Data Processing with IFEFFIT, ATHENA, & ARTEMIS

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Acknowledgments

John Rehr

FEFF

U. Washington

Bruce Ravel

ATHENA, ARTEMIS

Argonne

Sam Webb

SIXPACK

SSRL

ATHENA, ARTEMIS, and SIXPACK are GUI built on top of the IFEFFIT library:

- Data Management and Visualization
- XAFS Data Processing: background subtraction, Fourier Transforms.
- Simple XANES analysis: linear combination.
- Run FEFF for *ab initio* XAFS calculations.
- Fit XAFS data to calculations, build physical models.

The FEFF and IFEFFIT suite of XAFS Analysis Programs

FEFF6 *ab initio* EXAFS calculations (J. J. Rehr, *et al.*, 1990 – 1998)

- state-of-the-art photo-electron scattering physics.
- no built-in analysis – used by many analysis programs.

IFEFFIT Interactive (command-line) XAFS Analysis, building on earlier codes: AUTOBK and FEFFIT (MN, 2000).

ATHENA GUI for XAFS Data Processing, using IFEFFIT (Ravel, 2001).

ARTEMIS GUI for XAFS Fitting, using FEFF and IFEFFIT (Ravel, 2002).

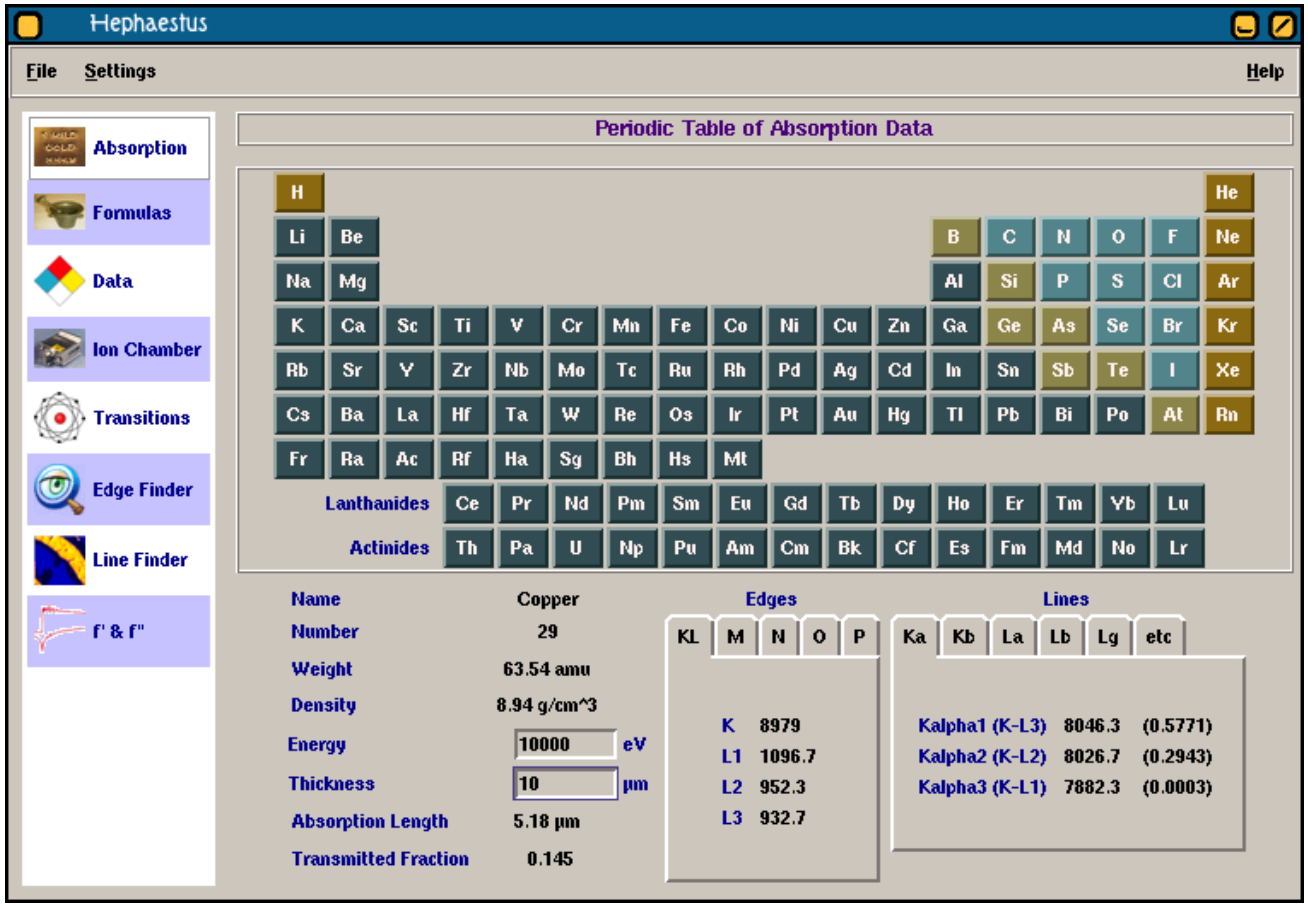
HEPHAESTUS GUI for XAFS information (edge energies,etc) (Ravel, 2004).

SIXPACK GUI for XAFS Analysis, using FEFF and IFEFFIT (Webb, 2003).

Not Included in the IFEFFIT Package:

FEFF8 necessary for *ab initio* XANES calculation. Helpful for some EXAFS Analysis (J. J. Rehr, *et al.*, 1998 – present)
Requires a license from U. Washington [∼US$400].

HEPHAESTUS: Periodic Table of X-ray Properties



Edge Energies, Fluorescence Line Energies, Absorption calculations

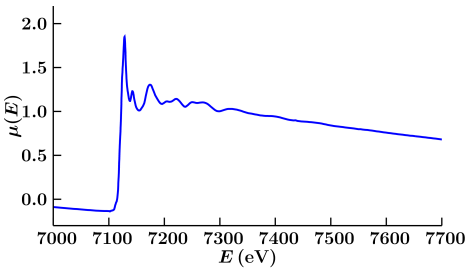
SIXPACK: Sam's XAS Programs

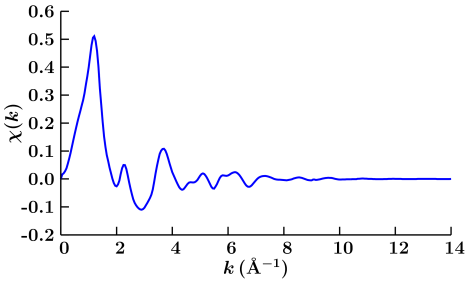
Well-supported GUIs, used heavily in Northern CA!

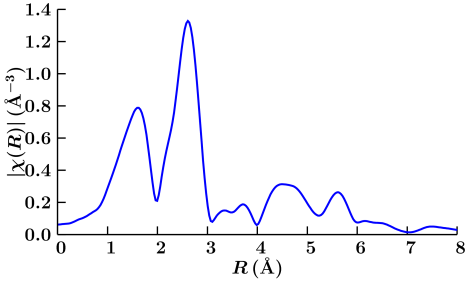
- Reading / Viewing Data from Many beamlines
- Linear Combinations and Principle Component Analysis (for XANES)
- EXAFS Fitting with simple FEFF models.

Data Processing with ATHENA / IFEFFIT

ATHENA provides a GUI for processing beamline data to $\chi(k)$.







Collected Spectra $\mu(E)$ $\Rightarrow$ Spline Subtracted $\chi(k)$ $\Rightarrow$ Fourier Transform of $\chi(k)$

- Read in beamline data, merge data sets.
- Deglitch, Align Spectra, Shift energies.
- Pre-edge subtraction, Find E_0, Normalize Spectra
- Background subtraction to $\chi(k)$.
- Fourier Transforms $\chi(k) \rightarrow \chi(R)$.
- Simple Data Plotting.
- Save/Read "Projects" of Analysis.

Other features, including:

- Correct for self absorption of fluorescence data.
- Linear combination fits, peak shape fitting for XANES / EXAFS.

Athena User Guide

ATHENA User's Guide

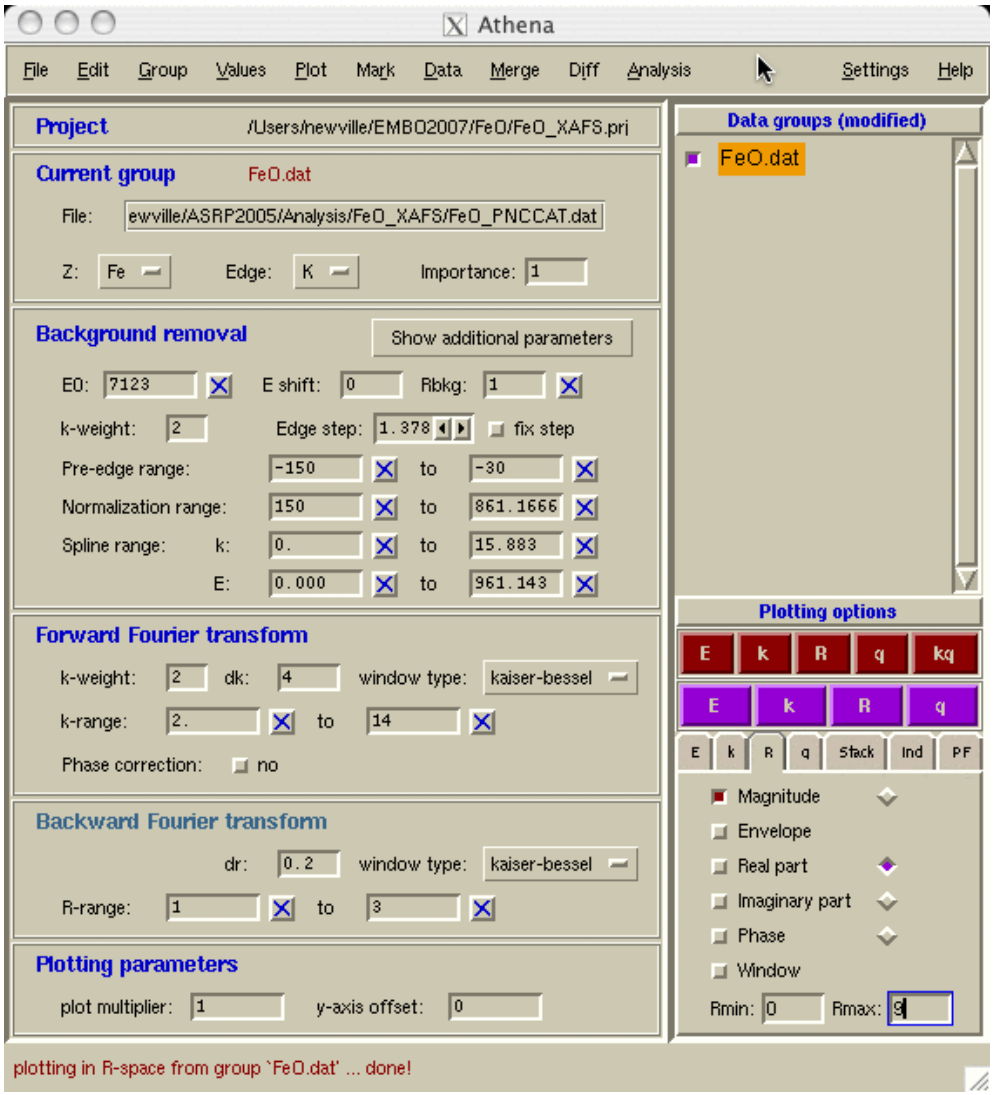
Bruce Ravel
bravel@anl.gov
http://cars9.uchicago.edu/~ravel/software/exafs/

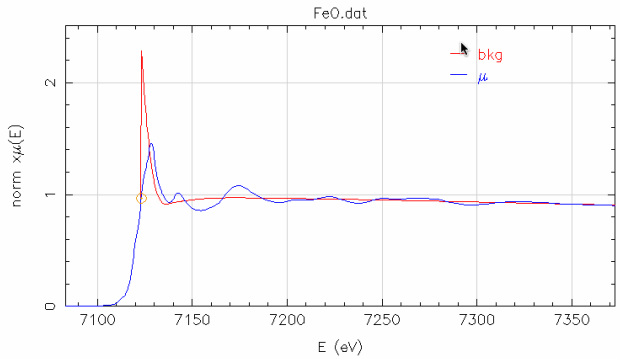
Document version 1.2

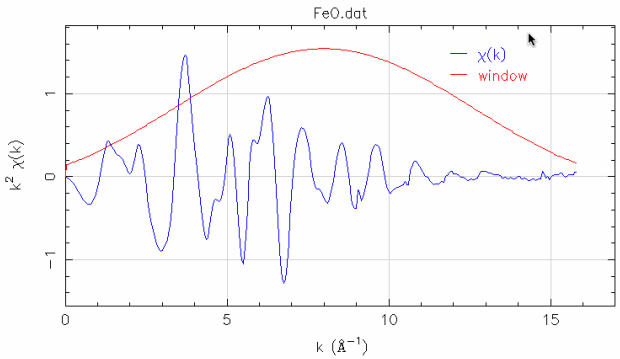
for ATHENA version 0.8.53
June 24, 2007

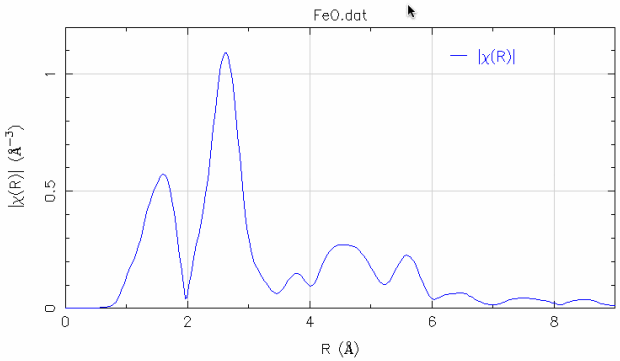
You may find this helpful.

Data Processing with ATHENA / IFEFFIT









Data Reduction: Strategy

Steps for reducing measured data to $\mu(E)$ and then to $\chi(k)$:

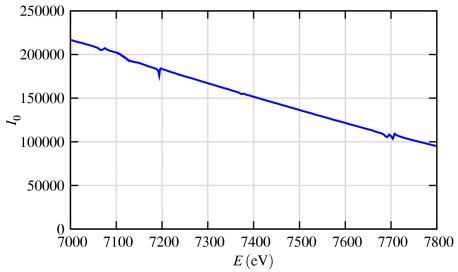
1. convert measured intensities to $\mu(E)$.
2. subtract a smooth pre-edge function, removing instrumental background and absorption from other edges.
3. normalize $\mu(E)$ to go from 0 to 1. *Analyze normalized $\mu(E)$ as XANES.*
4. remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS $\chi(k)$.
5. identify the threshold energy E_0, and convert from E to k space: $k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$
6. weight the XAFS $\chi(k)$ and Fourier transform from k to R space.

After we get this far, we'll model $\chi(k)$ with FEFF calculations.

Data Reduction: Converting Raw Data to $\mu(E)$

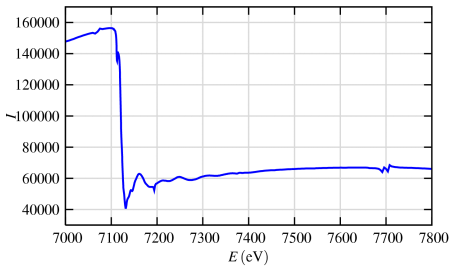
Starting with measured intensities before and after the sample, we construct $\mu(E)$:

Transmission XAFS: $\mu(E)t = \ln(I_0/I_t)$



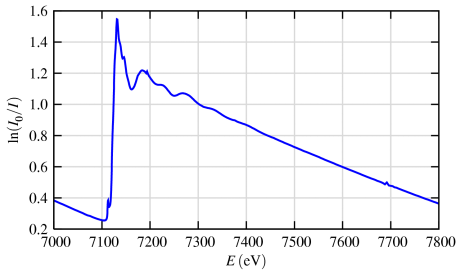
I_0

$\div$



I_t

$=$



$\mu(E)$

Fluorescence XAFS: $\mu(E) \propto I_f/I_0$

I_f may be the

- the intensity from a single fluorescence ion chamber (Lytle detector)
- the **sum** of several signals from a multi-element solid-state detector.

Merging Data, Aligning Data, Deglitching

Real Data is typically measured in several scans.

These scans can be *merged* together to give better statistics.
Important issues when processing real data

- The monochromator energy calibration may drift with time.
  - scans can be aligned so that E_0 is constant for all scans.
  - a *Reference Channel* – often a metal foil – can be measured **during the scan** and used for energy alignment.
  - if the drift is bad enough (every scan, etc), consult the beamline scientist.
- At certain energies, I_0 jumps – a *glitch* – that ma not normalize out of $\mu(E)$. These points should be removed.

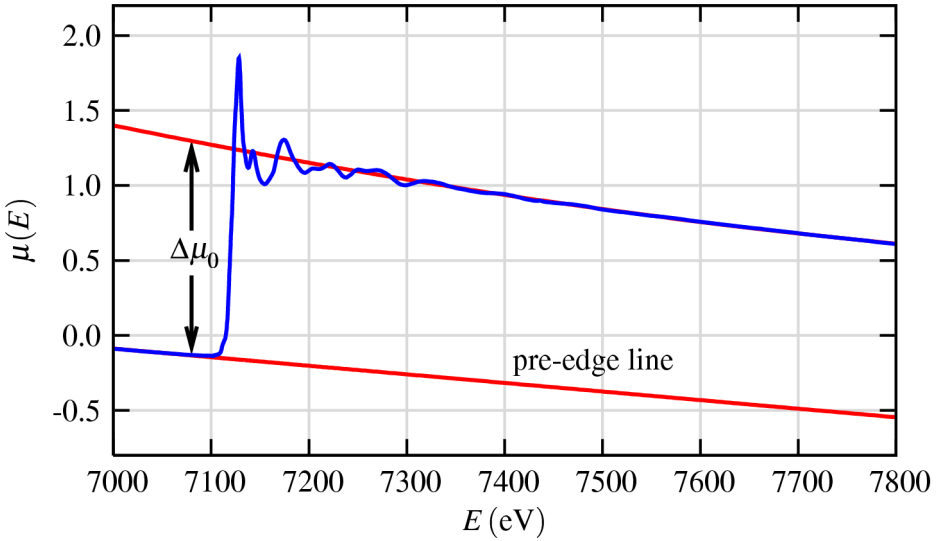
Other corrections that could be made:

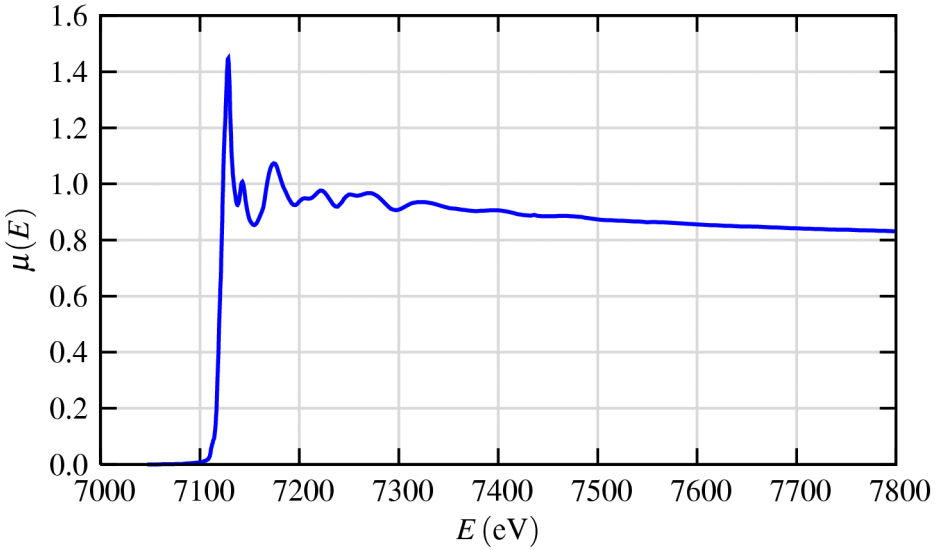
- *self-absorption* for concentrated samples measured in fluorescence.
- *detector dead-time* for fluorescence measurements with a solid-state detector.

ATHENA and/or SIXPACK can deal with all of these.

Data Reduction: Pre-Edge Subtraction, Normalization

Data reduction of $\mu(E)$ data goes like this:





Pre-Edge Subtraction

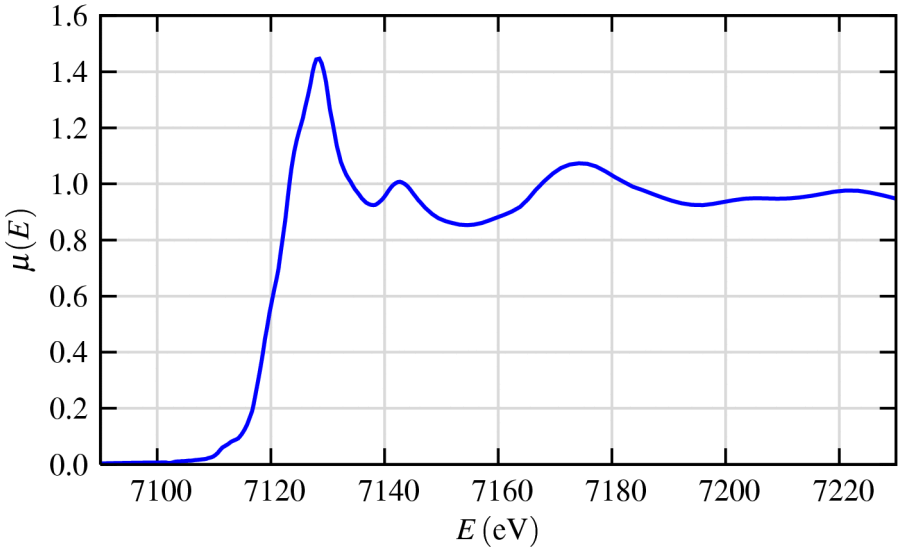
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other absorption edges (say, the Fe $\mathrm{L_{III}}$ edge).

Normalization

We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple curve the above $\mu(E)$ to the edge.

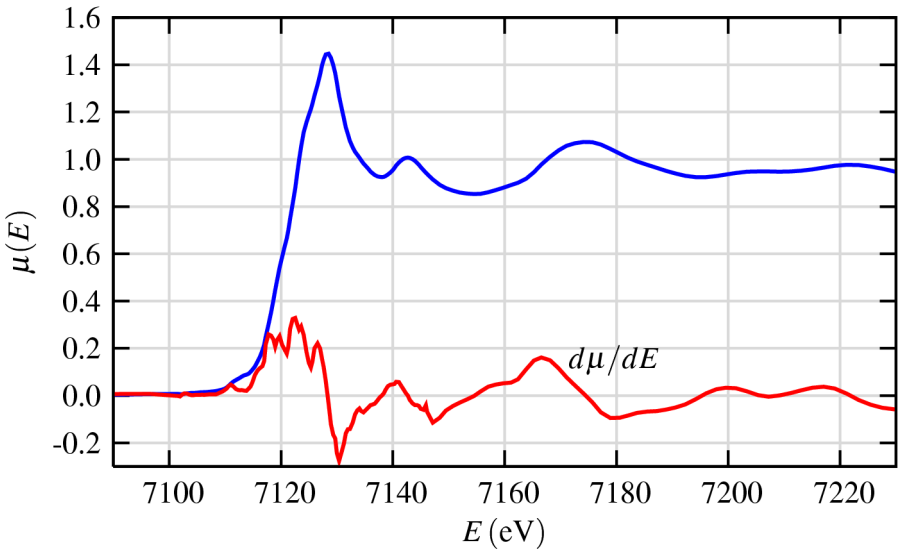
$$\mu_{\mathrm{Norm}}(E) = \mu(E)/\Delta\mu_0(E_0)$$

Data Reduction: Normalized XANES and E_0



XANES

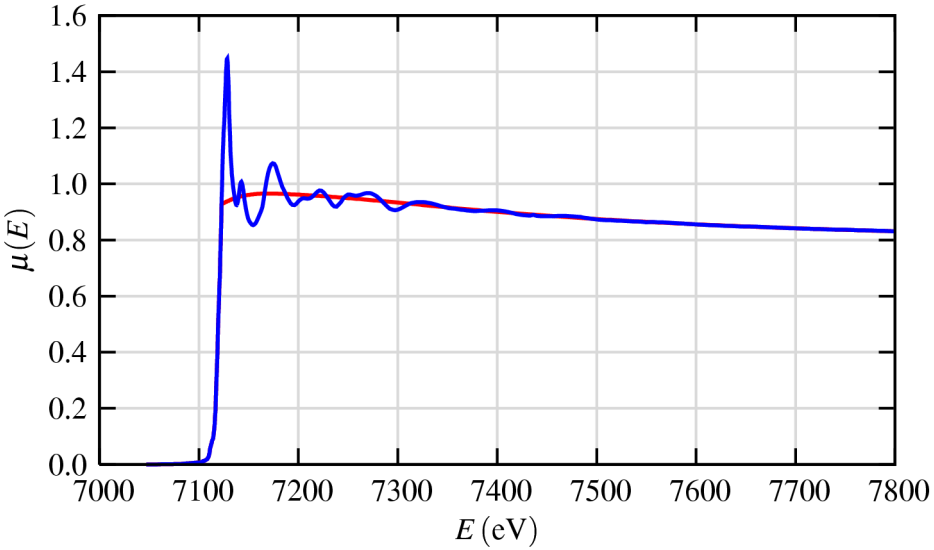
The XANES part of $\mu(E)$ shows a fairly rich spectral structure. We'll use this for XANES analysis.

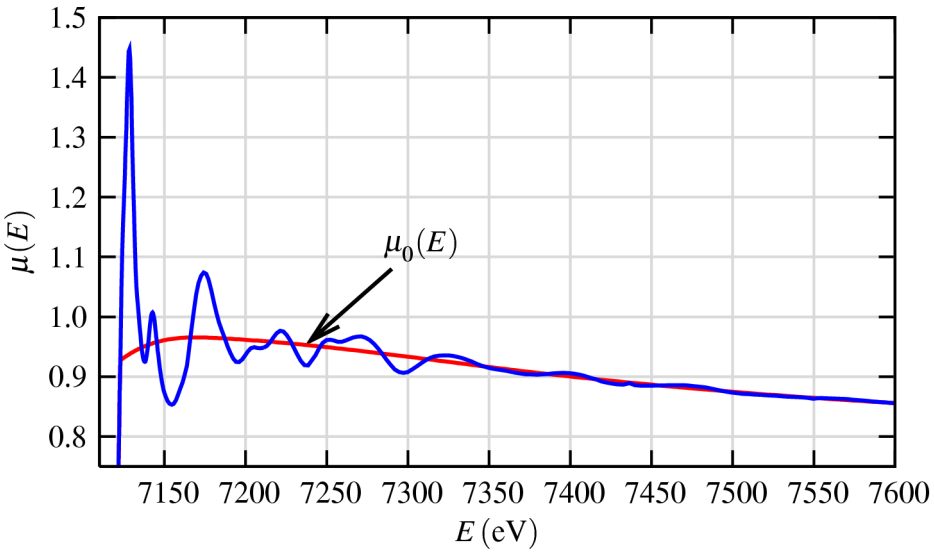


Derivative

We can select E_0 roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we'll keep in mind that we may need to refine this value later on.

Data Reduction: Post-Edge Background Subtraction





Post-Edge Background

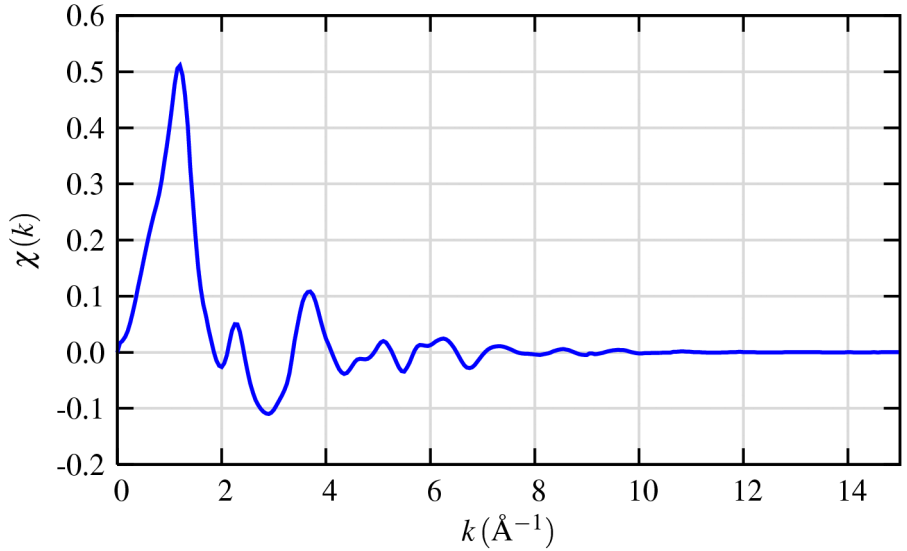
We don't have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).

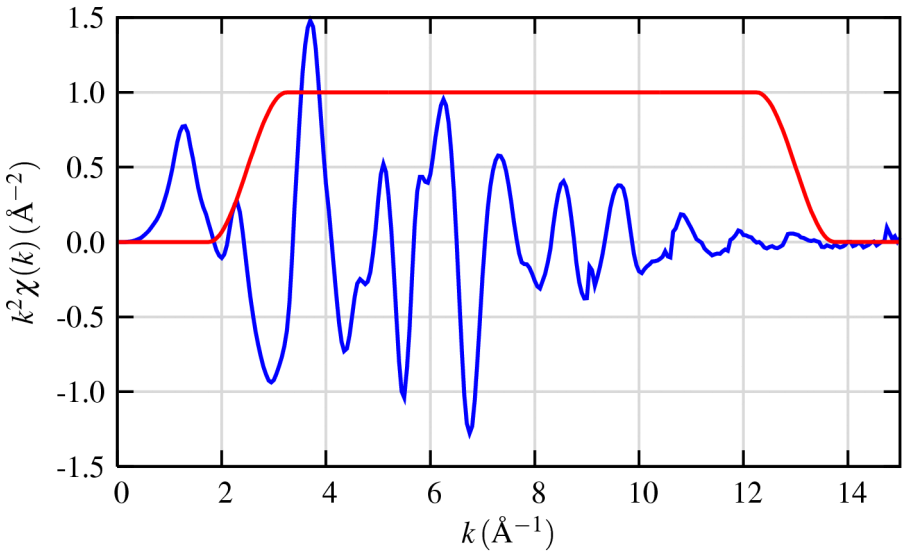
We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.

This can be somewhat dangerous – a flexible enough spline could match $\mu(E)$ and remove all the EXAFS!

We want a spline that will match the *low frequency* components of $\mu(E)$.

Data Reduction: $\chi(k)$, k-weighting





$\chi(k)$

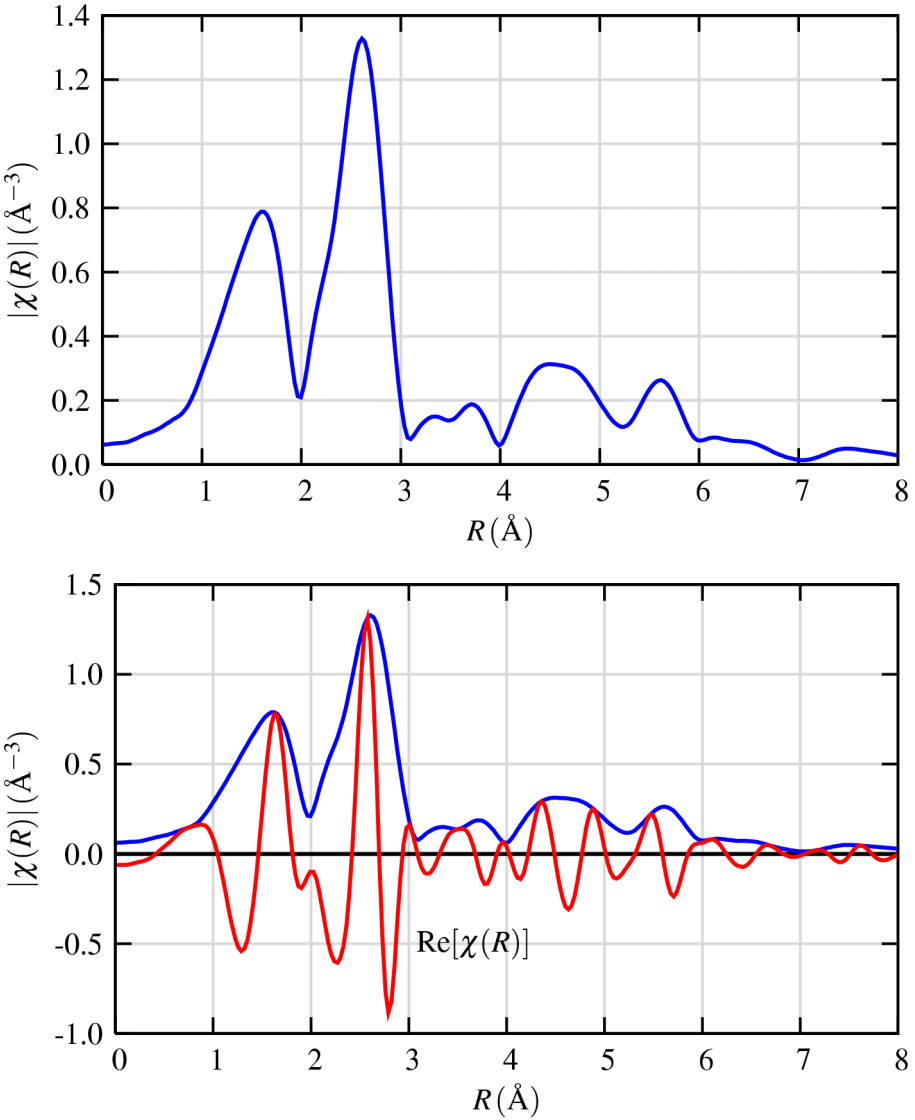
The raw EXAFS $\chi(k)$ decays quickly with k.

We emphasize the higher-k portion of the spectra by multiplying by k^2 or k^3.

k-weighted $\chi(k)$: $k^2\chi(k)$

$\chi(k)$ is composed of sine waves, so we'll Fourier Transform from k to R-space. To avoid "ringing", we'll multiply by a *window function*.

EXAFS Fourier Transform: $\chi(R)$



$\chi(R)$

Peaks in $\chi(R)$ often correspond to "coordination shells". The Fe-O distance in FeO is 2.14Å – the first peak is at 1.6Å.

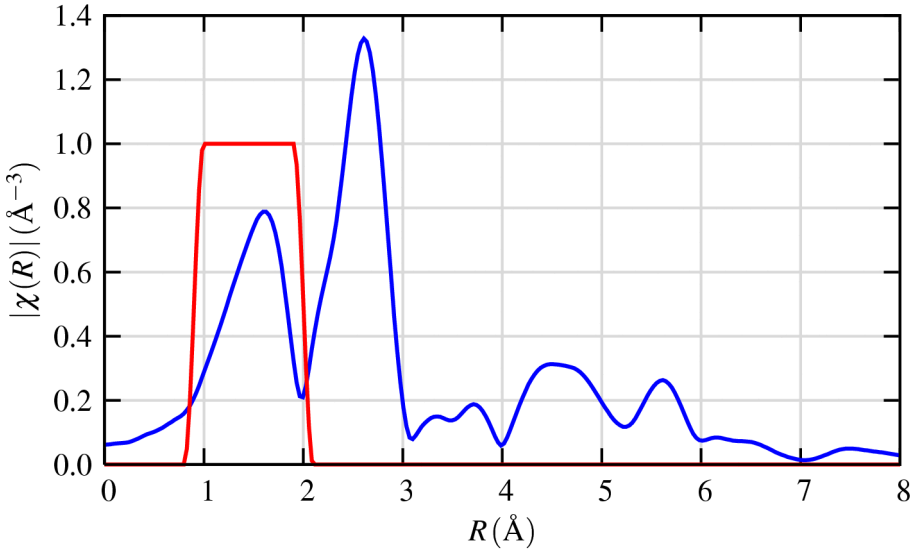
This distance shift is due to the *phase-shift*: $\sin[2kR + \delta(k)]$.

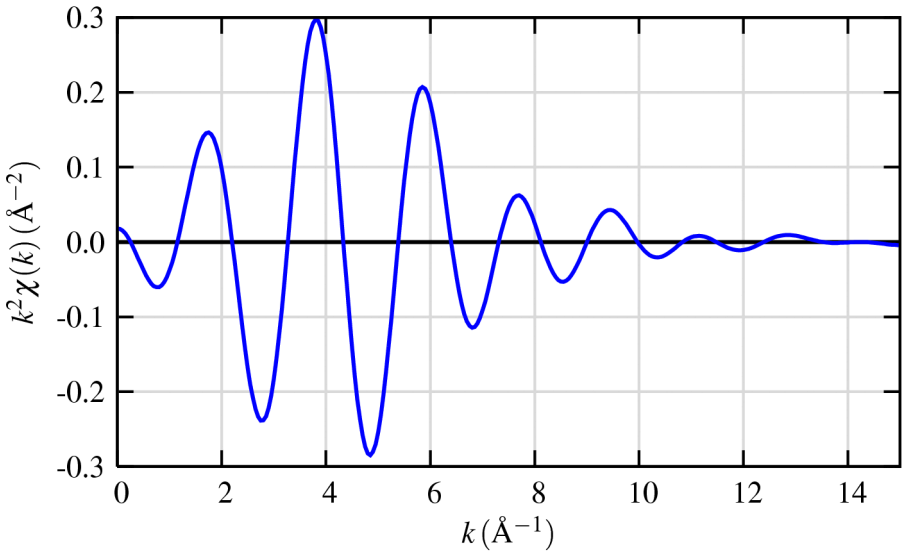
$\chi(R)$ is complex:

Usually only the amplitude is shown, but there are oscillations in $\chi(R)$.

Both real and imaginary parts are used in modeling.

Fourier Filtering





$\chi(R)$ often has well-separated peaks for different "shells".

This shell can be isolated by a Filtered Back-Fourier Transform, using the window shown for the first shell of FeO.

$\chi(q)$ ("Q-space")

This results in the filtered $\chi(k)$ for the selected shell.

Many analysis programs use such filtering to remove shells at higher R.

Don't do it – it's too hard.

Fourier Transforms

Fourier Transforms are an important part of XAFS Analysis:

$$\chi(R) = \mathrm{FT}[\chi(k)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, e^{i2kR}\, k^w\, \chi(k)\, \Omega(k)$$

- $\Omega(k)$ is the Window Function
- w is the k-weighting

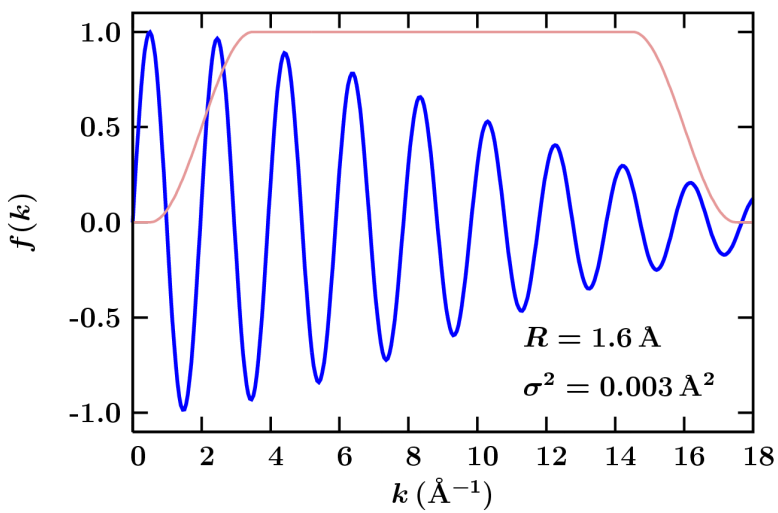
We really use a discrete version and Fast Fourier Transform

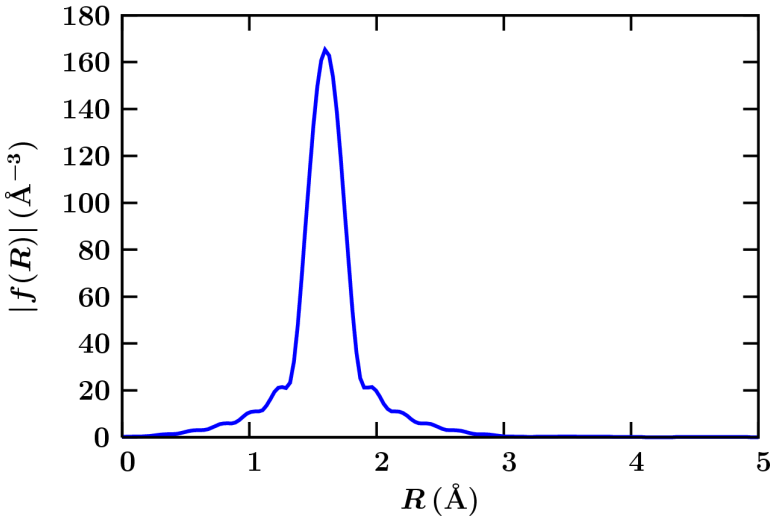
$$\chi(R_m) = \frac{i\delta k}{\sqrt{\pi N_{\mathrm{fft}}}} \sum_{n=1}^{N_{\mathrm{fft}}} e^{2\pi i n m / N_{\mathrm{fft}}}\, k_n^w\, \chi(k_n)\, \Omega(k_n)$$

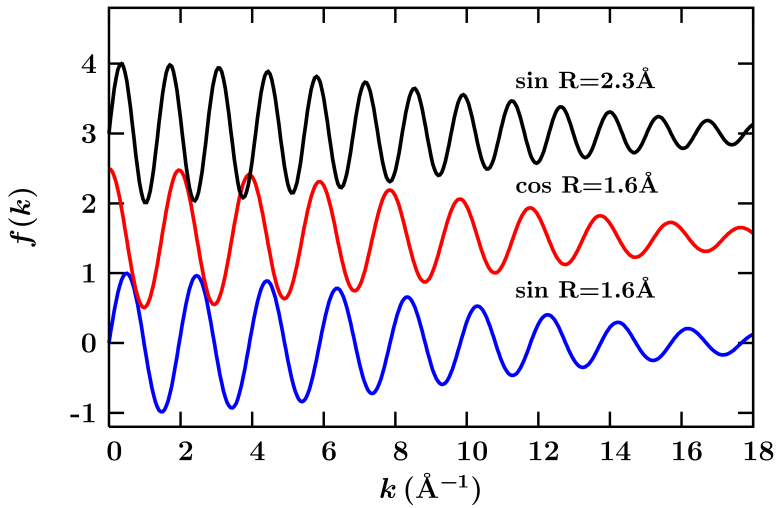
- $\chi(k)$ is put on a uniform k-grid with spacing of $\delta k = 0.05\,\mathrm{\AA}^{-1}$.
- $\chi(k)$ is filled with zeros past the real data range.
- $N_{\mathrm{fft}} = 2048$: $\chi(k)$ can go to $102.4\,\mathrm{\AA}^{-1}$ ($\sim 40\,\mathrm{keV}$) past the edge.
- $\chi(R)$ is on a R-grid with spacing $\sim 0.031\,\mathrm{\AA}$, and can go to $31.4\,\mathrm{\AA}$.

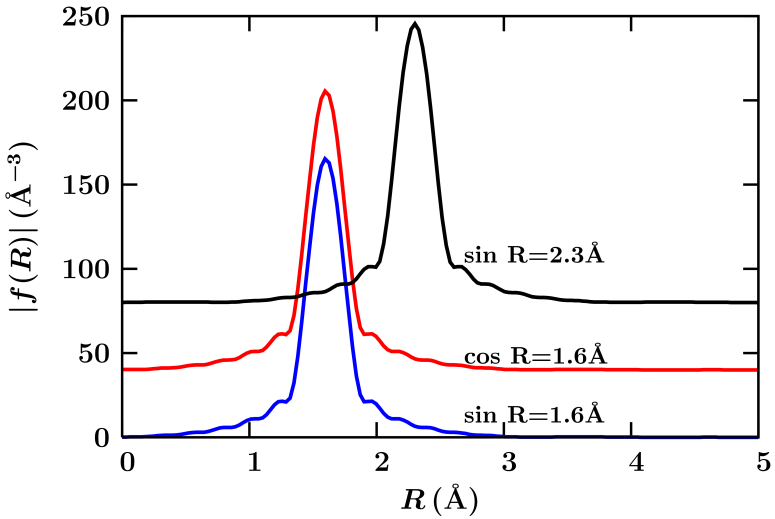
Fourier Transforms: Basic Properties

Fourier Transform of a sine wave:



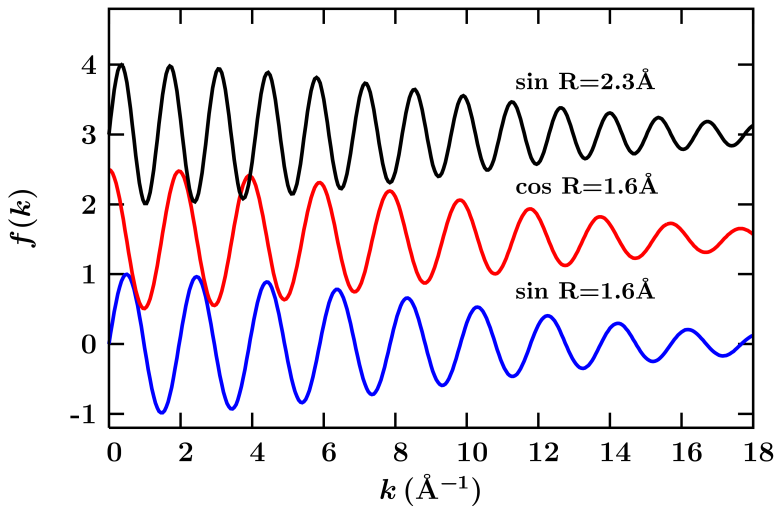






Fourier Transforms: Basic Properties(2)

Fourier Transforms are complex:



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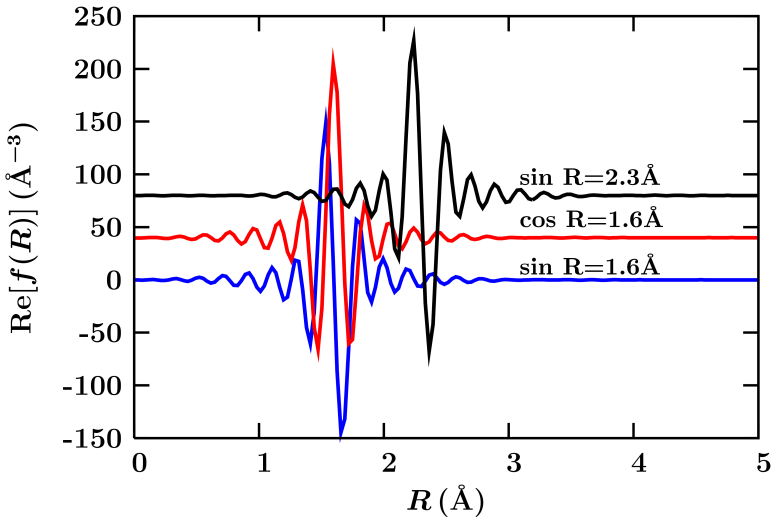
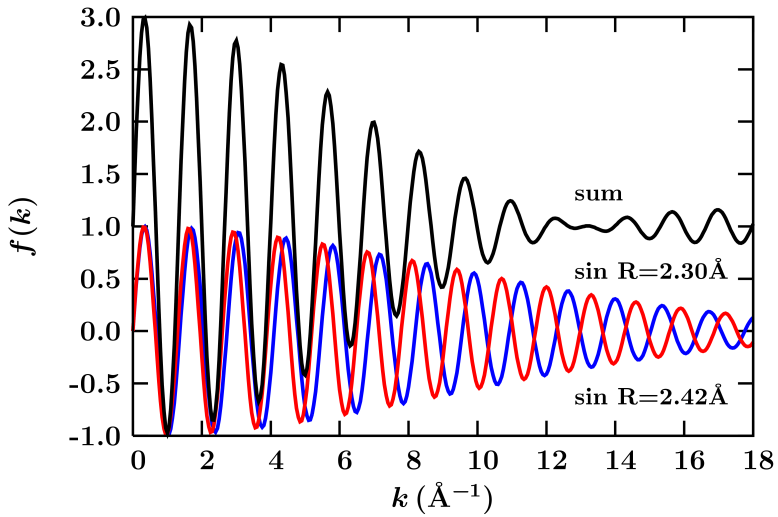


Frequencies that are close can "beat"



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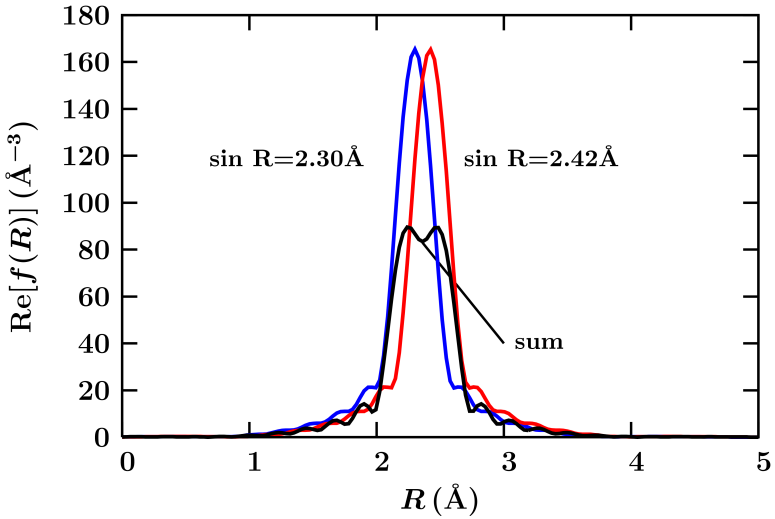
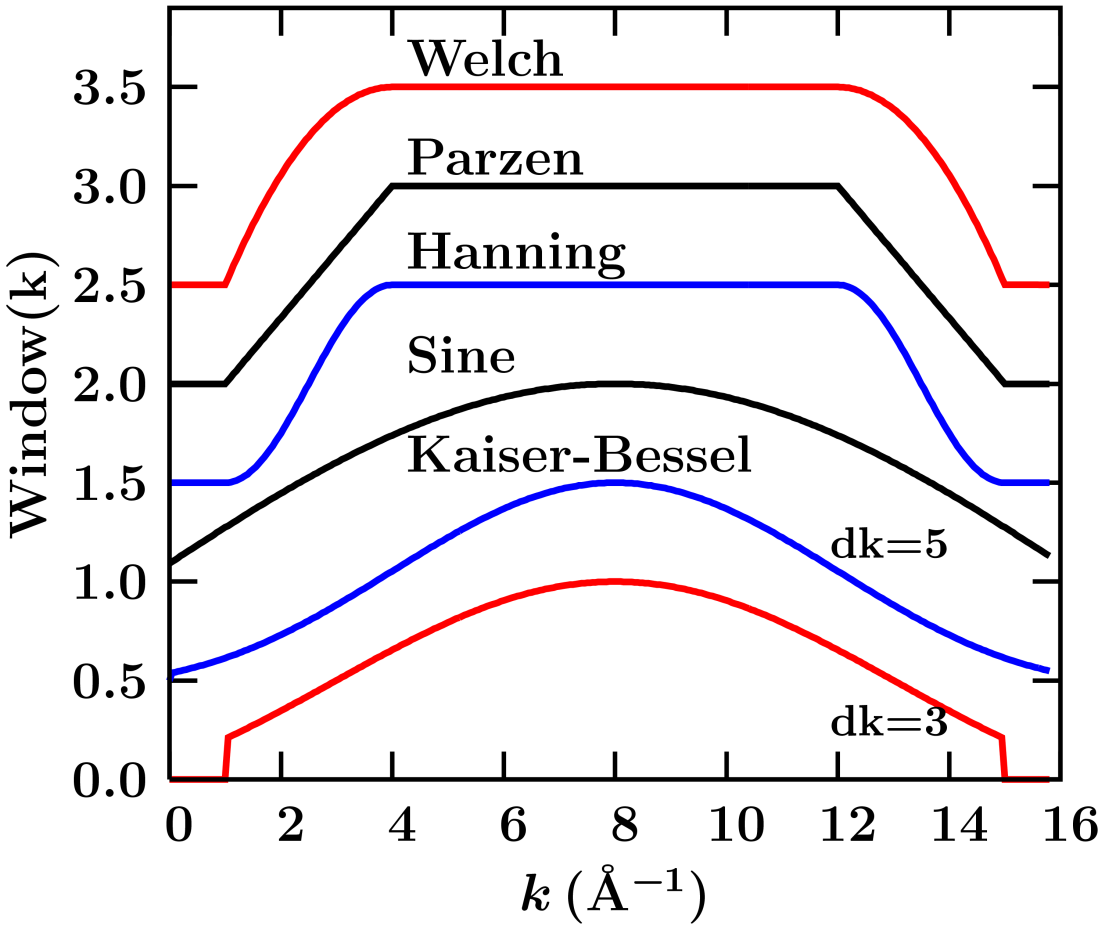


Fourier Transform Window Types



Typical Window Functions

A Window Function:

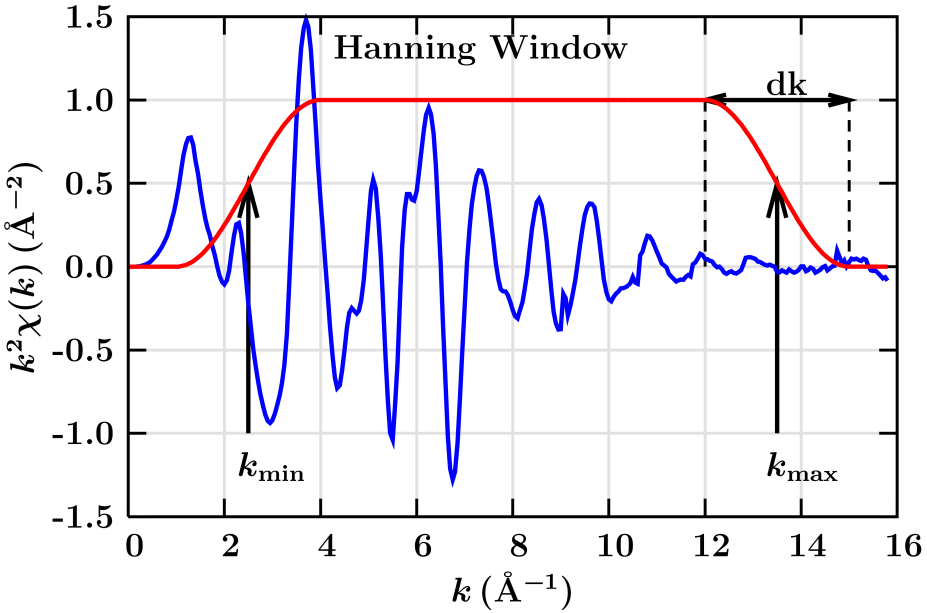
- goes from 0 to 1 and back to 0
- *dk* gives the width of the Window "sill"

Most important rule:

Pick a window type and stick with it.

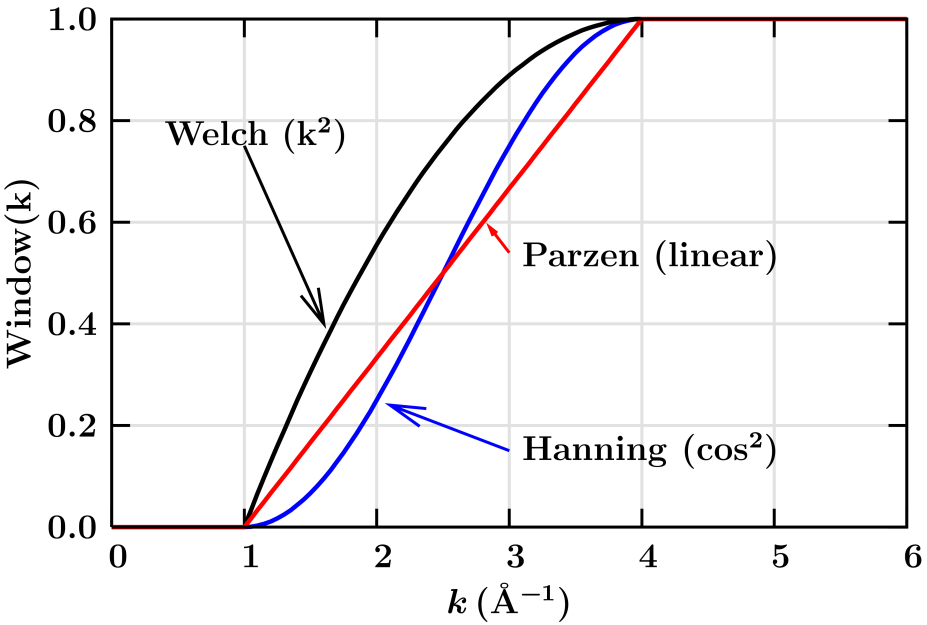
Kaiser-Bessel and Hanning are the most common.

Fourier Transform Window Types



Fourier Window Function

The meaning of k_{min}, k_{max}, and dk.

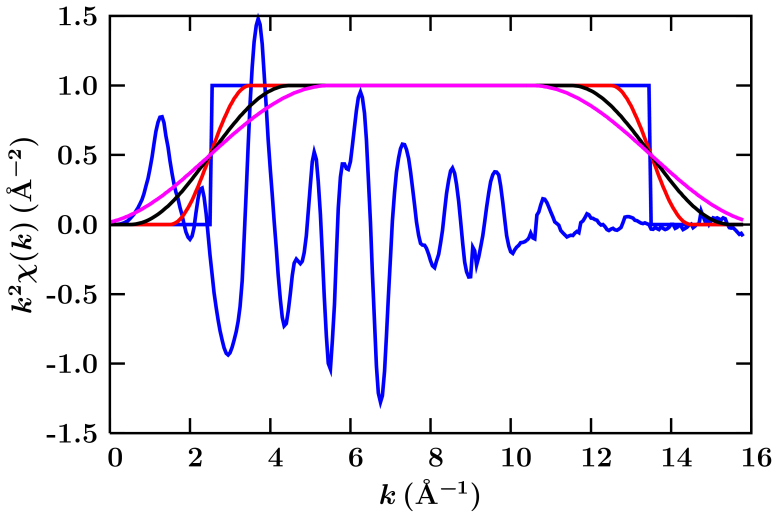


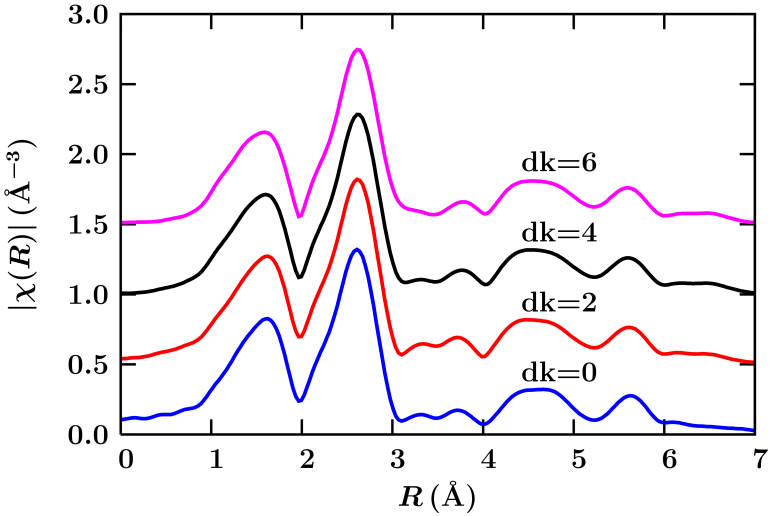
Parzen, Hanning, Welch

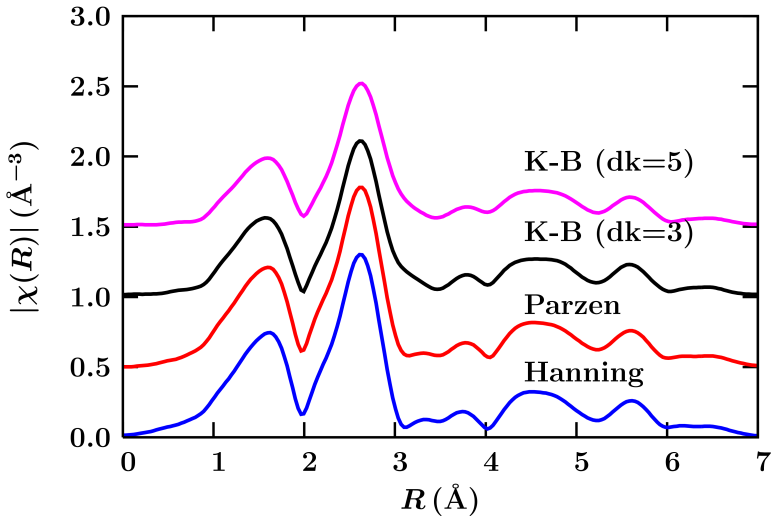
Details of the different Window "sills", all with $k_{\mathrm{min}} = 2\,\mathrm{Å}^{-1}$ and $dk = 3\,\mathrm{Å}^{-1}$.

Fourier Transform Window and real data

The effect of *dk* (for Hanning Window) and different Window Function:



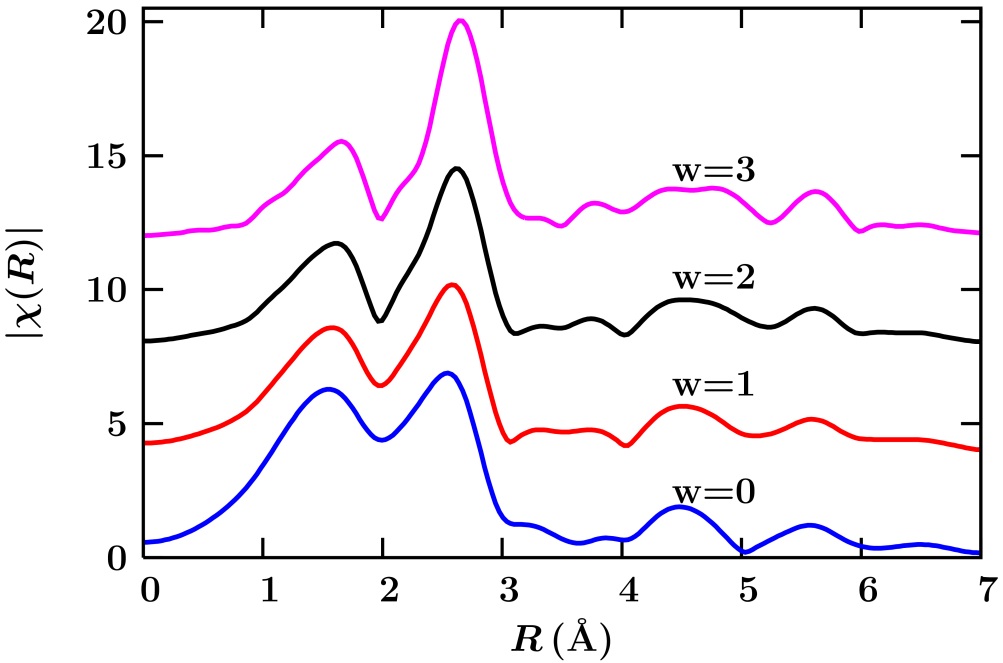




Changing *dk* and Window functions often gives small changes to $\chi(R)$.

Fourier Transform Window and k-weight

But changing the k-weighting has a significant impact:



Fe-Fe scattering dominates with higher w.

low w emphasizes low-k, and low-Z scatterers.

high w emphasizes high-k, and high-Z scatterers.

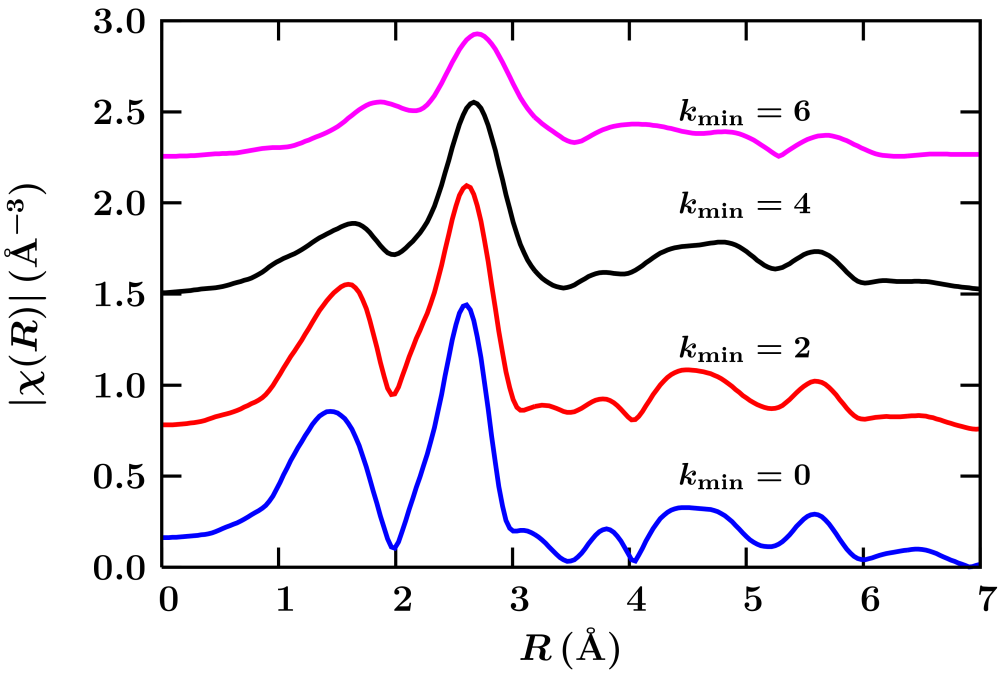
This is important when trying to determine the Z of a scatterer.

Again, $w = 2$ and $w = 3$ are most common, and recommended.

Fourier Transform Window and k_{min}

k_{min} and k_{max} are important too.

- k_{max} should be the end of useful data.
- With k-weight $= 2$, 3, it is not too important to avoid "very low k".



Conventional wisdom: keep $k_{\mathrm{min}} > 2\,\text{Å}^{-1}$

But: don't make it too big.

Use Kaiser-Bessel with $dk = 4$, $k_{\mathrm{min}} = 2\,\text{Å}^{-1}$

Use k-weight=2, or 3. Don't obsess too much.

Background Subtraction

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

We don't know $\mu_0(E)$, so use a *spline*: a smooth, adjustable function.

This is dangerous – a flexible enough spline could remove all the XAFS.

ATHENA chooses a background spline for $\mu_0(E)$ to

minimize the low-R components of χ

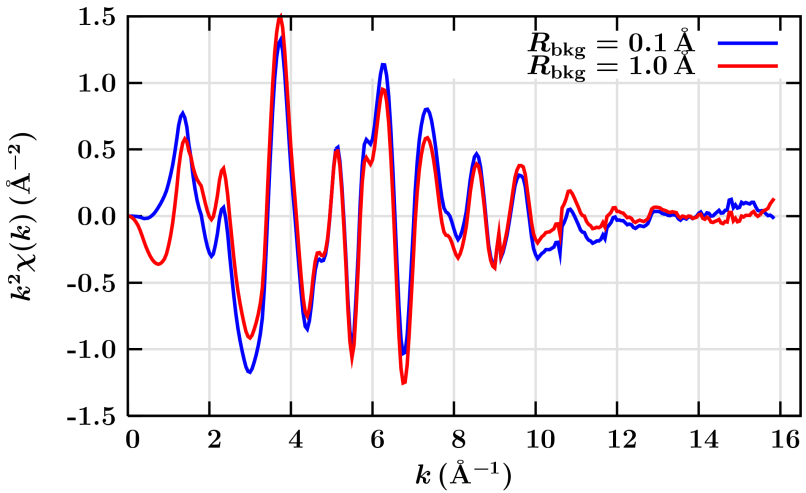
$\mu_0(E)$ is adjusted, $\chi(k)$ is Fourier Transformed, and $\chi(R)$ below $R_{\rm bkg}$ is minimized. $\chi(R)$ above $R_{\rm bkg}$ is ignored.

Most important parameters:

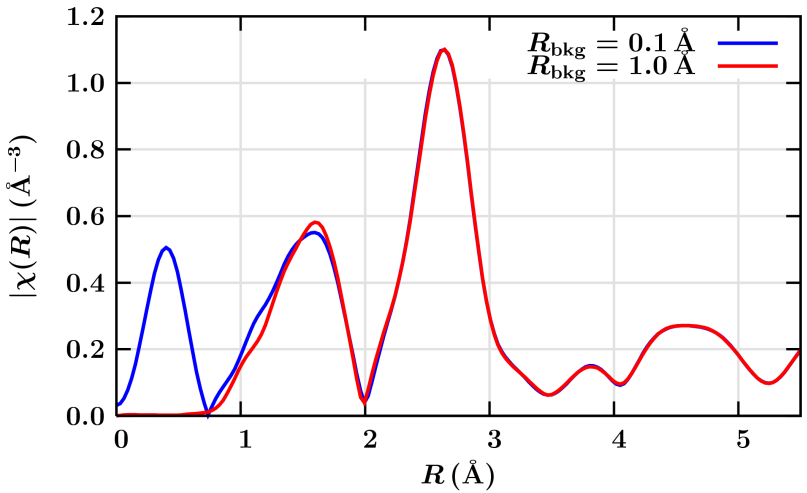
1. $R_{\rm bkg}$: R below which $\chi(R)$ is reduced.
2. k-weight: used for Fourier transform: use 1, or 2.
3. E_0: May need to adjust for initial guess (max of $d\mu/dE$).

Background Subtraction in ATHENA / IFEFFIT

Effect of R_{bkg} on XAFS $\chi(k)$ and $\chi(R)$:



$\chi(k)$ for FeO with $R_{\mathrm{bkg}} = 0.1$ Å (stiff spline) and $R_{\mathrm{bkg}} = 1.0$ Å.



$\chi(R)$ for FeO with $R_{\mathrm{bkg}} = 0.1$ Å (stiff spline) and $R_{\mathrm{bkg}} = 1.0$ Å.

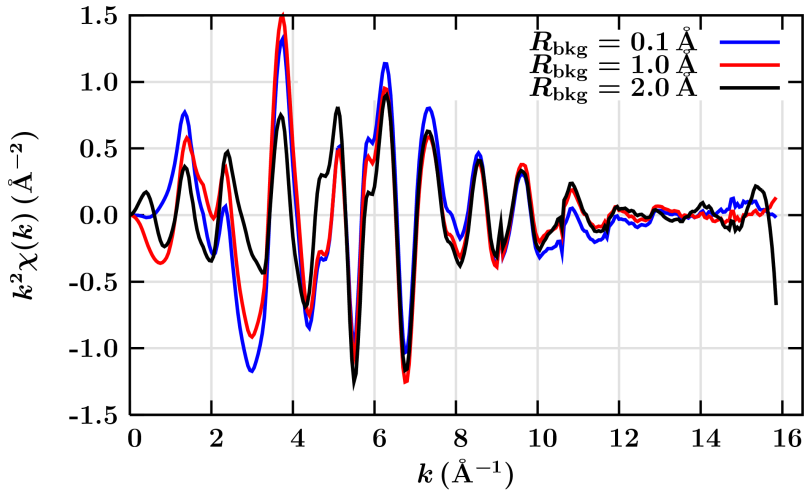
Rules of thumb:

Use $R_{\mathrm{bkg}} = 1.0$ Å or half the near-neighbor distance.

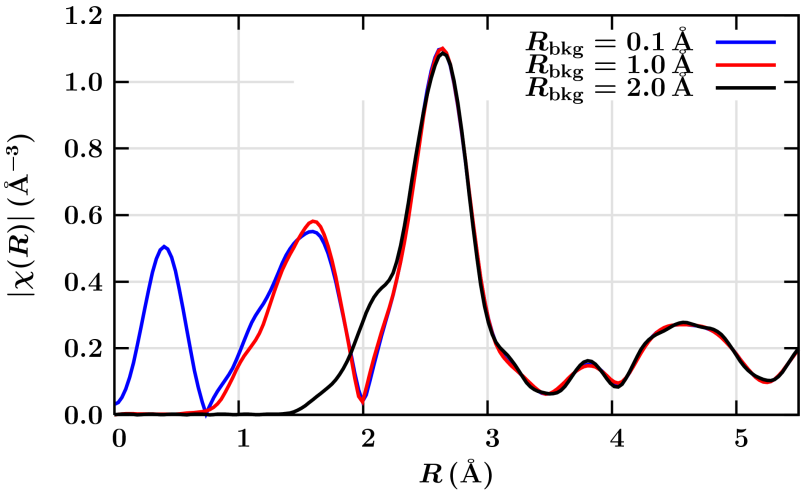
Don't spend too much time on background subtraction.

Background Subtraction in ATHENA / IFEFFIT

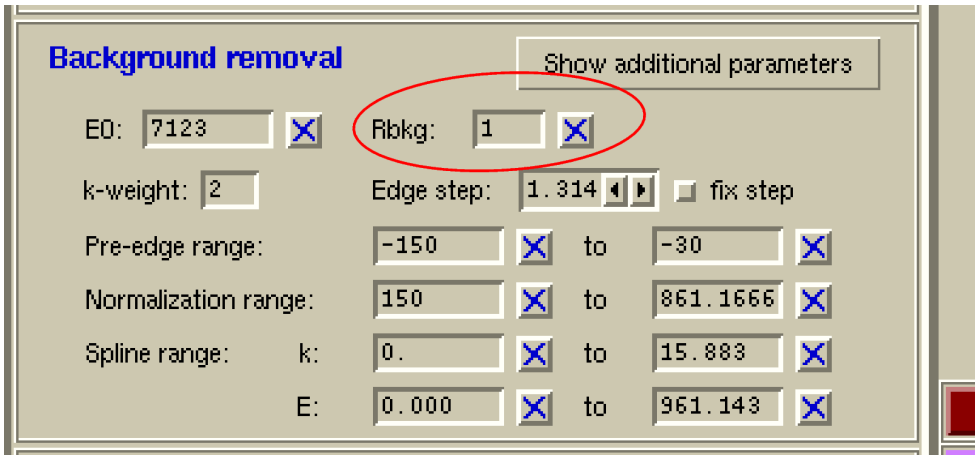
Don't make R_{bkg} too big!



$\chi(k)$ for FeO with $R_{\mathrm{bkg}} = 2.0$ Å



$\chi(R)$ for FeO with $R_{\mathrm{bkg}} = 2.0$ Å



Background removal Panel in ATHENA.

XAFS Analysis with FEFF & IFEFFIT

The XAFS Equation used with FEFF and IFEFFIT:

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

- The sum is over *Scattering Paths* of the photo-electron. Both:

  Single Scattering absorbing atom ⇒ neighbor atom ⇒ absorbing atom

  Multiple Scattering absorbing atom ⇒ neighbor atom ⇒ neighbor atom ⇒ . . . ⇒ absorbing atom

- $f(k)$ and $\delta(k)$ are photo-electron scattering amplitude and phases:
  - Energy (k) dependent.
  - Z dependent – Z of the scattering atoms(s).
  - non-trivial: must be calculated (or extracted from measured spectra).

Knowing $f(k)$ and $\delta(k)$, we can determine structural information:

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

FEFF Overview

FEFF calculates $f(k)$ and $\delta(k)$ for all *Scattering Paths* in a cluster of atoms:

1. build atomic potentials. To simplify calculations,

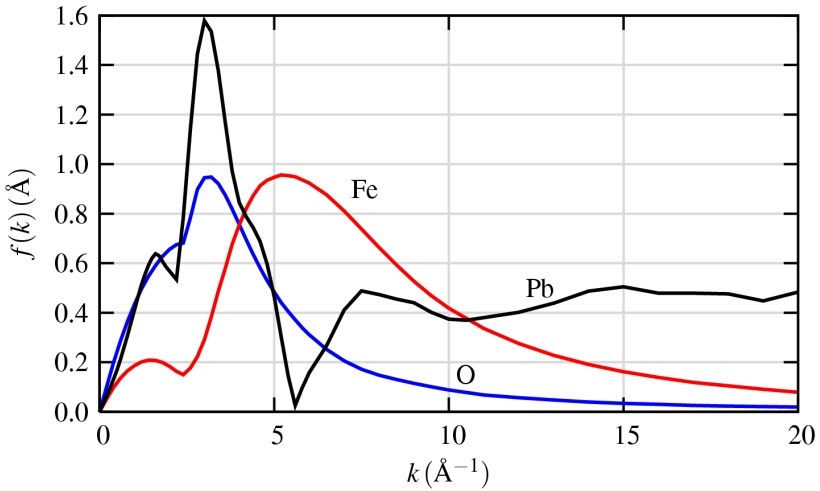
   Use the *Muffin Tin Approximation*: atomic potentials up to a uniform Fermi level (no chemical bonding).

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 δ as a function of k:

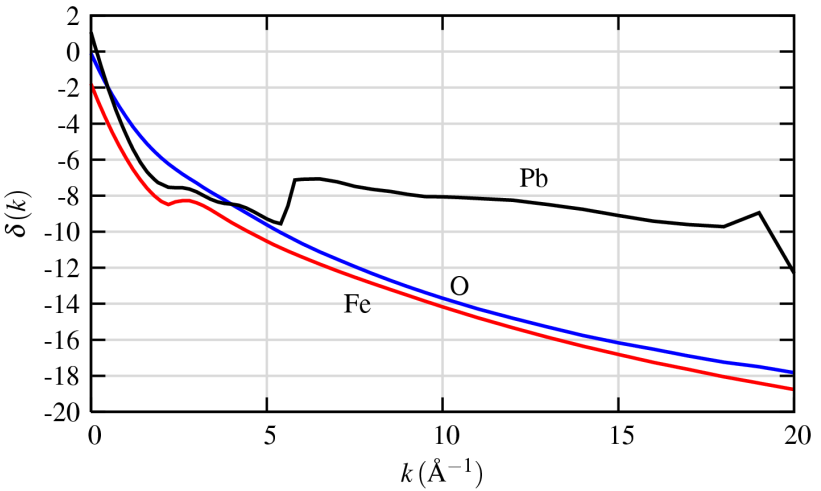
   propagate $\Rightarrow$ scatter $\Rightarrow$ propagate $\Rightarrow$ . . . .

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 heavy elements, there is a minimum in $f(k)$.



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

Z can usually be determined to ± 5.
Fe and O can be distinguished
N and O cannot be distinguished.

FEFF: what's so hard ??

FEFF includes sophisticated techniques to calculate of $f(k)$ and $\delta(k)$:

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, if approximate.

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

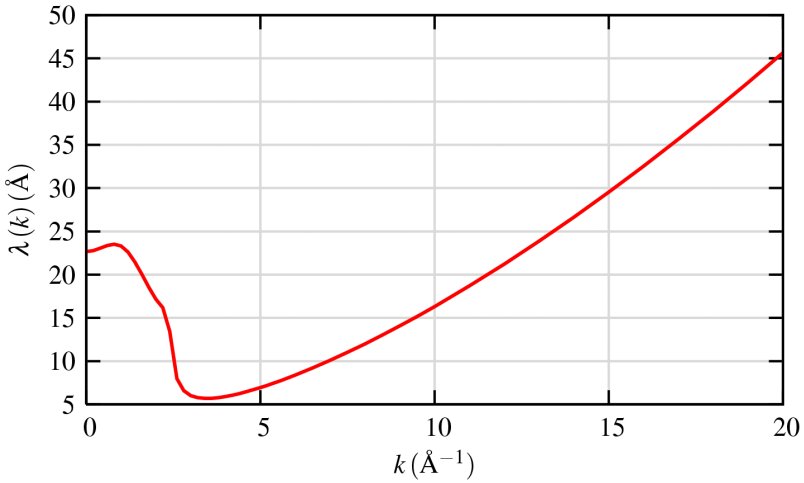
Intrinsic Losses S_0^2: the absorbing atom relaxes to the presence of the core hole.

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

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).

$\lambda(k)$: 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.



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

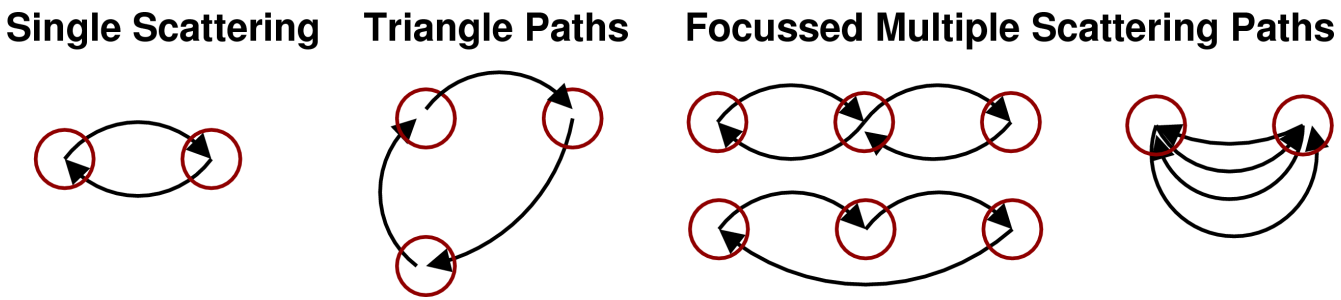
$5\text{Å} < \lambda < 25\,\text{Å}$ for the EXAFS k-range.

The λ and R^{-2} terms make EXAFS a *local probe*.

XANES ($k < 3\,\text{Å}^{-1}$) is sensitive to longer distances.

Multiple Scattering

The photo-electron can scatter multiple times:



A Path Formalism is used in the "Real Space" calculations:

$$G = G^0 + G^0 t G^0 + G^0 t G^0 t G^0 + G^0 t G^0 t G^0 t G^0 + \ldots$$

G^0 = propagation of the electron, t = scattering from neighboring atom.

Triangle Paths with angles $45 < \theta < 135^\circ$ are weak, 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!

S_0^2: 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 is used as a Fitting Parameter that multiplies χ:

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

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

S_0^2 can be determined with an *Experimental Standard* with known N.

Practical FEFF

Good News: you don't have to worry about most of this!

The normal scheme for using FEFF with ARTEMIS is:

1. Start with a structure close to the atomic structure of your sample, and generate x,y,z coordinates:
   - simple crystal structure? use ATOMS input format
   - Protein Data Bank? use CRYSTALLFF
2. Run FEFF, generating a list of *feffnnnn.dat* files for each path.
3. Use these for Paths in ARTEMIS to model measured XAFS.

May need to use a few structures to find appropriate paths for your system.

Having good starting structures is important!

XAFS Analysis with ARTEMIS and IFEFFIT

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	IFEFFIT Parameter	Meaning
NS_0^2	`amp`	Amplitude Factor: N and S_0^2
E_0	`e0`	Energy Shift (where $k = 0$)
ΔR	`delr`	Change in path length $R = \Delta R + R_{\rm eff}$
σ^2	`sigma2`	Mean-square-displacement in R

($R_{\rm eff}$ is the starting R value for the FEFF Path).

Each Path Parameter for Each Path could be refined.
OR: These can be tied together using mathematical constraints.
(Other Path Parameters: higher order cumulants, energy broadening, . . .)

XAFS Analysis: Information Content in XAFS

The Number of Parameters we can measure from our data is limited:

$$N \approx \frac{2\Delta k \Delta R}{\pi}$$

where Δk and ΔR are the k- and R-ranges of the data.
Typical: $k = [2.0, 12.0]\,\text{Å}^{-1}$ and $R = [1.0, 3.0]\,\text{Å}$, gives ~ 12 Parameters.

Fit statistics, and Error Bars need to reflect this limit.

Need to constrain Parameters R, N, σ^2 for different paths and different data sets (different edge elements, temperatures, etc)

It's also possible to add restraints to describe external knowledge of the system (crystallography, Bond Valence, etc).

Use as much other information about the system as possible!

XAFS Analysis: Building Models

The basic difficulties in EXAFS Analysis are

1. The scattering factors $f(k)$, $\delta(k)$ are non-trivial (we use FEFF).
2. The basis functions (Paths) are not very well resolved, and their number grows exponentially with R.
3. There's not much information in a real measurement:

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

We address these with methods to:

1. reduce the number of Paths to consider (Fourier analysis).
2. parameterize *ab initio* calculations of $f(k)$, $\delta(k)$ (use FEFF
3. cut down the number of independent variables in the fit, while keeping a meaningful analysis.

We parameterize the EXAFS with a physical model, and then put *Constraints* and *Restraints* on the parameters in a least-squares analysis.

Constraints in IFEFFIT / ARTEMIS

All Path Parameters written in terms of Generalized Variables:

Parameter = Variable

```
guess e0    = 1.0
path(1,  e0 = e0)
path(2,  e0 = e0)
```

mixed coordination shell

```
set S02   = 0.80

guess x   = 0.5

path(1,  Amp= S02 * x )
path(2,  Amp= S02 * (1-x))
```

Fit Einstein Temperature

```
 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   )
```

Other Examples:

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

Fitting with IFEFFIT / ARTEMIS

IFEFFIT optimizes the Fitting Parameters with a least-squares fit to the Data

Find the variables that make the Model best match the Data

χ^2 (don't confuse with EXAFS χ!!) describe the fit:

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

$N_{\rm fit}$ = number of data points, x = set of variables, ϵ = noise level in the data.
We should consider only $N_{\rm idp}$ data points:

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

Fitting is typically done in R-space to ignore higher shells.

Goodness of Fit and Error Bars

Goodness-of-Fit statistics:

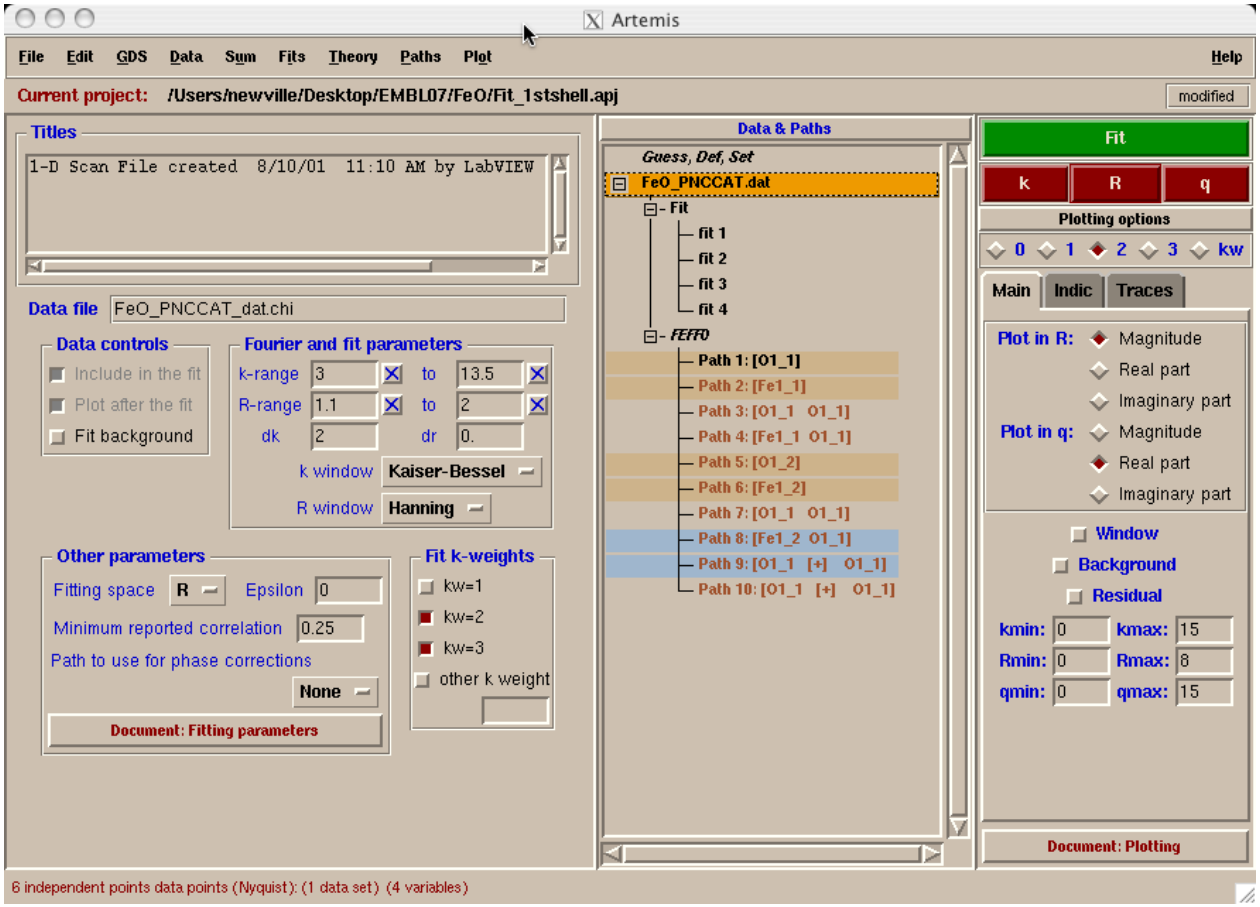
- chi-square: $\chi^2 = \frac{N_{\rm idp}}{\epsilon^2 N_{\rm fit}} \sum_i^{N_{\rm fit}} [\chi_i^{\rm data} - \chi_i^{\rm model}(x)]^2$
- reduced chi-square: scale χ^2 by the "degrees of freedom"
  $\chi^2_\nu = \chi^2/(N_{\rm idp} - N_{\rm varys})$
  A Good Fit should have $\chi^2_\nu \sim 1$. This *never* happens!
  $\chi^2_\nu \sim 10$ or higher, typically.
- R-factor: Fractional misfit.

$$\mathcal{R} = \sum_i^{N_{\rm fit}} [\chi_i^{\rm data} - \chi_i^{\rm model}(x)]^2 / \sum_i^{N_{\rm fit}} [\chi_i^{\rm data}]^2$$

Error bars for Fitting Parameters are calculated, and increase χ^2 by χ^2_ν.

Correlations between parameters are also calculated.

Fitting with ARTEMIS



ARTEMIS Main Page for selecting:

Data File(s)

Fit k and R ranges

Paths to use in Fit

Plot Results.

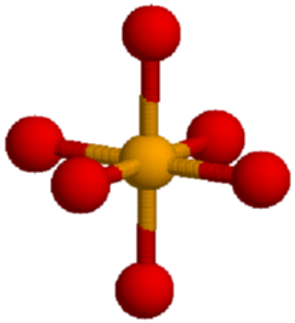
- Fit with multiple k-weights.
- Use Paths from multiple FEFF calculations
- Keep a history of fits.

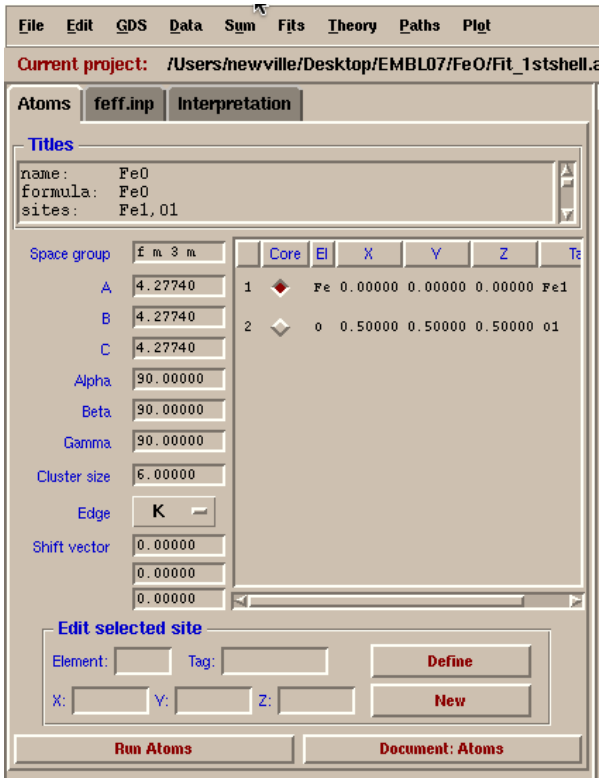
Simple ARTEMIS example: FeO

FeO has a rock-salt structure.

To model the FeO EXAFS, we'll run FEFF with the crystal structure for FeO, with Fe-O distance $R = 2.14\,\text{Å}$ (a regular octahedra).

We'll use ARTEMIS to *refine* R, N, σ^2, and E_0.



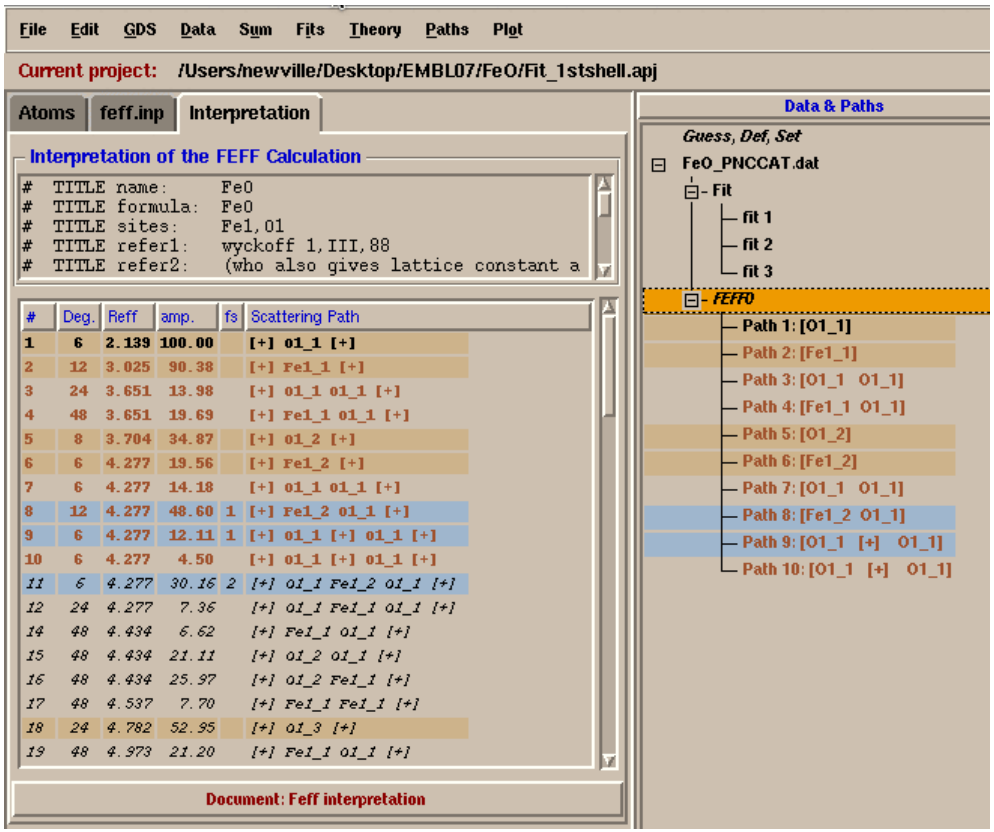


ATOMS Page in ARTEMIS:
Crystal structure → atomic cluster for FEFF
Put in space group, cell parameters, and fractional coordinates (or look them up) and push

Run ATOMS generate input for FEFF

Run FEFF calculate χ for all Paths.

Path List from Running FEFF



FEFF Paths for Fe-O, showing

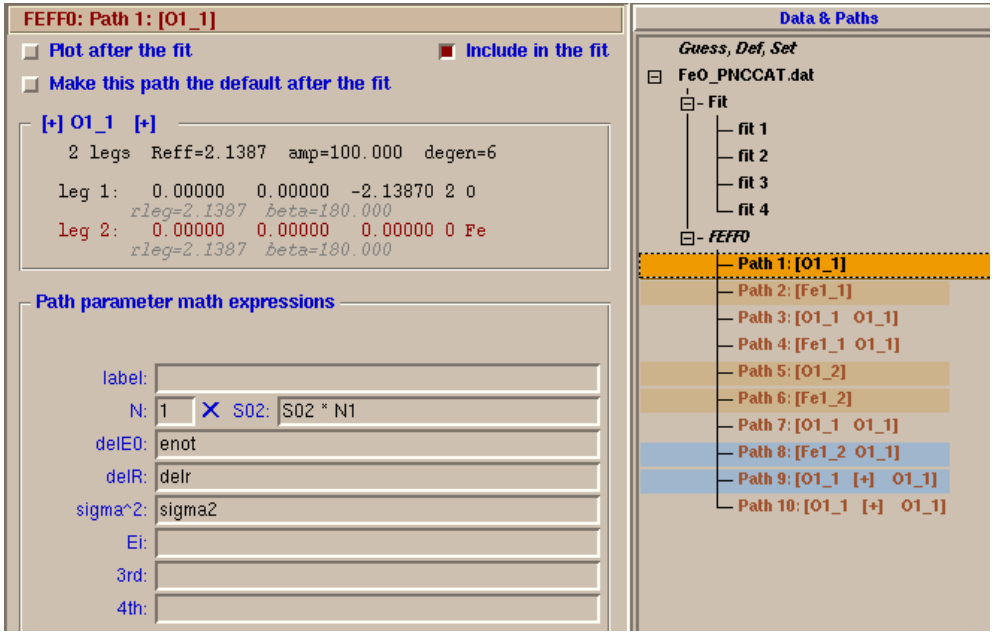
- Path Length: $R_{\rm eff}$
- Path Degeneracy: N
- Path Importance
- Path Geometry

Each FEFF Path includes a degeneracy (number of equivalent paths).
That gives *3* Amplitude terms:

$$N_{\rm total} = \texttt{DEGEN} \times S_0^2 \times N$$

This is a useful feature (really!), but it can cause confusion.

Path Parameters



Each Path has a list of Path Parameters

- $N \times S_0^2$
- E_0
- ΔR
- σ^2
- ...

Each Path Parameter can each be assigned a *Fit Variable*

More generally:

Path Parameters are functions of *Fit Variables*.

Also: FEFF's DEGENERACY can be set to 1 here so that the fitted N represents coordination number.

Fit Variables and Parameters

Guess, Def, Set Page:
The List of Variables, can be

guess	floated / refined in fit.
set	fixed / not refined.
def	defined in terms of other variables.

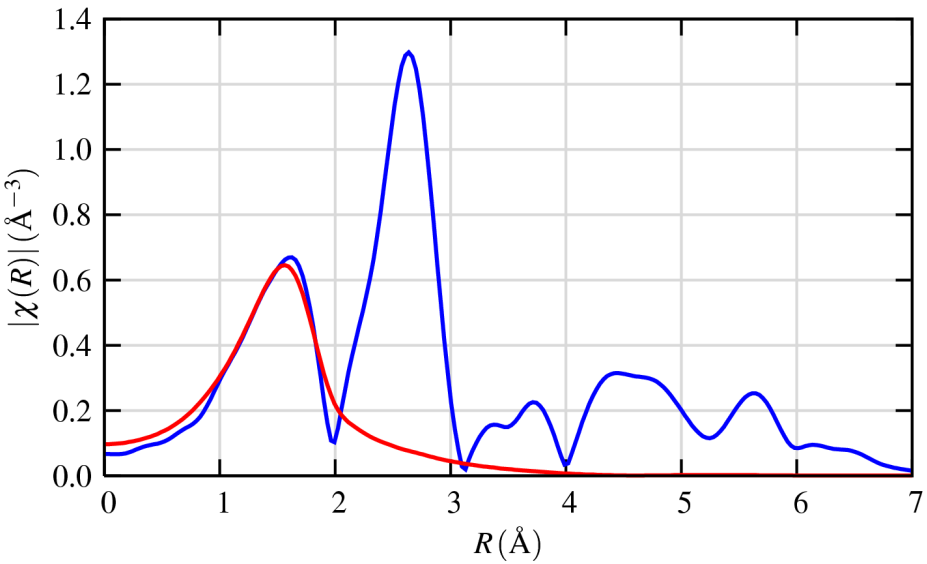
Variables can also be:

restraint	used as a restraint
skip	saved, but not used in fit
after	evaluated definition, bit used in fit.

First Shell Fit

Fit to 1^{st} shell of FeO: 1 Path (Fe-O)

We'll refine ΔR, N, σ^2, and E_0.

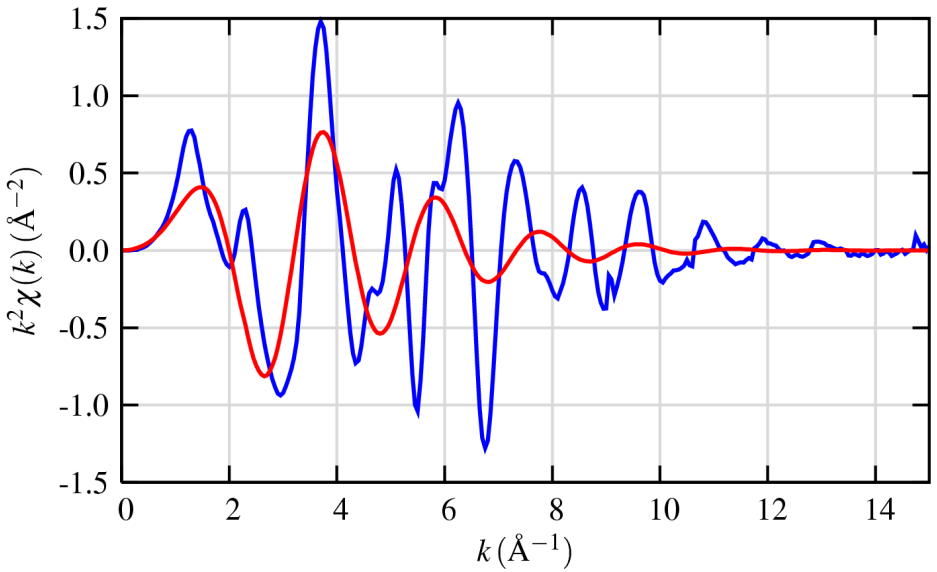


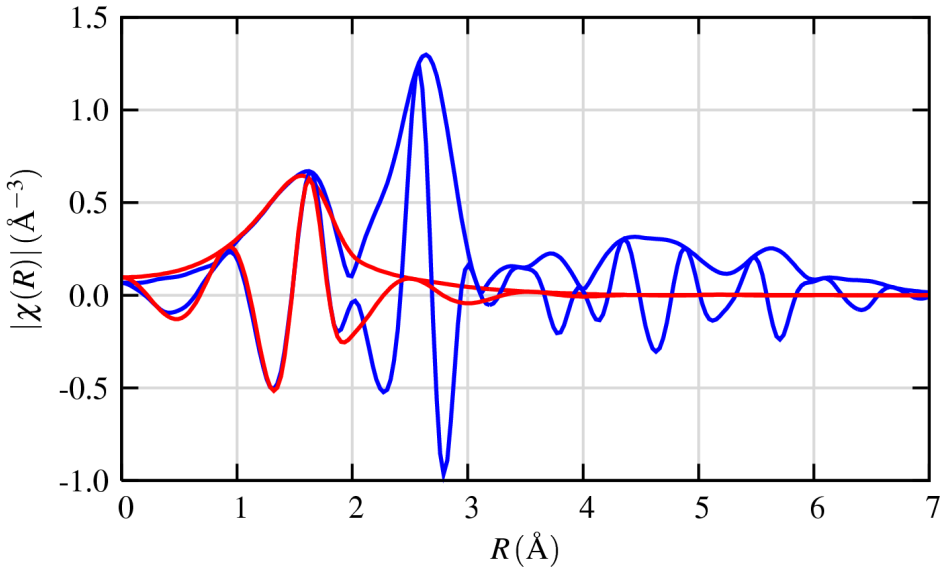
$|\chi(R)|$ for FeO data (blue) and fit (red).

Fit results:

$$
\begin{aligned}
N &= 5.2 \pm 0.8 \\
R &= 2.10 \pm 0.02\,\mathrm{Å} \\
E_0 &= -2.3 \pm 1.8\,\mathrm{eV} \\
\sigma^2 &= 0.013 \pm 0.003\,\mathrm{Å}^2.
\end{aligned}
$$

First Shell Fit (continued)





1^{st} shell fit to FeO in k space. There is clearly another component in the XAFS!

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).

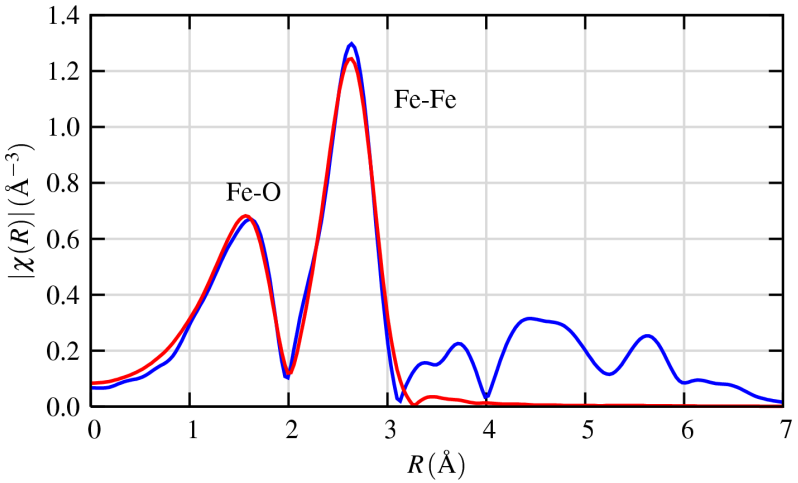
Though the fit to the magnitude didn't look great, the fit to $\mathrm{Re}[\chi(\mathrm{R})]$ looks very good.

Fit Results and Log Report

The Results Page gives detailed fit statistics, and results for Variables and Path Parameters.

2 Path Fit to FeO

Adding the Fe-Fe Path, and refining R, N, σ^2 (use the same E_0 as for Path 1):



$|\chi(R)|$ data for FeO (blue), and 2-Path fit (red).

Results are consistent with the known values for FeO:
6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results:

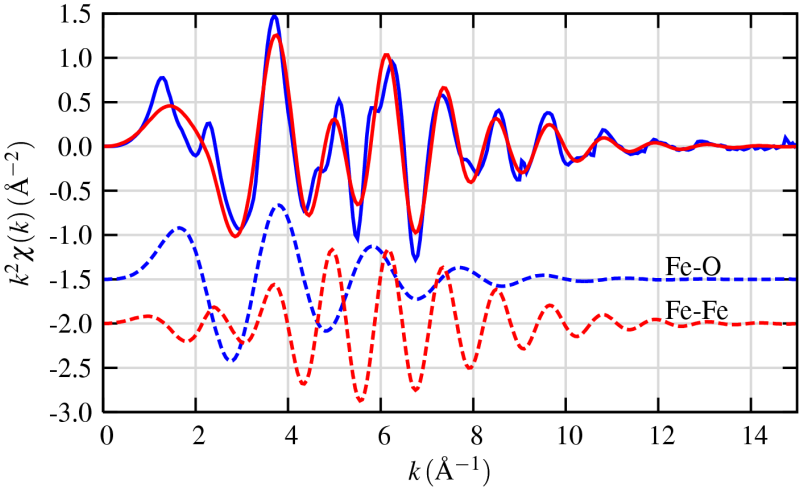
Path	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

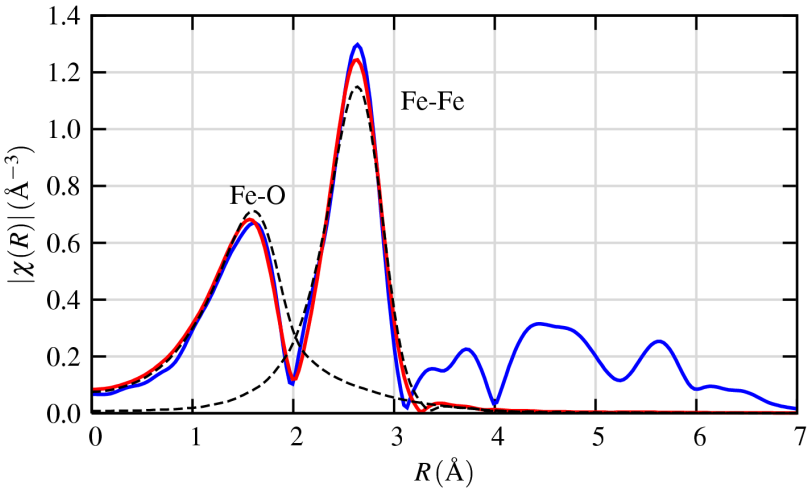
Fit Statistics: $R \approx 0.016$ $\chi^2_\nu \approx 100.$

These are typical even for a "very good fit" on known structures.

Second Shell Fit to FeO (continued)

Other views of the data and two-shell fit:

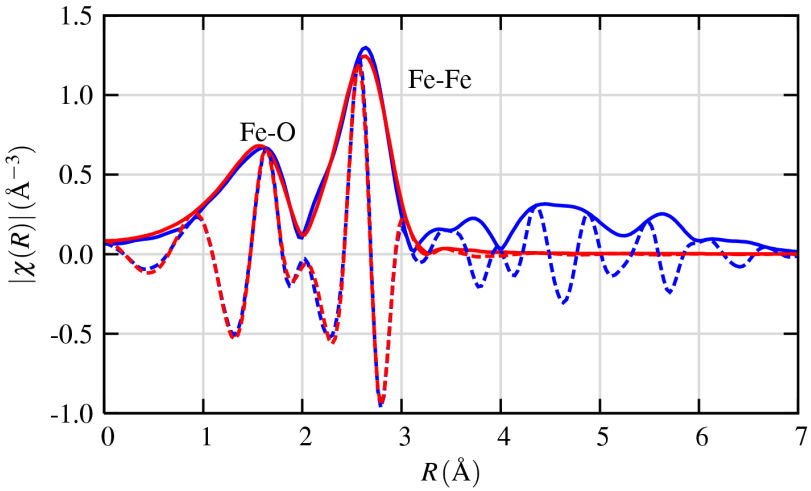




The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.

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

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



Multiple Scattering Example: Cp-$MnCO_3$

Cp-$MnCO_3$ = tricarbonyl(η^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 $\sim 2.13\,\text{Å}$

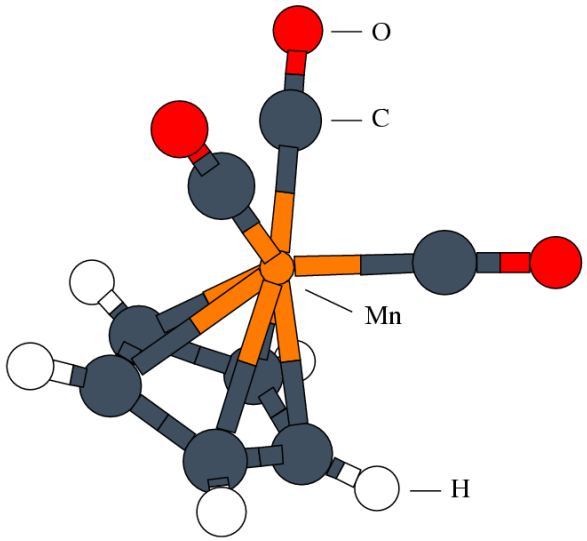
carbonyl

3 Mn-C at $\sim 1.78\,\text{Å}$

3 Mn-O at $\sim 2.93\,\text{Å}$

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

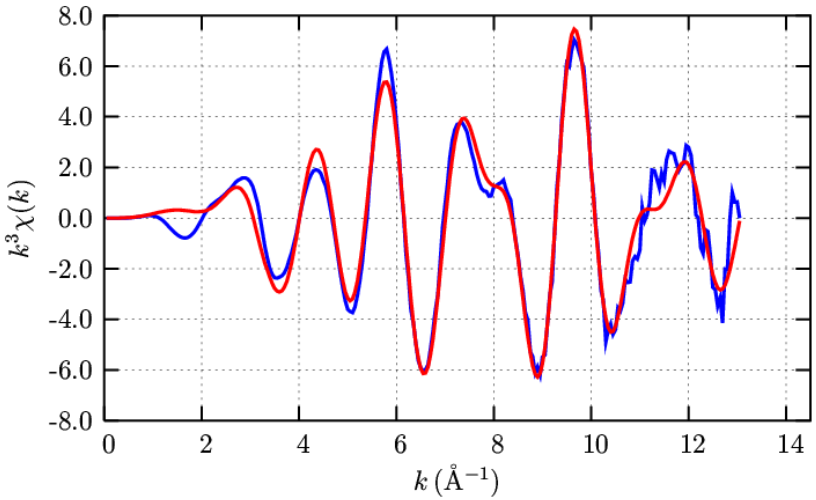
3 Mn-C-O-C paths at $\sim 2.93\,\text{Å}$



The Multiple Scattering Paths will overlap the longer Mn-C(ring) distance!!
Using only the single-scattering paths will gives:

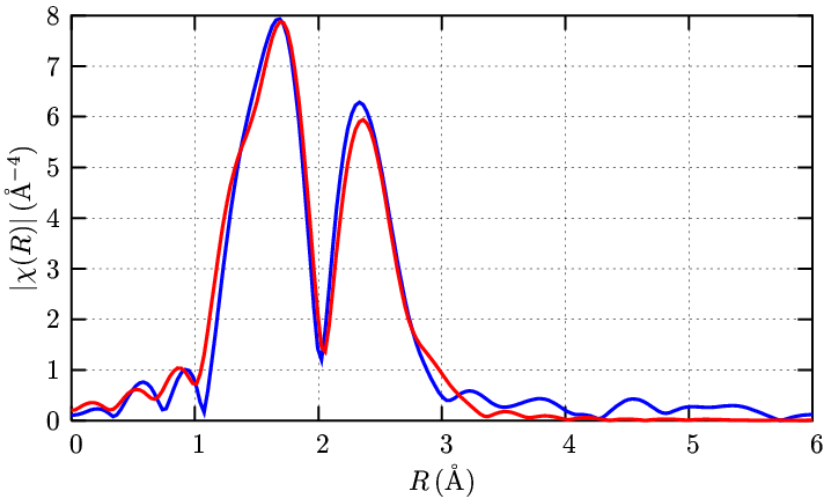
- large coordination numbers: 6 Mn-C(ring) at $2.10\,\text{Å}$, 10 Mn-C(carbonyl) at $1.80\,\text{Å}$, and 10 Mn-O (carbonyl) at $2.99\,\text{Å}$.
- E_0 of -13eV (pretty big!).

Multiple Scattering Example: Cp-$MnCO_3$

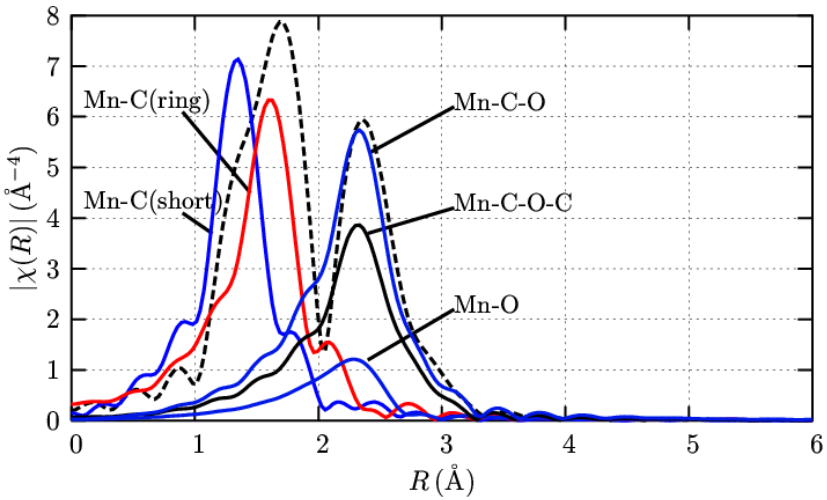


The Mn *K*-edge EXAFS data and fit with 5 paths.
Constrained $N_{\mathrm{Mn-O}} = N_{\mathrm{Mn-C(short)}}$ and used 1 E_0 $(-3.6 \pm 2.0\,\mathrm{eV}\ )$.

Path	N	R (Å)	σ^2 (Å^2)
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 overlap the 1st shell.



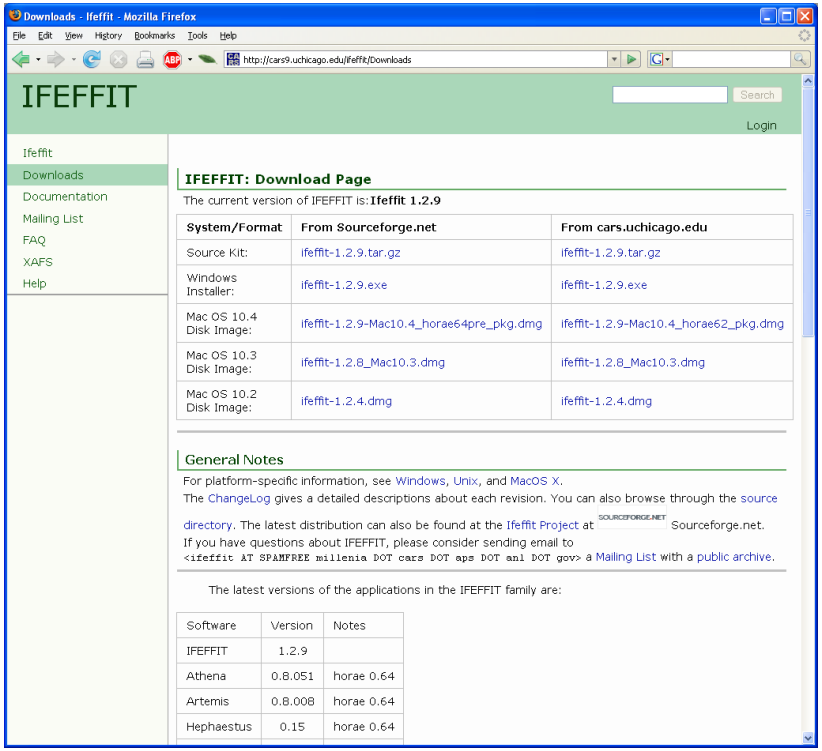
Some Final Thoughts on Fitting

Of course, FeO is very easy

. . . it can get more complicated . . . .

- Start out with a First Shell Fit
- Measure and Fit standards similar to your Systems.
- Use as much other information as possible.

IFEFFIT and its community



- Free Software.
- Mailing List (400 subscribers).
- Binary Installer for Windows.
- Binary Installer for Mac OS X.
- Linux Packages (debian).
- Source Code (configure/make).
- Decent Docs and Users Guides.
- On-line Tutorials, Examples.


B. Ravel
(ANL)


S. Webb
(SSRL)


S. Kelly
(ANL)


S. Calvin
(Sarah Lawrence)


P. Fons
(AIST, Japan)


C. Segre
(IIT)


J. Rehr
(UW)

http://cars.uchicago.edu/ifeffit/ http://xafs.org/

Where To Go From Here

IFEFFIT Home Page:

http://cars9.uchicago.edu/ifeffit

Documentation, Downloads, Mailing List, FAQ

xafs.org:

http://xafs.org: Wiki with more tutorials and other useful information.

International XAFS Society:

http://www.i-x-s.org/

Books and Review Articles:

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, in *Chemical Analysis* **92**, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988.

Basic Principles and Applications of EXAFS, Chapter 10 in *Handbook of Synchrotron Radiation*, pp 995–1014. E. A. Stern and S. M. Heald, E. E. Koch, ed., North-Holland, 1983

Thank you.