Using FEFF for EXAFS Data Analysis

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July-2021

Fundamentals of X-ray Absorption Fine-Structure

Virtual XAFS School at Illinois Institute of
Technology and Advanced Photon Source

The EXAFS Equation

The XAFS Equation used with FEFF:

$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

- $f(k)$ and $\delta(k)$ are *photo-electron scattering amplitude and phase*:
  - Energy dependent $\quad k \sim \sqrt{(E - E_0)}$.
  - Depend on Z of the scattering atom(s).
  - Non-trivial: must be calculated or carefully extracted from measured spectra.
- $\lambda(k)$ tells how far the photo-electron can travel.
- The sum is over *Scattering Paths* of the photo-electron, from absorbing atom to neighboring atom(s) and back. May include *multiple scattering*!

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> If we know $f(k)$, $\delta(k)$, and $\lambda(k)$, we can get:
> - R – near neighbor distance.
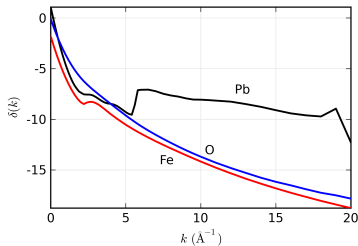> - N – coordination number.
> - σ^2 – mean-square disorder in R.

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on Z:
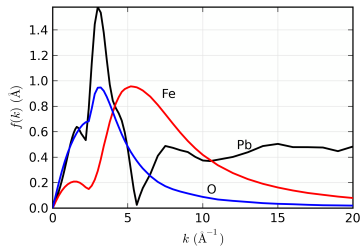
$f(k)$ peaks at higher k as Z increases. Heavy elements, have a characteristic dip in $f(k)$, and scatter to high k.
Note: O is done at $k > 15\text{Å}^{-1}$

The phase shift $\delta(k)$ also shows strong Z dependence, and has sharp jumps for heavy elements where $f(k)$ dips.
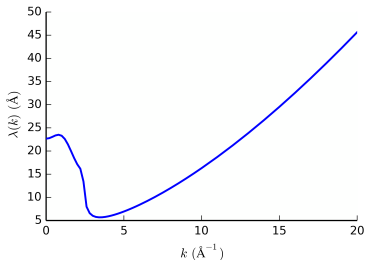**Note: $\delta(k) \approx -k$!**

Z can usually be determined to ± 5.

Fe and O can be distinguished.

N and O cannot be distinguished.

The $e^{-2R/\lambda(k)}$ term in the XAFS Equation accounts for how far the photo-electron can travel and still return (in phase) to the excited atom.

This includes both:

- inelastic scattering of photo-electron.
- finite lifetime of the core-hole (fs).

The photo-electron goes only 10 to 20 Å over most of the EXAFS region.

> The λ and $1/R^2$ terms make EXAFS a *local probe*.

$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

Steps:

1. Calculate theoretical XAFS spectra with FEFF, starting with a guess of the local structure.
2. *Refine* R, N, and σ^2 to best match experimental data.
3. Compare lots of refined models.

Questions you might have (and we might answer!):

- How do we run FEFF to generate $f(k)$, $\delta(k)$, and $\lambda(k)$?
- What correction factors do we need to worry about?
- How do we fit experimental data?
- How do we interpret the results?
- Any advice for making all this, um, easier?

FEFF calculates the EXAFS $\chi(k)$ by simulating the scattering of a photo–electron along all scattering paths from a selected absorbing atom within a cluster of atoms.

1. build atomic potentials. To simplify calculations,

   Use the *Cup-Cake Tin Approximation*: atomic potentials up to a uniform Fermi level -no chemical bonding. (Some people call this "Muffin-Tin" Approximation)

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3. move photo-electron along path to determine f and δ as a function of k:

$$\text{propagate} \Rightarrow \text{scatter} \Rightarrow \text{propagate} \Rightarrow \ldots.$$

FEFF includes sophisticated techniques to calculate of $f(k)$, $\delta(k)$, and $\lambda(k)$.

Curved Wave Effects the photo-electron goes out as spherical wave and scatters from atoms with finite size.

Muffin-Tin Approximation: Makes the calculations tractable, but is an approximation.

Multiple Scattering the photo-electron can scatter multiple times. Most important at low k and for *linear paths*.

*Extrinsic Losses* $\lambda(k)$: self-energy and core-hole lifetime.

Intrinsic Losses S_0^2: the absorbing atom relaxes to the presence of the hole left in the core electron level.

Polarization Effects synchrotron beams are highly polarized, which needs to be taken into account. This is simple for K edges ($s \rightarrow p$ is dipole), but slightly more complicated for L and M edges.

Usually, you don't have to worry about these things.

The photo-electron can scatter multiple times before getting back to the absorbing atom:
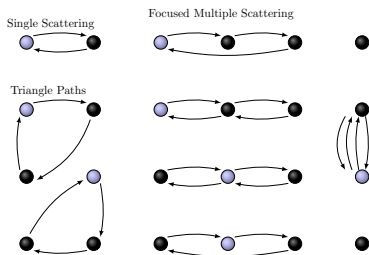
A Path Formalism is used in the calculation:

propagate $\Rightarrow$ scatter $\Rightarrow$ propagate $\Rightarrow$ ....

Single Scattering usually important.

Triangle Paths with angles $45 < \theta < 135°$ scatter weakly, but there are lots of them.

Linear paths with angles $\theta \approx 180°$ are very strong: the photo-electron is focused through an atom. Can be used to measure bond angles...

A FEFF Path looks the same for Single and Multiple Scattering

The *other* electrons in the absorbing atom can relax due to the core-hole, giving an Amplitude Reduction Term:

$$S_0^2 = |\langle \Phi_f^{N-1} | \Phi_0^{N-1} \rangle|^2$$

$|\Phi_0^{N-1}\rangle = (N-1)$ electrons in unexcited atom.
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S_0^2 is taken as a constant: $0.7 < S_0^2 < 1.0$.
and may be used as a Fitting Parameter that multiplies χ:

S_0^2 is Completely Correlated with N (!!!)

S_0^2 is usually constant for data measured on the same edge **and** beamline (energy resolution).

Most Common Approach: Determine S_0^2 from experimental data on a system with known N, and then use that for unknown data.

Good News: you don't have to worry about the hard parts (mostly)!

1. Start with a structure close to the *local* atomic structure of your sample, and generate x,y,z coordinates for the atoms. Often a crystal structure is close – it does not have to be perfect!

2. Run FEFF. This creates a `feffnnnn.dat` files for each path.

3. Use these Path Files in to model measured XAFS.

LARCH and XAS VIEWER helps you find crystal structures, create and edit input filess, run FEFF, and sort and use the results.

> **run FEFF in a specified folder**
>
> ```
> larch> feff8l('feff8.inp', folder='CuS_Feff')
> ```

Having good starting structures can be important, but you do not need the exact structure to use FEFF.

You can (may need to) mix structural models to model real data.

Anatomy of `feff.inp`

FEFF is a very old program that runs from an input file – it **must** be called `feff.inp`. LARCH can help with this.

Each calculation should be in its own folder/subdirectory.

`feff.inp` file (FEFF 8):

```
TITLE    FeO, rock salt structure
EDGE K
S02   1.0
CONTROL  1 1 1 1 1 1  # which parts of code to run
PRINT    1 0 0 0 0 3  # which output files to write
RPATH    6.0   # How far in R to build paths

POTENTIALS        # list of Atomic Potentials
* potential  z  label
     0    26  Fe   # Absorbing Atom
     1     8  O    # 1 Potential for each Z
     2    26  Fe

ATOMS # list of Atomic X, Y, Z, Potential
 0.00000    0.00000    0.00000    0   Fe
 0.00000    0.00000   -2.13870    1   O
-2.13870    0.00000    0.00000    1   O
 0.00000   -2.13870    0.00000    1   O
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 0.00000    2.13870    2.13870    2   Fe
 0.00000   -2.13870   -2.13870    2   Fe
```

`feff.inp` includes:

1. A list of unique Atomic Potentials:
   - 1 Absorbing Atom, always Potential 0
   - 1 Potential per atomic species (Z)

2. List of atomic coordinates (in Å):
   x, y, z, Pot
   for each atom in the cluster of atoms

   The cluster can be non-crystalline.

   The absorber can be at $(0, 0, 0)$, or not.

   Hint: better off removing H atoms!

You can edit the atomic positions, and add or change potentials.

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You can edit the atomic positions, and add or change potentials.

FEFF has many inputs, but only a few of them are really important for EXAFS Analysis (some are required, some optional):

EDGE	which edge absorbs the x-ray (K, L3, etc.)
POTENTIALS	list of atomic potentials (0 = absorbing atom)
ATOMS	list of atomic x, y, z, Potential
CONTROL	which "Modules" to run. Use "1 1 1 1 1 1".
PRINT	which "Outputs" to write. Use "1 0 0 0 0 3".
RPATH	how far out (in Å) to consider the cluster of atoms.
POLARIZATION	polarization vector of incident x-ray (in same coordinate system as atomic coordinates)
EXCHANGE	which model to use for the exchange energy. Use the default (Hedin-Lundqvist model) unless you know why.

LARCH comes with about 9000 crystral structures from the

American Mineralogist Crystal Structure Database

and can convert these as *Crystallographic Information Format* (CIF) files to FEFF input files.

It handles fractional site occupancy with weighted substitutions – use with caution!

It can also read some CIF files from other sources (work-in-progress!).

This is a convenient way to generate a FEFF input, but not necessary!

> The cluster used by FEFF does not need to be a crystal!

Atomic clusters may also come from:

Protein Data Bank, Molecular Dynamics Simulations, Density Functional Theory Calculations, ...

Using FEFF in a real analysis, we'll be *refining* bond lengths and coordination numbers. For this to work, here are some "rules of thumb":

1. refining distances by **more than** $0.1\,\text{Å}$ probably means the calculation should be re-run – the overlap of atomic potentials may not be accurate.

2. refining energy origins E_0 by **more than** $10\,\text{eV}$ may mean the calculation – or the selection of E_0 in the data reduction – is wrong or needs to be re-examined.

3. FEFF allows you set S_0^2 and σ^2 values in `feff.inp`. **Do not set these in** `feff.inp`.

4. You **should set** S_0^2 in the analysis for a particular group of data (central atom, beamline energy resolution, etc), based on an experimental standard, or have uncertain values for N.

To model XAFS as a Sum of Paths:

$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{k R_j{}^2} \sin[2k R_j + \delta_j(k)]$$

we may refine these Parameters *For Each Path*:

XAFS Equation	LARCH Paramaeter	Physical Meaning
$S_0^2 N_j$	s02	Amplitude Factor: Both N_j and S_0^2
E_0	e0	Energy Shift (where $k = 0$)
ΔR	deltar	Change in path length $R_j = \Delta R_j + R_{\text{eff}\,j}$
σ_j^2	sigma2	Mean-square-displacement in R_j

- R_{eff} is the starting R value for the FEFF Path.
- Other Parameters: higher order cumulants, energy broadening, . . .
- In principle, any parameter for any path could be refined.

FeO has a rock-salt structure.

To model the Fe K edge EXAFS of FeO, we'll calculate the `feffNNNN.dat` files (with $f(k)$ and $\delta(k)$), for Fe-O based on the FeO crystal structure.

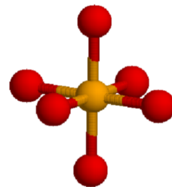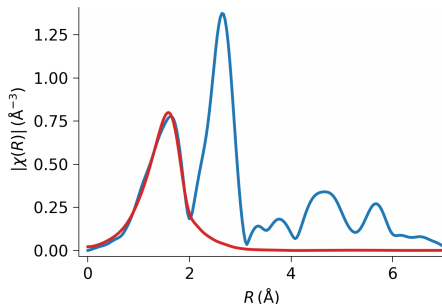We'll then *refine* the values R, N, σ^2, and E_0 so our model EXAFS function matches our data.

Fe-O octahedra,
$R = 2.14\,\text{Å}$.

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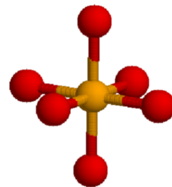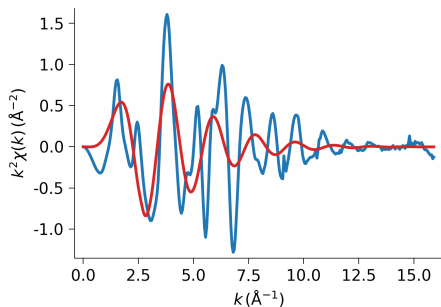

Fe-O octahedra,
$R = 2.14$ Å.

Results:

$$
\begin{aligned}
S_0^2 &= 0.7 \text{ (fixed)} \\
N &= 5.1 \pm 0.4 \\
R &= 2.09 \pm 0.01\text{Å} \\
\Delta E_0 &= \text{-1.3} \pm 0.9 \text{ eV} \\
\sigma^2 &= 0.012 \pm 0.002 \ \text{Å}^2.
\end{aligned}
$$

$|\chi(R)|$ for FeO data and 1st shell fit.

1st shell fit in k space.

Yes, that is the best fit! But only to the first shell, completely ignoring $R > 2$Å.

There is clearly another component in the XAFS besides just Fe-O.

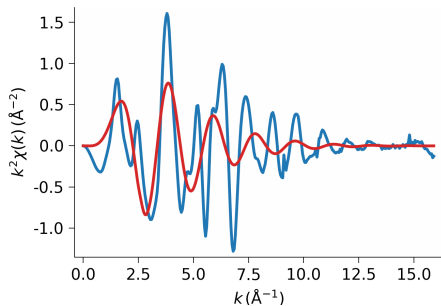1st shell fit in k space.

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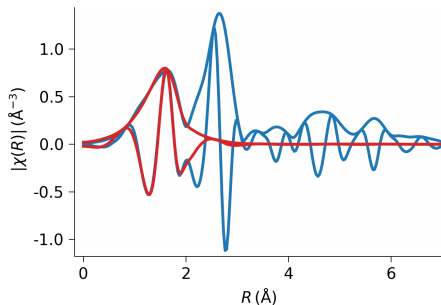1st shell fit in R space.

$|\chi(R)|$ and $\mathrm{Re}[\chi(\mathrm{R})]$ for FeO (blue), and a 1st shell fit (red).

Although the fit to the magnitude is not perfect, the fit to $\mathrm{Re}[\chi(\mathrm{R})]$ is very good.

Using FEFF to calculate the scattering factors does not need to be too hard.

- Start with a crystal structure that close to your structure.
- Make sure you have the absorbing element and edge right!
- Pay attention to the *degeneracy*, or coordination number for each path.
- Don't be afraid to alter the atoms list in `feff.inp`, especially replacing atom types or importing structures from simulations.
- Don't be afraid to mix paths from different calculations.
- Don't worry too much about the rest of it – let the GUI programs (XAS VIEWER, ARTEMIS) help you manage these calculations.

More information on X-rays and X-ray Absorption Spectroscopy:

https://xafs.xrayabsorption.org/

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