

X-ray Absorption Fine-Structure Spectroscopy

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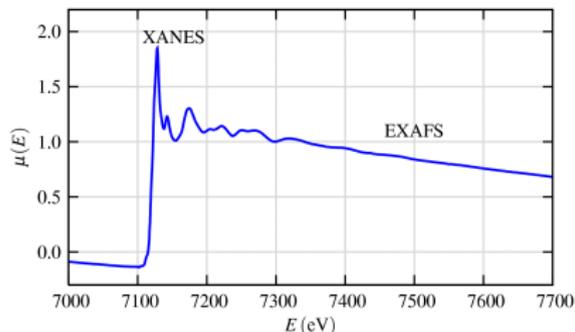
What Is XAFS?

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

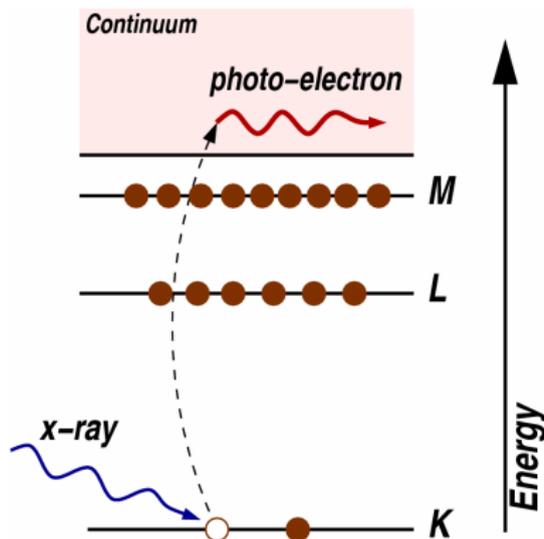
X-Ray Absorption

X-rays (light with wavelength $0.25 \text{ \AA} \lesssim \lambda \lesssim 250 \text{ \AA}$ and energy $500 \text{ eV} \lesssim E \lesssim 500 \text{ keV}$) 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).

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 an ejected *photo-electron*.

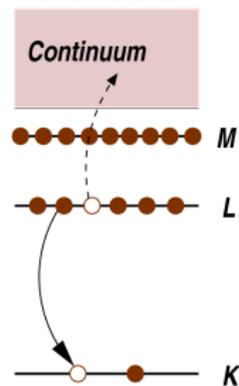
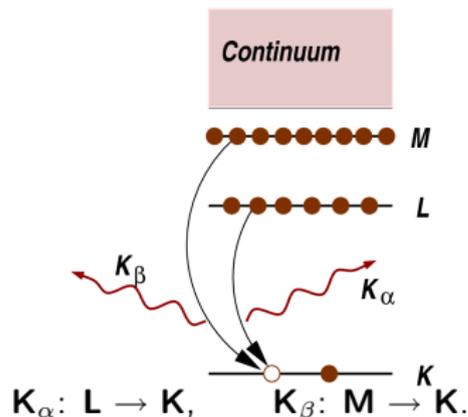


X-ray Fluorescence

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: Emit an x-ray with energy = the difference of the core-levels.

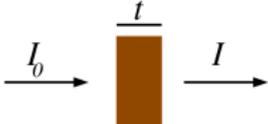
Auger Effect: Promote an electron from another core-level to the continuum.



X-ray fluorescence and Auger emission occur at discrete energies that are characteristic of the absorbing atom. They 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 :

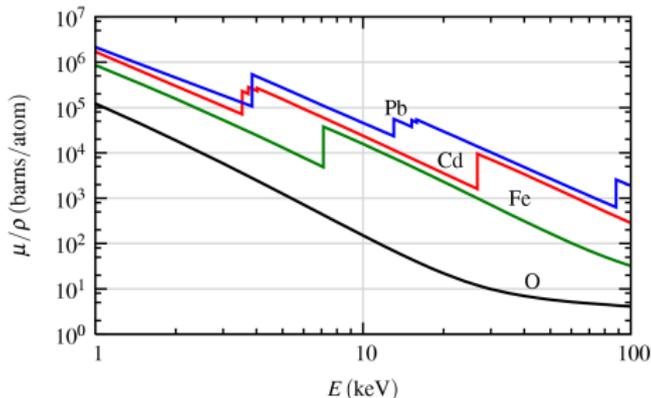
$$I = I_0 e^{-\mu t}$$


The diagram illustrates the absorption process. An arrow labeled I_0 points from the left towards a brown rectangular block representing a material of thickness t . 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 atomic number Z , and also on density ρ , and Atomic mass A :

$$\mu \sim \frac{\rho Z^4}{AE^3}$$



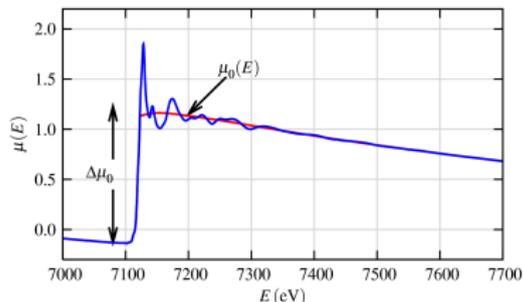
Plus: μ has sharp *Absorption Edges* corresponding to the characteristic core-level energies of the atom.

EXAFS: Extended X-ray Absorption Fine Structure

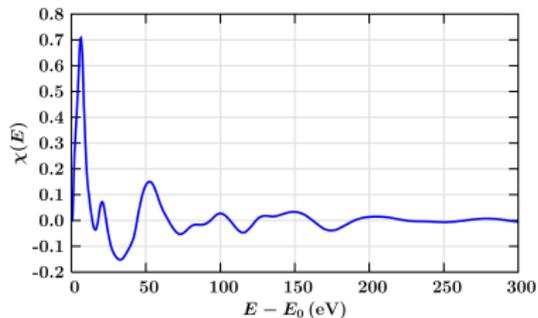
We're interested in the energy-dependent oscillations in $\mu(E)$, as these will tell us something about the neighboring atoms, so we define the EXAFS as:

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

We subtract off the smooth *"bare atom" background* $\mu_0(E)$, and divide by the *"edge step"* $\Delta\mu_0(E_0)$ to give the oscillations normalized to 1 absorption event:



$\mu(E)$ and smooth $\mu_0(E)$ for FeO



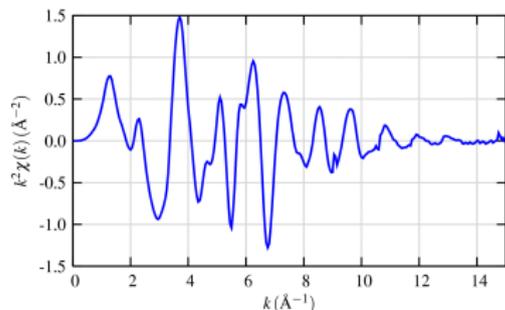
$\chi(E)$ for FeO, with $E_0 = 7122$ eV.

EXAFS: $\chi(k)$ and XAFS Fourier Transforms

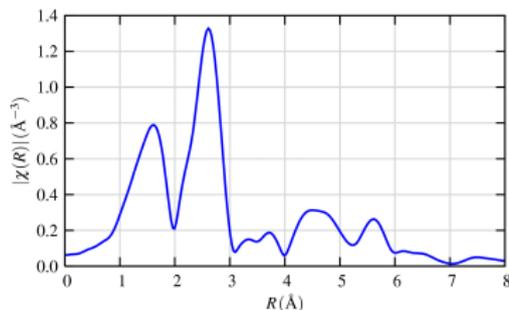
XAFS is an *interference effect*, using the wave-nature of the photo-electron. We express the XAFS in terms of *photo-electron wavenumber*, k :

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

We'll also then use Fourier Transforms to convert from k to R .



$k^2\chi(k)$ for FeO



Fourier Transform $|\chi(R)|$ for FeO.
Like "Pair Distribution Functions"
from other scattering techniques.

The EXAFS Equation

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

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

where $f(k)$ and $\delta(k)$ are *photo-electron scattering properties* of the neighboring atom. If we know these properties, we can determine:

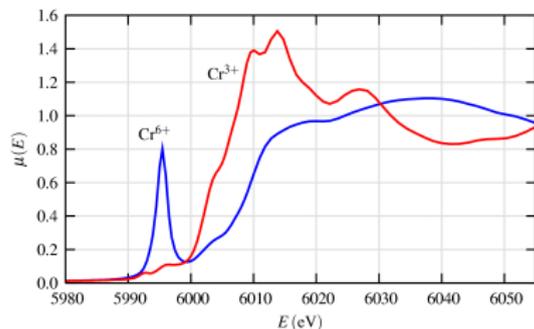
R distance to neighboring atom.

N coordination number of neighboring atom.

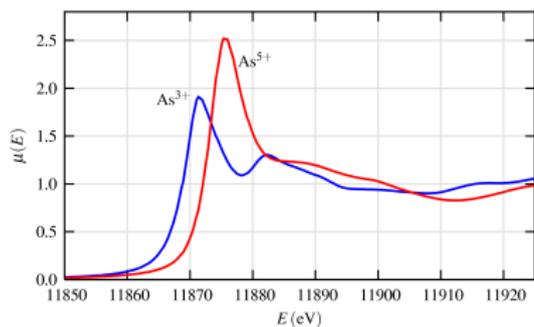
σ^2 mean-square disorder of neighbor distance.

Plus: $f(k)$ and $\delta(k)$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

XANES (within 30eV of the absorption edge) gives the chemical state and formal valence of selected element:



XANES for Cr^{3+} and Cr^{6+}



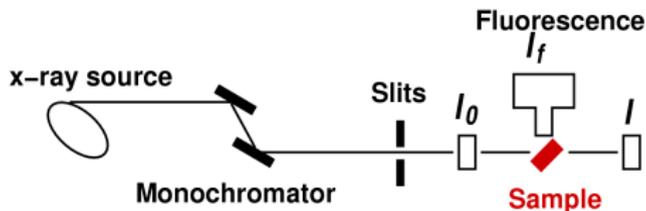
XANES for As^{3+} and As^{5+}

Many reliable spectral / empirical approaches to analyzing XANES:

Linearly combine known spectra to match measured spectra, giving chemical environment.

XANES calculations can help map spectra to electronic density of states

X-ray Absorption Measurements



$\mu(E)$ can be measured two ways:

Transmission measure what is transmitted through the sample:

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

Appropriate for concentration samples: $\gtrsim 10$ wt.%.

Fluorescence measure fluorescent x-rays from the re-filling the core hole:

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

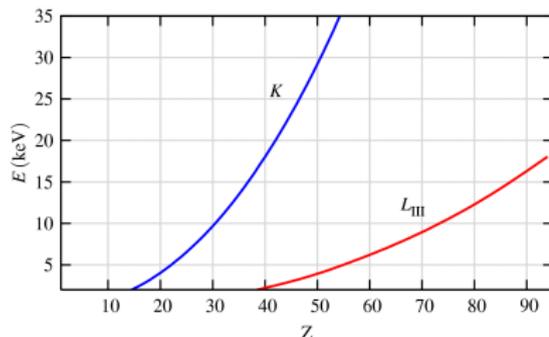
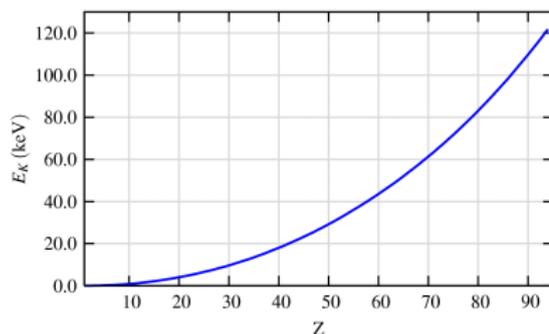
Appropriate for dilute elements: $\lesssim 2$ wt.%.

We need a measurement of $\mu(E)$ to $\sim 0.1\%$, but with an energy-tunable x-ray source, the measurements are fairly easy.

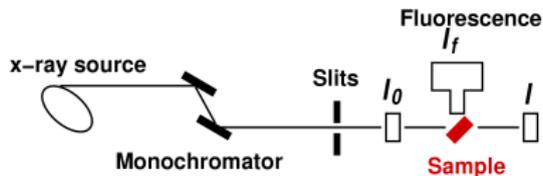
Absorption Edge Energies

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

Elements with $Z > 18$ have either a K -, or L -edge between 3 and 35 keV (hard x-rays), and can be accessed at many synchrotron sources. Lower Z elements (soft x-rays) can be measured as well.



X-ray Absorption Measurements: Transmission



For concentrated samples, XAFS is best measured in transmission. We need enough transmission through the sample to get x-rays through the sample. With,

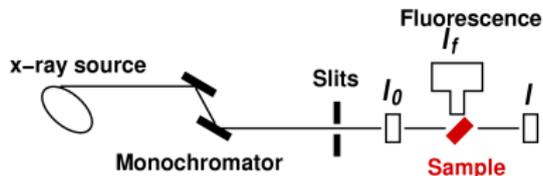
$$\mu(E)t = -\ln(I/I_0)$$

We make the sample thickness t so that $\mu(E)t \approx 1 < 3$.

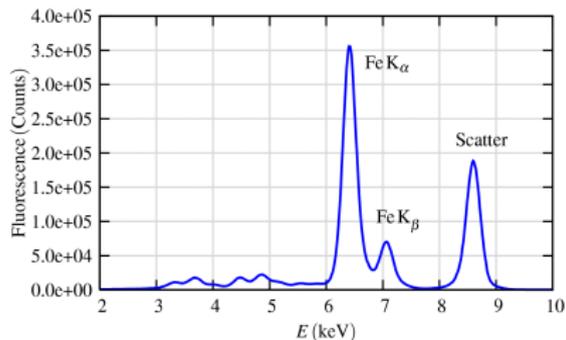
- Samples typically need to $10\mu m$ or less!
- They must be uniform, and free of pinholes.
- grain size cannot be much bigger than an absorption length.

Transmission measurements can give excellent data, but require careful sample preparation.

X-ray Absorption Measurements: Fluorescence



For low concentrations (down to the ppm level), monitoring the x-ray fluorescence is the preferred measurement.



x-rays emitted from the sample I include the fluorescence line of interest (here, both Fe K_α and Fe K_β) as well as *scattered* (elastic and inelastic) x-rays, and other fluorescence lines.

In many cases, the scatter or other fluorescence lines will dominate the fluorescence line of interest.

Fluorescence Measurements

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

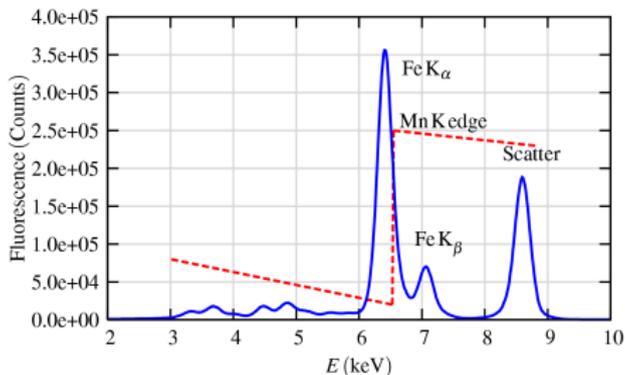
Energy Discrimination either physically or electronically filter the unwanted portions of the fluorescence/scatter spectra.

Solid Angle Fluorescence is emitted isotropically, so we'd like to collect as much of the 4π of solid angle as possible.

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 with no energy resolution.



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:

$$\Delta E \approx 1 \text{ eV at } 10 \text{ keV.}$$

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 ~ 1 absorption lengths. It should be free from pinholes. Powders need to be very fine-grained.

Counting Statistics: $\mu(E)$ should have a noise level of about 10^{-3} . That means we need to collect at least $\sim 10^6$ photons. For very low concentration samples, this may require hours of counting time.

X-ray Absorption Measurements: The Experiment

An XAFS measurement needs monochromatic x-ray that can be tuned in energy across the absorption edge. Typical scans are from ~ 200 eV below to ~ 800 eV an absorption edge, like this:

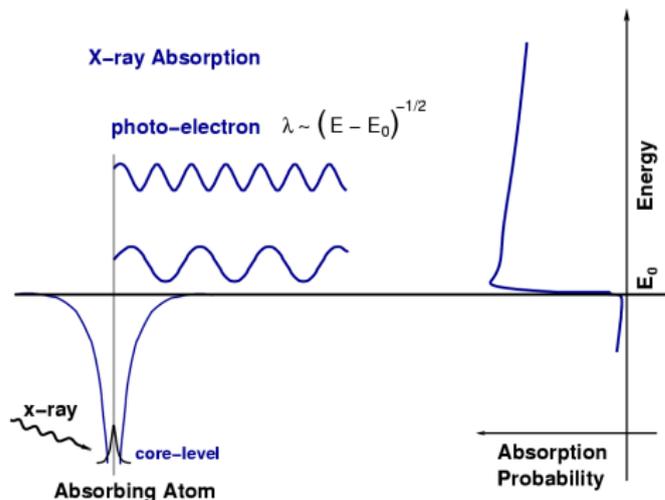
Region	Starting Energy (eV)	Ending Energy (eV)	Step Size (eV)
Pre-edge	-200	-20	5.0
XANES	-20	+30	0.25 – 0.50
EXAFS	+30	~ 800	0.05 \AA^{-1}

(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.
- Very fast measurements (1 second for the whole spectra) can be made at specialized beamlines.

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 hole** 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:

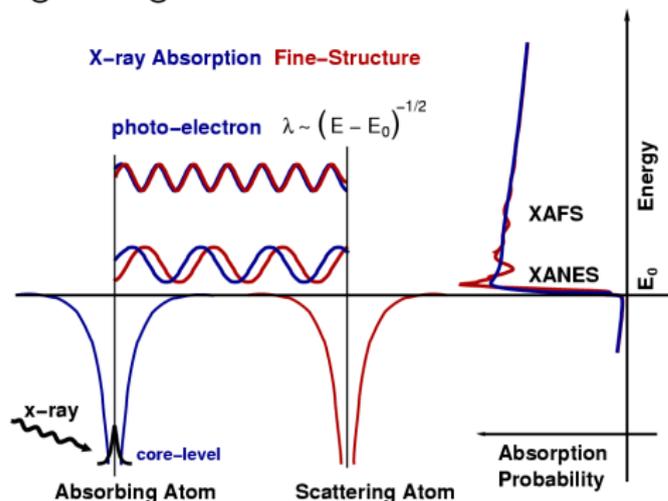
No available state:
No absorption

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

$\mu(E)$ 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.

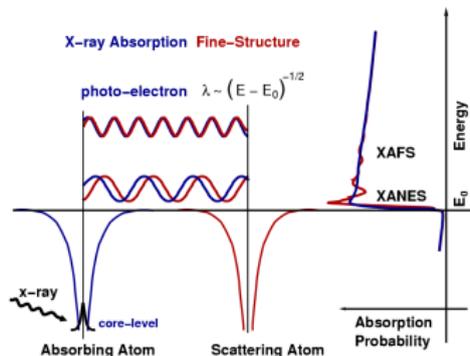
The XAFS oscillations are an interference effect of the photo-electron with itself, due to the presence of neighboring atoms.

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:

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

$|i\rangle$ the *initial state* has a core level electron and the photon.
This is **not** altered by the neighboring atom.

\mathcal{H} the *interaction*. In the dipole approximation, $\mathcal{H} = e^{ikr} \approx 1$.

$|f\rangle$ the *final state* has a photo-electron, a **hole** in the core, and no photon. This is altered by the neighboring atom:
the photo-electron scatters.

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

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

Compare this to our definition for χ :

$\mu(E) = \mu_0(E)[1 + \chi(E)]$, we recognize $\mu_0(E) = |\langle i|\mathcal{H}|f_0\rangle|^2$, so that

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

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

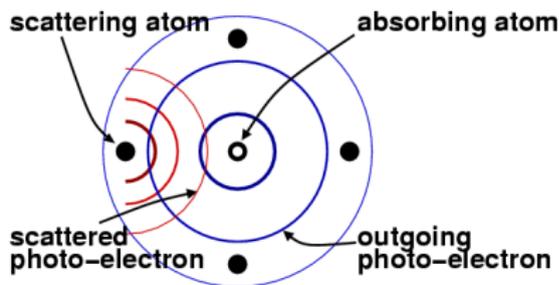
$$\chi(E) \approx \int dr \delta(r) \psi_{\text{scatt}}(r) = \psi_{\text{scatt}}(0).$$

χ is the portion of the photo-electron wave-function at the absorbing atom caused that was scattered back by neighboring atoms.

The EXAFS Equation: simple description

With $\chi \sim \psi_{\text{scatt}}(0)$, we can model χ from the photo-electron's journey:

- 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

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

where scattering from the neighboring atom gives the amplitude $f(k)$ and phase-shift $\delta(k)$ to the photo-electron.

Development of the EXAFS Equation

Combining terms (including the complex conjugate), we get

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

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

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

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:

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

The Photo-Electron Mean-Free Path

To get 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 . But ...

The photo-electron can also scatter *inelastically*, and may not be able to get back the absorbing atom.

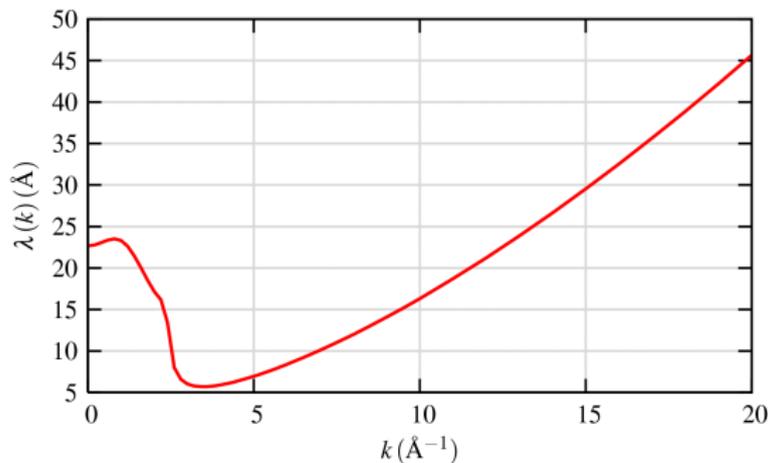
Plus: the core-level has a finite lifetime, limiting how far the photo-electron can go out and make it back coherently. Using a damped wave-function:

$$\psi(k, r) \sim \frac{e^{ikr} e^{-r/\lambda(k)}}{kr}$$

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

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

The Photo-Electron Mean-Free Path



λ depends strongly on k , but $\lambda < 25 \text{ \AA}$ for the EXAFS k -range. The λ and R^{-2} terms make EXAFS a *local atomic probe*.

Note: that λ (and R^{-2}) gets large at very low k (the XANES region).

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).

The EXAFS Equation

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

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

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: $f(k)$ and $\delta(k)$, and the mean-free-path $\lambda(k)$ we can determine:

R distance to neighboring atom.

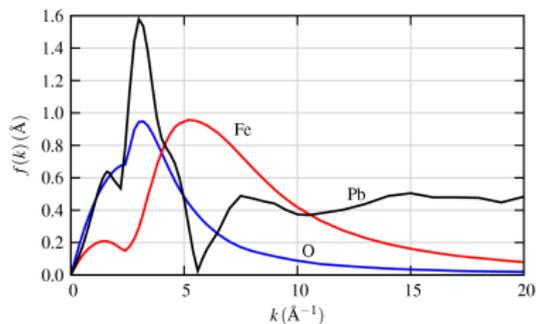
N coordination number of neighboring atom.

σ^2 mean-square disorder of neighbor distance.

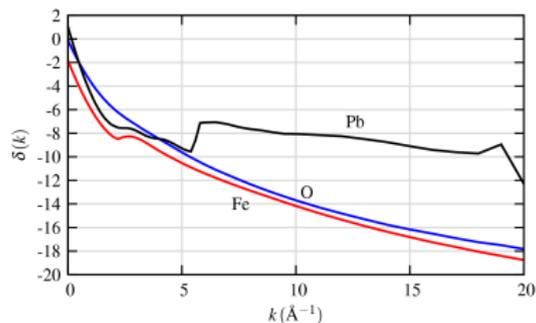
The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number, so that XAFS is also sensitive to Z of the neighboring atom.

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

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number.



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



The phase shift $\delta(k)$ shows sharp changes for very heavy elements.

These functions can be calculated accurately (say with the program FEFF) for modeling EXAFS.

Z can usually be determined to ± 3 . Fe and O can be distinguished, but Fe and Mn cannot be.

Calculating $f(k)$ and $\delta(k)$ with FEFF

These days, we can calculate $f(k)$ and $\delta(k)$ 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 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 $f(k)$, $\delta(k)$, $\lambda(k)$ for a particular scattering “shell” or “scattering path” for that cluster of atoms.

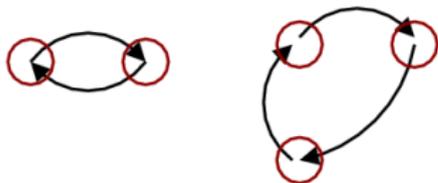
Many analysis programs use these FEFF files directly to model EXAFS data.

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, 3rd neighbor, ...), and can include **multiple-scattering paths**:

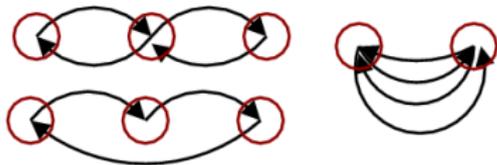
Single Scattering Triangle Paths



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.

Focussed Multiple Scattering Paths



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

Multiple Scattering is strongest when $\theta > 150^\circ$.

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

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

XAFS Data Reduction: Strategy

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

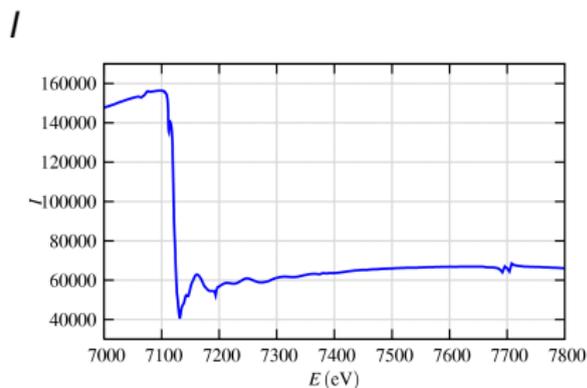
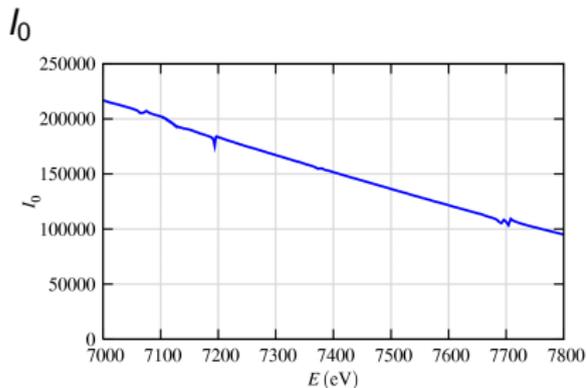
- 1 convert measured intensities to $\mu(E)$
- 2 subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
- 3 normalize $\mu(E)$ to go from 0 to 1, so that it represents the absorption of 1 x-ray.
- 4 remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS χ .
- 5 identify the threshold energy E_0 , and convert from E to k space:
$$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$$
- 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.

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

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

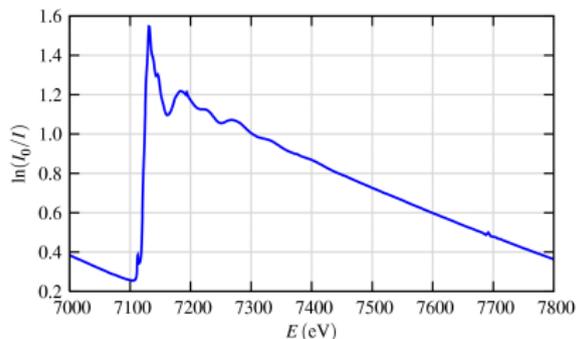
Starting with measured intensities before and after the sample, we construct

$\mu(E)$:



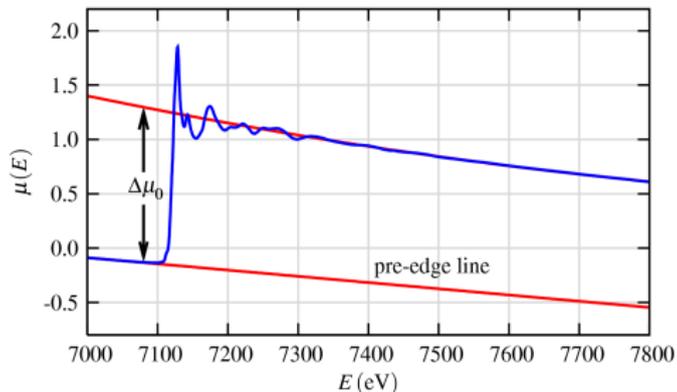
For Transmission XAFS

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



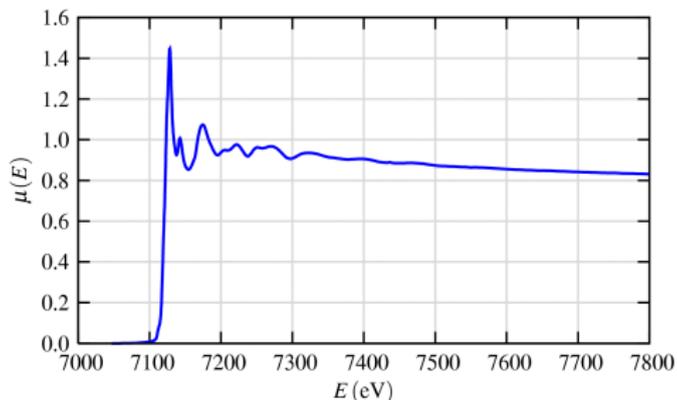
Data Reduction: Pre-Edge Subtraction, Normalization

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



Pre-Edge Subtraction

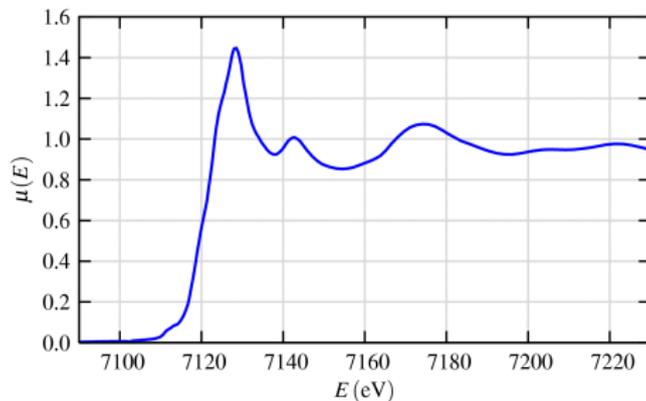
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

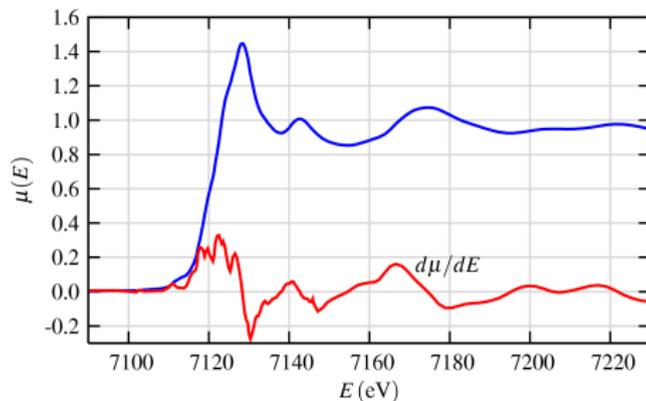
We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge. We normalize by this value to get the absorption from 1 x-ray.

Data Reduction: Normalized XANES and E_0



XANES

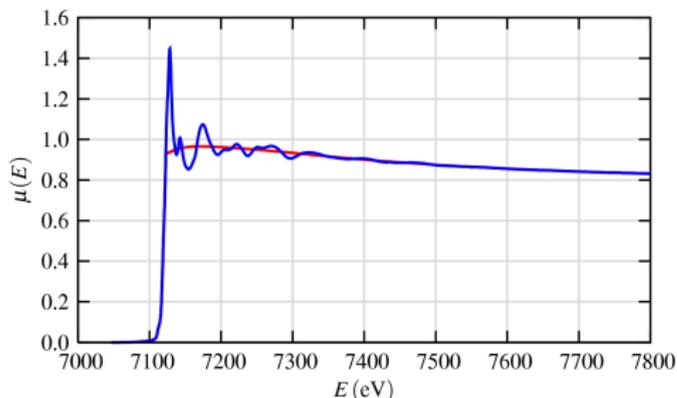
The XANES portion (below) shows a fairly rich spectral structure. We'll come back to this for XANES analysis.



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.

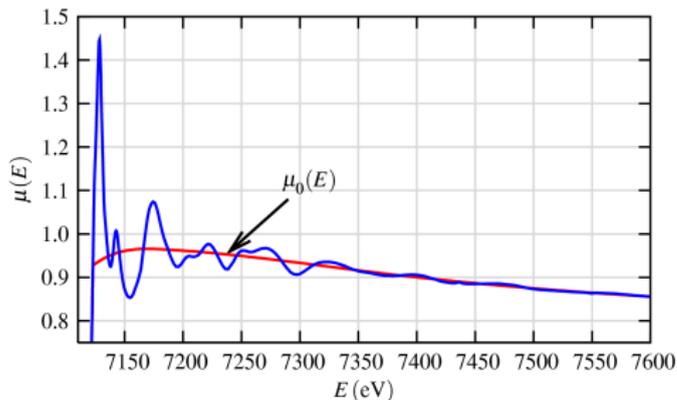
Data Reduction: Post-Edge Background Subtraction



Post-Edge Background

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

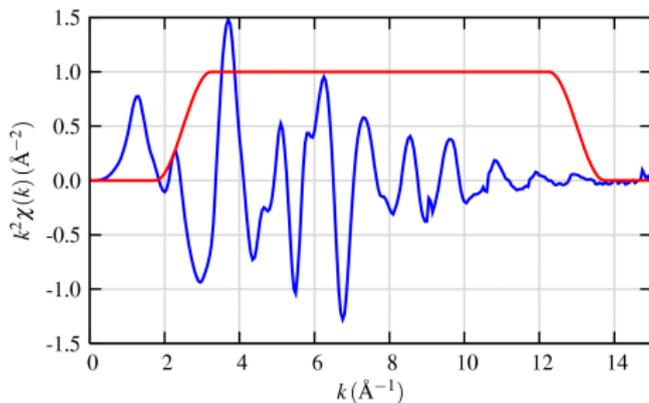
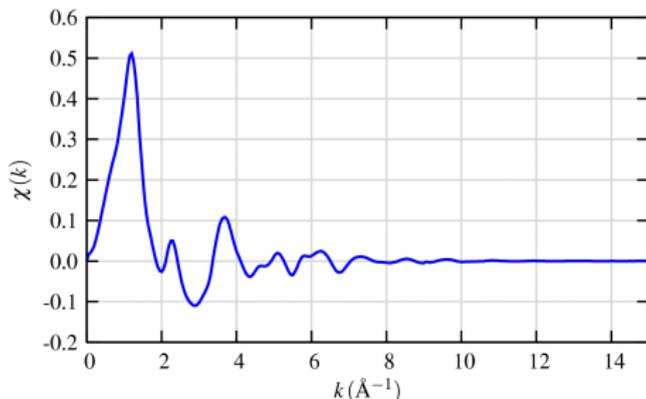
We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.



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



$\chi(k)$

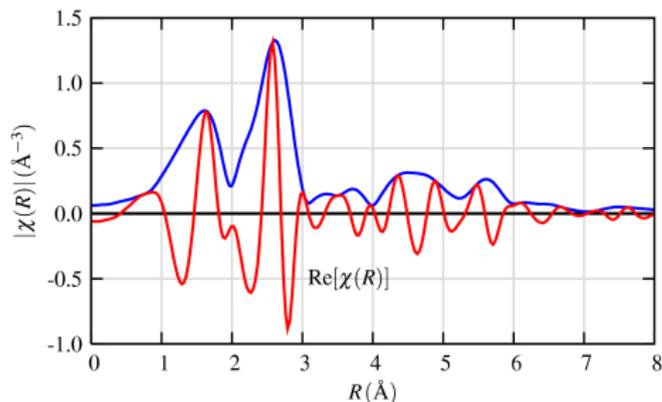
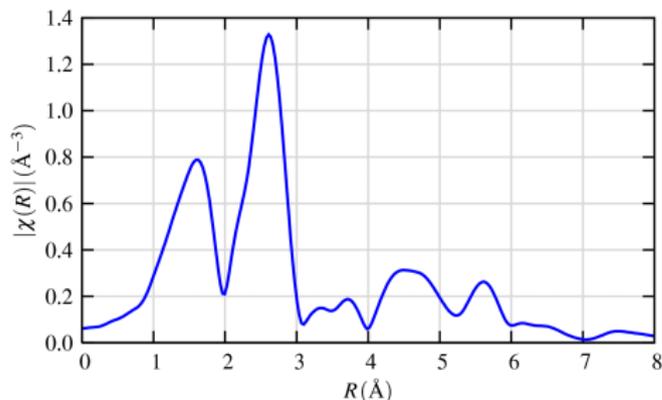
The raw EXAFS $\chi(k)$ usually decays quickly with k , and difficult to assess or interpret by itself.

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*.

EXAFS Fourier Transform: $\chi(R)$



$\chi(R)$

The Fourier Transform of $k^2\chi(k)$ has 2 main peaks for the Fe-O and Fe-Fe shells.

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

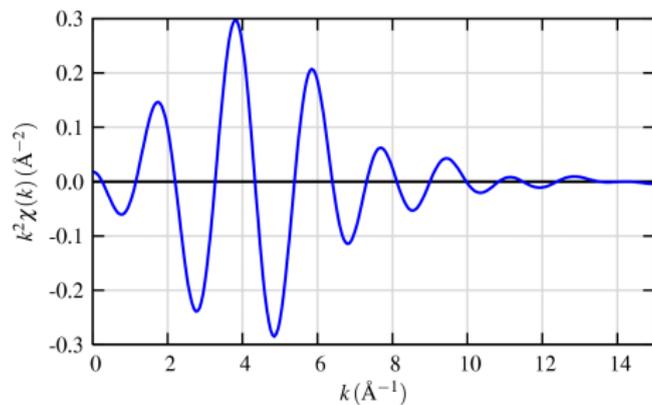
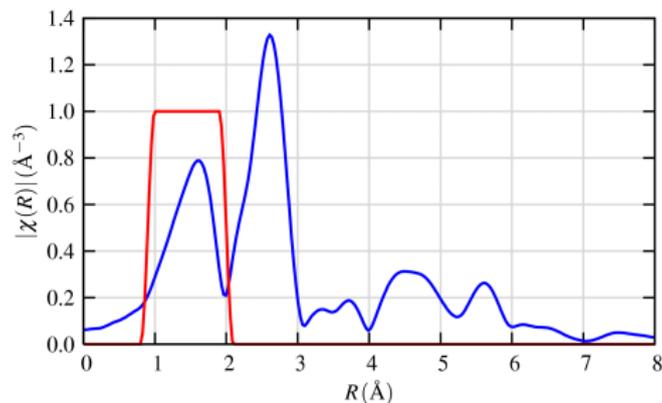
A shift of -0.5Å is typical.

$\chi(R)$ is complex:

The FT makes $\chi(R)$ complex. Usually only the amplitude is shown.

In data modeling, both real and imaginary components are used.

Fourier Filtering



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

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

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.

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)

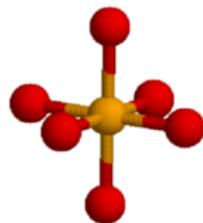
Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).

Use as much other information about the system as possible!

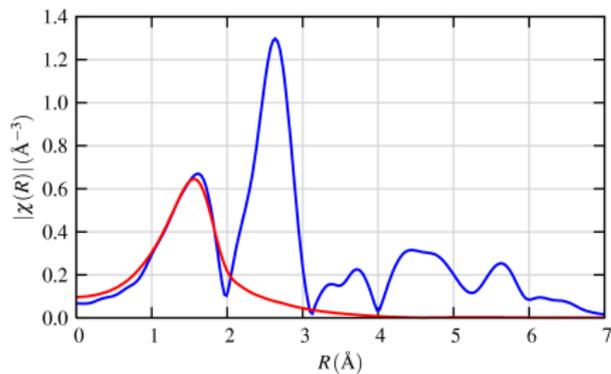
EXAFS Analysis: Modeling the 1st Shell of FeO

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude $f(k)$ and phase-shift $\delta(k)$, 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.

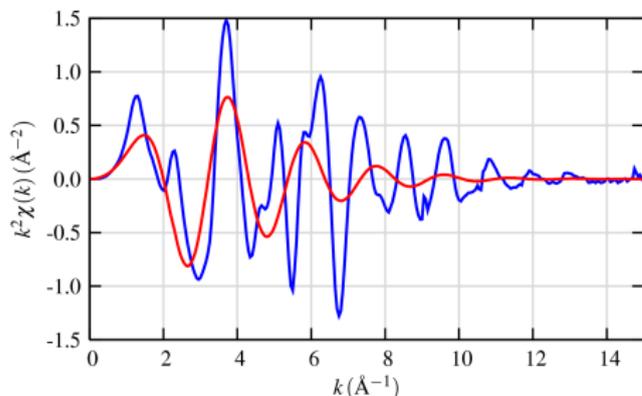


Fit results:

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

$|\chi(R)|$ for FeO data and 1st shell fit.

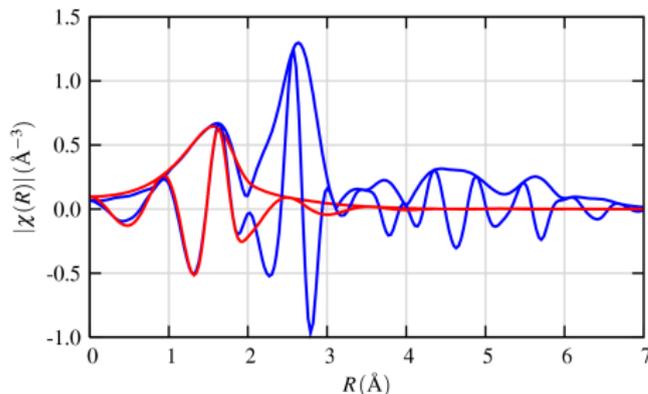
EXAFS Analysis: 1st Shell of FeO



1st shell fit in k space.

The 1st shell fit to FeO in k space.

There is clearly another component in the XAFS!



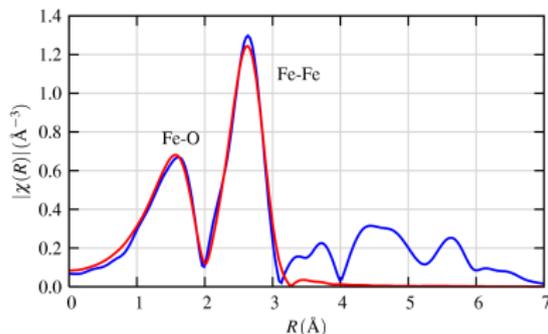
1st shell fit in R space.

$|\chi(R)|$ 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

Adding the second shell Fe to the model, with $f(k)$ and $\delta(k)$ for Fe-Fe, and refining R , N , σ^2 :



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

These results are consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

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

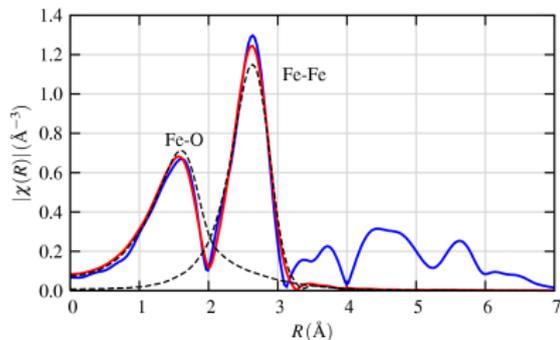
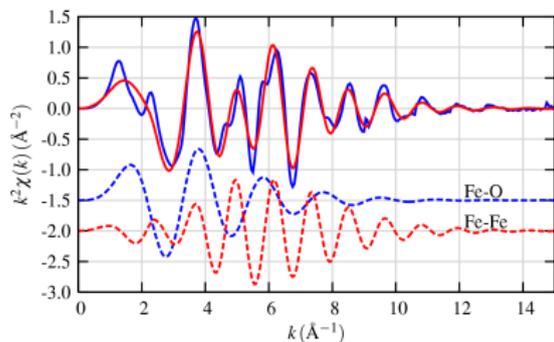
Shell	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

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

The calculation for $f(k)$ and $\delta(k)$ are good, but not perfect!

EXAFS Analysis: Second Shell of FeO

Other views of the data and fit:

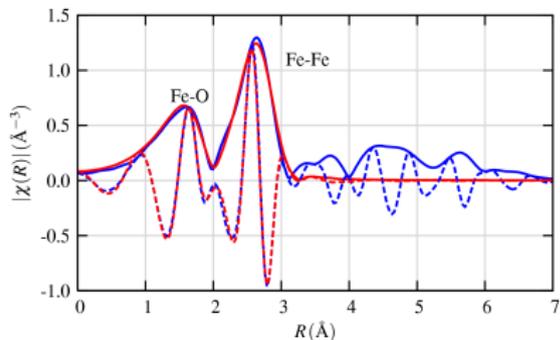


The Fe-Fe EXAFS extends to higher- k than the Fe-O EXAFS.

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!



Where To Go From Here

Lots more tutorial information: <http://xafs.org/>

Books and Review Articles: *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, in *Chemical Analysis* **92**, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988.
Basic Principles and Applications of EXAFS, Chapter 10 in *Handbook of Synchrotron Radiation*, pp 995–1014. E. A. Stern and S. M. Heald, E. E. Koch, ed., North-Holland, 1983