Part II

Fundamentals of X-ray Absorption Fine Structure: data analysis

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Data Analysis:

EXAFS Analysis: near neighbor R, N, and atomic species

XANES Analysis: formal valence and coordination chemistry

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XAFS Data Reduction

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Data Reduction: Strategy

Step for reducing measured data to μ(E) and then to χ(k):

1. convert measured intensities to μ(E).

2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.

3. normalize μ(E) to go from 0 to 1, so that it represents the absorption of 1 X-ray.

4. remove a smooth post-edge background function to approximate μ_0(E) to isolate the XAFS χ.

5. identify the threshold energy E_0, and convert from E to k space:

6. weight the XAFS χ(k) and Fourier transform from k to R space.

$$k = \frac{\sqrt{2m(E - E_0)}}{\hbar^2}$$

7. isolate the χ(k) for an individual "shell" by Fourier filtering.

After we get this far, we'll model f(k) and δ(k) and analyze χ(k) to get:

distance R
coordination number N
mean square relative displacement σ^2

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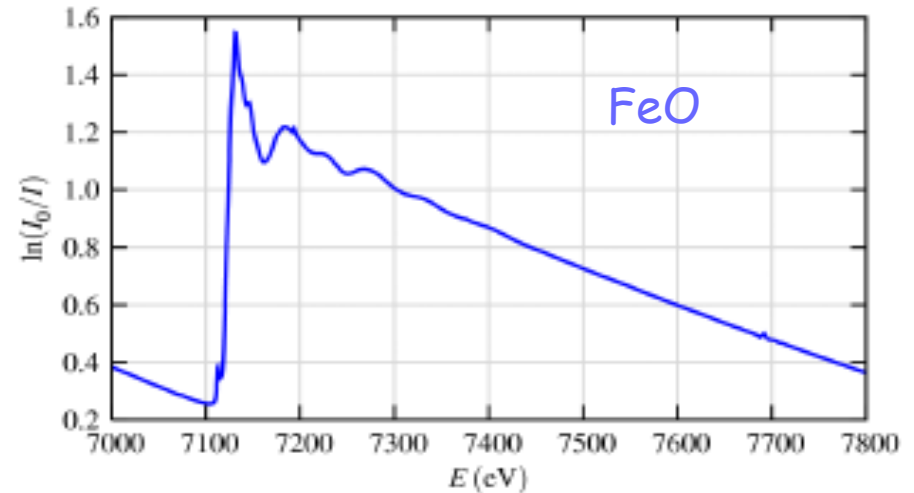
Data Reduction: Converting Raw Data to μ(E)

Starting with measured intensities before and after the sample, we construct μ(E):
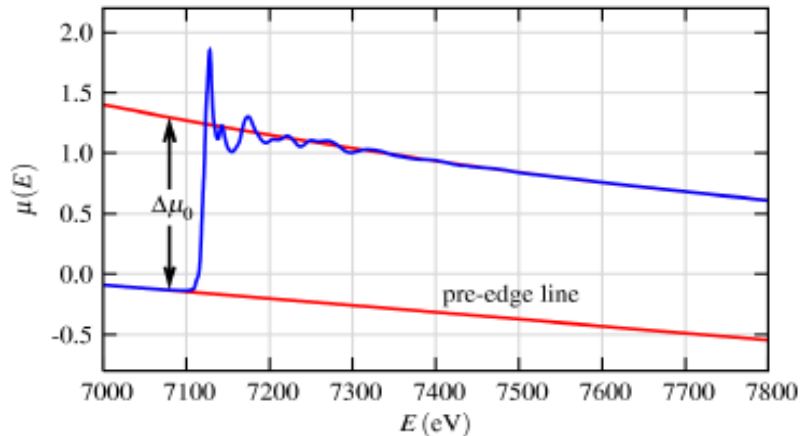
I$_0$

I
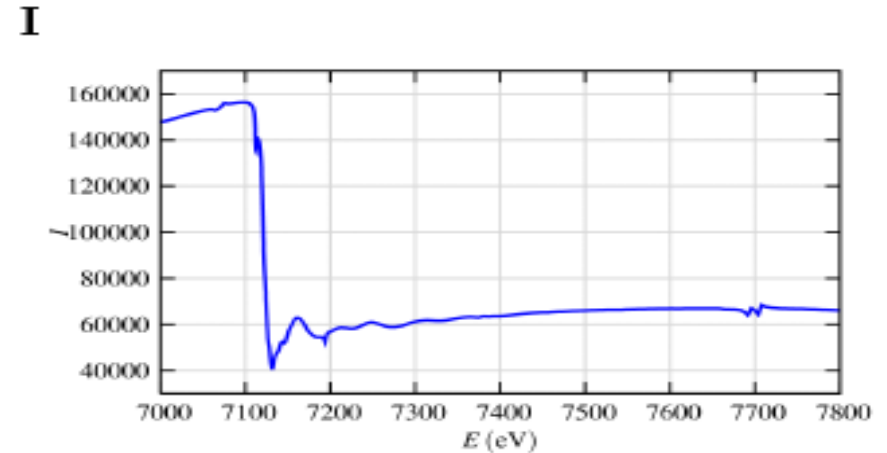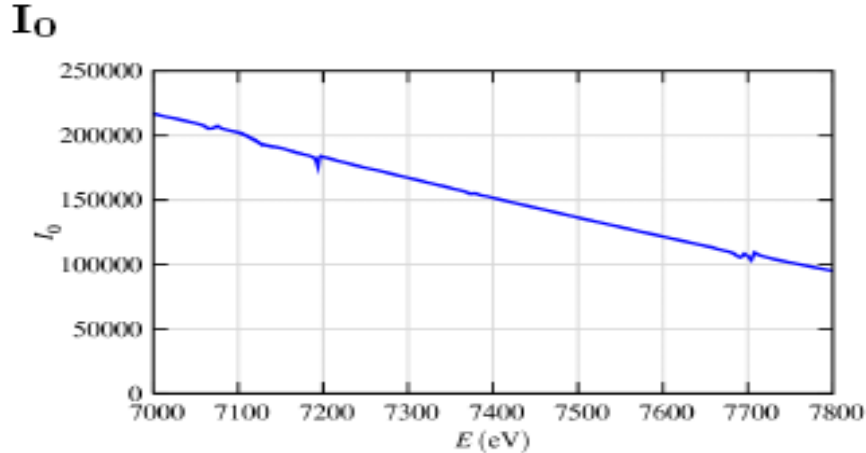
For transmission XAFS:

$$I = I_0 \exp[-\mu(E) \, t]$$

$$\mu(E) \, t = \ln[I_0/I]$$
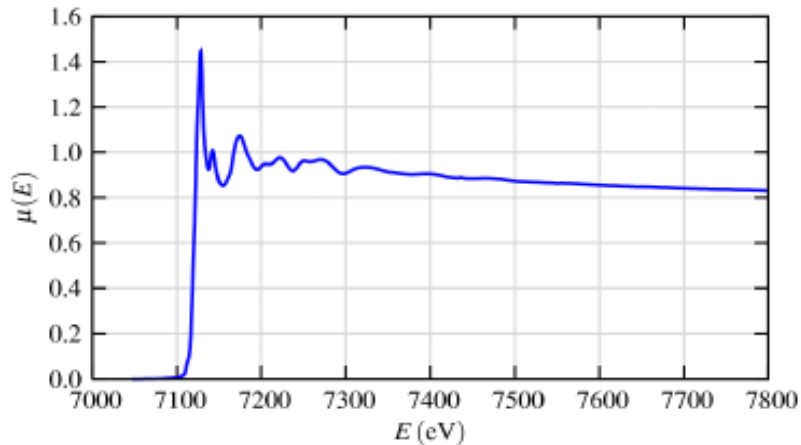
FeO

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Data Reduction: Pre-Edge Subtraction, Normalization

Data reduction of μ(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 edges (say, the Fe L_{III} edge).

Normalization
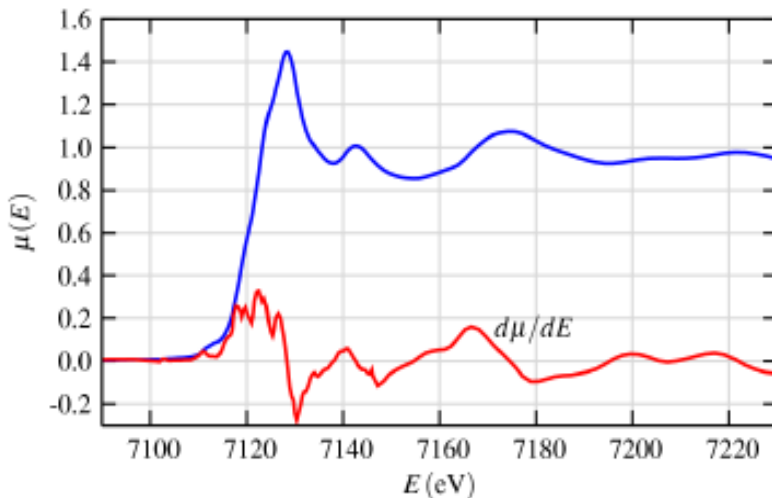
We estimate the edge step, $\mu_0(E_0)$ by extrapolating a simple fit to the above μ(E) to the edge.
We normalize by this value to get the absorption from 1 X-ray.

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# Data Reduction: Normalized XANES and E_0
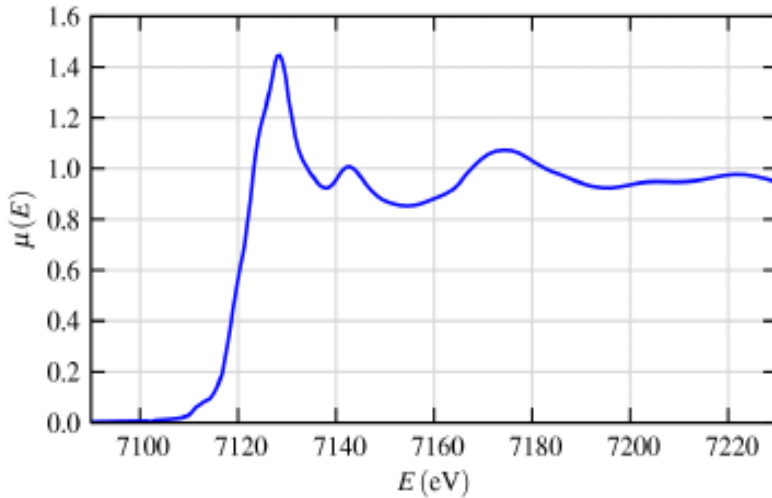
XANES

The XANES portion shows a fairly rich spectral structure. We'll come back to 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.
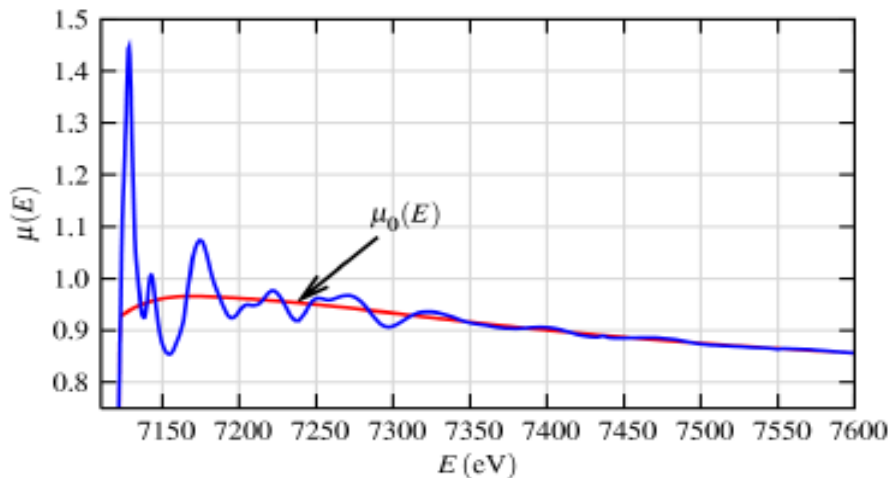
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Data Reduction: Post-Edge Background Subtraction
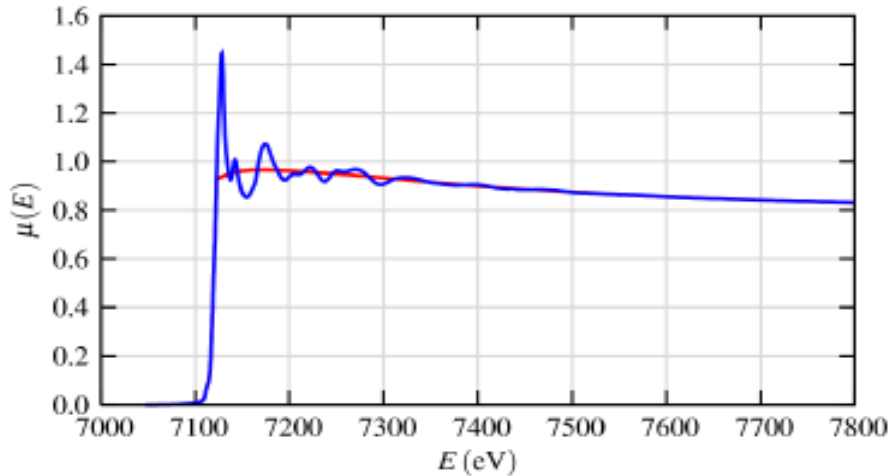
Post-Edge Background

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 the $\mu(E)$ and remove all the EXAFS!

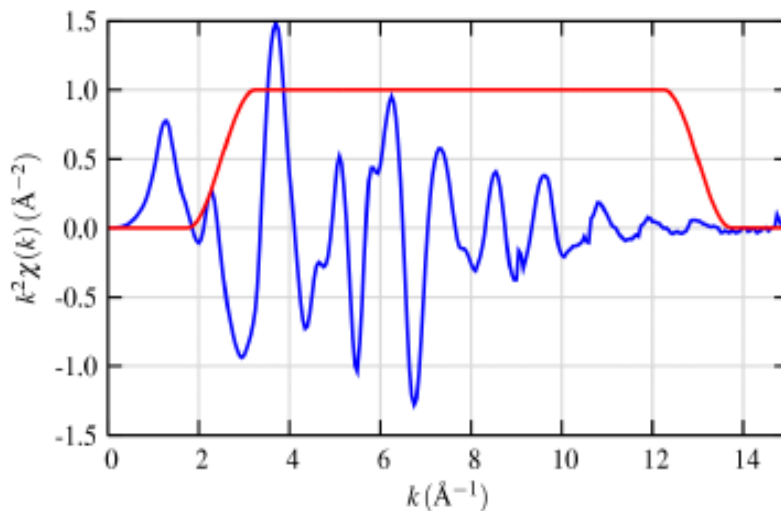We want a spline that will match the low frequency components of $\mu_0(E)$.

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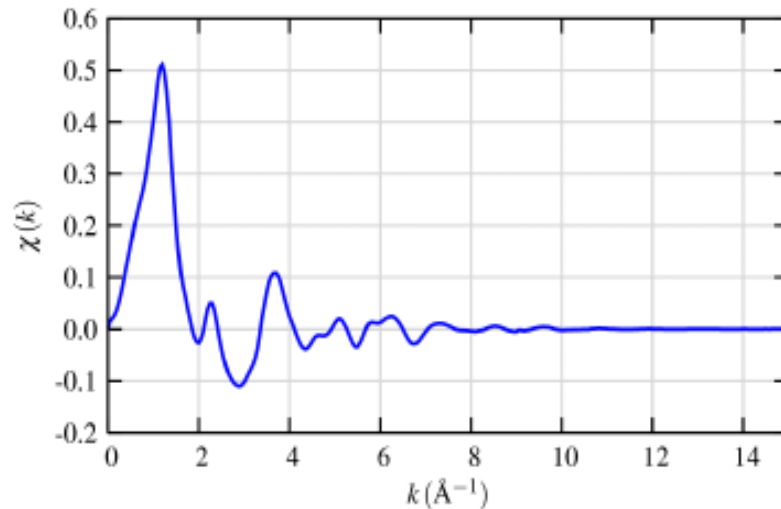
$\chi(k)$

The raw EXAFS $\chi(k)$ usually decays quickly with k, and difficult to assess or interpret by itself.

It is customary to weight 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.
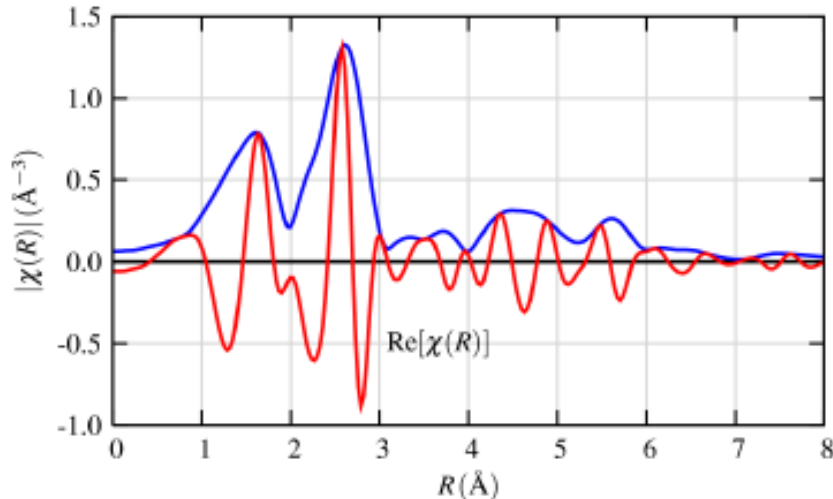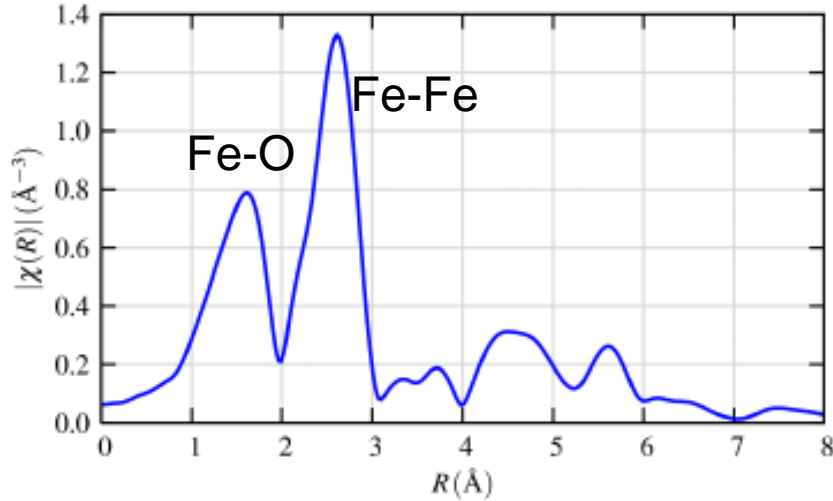
The Fourier Transform is a tool that breaks a waveform (a function or signal) into an alternate representation, characterized by sine and cosines.

The Fourier Transform shows that any waveform can be re-written as the sum of sinusoidal functions.

$$\mathscr{F}\{g(t)\} = G(f) = \int_{-\infty}^{\infty} g(t)e^{-i2\pi ft}\,dt$$

$$\mathscr{F}^{-1}\{G(f)\} = g(t) = \int_{-\infty}^{\infty} G(f)e^{i2\pi ft}\,df$$
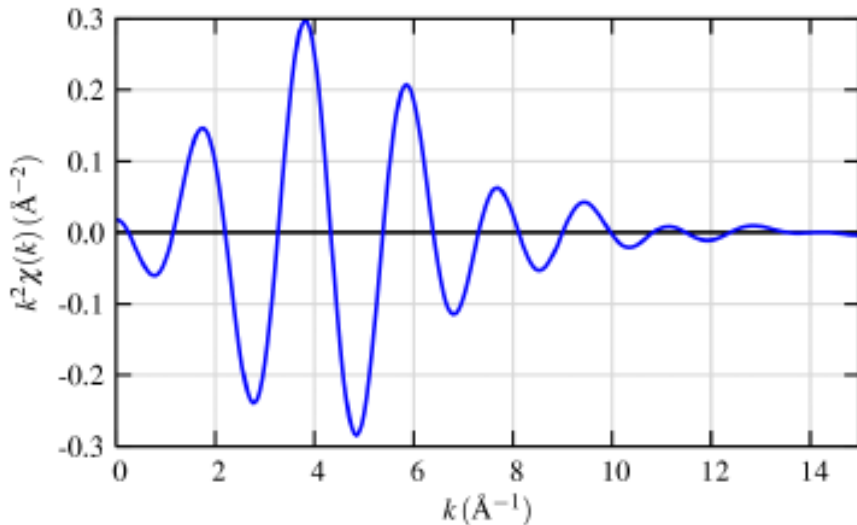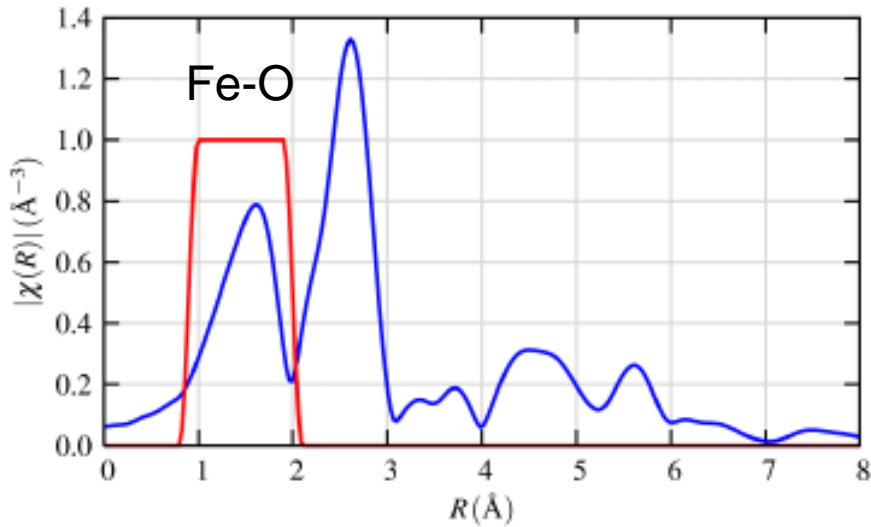
Fourier Transform: $\chi(R)$

$\chi(R)$

The Fourier Transform of $k^2(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe-Fe.

The Fe-O distance in FeO is 2.14Å, but the first peak is at 1.66Å. This shift in the first peak is due to the phase-shift, $\delta(k)$: $\sin[2kR + \delta(k)]$.

A shift of -0.5Å is typical.

$\chi(R)$ is complex

The FT makes $\chi(R)$ complex. Usually only the amplitude is shown, but there are really oscillations in $\chi(R)$. Both real and imaginary components are used in modeling.

χ**(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.

This results in the filtered χ(k) for the selected shell. Many analysis programs use such filtering to remove shells at higher R.

Beyond the first shell, isolating a shell in this way can be difficult.

EXAFS Data Modeling

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The Information Content of EXAFS

The number of parameters we can reliably 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 usable data.

For the typical ranges like k = [3.0, 12.0] Å^{-1} and R = [1.0, 3.0] Å, there are 11.5 parameters that can be determined from EXAFS.

The "Goodness of Fit" statistics, and confidence in the measured parameters need to reflect this limited amount of data.

It's often important to constrain parameters R, N, σ^2 for different paths or even different data sets (different edge elements, temperatures, etc)

Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).

Use as much other information about the system as possible!

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EXAFS Analysis: Modeling the 1ˢᵗ Shell of FeO

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude **f (k)** and phase-shift **δ(k),** based on a guess of the structure, with Fe-O distance R = 2.14 Å (a regular octahedral coordination).
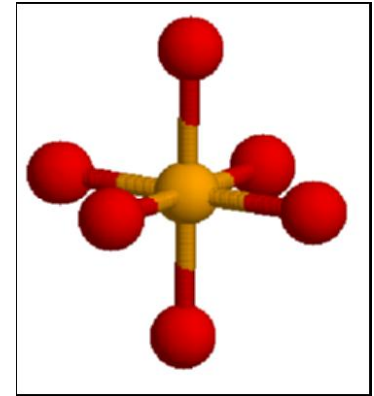
We'll use these functions to refine the values **R, N, σ², and E₀** so our model EXAFS function matches our data.
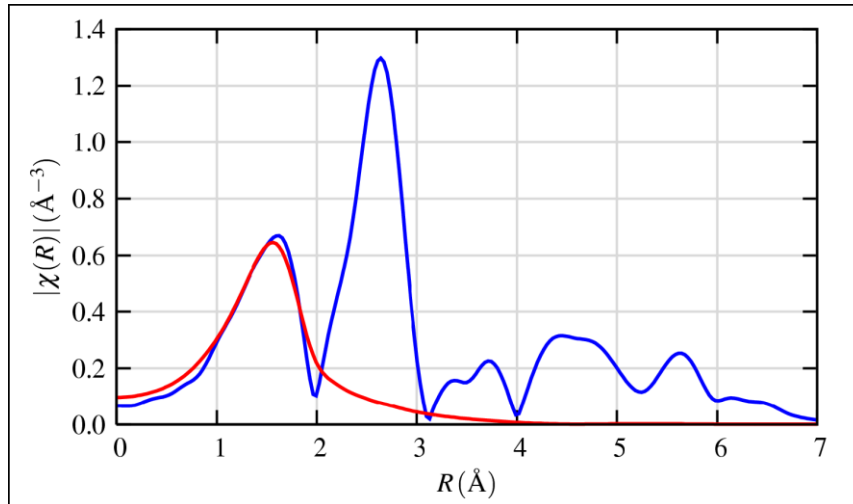
$|\chi(R)|$ for FeO (blue), and a 1ˢᵗ shell fit (red).

Fit results:

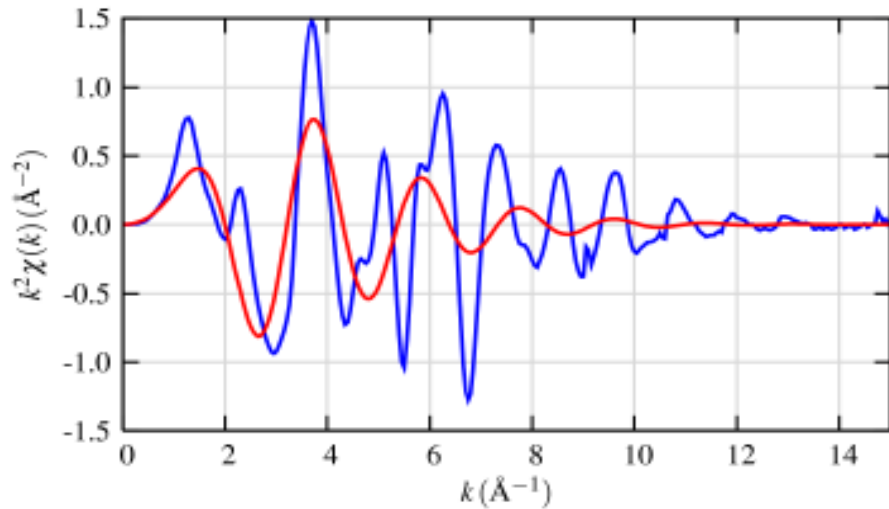$$N = 5.8 \pm 1.8$$
$$R = 2.10 \pm 0.02 \text{ Å}$$
$$E_0 = -3.1 \pm 2.5 \text{ eV}$$
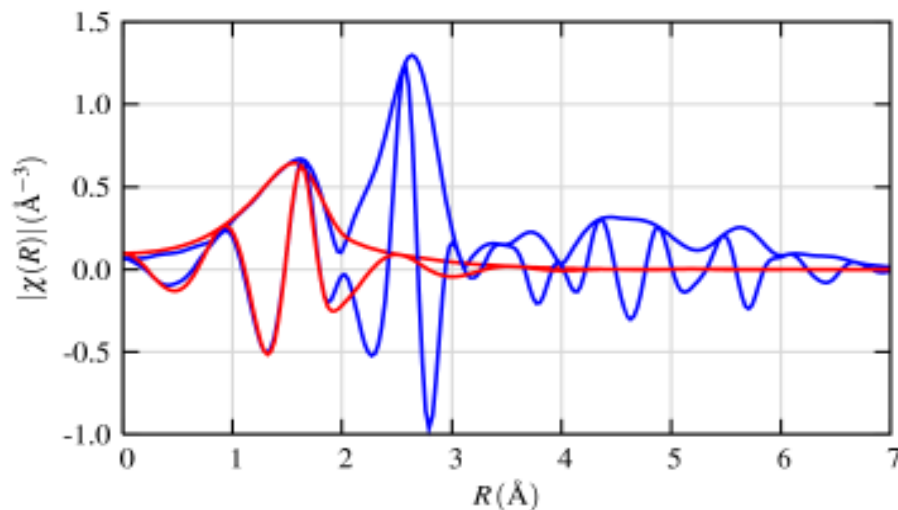$$\sigma^2 = 0.015 \pm 0.005 \text{ Å}^2$$

EXAFS Analysis: 1ˢᵗ Shell of FeO

1ˢᵗ shell fit in k space.

The 1ˢᵗ shell fit to FeO in k space.

There is clearly another component in the XAFS!

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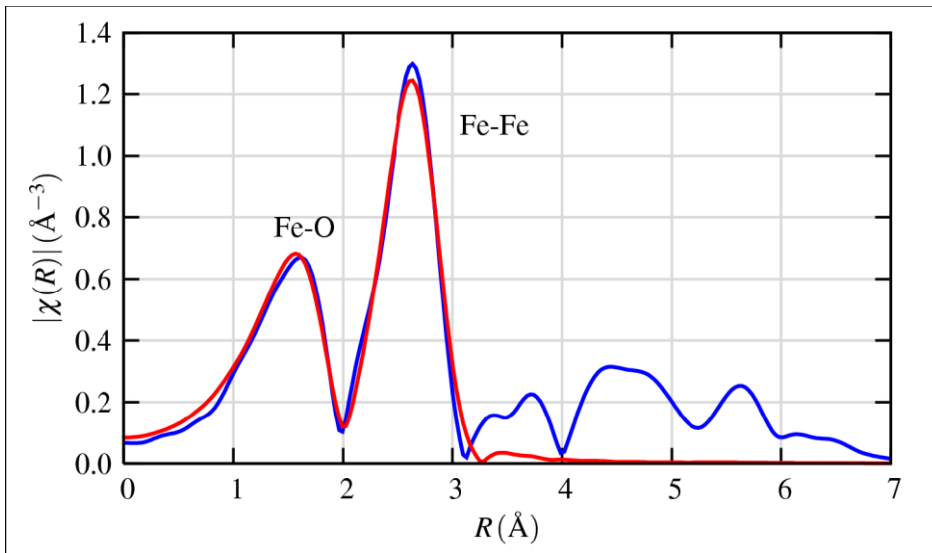
$|\chi(R)|$ and $Re[\chi(R)]$ for FeO (blue), and a 1ˢᵗ shell fit (red).

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

EXAFS Analysis: Second Shell of FeO

To add the second shell Fe to the model, we use calculation for **f(k)** and δ**(k)** based on a guess of the Fe-Fe distance, and refine the values **R,N, σ^2.**
Such a fit gives a result like this:

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

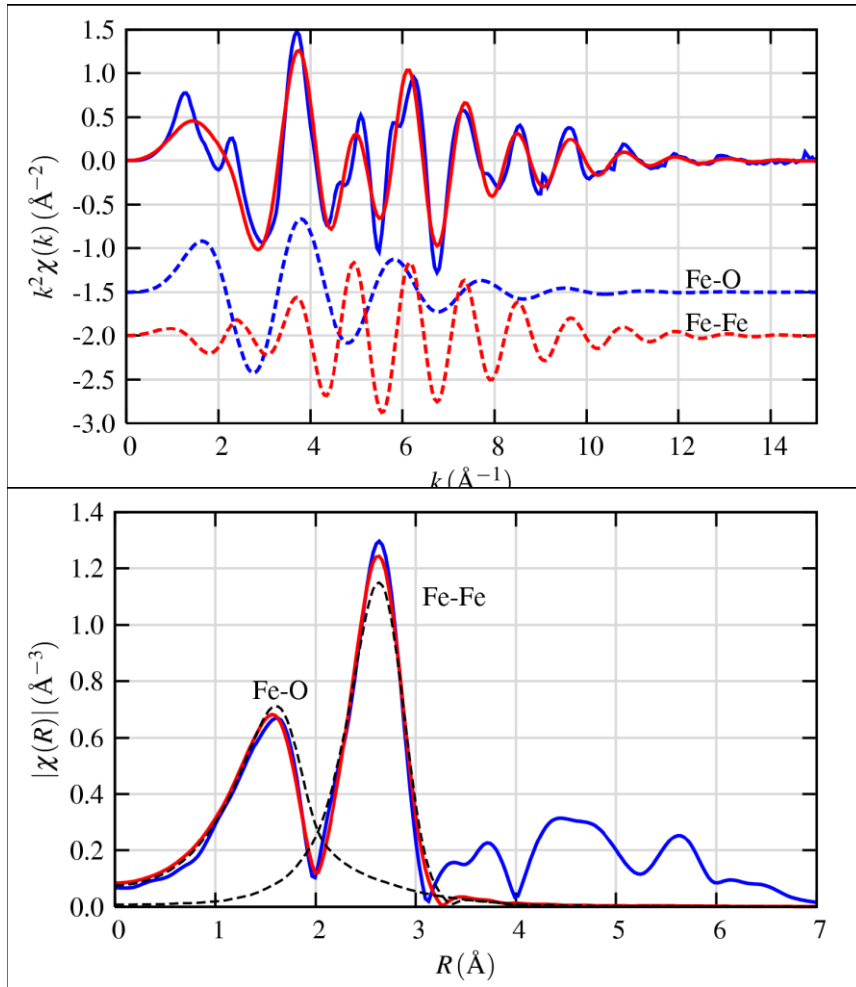The results are fairly consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

Shell	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)

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EXAFS Analysis: Second Shell of FeO
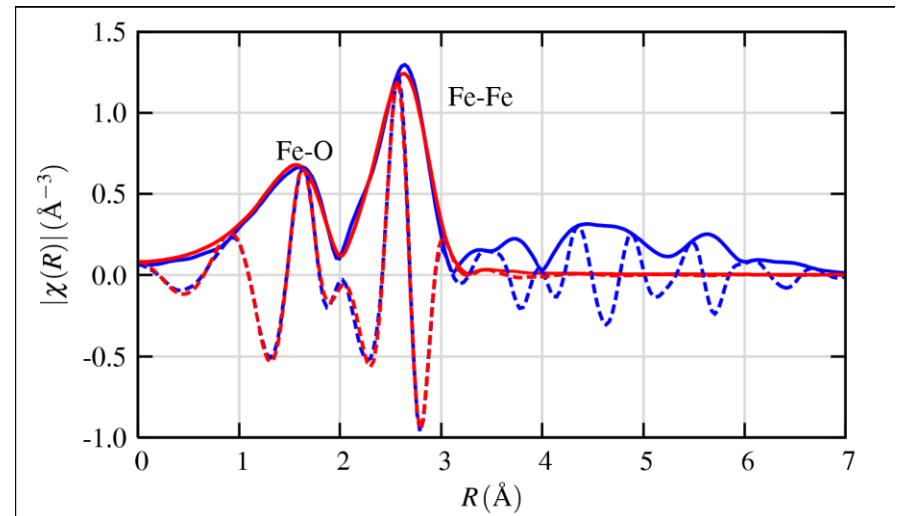
Other views of the data and two-shell fit:

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

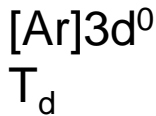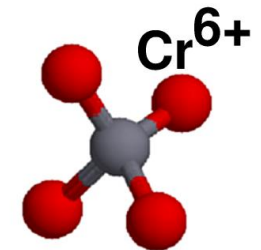Even in this simple system, there is some overlap of shells in R-space.
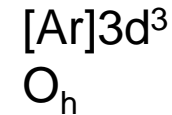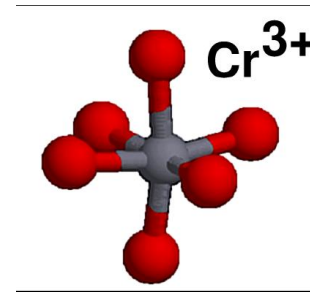The agreement in $Re[\chi(R)]$ look especially good – this is how the fits are done.

Of course, the modeling can get more complicated than this!

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XANES

XANES Analysis: Oxidation State and Coordination Chemistry
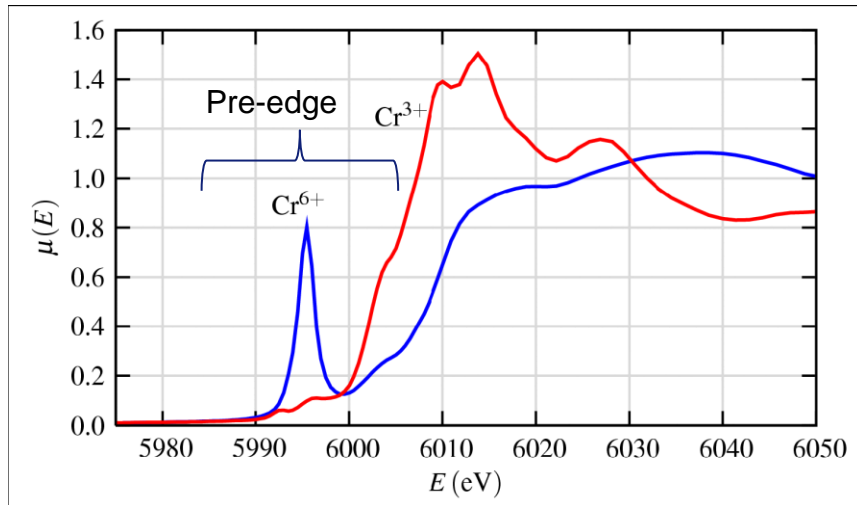
- The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

- For ions with partially filled d shells, the p-d hybridization changes dramatically as regular octahedra distort, and is very large for tetrahedral coordination.

- This gives a dramatic pre-edge peak – absorption to a localized electronic state.

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XANES Interpretation

The EXAFS Equation breaks down at low-k, and the mean-free-path goes up. This complicates XANES interpretation:

<div align="center">We do not have a simple equation for XANES.</div>

XANES can be described qualitatively (and nearly quantitatively) in terms of

coordination chemistry	regular, distorted octahedral, tetrahedral, . . .
molecular orbitals	p-d orbital hybridization, crystal-field theory, . . .
band-structure	the density of available electronic states
multiple-scattering	multiple bounces of the photoelectron

These chemical and physical interpretations are all related, of course:

<div align="center">What electronic states can the photoelectron fill?</div>

XANES calculations are becoming reasonably accurate and simple. These can help explain what bonding orbitals and/or structural characteristics give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are still rare, but becoming possible... **FDMNES Tutorial (Y. Joly)**

XANES Interpretation

Region	Transition	Information Content
Pre-edge	Electronic transitions to empty bound states (transition probability controlled by dipolar selection rules). e.g. 1s→4p/3d (1st transition series metals)	Local coordination environment around the absorbing atom. Dependence on the oxidation state and bonding.
Edge	Defines ionization threshold to continuum states.	Dependence on the oxidation state "Chemical shift": main edge (binding energy) shifts to higher energy with increasing oxidation state.
XANES	Feautures dominated by multiple-scattering resonances of the photoelectrons ejected at low $E_{kinetic}$.	Atomic positions of neighbours: Interatomic distances and bond angles.

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Edge Shifts and Pre-edge Peaks in Fe oxides
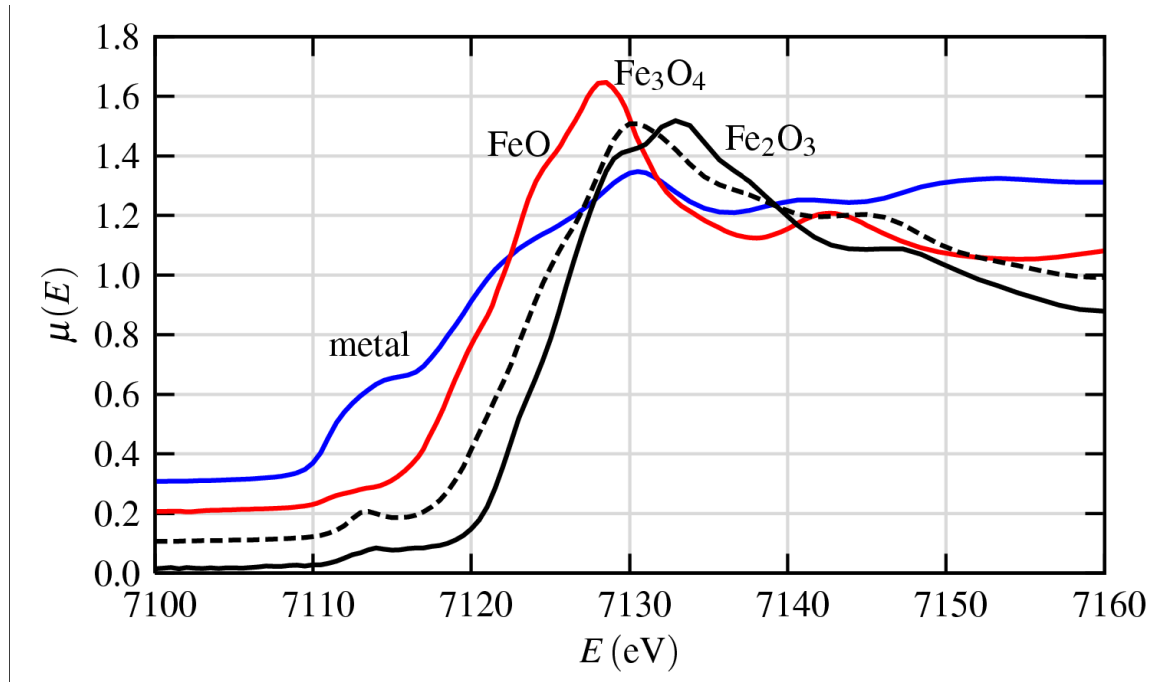
The shift of the edge position can be used to determine the valence state (J. García et al., J. Synchrotron Rad. **17** (2010))

The heights and positions of pre-edge peaks can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

XANES Analysis: Oxidation State

The Normalized XANES from several Fe compounds:
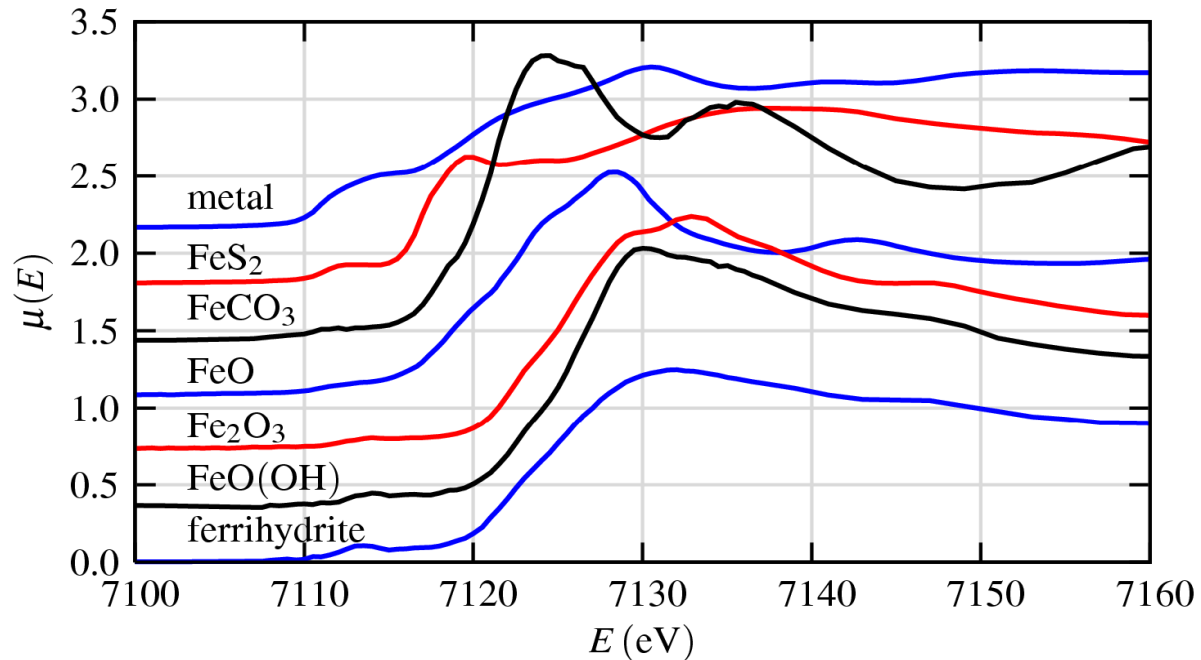
XANES can be used simply as a fingerprint of phases and oxidation state.

XANES Analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components.

XANES: Conclusions

XANES is a much larger signal than EXAFS
XANES can be done at lower concentrations, and less-than-perfect sample conditions.

XANES is easier to crudely interpret than EXAFS
For many systems, the XANES analysis based on linear combinations of known spectra from "model compounds" is sufficient.

XANES is harder to fully interpret than EXAFS
The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.

This situation is improving, so stay tuned to the progress in XANES calculations . . . .

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