

Fundamentals of X-ray Absorption Fine Structure

Matt Newville

Consortium for Advanced Radiation Sources

University of Chicago

Basic Principles:

X-ray absorption and fluorescence

Simple theoretical description

Multiple Scattering

Experiment Design

Data Analysis:

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

XANES Analysis: formal valence and coordination chemistry

(version 1.6.1, 20-July-2005: <http://cars.uchicago.edu/xafs/>)

What Is XAFS?

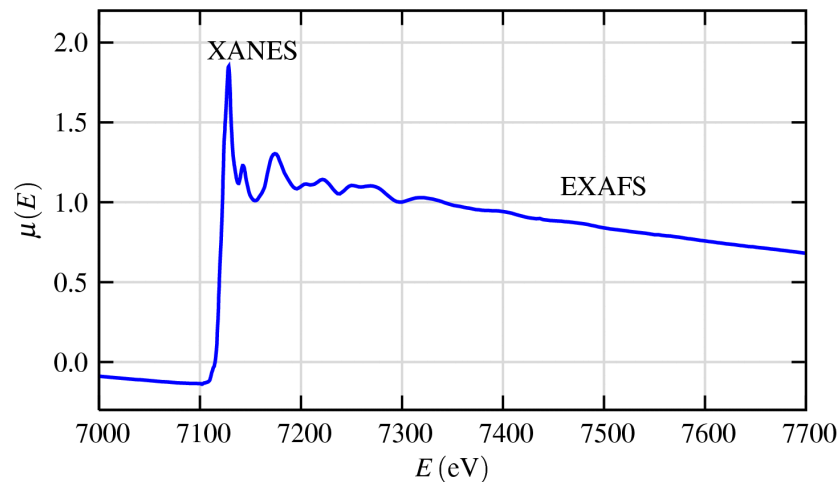
X-ray Absorption Fine-Structure (**XAFS**) is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge. XAFS is also referred to as X-ray Absorption Spectroscopy (**XAS**) and is broken into 2 regimes:

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:

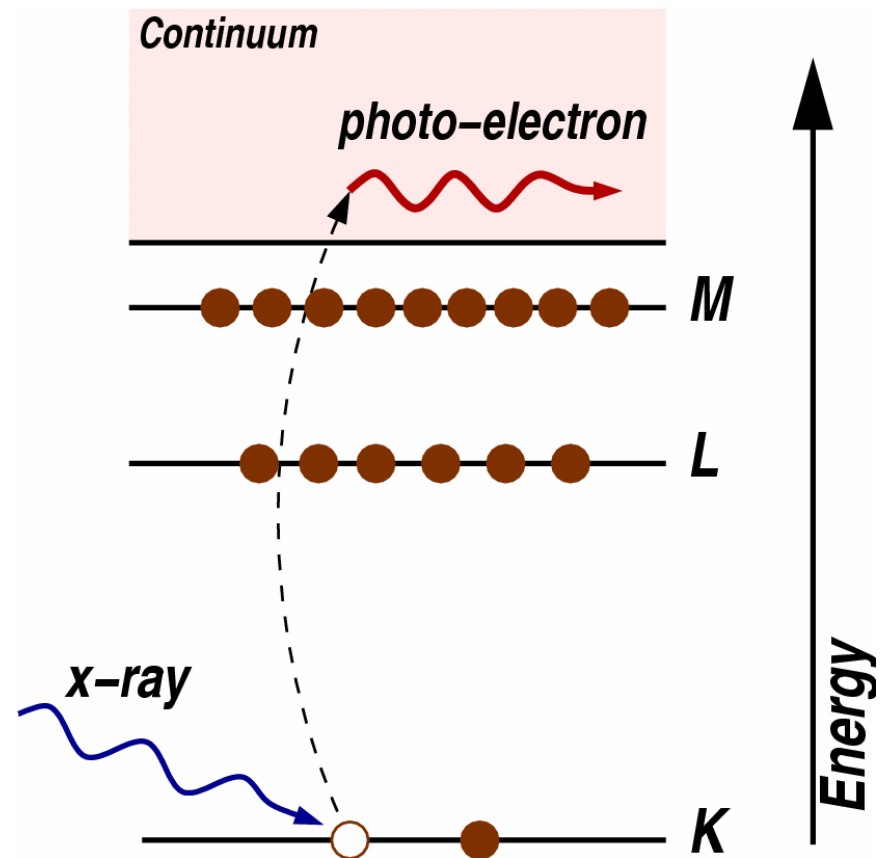
- local atomic coordination
- chemical / oxidation state
- applies to any element
- works at low concentrations
- minimal sample requirements

X-Ray Absorption

X-rays (light with wavelength $0.06 \lesssim \lambda \lesssim 12 \text{ \AA}$ or energy $1 \lesssim E \lesssim 200 \text{ keV}$) are absorbed by all matter through the **photo-electric effect**:

An x-ray is absorbed by an atom when the energy of the x-ray is transferred to a core-level electron (*K*, *L*, or *M* shell) which is ejected from the atom.

The atom is left in an **excited state** with an empty electronic level (a **core hole**). Any excess energy from the x-ray is given to the ejected **photo-electron**.

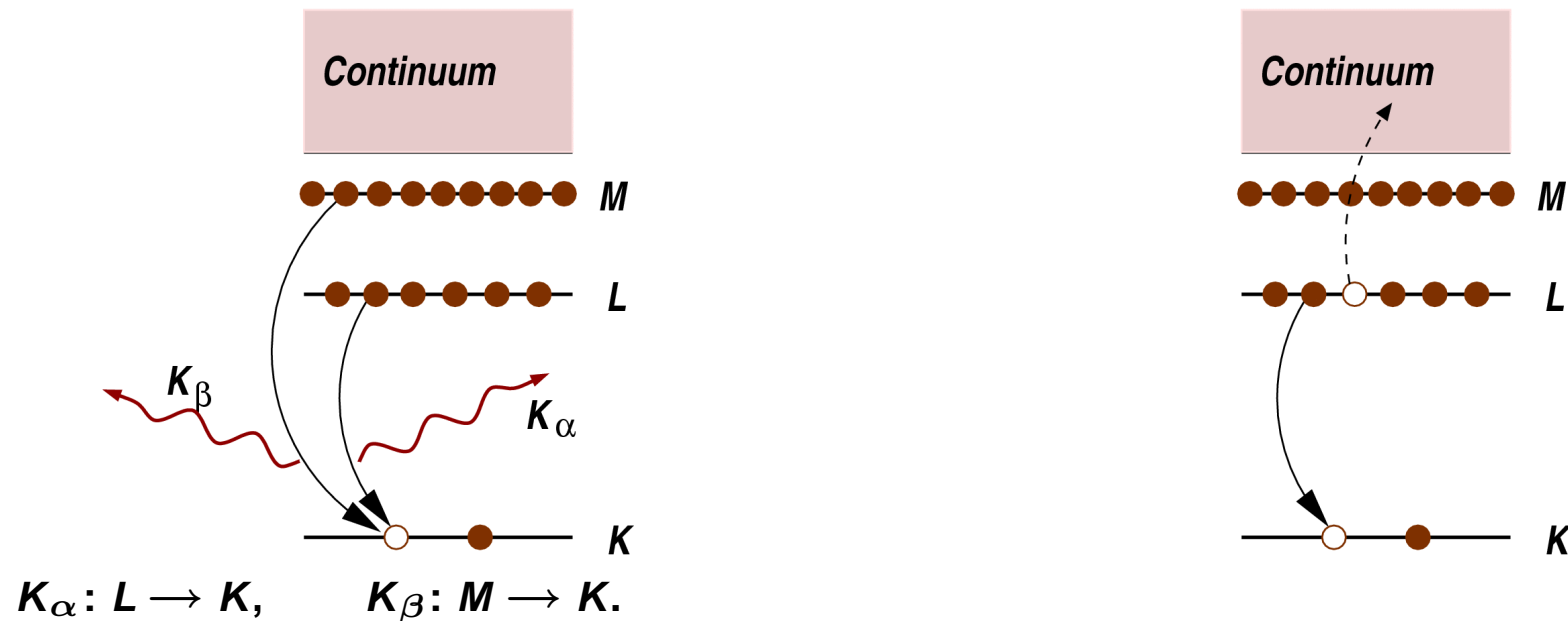


X-ray Fluorescence

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.

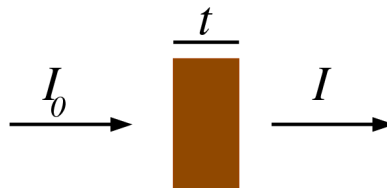
Auger Effect: An electron is promoted to the continuum from another core-level.



X-ray fluorescence and Auger emission occur 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 passing through a material of thickness t is given by the **absorption coefficient** μ :

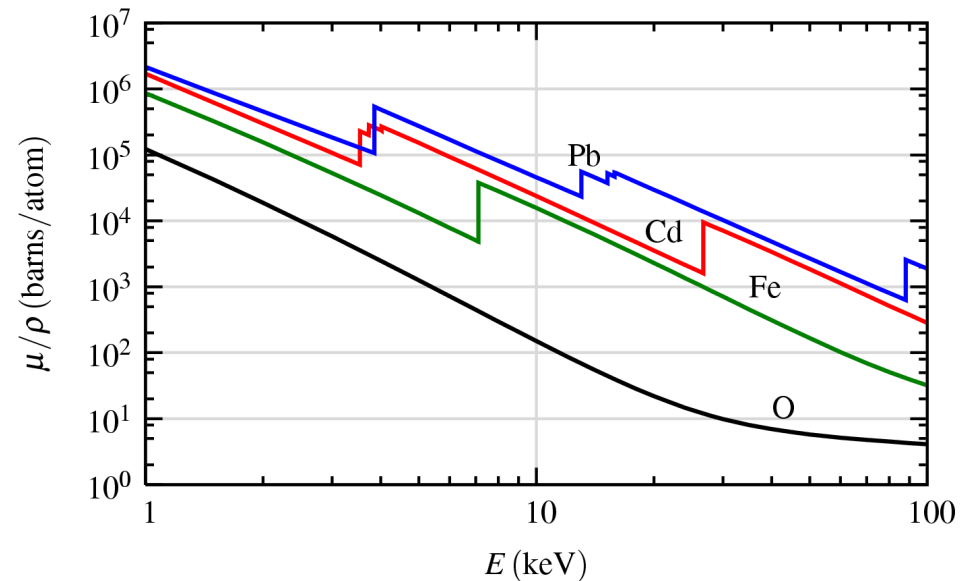
$$\boxed{I = I_0 e^{-\mu t}}$$


The diagram illustrates the absorption process. An arrow labeled I_0 points from the left towards a brown rectangular block representing the material. Above the block is a horizontal line labeled t , indicating its thickness. An arrow labeled I points from the right side of the block, representing the transmitted intensity.

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 :

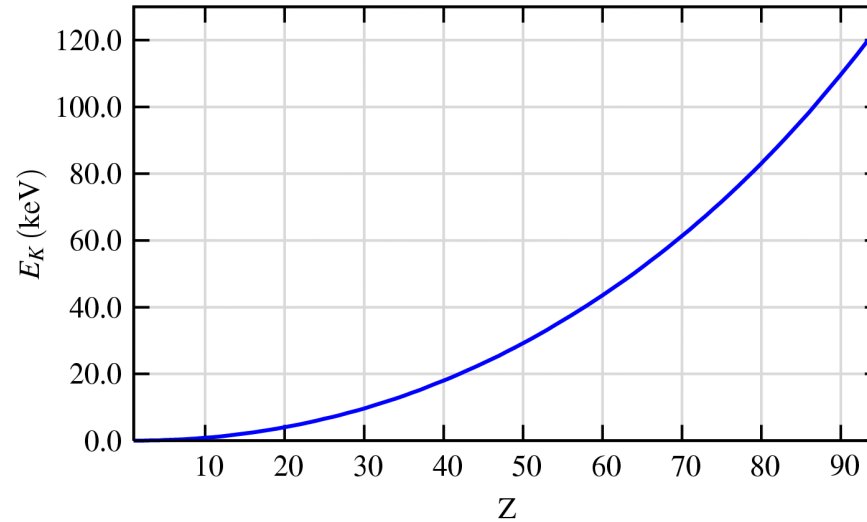
$$\mu \approx \frac{\rho Z^4}{A E^3}$$



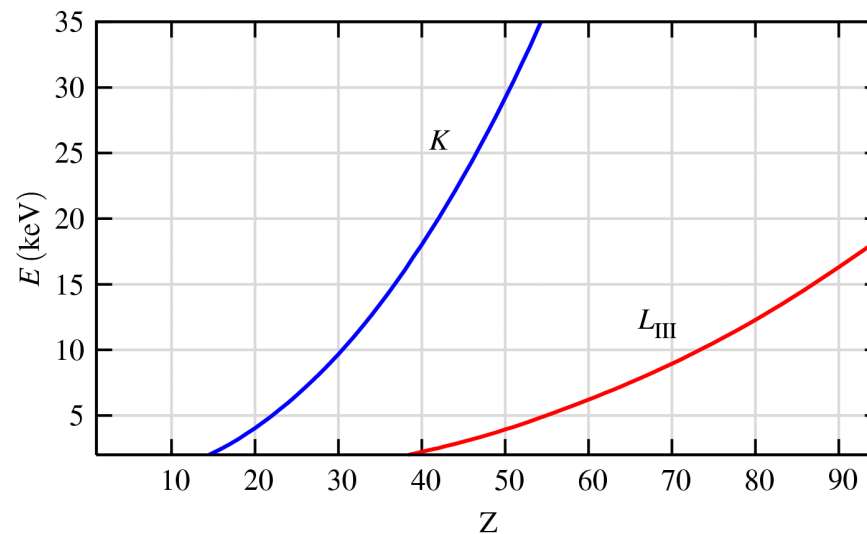
In addition, μ has sharp **Absorption Edges** corresponding to the characteristic core-level energies of the atom.

Absorption Edge Energies

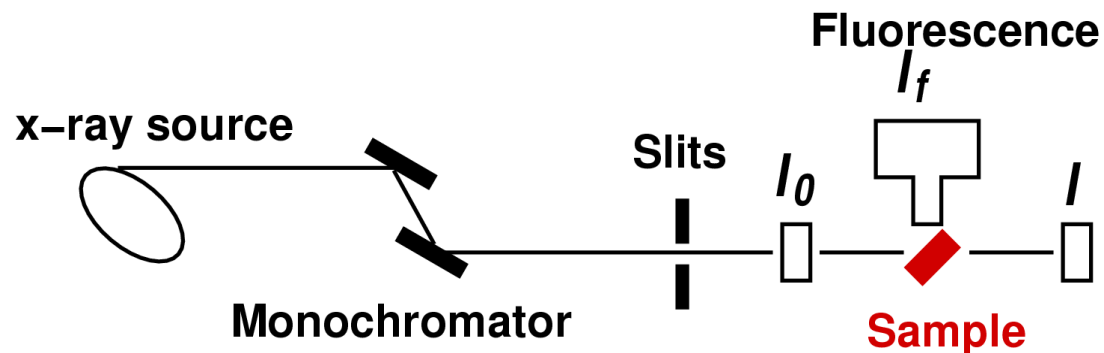
The energies of the *K*-edge absorption edges go roughly as $E_K \sim Z^2$



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.

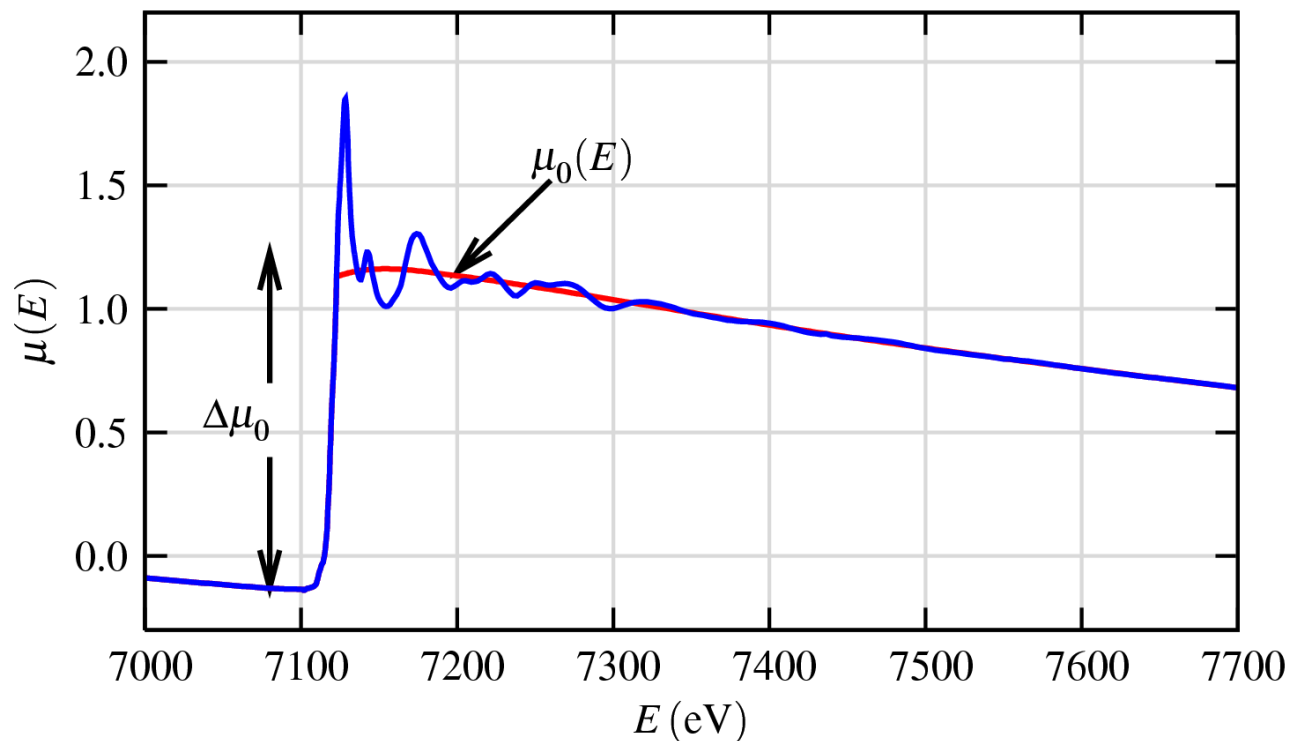
$$\mu(E) \propto I_f/I_0$$

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 we 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:

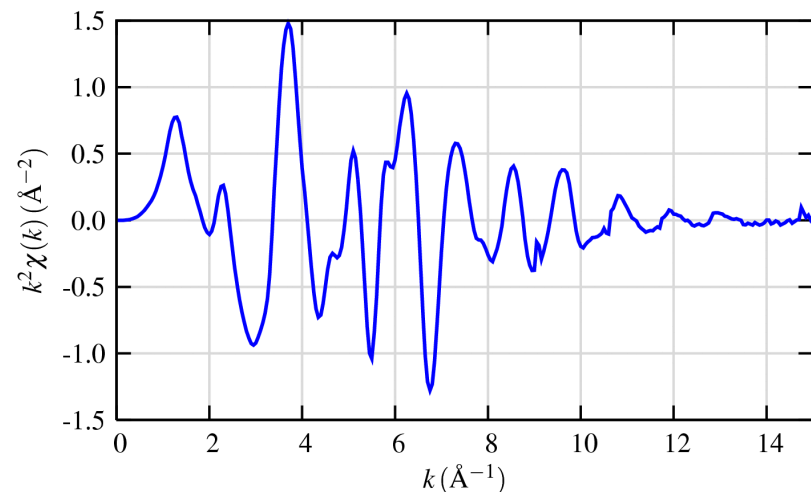
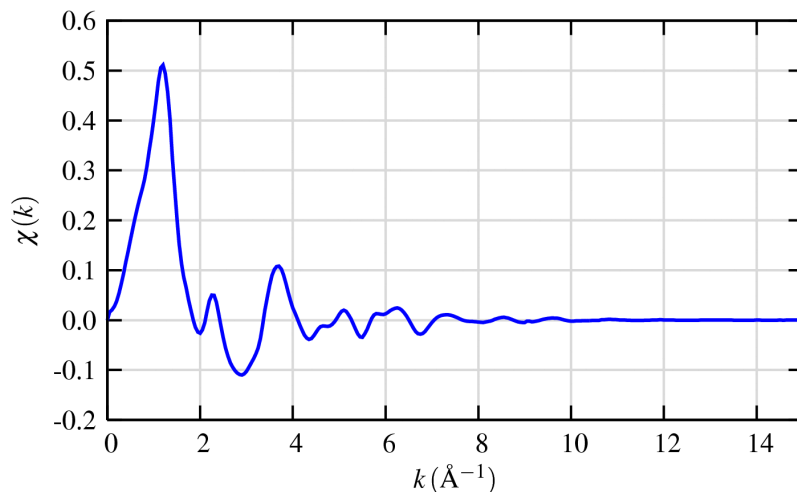


EXAFS: $\chi(k)$

XAFS is an **interference effect**, and depends on the wave-nature of the photo-electron. It's convenient to think of XAFS in terms of **photo-electron wavenumber**, k , rather than x-ray energy:

$$k = \sqrt{\frac{2m(\mathbf{E} - \mathbf{E}_0)}{\hbar^2}}$$

$\chi(k)$ 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 $\delta(\mathbf{k})$ are *photo-electron scattering properties* of the neighboring atom.

If we know these properties, we can determine:

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

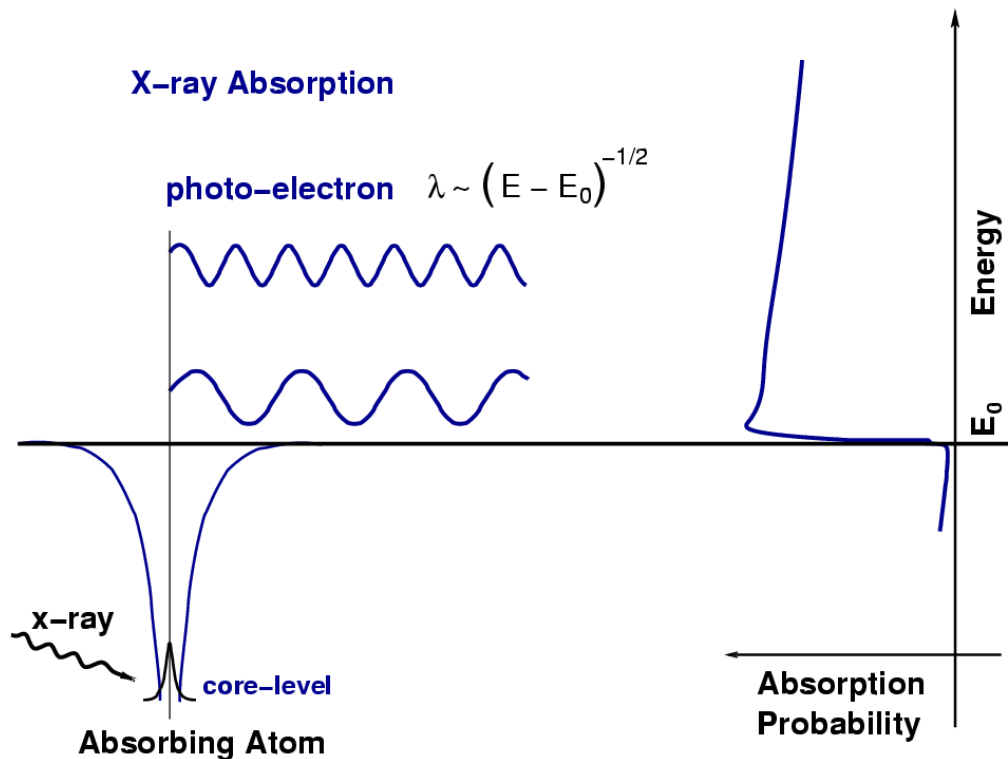
The scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta(\mathbf{k})$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

XAFS Theory

Development of the EXAFS Equation

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 Auger electron is ejected from the atom.



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

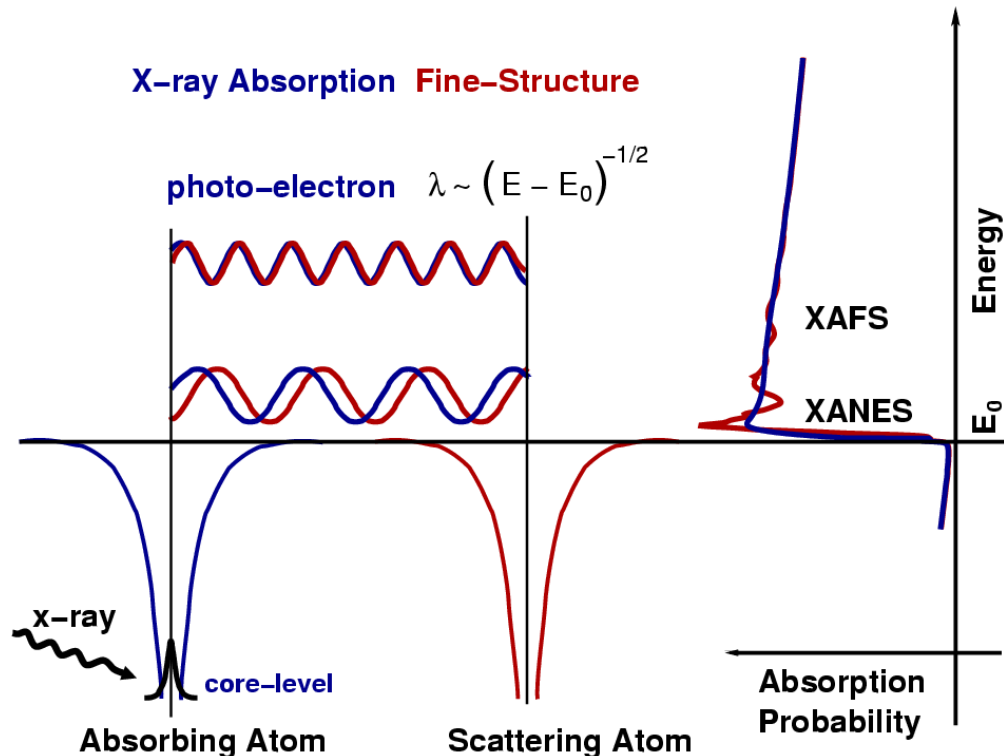
No available state:
No absorption

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.



The photo-electron scattered back will interfere with itself.

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

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

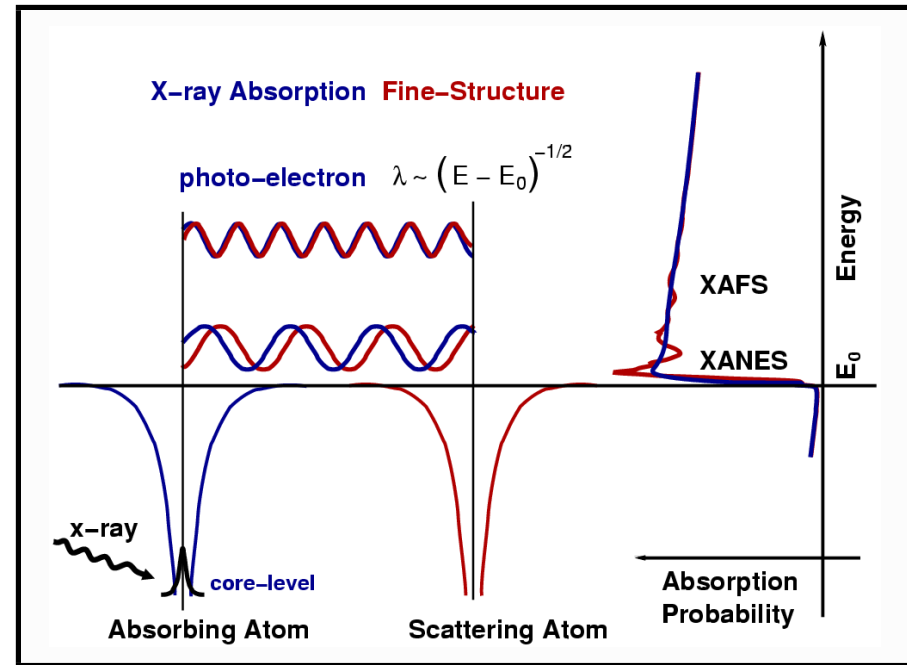
The XAFS oscillations are an interference effect of the photo-electron with itself, due to the presence of neighboring atoms.

EXAFS: Physical description

Going back to our definition

$$\chi(k[E]) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$

we'll work out a simple form for $\chi(k)$ to use in analysis.



Fermi's Golden Rule describes $\mu(E)$ as a transition between quantum states:

$$\mu(E) \sim |\langle i | \mathcal{H} | f \rangle|^2$$

$\langle i |$ the *initial state* describes the core level (and the photon). This **is not** altered by the neighboring atom.

\mathcal{H} the *interaction*. In the dipole approximation, $\mathcal{H} = e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$.

$|f\rangle$ the *final state* describes the photo-electron (and no photon). This **is** altered by the neighboring atom.

EXAFS: Physical description

Writing $|f\rangle = |f_0 + \Delta f\rangle$, where Δf gives the change in photo-electron final state due to backscattering from the neighboring atom, we can expand μ to get

$$\mu(\mathbf{E}) \sim |\langle i|\mathcal{H}|f_0\rangle|^2 \left[1 + \frac{\langle i|\mathcal{H}|\Delta f\rangle \langle f_0|\mathcal{H}|i\rangle^*}{|\langle i|\mathcal{H}|f_0\rangle|^2} + \text{C.C.} \right]$$

Comparing this to our definition for χ ,

$$\mu(\mathbf{E}) = \mu_0(\mathbf{E})[1 + \chi(\mathbf{E})],$$

and recognizing that $\mu_0(\mathbf{E})$ is given by $|\langle i|\mathcal{H}|f_0\rangle|^2$, we see that

$$\chi(\mathbf{E}) \sim \langle i|\mathcal{H}|\Delta f\rangle \sim \langle i|\Delta f\rangle.$$

Since the *initial state* for the core-level is very nearly a delta-function in space (centered at the absorbing atom), this becomes

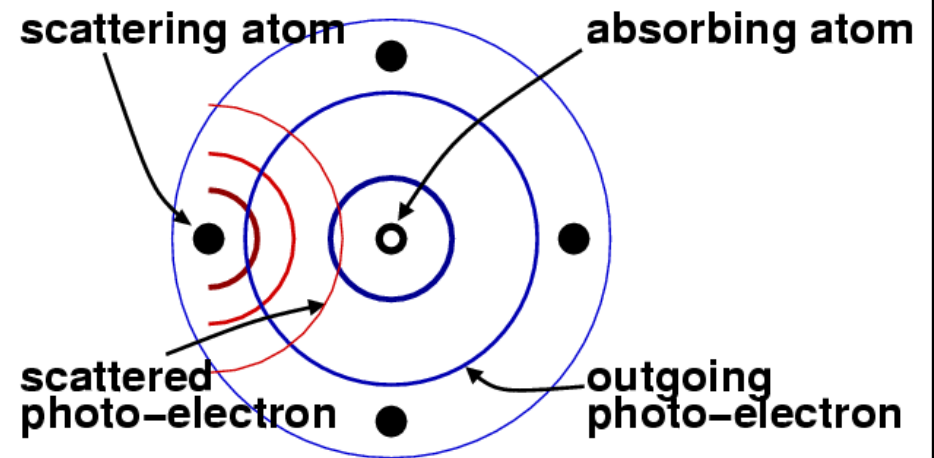
$$\chi(\mathbf{E}) \approx \int d\mathbf{r} \delta(\mathbf{r}) \psi_{\text{scatt}}(\mathbf{r}) = \psi_{\text{scatt}}(\mathbf{0}).$$

The XAFS χ is due to the oscillations in the photo-electron wave-function at the absorbing atom caused by it scattering from neighboring atoms.

The EXAFS Equation: simple description

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

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 types. 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

To get to

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

we used a spherical wave for the photo-electron: $e^{i\mathbf{k}\mathbf{r}}/kr$. But the photo-electron can also scatter *inelastically*, and may not be able to get back the absorbing atom.

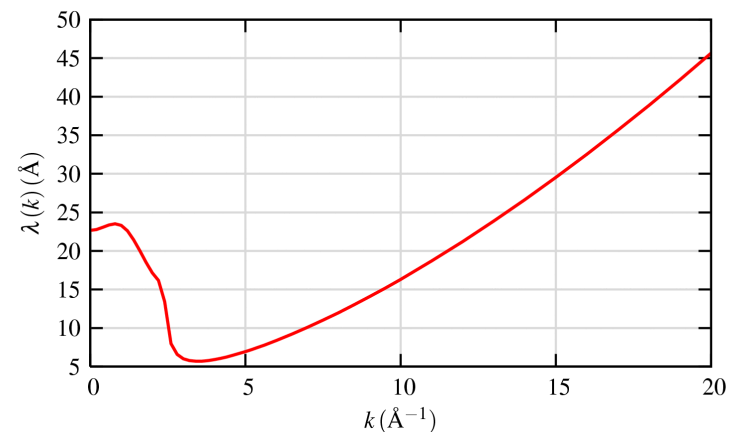
Also: The core-level has a finite lifetime, limiting how far the photo-electron can go.

Using a damped wave-function: $e^{i\mathbf{k}\mathbf{r}} e^{-r/\lambda(k)}/kr$ where $\lambda(k)$ is the photo-electron's *mean free path* (including core-hole lifetime), the EXAFS equation becomes:

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

The mean-free-path λ depends on k , but $\lambda < 25 \text{ \AA}$ for the EXAFS k -range.

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



S_0^2 : Amplitude Reduction Term

Another important **Amplitude Reduction Term** is due to the relaxation of all the other electrons in the absorbing atom to the hole in the core level:

$$S_0^2 = |\langle \Phi_f^{N-1} | \Phi_0^{N-1} \rangle|^2$$

where $\langle \Phi_f^{N-1} |$ accounts for the relaxation of the other $(N - 1)$ electrons relative to these electrons in the unexcited atom: $|\Phi_0^{N-1}\rangle$. Typically, S_0^2 is taken as a constant:

$$0.7 < S_0^2 < 1.0$$

which is found for a given central atom, and simply multiplies the XAFS χ .

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

This, and other experimental and theoretical issues, make EXAFS amplitudes (and therefore N) less precise than EXAFS phases (and therefore R).

Usually S_0^2 is found from a “standard” (data from a sample with well-known structure) and applied to a set of unknowns as a scale factor.

The EXAFS Equation

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

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

where the sum is over “shells” of atoms or “scattering paths” for the photo-electron – nearly the same concept.

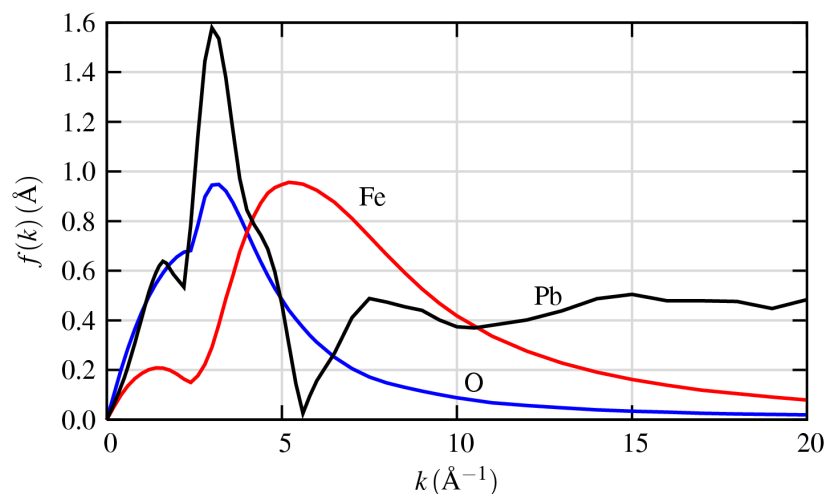
If we know the **scattering** properties of the neighboring atom: $f(\mathbf{k})$ and $\delta(\mathbf{k})$, and the mean-free-path $\lambda(\mathbf{k})$ we can determine:

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

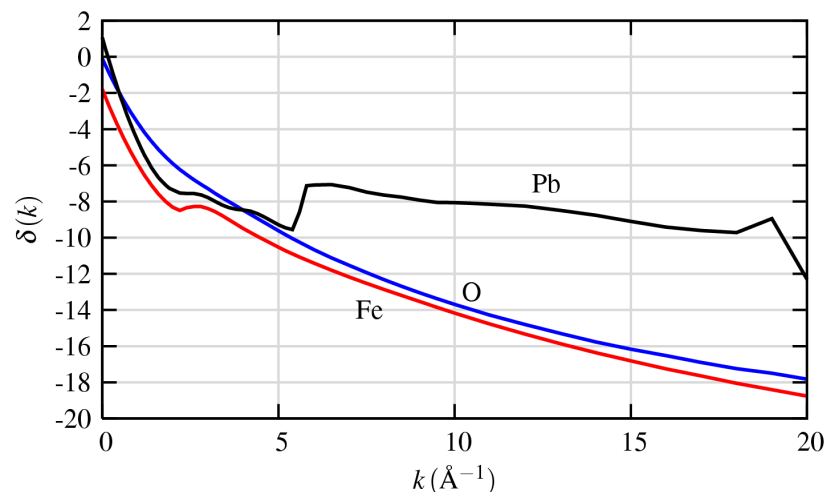
The scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta(\mathbf{k})$ depend on atomic number, so that XAFS is also sensitive to Z of the neighboring atom.

Scattering Amplitude and Phase-Shift: $f(\mathbf{k})$ and $\delta(\mathbf{k})$

The scattering amplitude $f(\mathbf{k})$ and phase-shift $\delta(\mathbf{k})$ 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 $\delta(\mathbf{k})$ shows sharp changes for very heavy elements.

These scattering functions can be accurately calculated (say with the program FEFF, and used in the EX-AFS modeling.

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

Calculating $f(\mathbf{k})$ and $\delta(\mathbf{k})$ with FEFF

These days, we can calculate $f(\mathbf{k})$ and $\delta(\mathbf{k})$ easily using the computer program FEFF. Though not necessarily “User-Friendly”, this program takes as input:

1. a list of atomic x,y,z coordinates for a physical structure (tools such as ATOMS and CRYSTALFF exist to use convert crystallographic data to the required list).
2. a selected central atom.

That’s it! (OK, it can be more painful than that, but is still pretty easy).

The result is a set of files:

feff0001.dat, *feff0002.dat*, ..., each containing the $f(\mathbf{k})$, $\delta(\mathbf{k})$, $\lambda(\mathbf{k})$ for a particular scattering “shell” or “scattering path” for that cluster of atoms.

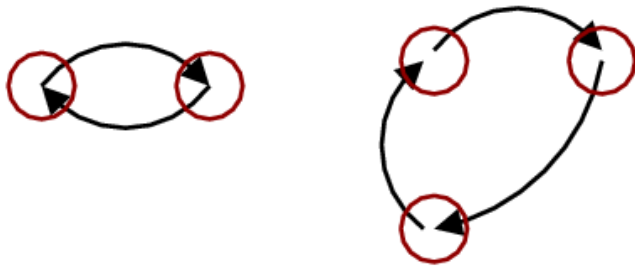
Many analysis programs use these FEFF files directly to model EXAFS data.

A structure that is close to the expected structure can be used to generate a FEFF model, and used in the analysis programs to refine distances and coordination numbers.

Multiple Scattering

The sum over paths in the EXAFS equation includes many shells of atoms (1st neighbor, 2nd neighbor, 3rd neighbor, ...), but can also include **multiple-scattering paths**, in which the photo-electron scatters from more than one atom before returning to the central atom:

Single Scattering Triangle Paths

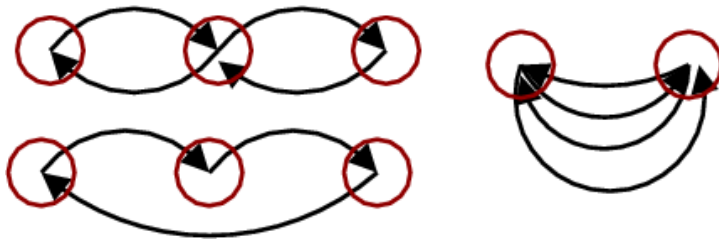


For multi-bounce paths, the total amplitude depends on the **angles** in the photo-electron path.

Triangle Paths with angles $45 < \theta < 135^\circ$ aren't strong, but there can be a lot of them.

Linear paths, with angles $\theta \approx 180^\circ$, are very strong: the photo-electron can be **focussed** through one atom to the next.

Focussed Multiple Scattering Paths



FEFF calculates these effects and includes them in **$f(\mathbf{k})$** and **$\delta(\mathbf{k})$** for the EXAFS equation so that all paths look the same in the analysis.

Multiple Scattering is most important when the scattering angle is $> 150^\circ$.

The strong angular dependence of the scattering can be used to measure bond angles.

For first shell analysis, multiple scattering is hardly ever needed.

XAFS Measurements

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 and detectors that are very linear in x-ray intensity (ion chambers). This usually means using a synchrotron source.

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

Counting Statistics: 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: The Experiment

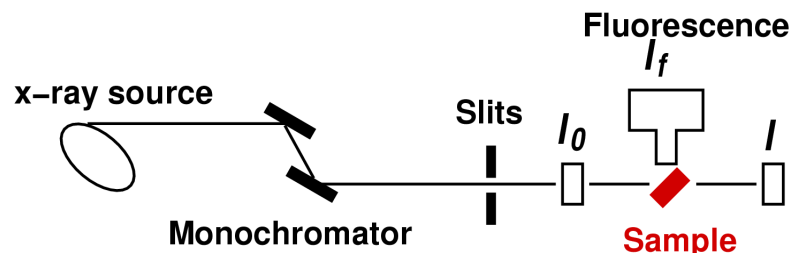
Energy Scanning The beamline needs to deliver monochromatic x-rays that are tunable so we can scan energy across the absorption edge. We'll scan from ~ 200 eV below to ~ 800 eV above the Fe K-edge, like this:

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}

(all values relative to a nominal x-ray absorption edge energy.)

- In the EXAFS region, it's common to step in k rather than energy.
- Typical count times are 1 to 15 seconds per point, so that EXAFS measurements take 10 minutes to several hours (dilute samples take longer than concentrated samples!).
- Very fast measurements (1 second for the whole spectra) can be made at specialized beamlines.

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,

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

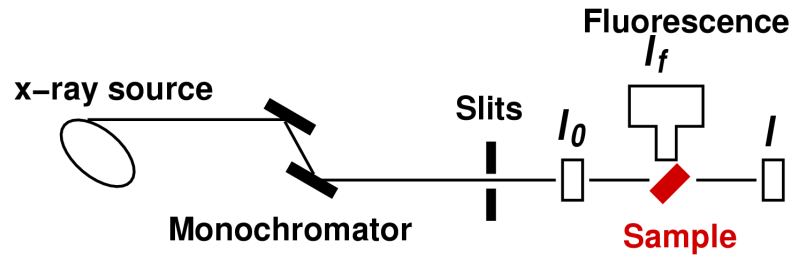
We adjust the sample thickness t so that $\mu(E)t \approx 2.5$ above the absorption edge and/or the edge step $\Delta\mu(E)t \approx 1$.

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.

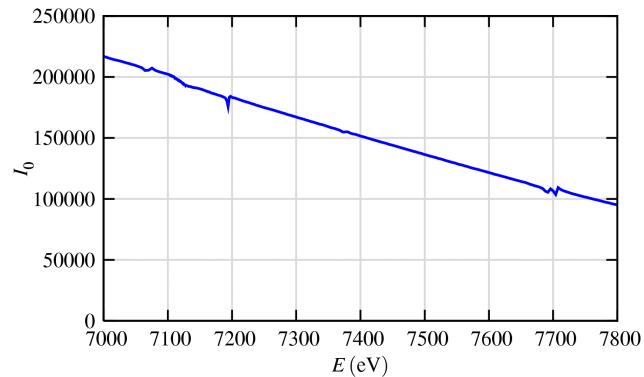
If a transmission experiment can be done, this is an easy measurement and gives excellent data. It's usually appropriate for model compounds, and concentrations $> 10\%$.

X-ray Absorption Measurements: Transmission

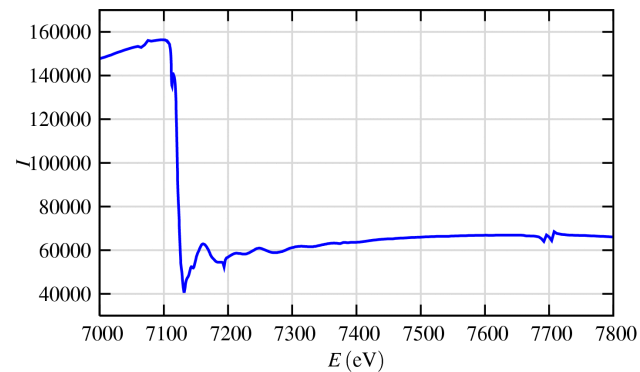


Scanning the x-ray energy across the Fe *K*-edge (~ 7112 eV), we measure the intensities of the incident beam and that transmitted through a sample (Fe_2O_3):

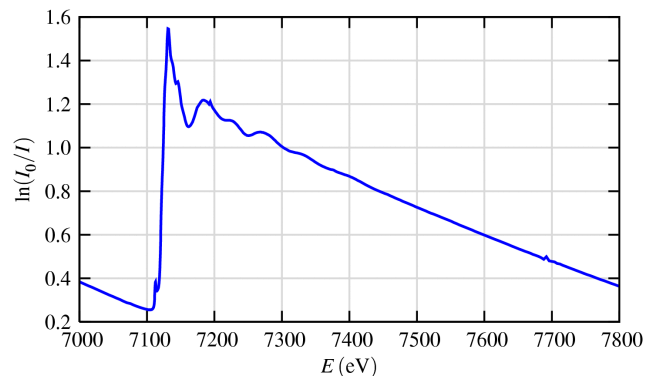
I_0 :



I :

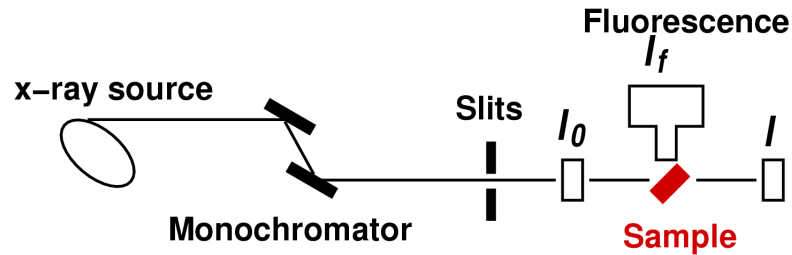


$\mu(E)t$:

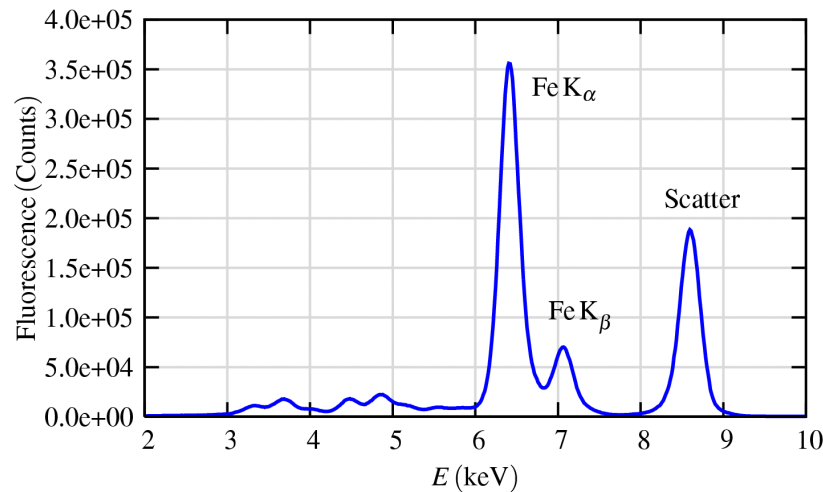


$$\mu(E)t = -\ln(I/I_0)$$

X-ray Absorption Measurements: Fluorescence



For thick samples or low 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

There are two main considerations for getting a good fluorescence measurement:

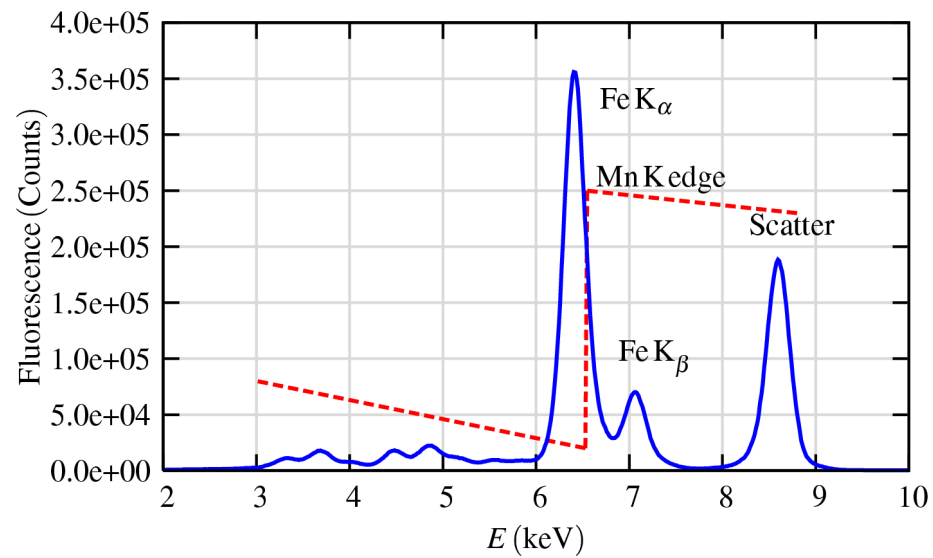
Energy Discrimination either physically or electronically filter the unwanted portions of the fluorescence/scatter spectra is helpful.

Solid Angle The fluorescence is emitted isotropically in all directions, so collecting as much of the 4π of solid angle as possible is good.

A simple method of energy discrimination uses a **filter** of “Z-1” from the element of interest.

For Fe, a Mn filter absorbs the scatter, while passing the Fe K_{α} line.

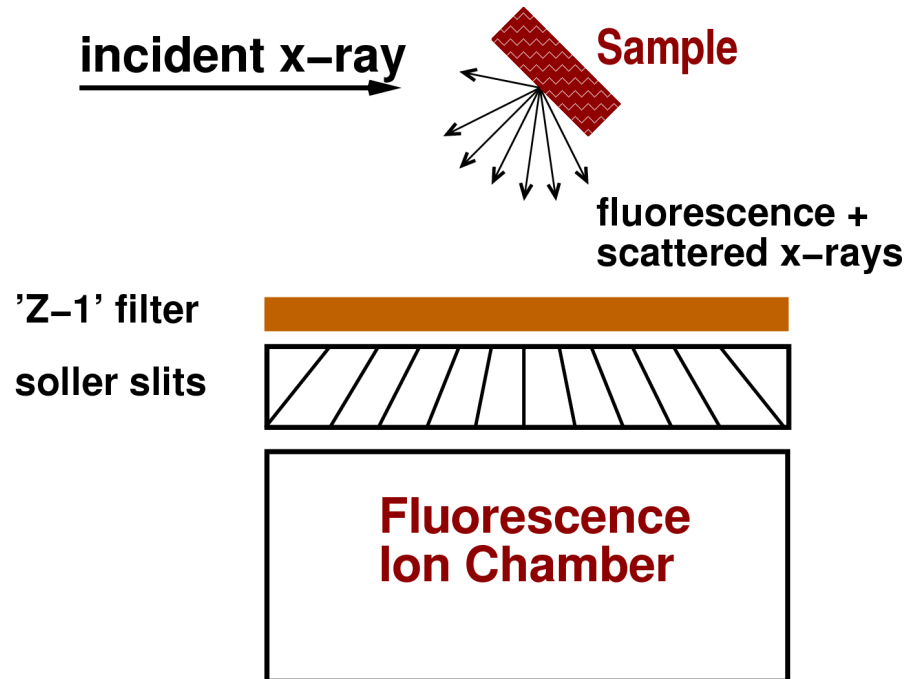
This can be used with a detector without any energy resolution.



Fluorescence Measurements: Filters

A typical fluorescence setup with a 'Z-1' filter uses a simple ion chamber which has no energy resolution, but high count rate and linearity.

Because the filter absorbs the scattered beam, it can itself re-radiate!!



A set of **Soller slits** can be used to see the sample, but absorb most of the re-radiate scatter from the filter.

This arrangement can be very effective especially when the signal is dominated by **scatter**, and when the concentration is at per cent levels.

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.

Fluorescence Measurements: Self-Absorption

The fluorescent x-ray has to get out of the sample, and can be attenuated by the sample itself. This **self-absorption** can damp the XAFS – even completely wiping it out for highly concentrated elements.

The measured fluorescence intensity goes as:

$$I_f = I_0 \frac{\epsilon \Delta\Omega}{4\pi} \frac{\mu_\chi(\mathbf{E})}{\mu_{\text{tot}}(\mathbf{E}) + \mu_{\text{tot}}(\mathbf{E}_f)} \left[1 - e^{-[\mu_{\text{tot}}(\mathbf{E}) + \mu_{\text{tot}}(\mathbf{E}_f)]t} \right]$$

where

ϵ is the fluorescence efficiency.

$\Delta\Omega$ is the solid angle of the detector.

\mathbf{E}_f is the energy of the fluorescent x-ray.

$\mu_\chi(\mathbf{E})$ is the absorption from the element of interest.

$\mu_{\text{tot}}(\mathbf{E})$ is the *total* absorption in the sample:

$$\mu_{\text{tot}}(\mathbf{E}) = \mu_\chi(\mathbf{E}) + \mu_{\text{other}}(\mathbf{E})$$

When $\mu_\chi(\mathbf{E})$ dominates $\mu_{\text{tot}}(\mathbf{E})$, the fluorescence intensity will be severely attenuated.

XAFS Data Reduction

Data Reduction: Strategy

Step for reducing measured data to $\mu(\mathbf{E})$ and then to $\chi(\mathbf{k})$:

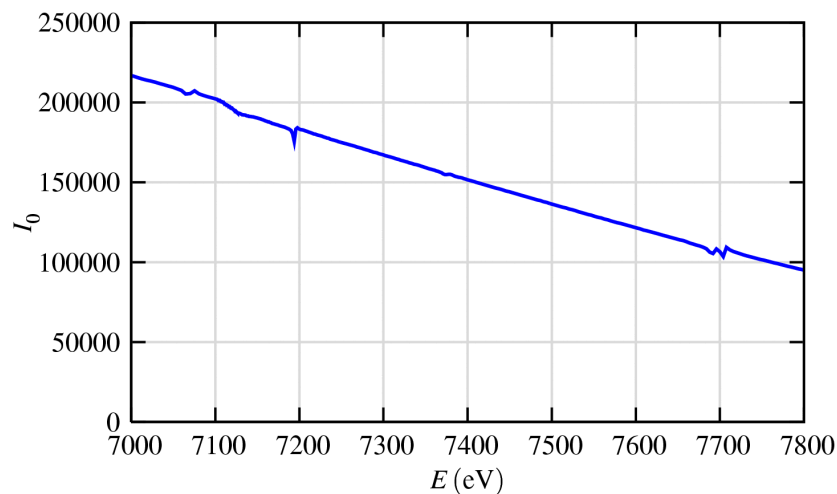
1. convert measured intensities to $\mu(\mathbf{E})$
2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
3. normalize $\mu(\mathbf{E})$ to go from 0 to 1, so that it represents the absorption of 1 x-ray.
4. remove a smooth post-edge background 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.
7. isolate the $\chi(\mathbf{k})$ for an individual “shell” by Fourier filtering.

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} .

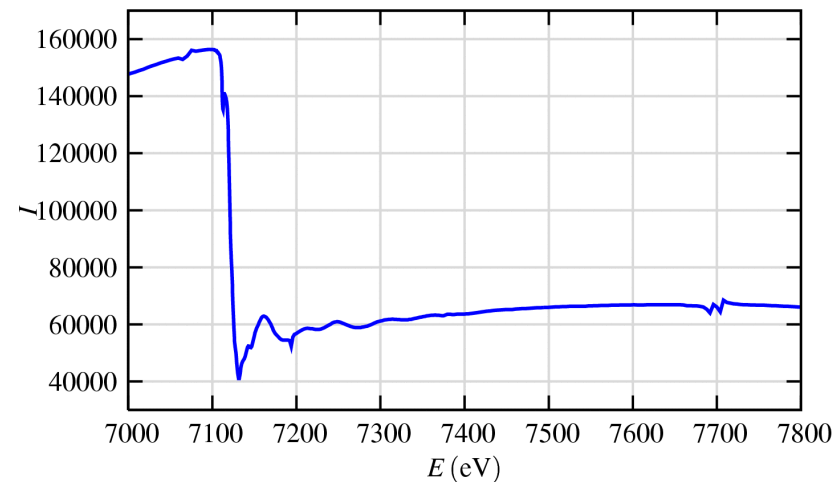
Data Reduction: Converting Raw Data to $\mu(E)$

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

I_0

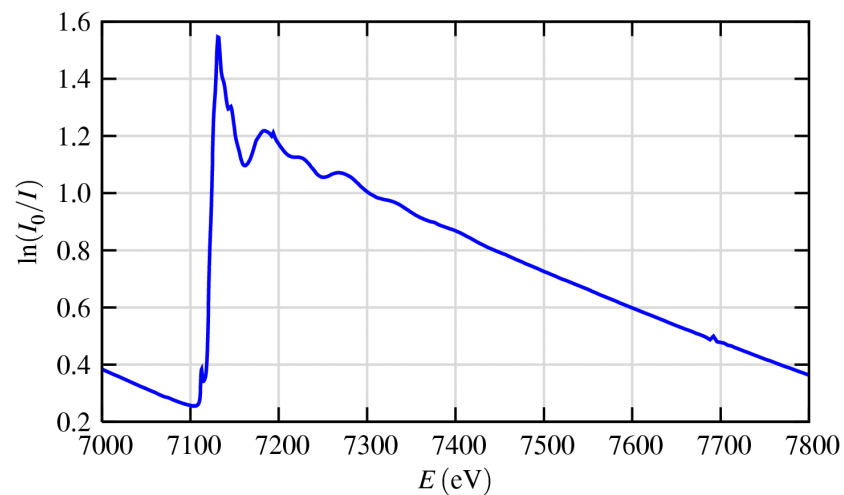


I



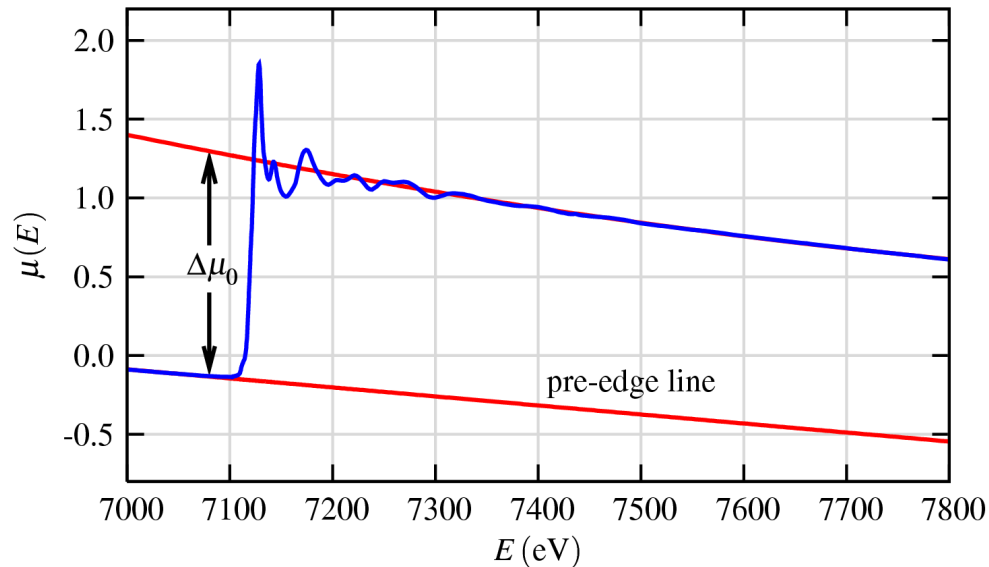
For Transmission XAFS

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



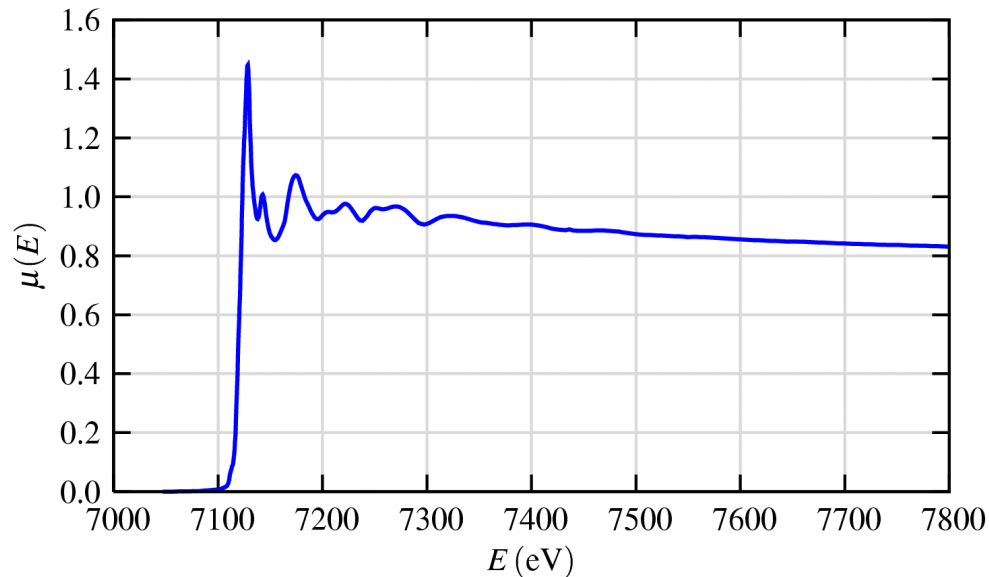
Data Reduction: Pre-Edge Subtraction, Normalization

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



Pre-Edge Subtraction

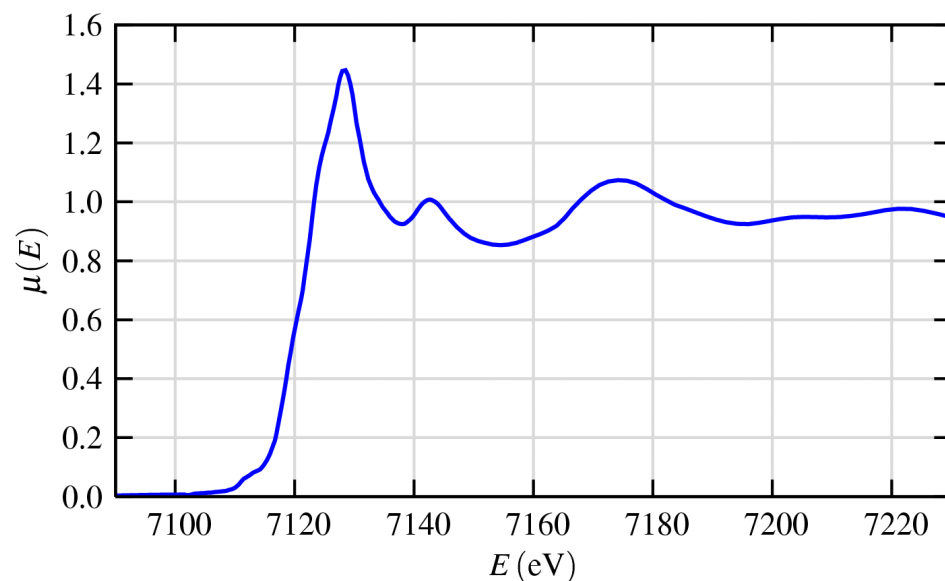
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

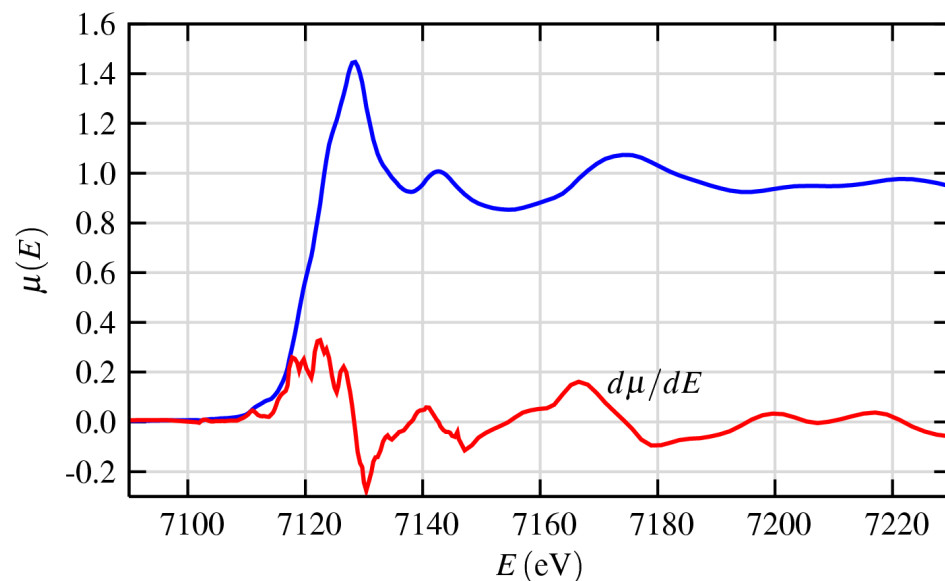
We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge. We normalize by this value to get the absorption from 1 x-ray.

Data Reduction: Normalized XANES and E_0



XANES

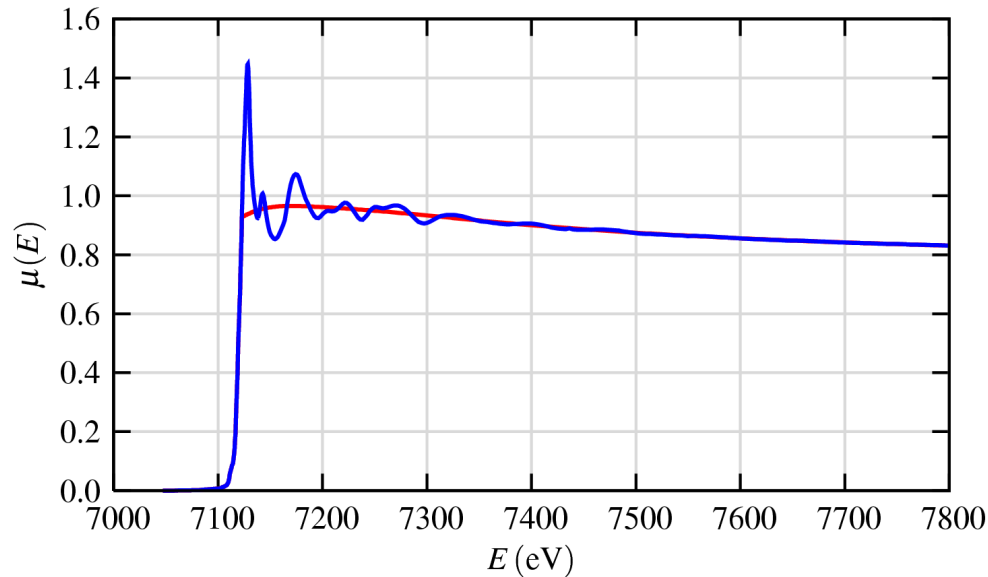
The XANES portion (below) shows a fairly rich spectral structure. We'll come back to this for XANES analysis.



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.

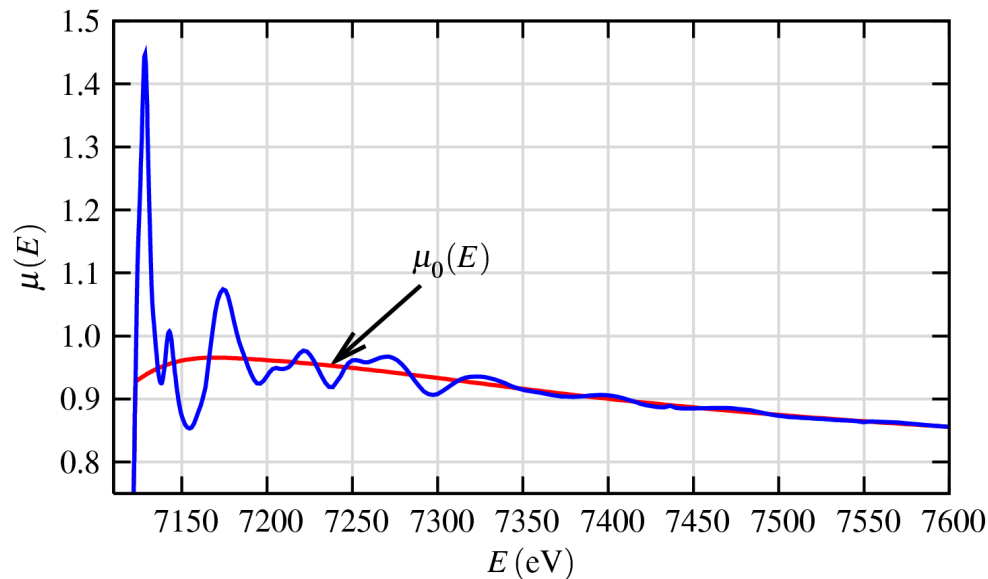
Data Reduction: Post-Edge Background Subtraction



Post-Edge Background

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

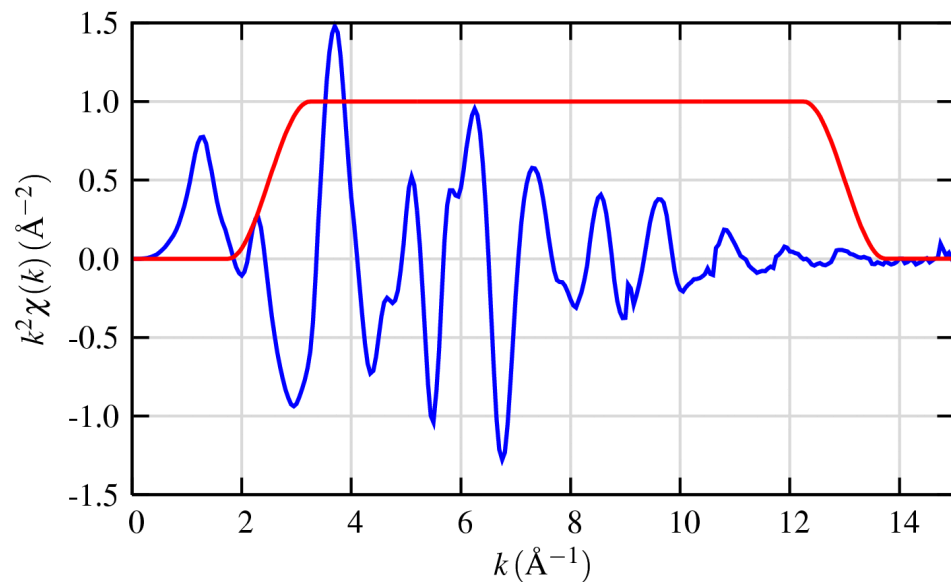
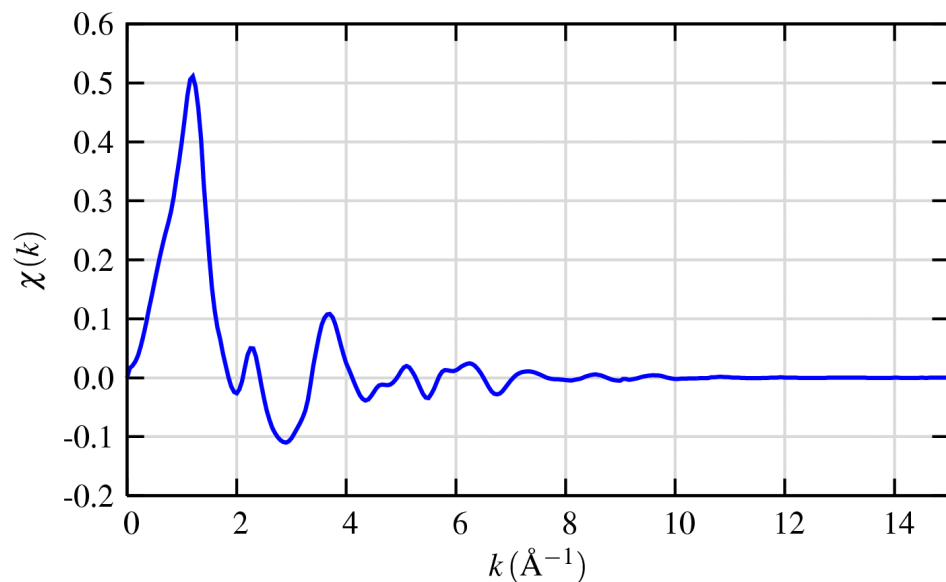
We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.



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



$\chi(k)$

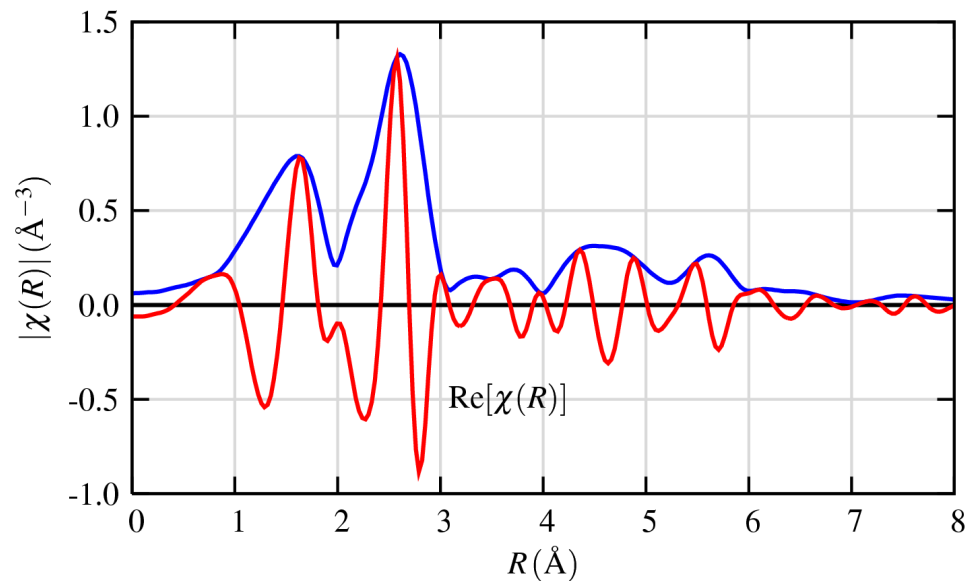
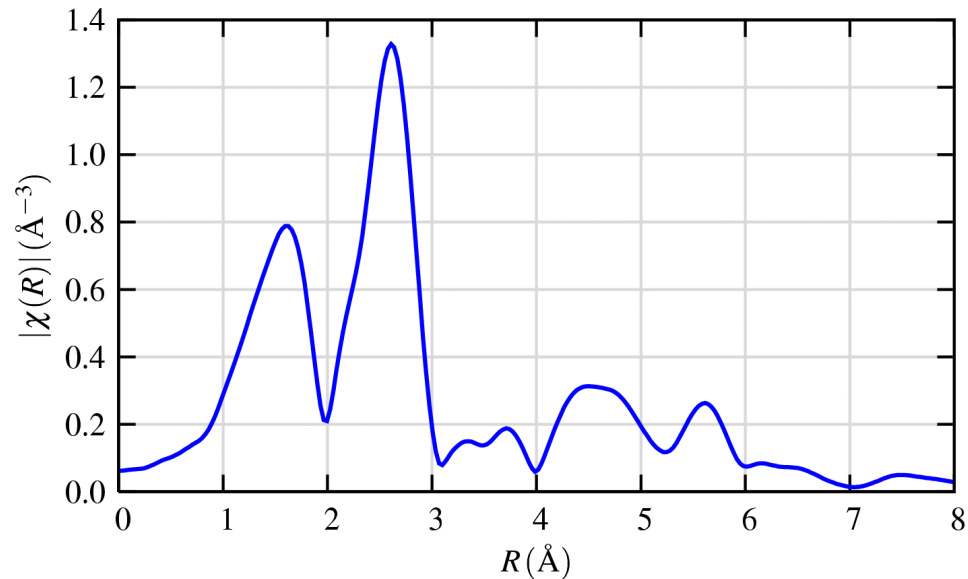
The raw EXAFS $\chi(k)$ usually decays quickly with k , and difficult to assess or interpret by itself.

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**, $\delta(\mathbf{k})$: $\sin[2kR + \delta(\mathbf{k})]$.

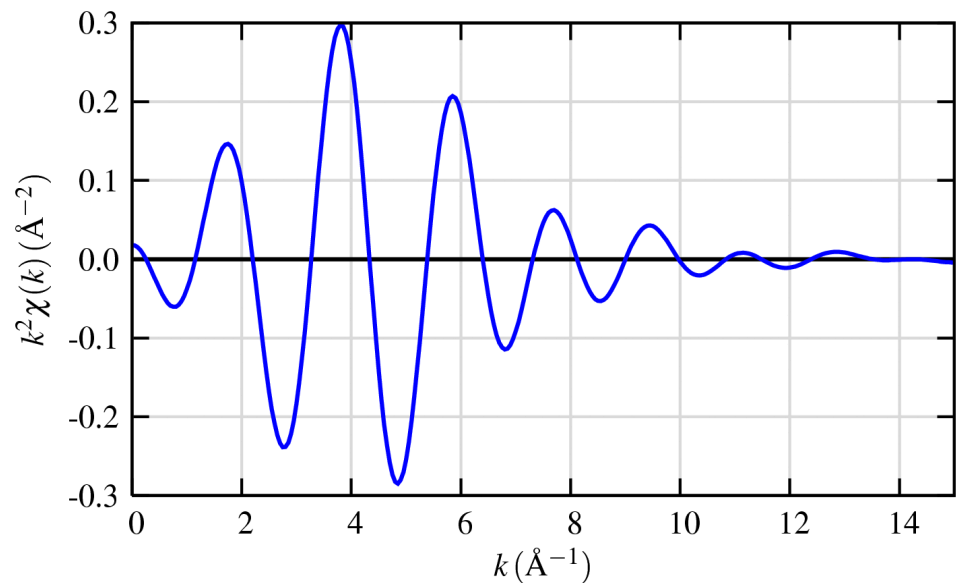
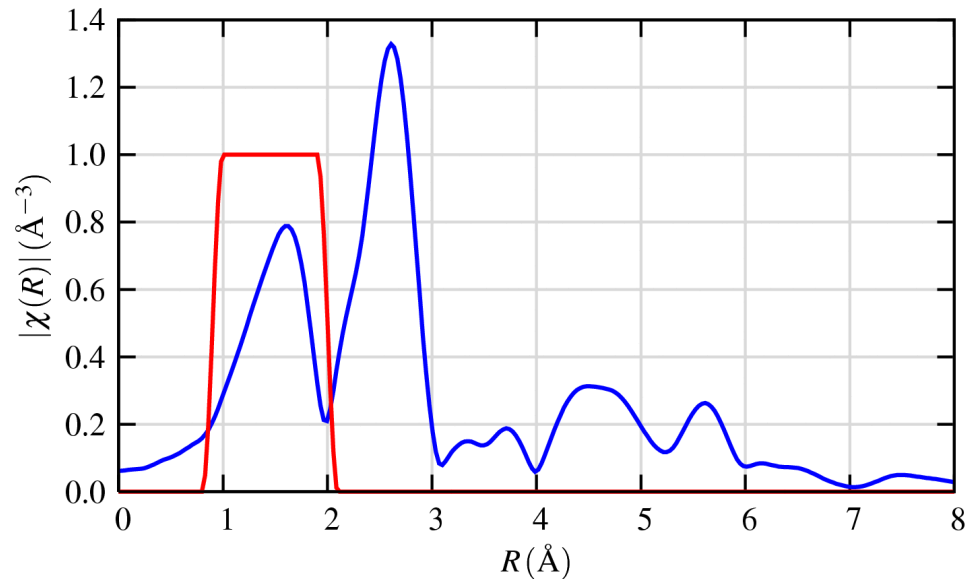
A shift of -0.5 \AA is typical.

$\chi(\mathbf{R})$ 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.

Fourier Filtering



$\chi(\mathbf{R})$ 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 $\chi(\mathbf{k})$ 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 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 are $k = [3.0, 12.0] \text{ \AA}^{-1}$ 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)

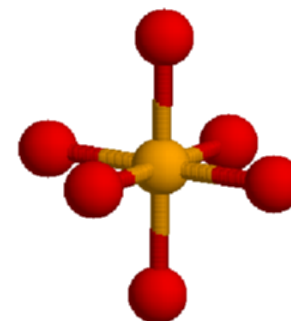
Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).

Use as much other information about the system as possible!

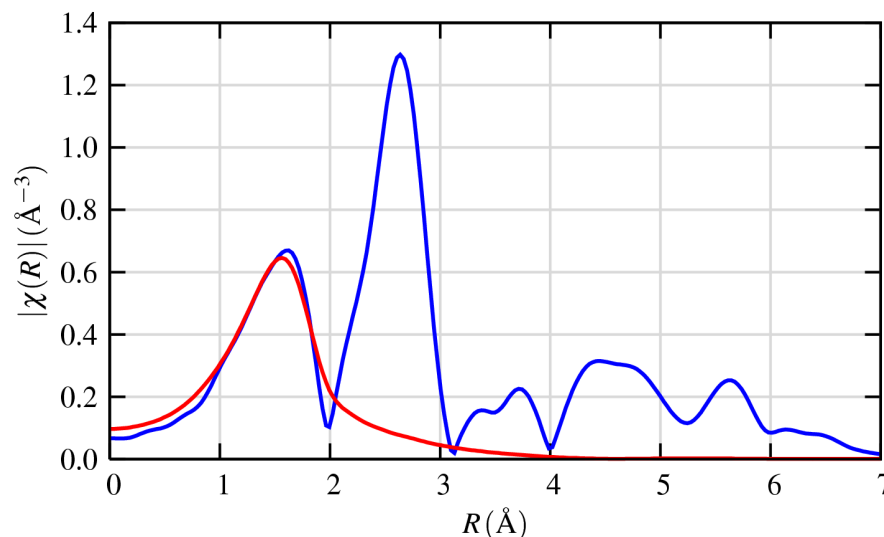
EXAFS Analysis: Modeling the 1st Shell of FeO

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.

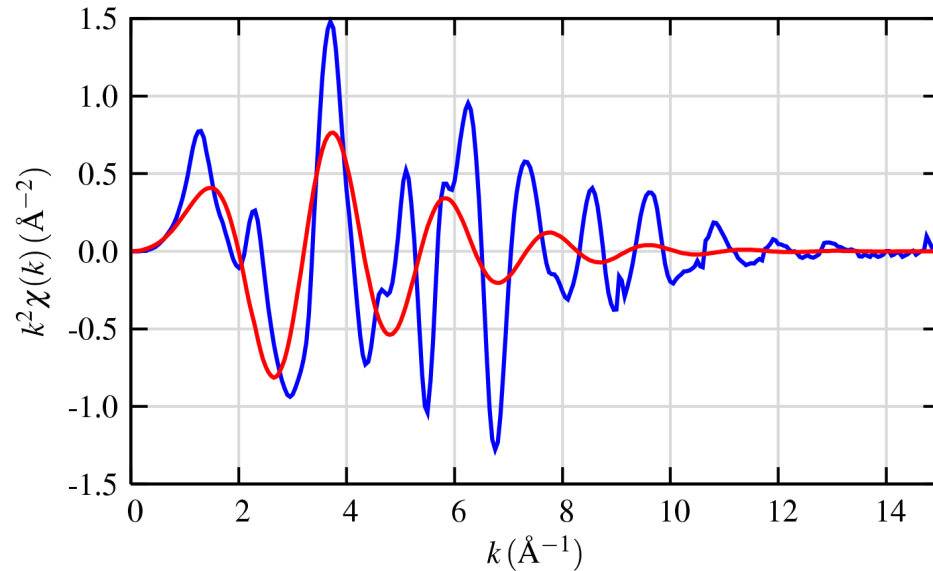


Fit results:

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

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

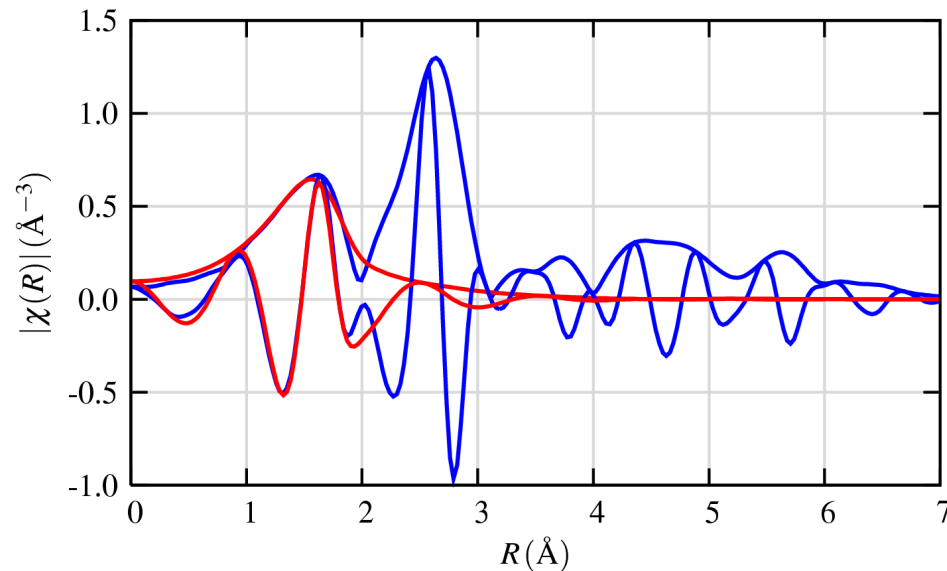
EXAFS Analysis: 1st Shell of FeO



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.

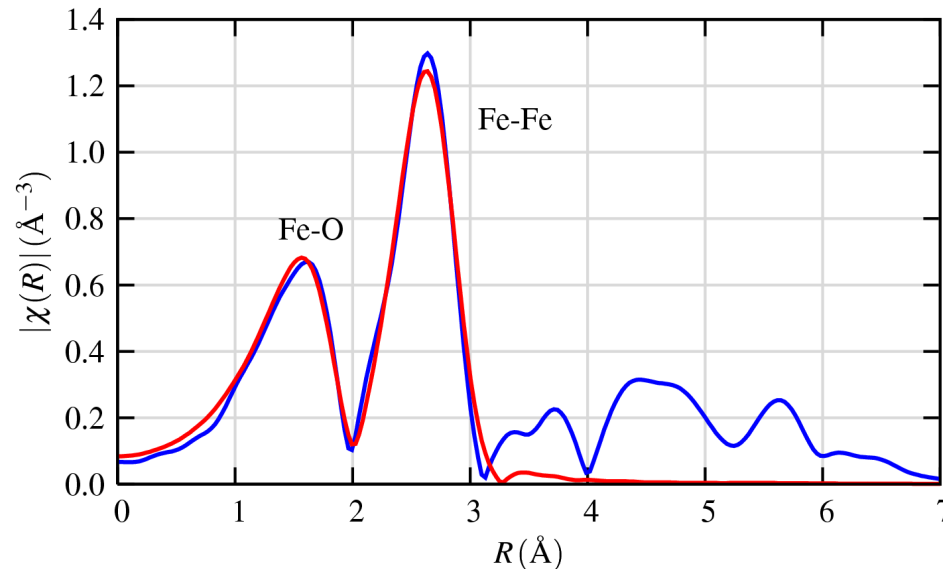
$|\chi(R)|$ and $\text{Re}[\chi(R)]$ for FeO (blue), and a 1st shell fit (red).

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:

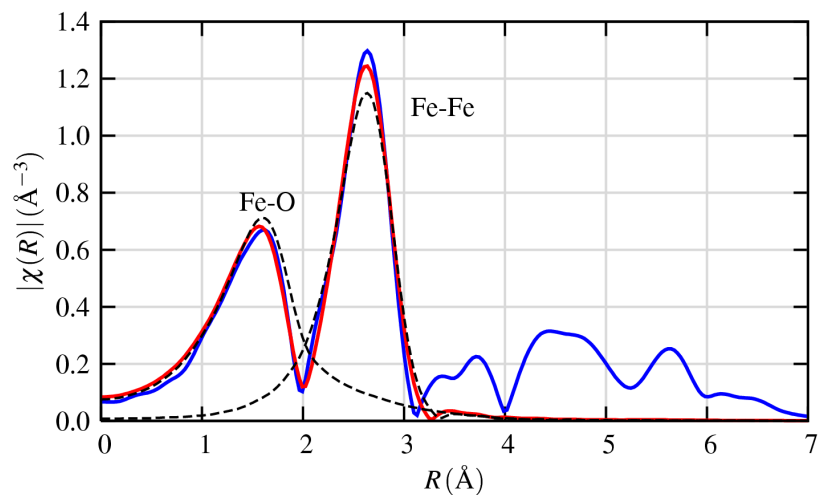
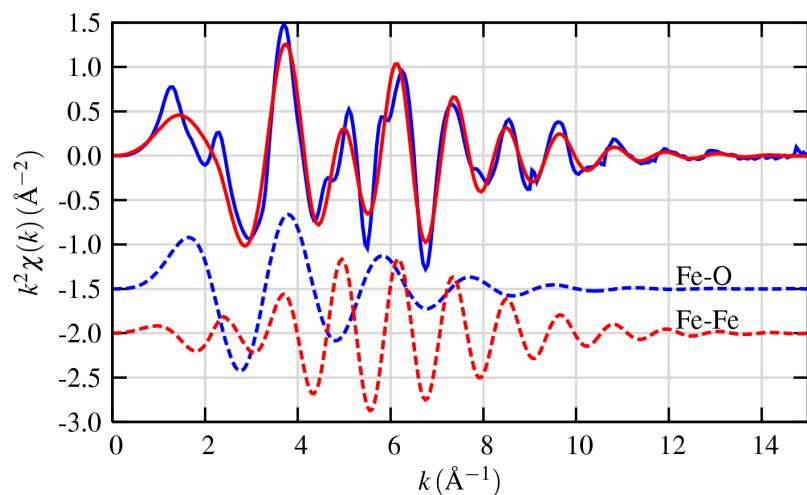
6 O at 2.13Å, 12 Fe at 3.02Å.

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:

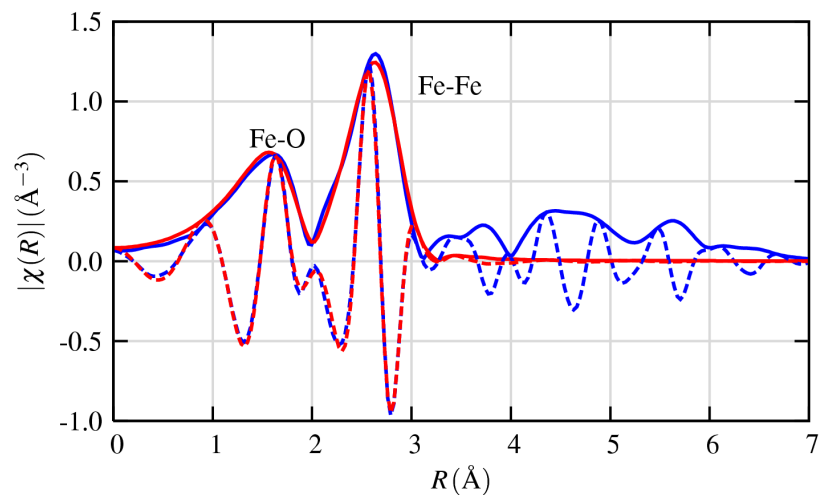


The Fe-Fe EXAFS extends to higher- k than the Fe-O EXAFS.

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

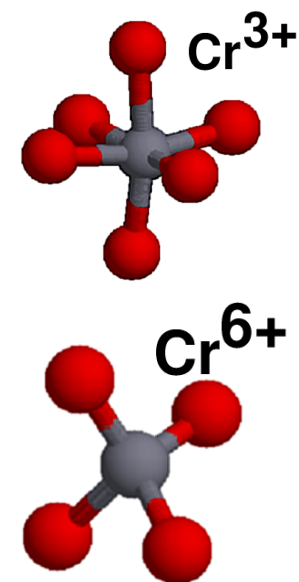
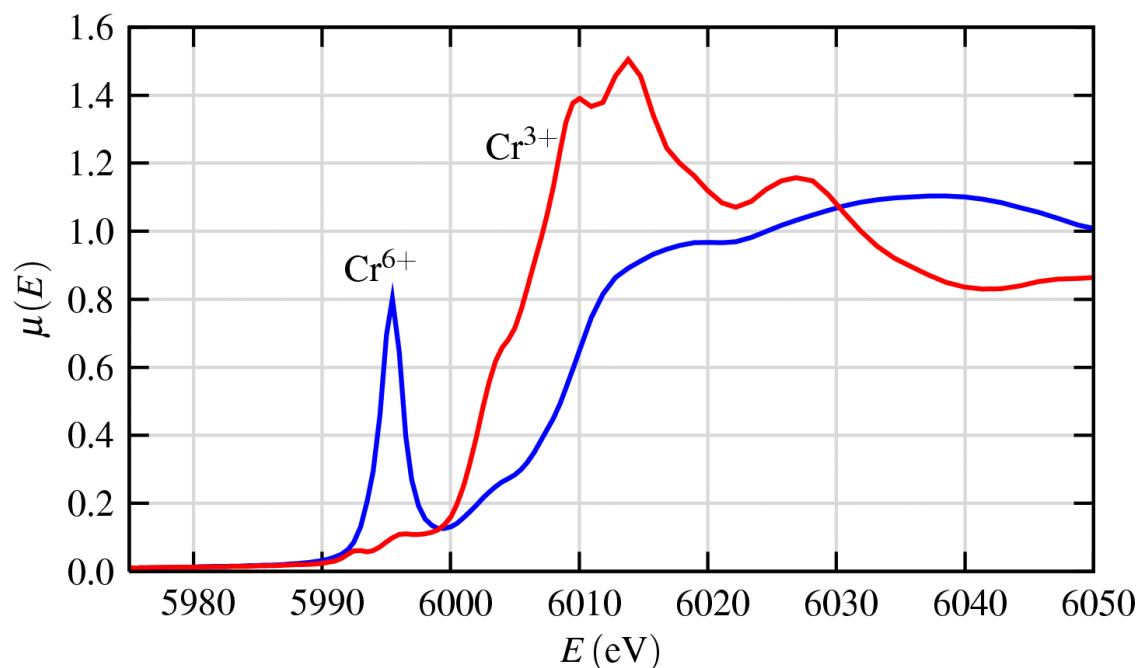
The agreement in $\text{Re}[\chi(R)]$ look especially good – this is how the fits are done.

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



XANES

XANES Analysis: Oxidation State 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.

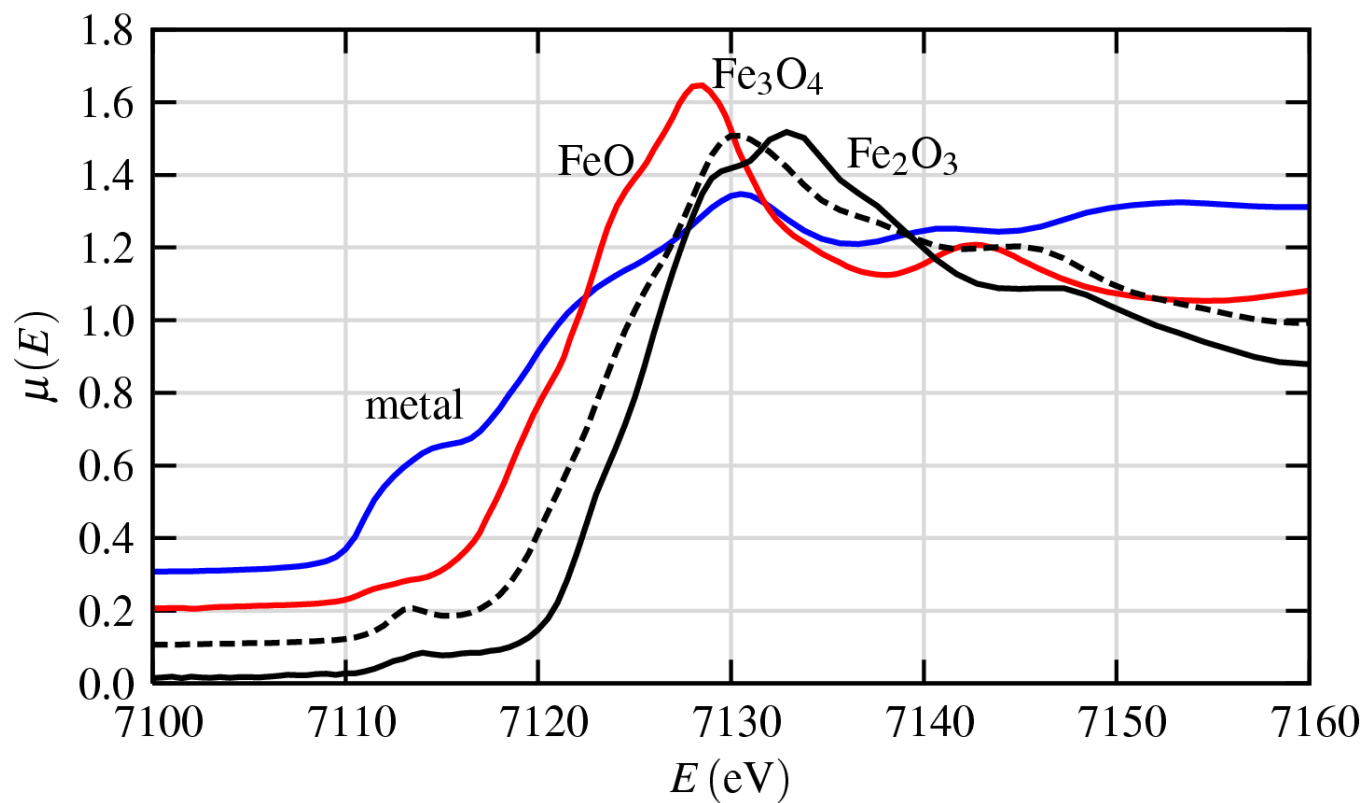
These chemical and physical interpretations are all related, of course:

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 still rare, but becoming possible...

Edge Shifts and Pre-edge Peaks in Fe oxides

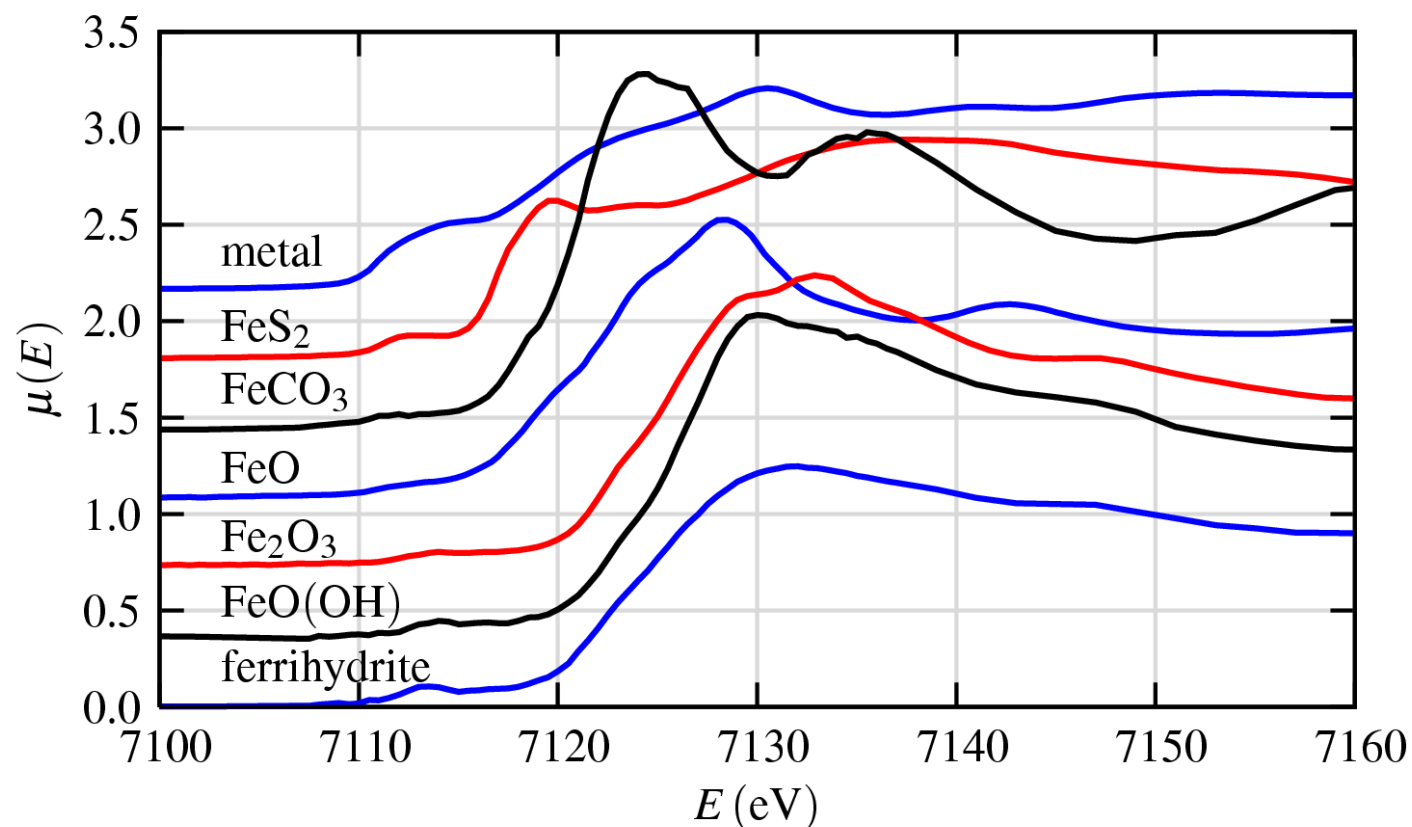


XANES for Fe oxides and metal. The shift of the edge position can be used to determine the valence state.

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).

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

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/>.