EXAFS Data Analysis with FEFF

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2022-July-28

2022 XAFS School

The EXAFS Equation

The XAFS Equation used with FEFF:

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

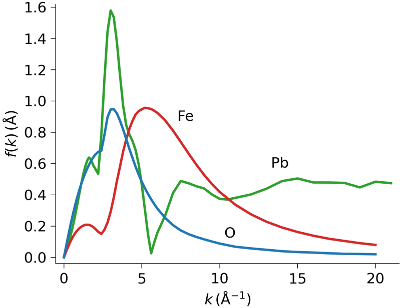
- $f(k)$ and $\delta(k)$ are *photo-electron scattering amplitude and phase*:
  - Energy dependent $k \sim \sqrt{(E - E_0)}$.
  - Depend on Z of the scattering atom(s).
  - Non-trivial: must be calculated or carefully extracted from measured spectra.
- $\lambda(k)$ tells how far the photo-electron can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

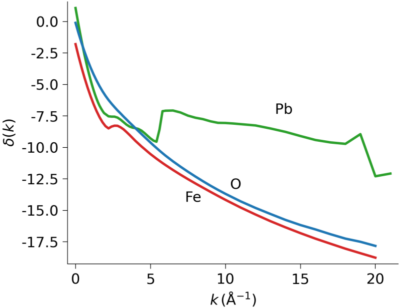
If we know $f(k)$, $\delta(k)$, and $\lambda(k)$, we can get:

- R – near neighbor distance.
- N – coordination number.
- σ^2 – mean-square disorder in R.

Scattering Amplitude and Phase-Shift

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number.





$f(k)$ extends to higher k values for higher Z elements. For very heavy elements, there is structure in $f(k)$.

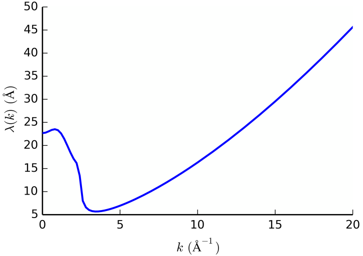
$\delta(k)$ shows sharp changes for very heavy elements. **Note:** $\delta(k) \approx -k$**!**

These complex scattering factors allow EXAFS to distinguish the species of neighboring atom:

Z can usually be determined to ± 5.
Fe and O can be distinguished, but not Fe and Mn.

$\lambda(k)$: The Photo-Electron Mean-Free Path

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*.

EXAFS Analysis Strategy: How to get N, R, etc?

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

Steps:

1. Calculate theoretical XAFS spectra with FEFF, starting with a guess of the local structure. This gives $f(k)$ and $\delta(k)$ for each Scattering Path.
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 Calculation Overview: What does FEFF do?

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)

2. determine important scattering paths.
   - Build paths from a selected *central atom* in a cluster of atoms
   - decide which ones are "degenerate" (="'equivalent", !="degraded state")
   - decide which ones are unimportant for XAFS
3. move photo-electron along path to determine f and δ as a function of k:

   propagate ⇒ scatter ⇒ propagate ⇒ . . . .

FEFF: what's so hard about that??

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.

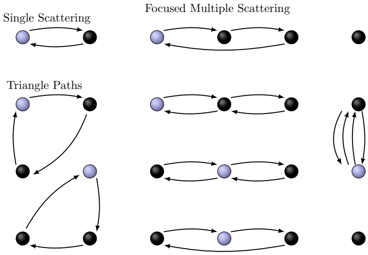
Intrinsic Losses S_0^2: the absorbing atom relaxes to the presence of the hole left in the core electron level.

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.

FEFF complication #1: Multiple Scattering

The photo-electron can scatter multiple times before getting back to the absorbing atom:



A Path Formalism is used in the calculation:

propagate ⇒ scatter ⇒ propagate ⇒ . . . .

Single Scattering usually important.

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

Linear paths with angles $\theta \approx 180^\circ$ 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

FEFF complication #2: S_0^2, the Amplitude Reduction Term

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.
$\langle \Phi_f^{N-1}| = (N-1)$ electrons, relaxed by core-hole.

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.

Practical FEFF

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 and XAS VIEWER can help manage running and organizing FEFF runs.

Each calculation should be in its own folder/subdirectory.

`feff.inp` file (FEFF 8):

```
TITLE    FeO, rock salt structure
EDGE K
SO2   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
 0.00000     0.00000     2.13870    1   O
 2.13870     0.00000     0.00000    1   O
 0.00000     2.13870     0.00000    1   O
 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.

Input Parameters for *feff.inp* (FEFF 8)

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.

Converting CIF data into FEFF inputs

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

FEFF: what *should* you worry about?

We treat FEFF as a reliable EXAFS calculation tool.
That is, once you set up the calculation, you can just use the results.

When using FEFF to fit EXAFS data, we'll be *refining* bond lengths and coordination numbers (and other parameters). For this to work best, 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** $10\,\mathrm{eV}$ may mean the calculation – or the selection of E_0 in the data reduction – is wrong or needs to be re-examined.
3. FEFF can set S_0^2 and make a simple attempt at σ^2 values. **don't use these**.
4. You **should set** S_0^2 for a particular group of data (central atom, beamline energy resolution, etc), based on an experimental standard, or have uncertain values for N.

XAFS Analysis with FEFF and LARCH (and ARTEMIS)

To model XAFS as a Sum of Paths:

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

we may refine these Parameters *For Each Path*:

XAFS Equation	LARCH Parameter	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 $R_j = \Delta R_j + R_{\mathrm{eff}\,j}$
σ_j^2	`sigma2`	Mean-square-displacement in R_j

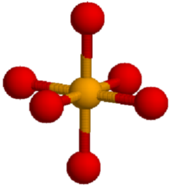
- R_{eff} is the starting R value for the FEFF Path.
- Other Parameters: higher order cumulants, energy broadening, . . .
- In principle, any parameter for any path could be refined.

EXAFS Analysis: Modeling the 1st Shell of FeO

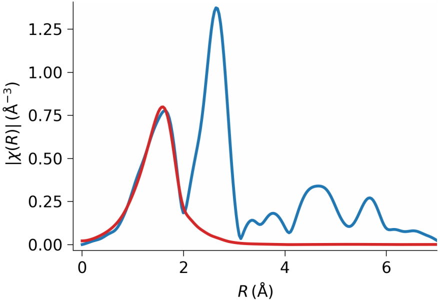
FeO has a rock-salt structure.

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,
$R = 2.14\,\text{Å}$.

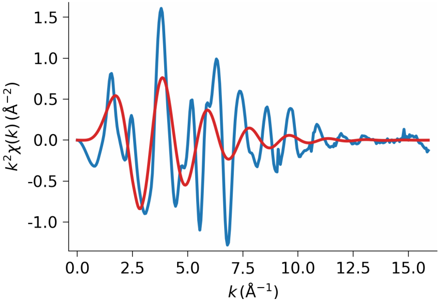


Results:

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

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

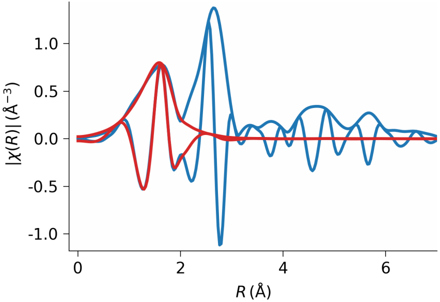
Analysis Example: 1st Shell of FeO



1^{st} shell fit in *k* space.

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

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



1^{st} shell fit in *R* space.

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

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

Fitting Strategies

Reminder: Data analysis seeks a *Model* that best matches a *Measurement*.

We'll use χ^2 (don't confuse with EXAFS χ!!) to describe how good the match is:

$$\chi^2 = \sum_{i}^{N_{\rm fit}} \frac{[\chi_i^{\rm measured} - \chi_i^{\rm model}(x)]^2}{\epsilon^2}$$

where

- $N_{\rm fit} =$ number of points in the data to fit.
- $\epsilon =$ the estimated noise level in the data.
- x is the set of parameters to be varied in the analysis

The Best Fit is the one with lowest χ^2.

Questions:

1. How do I know how many independent measurements I have?
2. What is ϵ for my data?
3. What parameters can/should I vary?

The Information Content of EXAFS

The number of parameters we can reliably extract from our data is limited:

$$N_{\mathrm{idp}} \approx \frac{2\Delta k \Delta R}{\pi}$$

where Δk and ΔR are the k- and R-ranges of the usable data.

For a typical range of $k = [3.0, 12.5]\,\mathrm{\mathring{A}}^{-1}$ and $R = [1.0, 3.0]\,\mathrm{\mathring{A}}$, there are ~ 12 parameters that can be determined from EXAFS. That's not much!

The Fit statistics and confidence in the measured parameters need to reflect this. But we usually oversample our data ($N_{\mathrm{fit}} > N_{\mathrm{idp}}$) so we have

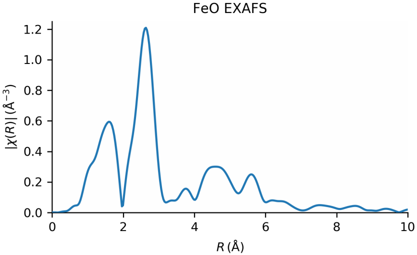
$$\chi^2 = \frac{N_{\mathrm{idp}}}{\epsilon^2 N_{\mathrm{fit}}} \sum_i^{N_{\mathrm{fit}}} [\chi_i^{\mathrm{measured}} - \chi_i^{\mathrm{model}}(x)]^2$$

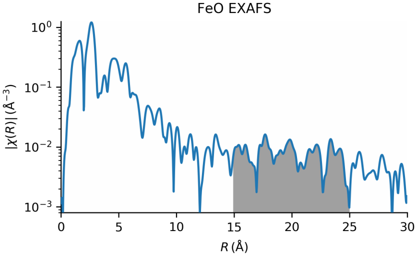
Note: I also assumed ϵ is a constant.

Propagation of uncertainties in $\chi(k)$

Estimating uncertainties in $\chi(k)$ has always been a challenge.

We have (by default) estimated the uncertainty in $\chi(k)$ as *white noise* (Newville, Boyanov, and Sayers, *J Synch Rad*, 1999), using $\chi(R)$ between [15, 25] Å.





The “high-R” portion of $\chi(R)$ can estimate the “white noise” in the data pretty well.

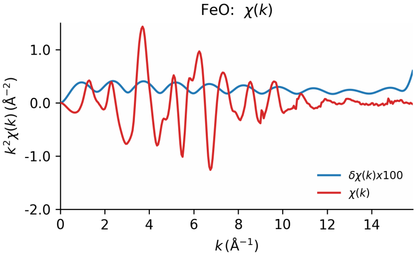
This is easy to do, but we know it misses an important component:

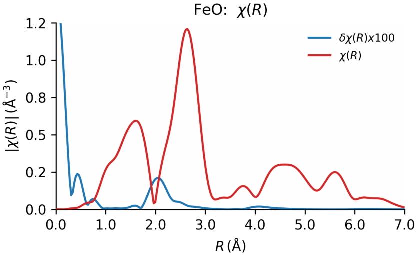
uncertainties from background subtraction

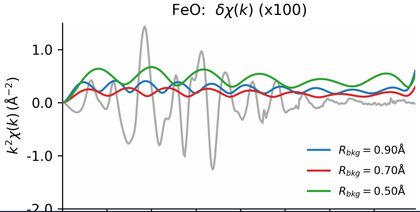
Uncertainties in $\chi(k)$ from background subtraction

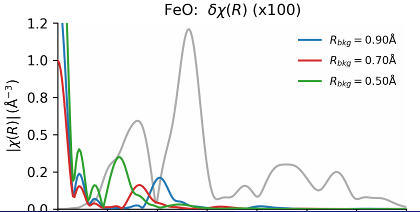
We can propagate the uncertainties from the fit of the background spline to estimate the uncertainty in $\chi(k)$ from the background subtraction.

This is *not white noise*. In fact, it tends to have a peak somewhat above $2R_{\rm bkg}$


FeO: $\chi(k)$


FeO: $\chi(R)$

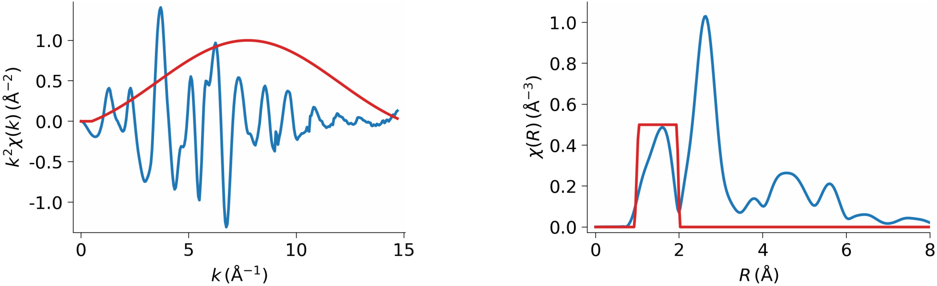

FeO: $\delta\chi(k)$ (x100)


FeO: $\delta\chi(R)$ (x100)

Fitting in *R*- or *k*-space: What do we model?

The χ^2 definition didn't say anything about what our data $\chi_i^{\mathrm{measured}}$ actually is . . .

We usually fit in *R*-space, so that we can select which “shells” to ignore:



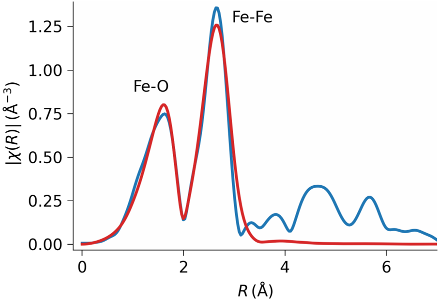
Fitting $\chi(R)$ (both real and imaginary parts!) gives more meaningful fit statistics – we know that we're not fitting all the spectral features.

Plus: We can have $\chi_i^{\mathrm{measured}}$ extend over multiple data sets, multiple *k*-weightings, etc.

as long as we generate the corresponding $\chi_i^{\mathrm{model}}(x)$ to match these data.

EXAFS Analysis: Second Shell of FeO

Adding the 2nd shell Fe – `feffNNNN.dat` for Fe-Fe – and refining R, N, σ^2:



$|\chi(R)|$ data for FeO (blue), and fit of 1^{st} and 2^{nd} shells (red).

These results are consistent with the known values for FeO:
6 O at 2.14Å, 12 Fe at 3.03Å.

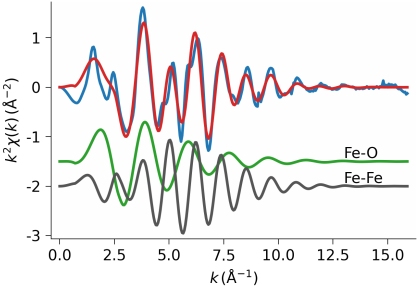
Fit results: Statistics: $R \approx 0.01$ $\chi^2_\nu \approx 3$.

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	4.6(0.6)	2.11(.01)	0.011(.002)	1.8(0.7)
Fe-Fe	14.1(1.7)	3.08(.01)	0.015(.002)	1.8(0.7)

These are typical even for a "very good fit" on known structures.
The calculation for $f(k)$ and $\delta(k)$ are good, but not perfect!

EXAFS Analysis: Second Shell of FeO

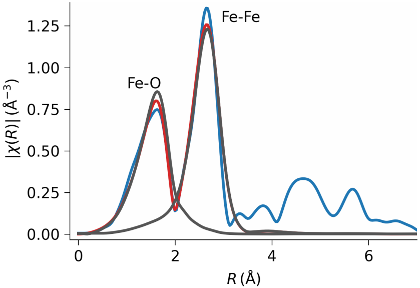
Other views of the data and fit:

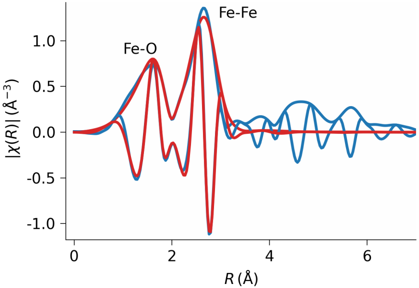


The Fe-Fe EXAFS extends to higher-*k* than the Fe-O EXAFS.

Even in this simple system, there is some *overlap* of shells in *R*-space.

The fit in $\mathrm{Re}[\chi(\mathrm{R})]$ look especially good – this is how the fits are done.





Path Parameters: what can we vary in a fit?

The EXAFS Equation has at least 4 adjustable parameters *Per Path*:

$$E_0,\ NS_0^2,\ R, \text{ and } \sigma^2.$$

But $N_{\rm idp}$ is low:

$$N_{\rm idp} = 8 \ \text{ for } \Delta R = 1\,\text{Å} \ \text{ and } \ \Delta k = 12.5\,\text{Å}^{-1}$$

For simple crystalline structures with well-isolated, single-scattering:
path (like FeO), it's OK to fit N, R, σ^2, and E_0 for every path.

For more complicated problems, we need a way to limit the number of parameters varied.

We might *want* to impose relationships between parameters to get more meaningful results...

Constraints and Generalized Variables

Instead of varying the Path Parameters directly, we write them in terms of *Generalized Variables*. This allows simple *Constraints* and model building:

Parameter=Variable

```
# one variable e0 for 2 paths
params = group(e0 = guess(1.0), ...)

path1  = feffpath(’feo.dat’, e0=’e0’)
path2  = feffpath(’fefe.dat’, e0=’e0’)
```

Mixed Coordination Shell

```
# mix O and S in 1st coordination shell
params = group(s02   = param(0.80, vary=False),
               sfrac = guess(0.5))

path1 = feffpath(’feo.dat’, s02=’s02*sfrac’)
path2 = feffpath(’fes.dat’, s02=’s02*(1-sfrac)’)
```

Einstein Temperature

```
# Use 1 ‘‘theta’’ to set sigma2 for multiple paths

params = group(amp=param(1, vary=True),
               theta=param(250, min=0, vary=True), ...)

path1_100K = feffpath(’fefe.dat’, s02=’amp’, ...,
                      sigma2=’sigma2_eins(100, theta)’)

path1_200K = feffpath(’fefe.dat’, s02=’amp’, ...,
                      sigma2=’sigma2_eins(200, theta)’)

path1_300K = feffpath(’fefe.dat’, s02=’amp’, ...,
                      sigma2=’sigma2_eins(300, theta)’)
```

This allows us to use *Prior Knowledge* into the data analysis, and consider more complicated problems:

- force one R for the same bond for data taken from different edges.
- model complex distortions (height of a sorbed atom above a surface).

Also: Each Parameter can have upper and lower bounds, say to ensure that $\sigma^2 \geq 0$.

Example: Cu metal at 3 temperature

A very simple example of a Multi-Data-Set Fit:
Cu metal, at 3 different temperatures: 10K, 50K 150K.

Path Parameters:

- E_0: Same for all T
- S_0^2 Same for all T
- R: expands linearly with T (slope + offset).
- σ^2: goes as Einstein temperature (as before).

12 parameters become 5.

Fit range:

$$R = [1.60, 2.75]\,\text{Å}$$

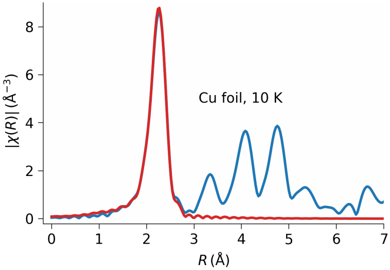
$$k = [1.50, 18.50]\,\text{Å}^{-1}$$

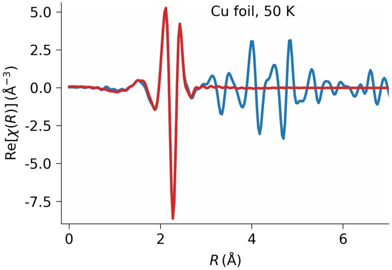
Cu at three temperatures

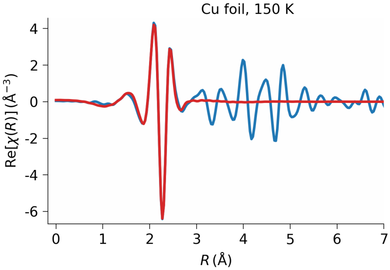
```
# define fitting parameter group
pars = group(amp      = param(1, vary=True),
             del_e0   = guess(2.0),
             theta    = param(250, min=10, vary=True),
             dr_off   = guess(0),
             dr_slope = guess(0) )

# define 3 Feff Path, give expressions for Path Parameters
path1_10  = feffpath(’feff0001.dat’,
                     s02=’amp’, e0=’del_e0’,
                     deltar=’dr_off + 10*dr_slope’,
                     sigma2=’sigma2_eins(10, theta)’)

path1_50  = feffpath(’feff0001.dat’,
                     s02=’amp’, e0=’del_e0’,
                     deltar=’dr_off + 50*dr_slope’,
                     sigma2=’sigma2_eins(50, theta)’)

path1_150 = feffpath(’feff0001.dat’,
                     s02=’amp’, e0=’del_e0’,
                     deltar=’dr_off + 150*dr_slope’,
                     sigma2=’sigma2_eins(150, theta)’)
```

Example: Cu metal Results

`amp`	$0.91(0.08)$
`theta`	$233.5(19.6)\,\mathrm{K}$
`del_e0`	$0.4(1.3)\,\mathrm{eV}$
`dr_off`	$0.002(0.003)\,\mathrm{\AA/K}$
`dr_slope`	$0.5(1.8)\times 10^{-5}\,\mathrm{\AA}$







EXAFS Data Analysis with FEFF

Using FEFF to model EXAFS mostly means paying attention to:

- $N_{\rm idp}$ – not very many Parameters can be varied for a limited k and R range.
- Always look at the uncertainties in the Parameters, not just best-fit values.
- Check (or require in the fit) that $\sigma^2 > 0$, $N > 0$.
- Think about how you combine Parameters for different Paths, ideally making a physical model.
- Try a third cumulant now and then – it might be needed.
- For very disordered systems, cumulants might not be enough.

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

https://xafs.xrayabsorption.org/

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