

# Larch for XAFS Analysis Using Feff and Feffit @ XAFS2021

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# 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  $k \sim \sqrt{(E - E_0)}$ .
  - ▶ 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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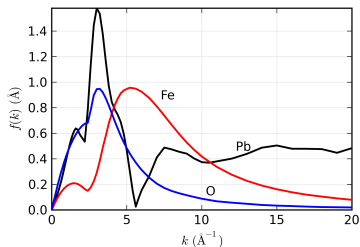
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If we know  $f(k)$ ,  $\delta(k)$ , and  $\lambda(k)$ , we can get:

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

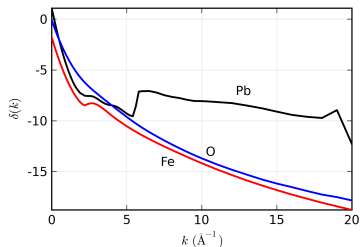
# Scattering Amplitude and Phase-Shift: $f(k)$ and $\delta(k)$

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  $k > 15 \text{ \AA}^{-1}$



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

**Note:**  $\delta(k) \approx -k!$

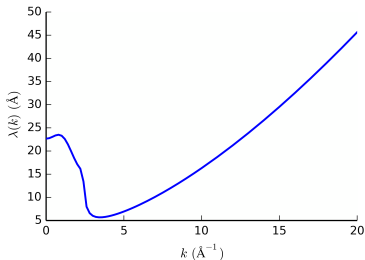
$Z$  can usually be determined to  $\pm 5$ .

Fe and O can be distinguished.

N and O cannot be distinguished.

## $\lambda(k)$ : 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  $\text{\AA}$  over most of the EXAFS region.

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

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

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

Steps:

- 1 Calculate theoretical XAFS spectra with FEFF, starting with a guess of the local structure.
  - 2 *Refine*  $R$ ,  $N$ , and  $\sigma^2$  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.  
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  - ▶ 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

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- 3 move photo-electron along path to determine  $f$  and  $\delta$  as a function of  $k$ :

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

## 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.

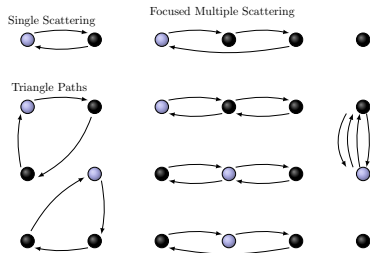
Usually, you don't have to worry about these things.

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



**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.

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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  $\chi$ :

**$S_0^2$  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 XASVIEWER helps you find crystal structures, create and edit input files, run FEFF, and sort and use the results.

run FEFF in a specified folder

```
larch> feff81('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   Fe0, 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 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 0 # 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 0
-2.13870 0.00000 0.00000 1 0
0.00000 -2.13870 0.00000 1 0
0.00000 0.00000 2.13870 1 0
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0.00000 2.13870 0.00000 1 0
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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Hint: better off removing H atoms!

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## 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 crystal 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, . . . .

## FEFF: what *should* you worry about?

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**  $0.1 \text{ \AA}$  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 can set  $S_0^2$  and make a simple attempt at  $\sigma^2$  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  $N$ .

To model XAFS as a Sum of Paths:

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

we may refine these Parameters *For Each Path*:

In XAFS Equation	LARCH Parameter	Physical Meaning
$NS_0^2$	s02	Amplitude Factor: $N$ and $S_0^2$
$E_0$	e0	Energy Shift (where $k = 0$ )
$\Delta R$	deltar	Change in path length $R = \Delta R + R_{\text{eff}}$
$\sigma^2$	sigma2	Mean-square-displacement in $R$

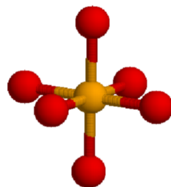
- $R_{\text{eff}}$  is the starting  $R$  value for the FEFF Path.
- Other Parameters: higher order cumulants, energy broadening, ...
- In principle, any parameter for any path could be refined.

# 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 use these functions to *refine* the values  $R$ ,  $N$ ,  $\sigma^2$ , and  $E_0$  so our model EXAFS function matches our data.



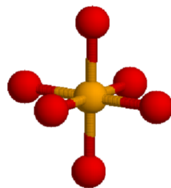
Fe-O octahedra,  
 $R = 2.14 \text{ \AA}$ .

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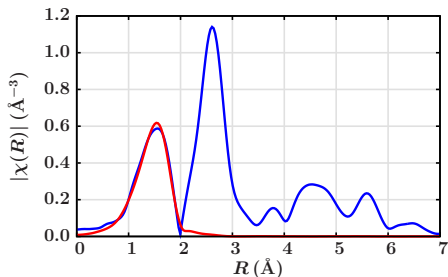
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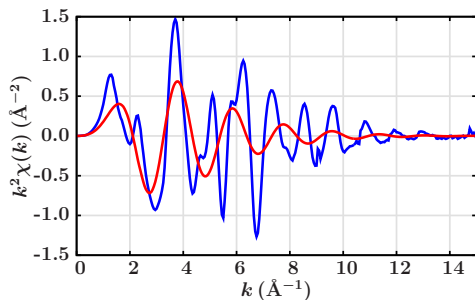


$|\chi(R)|$  for FeO **data** and **1<sup>st</sup> shell fit**.

Results:

$$\begin{aligned} S_0^2 &= 0.7 \text{ (fixed)} \\ N &= 5.0 \pm 1.0 \\ R &= 2.10 \pm 0.02 \text{ \AA} \\ \Delta E_0 &= -3.3 \pm 2.5 \text{ eV} \\ \sigma^2 &= 0.012 \pm 0.003 \text{ \AA}^2. \end{aligned}$$

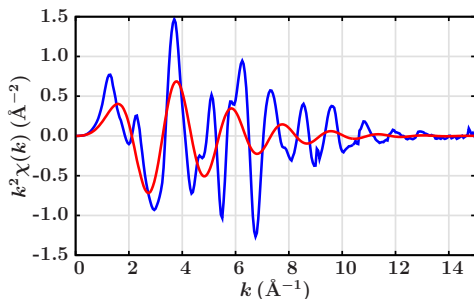
## Analysis Example: 1st Shell of FeO



1<sup>st</sup> shell fit in  $k$  space.

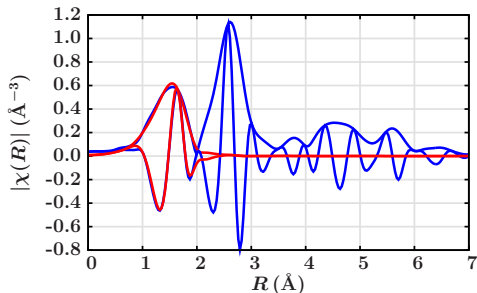
There is clearly another component in the XAFS!

## Analysis Example: 1st Shell of FeO



1<sup>st</sup> shell fit in  $k$  space.

There is clearly another component in the XAFS!



1<sup>st</sup> shell fit in  $R$  space.

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

Though the fit to the magnitude isn't perfect, the fit to  $\text{Re}[\chi(R)]$  looks very good.

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

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

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

where

- $N_{\text{fit}}$  = 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  $\chi^2$ .*

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Questions:

- 1 How do I know how many independent measurements I have?
- 2 What is  $\epsilon$  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:

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

where  $\Delta k$  and  $\Delta R$  are the  $k$ - and  $R$ -ranges of the usable data.

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where  $\Delta k$  and  $\Delta R$  are the  $k$ - and  $R$ -ranges of the usable data.

For a typical range of  $k = [3.0, 12.5] \text{ \AA}^{-1}$  and  $R = [1.0, 3.0] \text{ \AA}$ , there are  $\sim 12$  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 ( $N_{\text{fit}} > N_{\text{idp}}$ ) so we have

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

Note: I also assumed  $\epsilon$  is a constant.

## Other Fitting Statistics

Other “goodness-of-fit statistics”:

*chi-square*: As before:

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

*reduced chi-square*: scale  $N_{\text{varys}}$  by the “degrees of freedom” :

$$\chi_\nu^2 = \chi^2 / (N_{\text{idp}} - N_{\text{varys}})$$

For a “Good Fit”,  $\chi_\nu^2$  should be  $\sim 1$ . This *never* happens!

*R-factor*:  $\mathcal{R}$  gives a “fractional misfit” (and not scaled by the data uncertainty  $\epsilon$ ):

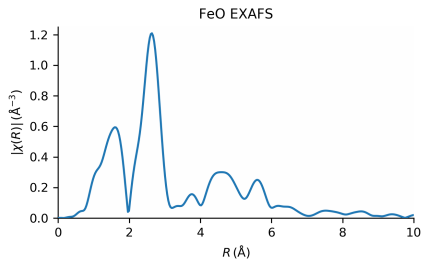
$$\mathcal{R} = \frac{\sum_i^{N_{\text{fit}}} [\chi_i^{\text{measured}} - \chi_i^{\text{model}}(x)]^2}{\sum_i^{N_{\text{fit}}} [\chi_i^{\text{measured}}]^2}$$

# 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.

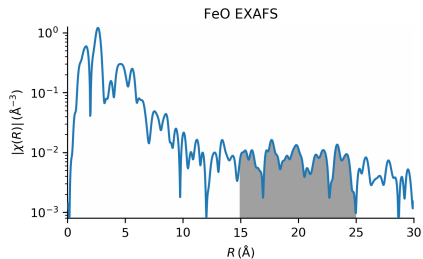
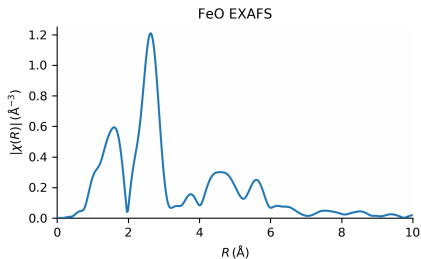


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The “high- $R$ ” portion of  $\chi(R)$  can estimate the “white noise” in the data pretty well.

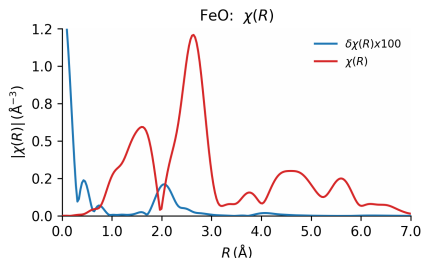
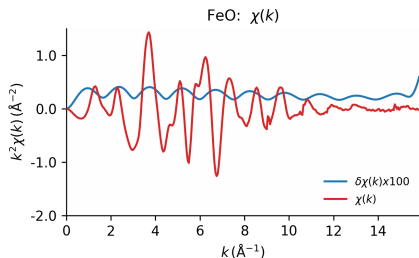
This is easy to do, but we know it misses an important component:

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.

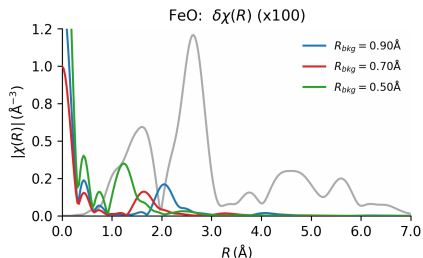
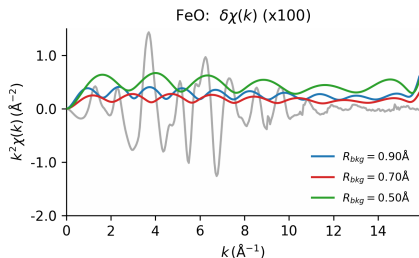
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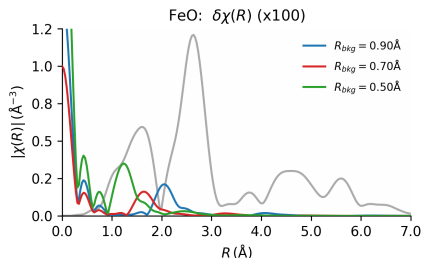
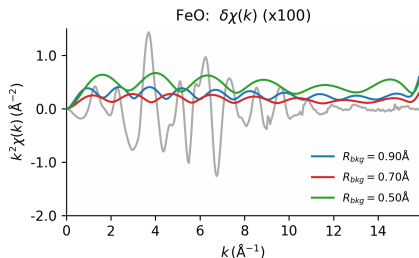
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Using this  $\delta\chi(k)$  array reduces the  $\chi^2$  statistic by  $2\times$  or more.

## Error Bars: the uncertainties in the fit variables

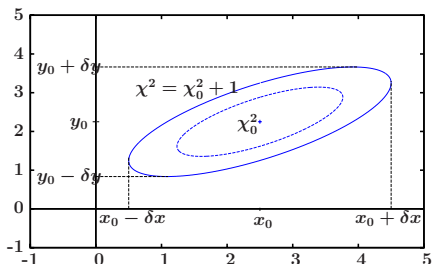
A fit finds a set of values  $x_0$  that are the “best fit” of the variables  $x$  – they give the lowest value of  $\chi^2$ .

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Some Parameters are *Correlated*:

Changing  $x$  away from its best value will change the best value for  $y$ .

For EXAFS,  $(R, E_0)$  and  $(N, \sigma^2)$  are usually very highly correlated ( $> 0.85$ ).

*Increasing  $\chi^2$  by 1 assumes we have a “Good Fit”, with  $\chi^2_{\nu} \approx 1$ .*

We typically have  $\chi^2_{\nu} \gtrsim 50$  (Actually, we *can now do better!*).

We increase the best  $\chi^2$  by  $\chi^2_{\nu}$  to estimate error bars.

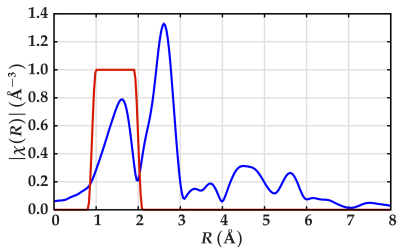
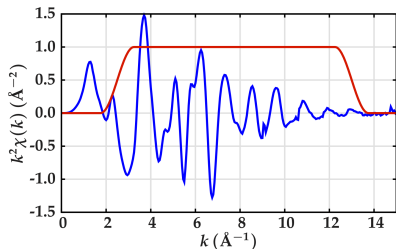
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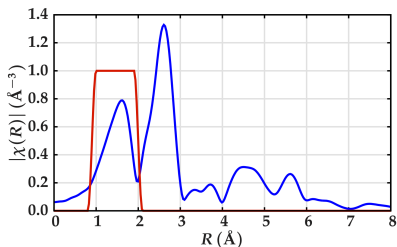
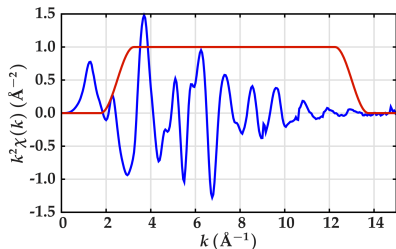
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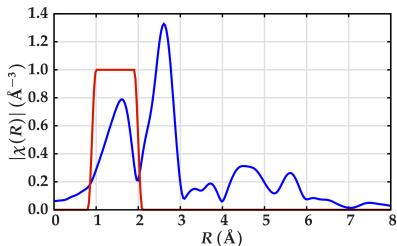
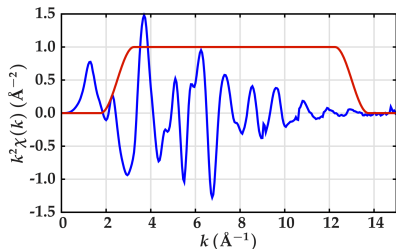


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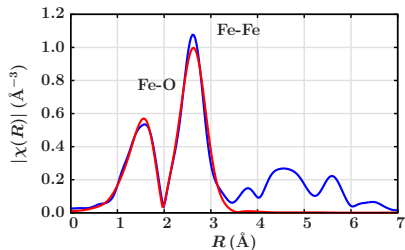
**Plus:** We can have  $\chi_i^{\text{measured}}$  extend over

multiple data sets, multiple  $k$ -weightings, etc,

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

# EXAFS Analysis: Second Shell of FeO

Adding the 2nd shell Fe – *feffNNNN.dat* for Fe-Fe – and refining  $R$ ,  $N$ ,  $\sigma^2$ :



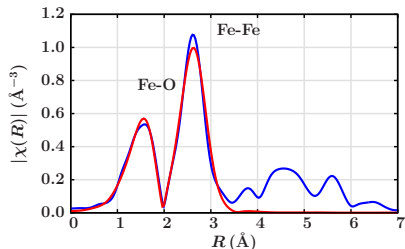
$|\chi(R)|$  data for FeO (blue), and fit of 1<sup>st</sup> and 2<sup>nd</sup> shells (red).

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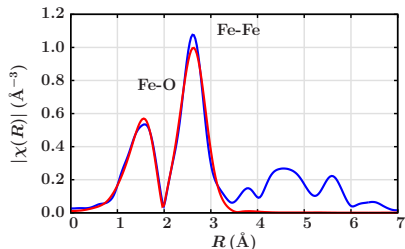
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Fit results: Statistics:  $R \approx 0.011$   $\chi^2_{\nu} \approx 4$ .

Shell	$N$	$R$ (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
Fe-O	4.9(0.8)	2.11(.01)	0.011(.002)	0.7(0.9)
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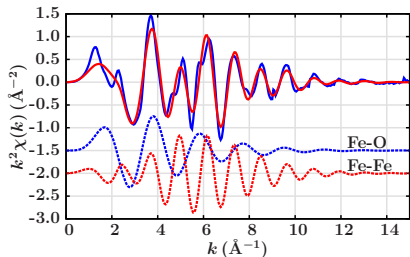
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These are typical even for a “very good fit” on known structures.  
The calculation for  $f(k)$  and  $\delta(k)$  are good, but not perfect!

# EXAFS Analysis: Second Shell of FeO

Other views of the data and fit:

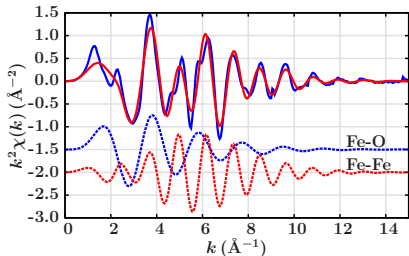


The Fe-Fe EXAFS extends to higher- $k$  than the Fe-O EXAFS.

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

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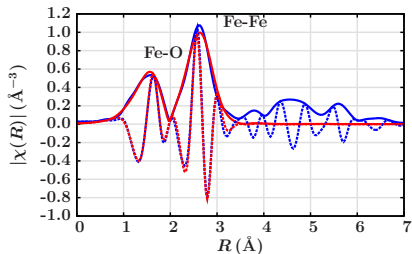
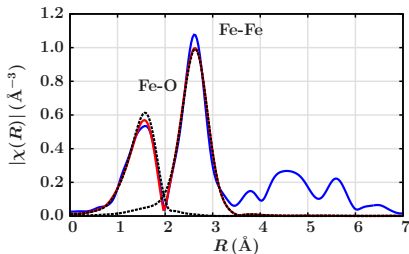
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The fit in  $\text{Re}[\chi(R)]$  look especially good – this is how the fits are done.



## Path Parameters: what can we vary in a fit?

The EXAFS Equation has at least 4 adjustable parameters *Per Path*:  $E_0$ ,  $NS_0^2$ ,  $R$ , and  $\sigma^2$ . But  $N_{\text{idp}}$  is low:

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

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For simple crystalline structures with well-isolated, single-scattering path (like FeO), it's OK to fit  $N$ ,  $R$ ,  $\sigma^2$ , 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')
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## 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')
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## 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).

## 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).
- $\sigma^2$ : goes as Einstein temperature (as before).

*12 parameters become 5.*

Fit range:

$$R = [1.60, 2.75] \text{ \AA}$$

$$k = [1.50, 18.50] \text{ \AA}^{-1}$$

### 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) )

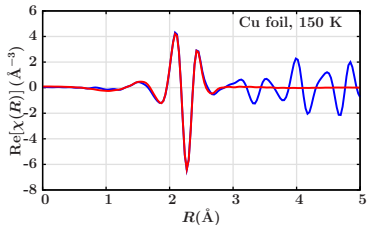
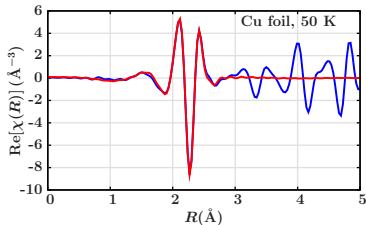
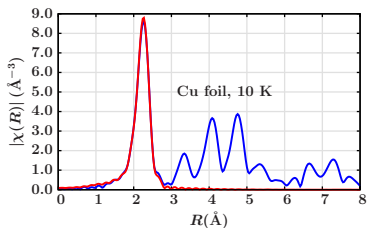
# define 3 Feff Path, give expressions for Path Parameters
path1_10 = feffpath('feff0001.dat',
                   s02='amp', e0='del_e0',
                   deltar='dr_off + 10*dr_slope',
                   sigma2='sigma2_eins(10, theta)')

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) K  
del\_e0 0.4(1.3) eV  
dr\_off 0.002(0.003) Å/K  
dr\_slope  $0.5(1.8) \times 10^{-5}$  Å



# Questions?