X-ray Absorption Fine-Structure Spectroscopy

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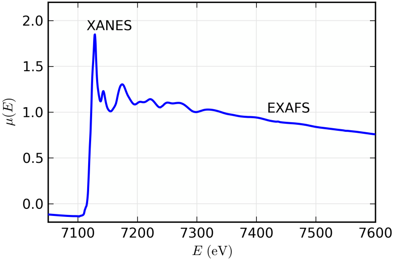
X-ray Absorption Spectroscopy: XAS, XAFS, EXAFS and XANES.

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.

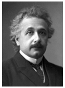
X-Ray Absorption and the Photo-Electric Effect

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

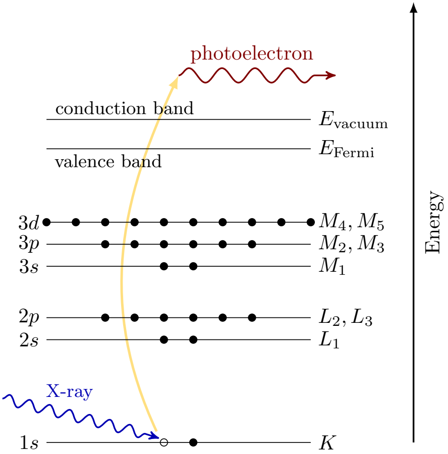
An atom absorbs an x-ray when the x-ray energy is transferred to a core-level electron (*K*, *L*, or *M* shell).

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*.



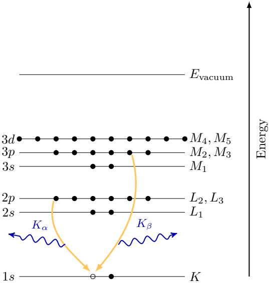
A. Einstein, Nobel Prize, 1921 "For his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect".



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.



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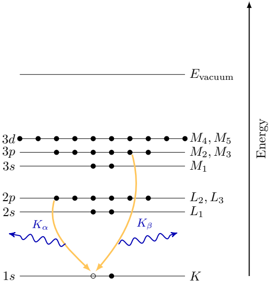

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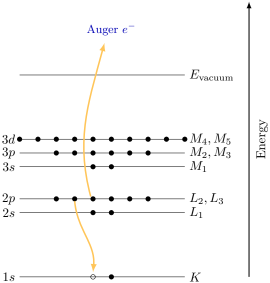
Auger Effect: Promote an electron from another core-level to the continuum.



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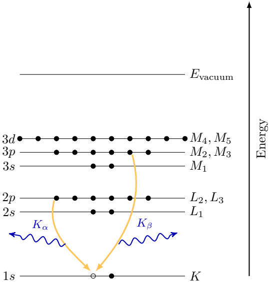

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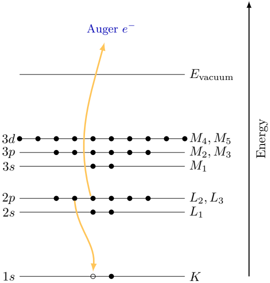

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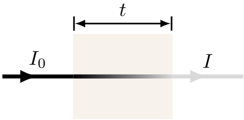
X-ray fluorescence and Auger emission have discrete energies, characteristic of the absorbing atom – very useful for identifying atoms!

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:

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



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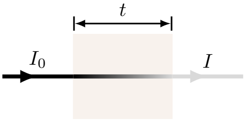

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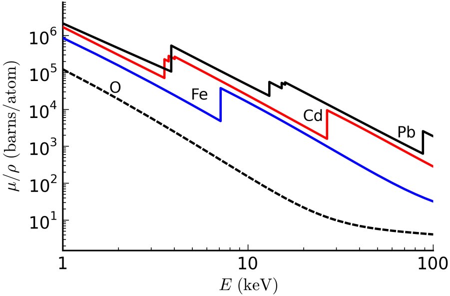
μ depends strongly on x-ray energy E atomic number Z, and also on density ρ, and Atomic mass A:

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



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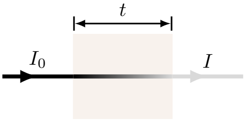

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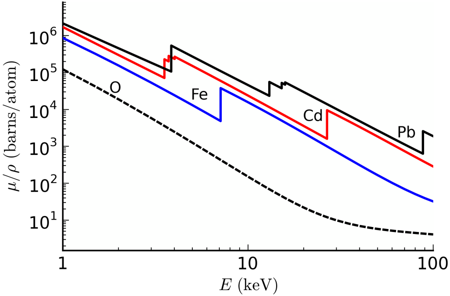
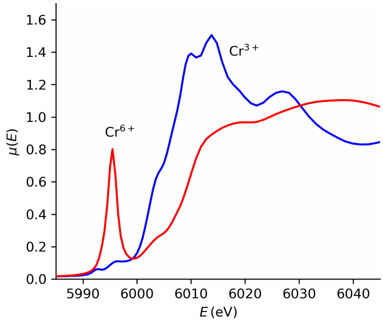


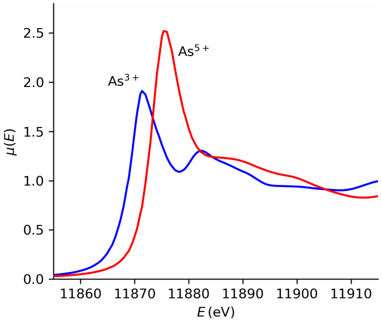
Plus: μ has sharp *Absorption Edges* corresponding to the characteristic core-level energies of the atom.

XANES: X-ray Absorption Near-Edge Spectra

Within ∼50eV of the absorption edge, the X-ray Absorption Spectra is highly sensitive to the chemical state and formal valence of absorbing element:



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



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

what are the unoccupied electronic states that the photo-electron can fill?

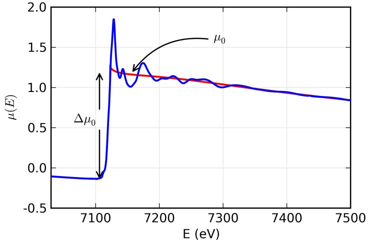
EXAFS: Extended X-ray Absorption Fine Structure

Even far above the edge, there are oscillations in $\mu(E)$ that are sensitive to the positions and types of atoms neighboring the absorbing atom.

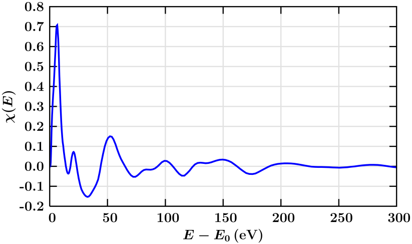
We define the EXAFS as:

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

We subtract off a smooth *"bare atom" background* $\mu_0(E)$, and divide by the *"edge step"* $\Delta\mu_0(E_0)$ to get χ, the EXAFS oscillations:



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



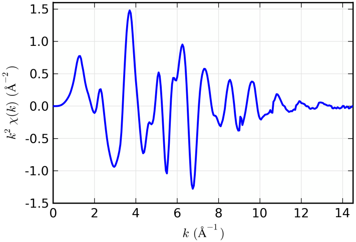
$\chi(E)$ for FeO, with $E_0 = 7122$ eV.

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

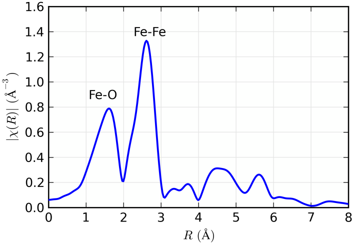
XAFS is an *interference effect*, using the wave-nature of the photo-electron. We express the XAFS in terms of *photo-electron wavenumber*, k:

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

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:

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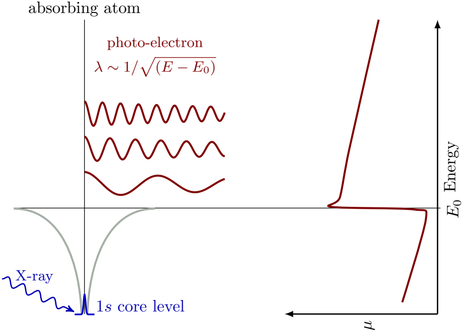
R	distance to neighboring atom.
N	coordination number of neighboring atom.
σ^2	mean-square disorder of neighbor distance.

$f(k)$ 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

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.



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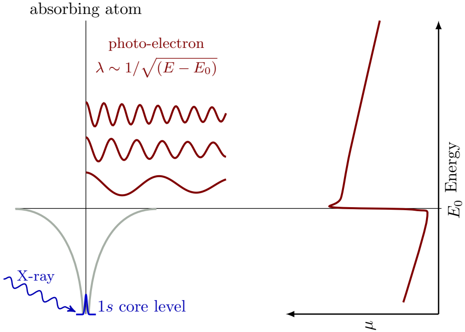

X-ray absorption needs an available state for the photo-electron to go into:

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.

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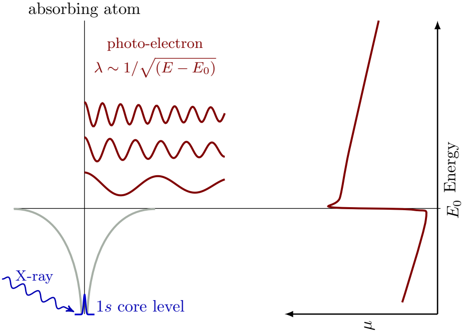

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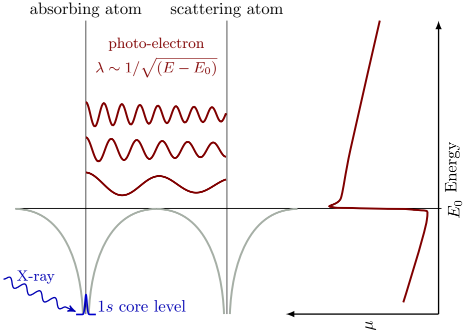
$\mu(E)$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

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 $\mu(E)$.



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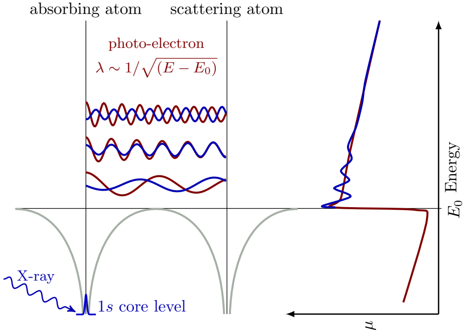

The photo-electron scattered back will interfere with itself.

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.

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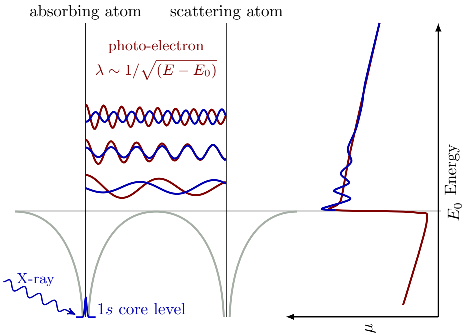

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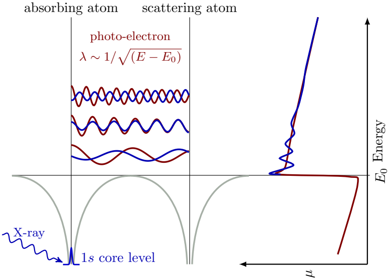
XAFS oscillations are due to the interference of the outgoing photo-electron with the photo-electron scattered from neighboring atoms.

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.



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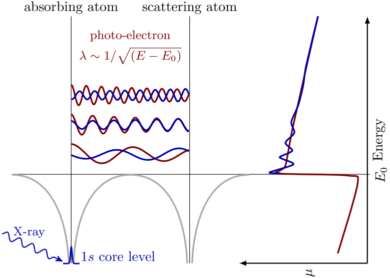

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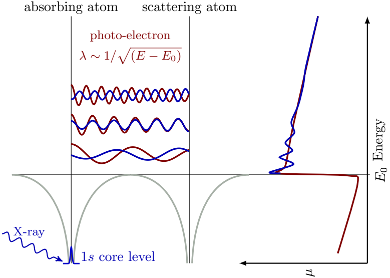

Fermi's Golden Rule describes $\mu(E)$ as a transition between quantum states:

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

$\langle i|$ 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.

μ and χ and the photo-electron wavefunction

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

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

Compare this to $\mu(E) = \mu_0(E)[1 + \chi(E)]$ and we see

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

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

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

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

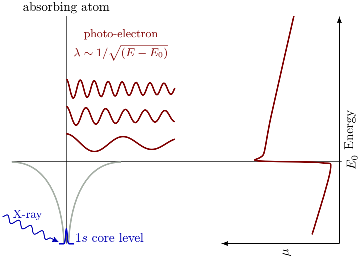
The EXAFS Equation: simple description

With $\chi \sim \psi_{\rm scatt}(0)$, 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



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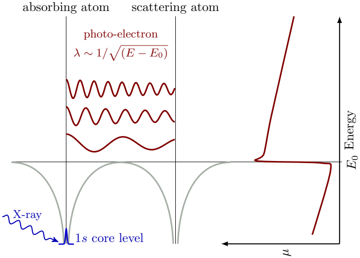
2. scatters from the neighbor atom



$$\chi(k) \sim \psi_{\rm scatt}(0) = \frac{e^{ikR}}{kR}\left[2kf(k)e^{i\delta(k)}\right]$$

where scattering from the neighboring atom gives:

$f(k)$	the scattering amplitude for the atom.
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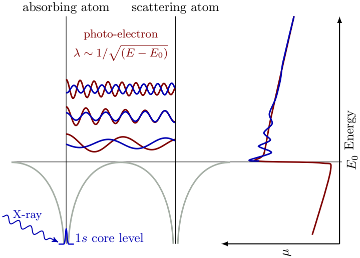
1. leaves the absorbing atom
2. scatters from the neighbor atom
3. returns to the absorbing atom



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turning complex number into real numbers gives the EXAFS Equation. . .

Development of the EXAFS Equation

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

The EXAFS Equation for 1 scattering atom.

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The EXAFS Equation 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

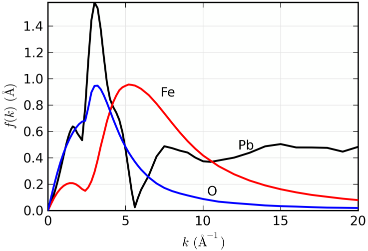
$$\chi(k) = \frac{Nf(k)e^{-2k^2\sigma^2}}{kR^2}\sin\left[2kR + \delta(k)\right]$$

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:

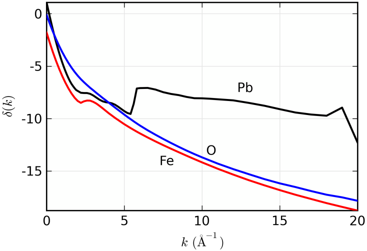
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{k{R_j}^2}\sin[2kR_j + \delta_j(k)]$$

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 $f(k)$.



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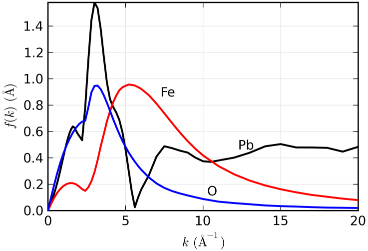

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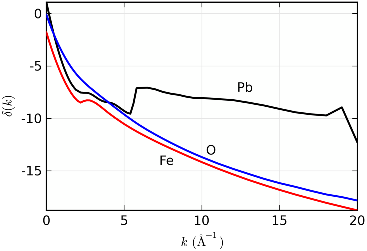

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These complex factors allow EXAFS to distinguish the species of neighboring atom:

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

The EXAFS Equation: 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.

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

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

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Photo-Electron Mean-Free Path (extrinsic losses)

To get to

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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* (λ) 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.

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Photo-Electron Mean-Free Path

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

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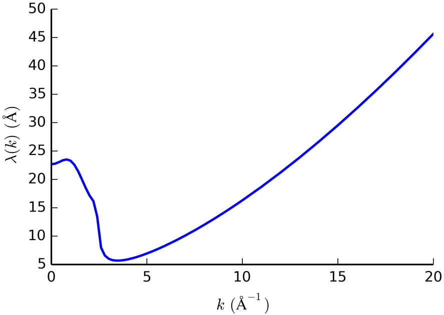
The Photo-Electron Mean-Free Path



λ is mostly independent of the system, and depends strongly on k:

- For $3\,\text{Å}^{-1} < \mathrm{k} < 15\,\text{Å}^{-1}$, $\lambda < 30\,\text{Å}$
- This (and the R^{-2} term) makes EXAFS a *local atomic probe*.
- For XANES ($k < 3\,\text{Å}^{-1}$) Both λ 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.
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S_0^2 is Completely Correlated with N (!!!)

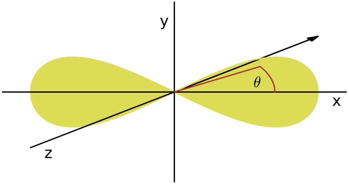
This – along with normalization of spectra – makes EXAFS amplitudes (and therefore N) less precise than EXAFS phases (and therefore R).

X-ray Polarization

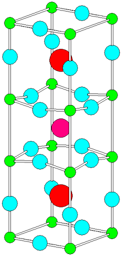
A synchrotron is highly polarized ($> 99.9\%$) in the horizontal plane.

A photo-electron from a *K* shell goes as a *p* orbital ($\cos^2\theta$), mostly in the horizontal plane.

It *never* sees atoms in the vertical (y) plane or along the beam direction (z).



For anisotropic systems (surfaces, non-cubic crystals, . . .) this can be important: It can be either confounding or useful!



Anistropy of the *crystal* doesn't really matter – anisotropy in the *local structure* does.

A sorbed ion on a surface, or ion intercalated in a layered material, may show very strong polarization dependence.

The EXAFS Equation: Sum over Scattering Paths

We need some way to account for different neighbor species (Fe-O, Fe-Fe):

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

This sum could be over "shells" of atoms, but more generally it is over *scattering paths* for the photo-electron. This allows *multiple scattering* to be taken into account.

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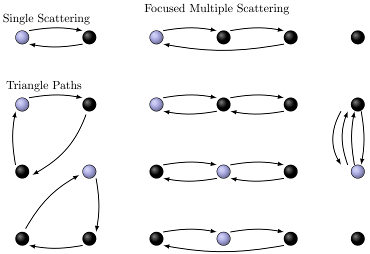

Triangle Paths with angles $45 < \theta < 135^\circ$ aren't strong, but there can be a lot of them.

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

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

This can be used to measure bond angles.

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

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.
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 for now.

The EXAFS Equation (one last time!)

Even with all those complications and caveats, we still 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.

> But now we will keep in mind that $f(k)$, $\delta(k)$, and $\lambda(k)$ might include some of the complications *AND* the sum over paths includes multiple-scattering

Again, if we know these properties, we can determine:

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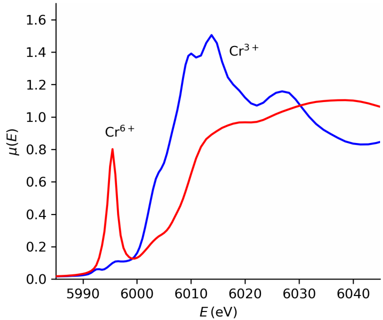
R distance to neighboring atom.
N coordination number of neighboring atom.
σ^2 mean-square disorder of neighbor distance.

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

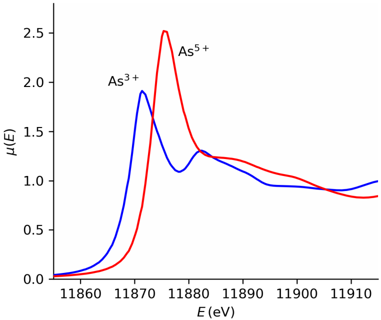
XANES

XANES: X-ray Absorption Near-Edge Spectra

Within ~50eV of the absorption edge, the X-ray Absorption Spectra is highly sensitive to the chemical state and formal valence of absorbing element:



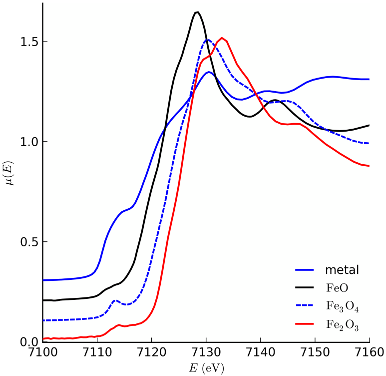
XANES for Cr^{3+} and Cr^{6+}



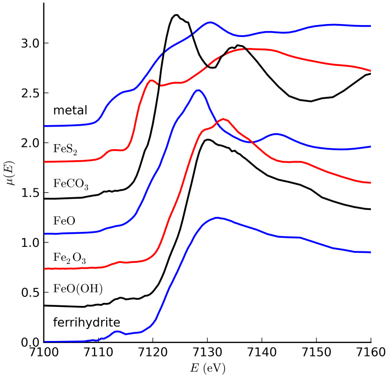
XANES for As^{3+} and As^{5+}

what are the unoccupied electronic states that the photo-electron can fill?

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 (FEFF9, FDMNES) are becoming reasonably accurate. These can help interpret spectra in terms of *bonding orbitals* and/or *density of states*.

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XANES: Summary

- *XANES is a much larger signal than EXAFS*

  XANES can be done at lower concentrations, and less-than-perfect sample conditions (small beam/sample size, complex sample environments).

- *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.

- *XANES lends itself to linear spectroscopic methods*

  XANES is not highly affected by thermal disorder, so maps well to "coordination geometry".

  For many systems, the XANES analysis based on linear combinations of other measured spectra – either from "model compounds" or from a large series of measured spectra – is informative and valuable.

  These *linear analysis* methods can be very easy to apply and can make use of more sophisticated statistical methods used in other spectroscopies.