

XAFS: X-ray Absorption Fine-Structure

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Basic Principles:

X-ray absorption and fluorescence

Simple theoretical description

Experiment Design:

Transmission v. Fluorescence modes

Fluorescence detectors

Data Analysis:

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

XANES Analysis: formal valence and coordination chemistry

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What Is XAFS?

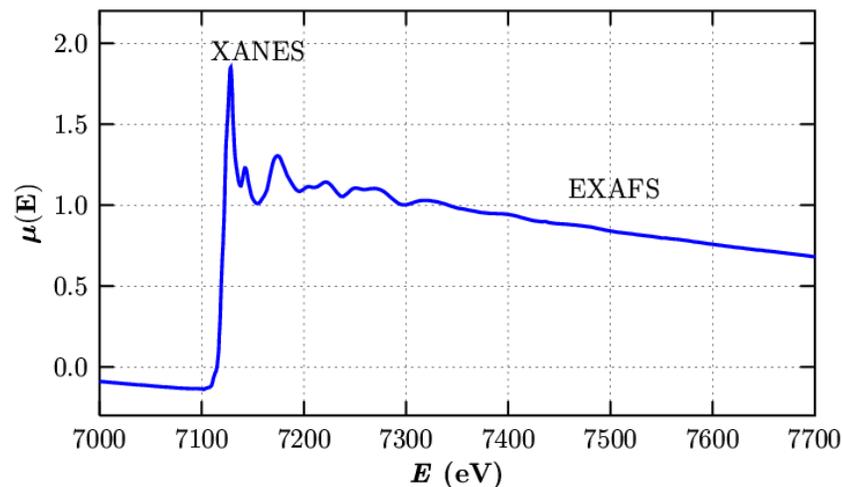
X-ray Absorption Fine-Structure (**XAFS**) is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge. XAFS is also referred to as X-ray Absorption Spectroscopy (**XAS**) and is broken into 2 regimes:

XANES X-ray Absorption Near-Edge Spectroscopy

EXAFS Extended X-ray Absorption Fine-Structure

which contain related, but slightly different information about an element's local coordination and chemical state.

Fe K-edge XAFS for FeO:



XAFS Characteristics:

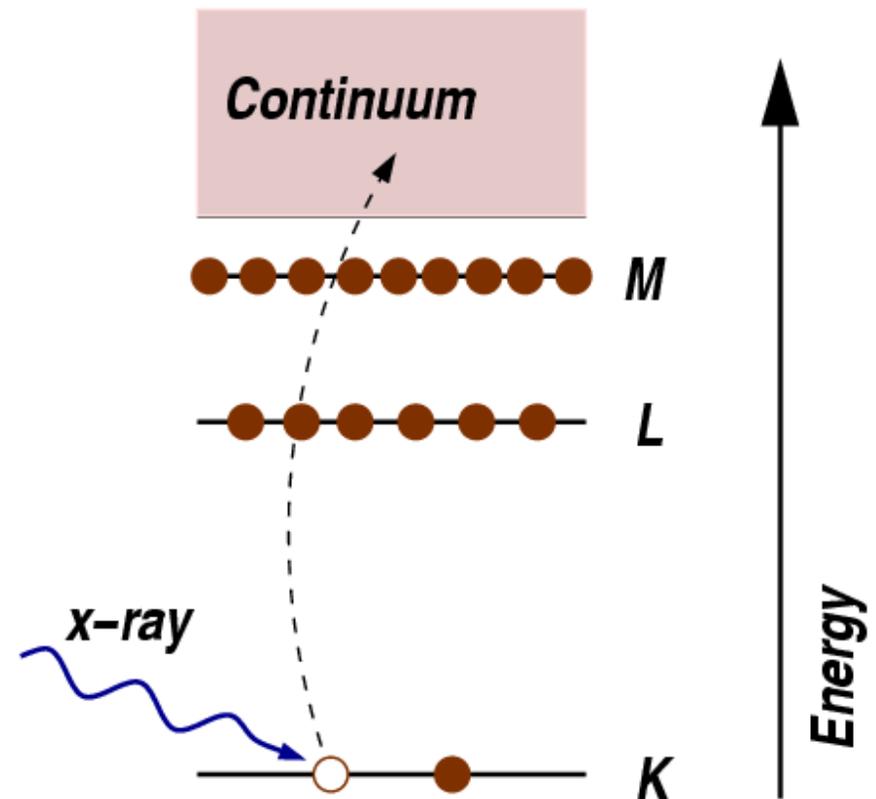
- local atomic coordination
- chemical / oxidation state
- applies to any element
- works at low concentrations
- minimal sample requirements

X-ray Absorption

X-rays (light with wavelength $0.03 \lesssim \lambda \lesssim 12 \text{ \AA}$ or energy $1 \lesssim E \lesssim 500 \text{ keV}$) are absorbed by all matter through the **photo-electric effect**:

An x-ray is absorbed by an atom, promoting a core-level electron (*K*, *L*, or *M* shell) out of the atom and into the continuum.

The atom is left in an **excited state** with an empty electronic level (a **core hole**). The electron ejected from the atom is called the **photo-electron**.

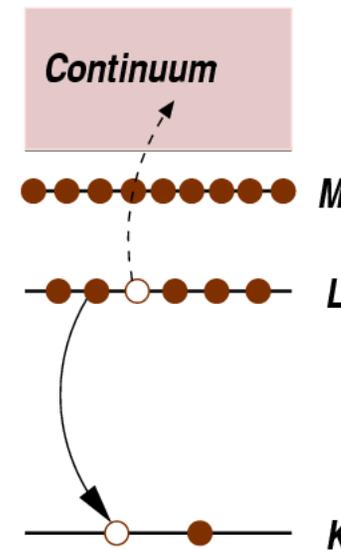
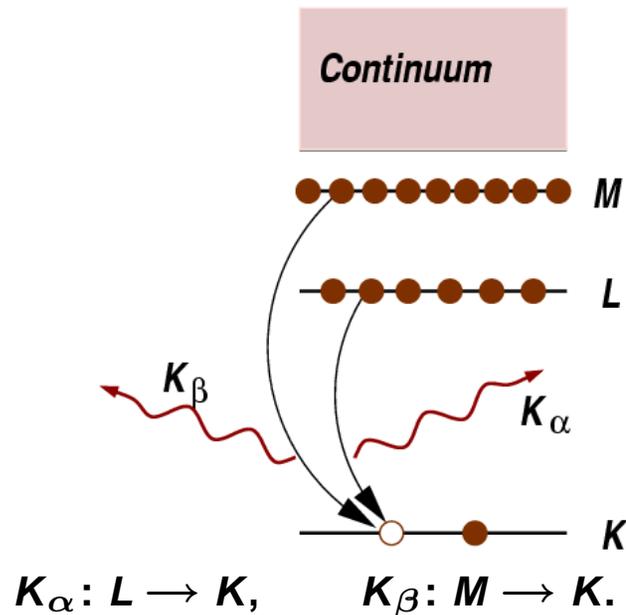


X-ray Fluorescence

When x-rays are absorbed by the photo-electric effect, the excited core-hole will relax back to a “ground state” of the atom. A higher level core electron drops into the core hole, and a **fluorescent x-ray** or **Auger electron** is emitted.

X-ray Fluorescence: An x-ray with energy = the difference of the core-levels is emitted.

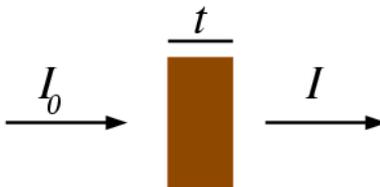
Auger Effect: An electron is promoted into the continuum from another core-level.



X-ray fluorescence occurs at discrete energies that are characteristic of the absorbing atom, and can be used to identify the absorbing atom.

The X-ray Absorption Coefficient: μ

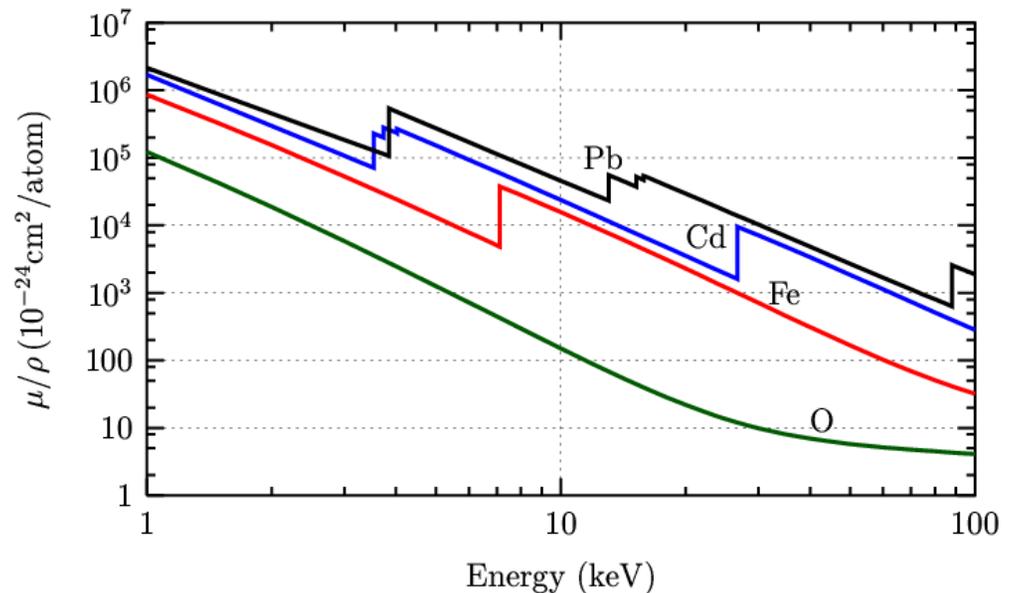
The intensity of an x-ray beam as it passes through a material of thickness t is given by the **absorption coefficient** μ :

$$\boxed{I = I_0 e^{-\mu t}}$$


where I_0 is the x-ray intensity hitting the material, and I is the intensity transmitted through the material.

μ depends strongly on x-ray energy E and atomic number Z , and on the density ρ and Atomic mass A :

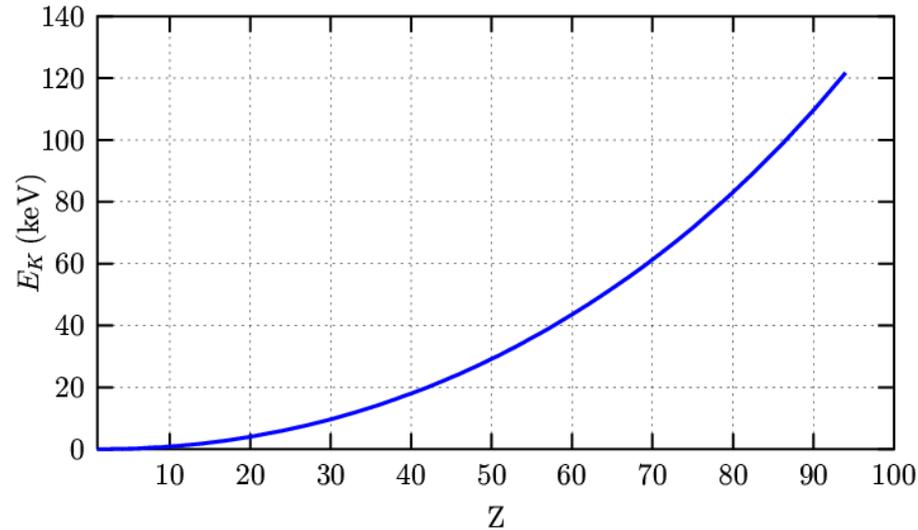
$$\mu \approx \frac{\rho Z^4}{A E^3}$$



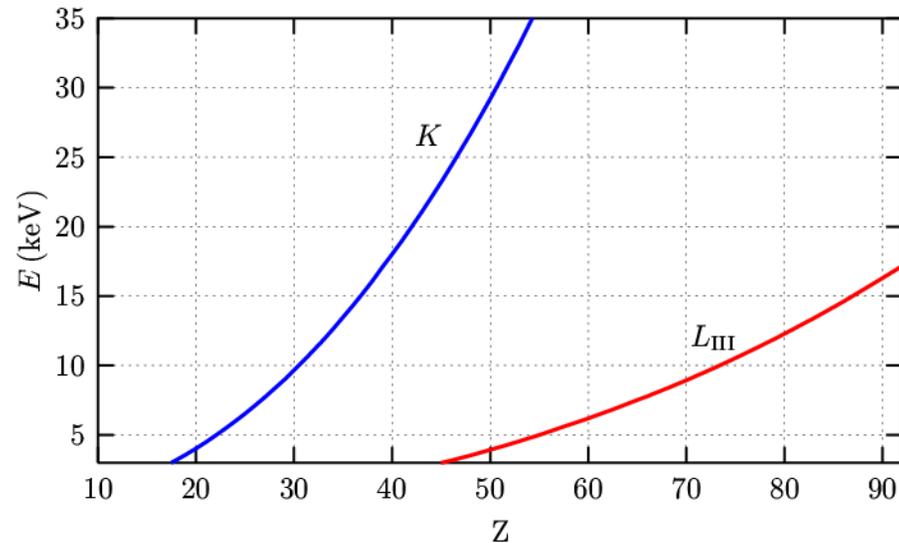
In addition, μ has sharp **Absorption Edges** corresponding to the characteristic core-level energies of the atom.

Absorption Edge Energies

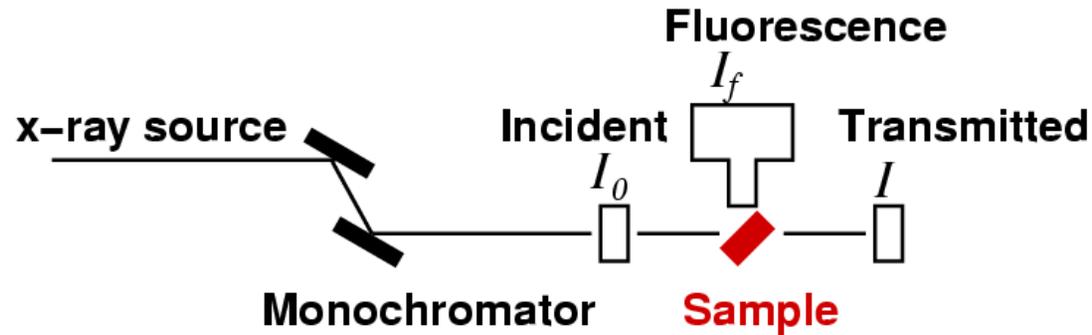
The energies of the *K*-edge absorption edges go roughly as $E_K \sim Z^2$



All elements with $Z > 18$ have either a *K*-, or *L*-edge between 3 and 35 keV, which can be accessed at many synchrotron sources:



X-ray Absorption Measurements



XAS measures the energy dependence of the x-ray absorption coefficient $\mu(E)$ at and above the absorption edge of a selected element. $\mu(E)$ can be measured two ways:

Transmission: The absorption is measured directly by measuring what is transmitted through the sample:

$$I = I_0 e^{-\mu(E)t}$$
$$\mu(E)t = \ln(I/I_0)$$

Fluorescence: The re-filling the deep core hole, is detected. Typically the fluorescent x-ray is measured.

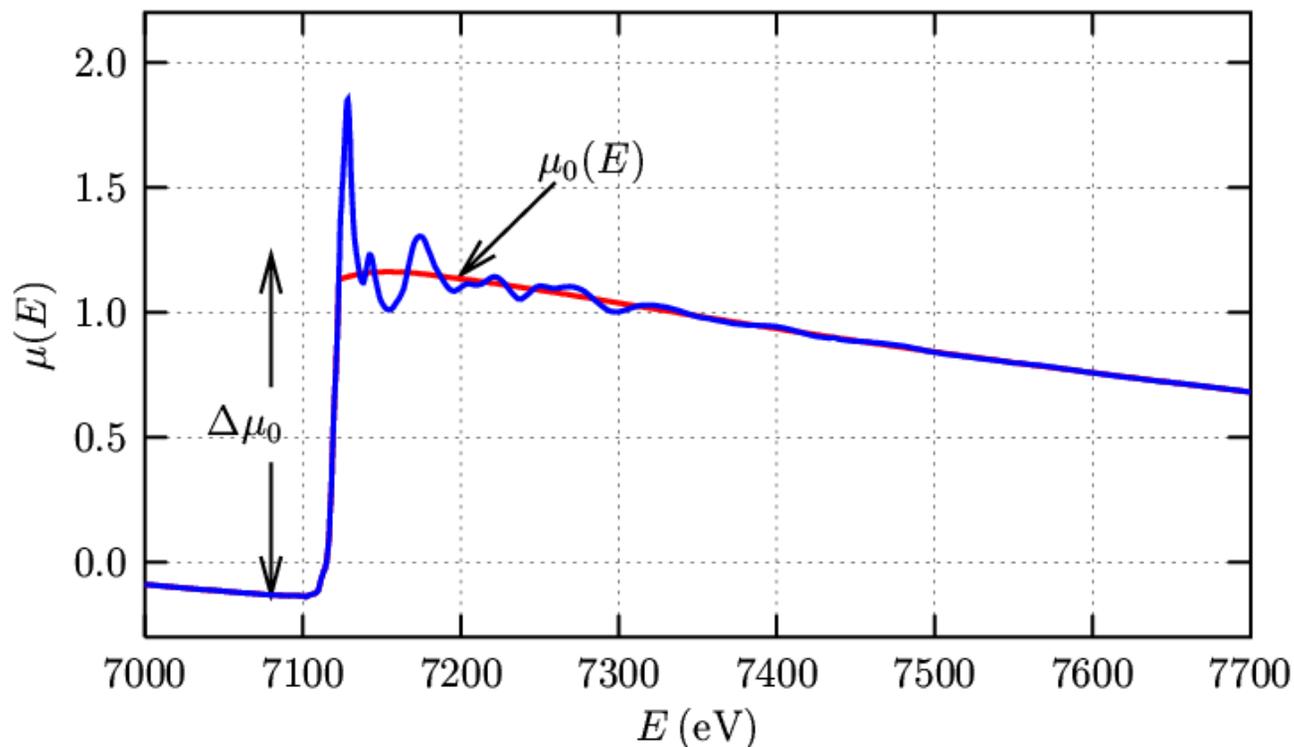
$$\mu(E) \sim I_f/I_0$$

X-ray Absorption Fine Structure

We're interested in the energy-dependent oscillations in $\mu(\mathbf{E})$, as these will tell us something about the neighboring atoms, so define the EXAFS as:

$$\chi(\mathbf{E}) = \frac{\mu(\mathbf{E}) - \mu_0(\mathbf{E})}{\Delta\mu_0(\mathbf{E}_0)}$$

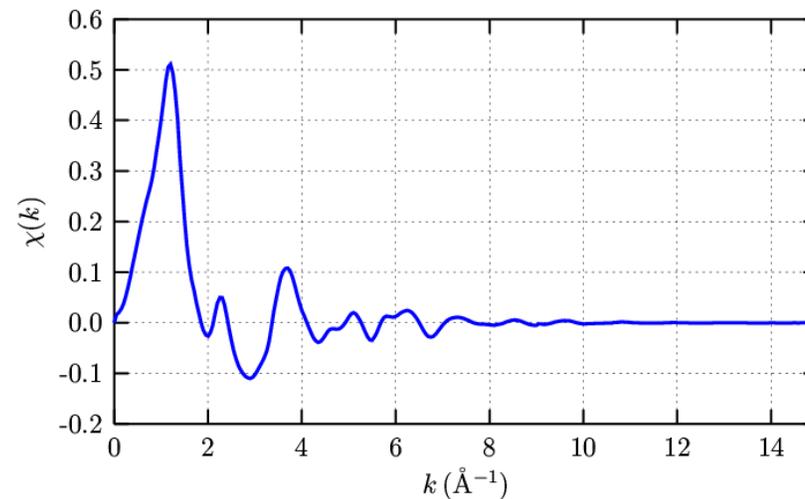
We subtract off the smooth *“bare atom” background* $\mu_0(\mathbf{E})$, and divide by the *“edge step”* $\Delta\mu_0(\mathbf{E}_0)$ to give the oscillations normalized to 1 absorption event:



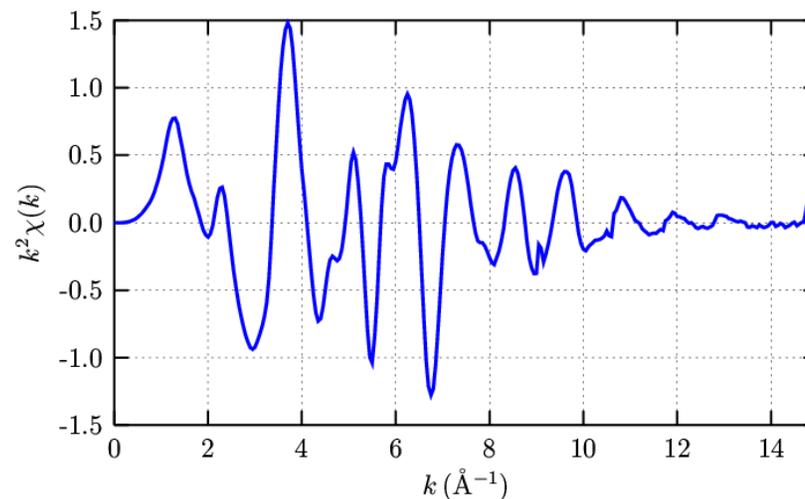
EXAFS: $\chi(k)$

It's convenient to think of the XAFS in terms of *photo-electron wavenumber* k :

$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$ rather than x-ray energy, so that we have $\chi(k) = \chi(k[E])$:



$\chi(k)$ is often shown weighted by k^2 or k^3 to amplify the oscillations at high- k :



The EXAFS Equation

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

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

where $f(\mathbf{k})$ and $\delta_j(\mathbf{k})$ are *scattering* properties of the neighboring atom.

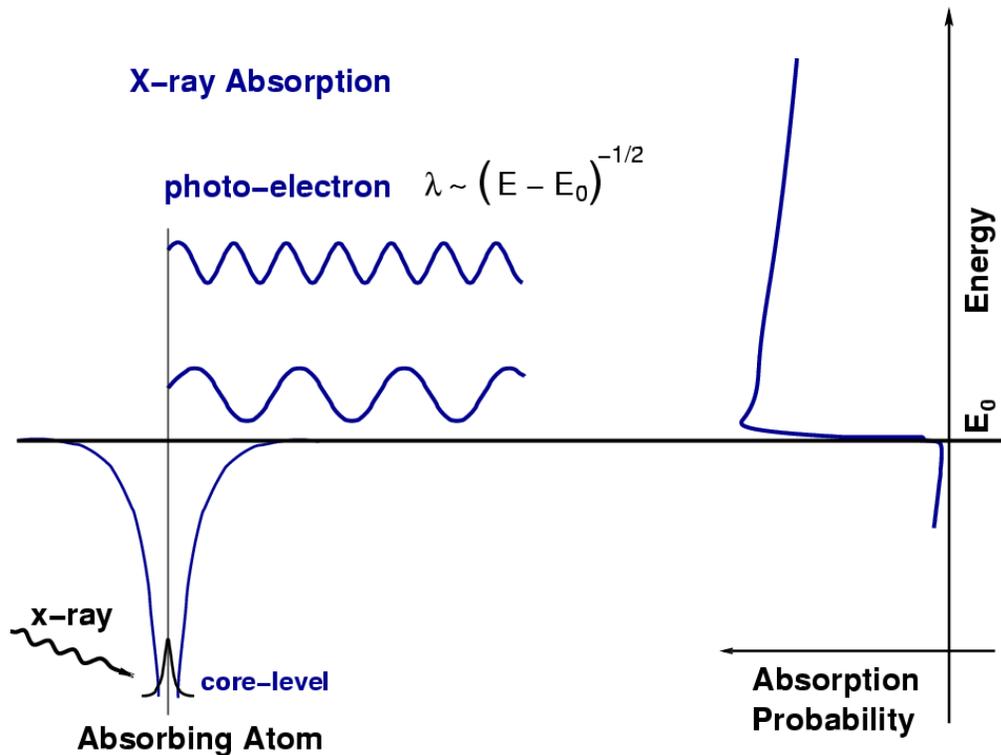
Knowing these, we can determine:

- R distance to neighboring atom.
- N coordination number of neighboring atom.
- σ^2 mean-square disorder of neighbor distance.

The scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta_j(\mathbf{k})$ depend on atomic number Z of the scattering atom.

XAFS Theory: X-ray Absorption by a Free Atom

An atom absorbs an x-ray of energy E , destroying a core electron with energy E_0 and creating a photo-electron with energy $(E - E_0)$. The core level is eventually filled, and a fluorescence x-ray or an Auger electron is ejected from the atom.



x-ray absorption needs an available state for the photo-electron to go into:

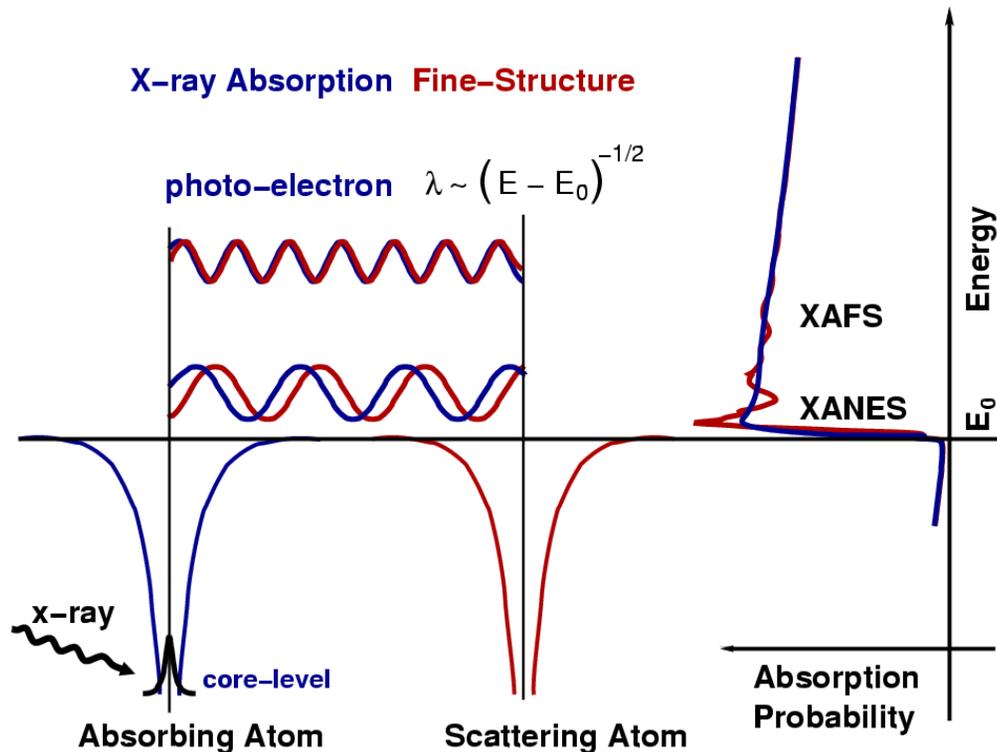
No available state:
No absorption

Once the x-ray energy is large enough to promote a core-level to the continuum, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

X-ray Absorption with Photo-Electron Scattering

With another atom nearby, the ejected photo-electron can **scatter** from a neighboring atom and return back to the absorbing atom.



When this happens, the photo-electron scattered back will interfere with itself.

μ depends on the presence of an electron state with energy $(E - E_0)$ and at the absorbing atom.

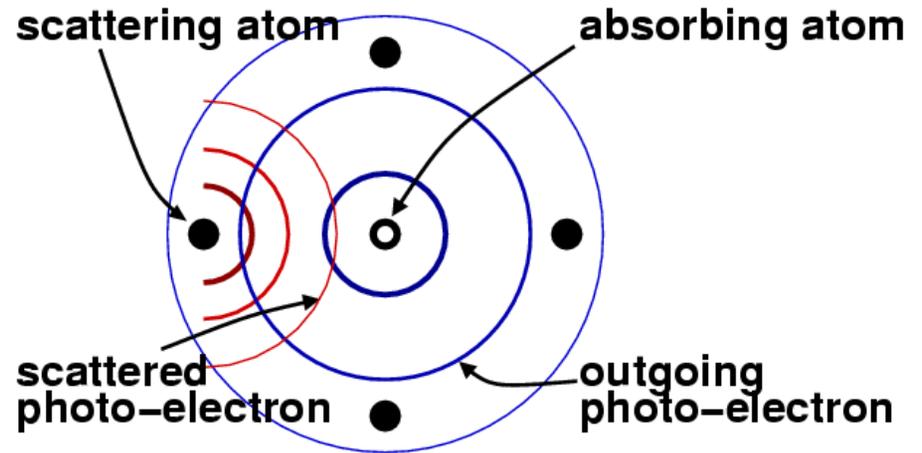
The amplitude of the back-scattered photo-electron **at the absorbing atom** will oscillate with energy, causing oscillations in $\mu(E)$.

The XAFS oscillations are an interference effect due to the presence of neighboring atoms.

The EXAFS Equation: simple description

Starting with $\chi \sim \psi_{\text{scatt}}(0)$, we can build a simple model for the EXAFS from the photo-electron as:

1. leaving the absorbing atom
2. scattering from the neighbor atom
3. returning to the absorbing atom



With spherical wave e^{ikr}/kr for the propagating photo-electron, and a scattering atom at a distance $r = R$, we get

$$\chi(\mathbf{k}) = \frac{e^{ikR}}{kR} [2k\mathbf{f}(\mathbf{k})e^{i\delta(\mathbf{k})}] \frac{e^{ikR}}{kR} + \text{C.C.}$$

where the neighboring atom gives the amplitude $\mathbf{f}(\mathbf{k})$ and phase-shift $\delta(\mathbf{k})$ to the scattered photo-electron.

Development of the EXAFS Equation

Combining terms (including the complex conjugate), we get

$$\chi(\mathbf{k}) = \frac{f(\mathbf{k})}{kR^2} \sin[2kR + \delta(\mathbf{k})]$$

for 1 scattering atom.

For N neighboring atoms, and with thermal and static disorder of σ^2 , giving the *mean-square disorder* in R , we have

$$\chi(\mathbf{k}) = \frac{Nf(\mathbf{k})e^{-2k^2\sigma^2}}{kR^2} \sin[2kR + \delta(\mathbf{k})]$$

A real system will have neighboring atom at different distances and of different type. We add all these contributions to get a version of the EXAFS equation:

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

The Photo-Electron Mean-Free Path

Getting to

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

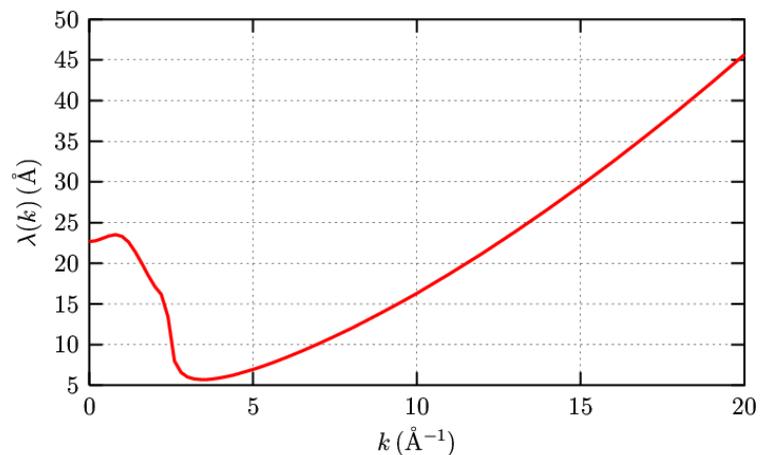
we used a spherical wave for the photo-electron: e^{ikr}/kr . The photo-electron can also scatter *inelastically*, and may not be able to get back the absorbing atom.

Using a damped wave-function: $e^{ikr} e^{-r/\lambda(k)} / kr$

where $\lambda(k)$ is the photo-electron's *mean free path*, the EXAFS equation becomes:

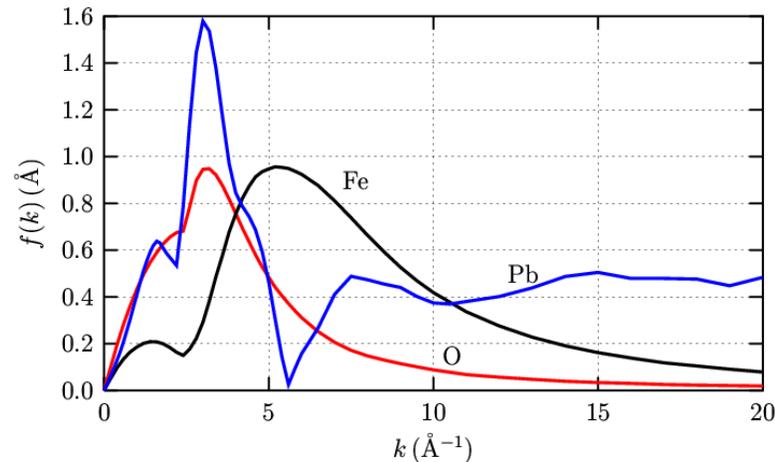
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2k R_j + \delta_j(k)]$$

The mean-free-path is $< 25 \text{ \AA}$
for much of the EXAFS range.
 λ and the R^{-2} term make
EXAFS a *local atomic probe*.

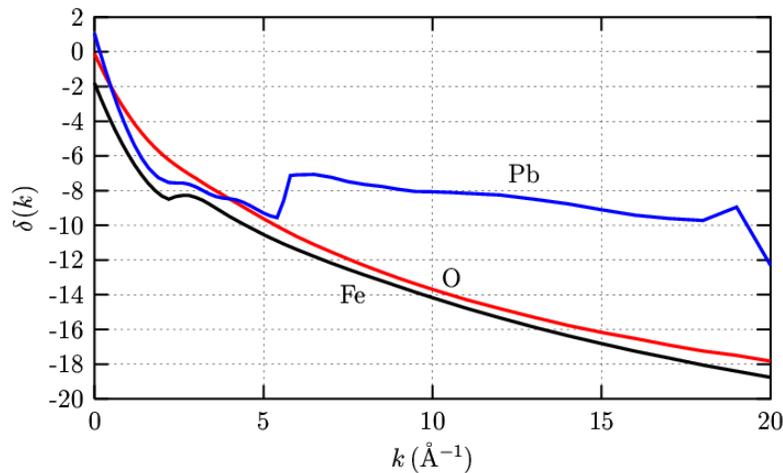


Scattering Amplitude and Phase-Shift

The scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta_j(\mathbf{k})$ depend on atomic number.



The scattering amplitude $f(\mathbf{k})$ peaks at different k values and extends to higher- k for heavier elements. For very heavy elements, there is structure in $f(\mathbf{k})$.



The phase shift $\delta_j(\mathbf{k})$ shows sharp changes for very heavy elements.

These scattering functions can be accurately calculated, and used in the EXAFS modeling.

Z can usually be determined to within 5 or so. Fe and O can be distinguished, but Fe and Mn cannot be.

The EXAFS Equation

Finally we have an equation we can use to model and interpret EXAFS:

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

If we know the *scattering* properties of the neighboring atom: $f(\mathbf{k})$ and $\delta_j(\mathbf{k})$, and the mean-free-path $\lambda(\mathbf{k})$ we can determine:

- R distance to neighboring atom.
- N coordination number of neighboring atom.
- σ^2 mean-square disorder of neighbor distance.

Since the scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta_j(\mathbf{k})$ depend strongly on atomic number, XAFS is also sensitive to Z of the scattering atom.

X-ray Absorption Measurements: Experimental Design

Important points to consider for measuring XAFS are:

Monochromatic x-rays: Need x-rays with a small energy spread or bandwidth: $\Delta E \approx 1 \text{ eV}$ at 10keV.

Linear Detectors: The XAFS $\chi(k) \sim 10^{-2}$ or smaller, so we need a lot of photons (ie, a synchrotron) and detectors that are very linear in x-ray intensity (ion chambers).

Well-aligned Beam: The x-ray beam hitting the detectors has to be the same hitting the sample.

Homogeneous sample: For transmission measurements, we need a sample that is of uniform and appropriate sample thickness of ~ 2 absorption lengths. It should be free from pinholes. If a powder, the grains should be very fine-grained (absorption length) and uniform.

X-ray Absorption Measurements: The Experiment

Energy Scanning The beamline needs to deliver monochromatic x-rays that are tunable so we can scan energy across the absorption edge. We'll scan from ~ 200 eV below to ~ 800 eV above the Fe K-edge, like this:

Region	Starting Energy (eV)	Ending Energy (eV)	Step Size (eV)
Pre-edge	-200	-20	5.0
XANES	-20	+30	0.5
EXAFS	+30	~ 800	0.05 \AA^{-1}

Notes: all values relative to a nominal value of the edge energy.

In the EXAFS region, it's common to step in k rather than energy.

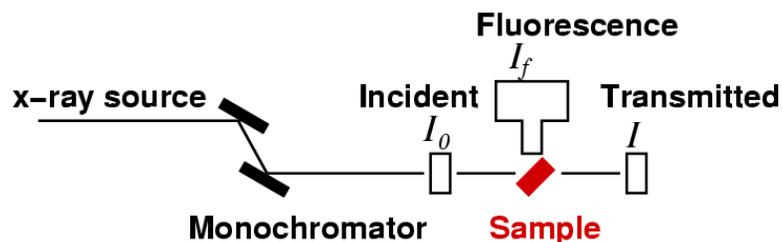
Counting Statistics: The EXAFS is a fairly small signal, so for good data $\mu(E)$ should have a noise level of about 10^{-3} . That means we need to collect at least $\sim 10^6$ photons.

Transmission : Fluxes at synchrotrons are $> 10^8$ photons/sec.

Count rate is not much of an issue.

Fluorescence : May be a concern, especially when concentrations are very low.

X-ray Absorption Measurements: Transmission



For concentrated samples, XAFS is best measured in transmission. To do this, we need enough transmission through the sample to get a decent signal for I . With,

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

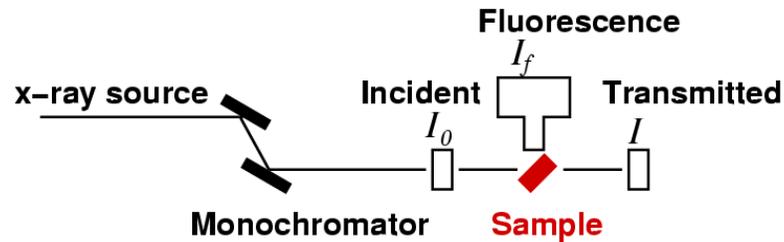
We adjust the sample thickness t so that $\mu(E)t \approx 2.5$ above the absorption edge and/or the edge step $\Delta\mu(E)t \approx 1$.

For Fe foil, $t \approx 7 \mu\text{m}$.

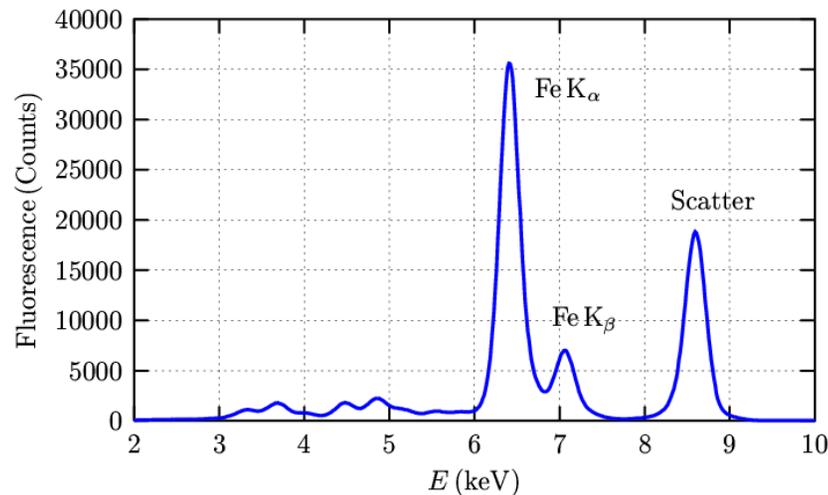
Also: the sample must be uniform, and free of pinholes. For a powder, the grain size cannot be much bigger than an absorption length.

If a transmission experiment can be done, this is an easy measurement and gives excellent data. It's usually appropriate for model compounds, and concentrations $> 10\%$.

X-ray Absorption Measurements: Fluorescence



For thick samples or lower concentrations (down to the ppm level), monitoring the x-ray fluorescence is the preferred measurement.



The x-rays emitted from the sample will include the fluorescence line of interest (here, both Fe K_{α} and Fe K_{β}) as well as *scattered* x-rays, and other fluorescence lines (here, Ca, Ti, and V).

There are both *elastically scattered* (at the same energy as the incident beam), and *inelastically scattered* (Compton effect) x-rays.

In many cases the scatter or other fluorescence lines will dominate the fluorescence spectra.

Fluorescence Measurements: Solid-State Detectors

An alternative is to use a **solid-state detector** with Ge or Si as the x-ray absorber. This uses electronic energy discrimination.

This has an advantage of being able to measure the **Full XRF Spectra**, for identifying other elements.

This can be used for XAFS measurements with concentrations down to 10's of ppm.



Though this has many advantages, it has a few drawbacks:

Dead time The electronic discrimination saturates at $\sim 10^5$ Hz or so. Ten (or more) detectors are often used in parallel, but XAFS measurements are still often limited by these detectors.

Complicated Maintaining, setting up, and using one of these is more work than an ion chamber.

Data Reduction: Strategy

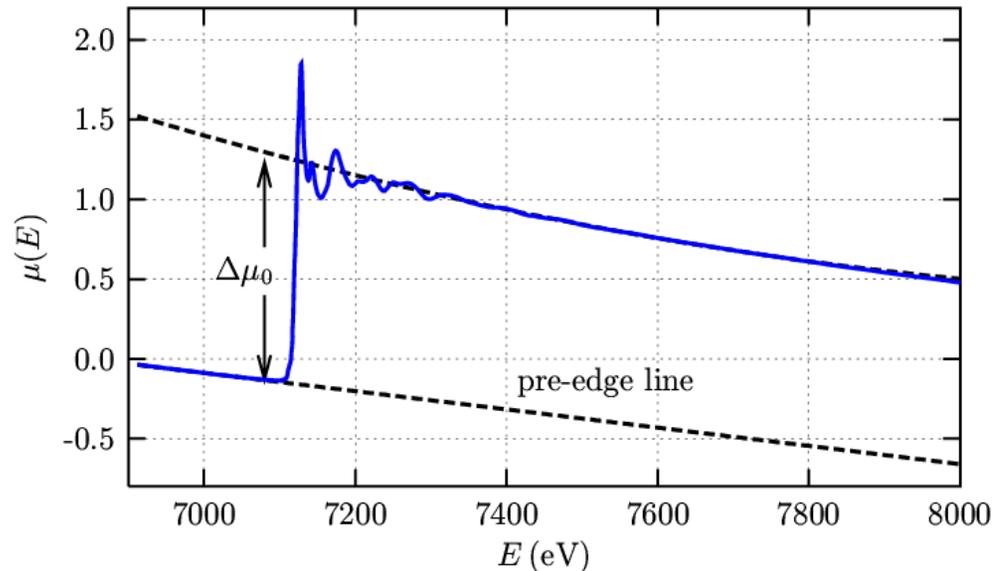
No matter how we measure $\mu(\mathbf{E})$, we'll use these steps to reduce the data to $\chi(\mathbf{k})$ begin the analysis:

1. convert measured intensities to $\mu(\mathbf{E})$
2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
3. normalize $\mu(\mathbf{E})$ 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 $\mu_0(\mathbf{E})$ to isolate the XAFS χ .
5. identify the threshold energy \mathbf{E}_0 , and convert from \mathbf{E} to \mathbf{k} space:
$$\mathbf{k} = \sqrt{\frac{2m(\mathbf{E}-\mathbf{E}_0)}{\hbar^2}}$$
6. weight the XAFS $\chi(\mathbf{k})$ and Fourier transform from \mathbf{k} to \mathbf{R} space.

After we get this far, we'll model $f(\mathbf{k})$ and $\delta(\mathbf{k})$ and analyze $\chi(\mathbf{k})$ to get distance \mathbf{R} , coordination number \mathbf{N} .

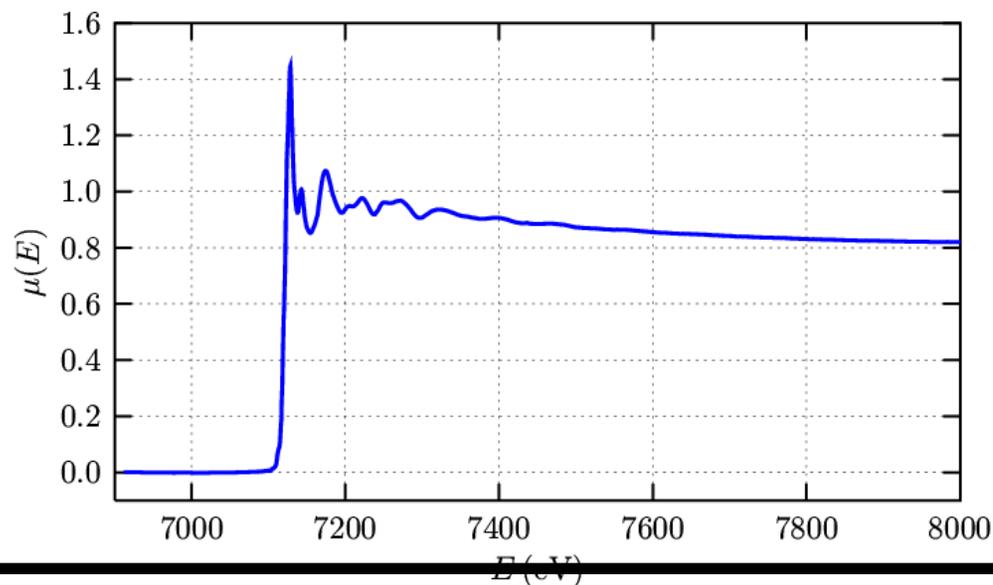
Data Reduction: Pre-Edge Subtraction, Normalization

Starting with $\mu(E)$ data for Fe_2O_3 , the data reduction goes like this:



Pre-Edge Subtraction

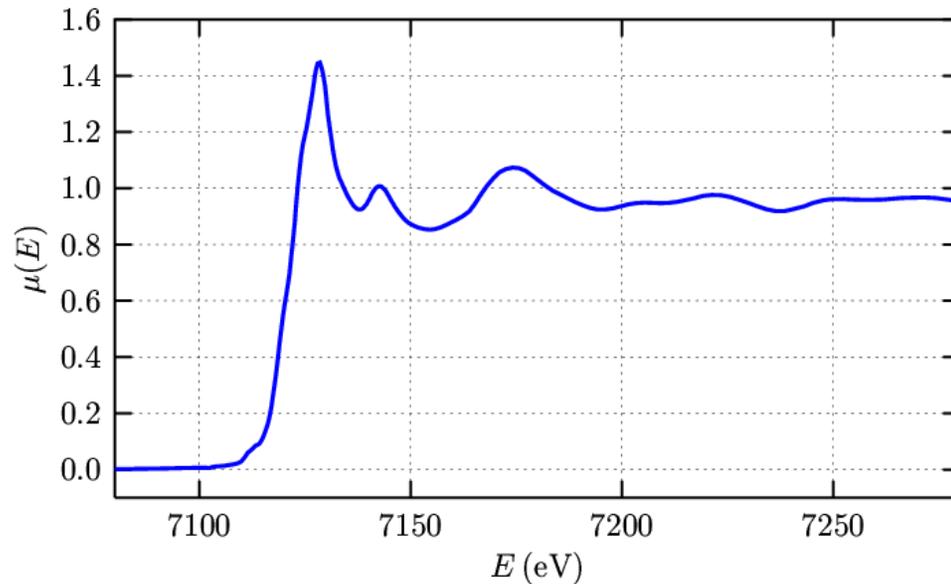
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

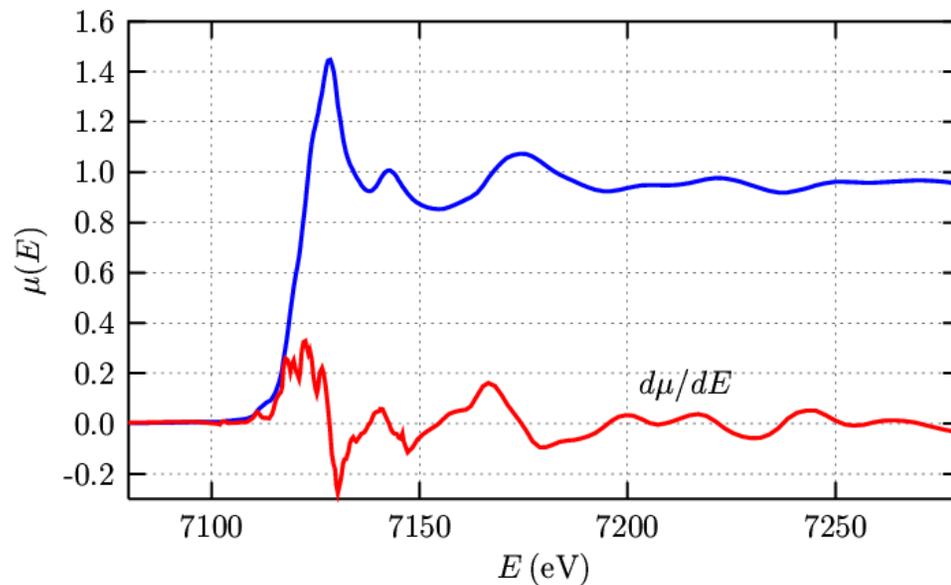
We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge. We normalize by this value to get the absorption from 1 x-ray.

Data Reduction: Normalized XANES and E_0



XANES

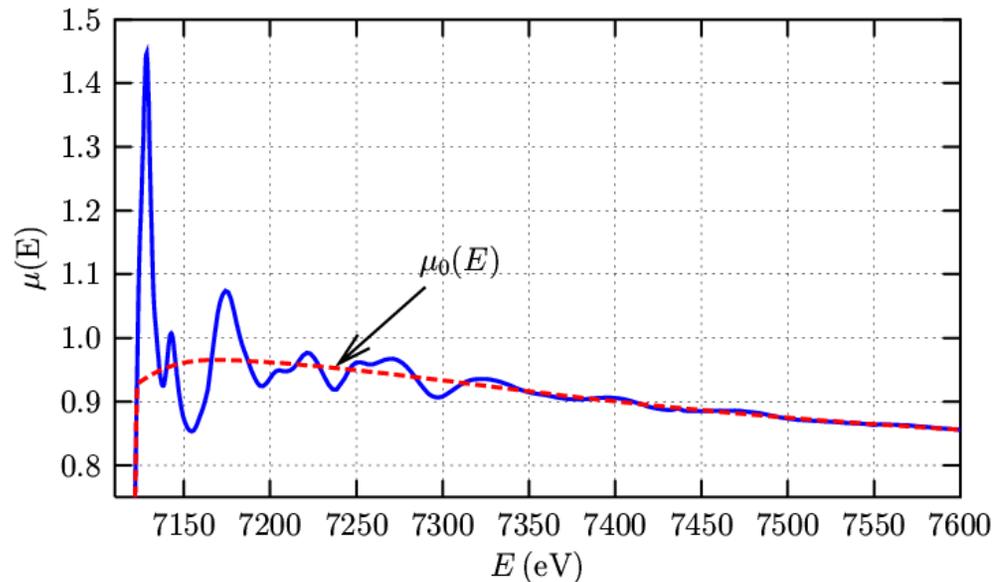
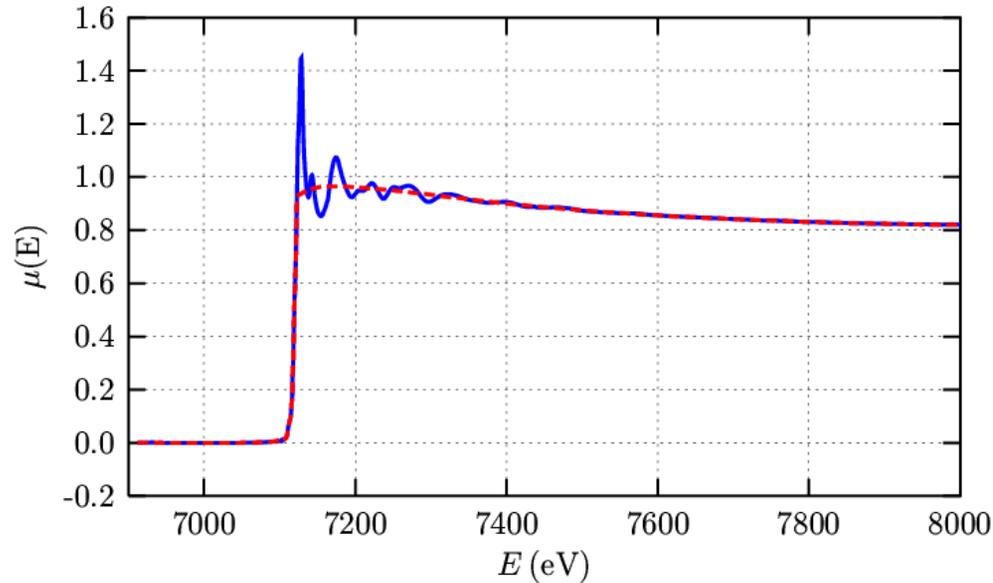
The XANES portion (below) shows a fairly rich spectral structure. We'll come back to this for XANES analysis.



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

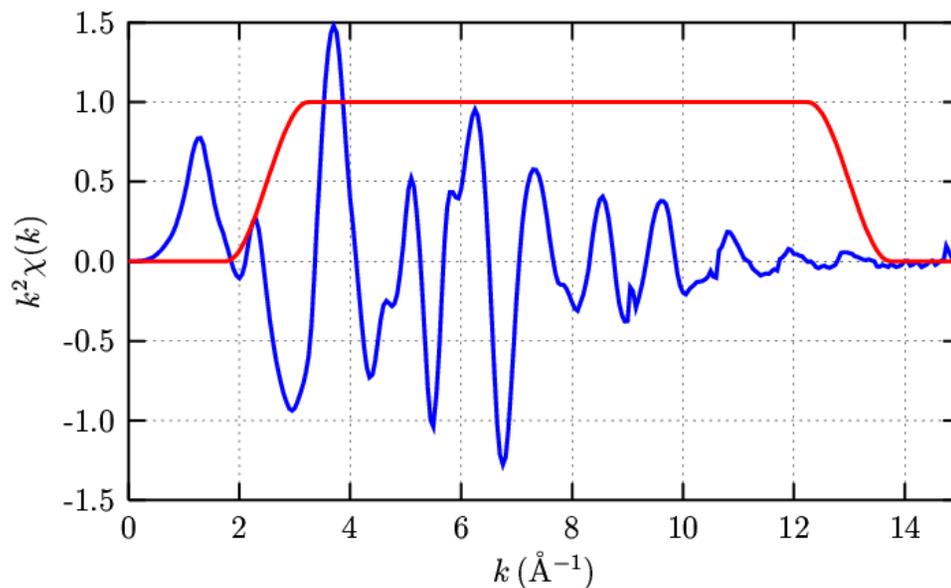
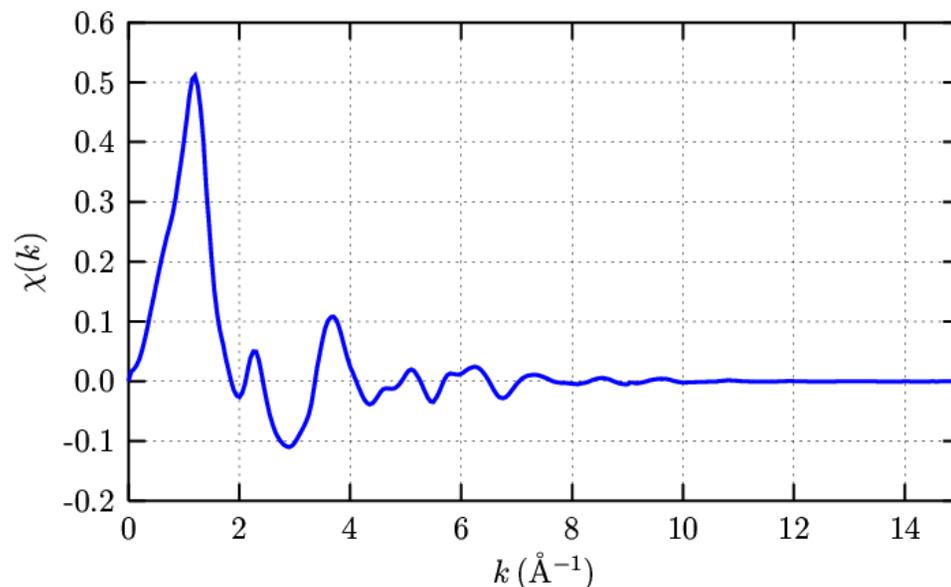
We don't have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).

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



$\chi(k)$

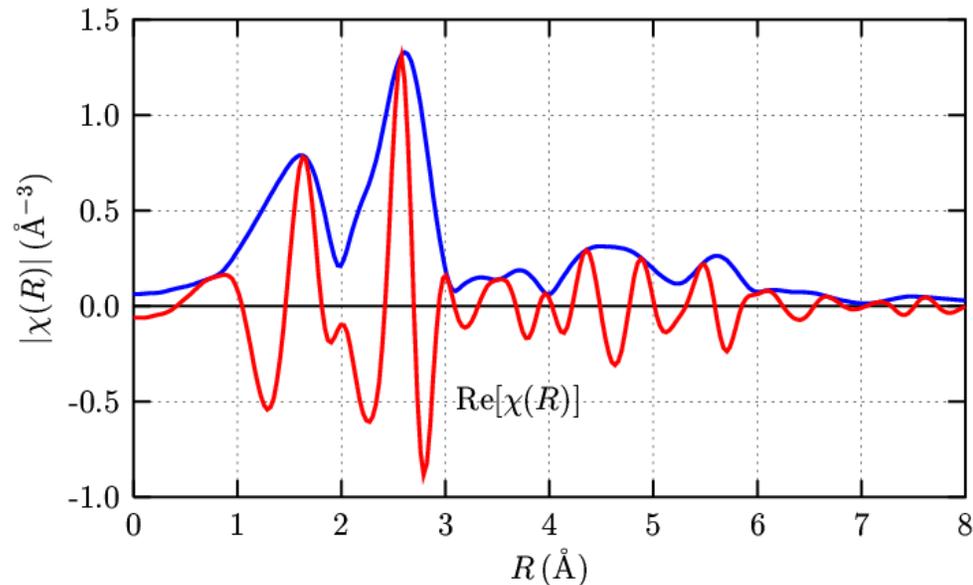
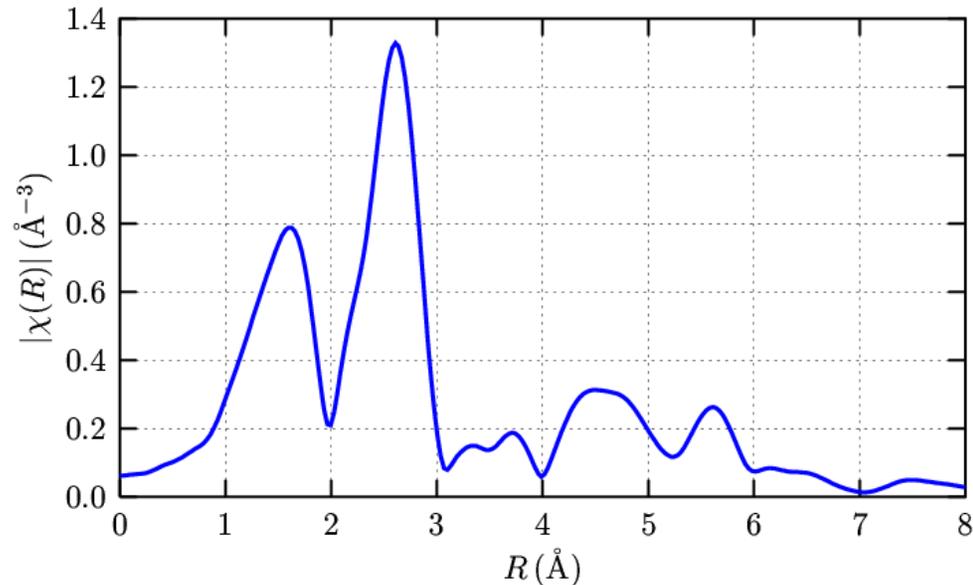
The raw EXAFS $\chi(k)$ usually decays quickly with k , and difficult to assess or interpret by itself.

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*.

Fourier Transform: $\chi(\mathbf{R})$



$\chi(\mathbf{R})$

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

The Fe-O distance in FeO is 2.14 \AA , but the first peak is at 1.6 \AA . This shift in the first peak is due to the *phase-shift*, $\delta(\mathbf{k})$: $\sin[2kR + \delta(\mathbf{k})]$.

A shift of -0.5 \AA is typical.

$\chi(\mathbf{R})$ is complex:

The FT makes $\chi(\mathbf{R})$ complex. Usually only the amplitude is shown, but there are really oscillations in $\chi(\mathbf{R})$.

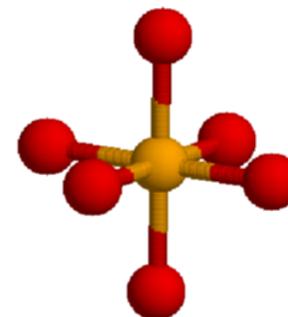
Both real and imaginary components are used in modeling.

EXAFS Data Modeling

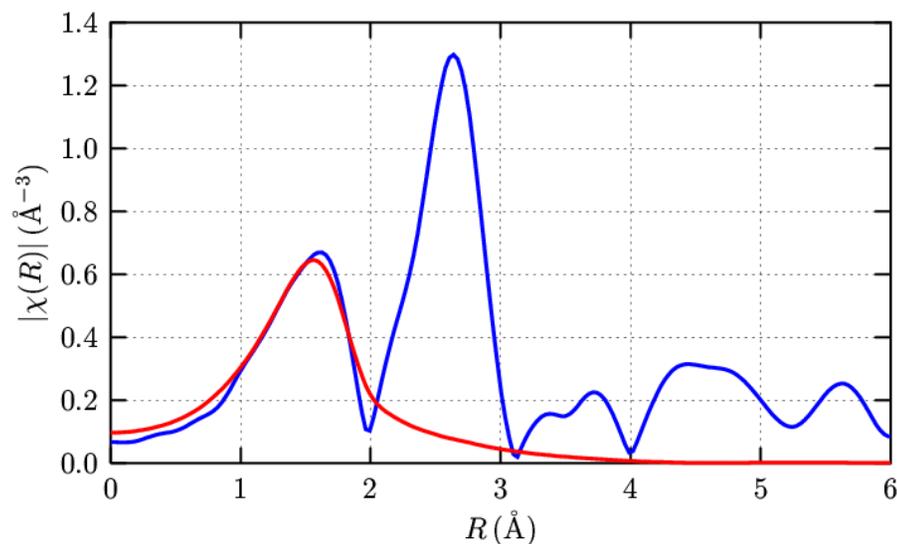
EXAFS Analysis: Modeling the 1st Shell of FeO

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.

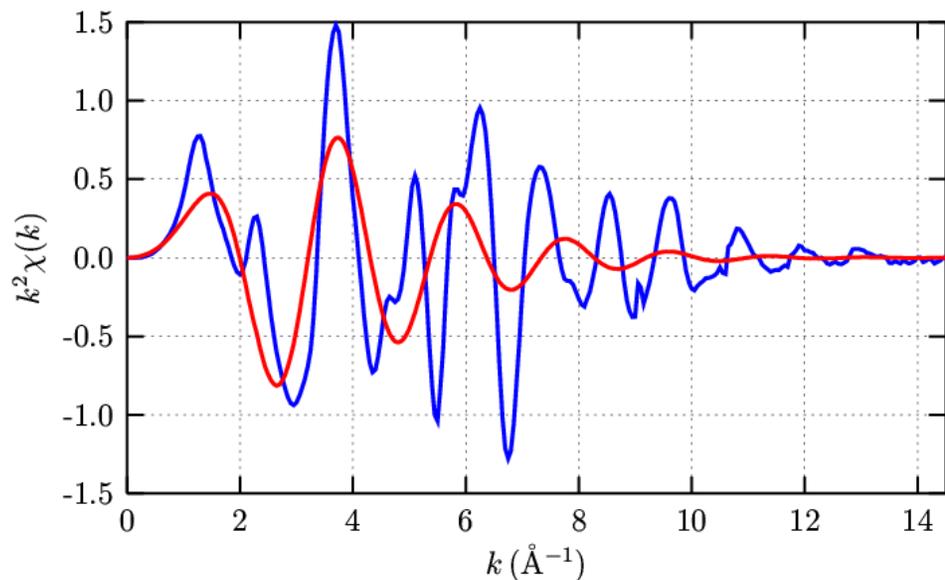


Fit results:

$$\begin{aligned} N &= 5.8 \pm 1.8 \\ R &= 2.10 \pm 0.02 \text{ \AA} \\ \Delta E_0 &= -3.1 \pm 2.5 \text{ eV} \\ \sigma^2 &= 0.015 \pm 0.005 \text{ \AA}^2. \end{aligned}$$

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

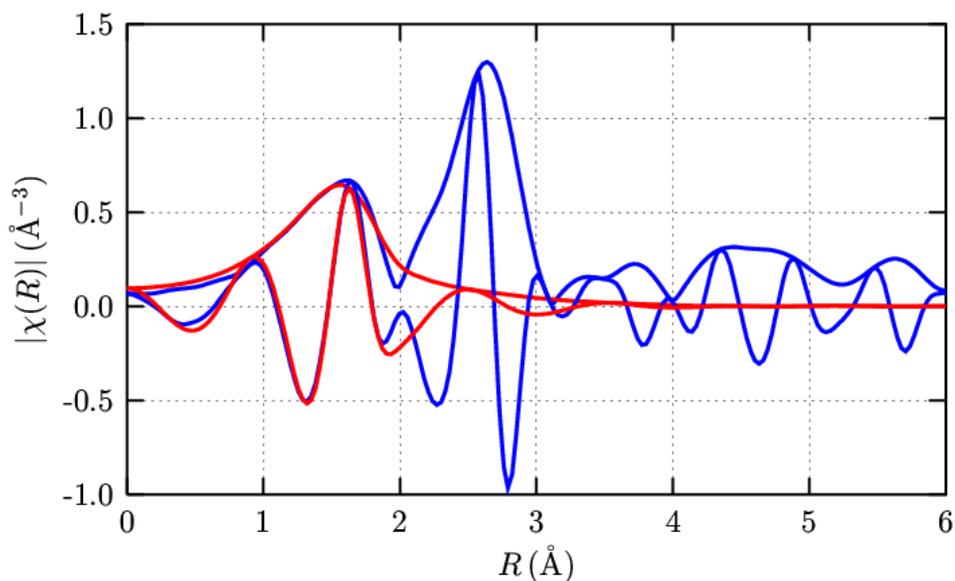
EXAFS Analysis: 1st Shell of FeO



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.

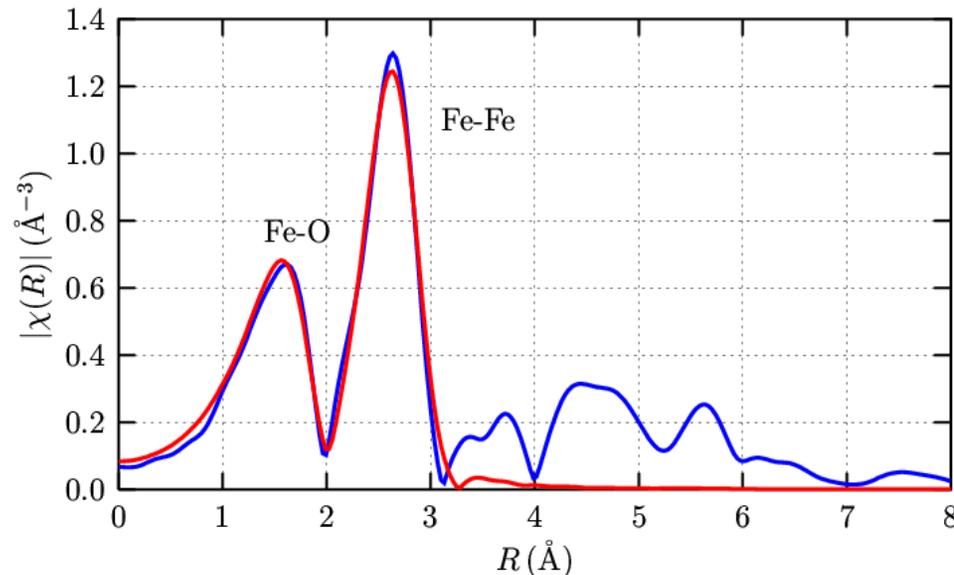
$|\chi(R)|$ and $\text{Re}[\chi(R)]$ for FeO (blue), and a 1st shell fit (red).

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 adding 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:

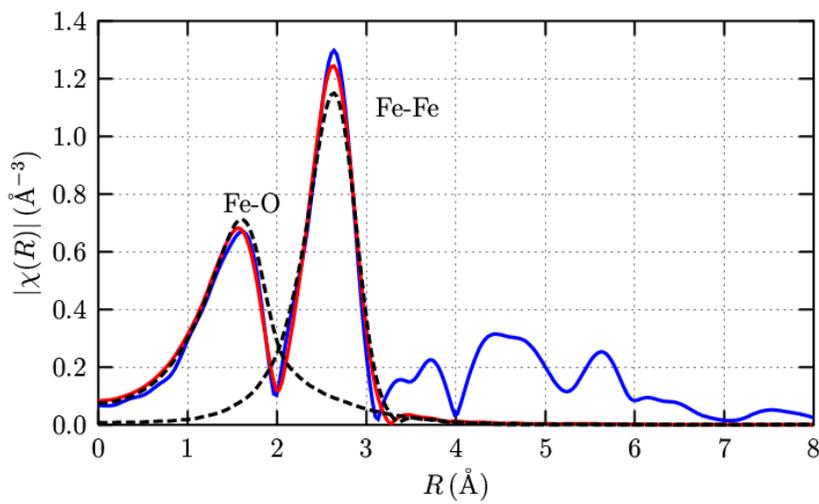
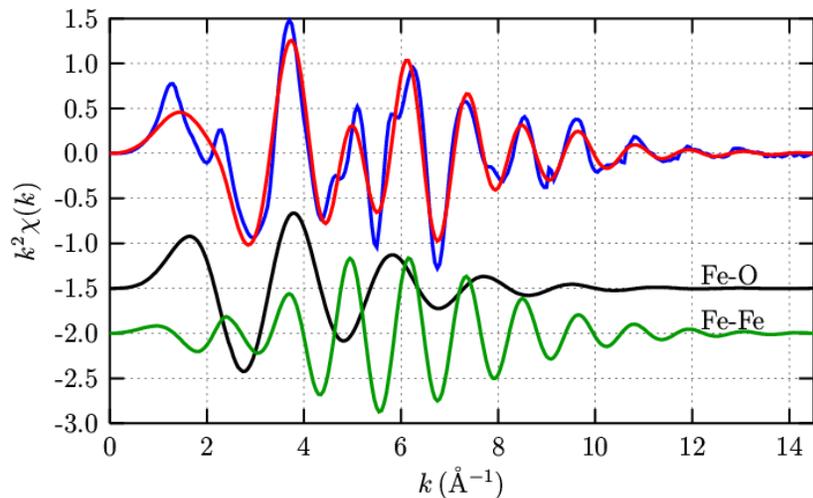
6 O at 2.13Å, 12 Fe at 3.02Å.

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:

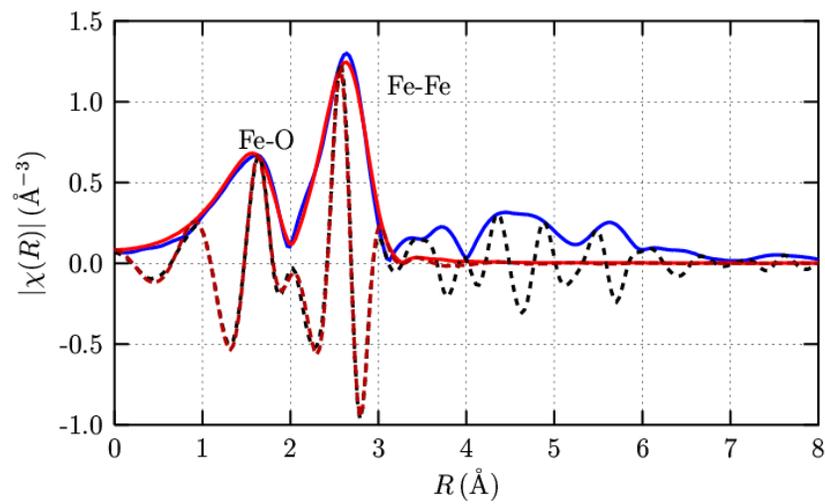


The Fe-Fe EXAFS extends to higher- k than the Fe-O EXAFS.

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.

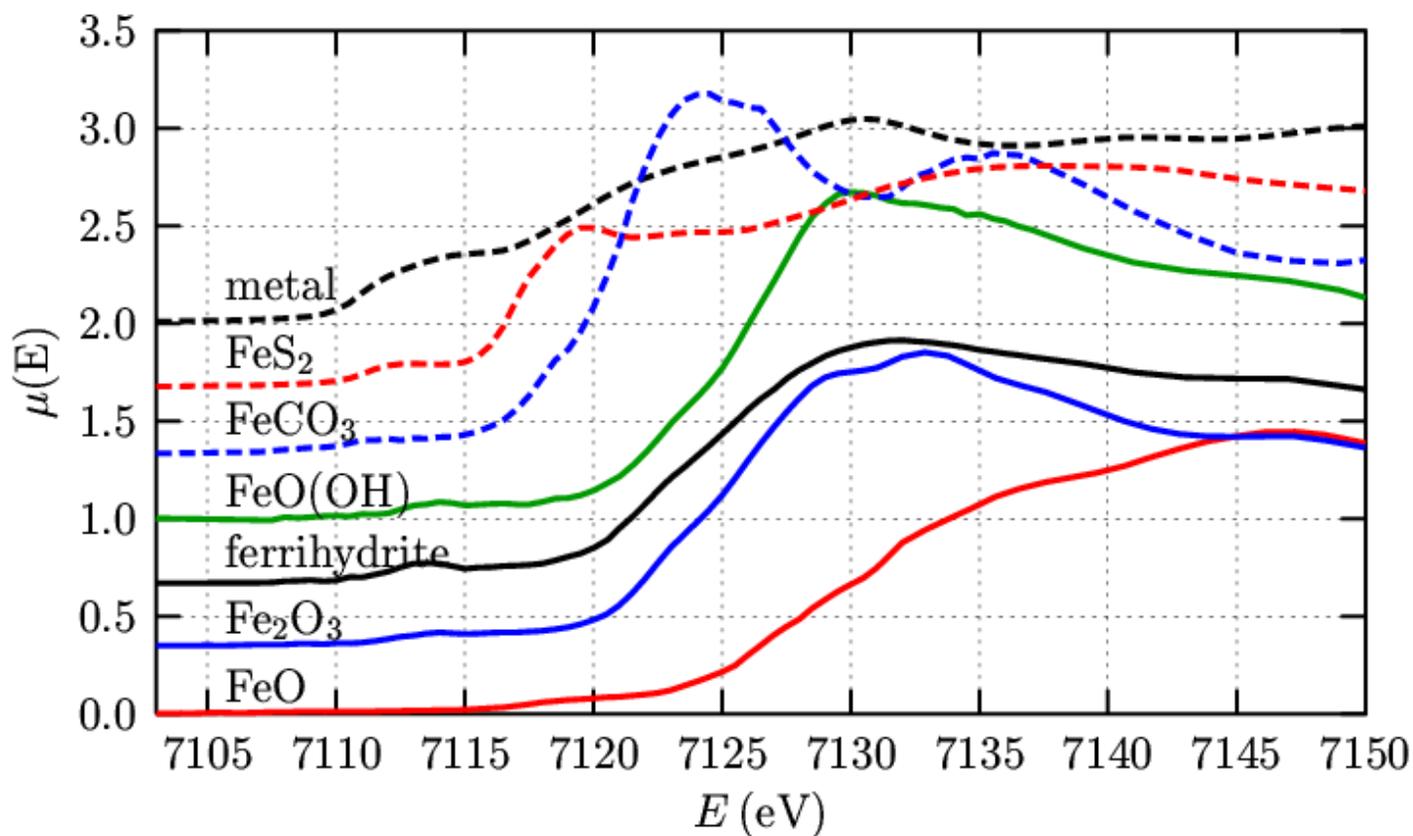
Of course, the modeling can get more complicated than this!



XANES

XANES Analysis: Oxidation State

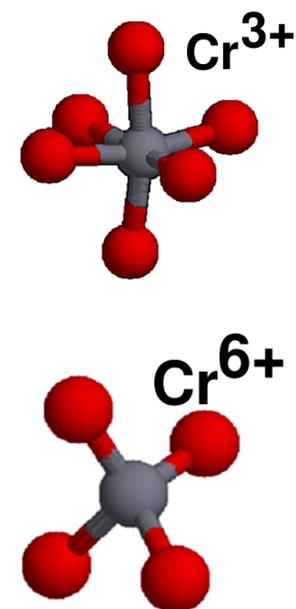
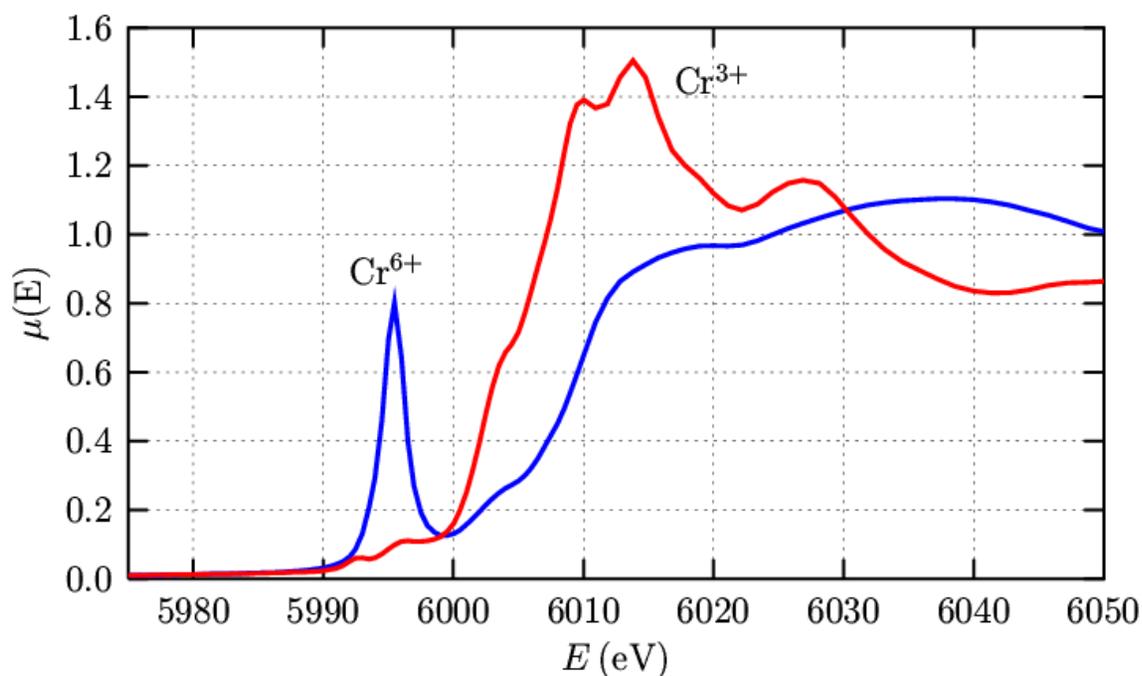
The Normalized XANES from several Fe compounds:



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 Analysis: Oxidation State and Coordination Chemistry



The XANES of Cr³⁺ and Cr⁶⁺ 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 photo-electron.

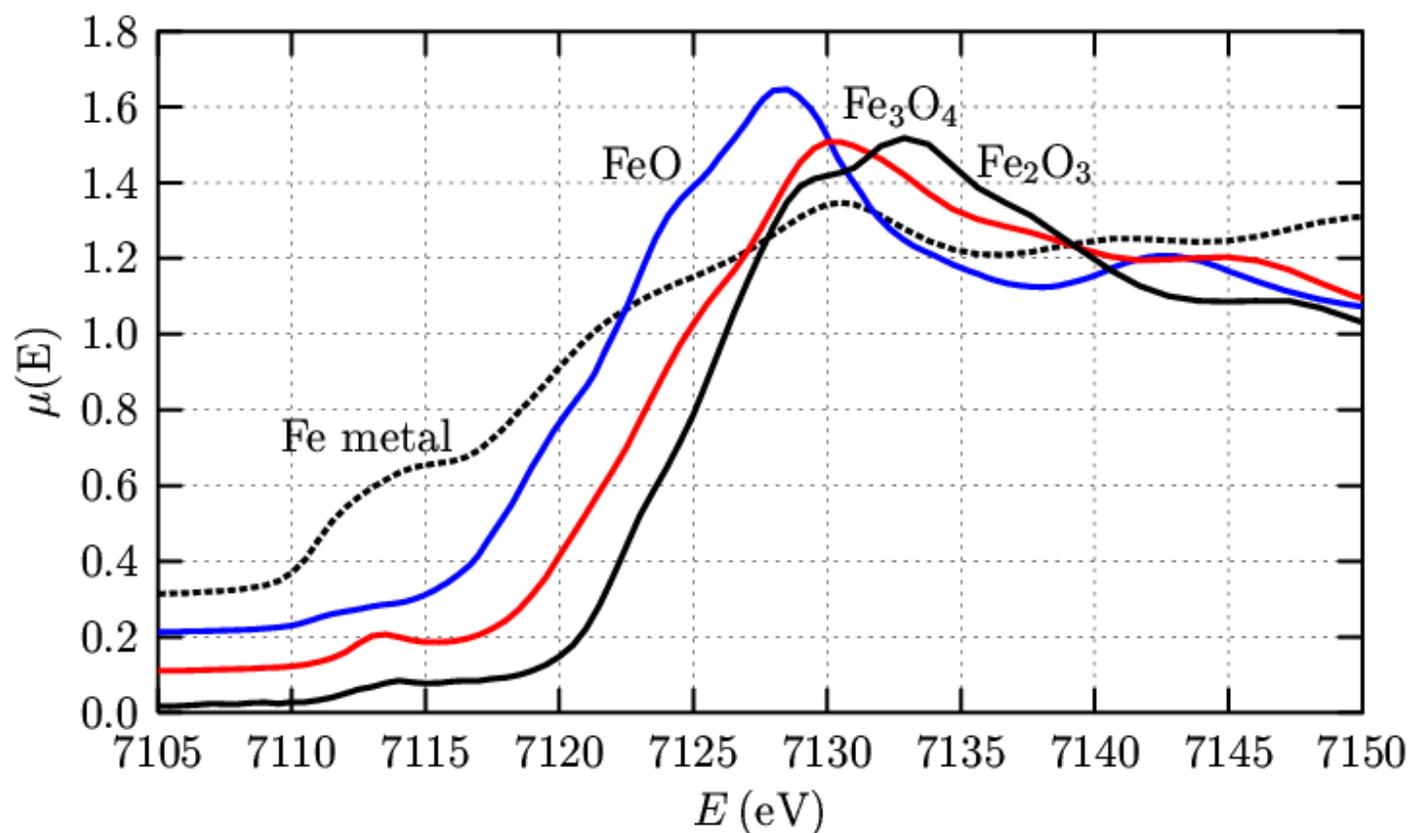
These chemical and physical interpretations are all related, of course:

What electronic states can the photo-electron 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 rare.

Edge Shifts and Pre-edge Peaks in Fe oxides



XANES for Fe oxides and metal. 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).

Where To Go From Here

International XAFS Society:

<http://ixs.iit.edu/>

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

Tutorials and other Training Material:

<http://gbxafs.iit.edu/training/tutorials.html> Grant Bunker's tutorials

<http://srs.dl.ac.uk/XRS/courses/> Tutorial from Daresbury Lab, UK

<http://leonardo.phys.washington.edu/~ravel/course/> Bruce Ravel's Course on Advanced EXAFS Analysis.

Software Resources:

<http://www.esrf.fr/computing/scientific/exafs/>

http://cars9.uchicago.edu/IXS-cgi/XAFS_Programs

<http://leonardo.phys.washington.edu/feff>

This tutorial and more links can be found at: <http://cars.uchicago.edu/xafs/>.