An Introduction to XAFS

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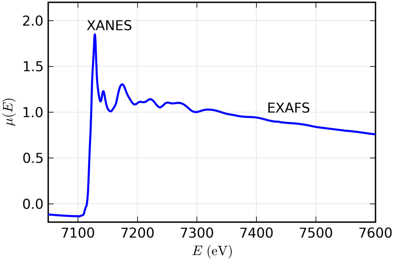
Slides for this talk: https://tinyurl.com/Larch2018
https://millenia.cars.aps.anl.gov/gsecars/Data/Larch/2018Workshop

X-ray Absorption Spectroscopy: XAS, XAFS, EXAFS and XANES.

X-ray Absorption Spectroscopy (XAS) is the modulation of the X-ray absorption coefficient at energies at and above an X-ray absorption edge.

XAFS	X-ray Absorption Fine-Structure Spectroscopy (= XAS)
XANES	X-ray Absorption Near-Edge Spectroscopy
EXAFS	Extended X-ray Absorption Fine-Structure

These contain information about an element's chemical state (XANES) and local atomic environment (EXAFS).



Fe *K*-edge XAFS for FeO.

Main XAS Characteristics:

- local atomic coordination
- valence, oxidation state
- applies to any element ($Z > 2$) .
- works at low concentrations (ppm, μM)
- minimal sample requirements.
- independent of crystal structure, isotope.

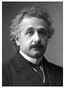
X-Ray Absorption and the Photo-Electric Effect

X-rays are absorbed by all matter through the *photo-electric effect*:

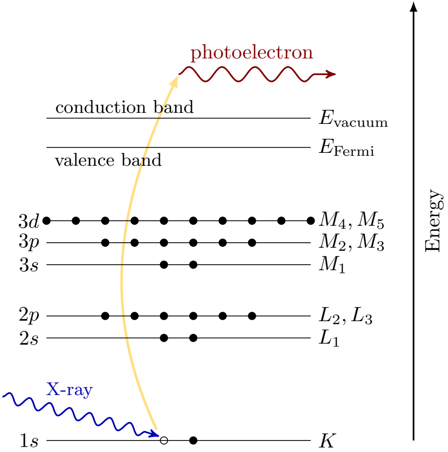
An atom absorbs an x-ray when the x-ray energy is transferred to a core-level electron (*K*, *L*, or *M* shell).

The atom is left in an *excited state* with a *core hole* – an empty electronic level.

Any excess energy from the x-ray is given to an ejected *photo-electron*.



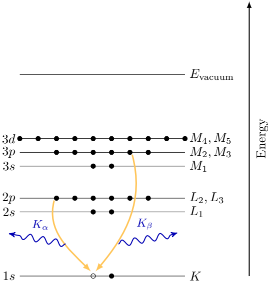
A. Einstein, Nobel Prize, 1921 "For his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect".



X-ray Fluorescence and Auger emission

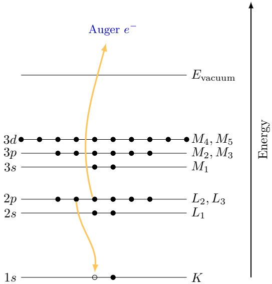
After X-ray absorption, the excited atom relaxes to the ground state. A higher level electron fills the core hole, and a *fluorescent X-ray* or *Auger electron* is emitted.

X-ray Fluorescence: Emit an X-ray with energy given by core-levels energies.



Charles Barkla, Nobel Prize, 1917 “discovery of the characteristic Röntgen radiation of the elements”

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



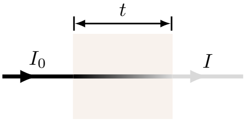
Lise Meitner, no Nobel Prize, first to discover Auger effect, explained nuclear fission.

X-ray fluorescence and Auger emission have discrete energies, characteristic of the absorbing atom – very useful for identifying atoms!

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:

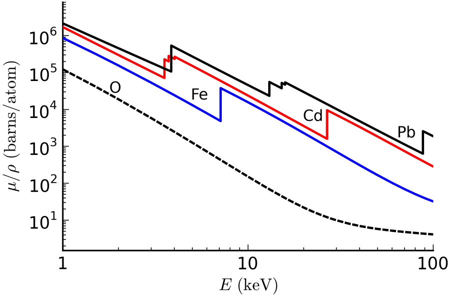
$$I = I_0 e^{-\mu t}$$



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:

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



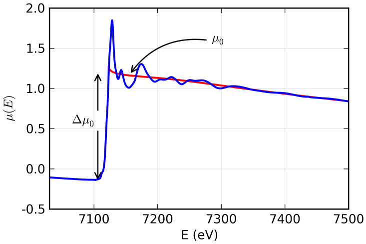
Plus: μ has sharp *Absorption Edges* corresponding to the characteristic core-level energies of the atom.

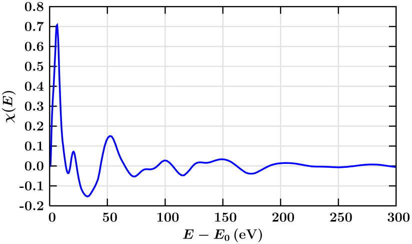
EXAFS: Extended X-ray Absorption Fine Structure

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

$$\mu(E) = \mu_0(E)[1 + \chi(E)] \qquad\qquad \chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

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





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

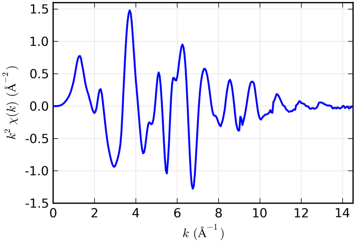
$\chi(E)$ for FeO, with $E_0 = 7122$ eV.

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

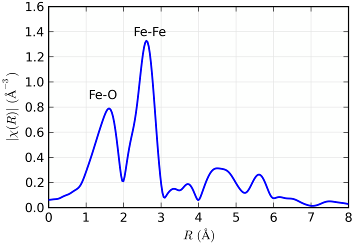
XAFS is an *interference effect*, using the wave-nature of the photo-electron. We express the XAFS in terms of *photo-electron wavenumber*, k:

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

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. Similar to a Pair Distribution Function from scattering techniques.

The EXAFS Equation

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

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

where $f(k)$ and $\delta(k)$ are *photo-electron scattering properties* of the neighboring atom [and $\lambda(k)$ is the photo-electron mean-free-path].

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.

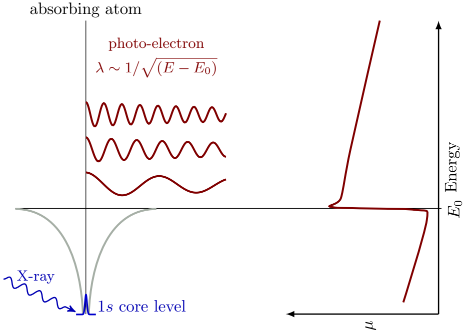
$f(k)$ and $\delta(k)$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

Development of the EXAFS Equation

the short version

X-ray Absorption by a Free Atom

An atom absorbs an x-ray (energy E), destroying a core electron (energy E_0) and creating a photo-electron (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:

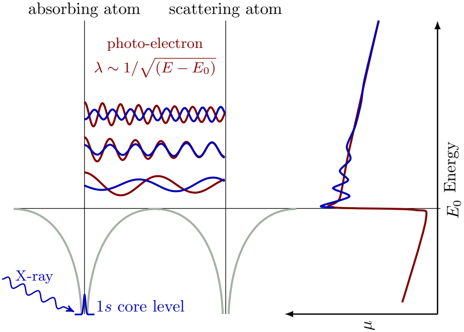
No available state:
No absorption

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. The amplitude of the photo-electron scattered back to *the absorbing atom* will cause oscillations in $\mu(E)$.



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 scattered photoelectron partially fills that state.

XAFS oscillations are due to the interference of the outgoing photo-electron with the photo-electron scattered from neighboring atoms.

The EXAFS Equation: simple description

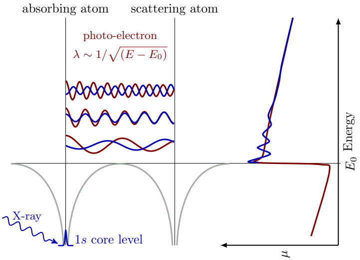
The XAFS – the change in μ – is the *overlap* of the returning, scattered photo-electron with the tightly bound core electron

With a spherical wave for the photo-electron:

$$\psi(k,r) = e^{ikr}/kr$$

$\chi(k)$ is due to the photo-electron:

1. leaves the absorbing atom
2. scatters from the neighbor atom
3. returns to the absorbing atom



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

$f(k)$ the scattering amplitude for the atom.

$\delta(k)$ the scattering phase-shift for the atom.

Development of the EXAFS Equation: Coordination Sphere

Including the complex conjugate, and insisting on a real result, we get

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

The EXAFS Equation for 1 scattering atom.

For N neighboring atoms, with (thermal and static) disorder in the distribution of R described by σ^2, we have

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

In general, we would integrate over the *Partial* Pair distribution function, $g(R)$. Using N, R, and σ^2, is a common simplification.

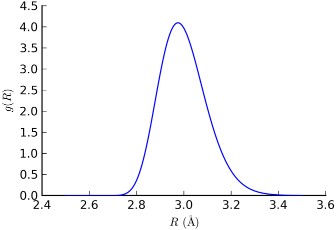


Photo-Electron Mean-Free Path

We used a spherical wave for the photo-electron, $\psi(k,r) \sim e^{ikr}/kr$ to get to

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

The photo-electron can also scatter *inelastically*, and may not be able to get back the absorbing atom in tact (in phase, at energy).

Plus: the core-level has a *finite lifetime*, before it is filled. This also limits how far the photo-electron can go out.

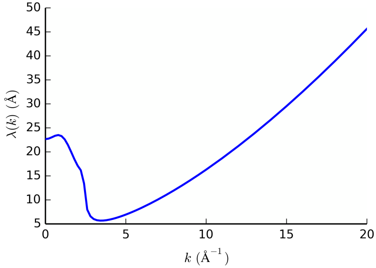
A *mean free path* – λ – describes how far the photo-electron can go before it loses energy/coherence.

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

Photo-Electron Mean-Free Path

Using $\psi(k,r) \sim \dfrac{e^{ikr}e^{-r/\lambda(k)}}{kr}$ adds a term to the EXAFS equation:

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

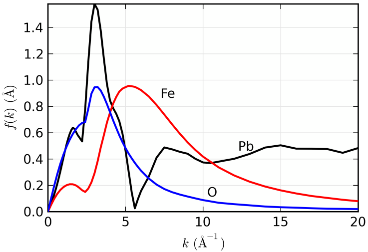


- $\lambda \lesssim 30\,\text{Å}$ for $k > 3\,\text{Å}^{-1}$.
- This (and the R^{-2}) makes EXAFS a *local atomic probe*.
- λ increases at low k.
- XANES is less a *local probe* than EXAFS.

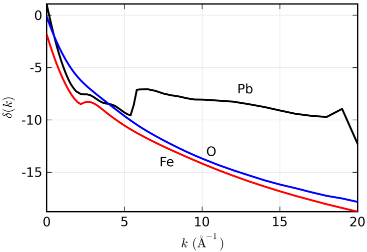
λ has a universal and strong k dependence, but is mostly independent of the material.

Scattering Amplitude and Phase-Shift

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



$f(k)$ extends to higher k values for higher Z elements. For very heavy elements, there is structure in $f(k)$.



$\delta(k)$ shows sharp changes for very heavy elements. These functions can be calculated for modeling EXAFS.

These complex factors allow EXAFS to distinguish the species of neighboring atom:

Z can usually be determined to ± 5.
Fe and O can be distinguished, but not Fe and Mn.

The EXAFS Equation

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

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where $f(k)$ and $\delta(k)$ are *photo-electron scattering properties* of the neighboring atom [and $\lambda(k)$ is the photo-electron mean-free-path].

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

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XAFS Data Reduction

XAFS Data Reduction

We begin with *Data Reduction*:

Converting measured data to $\mu(E)$ and then to $\chi(k)$

This won't tell us R, N, and neighbor species, but it will:

1. help us determine data quality
2. can be useful for "spectroscopic" analysis: fingerprinting, linear combinations of spectra, etc.
3. needed to get to $\chi(k)$ for further modeling.

XAFS Data Reduction: Strategy

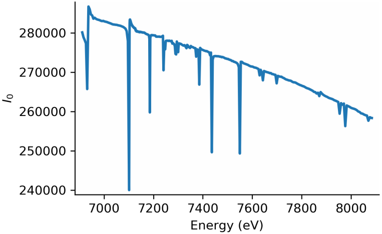
Step for reducing measured data to $\mu(E)$ and then to $\chi(k)$:

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. (optional) weight the XAFS $\chi(k)$ and Fourier transform from k to R space.
7. (optional) isolate the $\chi(k)$ for an individual "shell" by Fourier filtering.

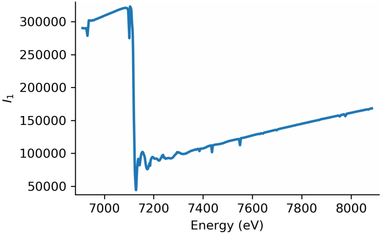
Data Reduction: Converting Raw Data to $\mu(E)$

Starting with measured intensities, we construct $\mu(E)$:

I_0

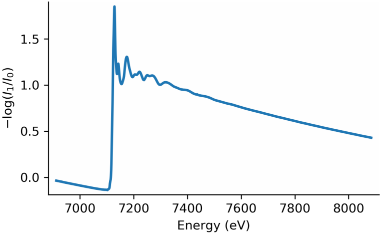


I

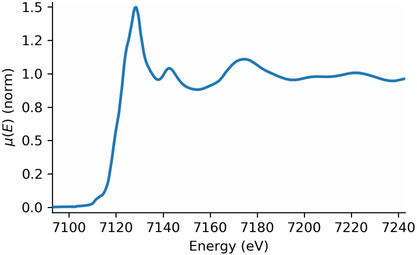


For Transmission XAFS

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

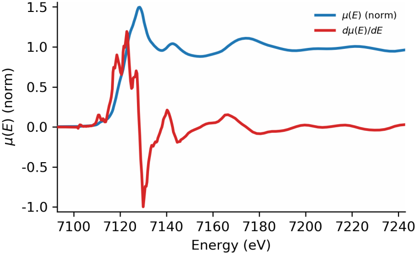


Data Reduction: Normalized XANES and E_0



XANES

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

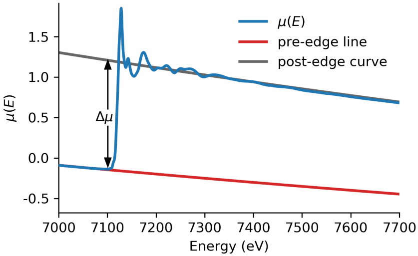


Derivative

We can select E_0 easily as the energy with the maximum derivative. This is somewhat arbitrary, so we may need to refine this value later on.

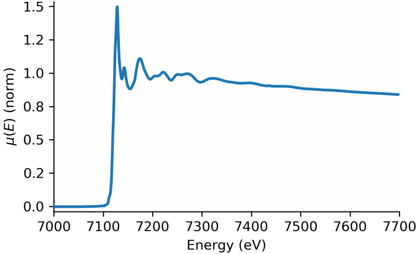
Data Reduction: Pre-Edge Subtraction, Normalization

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



Pre-Edge Subtraction

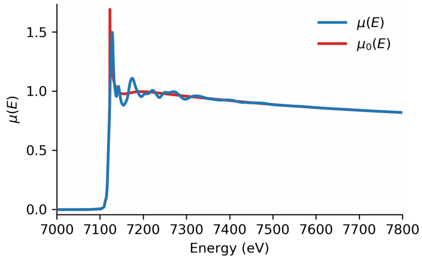
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe $\mathrm{L_{III}}$ edge).



Normalization

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

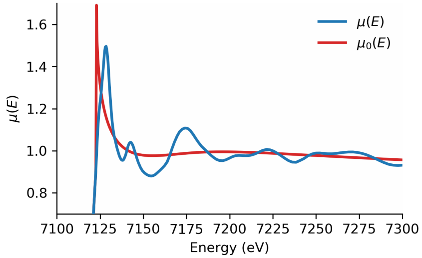
Data Reduction: Post-Edge Background Subtraction



Post-Edge Background

We can't measure $\mu_0(E)$ (the absorption coefficient without neighboring atoms).

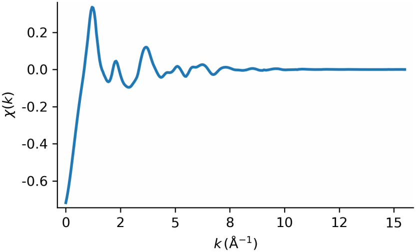
We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.



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 $\mu_0(E)$.

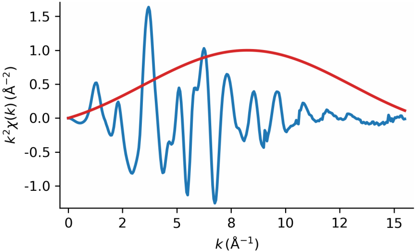
Data Reduction: $\chi(k)$, k-weighting



$\chi(k)$

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

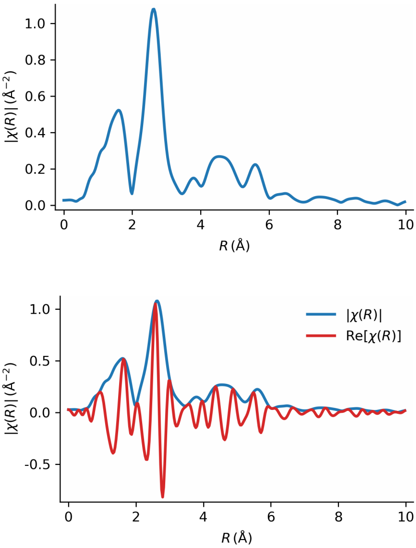
It is customary to weight the higher-k portion of the spectra by multiplying by k^2 or k^3.



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.

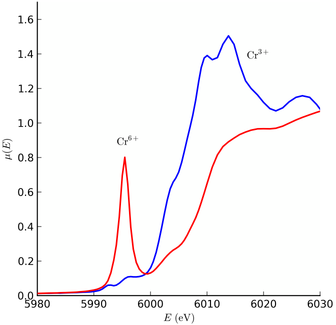
In data modeling, both real and imaginary components are used.

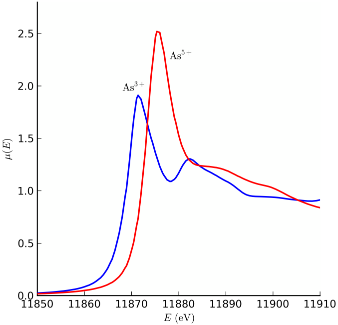
XANES

XANES: X-ray Absorption Near-Edge Spectra

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

what are the lowest-energy unoccupied states?



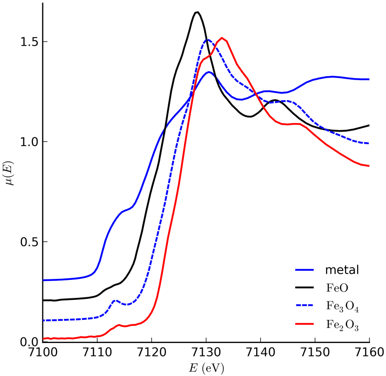


XANES Analysis approaches:

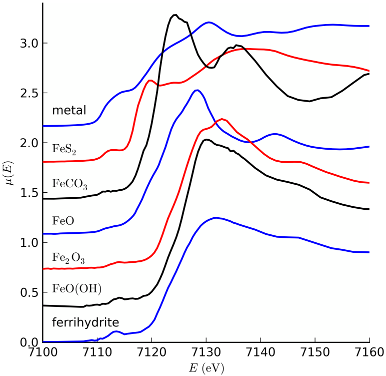
Linearly combine known spectra to match measured spectra.

ab initio calculations to map features to electronic density of states.

Fe K-edge XANES



Edge shifts and Heights and positions of *pre-edge peaks* can also determine valence state.



Fe *K*-edge XANES for several compounds. XANES can be used to *fingerprint* chemical and mineral phases.

XANES Interpretation

The EXAFS Equation breaks down at low-k, as 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 *semi-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.

What electronic states can the photo-electron fill?

XANES calculations are becoming reasonably accurate. These can help interpret spectra in terms of *bonding orbitals* and/or *density of states*.

XANES: Summary

- *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 . . . .