts counting at 1. What do notice about these orbitals? What is the difference between  $[\text{FeCl}_4]^{1-}$  and  $[\text{FeCl}_6]^{3-}$ ? Note, that it is generally possible to plot orbitals using any visualizer, and it is possible to plot the orbitals from any calculation for which you have a .gbw file. This can be done using the **orca\_plot** utility to generate a .cube file, and it is described in the orca manual.

## Exercise 2: TDDFT Fe and Cl K-edge XAS

### *A) Background*

The calculation process of an X-ray absorption spectrum is similar to that of an optical absorption spectrum, and the typical approaches that are used to calculate UV/Vis excitation energies and transition strengths may be applied for XAS. However, for X-ray absorption, high-energy incident radiation excites core-electrons as opposed to lower-energy valence electrons in UV/Vis absorption spectroscopy, and before starting calculations, one must consider the nature of these core-level excitations. It is convenient to classify the nature of the final states in XAS with regions of the X-ray spectrum.

These regions are traditionally referred to as the XANES (or NEXAFS) and EXAFS regions. The EXAFS region contains transitions to unbound states that report on the geometric structure around the absorber. On the other hand, the XANES region, divided into pre-edge and rising-edge, contains electronic structure information. The pre-edge contains transitions from the 1s core to lowest lying acceptor orbitals. In the case of transition metals, the pre-edges are comprised of transitions from the 1s to the unoccupied 3d orbitals. The rising-edge region contains 1s  $\rightarrow$  *np* transitions mixed with transitions to Rydberg states and many-electron processes (i.e. shakedown).

In this exercise you will apply TDDFT to calculate the pre-edge region of Fe K-edge and Cl K-edge XAS. There are several reasons for focusing on the pre-edge region. In the case of metal K-edges, the pre-edge is dominated by 1s  $\rightarrow$  *nd* transitions. The excitation energies and intensity distributions report directly on the d-electron configuration and ligand environment. In the case of Cl K-edge can be used to investigate metal—ligand covalency in transition metal complexes. While there is certainly interesting chemical information contained in the rising-edge region, the use of finite basis sets and presence of many-electron processes complicates the application of TDDFT to this region.

The calculation of K-edge pre-edge absorption spectra by TD-DFT is fairly straightforward; however, it is important to carefully consider the transition moments. Due to the short wavelengths of X-ray radiation, the dipole approximation begins to break down, and one must consider quadrupole and magnetic dipole contributions to the spectrum. This is particularly important for pre-edges of transition metal compounds where 1s  $\rightarrow$  3d are dipole forbidden for octahedral complexes and pre-edge intensity arises from quadrupole contributions. Consequently, ORCA contains the ability to include 1<sup>st</sup>-order intensity contributions from the

multipole expansion instead of just the 0-order term (dipole). The total oscillator strength is given by

$$f = f_D + f_M + f_Q$$

$$f_D = \frac{2m_e}{3\hbar^2 e^2} E_{if} |\overrightarrow{D}_{if}|^2$$

$$f_M = \frac{2m_e}{3\hbar^2 e^2} E_{if} |\overrightarrow{M}_{if}|^2$$

$$f_Q = \frac{m_e}{20\hbar^4 e^2 c^2} E_{if}^3 \sum_{a,b} |(Q_{ab})_{if}|^2$$

Where  $f_D$ ,  $f_M$ , and  $f_Q$  are dipole, magnetic dipole and quadrupole terms, respectively.

The last ingredient required to perform a TDDFT calculation of XAS is to choose a clever way to solve the TDDFT eigenvalue problem. In typical implementations of TDDFT selects the number of roots (excitations) that are desired, and the solver finds this many excitations beginning with the lowest energy. This is problematic for X-ray calculations because one would have to calculate an unreasonably large number of roots to get an X-ray spectrum from a standard TDDFT implementation. Consequently, ORCA makes use of an orbital window, which defines the donor and acceptor spaces in terms of molecular orbital number. To perform X-ray calculations users place only the relevant core orbitals in the donor space.

### **B) Metal K-edge XAS**

Perform TDDFT calculations to calculate the pre-edge of  $[\text{FeCl}_4]^{1-}$  and  $[\text{FeCl}_6]^{3-}$  using the geometries that you optimized in the first exercise. Inputs similar to the inputs in Exercise 1 maybe be used with the addition of a **%tddft** block. A partially completed block is given below. Look up how to complete the **OrbWin** keyword in the manual.

```
%tddft NRoots      40
        MaxDim     400
        OrbWin[0] = ...
        OrbWin[1] = ...
        DoQuad     True
        TDA        True
        end
```

## Notes on Input:

- **NRoots**: Number of excitations to be computed.
- **MaxDim**: Maximum size of the expansion space used by the solver. Typically, MaxDim should be between 5 and 10 times the number of excitations.
- **OrbWin**: This argument takes four numbers separated by commas (i.e. 5, 10, -1, -1) where the first two numbers define the range of donor orbitals, and the last two are the range of acceptor orbitals. Using -1 indicates that the whole acceptor space is used in the calculation. Determine the numbers you should use in your calculations. OrbWin[0] and OrbWin[1] refer to the alpha and beta orbitals, respectively.
- **DoQuad**: Requests calculation of transition quadrupole moments.
- **TDA**: This requests the use of the Tamm-Dancoff approximation to the full linear response formalism of TDDFT. It is worth noting that this is a very good approximation for calculations of X-ray spectra. This is also the default mode if hybrid functionals (those including HF exchange) are used in the calculation. Consequently, comparisons between pure DFT functionals (BP86, BLYP, PW91, etc.) and hybrid functionals (B3LYP, PBE0, TPSSh, etc.) should be carried out at the TDA level. Future versions of ORCA will include full TDDFT response for hybrid functionals.

There are several other keywords that are useful for X-ray calculations. Firstly, anions are commonly unstable (due to the fact that the highest lying MO's have positive orbital eigenvalues) when counter-ions are not included in calculations, and including counter ions is often not practical. The passivation of excess charge may be achieved by using a solvent model. For this purpose ORCA includes the COSMO model, which is invoked by the **! COSMO** directive. Secondly, while spin—coupling does not play a significant role in K-edge spectra, scalar relativistic effects can be significant, and they can be accounted for by including either **! ZORA** or **! DKH**. More information regarding solvent models and relativistic effects can be found in the manual.

When the calculation has finished, confirm that it has finished correctly: (1) make sure that the SCF converged (2) verify that orca terminated correctly. Now look for the output from the TDDFT calculation. The origin adjusted transition energies and intensities are given following this header:

```
-----  
COMBINED ELECTRIC DIPOLE + MAGNETIC DIPOLE + ELECTRIC QUADRUPOLE SPECTRUM (origin adjusted)  
-----  
State  Energy Wavelength  D2      M2      Q2      D2+M2+Q2  D2/TOT  M2/TOT  Q2/TOT  
      (cm-1)  (nm)                (*1e6)  (*1e6)  
-----
```

The details of the individual roots can be found above, where each root is listed with its excitation energy and the dominant components of its transition vector.

The first step of analyzing the simulated X-ray spectrum is to visualize it. For this purpose ORCA is packaged with the **orca\_mapspc** utility that generates spectra from the orca output, and saves them as easy to plot ascii files. An example of how to generate plots for your spectrum is as follows:

```
orca_mapspc my_xas.out ABSQ -eV -07000 -17100 -n500 -w1.0
```

All of the orca\_mapspc options may be seen by typing orca\_mapspc at the command line with no arguments. Here, we are generating the absorption spectrum with quadrupole contributions (**ABSQ**), in the units of eV (**-eV**) over a selected range (**-x0####** to **-x1####**) with 500 points (**-n###**) and a Gaussian linewidth (full-width-at-half-maximum) of 1 eV (**-w##**). The above command will generate two files. The first file is a .dat file that contains the XA spectrum where the transitions have been convoluted with Gaussian functions with a full-width-at-half-maximum of 1.0 eV. The second file is a .stk file that contains the energies of the individual transitions along with their intensities. After you have generated these file, plot the spectra in your favorite plotting program (MATLAB, gnuplot, Origin, Excel, etc.). For this purpose you may have to transfer the files to your own computer. Alternatively, you could use gnuplot, octave or Grace, all of which are available on Rhea.

### Analysis

Now that you have plotted the spectra, what do you see? The lowest energy transitions should be the pre-edge. How many features do you expect? How many are there? Consider the 3d orbital occupations and energetic arrangement from Group Theory to make your predictions.

Do the energies match what you expect to observed experimentally? If not, are they too high or low? Various functions and methods, including relativistic effects and solvation models affect the calculated pre-edge energy. It has been observed previously that a linear correlation is achieved for experimental and calculated pre-edge energies and only an energy shift, depending on the method, is necessary to achieve proper reproduction of experimental values. Therefore, it is necessary to calibrate TDDFT calculations to experimental observables for each edge of interest.<sup>1</sup>

There are several ways to obtain a qualitative understanding of the transitions. Firstly, identify the most intense transitions in the pre-edge region, and then examine the transition vectors for

---

<sup>1</sup> See: S. DeBeer George, T. Petrenko, F. Neese, "Prediction of iron K-edge absorption spectra



these transitions. Is there a dominant component? For example, a transition has single donor-acceptor pair that is greater than 90% indicates that the transition is dominated by one singly-excited determinant.

The individual excited states may be comprised of a single molecular orbital transition or many. This is denoted in the output as ‘##a/b -> ##a/b’, where ‘a’ and ‘b’ denote alpha and beta spin, respectively. As we performing a K-edge calculation, the initial state is always 0a/b. Once you determine which transitions are of interest, their composition may be determined from the “**REDUCED ORBITAL POPULATIONS.**” Be sure to look at the correct set, either “**SPIN UP**” or “**SPIN DOWN.**”

Useful output search keywords:

“LOEWDIN REDUCED ORBITAL POPULATIONS PER MO”

“TD-DFT/TDA EXCITED STATES”

“COMBINED ELECTRIC DIPOLE + MAGNETIC DIPOLE + ELECTRIC QUADRUPOLE SPECTRUM”

Plot the acceptor orbitals that dominate the important transitions in your spectra using Avogadro. Are these orbitals what you expected?

A second way to examine transitions is to plot difference densities. These are useful for visualizing transitions where multiple acceptor orbitals contribute to the excited state. This is especially useful when using hybrid functionals because the core-excited states typically contain contributions from several acceptor orbitals. For this purpose, use the `orca_plot` utility. This program is invoked by typing

```
orca_plot my_xas.gbw -i
```

at the terminal. This program allows you to interactively generate files for plotting surfaces. First select “Gaussian cube” as the output format. Choose to plot TDDFT/CIS Difference Densities, and enter the excited states of interest. The difference density is defined by the following equation:

$$\Delta\rho = \rho_{excited\ state} - \rho_{ground\ state}$$

Since the negative part of the difference density lies at the core of the absorber, the positive part gives some indication of the spatial distribution of the core-excited electron.

Finally, compare the spectra of  $[\text{FeCl}_4]^{1-}$  and  $[\text{FeCl}_6]^{3-}$ . How do the intensities differ? Compare dipole and quadrupole contributions to the spectra. What conclusions can be drawn about the metal—ligand bonding based on the energies and intensities of the pre-edge transitions? Some of the observations made in Exercise 1 could be helpful in analyzing these results.

*OPTIONAL:* An additional useful tool for analyzing transitions is to use natural transition orbitals (NTOs). ORCA can generate a set of NTOs, but it is required to redo the TDDFT calculation for this. While the theory behind NTO is a bit technical,<sup>2</sup> they provide a set of orbitals that has been broken donor-acceptor pairs weighted by their contribution to the transition. Choose a few transitions of interest from one of your calculations and add the following lines to the `%tddft` block of the input:

```
DoNTO    true
NTOSTates 1, 3, 4
```

This would generate a .nto file containing for each of the transitions. When you search for “**NATURAL TRANSITION ORBITALS**”, you will find the name of the .nto file that contains the orbitals, and there will be a list of the important NTOs.

### C) Cl K-edge XAS

Now calculate Cl K-edge XAS. In these compounds there are multiple symmetry equivalent Cl atoms, and in many cases the 1s orbitals will be delocalize. However, the core-hole created by X-ray radiation is localized to a single atom. To ensure that your DFT calculations truly mimic the physics, you first must localize the 1s orbitals. This is achieved by modifying the `%tddft` input block as follows:

```
%tddft NRoots    40
        MaxDim    400
        OrbWin[0] = ...
        OrbWin[1] = ...
        XASLoc[0] = Orb_Start, Orb_End
        XASLoc[1] = Orb_Start, Orb_End
        DoQuad    True
        TDA       True
end
```

In this input *Orb\_Start* and *Orb\_End* are the indexes the range of orbitals that you want to localize. Finally, the calculation may be carried out for single symmetry equivalent Cl atom, so only one orbital is required in the donor space.

---

<sup>2</sup>Martin, R. L., “Natural transition orbitals.” *J. Chem. Phys.* **2003**, 118, 4775.

### Analysis

Now, compare the results for  $[\text{FeCl}_4]^{1-}$  and  $[\text{FeCl}_6]^{3-}$ . What conclusions can you draw about metal—ligand covalency from these results? How do these conclusions relate to the Fe K-edge spectra?

Can you determine the amount of metal-ligand covalency? For a  $d^9$  metal center, this is very straight forward as the only possible final electronic configuration is  $d^{10}$ . However, for metal centers with multiple d holes, several final electronic configurations may exist for the  $dn+1$  state, giving rise to a multiplet structure. To extract information about metal-ligand covalency, the intensity of the pre-edge transition of  $d^n$  and  $d^{n+1}$  state (where  $1 > n > 9$ ) must be relation to the amount of ligand 3p (for Cl) in the one-electron  $t_2$  and e orbitals. Will Fe(II) tetrachloride be more or less covalent than Fe(III)?

## DAY 2

### Exercise 3: ROCIS Calculation of L-edge XAS

#### A) Overview

L-edge XAS is an important technique for understanding the electronic structure of transition metal complexes. L-edge absorption spectra make use of the dipole allowed nature of the  $2p \rightarrow nd$  transitions to directly probe the d orbitals of transition metals. While L-edge XAS can be a powerful and direct approach for investigating the bonding in transition metal complexes, several strong atomic effects complicate the interpretation of the measurements. Firstly, large 2p spin-orbit coupling (SOC) splits the L-edge into  $L_{3-}$  and  $L_{2-}$  edges. This enables contributions to the L-edges from transitions that are spin-forbidden in the non-relativistic limit. Consequently, any realistic simulation of the L-edge XAS spectra must include SOC. Secondly, in the case of 3d transition metals, the overlap between the 2p and 3d orbitals results in strong 2p3d exchange interaction that give the L-edges of 3d transition metals a rich multiplet structure.

With the goal of accounting for both of these interactions while using a quantum chemical method that is applicable to large chemical and materials systems, the ORCA team has recently developed the restricted-open-shell configuration interaction singles (ROCIS) method. Within this approach, all possible spin-adapted configurations resulting from the single excitation of 2p electrons are used as a basis for calculation of 2p excited states. Once these excited states have been determined, they are allowed to interact via SOC.

While the ROCIS treatment rigorously generates the multiplet structure required to calculate L-edge spectra, it is based on a Hartree-Fock reference determinant, and it is well-known that HF theory poorly describes transition metal bonding due to a lack of dynamic electron correlation. To remedy this problem the DFT/ROCIS methodology have been developed. This approach combines DFT orbitals with a CI treatment of the excited states.

#### B) DFT/ROCIS Calculation Fe L-edges

Proceed with the calculation of the L-edge spectra for  $[\text{FeCl}_4]^{1-}$ . An example input block for ROCIS is given here

```
! def2-TZVP def2-TZVP/J grid4 NoFinaGrid
#ROKS B3LYP transfer this in the command line to perform a DFT/ROCIS

! Grid4 NoFinalGrid
```

```

%maxcore 4000

%rocis NRoots 30
  MaxDim 300
  maxcore 4000
  DoQuad true
  DoRI true
  SOC true
  OrbWin = 6, 8, 0, 2000
  DoLowerMult True
  PrintLevel 3
  DoDFTCIS true #quote this out for pure ROCIS calculation
  DFTCIS_c = 0.18, 0.20, 0.40 #quote this out for pure ROCIS calculation
  MaxIter 200
end

* xyzfile -1 6 fecl4-opt.xyz

```

Notes on Input:

- **ROKS**: It is instructive but not strictly required to use a restricted reference for the ROCIS method (**UKS** can be used as well). Be sure to check that the SCF converges.
- **DFTCIS\_c**: Coefficients used for scaling when ROCIS is combined with DFT orbitals.
- **DoLowerMult**: Requests that the excited states of lower multiplicity are also computed. This is important given the presence of SOC. Note that in some cases DoHigherMult is also important.

The results of ROCIS or DFT-ROCIS calculations can be plotted using the orca\_mapspc. To instruct orca\_mapspc to extract the spectrum including SOC use **SOCABS**.

### ROCIS vs DFT-ROCIS

Perform the ROCIS and DFT/ROCIS calculations, plot the spectra and observed the differences. User orca\_mapspc and plot the 3d orbitals of the two calculations. Can you relate what you see to the actual calculated spectra?

### Influence of relativity (DKH, ZORA)

Perform the DFT-ROCIS calculations accounting for relativistic corrections through DKH and ZORA hamiltonians. Compare the DFT/ROCIS spectrum with the respective DFT/ROCIS + ZORA and DFT/ROCIS + DKH ones. Can you discuss the observed differences?

*[FeCl<sub>4</sub>]I<sup>-</sup> vs [FeCl<sub>6</sub>]<sup>3-</sup>*

Now repeat the calculation for [FeCl<sub>6</sub>]<sup>3-</sup>. In the case of the octahedral complex, you may encounter convergence problems in the SCF. One approach to solve this problem is to start your SCF with a good guess for the starting orbitals. A good set of orbitals is often the quasi-restricted orbitals from a unrestricted DFT calculation. These orbitals can be generated by performing a single-point calculation including the keyword **! UNO**.

### Analysis

Upon plotting the spectra identify the two absorption edges (L<sub>3</sub> and L<sub>2</sub>). Do the intensity ratios of the edges make sense? Focusing on the L<sub>3</sub>-edge Do you observe a splitting in the features. Can you relate this splitting to what you know about the differences between octahedral and tetrahedral ligand fields. Lastly, note the significance of quadrupole transitions in these spectra? Do you think that you typically require the **DoQuad** keyword?

## Exercise 4: X-ray Emission Mainlines (Tutorial): The RAS-CI calculation protocol for XES spectra. The Fe<sup>(II)</sup>Cl<sub>6</sub> case study

### A) Geometry Optimization

Use the following input and perform a geometry optimization on the Fe<sup>(II)</sup>Cl<sub>6</sub>

```
! UKS BP86 def2-TZVP def2-TZV/J TightSCF SlowConv SCFConv7 COSMO ZORA
! Grid4 NoFinalGrid Normalprint
! OPT
%scf
MaxIter 500
end
%maxcore 1024
%method SpecialGridAtoms 26
SpecialGridIntAcc 7
end

* xyzfile -2 5 FeCl6_opt.xyz
```

### B) Generate the Quasi Restricted Orbitals

1) Use the following input (**FeCl6\_qro.inp**) to generate the quasi-restricted orbitals FeCl6\_qro.qro

```
! UKS BP86 def2-TZVP def2-TZV/J TightSCF SlowConv SCFConv7 COSMO ZORA UNO
! Grid4 NoFinalGrid Normalprint
%scf
MaxIter 500
end
%maxcore 1024
%method SpecialGridAtoms 26
SpecialGridIntAcc 7
End

* xyzfile -3 6 FeCl6_opt.xyz
```

1) Realize the meaning of the Quasi-Restricted orbitals.

Search the FeCl6\_gro.out for the HEADER:

\*\*\*Quasi-Restricted Orbitals were saved in FeCl6\_gro.qro\*\*\*

Orbital Energies of Quasi-Restricted MO's

```
0( 2) : -259.538124 a.u. -7062.391 eV
1( 2) : -101.412661 a.u. -2759.579 eV
2( 2) : -101.412651 a.u. -2759.579 eV
3( 2) : -101.400958 a.u. -2759.260 eV
4( 2) : -101.400944 a.u. -2759.260 eV
5( 2) : -101.399975 a.u. -2759.234 eV
6( 2) : -101.399966 a.u. -2759.233 eV
...
63( 1) : -0.202477 a.u. -5.510 eV alpha= -7.446 beta= -3.574
64( 1) : -0.198014 a.u. -5.388 eV alpha= -7.265 beta= -3.511
65( 1) : -0.197962 a.u. -5.387 eV alpha= -7.265 beta= -3.509
66( 1) : -0.147460 a.u. -4.013 eV alpha= -5.445 beta= -2.580
67( 1) : -0.130914 a.u. -3.562 eV alpha= -4.956 beta= -2.169
68( 0) : 0.042837 a.u. 1.166 eV
69( 0) : 0.100215 a.u. 2.727 eV
70( 0) : 0.169615 a.u. 4.615 eV
...
```

2) Identify the character of these orbitals.

Search the FeCl6\_gro.out for the HEADER:

-----  
LOEWDIN FRAGMENT POPULATIONS PER MO  
-----

SPIN UP

```
0 -259.5384 1.0000: 100.0 0.0      Fe 1s
1 -101.4139 1.0000: 0.0 100.0
2 -101.4139 1.0000: 0.0 100.0
...
35 -3.4835 1.0000: 98.6 1.4
36 -2.2330 1.0000: 99.7 0.3      Fe 3p
37 -2.2330 1.0000: 99.7 0.3
38 -2.2320 1.0000: 99.4 0.6
```

3) Search the FeCl6\_gro.out for the HEADER:

-----  
LOEWDIN REDUCED ORBITAL POPULATIONS PER UNO  
-----



THRESHOLD FOR PRINTING IS 0.1%

	0	1	2	3	4	5
	-259.53843	-101.41393	-101.41392	-101.40196	-101.40194	-101.40096
	2.00000	2.00000	2.00000	2.00000	2.00000	2.00000
0 Fe s	100.0	0.0	0.0	0.0	0.0	0.0
1 Cl s	0.0	0.0	0.0	0.0	0.0	52.5
2 Cl s	0.0	52.7	0.0	45.4	1.8	0.0
3 Cl s	0.0	0.0	54.2	1.5	44.2	0.0
4 Cl s	0.0	0.0	45.8	2.1	52.1	0.0
5 Cl s	0.0	0.0	0.0	0.0	0.0	47.5
6 Cl s	0.0	47.2	0.0	50.9	1.8	0.0

2) Use the orca\_plot interactive module and plot the 3d Orbitals:

```
orca_plot -i FeCl6_qro.qro
```

- Use the Avogadro program to visualize these orbitals.
- Identify their character.

### C) Perform the RAS-CI calculation

1) Use the following input (**FeCl6\_rasci.inp**) and perform the core RAS-CI calculation

```
! RHF AllowRHF def2-TZVP def2-TZV/J COSMO ZORA
! NormalPrint
! MOREAD NOITER #Read The Orbitals
! NoLoewdin NoMulliken
%moinp "FeCl6_qro.qro"
%basis gtoaux autobuild
end

%scf
#Rotate the 1s and 3p orbitals below the SOMOs by using the rotate option
rotate {0,59,90} {36,60,90} {37,61,90} {38,62,90} end
end

%mrci citype mrci
Etol 1e-5
IntMode ritrafo
```

```

newblock 7 * #Multiplicity
excitations none #Type Of Excitations
nroots 4 #Number of Roots
refs RAS(12:4 1/5/0 0) end #RAS(nel: m1 h/m2/m3 p)
end
newblock 5 *
excitations none
nroots 105
refs ras(12:4 1/5/0 0) end
end
soc
dosoc true #Perform SOC calculation
Ninitstates 500 #Number of SOC states to account
end
end
%method SpecialGridAtoms 26 #Increase the radial integration accuracy on Fe
SpecialGridIntAcc 7#Requested radial integration accuracy values
end
* xyzfile -2 5 FeCl6_opt.xyz

```

2) Plot the FeCl6\_racsi.out.socabs.dat spectrum that is located in the directory **Exercise\_4/Spectra**. Use the FeCl6\_racsi.out to assign the observed spectral features,

## Suggested Literature

### XAS or XES (TD-DFT)

- 1) Roemelt, M.; Beckwith, M. A.; Duboc, C.; Collomb, M.-N.; Neese, F.; DeBeer, S. (2012), *Inorg. Chem.*, 51, 680-687.
- 2) Chandrasekaran, P.; Stieber, S. C. E.; Collins, T. J.; Que, L.; Neese, F.; DeBeer, S. (2011), *Dalton Trans.*, 40, 11070-11079.
- 3) Beckwith, M. A.; Roemelt, M.; Collomb, M. N.; Duboc, C.; Weng, T. C.; Bergmann, U.; Glatzel, P.; Neese, F.; DeBeer, S. (2011), *Inorg. Chem.*, 50, 8397-8409.
- 4) Lee, N.; Petrenko, T.; Bergmann, U.; Neese, F.; DeBeer, S. (2010), *J. Am. Chem. Soc.*, 132, 9715-9727.
- 5) DeBeer-George, S.; Neese, F. (2010), *Inorg. Chem.*, 49, 1849.

6) DeBeer-George, S.; Petrenko, T.; Neese, F. (2008), J. Phys. Chem. A., 112, 12936-12943.

7) DeBeer-George, S.; Petrenko, T.; Neese, F. (2008), Inorg. Chim. Acta (60th birthday issue of Prof. E.I. Solomon), 361, 965-972.

#### **XES(RASCI)**

1) Pollock, C.J.; Delgado-Jaime, M.U., Atanasov, M., Neese, F., DeBeer, S., (2014) J. Am. Chem. Soc., 136, 9453-9463.

2) Lee, Nn, Petrenko, T., Bergmann, U., Neese, F., DeBeer, S., (2010), J. Am. Chem. Soc. 132, 9715.

#### **XAS(DFT/ROCIS)**

1) Roemelt, M., Maganas, D., DeBeer, S, Neese, F. (2013), J. Chem. Phys., 138, 204101

2) Maganas, D.; Roemelt, M.; Weyhermuller, T.; Blume, R.; Havecker, M.; Knop-Gericke, A.; DeBeer, S.; Schlögl, R.; Neese, F. (2014) Physical Chemistry Chemical Physics : PCCP, 16, 264.