

# EXAFS Analysis

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# The EXAFS Equation

The XAFS Equation used with FEFF:

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

- $f(k)$  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 atoms 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.
- $\sigma^2$  – mean-square disorder in  $R$ .

# EXAFS Analysis Strategy: How to get $N$ , $R$ , and more

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

Step 1 Look up  $f(k)$ ,  $\delta(k)$ , and  $\lambda(k)$  in a book.

Step 2 Extract  $R$ ,  $N$ , and  $\sigma^2$  with a ruler and a calculator.

Step 3 Publish, Profit!!

Only Kidding!!!!

# EXAFS Analysis Strategy: How to get $N$ , $R$ , and more

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

**Step 1** Calculate theoretical XAFS spectra with FEFF, starting with a rough guess of the local structure.

**Step 2** *Refine*  $R$ ,  $N$ , and  $\sigma^2$  to best match experimental data.

**Step 3** Compare lots of refined models.

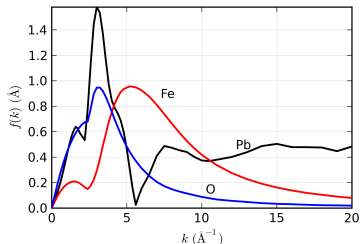
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Topics to try to cover:

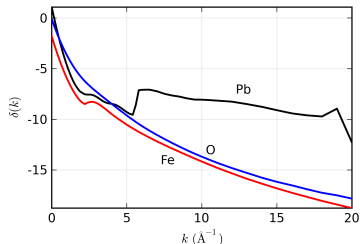
- How do we run FEFF to generate  $f(k)$ ,  $\delta(k)$ , and  $\lambda(k)$ ?
- What Correction Factors do we need to worry about?
- How do we fit experimental data?
- How do we interpret the results?
- What tips and tricks can help fitting EXAFS data with FEFF calculations?

# 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. For very heavy elements, there is a characteristic dip in  $f(k)$ .



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

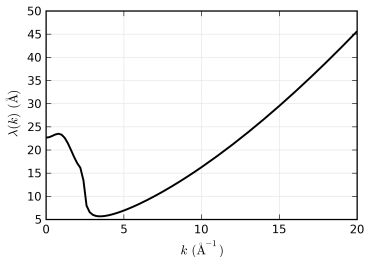
$Z$  can usually be determined to  $\pm 5$ .

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

XANES is more sensitive to longer distances than EXAFS.

# FEFF Calculation Overview

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).  
(aka 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” .
- ▶ decide which ones are unimportant for XAFS

- 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!

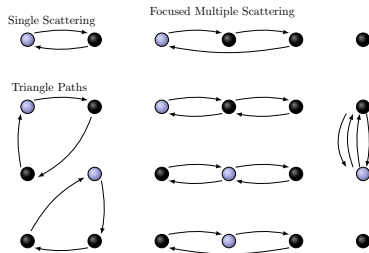


# FEFF complication #1: Multiple Scattering

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  $45^\circ < \theta < 135^\circ$  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  $\chi$ :

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

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

Usual strategy: Determine  $S_0^2$  from experimental data on a system with known  $N$  (an *Experimental Standard*).

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

The normal scheme for using FEFF for EXAFS data analysis is:

- 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 in your structure.
- 3 Use these Path Files in to model measured XAFS in an analysis program.

ARTEMIS and SIXPACK makes this even easier: they run and manages FEFF for you.

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*. No Kidding!

*feff.inp* file:

```
TITLE      Fe0, rock salt structure

HOLE       1   1.0   # K Edge, S02
CONTROL    1 1 1 1   # which parts of code to run
PRINT      1 0 0 3   # which output files to write

POTENTIALS      # list of Atomic Potentials
* potential    z  label
    0          26  Fe   # Absorbing Atom Potential=0
    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
2.13870 0.00000 0.00000 1 0
0.00000 2.13870 0.00000 1 0
0.00000 2.13870 2.13870 2 Fe
0.00000 -2.13870 -2.13870 2 Fe
-2.13870 2.13870 0.00000 2 Fe
2.13870 -2.13870 0.00000 2 Fe
0.00000 -2.13870 2.13870 2 Fe
```

*feff.inp* includes:

- 1 A list of unique Atomic Potentials:
  - ▶ Pot 0 = Absorbing Atom
  - ▶ 1 Potential per atomic species (Z)
- 2 List of atomic coordinates:
  - $x, y, z, Pot$for the cluster of atoms (in Å).

The cluster does not need to be crystalline!

The absorbing atom does not have to be at (0, 0, 0).

There can be only one absorbing atom!

# Input Parameters for *feff.inp*

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

- HOLE** which orbital absorbs the x-ray ( $1 = K$ ,  $4 = L_{III}$  )
- 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”.
- PRINT** which “Outputs” to write. Use “1 0 0 0”.
- RMAX** 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.

## ATOMS and *atoms.inp*

One convenient way to make *feff.inp* is with the ATOMS program which converts Crystal Structure to Atomic Cluster:

*atoms.inp* file:

```
TITLE      FeO, rock salt structure

space f m 3 m      # Space Group

a  = 4.2774      # Lattice Constant
rmax = 6.00      # Cluster Size
core = Fe1      # Central Atom

atom      # List of Cell Parameters
Fe  0.0000  0.0000  0.0000  Fe1
O   0.5000  0.5000  0.5000  01
-----
```

Using ATOMS is convenient, but not necessary!

ATOMS does not allow “doping”, or fractional substitution – you can edit the *feff.inp* file for that, or combine paths from multiple FEFF runs.

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

Atomic clusters may also come from:

Protein Data Bank, CIF Format data, Density Functional Theory Calculations, . . . .

## *feffNNNN.dat*: FEFF's output

FEFF writes out a separate file for each Scattering Path:  
*feff0001.dat*, *feff0002.dat*, ...

*feff.dat* file:

```
FeO, rock salt structure                                Feff XX 6.10
Abs  Z=26 Rmt= 1.197 Rnm= 1.402 K shell
Pot 1 Z= 8 Rmt= 0.937 Rnm= 1.103
Pot 2 Z=26 Rmt= 1.203 Rnm= 1.418
Gam_ch=1.325E+00 H-L exch
Mu=-4.210E+00 kf=2.067E+00 Vint=-2.048E+01 Rs_int= 1.755
Path  1      icalc      2
-----
 2  1.000  2.1387  2.4356  -4.21002 nleg, deg, reff, rnrnav(bohr), edge
    x      y      z  pot at
    0.0000  0.0000  0.0000  0 26 Fe      absorbing atom
    0.0000  2.1387  0.0000  1 8 0
k  real[2*phc]  mag[feff]  phase[feff]  red factor  lambda  real[p]
0.000  2.9505E+00  0.0000E+00  -3.0508E+00  0.1009E+01  2.3773E+01  2.0669E+00
0.200  2.9485E+00  9.9421E-02  -3.8738E+00  0.1009E+01  2.3876E+01  2.0762E+00
0.400  2.9424E+00  1.9477E-01  -4.6322E+00  0.1009E+01  2.4141E+01  2.1037E+00
0.600  2.9320E+00  2.8278E-01  -5.3276E+00  0.1010E+01  2.4444E+01  2.1488E+00
0.800  2.9172E+00  3.6142E-01  -5.9621E+00  0.1011E+01  2.4599E+01  2.2105E+00
1.000  2.8976E+00  4.2991E-01  -6.5379E+00  0.1012E+01  2.4410E+01  2.2878E+00
1.200  2.8723E+00  4.8834E-01  -7.0570E+00  0.1014E+01  2.3748E+01  2.3798E+00
```

This file contains:

- 1 Path geometry
- 2 Data for  $f(k)$ ,  $\delta(k)$ , and  $\lambda(k)$ .

You *never* have to read this file – the analysis program will do that.

You may have to move or rename files.

Analysis programs will use these files to model EXAFS as a *Sum of Paths*.

## 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  $N$ .



# Structural Disorder and the Pair Distribution Function

An EXAFS measurement averages billions of *snapshots* of the local structure:

- Each absorbed x-ray generates 1 photo-electron.
- the photo-electron / core-hole pair lives for about  $10^{-15}$  s – much faster than the thermal vibrations ( $10^{-12}$  s).
- An EXAFS measurement samples  $10^4$  (dilute fluorescence) to  $10^{10}$  absorbed x-rays for each energy point.

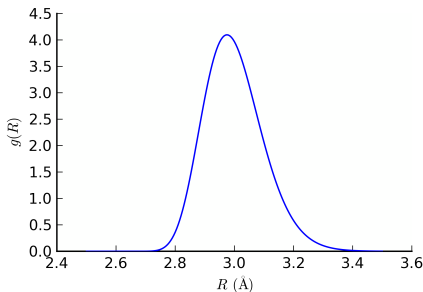
So far, we've put this in the EXAFS Equation as  $\chi \sim N \exp(-2k^2\sigma^2)$

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More generally, EXAFS samples the

*Partial Pair Distribution Function*

$g(R)$  = probability that an atom is a distance  $R$  away from the absorber.



# EXAFS and The Pair Distribution Function

To fully account for a highly disordered local structure, we should use

$$\chi(k) = \left\langle \sum_j \frac{f_j(k) e^{i2kR_j + \delta_j(k)}}{kR_j^2} \right\rangle$$

where  $\langle x \rangle = \int dR x g(R) / \int dR g(R)$  – averaging over the billions+ of snapshots.

$R$  won't change too much, so we'll neglect the changes to  $1/R^2$ :

$$\chi \approx \sum_j f_j(k) \frac{e^{i\delta_j(k)}}{kR_j^2} \left\langle e^{i2kR_j} \right\rangle$$

each path in the sum now has a  $g(R)$  with respect to the absorbing atom.

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The *the cumulant expansion* relates  $\langle e^x \rangle$  to  $\langle x \rangle$ , the moments of  $g(x)$ :

$$\left\langle e^{i2kR} \right\rangle = \exp \left[ \sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} C_n \right].$$

# The Cumulants and Moments of a Distribution Function

The cumulants  $C_n$  of  $g(R)$  are related to the moments of  $g(R)$ :  $\langle r^n \rangle$ , with  $r = R - R_0$  and  $R_0$  is the centroid of the distribution:

$$C_1 = \langle r \rangle = \Delta R$$

$$C_2 = \langle r^2 \rangle - \langle r \rangle^2 = \sigma^2$$

$$C_3 = \langle r^3 \rangle - 3\langle r^2 \rangle \langle r \rangle + 2\langle r \rangle^3$$

$$C_4 = \langle r^4 \rangle - 3\langle r^2 \rangle^2 - 4\langle r^3 \rangle \langle r \rangle + 12\langle r^2 \rangle \langle r \rangle^2 - 6\langle r \rangle^4$$

$C_3$  (the *third cumulant*) can be important For many EXAFS problems.

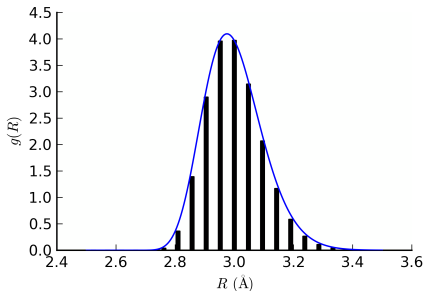
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Sometimes, the cumulant expansion isn't good enough. One can build more complicated models . . . .

*Example:*

Use many closely spaced paths to allow for nearly any distribution.

Model the amplitude of each Path.



# XAFS Analysis with ARTEMIS, IFEFFIT, and FEFF

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*:

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

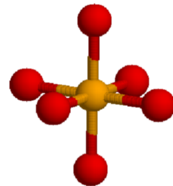
- $R_{\text{eff}}$  is the starting  $R$  value for the FEFF Path.
- Other Parameters: higher order cumulants, energy broadening, ...
- In principle, any parameter for any path could be refined.

# EXAFS Analysis: Modeling the 1st Shell of FeO

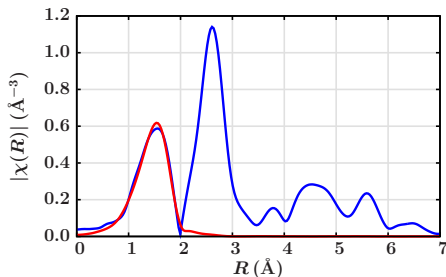
FeO has a rock-salt structure.

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,  
 $R = 2.14 \text{ \AA}$ .

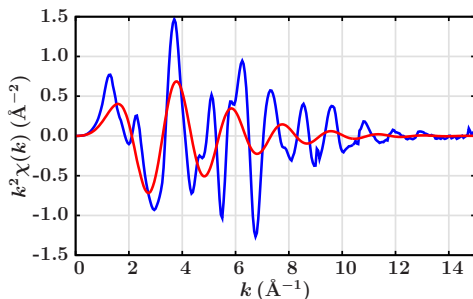


$|\chi(R)|$  for FeO *data* and *1<sup>st</sup> shell fit*.

Results:

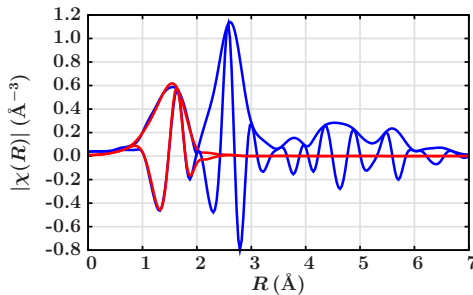
$$\begin{aligned} S_0^2 &= 0.75 \text{ (fixed)} \\ N &= 4.7 \pm 0.4 \\ R &= 2.10 \pm 0.01 \text{ \AA} \\ \Delta E_0 &= -3.5 \pm 1.0 \text{ eV} \\ \sigma^2 &= 0.011 \pm 0.001 \text{ \AA}^2. \end{aligned}$$

## Analysis Example: 1st Shell of FeO



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

There is clearly another component in the XAFS!



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.

# Fitting Strategies

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.

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!

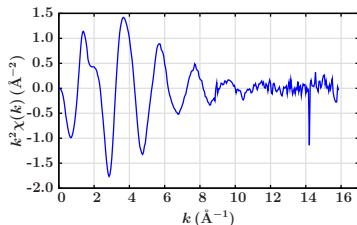
*R-factor*:  $\mathcal{R}$  gives a “fractional misfit” (and not scaled by the data uncertainty  $\epsilon$ ):

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

## $\epsilon$ : The Noise Levels in Data

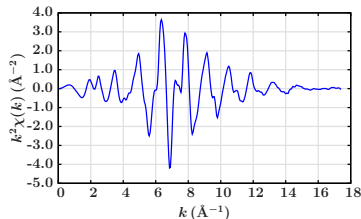
Here are some typical EXAFS spectra (both transmission, 1 sec/point), and their estimated noise  $\epsilon$  in  $\chi(k)$ :

0.2 mM Zn nitrate solution



$$\epsilon \approx 6.6 \times 10^{-4} \text{ "Normal Data"}$$

Cu foil Room Temperature

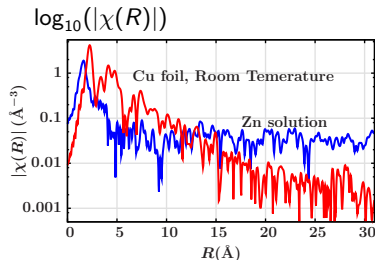
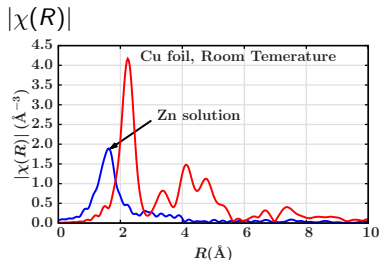


$$\epsilon \approx 1.6 \times 10^{-4} \text{ "Good Data"}$$

For the Zn solution, this noise level is consistent with counting statistics for "Number of Photons in Ion Chambers"!

## $\epsilon$ : Noise Levels in Data

$\epsilon$  here is estimated from the high- $R$  [15 to 25 Å] components of the data:



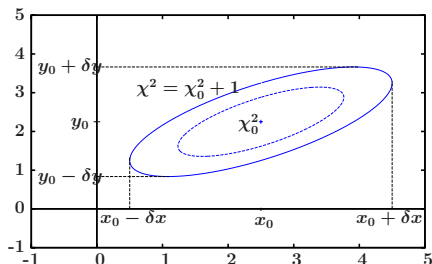
- The Zn data really shows “white noise”.
- The Cu data has signal well above the noise level past 10Å!
- Using the range  $R = [15, 25]$  Å may *overestimate*  $\epsilon$  for good data.

A general property of Fourier transforms allows us to translate the noise in  $\chi(R)$  to the noise in  $\chi(k)$ .

# 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  $\chi^2$ .

Uncertainties in  $x$  are estimated by increasing the  $\chi^2$  by 1:



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  $\chi_\nu^2 \approx 1$ .*

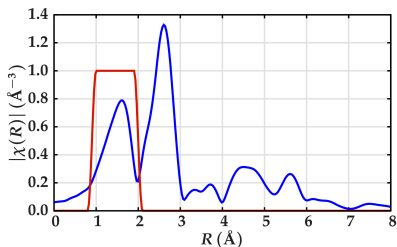
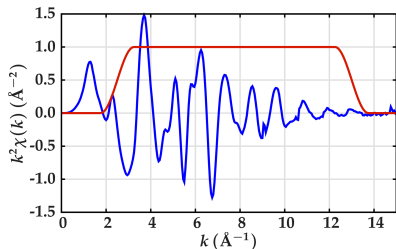
We typically have  $\chi_\nu^2 \gtrsim 50$  (Yikes!).

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

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

The  $\chi^2$  definition didn't say anything about what our data  $\chi_i^{\text{measured}}$  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.

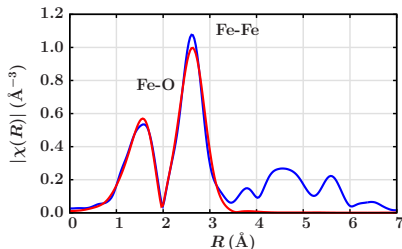
**Plus:** We can have  $\chi_i^{\text{measured}}$  extend over

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).

These results are consistent with the known values for FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results: Statistics:  $R \approx 0.015$   $\chi^2_\nu \approx 165$ .

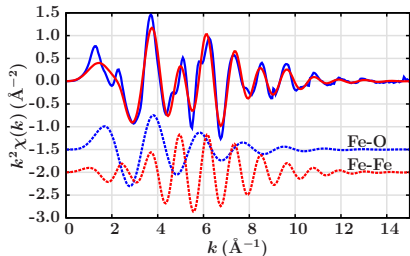
| Shell | $N$       | $R$ (Å)   | $\sigma^2$ (Å <sup>2</sup> ) | $\Delta E_0$ (eV) |
|-------|-----------|-----------|------------------------------|-------------------|
| Fe-O  | 5.1(0.8)  | 2.10(.01) | 0.012(.003)                  | -1.4(0.9)         |
| Fe-Fe | 12.6(1.6) | 3.07(.01) | 0.013(.001)                  | -1.4(0.9)         |

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

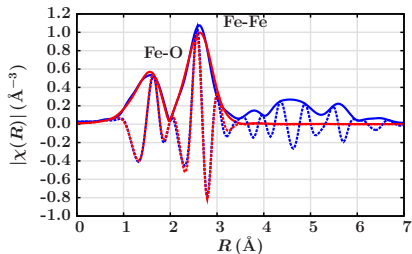
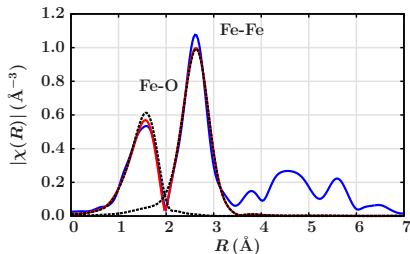
Other views of the data and fit:



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  $\text{Re}[\chi(R)]$  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:

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

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 e0 for 2 paths
guess e0 = 1.0
path(1, feff= feo.dat, e0 = e0)
path(2, feff= fefe.dat, e0 = e0)
```

## Mixed Coordination Shell

```
# mix O and S in 1st coordination shell
set S02 = 0.80
guess xSulfur = 0.5

path(1, feff= feo.dat, amp=S02* xSulfur )
path(2, feff= fes.dat, amp=S02* (1-xSulfur) )
```

## Einstein Temperature

```
# 1 parameter to set sigma2 for all paths
set factor = 24.254337  # = (hbar*c)^2/(2 k_boltz)
# mass and reduced mass in amu
set mass1 = 63.54, mass2 = 63.54
set r_mass = 1/ (1/mass1 + 1/mass2)

# the Einstein Temp will be adjusted in the fit!
guess thetaE = 200

# use for data set 1, T=77
set temp1 = 77
def ss2_path1 = factor*coth(thetaE/(2*temp1))/r_mass )
path(101, sigma2 = ss2_path1 )

# use for data set 2, T=300
set temp2 = 300
def ss2_path2 = factor*coth(thetaE/(2*temp2))/r_mass )
path(201, sigma2 = ss2_path2 )
```

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

```
guess s02      = 0.93
guess theta    = 240
guess e0       = 3.5
guess alpha    = 0.0
guess a_t      = 0.00

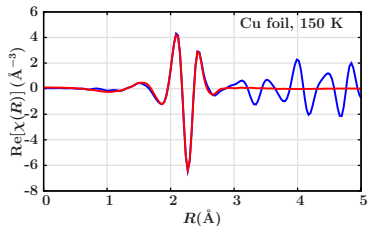
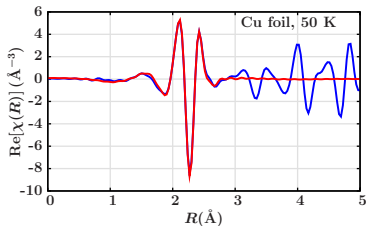
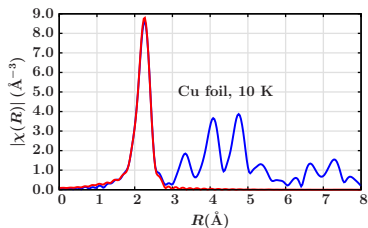
path(index     = 101, feff = feffcu01.dat,
  label       = "Cu metal first shell, for 10K",
  s02         = s02,
  sigma2      = eins(10, theta),
  delr        = reff * (alpha + 10.0 * a_t) ,
  e0          = e0)

path(index     = 201, feff = feffcu01.dat,
  label       = "Cu metal first shell, for 50K",
  s02         = s02,
  sigma2      = eins(50, theta),
  delr        = reff * (alpha + 50.0 * a_t) ,
  e0          = e0 )

path(index     = 301, feff = feffcu01.dat,
  label       = "Cu metal first shell, for 150K",
  s02         = s02,
  sigma2      = eins(150, theta),
  delr        = reff * (alpha + 150.0 * a_t) ,
  e0          = e0 )
```

# Example: Cu metal Results

$$\begin{aligned} S_0^2 &= 0.91(0.08) \\ \theta &= 233.5(19.6) \text{ K} \\ e_0 &= 0.4(1.3) \text{ eV} \\ \alpha &= 0.002(0.003) \text{ \AA/K} \\ a_t &= 0.5(1.8) \times 10^{-5} \text{ \AA} \end{aligned}$$



## Multiple Scattering Example: $\text{Cp-MnCO}_3$

$\text{Cp-MnCO}_3$  = tricarbonyl( $\eta^5$ -cyclopentadienyl)manganese(I)

This molecule has linear Mn-C-O bonds, and two distinct Mn-C distances.

To model the EXAFS, we need these paths:

ring

5 Mn-C at  $\sim 2.13 \text{ \AA}$

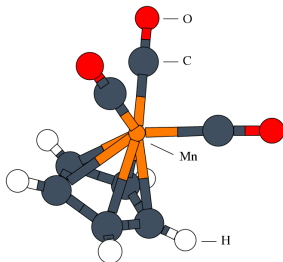
carbonyl

3 Mn-C at  $\sim 1.78 \text{ \AA}$

3 Mn-O at  $\sim 2.93 \text{ \AA}$

6 Mn-C-O paths at  $\sim 2.93 \text{ \AA}$

3 Mn-C-O-C paths at  $\sim 2.93 \text{ \AA}$



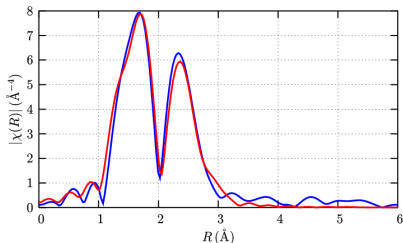
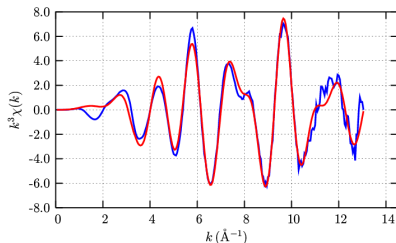
The Multiple Scattering Paths will overlap the longer Mn-C(ring) distance!!

Using only the single-scattering paths will gives:

- large coordination numbers: 6 Mn-C(ring) at  $2.10 \text{ \AA}$ , 10 Mn-C(carbonyl) at  $1.80 \text{ \AA}$ , and 10 Mn-O (carbonyl) at  $2.99 \text{ \AA}$ .
- $E_0$  of  $-13\text{eV}$  (pretty big! A hint!).

# Cp-MnCO<sub>3</sub> with Multiple Scattering

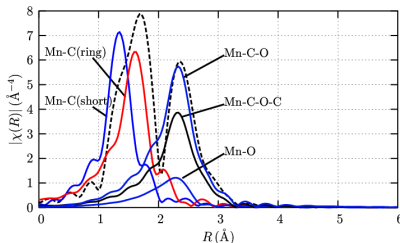
The Mn *K*-edge EXAFS, and fit with 5 paths.



Constrained  $N_{\text{Mn-O}} = N_{\text{Mn-C(short)}}$ , and used 1  $E_0$  for all paths. This refined to  $-3.6 \pm 2.0$  eV.

| Path        | N        | R (Å)     | $\sigma^2$ (Å <sup>2</sup> ) |
|-------------|----------|-----------|------------------------------|
| Mn-C(short) | 3.6(1.0) | 1.80(.02) | 0.005(.002)                  |
| Mn-C(long)  | 5.2(1.3) | 2.11(.02) | 0.004(.002)                  |
| Mn-O        | 3.6(1.3) | 2.92(.04) | 0.003(.006)                  |

The MS paths are very important here, and overlap the 1st shell.



EXAFS Analysis is challenging:

- ① Lots of Paths.
  - ②  $f(k)$ ,  $\delta(k)$  are not trivial.
  - ③ There's not much information in a real measurement:  $N_{\text{idp}} \approx \frac{2\Delta k \Delta R}{\pi}$
- 

We need to:

- ① **reduce** the number of Paths to consider (Fourier analysis).
  - ② **re-use** FEFF calculations for  $f(k)$  and  $\delta(k)$ .
  - ③ **recycle** parameters to cut down the number of independent variables in the fit, while keeping a meaningful analysis.
- 

Build physical models with *Constraints*

Study the error bars and correlations.

Find the simplest interpretation of your data.