



| The European Synchrotron

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

XAFS Data Reduction

Data Reduction: Strategy

Step 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, to get rid of any instrumental background, and absorption from other edges.
3. normalize $\mu(E)$ 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 $\mu_0(E)$ to isolate the XAFS χ .
5. identify the threshold energy E_0 , and convert from E to k space:
6. weight the XAFS $\chi(k)$ and Fourier transform from k to R space.
7. isolate the $\chi(k)$ for an individual “shell” by Fourier filtering.

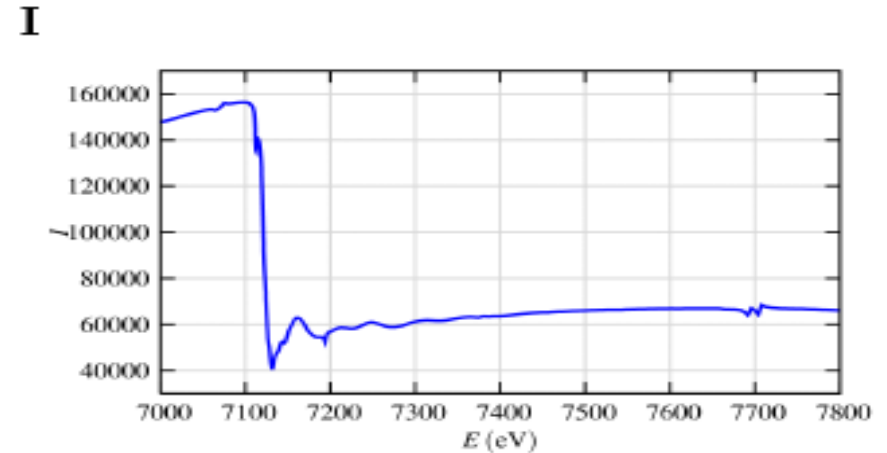
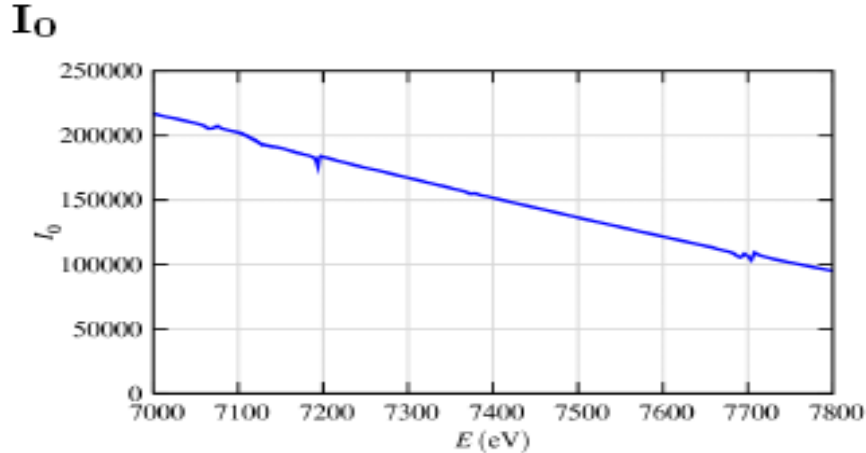
$$k = \frac{\sqrt{2m(E - E_0)}}{\hbar^2}$$

After we get this far, we'll model $f(k)$ and $\delta(k)$ and analyze $\chi(k)$ to get:

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

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

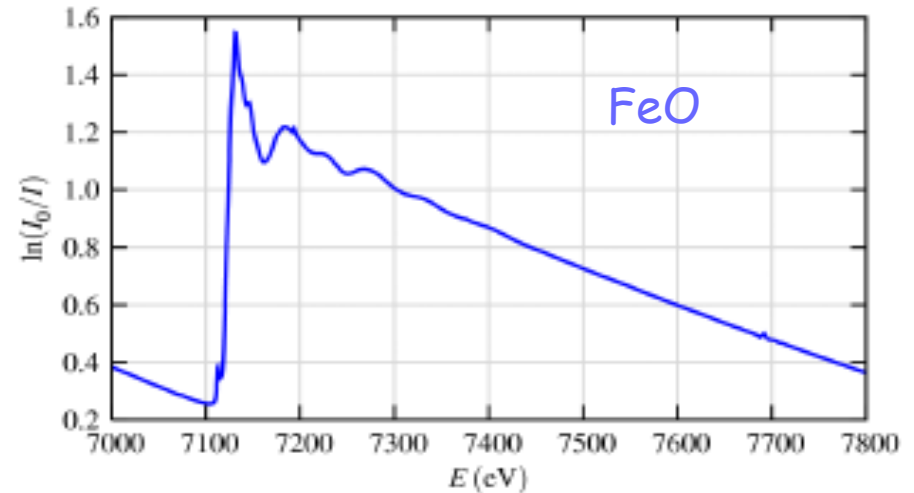
Starting with measured intensities before and after the sample, we construct $\mu(E)$:



For transmission XAFS:

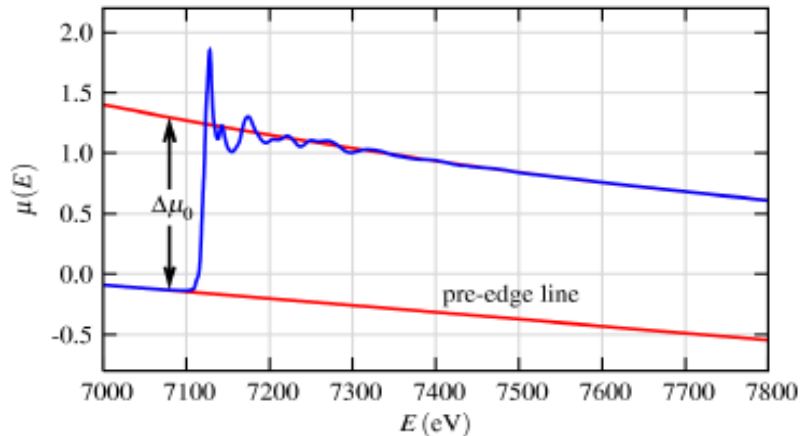
$$I = I_0 \exp[-\mu(E) t]$$

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



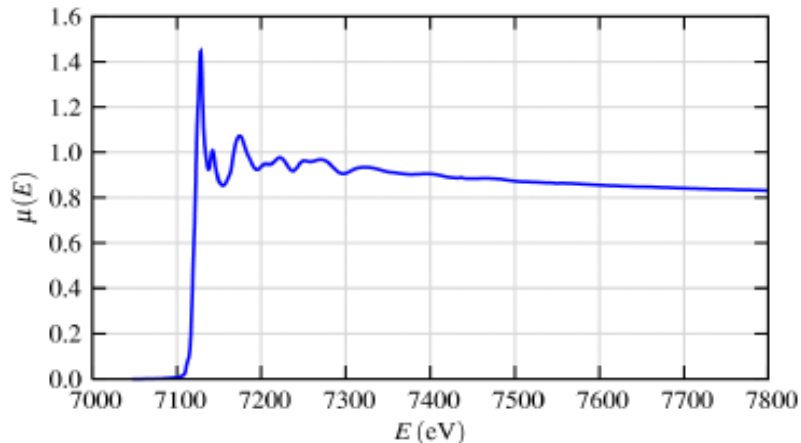
Data Reduction: Pre-Edge Subtraction, Normalization

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



Pre-Edge Subtraction

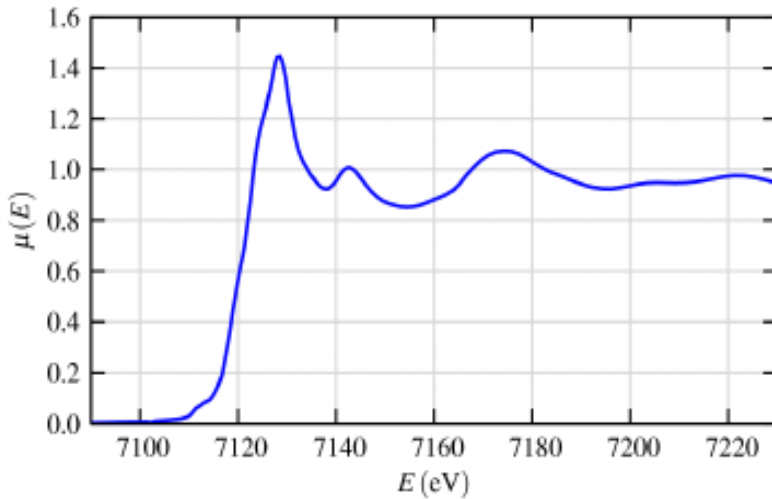
We subtract away the background that fits the **pre edge** region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

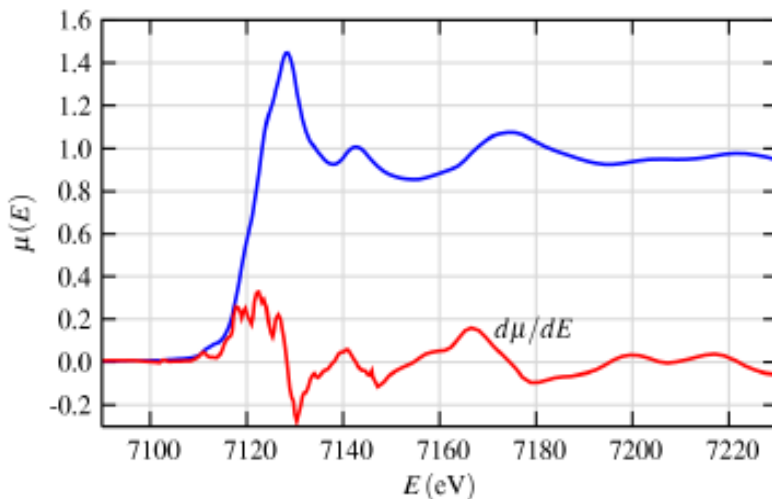
We estimate the **edge step**, $\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge. We normalize by this value to get the absorption from 1 X-ray.

Data Reduction: Normalized XANES and E_0



XANES

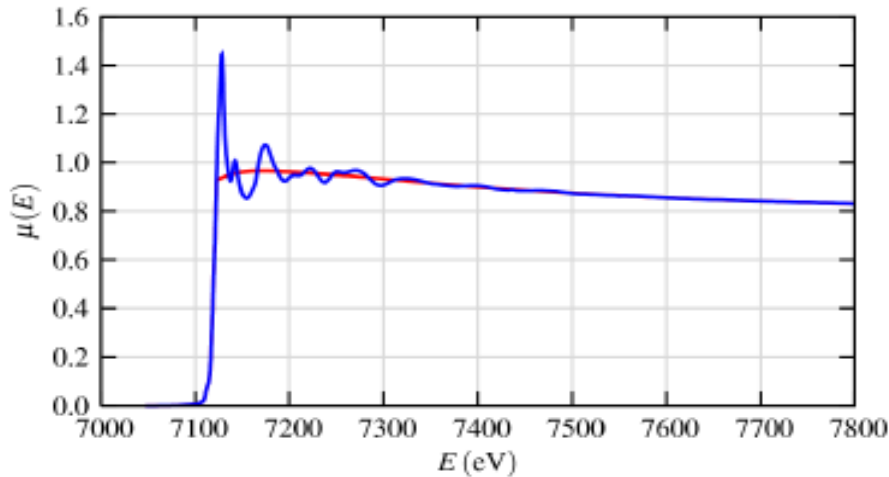
The XANES portion shows a fairly rich spectral structure. We'll come back to this for XANES analysis.



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.

Data Reduction: Post-Edge Background Subtraction



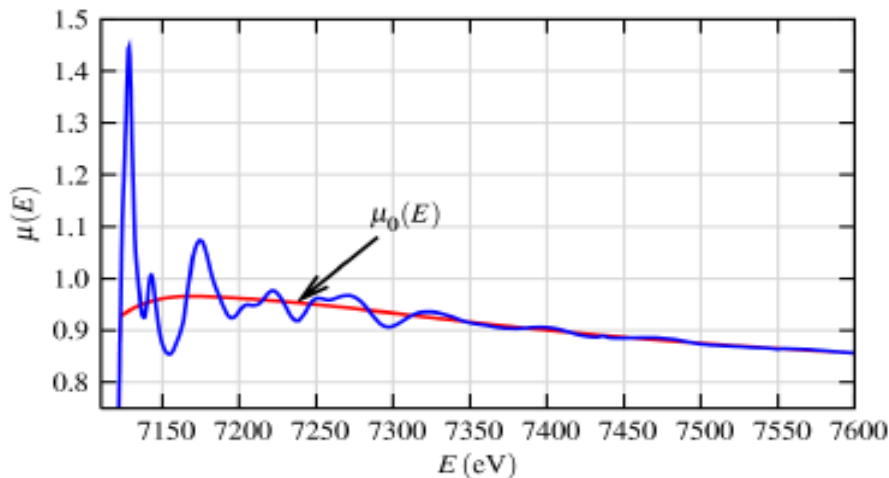
Post-Edge Background

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

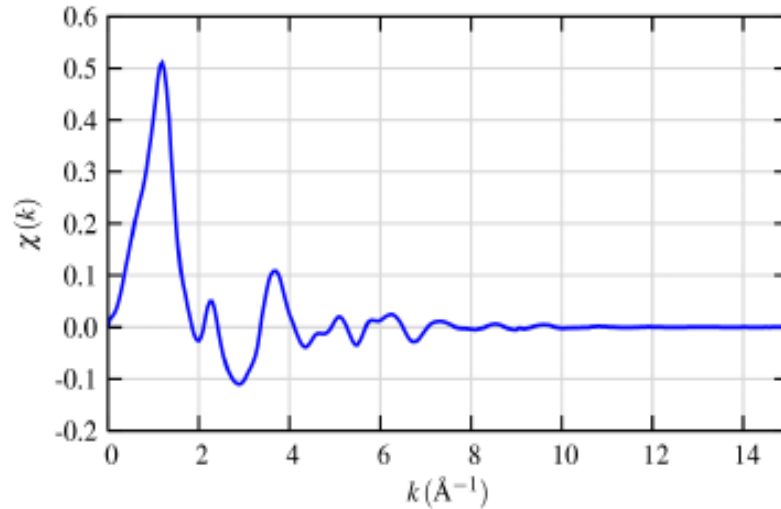
We approximate $\mu_0(E)$ by an adjustable, smooth function: a **spline**.

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 $\mu_0(E)$.



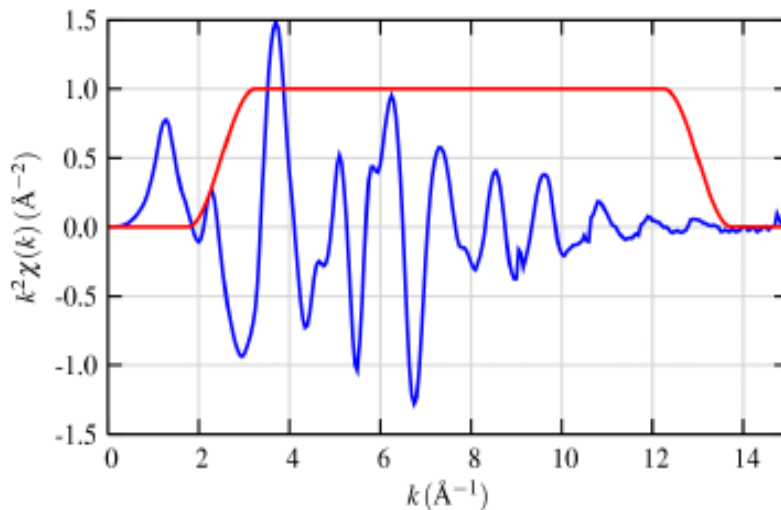
Data Reduction: $\chi(k)$, k-weighting



$\chi(k)$

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**.

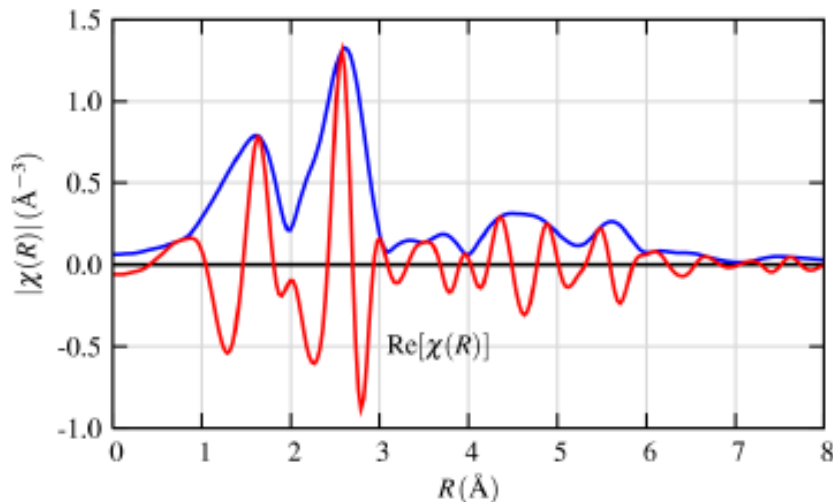
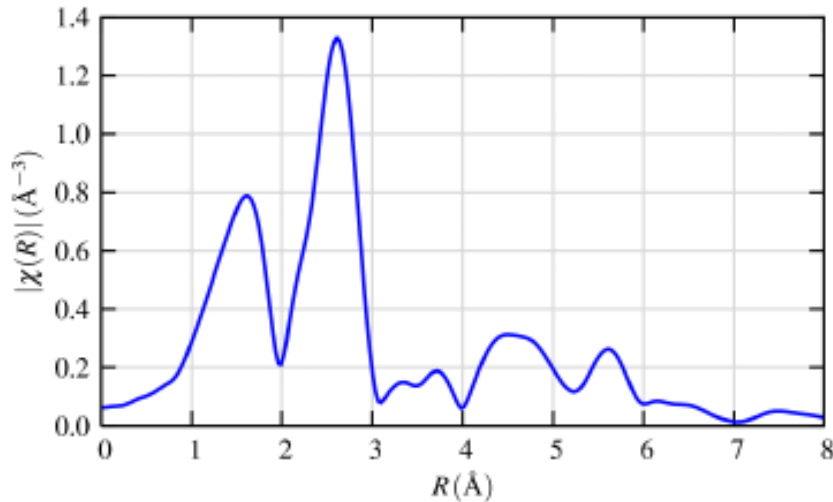
The Fourier Transform is a tool that breaks a waveform (a function or signal) into an alternate representation, characterized by sine and cosines.

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

$$\mathcal{F}\{g(t)\} = G(f) = \int_{-\infty}^{\infty} g(t)e^{-i2\pi ft} dt$$
$$\mathcal{F}^{-1}\{G(f)\} = g(t) = \int_{-\infty}^{\infty} G(f)e^{i2\pi ft} df$$



Fourier Transform: $\chi(R)$



$\chi(R)$

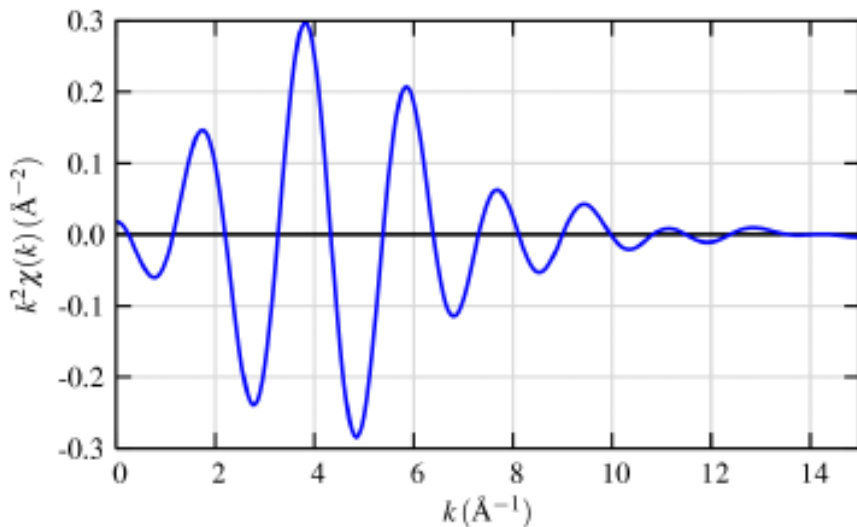
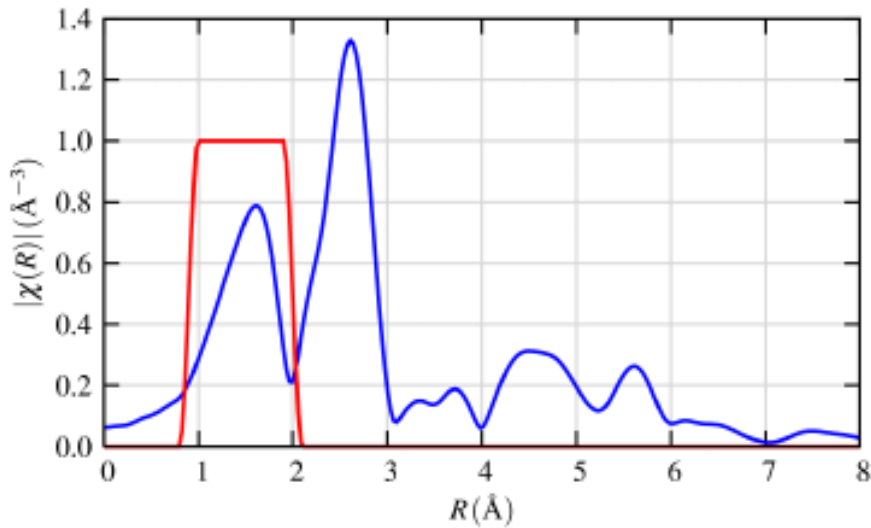
The Fourier Transform of $k^2(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe- Fe.

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.



$\chi(R)$ 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.

This results in the filtered $\chi(k)$ 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

The EXAFS equation

To model the EXAFS, we use the **EXAFS Equation**

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

where $f(k)$ and $\delta(k)$ are **photoelectron scattering properties** of the neighboring atom.

(the sum is over “shells” of similar neighboring atoms)

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

R distance to neighboring atom.

N coordination number of neighboring atom.

σ^2 mean-square disorder of neighbor distance.

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

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 $k = [3.0, 12.0] \text{ \AA}^{-1}$ and $R = [1.0, 3.0] \text{ \AA}$, 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)

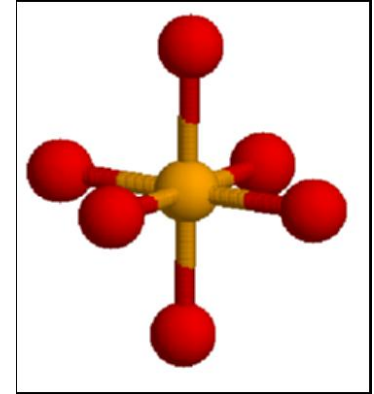
Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).

Use as much other information about the system as possible!

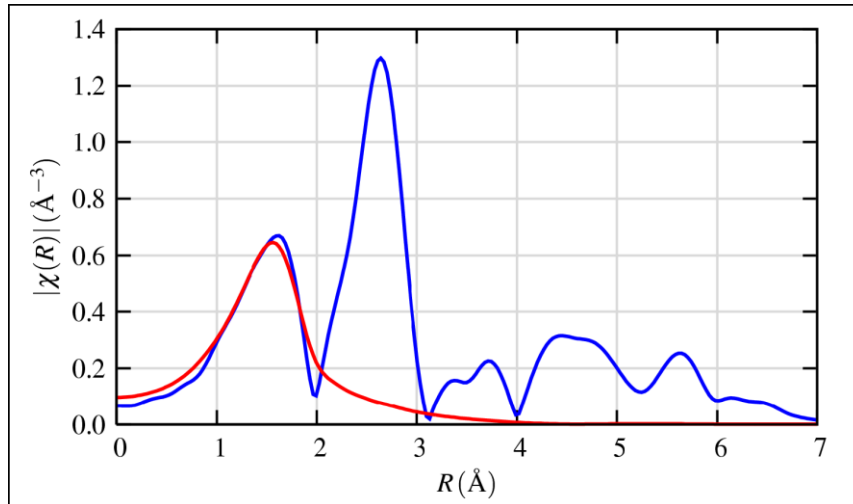
EXAFS Analysis: Modeling the 1st Shell of FeO

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta(\mathbf{k})$, based on a guess of the structure, with Fe-O distance $R = 2.14 \text{ \AA}$ (a regular octahedral coordination).



We'll use these functions to refine the values R , N , σ^2 , and E_0 so our model EXAFS function matches our data.



$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).

Fit results:

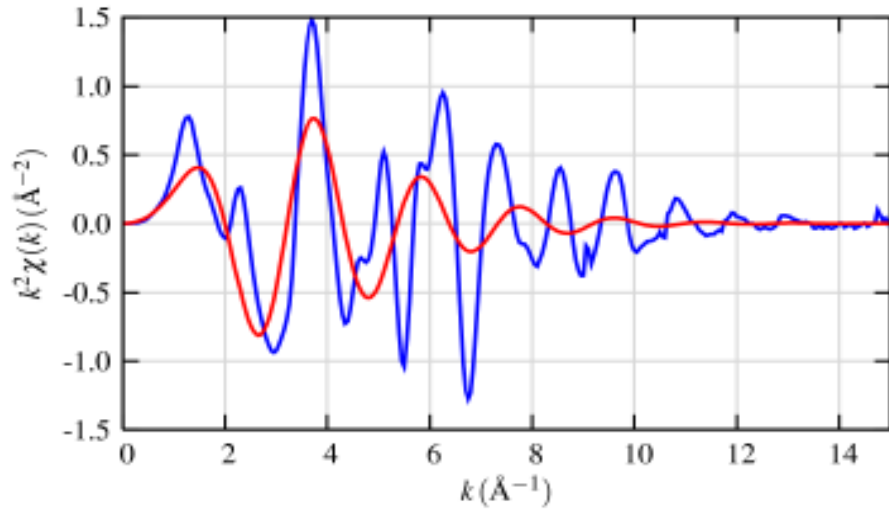
$$N = 5.8 \pm 1.8$$

$$R = 2.10 \pm 0.02 \text{ \AA}$$

$$E_0 = -3.1 \pm 2.5 \text{ eV}$$

$$\sigma^2 = 0.015 \pm 0.005 \text{ \AA}^2$$

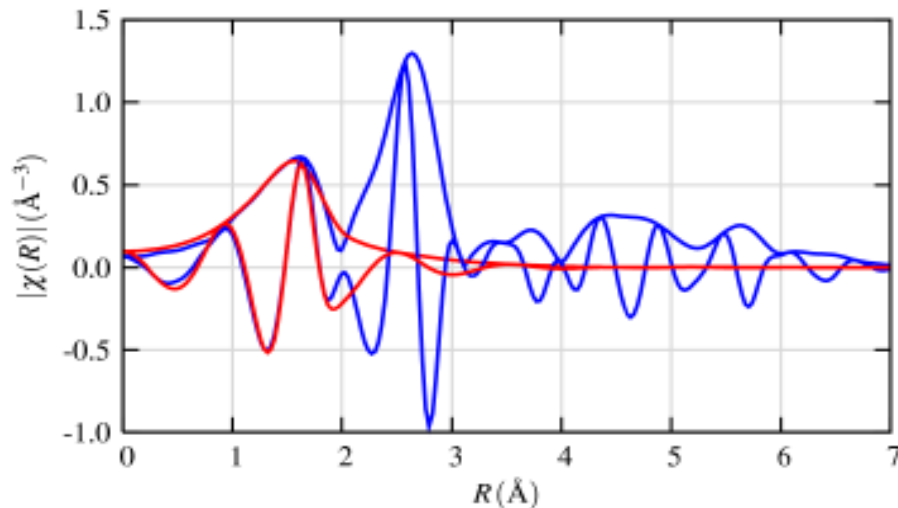
EXAFS Analysis: 1st Shell of FeO



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.

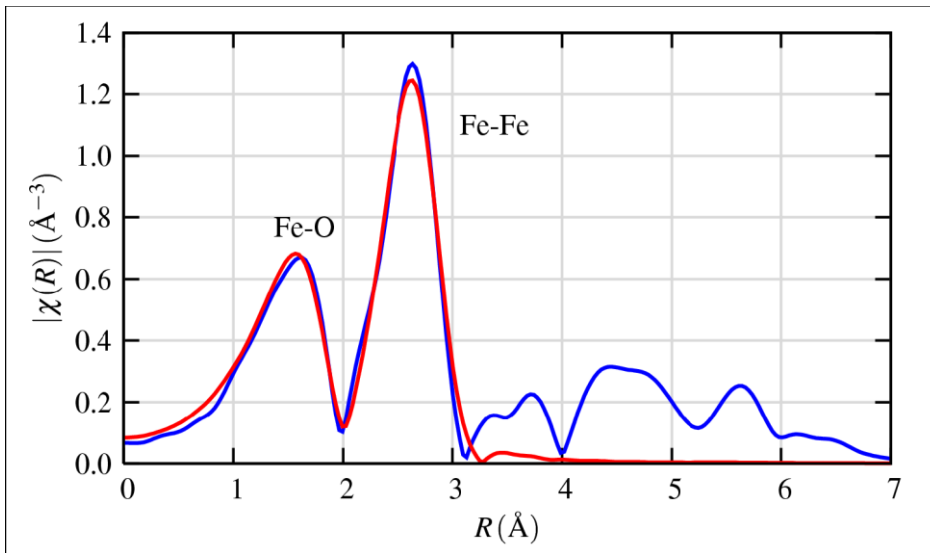
$|\chi(R)|$ and $\text{Re}[\chi(R)]$ for FeO (blue), and a 1st shell fit (red).

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

EXAFS Analysis: Second Shell of FeO

To add the second shell Fe to the model, we use calculation for $f(\mathbf{k})$ and $\delta(\mathbf{k})$ 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:

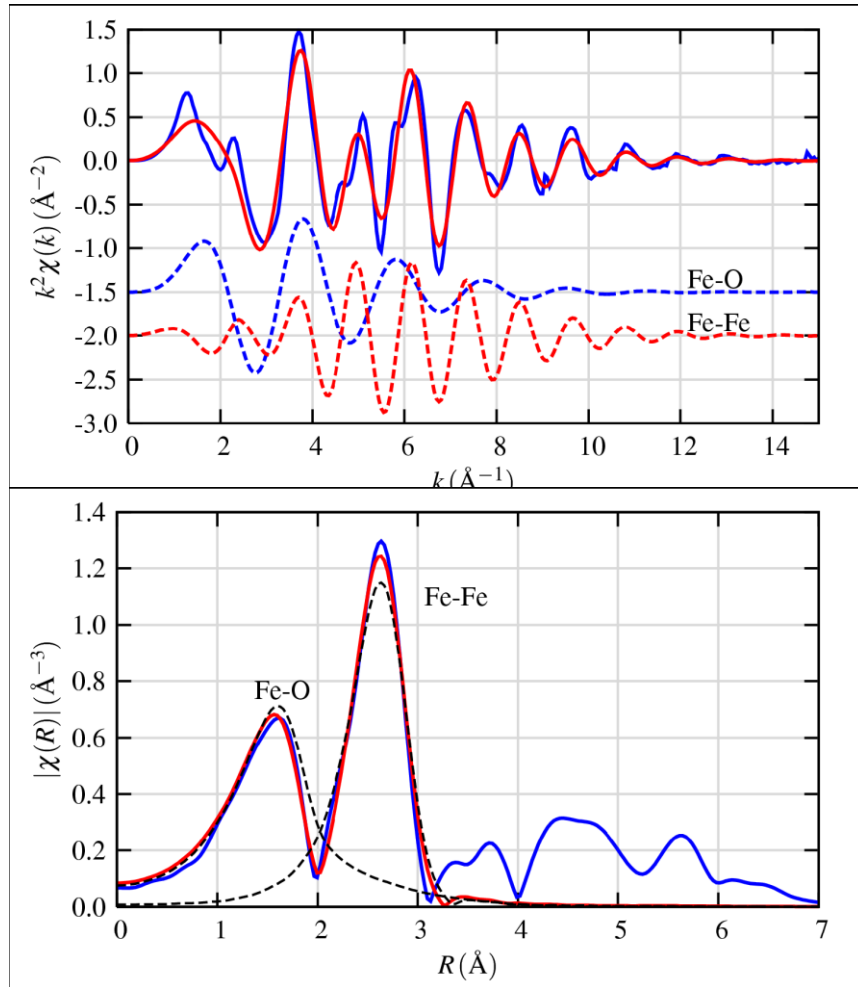
6 O at 2.13Å, 12 Fe at 3.02Å.

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)

EXAFS Analysis: Second Shell of FeO

Other views of the data and two-shell fit:

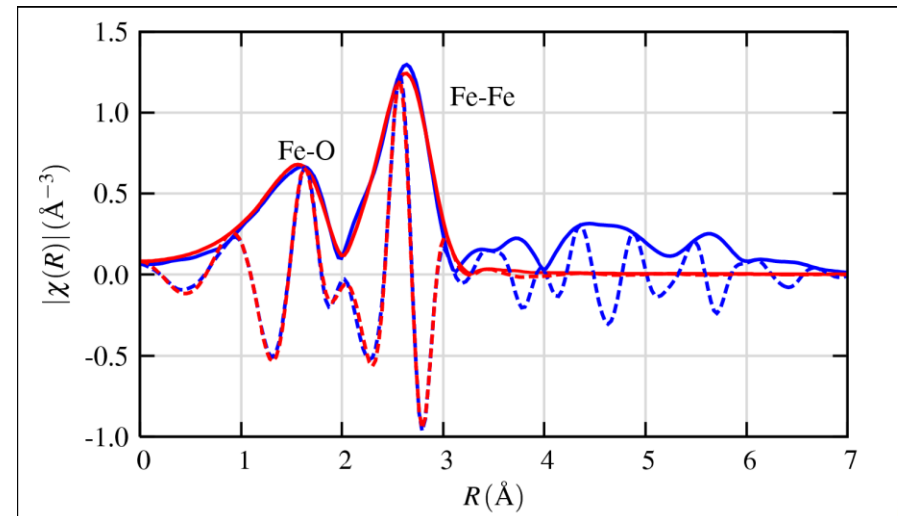


The Fe-Fe EXAFS extends to higher- k than the Fe-O EXAFS.

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

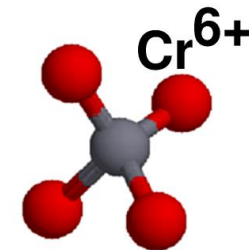
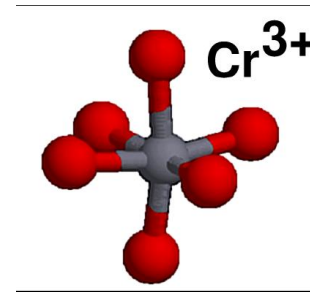
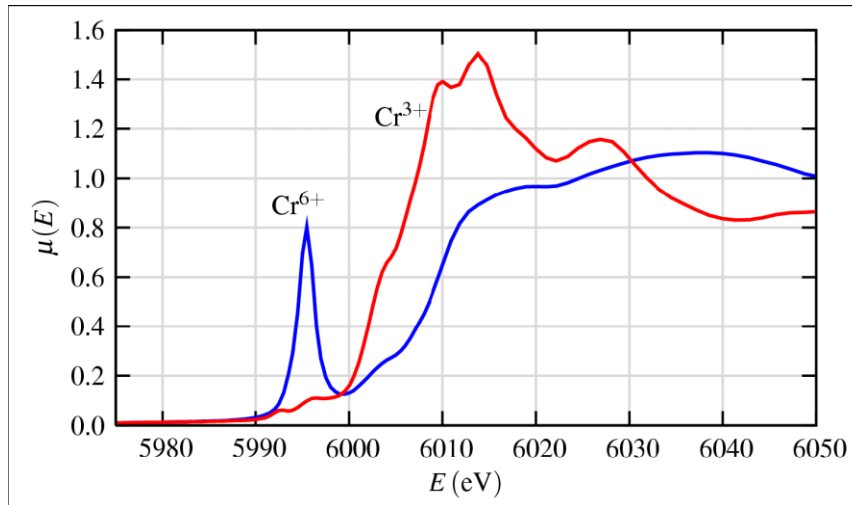
The agreement in $\text{Re}[\chi(R)]$ look especially good – this is how the fits are done.

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



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.

XANES Interpretation

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

We do not have a simple equation for XANES.

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

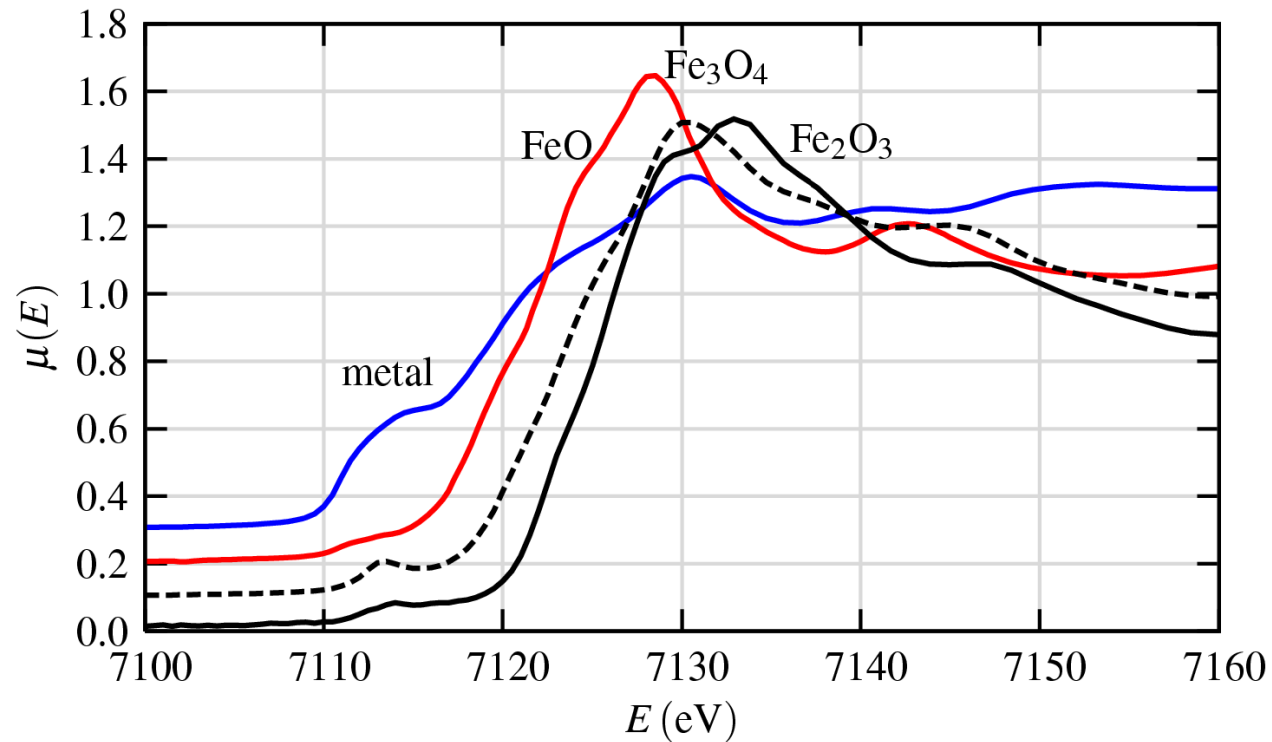
These chemical and physical interpretations are all related, of course:

What electronic states can the photoelectron fill?

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...

Edge Shifts and Pre-edge Peaks in Fe oxides

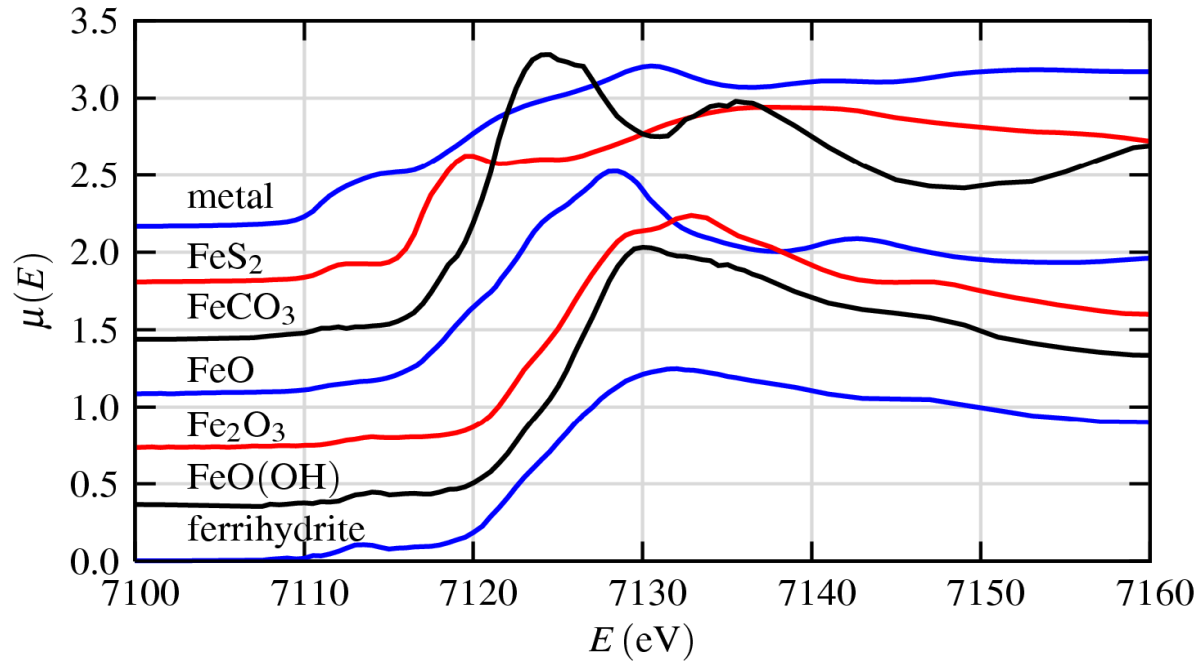


The shift of the edge position can be used to determine the valence state

The heights and positions of pre-edge peaks can also be reliably used to determine $\text{Fe}^{3+}/\text{Fe}^{2+}$ 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