

# X-ray Absorption Fine-Structure Spectroscopy

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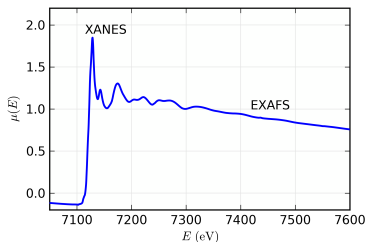
# What Is XAFS?

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

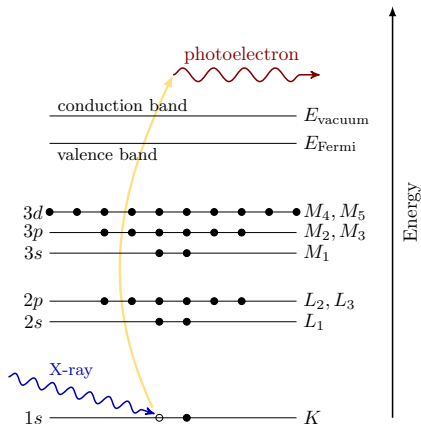
# X-Ray Absorption

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

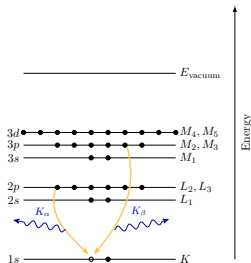


# X-ray Fluorescence

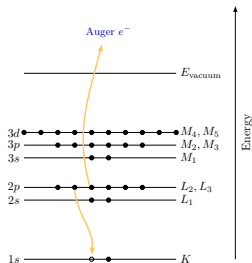
When x-rays are absorbed by the photo-electric effect, the excited core-hole will relax back to a “ground state” of the atom. A higher level core electron drops into the core hole, and a *fluorescent x-ray* or *Auger electron* is emitted.

**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.



$K_{\alpha}$ : L  $\rightarrow$  K,       $K_{\beta}$ : M  $\rightarrow$  K.

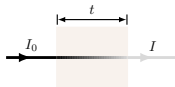


X-ray fluorescence and Auger emission have discrete energies, characteristic of the absorbing atom. They can be used to identify the absorbing atom.

# The X-ray Absorption Coefficient: $\mu$

The intensity of an x-ray beam passing through a material of thickness  $t$  is given by the *absorption coefficient*  $\mu$ :

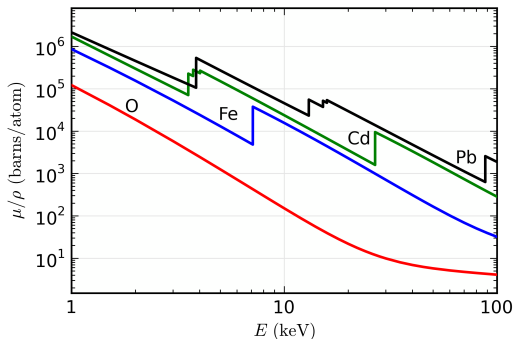
$$I = I_0 e^{-\mu t}$$



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

$\mu$  depends strongly on x-ray energy  $E$  atomic number  $Z$ , and also on density  $\rho$ , and Atomic mass  $A$ :

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

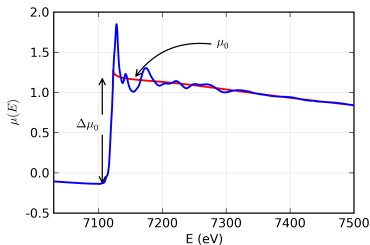


# EXAFS: Extended X-ray Absorption Fine Structure

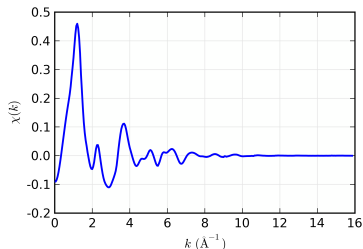
We're interested in the energy oscillations in  $\mu(E)$ , as these will tell us something about the neighboring atoms. We define the EXAFS as:

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

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  $\chi$  normalized to 1 absorption event:



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



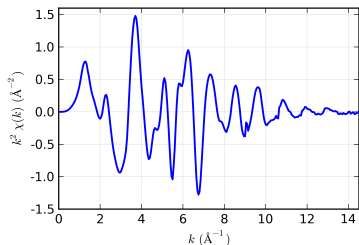
$\chi(E)$  for FeO, with  $E_0 = 7122$  eV.

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

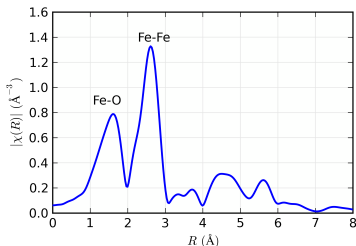
XAFS is an *interference effect*, using the wave-nature of the photo-electron. We express the XAFS in terms of *photo-electron wavenumber*,  $k$ :

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

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 "Pair Distribution Functions" from other scattering techniques.

# The EXAFS Equation

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

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

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.
- $\sigma^2$  mean-square disorder of neighbor distance.

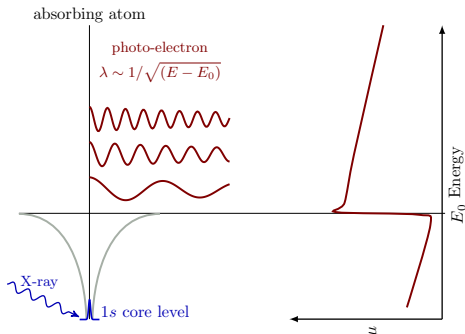
$f(k)$  and  $\delta(k)$  depend on atomic number  $Z$  of the scattering atom, so we can also determine the species of the neighboring atom.



*Development of the EXAFS Equation*

# 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:

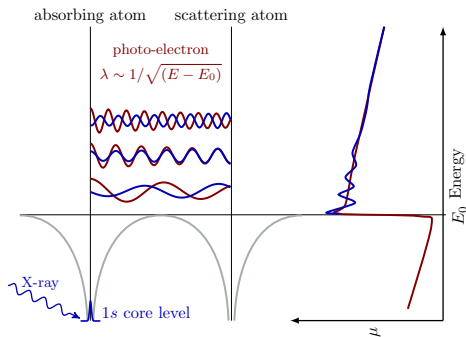
No available state:  
No absorption

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.

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

The scattered photoelectron partially fills that state.

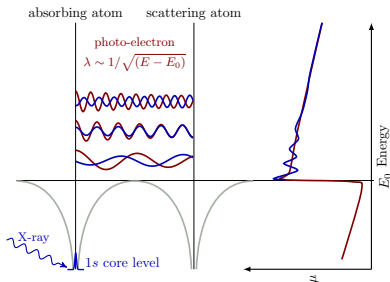
The XAFS oscillations are an interference effect of the photo-electron with itself, due to the presence of neighboring atoms.

# X-ray Absorption: Fermi's Golden Rule

Going back to our definition

$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$

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* 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.

## $\mu$ and $\chi$ and the photo-electron wavefunction

Writing  $|f\rangle = |f_0 + \Delta f\rangle$ , where  $\Delta f$  gives the change in photo-electron final state due to backscattering from the neighboring atom, we can expand  $\mu$  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  $\mu(E) = \mu_0(E)[1 + \chi(E)]$  and we see

$$\begin{aligned} \mu_0(E) &\sim |\langle i|\mathcal{H}|f_0\rangle|^2 && \text{(atomic background)} \\ \chi(E) &\sim \langle i|\mathcal{H}|\Delta f\rangle \sim \langle i|\Delta f\rangle && \text{(XAFS oscillations)} \end{aligned}$$

Since the *initial state* – the core-level – is very nearly a delta-function in space, centered at the absorbing atom:

$$\chi \sim \langle i|\Delta f\rangle \sim \int dr \delta(r) \psi_{\text{scatt}}(r) = \psi_{\text{scatt}}(r=0).$$

$\chi$  is due to the portion of the photo-electron wave-function at the absorbing atom caused that was scattered back by neighboring atoms.

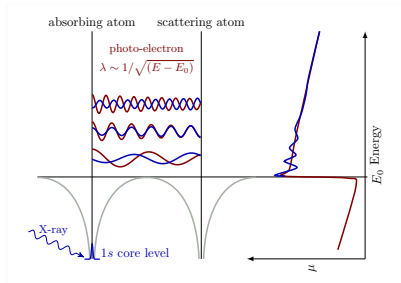
# The EXAFS Equation: simple description

With  $\chi \sim \psi_{\text{scatt}}(0)$ , and a spherical wave for the photo-electron

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

we can model  $\chi(k)$  as the photo-electron

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



$$\chi(k) \sim \psi_{\text{scatt}}(0) = \frac{e^{ikR}}{kR} [2kf(k)e^{i\delta(k)}] \frac{e^{ikR}}{kR} + \text{C.C.}$$

where scattering from the neighboring atom gives:

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

## Development of the EXAFS Equation

Including the complex conjugate, and insisting on a Real value, we get

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

The EXAFS Equation for 1 scattering atom.

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

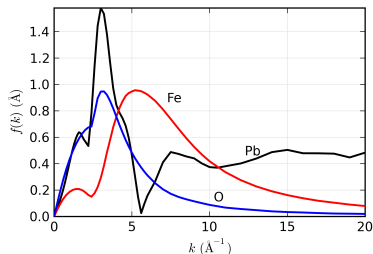
$$\chi(k) = \frac{Nf(k)e^{-2k^2\sigma^2}}{kR^2} \sin[2kR + \delta(k)]$$

A real system has atoms at different distances and of different types. We add all these contributions to get a better version of the EXAFS equation:

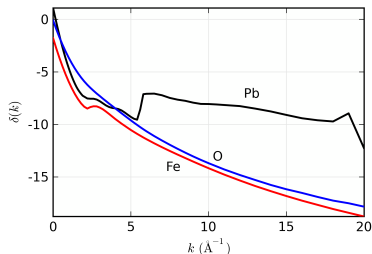
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

# 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 (say with the program FEFF) for modeling EXAFS.

$Z$  can usually be determined to  $\pm 5$ . Fe and O can be distinguished, but Fe and Mn cannot be.



# The EXAFS Equation: What we left out

This simple description so far is qualitatively right, but for quantitative EXAFS calculations, it's important to consider several other points:

*Inelastic Losses* Processes that alter the absorbing atom or photo-electron before the photo-electron scatters back home.

*Extrinsic Losses* photo-electron mean-free path, including complex self-energy and finite core-hole lifetime.

*Intrinsic Losses* relaxation of absorbing atom due to the presence of the core hole.

*Multiple Scattering* the photo-electron can scatter multiple times, which is important at low  $k$ , and can be important at high  $k$  for some systems.

Calculations *should* include these effects, and mostly do.

We'll discuss these in more detail . . . .

## The EXAFS Equation: Even more stuff we left out ...

These effects also need to be considered for quantitative EXAFS calculations:

*Curved Wave Effects* scattering calculation needs a partial wave expansion.

*Muffin-Tin Approximation*: scattering calculation needs a real-space potential, and a muffin-tin approximation is tractable, but not perfect.

*Polarization Effects* synchrotron beams are highly polarized, which needs to be taken into account in anisotropic samples. This is simple for  $K$ -edges ( $s \rightarrow p$  is dipole), and less so for  $L$ -edges (where both  $p \rightarrow d$  and  $p \rightarrow s$  contribute).

*Disorder Terms* thermal and static disorder in real systems should be properly considered: A topic of its own.

We'll skip the details on these.

## Photo-Electron Mean-Free Path (extrinsic losses)

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:

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

But ...

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

A *mean free path* ( $\lambda$ ) describes how far the photo-electron can go before it scatters, losing energy to other electrons, phonons, etc.

*Plus*: the core-level has a *finite lifetime*, also limiting how far the photo-electron can go out and make it back to “the same” absorbing atom.

# Photo-Electron Mean-Free Path

To account for the mean-free-path, we can replace the spherical photo-electron wavefunction:

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

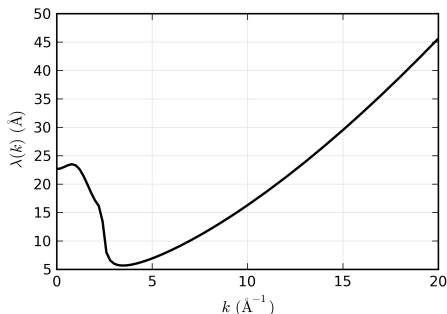
with a damped wave-function:

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

which simply adds another term to the EXAFS equation:

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

# The Photo-Electron Mean-Free Path



$\lambda$  is mostly independent of the system, and depends strongly on  $k$ :

- For  $3 \text{\AA}^{-1} < k < 15 \text{\AA}^{-1}$ ,  $\lambda < 30 \text{\AA}$
- This (and the  $R^{-2}$  term) makes EXAFS a *local atomic probe*.
- For XANES ( $k < 3 \text{\AA}^{-1}$ ) Both  $\lambda$  and  $R^{-2}$  get large:  
XANES is not really a *local probe*.

## $S_0^2$ : Amplitude Reduction Term (intrinsic losses)

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

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

$|\Phi_0^{N-1}\rangle = (N - 1)$  electrons in unexcited atom.

$|\Phi_f^{N-1}\rangle = (N - 1)$  electrons, relaxed by core-hole.

$S_0^2$  is usually taken as a constant:

$$0.7 < S_0^2 < 1.0$$

and is used as a Fitting Parameter that multiplies  $\chi$ :

$S_0^2$  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: Sum over Paths (vs. "Shells")

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

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

where the sum could be over *shells* of atoms (Fe-O, Fe-Fe) or ...  
over *scattering paths* for the photo-electron.

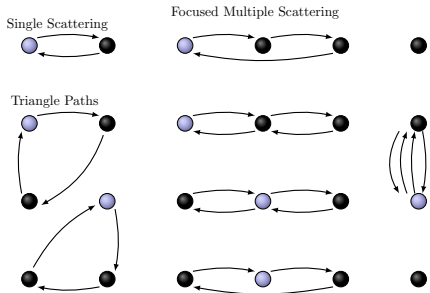
These are nearly the same concept.

Using *scattering path* more easily allows multiple-scattering.

If we know the  $f(k)$  and  $\delta(k)$ , and  $\lambda(k)$  we can determine  $Z$ ,  $R$ ,  $N$ , and  $\sigma^2$  for scattering paths to the neighboring atoms.

# Sum over Paths and Multiple Scattering

A sum over scattering paths allows *multiple-scattering paths*: the photo-electron scatters from *more than one atom* before returning to the central atom:



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 **focused** through one atom to the next.

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

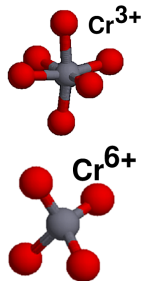
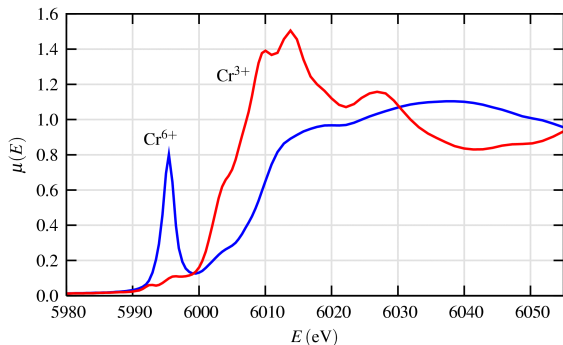
The strong angular dependence can be used to measure bond angles.

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



# *XANES*

# XANES: Oxidation State and Coordination Chemistry



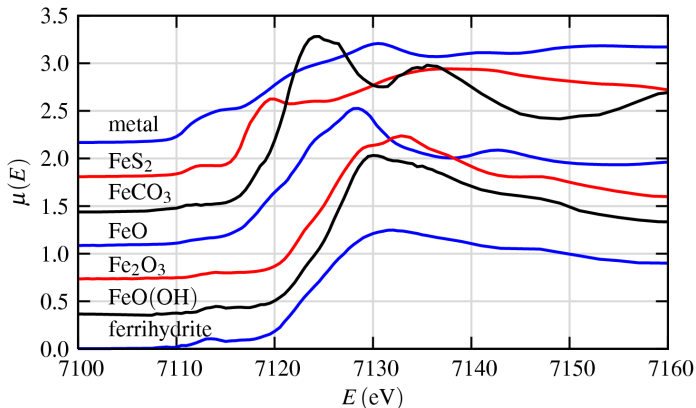
The XANES of Cr<sup>3+</sup> and Cr<sup>6+</sup> shows a dramatic dependence on oxidation state and coordination chemistry.

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.

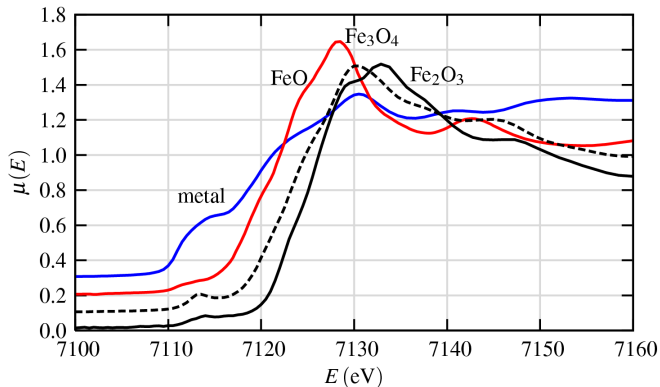
# XANES: Oxidation State

Fe K-edge XANES from several compounds:



XANES can be used as a fingerprint of phases.

# 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 ions).

# 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.

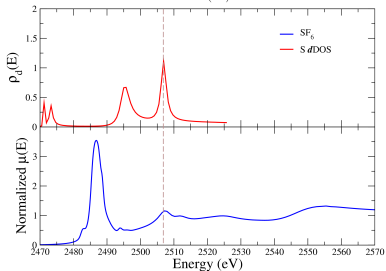
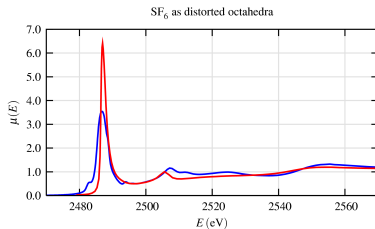
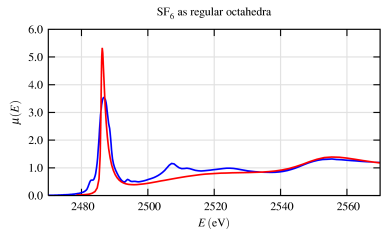
What electronic states can the photo-electron fill?

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

# XANES calculation: SF<sub>6</sub>

A typical *ab initio* XANES calculation FEFF8:

Can model principle features and show sensitivity to structural changes:



SF<sub>6</sub> : an octahedral complex with bond length 1.54 Å.

Including an off-center distortion mixes *d* character into the final *p* state. The peak near 2507 eV in the *d*DOS gives a peak in the XANES.

*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 . . . .