Theoretical calculations of X-ray absorption spectra of a copper mixed ligand complex using computer code FEFF9

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Abstract. The terms X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) refer, respectively, to the structure in the X-ray absorption spectrum at low and high energies relative to the absorption edge. Routine analysis of EXAFS experiments generally makes use of simplified models and several many-body parameters, e.g., mean free paths, many-body amplitude factors, and Debye–Waller factors, as incorporated in EXAFS analysis software packages like IFEFFIT which includes Artemis. Similar considerations apply to XANES, where the agreement between theory and experiment is often less satisfactory. The recently available computer code FEFF9 uses the real-space Green’s function (RSGF) approach to calculate dielectric response over a broad spectrum including the dominant low-energy region. This code includes improved treatments of many-body effects such as inelastic losses, core-hole effects, vibrational amplitudes, and the extension to full spectrum calculations of optical constants including solid state effects. In the present work, using FEFF9, we have calculated the X-ray absorption spectrum at the K-edge of copper in a complex, viz., aqua (diethylenetriamine) (isonicotinato) copper(II), the crystal structure of which is unknown. The theoretical spectrum has been compared with the experimental spectrum, recorded by us at the XAFS beamline 11.1 at ELETTRA synchrotron source, Italy, in both XANES and EXAFS regions.

1. Introduction
X-ray absorption fine structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. For this reason, XAFS is a very important probe of materials, since knowledge of local atomic structure, i.e., the species of atoms present and their locations, is essential to progress in many scientific fields: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology [1]. The XAFS is typically divided into two regimes: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The terms XANES and EXAFS refer, respectively, to the structure in the X-ray absorption spectrum at low and high energies relative to the absorption edge, with the crossover at about 30 eV above threshold. [2]

As experimental techniques and facilities have improved, including third generation synchrotron sources and the advent of X-ray free-electron lasers, measurements have been taken on wider ranges of systems, exploring the effects of temperature and pressure, and at higher resolutions than before. Hence, theoretical techniques have to be improved to keep abreast with the experimental advancements so that better information may be extracted from the experimental data.

Mostly, the analysis of experimental EXAFS data makes use of EXAFS analysis software packages like IFEFFIT [3]. This package includes Artemis which uses FEFF6L to generate simplified theoretical models in which mean free paths, many-body amplitude factors, and Debye–Waller factors...
are incorporated. This software does not perform XANES calculations. FEFF9 [2, 4] is a software package which does both XANES as well as EXAFS calculations in an advanced manner. This computer code uses the real-space Green’s function (RSGF) approach and includes improved treatments of many-body effects such as inelastic losses, core-hole effects, vibrational amplitudes, and the extension to full spectrum calculations of optical constants including solid state effects. In the present work, we have demonstrated the use of FEFF9 with an example of analysis of XAFS data of a copper complex. The theoretical spectrum generated by FEFF9 has been compared with the experimental spectrum.

2. Experimental
The copper complex aqua (diethylenetriamine) (isonicotinato) copper(II), Cu(dien)(ina) 4H2O.1/2SO4, has been prepared and characterized by following the standard methods [5]. The complex was in powder form (solid state). The absorption screens were in the form of pellets which were prepared by mixing calculated amount of the sample uniformly with a filler/binder material, viz., boron nitride (BN) and then using a press (pelletizer). X-ray absorption experiments were performed at ELETTRA Synchrotron Light Laboratory, Basovizza, Italy at the XAFS beam line 11.1. Other experimental details were similar to those described elsewhere. [6]

3. Description of FEFF9
FEFF uses an ab initio self-consistent real space multiple scattering (RSMS) approach, including polarization dependence, core-hole effects, and local field corrections, based on self consistent, spherical muffin-tin scattering potentials. Calculations are based on an all-electron, real space relativistic Green's function formalism with no symmetry requirements. The code builds in inelastic losses in terms of a self-energy, and includes vibrational effects in terms of Debye-Waller factors. For periodic structures reciprocal space calculations based on periodic boundary conditions are also available. FEFF can use both full multiple scattering based on Lanczos algorithms and a high-order path expansion based on the Rehr-Albers multiple scattering formalism. The name FEFF is derived from \( f_{\text{eff}} \), the effective curved wave scattering amplitude in the modern EXAFS equation. [7]

A FEFF calculation starts with two basic tasks: calculation of the potentials, followed by calculation of the scattering phase shifts. Using these phase shifts, scattering paths are found and their scattering amplitudes calculated. There are two ways to do this: either using an explicit enumeration and summation, most appropriate for extended absorption spectra; or using the implicit summation of full multiple scattering, appropriate for near-edge absorption spectra. [7]

FEFF9 can be used for a number of different calculations. In the present work, we have demonstrated its use for XANES and EXAFS calculations. In order to use FEFF9 a program must be used to create the atomic structure that indicates the position of all the atoms in the lattice. ATOMS on the web was used in order to create an input file for the FEFF9 program. The parameters that are required to create the atomic structure in ATOMS is the space group, the edge of interest (Copper K edge in the present case), lattice constants, angles and finally the sites of the elements in the unit cell and the central atom of the crystal structure.

4. Data analysis
The crystallographic data is unavailable for the complex. Hence, for the analysis of the XAFS data of the complex, the crystal structure of an analogous complex aqua(diethylenetriamine) (isonicotinato)-copper(II) hexafluorophosphate \([\text{Cu}-(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_6\text{N}_3)(\text{H}_2\text{O})]\text{PF}_6\) [5], has been used. The following parameters have been used for generating the feff input file.

Space group: \( \text{Pnma} \), Cell constants: \( a = 22.826 \) Å, \( b = 6.971 \) Å, \( c = 16.593 \) Å, 
\[ \alpha = 90.00^\circ, \beta = 90.00^\circ, \gamma = 90.00^\circ \] and Cluster size = 8 Å.

The remaining input positional parameters are given in ref. [5].

The FEFF program consists of a set of program modules driven by a single input file `feff.inp` [7]. One can either supply this file or can set all input options through the JFEFF GUI, which runs FEFF.
without the need for manual text editing. The input file `feff.inp' is a loosely formatted, line-oriented text file. Each type of input read by the program is on a line starting with a CARD: a keyword possibly followed by some numbers or words. The sequence of keyword cards is arbitrary. If any card or optional data is omitted, default values are used. Most calculations do require the POTENTIALS card, and either the ATOMS card or the OVERLAP card. Together, the POTENTIALS and ATOMS/OVERLAP cards specify the physical structure of the molecule or solid one is interested in. FEFF uses Cartesian coordinates and Angstrom units. Hence it is easy to copy atom positions from, e.g., an `xyz' file or other popular file formats. It is also possible to import CIF files (`*.cif'). There are many optional cards to specify the material property to calculate and to control how FEFF calculates it. All distances are in Angstrom (Å) and energies are in electron-volts (eV). Separate input files have to be generated for XANES as well as EXAFS calculations. For example, in the case of present sample, some components of the feff input file for XANES and EXAFS are shown in Table 1.

### 5. Results and discussions

#### 5.1 XANES calculations

For XANES calculations in FEFF9, the self-consistent potential (SCF) and full multiple scattering (FMS) must be specified in order to run the calculation. The SCF and FMS adjust the amount of atoms used in the calculation. Convergence is reached when increasing the amount of atoms included in the calculation produces no distinct changes in the graph of the simulated spectrum. The XANES calculations performed using FEFF9 include the many-pole self-energy, the treatment of the core-hole within the random phase approximation (RPA), and the many-body spectral function convolution.[8]

![Figure 1. Comparison of experimental Cu K-edge XANES (μ(E) vs. E) with calculations from FEFF9 for the complex](image1)

![Figure 2. Comparison of experimental Cu K-edge EXAFS (χ(k) vs. k) with calculations from FEFF9 for the complex](image2)

In the present case, for calculating the XANES spectra, self consistent potentials with a cluster radius of 3 Å have been used. The full multiple scattering (FMS) cluster size has also been kept as 3 Å. The calculated spectrum has been shifted to align the white-line peak with experiment. The

| Table 1. Some components of feff input file |
|------------------------------------------------|
| **XANES** | **EXAFS** |
| TITLE Cu complex | TITLE Cu complex |
| CONTROL 1 1 1 1 1 | |
| EXCHANGE 0 0 0 0 | |
| SCF 3.0 0 0 0.2 1 | |
| COREHOLE RPA | |
| SIG2 0.009 | |
| XANES 8.0 0.07 0.0 | |
| FMS 3.0 0 | |
| POTENTIALS | |
| 0 29 Cu | |
| 1 29 Cu | |
| 2 8 O | |
| 3 7 N | |
| 4 6 C | |
XANES spectrum (μ(E) vs. E) thus obtained for the studied copper complex is given in figure 1. In this figure the experimental spectrum has also been given in order to show the comparison between theoretical and experimental spectra.

5.2 EXAFS calculations
In the present case, the calculation of potentials and phase shifts has been done only once and then the results have been used while studying the paths. Because the number of possible paths increases exponentially with total path length, we have started with a short total path length and then examined few paths (representing scattering from the nearest neighbors), and gradually increased the total path length, studying the path importance coefficients and using the filters to limit the number of paths. The paths so generated using FEFF9 for the present complex are listed in Table 2.

| Table 2. Paths generated by FEFF9 |
|----------------------------------|
| FEFF 9.6.4, PATH R_{max}= 3.500, S_{0}^{2}=1.0 |
| Curved wave amplitude ratio filter 4.000% |
| File | sig2 | cw amp ratio | deg | nlegs | reff |
| 1   | 0.00600 | 100.00 | 1.00 | 2 | 2.0049 |
| 2   | 0.00600 | 99.05  | 1.00 | 2 | 2.0133 |
| 3   | 0.00600 | 98.80  | 1.00 | 2 | 2.0156 |
| 4   | 0.00600 | 98.57  | 1.00 | 2 | 2.0176 |
| 5   | 0.00600 | 70.10  | 1.00 | 2 | 2.3159 |
| 6   | 0.00600 | 13.26  | 2.00 | 3 | 3.3516 |
| 7   | 0.00600 | 12.97  | 2.00 | 3 | 3.3633 |
| 8   | 0.00600 | 10.13  | 2.00 | 3 | 3.4829 |

The EXAFS spectrum (χ(k) vs. k) has been obtained as the sum of these paths for the studied copper complex and the spectrum so obtained is given in figure 2. In this figure the experimental spectrum has also been given for comparison between theoretical and experimental spectra.

6. Conclusions
In the present work, both XANES spectra as well as EXAFS spectra at the K-edge of copper in a copper complex have been calculated using the computer code FEFF9. The calculations are based on extensions of the quasi-particle theory and the RSGF formalism which make possible general treatment of XAFS, encompassing XANES and EXAFS. New approaches for calculating inelastic losses, self-energies, and Debye–Waller factors yield significant improvements in amplitude and phase for XAFS spectra. Details of generating the feff input file for FEFF9 has been outlined. The theoretical spectra obtained from FEFF9 are comparable with the experimental spectra recorded on a standard XAFS beamline.

The use of recent and advance softwares for XAFS data analysis are important because the EXAFS beamlines at the 2.5 GeV Indus-2 synchrotron at Raja Ramanna Center for Advanced Technology (RRCAT), Indore have become easily available to Indian workers which were not available until now. The beamline BL-8 is a dispersive EXAFS beamline and beamline BL-9 is a DCM EXAFS beamline which have become operational. It is hoped that research workers from Indian laboratories will do experiments on these synchrotron beamlines and the present paper will help them in doing better theoretical calculations.
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