X-ray absorption spectroscopy: principles, methods and data analysis

Giuliana Aquilanti

giuliana.aquilanti@elettra.eu
Outline

• X-ray absorption
• X-ray absorption fine structure
• XANES
• EXAFS data analysis
X-ray absorption
Introduction: x-rays-matter interaction
X-rays – matter interaction

• Photoelectric absorption
  one photon is absorbed and the atom is ionized or excited

• Scattering
  photons are deflected form the original trajectory by collision with an electron
  • Elastic (Thomson scattering): the photon wavelength is unmodified by the scattering process
  • Inelastic (Compton scattering): the photon wavelength is modified
X-ray – matter interaction

- Fluorescence
- Auger Electrons
- Photoelectrons
- Inelastic Scattered beam
- Elastic scattered beam
- Transmitted beam
- Incoming beam
Main x-ray experimental techniques

• **Spectroscopy**

  atomic and electronic structure of matter
  
  • *Absorption*
  • *Emission*
  • *Photoelectron spectroscopy*

• **Imaging**

  macroscopic pictures of a sample, based on the different absorption of x-rays by different parts of the sample (medical radiography and x-ray microscopy)

• **Scattering**

  • *Elastic*: Microscopic geometrical structure of condensed systems
  • *Inelastic*: Collective excitations
Spectroscopic methods

• They measure the response of a system as a function of energy

• The energy that is scanned can be that of the incident beam or the energy of the outgoing particles (photons in x-ray fluorescence, electrons in photoelectron spectroscopy)
The absorption coefficient - 1

• Quantitatively, the absorption is given by the linear absorption coefficient $\mu$

• $\mu dz$: attenuation of the beam through an infinitesimal thickness $dz$ at a depth $z$ from the surface
The intensity $I(z)$ through the sample fulfills the condition

$$-dI = I(z)\mu dz$$

which leads to the differential equation

$$\frac{dI}{I(z)} = -\mu dz$$

If $I(z = 0) = I_0$, ($I_0$: incident beam intensity at $z = 0$) then

$$I(z) = I_0 e^{-\mu z}$$
The absorption coefficient - 3

\[ I(z) = I_0 e^{-\mu z} \Rightarrow \ln \frac{I_0}{I} = \mu z \]

Experimentally, \( \mu \) can be determined as the log of the ratio of the beam intensities with and without the samples (or beam intensity before and after the sample)
 Atomic cross section

\[ \mu = \rho_{\text{at}} \sigma_a = \left( \frac{\rho_m N_A}{A} \right) \sigma_a \]

- mass density
- Avogadro’s number
- Atomic number density
- Atomic mass

\[ \sigma_a [\text{cm}^2] \]
\[ \sigma_a [\text{barn}] \quad 1 \text{ barn} = 10^{-28} \text{ m}^2 \]

\[ \sigma_a \left[ \frac{\text{cm}^2}{g} \right] = \frac{N_A}{A} \sigma_a [\text{cm}^2] = \frac{\mu}{\rho_m} \]
Photoelectric absorption

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

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

- Any excess energy from the X-ray is given to the ejected *photoelectron*.
Absorption measurements in real life

Transmission

The absorption is measured directly by measuring what is transmitted through the sample

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

\[ \mu(E)t = \alpha = \ln \frac{I_0}{I_1} \]

Fluorescence

The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured

\[ \alpha \propto \frac{I_F}{I_0} \]
\( \mu \) depends strongly on:

- x-ray energy \( E \)
- atomic number \( Z \)
- density \( \rho \)
- atomic mass \( A \)

\[
\mu \approx \frac{\rho Z^4}{AE^3}
\]

In addition, \( \mu \) has sharp \textit{absorption edges} corresponding to the characteristic core-level energy of the atom which originate when the photon energy becomes high enough to extract an electron from a deeper level.
\[ \mu \approx \frac{\rho Z^4}{AE^3} \]
The absorption coefficient

• It is element-specific and a function of the x-ray energy
• It increases with the atomic number of the element ($\propto Z^4$)
• It decreases with increasing photon energy ($\propto E^{-3}$)
• The absorption coefficient is essentially an indication of the electron density in the material and the electron binding energy.
• For instance, if a particular chemical substance can assume different geometric (‘allotropic’) forms and thereby have different densities, will be different accordingly
• Conversely, compounds that are chemically distinct but contain the same number of electrons per formula unit and have similar mass densities will have similar absorption properties (except close to absorption edges).
The absorption coefficient

Attenuation length: $1/\mu$
Table 2.1 Correspondence between x-ray absorption edges and their electronic configurations.

<table>
<thead>
<tr>
<th>Edge</th>
<th>Configuration</th>
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<td>3d_{5/2}</td>
<td>O_2</td>
<td>5p_{1/2}</td>
</tr>
</tbody>
</table>

Continuum

3d_{5/2} - 3d_{3/2} - 3p_{3/2} - 3p_{1/2} - 2p_{3/2} - 2p_{1/2} - 2s - 1s
Absorption edge energies

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

All elements with $Z > 16$ have either a $K$-, or $L$- edge between 2 and 35 keV, which can be accessed at many synchrotron sources.
De-excitation process

Absorption → Excited state → Decay to the ground state

Core hole + photoelectron

**X-ray Fluorescence**

An x-ray with energy equal to the difference of the core-levels is emitted

**Auger Effect**

An electron is promoted to the continuum from another core-level

X-ray fluorescence and Auger emission occur at discrete energies characteristic of the absorbing atom, and can be used to identify the absorbing atom.
Secondary effects

Fluorescence

Auger emission
X-ray fluorescence

• These characteristic x-ray lines result from the transition of an outer-shell electron relaxing to the hole left behind by the ejection of the photoelectron from the atom.
• This occurs on a timescale of the order of 10 to 100 fs.
• As the energy difference between the two involved levels is well defined, these lines are exceedingly sharp.
• From Heisenberg’s uncertainty principle $\Delta E \Delta t \sim \hbar$, the natural linewidth is therefore of the order of 0.01 eV, although this depends on the element and the transition.
Emission lines nomenclature

\[ \nu = K(Z - 1)^2 \]

Characteristic energy of the K\(\alpha\) line (Moseley law)
Auger Emission - 1

• It is a three-electron process
• Auger electrons are produced when an outer shell electron relaxes to the core-hole produced by the ejection of a photoelectron.
• The excess energy produced in this process is $|E_c - E_n|$, whereby $E_c$ and $E_n$ are the core- and outer-shell binding energies, respectively
• Instead of being manifested as a fluorescence x-ray photon, the energy can also be channelled into the ejection of another electron if its binding energy is less than the excess energy.
• In case the Auger electron comes from the same shell as that of the electron which relaxed to the core-level hole, then the electron energy is $|E_c - 2E_n|$

• More generally, the kinetic energy is $|E_c - E_n - E_m'|$, where $E_m'$ is the binding energy of the Auger electron. The prime shows that the binding energy of this level has been changed (normally increased) because the electron ejected from this level originates from an already ionized atom.

• Typical Auger electron energies are in the range of 100 to 500 eV which have escape depths of only a few nanometres, hence Auger spectroscopy is very surface sensitive.

• In contrast to photoelectrons, the energies of Auger electrons ($|E_c - E_n - E_m'|$) are independent of the incident photon energy, although the amount of Auger electrons emitted is directly proportional to the absorption cross-section in the surface region.
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Fluorescence or Auger?

- Auger-electron emission and x-ray fluorescence are competitive processes.
- The rate of spontaneous fluorescence, is proportional to the third power of the energy difference between the upper and lower state. Hence, for a given atom, $K$-emission lines are more probable than $L$-emission.
- Fluorescence is stronger for heavier atoms, which have a more attractive positive nuclear charge and therefore a larger energy difference separating adjacent shells.
Fluorescence or Auger?

• The probability of an Auger electron being emitted increases with decreasing energy difference between the excited atom and the atom after Auger emission.
• LMM events are more likely than KLL events.
• Low atomic-number atoms have higher Auger yields than do heavier atoms.
• High atomic-number elements have a large positive charge at the nucleus, which binds electrons more tightly, reducing the probability of Auger emission.
Fluorescence or Auger?

The diagram illustrates the normalized fluorescence and Auger yield as a function of atomic number, Z. It shows two distinct features:

- **K-edge**: A sharp increase in fluorescence yield with a corresponding decrease in Auger yield. This is typical for K-shell excitation.
- **L-edge**: A more gradual increase in fluorescence yield and a decline in Auger yield over a wider range of atomic numbers. This is characteristic of L-shell excitation.

The Auger yield (average) is depicted by a line that crosses the fluorescence yield, indicating the balance between these two processes as a function of atomic number.
XAFS at Elettra
Summary Absorption

Absorption efficiency can be approximated by the following equation:

\[ \mu \approx \frac{\rho Z^4}{AE^3} \]

where:
- \( \mu \) is the linear absorption coefficient (in barns/atom)
- \( \rho \) is the density of the material
- \( Z \) is the atomic number
- \( A \) is the atomic mass number
- \( E \) is the energy of the X-ray photon

The relationship between the intensity of the X-ray beam before and after passing through a material can be described by:

\[ \ln \frac{I_0}{I} = \mu z \]

where:
- \( I_0 \) is the initial intensity
- \( I \) is the intensity after passing through thickness \( z \)
- \( \mu \) is the linear absorption coefficient
- \( z \) is the thickness of the material
X-ray absorption
fine structure
**What?** Oscillatory behaviour of the x-ray absorption as a function of photon energy beyond an absorption edge  
**When?** Non isolated atoms  
**Why?** Proximity of neighboring atoms strongly modulates the absorption coefficient
A little history

1895  Discovery of x-rays (Röntgen) (high penetration depth)
1912  First x-ray diffraction experiments (Laue, Bragg)
1913  Bohr’s atom electron energy levels
1920  First experimental observation of fine structure
1931  First attempt to explain XAFS in condensed matter (Krönig)

1970  Availability of synchrotron radiation sources for XAFS
1971  XAFS becomes a quantitative tool for structure determination

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New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray—Absorption Fine Structure*

Dale E. Sayers† and Edward A. Stern‡

Department of Physics, University of Washington, Seattle, Washington 98165

and

Farrel W. Lytle

Boeing Scientific Research Laboratories, Seattle, Washington 98124

(received 16 July 1971)

We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).
XANES and EXAFS - 1

**X-ray Absorption Near Edge Structure (XANES)**
- up to ~ 60 eV above the edge

**Extended X-ray Absorption Fine Structure (EXAFS)**
- from ~ 60 eV to 1200 eV above the edge

![Graph showing XANES and EXAFS](image)
XANES and EXAFS - 2

\[ \text{XANES} \iff \text{same physical origin} \iff \text{EXAFS} \]

transitions to
\textit{unfilled bound states, nearly bound states, continuum}

- Oxidation state
- Coordination chemistry (tetrahedral, octahedral) of the absorbing atom
- Orbital occupancy

transitions to
\textit{the continuum}

- Radial distribution of atoms around the photoabsorber (bond distance, number and type of neighbours)
EXAFS qualitatively – isolated atom

- X-ray photon with enough energy ejects one core (photo)electron (photoelectric effect)
  
  \[ E_k = E_{\text{h}v} - E_0 = \frac{p^2}{2m} = \frac{(hk)^2}{2m} \]  

  Kinetic energy of the p.e.
  
  \[ k = \sqrt{2m(E_{\text{h}v} - E_0)/\hbar^2} \]  

  wavevector of the p.e.
  
  \[ \lambda = 2\pi/k \]  

  wavelength of the p.e.
  
- The photoelectron can be described by a wave function approximated by a spherical wave

  \[ \lambda \propto 1/E - E_0 \]
EXAFS qualitatively – condensed matter

- The photoelectron can scatter from a neighbouring atom giving rise to an incoming spherical wave coming back to the absorbing atom
- The outgoing and ingoing waves may interfere

\[ \lambda \propto \frac{1}{E - E_0} \]
Origin of the fine structure (oscillations)

- The **interference** between the outgoing and the scattering part of the photoelectron at the absorbing atom changes the probability for an absorption of x-rays i.e. alters the absorption coefficient $\mu(E)$ that is no longer smooth as in isolated atoms, but **oscillates**.

- In the extreme of **destructive interference**, when the outgoing and the backscattered waves are completely out of phase, they will cancel each other, which means that no free unoccupied state exists in which the core-electron could be excited to.

- Thus absorption is unlikely to occur and the EXAFS oscillations will have a minimum.

- The **phase relationship** between outgoing and incoming waves depends on photoelectron wavelength (and so on the energy of x-rays) and **interatomic distance** $R$.

- The **amplitude** is determined by the **number and type of neighbours** since they determine how strongly the photoelectron will be scattered.
Which information

- Frequency of the oscillations
  - Distance from neighbours

- Amplitude of the oscillations
  - Number and type of neighbours
Some spectra

Kr gas

Rh metal
Fermi’s Golden rule

According to the time dependent perturbation theory, the Fermi’s Golden rule gives the transition rate (probability of transition per unit time) per unit volume between an initial and a final eigenstate due to a perturbation.

\[ \omega_{fi} = \frac{2\pi}{\hbar} \left| \langle \Psi_f | \mathcal{H}_{int} | \Psi_i \rangle \right|^2 \rho(E_f) \]

\[ \mu = -\frac{1}{I} \frac{dI}{dz} = \sum_f \frac{2\pi c}{\omega^2 A_0^2} N \hbar \omega \omega_{fi} \]

Density of final states compatible with the energy conservation \( E_f = E_i + \hbar \omega \)

Number of microscopic absorbing element per unit volume

Sum over all final states

giuliana.aquilanti@elettra.eu
Absorption process

\[ \mu \propto \sum_{f} |\langle \psi_f | \hat{\mathbf{E}} \cdot \mathbf{r} | \psi_i \rangle|^2 \rho(E_f) \]

\( |i\rangle \): initial state of energy \( E_i \)
- core electron (e.g. 1s electron wave function)
- very localized
- NOT altered by the presence of the neighboring atoms

\( |f\rangle \): final state of energy \( E_f = E_i + \hbar \omega \)
- core hole + photoelectron
- multibody process
- altered by neighbouring atoms
Initial and final states

Wavefunction of the initial state:

\[ |i> = Y_{l_0,m_0}(\hat{r}) R_{l_0}^0(r) \]

Where \( l_0 \) angular momentum of the electron
\( Y_{l_0,m_0} \) spherical harmonic functions

(solution of the angular part of the Schrödinger equation)

For the final state a potential must take into account that the electron moves in the condensed matter

Muffin Tin Potential

Spherical regions centered on each atom in which the potential has a spherical symmetry. Wavefunctions described by a radial + angular part

Interstitial region with a constant potential. Wavefunctions described by plane waves
Dipole selection rules

The dipolar selection rules determine the transition from the initial to the final state

\[ \Delta \ell = \pm 1 \]
\[ \Delta s = 0 \]
\[ \Delta j = \pm 1, 0 \]
\[ \Delta m = 0 \]

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<tr>
<td>L₂, L₃</td>
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<td>s ((\ell=0), d ((\ell=2))</td>
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</table>
The EXAFS signal $\chi(k)$ - 1

- The EXAFS signal is generally expressed as a function of the wavevector of the photoelectron $k = \sqrt{2m(E_{hv} - E_0)/\hbar^2}$
- The oscillatory part of the spectrum contains the structural information
- We define the EXAFS function as $\chi(k) = \frac{\mu - \mu_0}{\Delta\mu_0}$

$\mu_0(E)$ Smooth function representing the bare atomic background

$\Delta\mu_0$ Edge step at the absorption edge normalized to one absorption event
XAFS originates from an *interference effect*, and depends on the wave-nature of the photoelectron.

\[ \chi(k) \] is often shown weighted by \( k^2 \) or \( k^3 \) to amplify the oscillations at high-\( k \)
\( \chi(k) \): sum of damped waves

\( \chi(k) \) is the sum of contributions \( \chi_j(k) \) from backscattered wavelets:

\[
\chi(k) = \sum_j \chi_j(k)
\]

Each \( \chi_j(k) \) can be approximated by a \textit{damped} sine wave of the type:

\[
\chi_j(k) = A_j(k) \sin(\varphi_j(k)) e^{-2k^2\sigma^2}
\]

The larger the number of neighbours, the larger the signal.

The stronger the scattering amplitude, the larger the signal.

Damping of the amplitude at large \( k \), due to static and thermal disorder.

Each shell contributes a sinusoidal signal which oscillates more rapidly the larger the distance.

\( \delta_j(k) \)
EXAFS formula

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

- \( f(k) \) : scattering amplitude
- \( \delta_j(k) \) : phase-shift

\( R \) : Distance to the neighbouring atom

\( N \) : Coordination number of the neighbouring atom

\( \sigma^2 \) : Disorder in the neighbouring distance

scattering properties of the atoms neighbouring the photoabsorber (depend on the atomic number)
The shape of the envelope of each wave is indicative of the nature of backscatterer atom.

AgF (rocksalt structure)

- Ag-F: 2.46 Å
- Ag-Ag: 3.48 Å
The frequency of the single wave, for the same atomic pair, is indicative of the distance of the backscatterer atom (the lower the frequency the closer the neighbour).

AgF (rocksalt structure)
The scattering amplitude $F(k)$ and phase shift $\delta(k)$ depend on the atomic number. These scattering functions can be accurately calculated and used in the EXAFS modeling. $Z$ can usually be determined to within 5 or so. Fe and O can be distinguished, but Fe and Mn cannot.
Multiple scattering events may occur

The photoelectron can scatter from more than one atom before returning to the central atom.

\[
\begin{align*}
SS & \quad \rightarrow \quad g_2(r) \\
& \quad f = 2 \ R_1 \\
MS & \quad \rightarrow \quad g_2(r) \\
& \quad f = 4 \ R_1 \\
MS & \quad \rightarrow \quad g_3(r) \\
& \quad f = R_1 + R_2 + R_3 \\
MS & \quad \rightarrow \quad g_3(r) \\
& \quad f = 2R_1 + 2R_3
\end{align*}
\]

Through multiple scattering EXAFS can give information on the n-body distribution functions \( g_n(r) \)
Qualitative picture of local coordination in R space

The frequencies contained in the EXAFS signal depend on the distance between the absorbing atom and the neighbouring atoms (i.e. the length of the scattering path).

A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.
Quantitative structural determination

Structural determinations depend on the feasibility of resolving the data into individual waves corresponding to the different types of neighbours (SS) and bonding configurations (MS) around the absorbing atom.
XAS vs diffraction methods

Diffraction Methods (x-rays, Neutrons)

• Crystalline materials with long-range ordering -> 3D picture of atomic coordinates
• Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D RDF containing interatomic distances due to all atomic pairs in the sample

XAFS

• 1D radial distribution function (centered at the absorber)
• Element selectivity
• Higher sensitivity to local distortions (i.e. within the unit cell)
• Charge state sensitivity (XANES)
• Structural information on the environment of each type of atom:
  • distance, number, kind, static and thermal disorder
  • 3-body correlations
EXAFS: typical applications

- Local selectivity
- Local structure sensitivity

- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure
Summary X-ray absorption fine structure

EXAFS

What?
When?
Why?

- Chemical selectivity
- Local structure
- Electronic structure
- Same degree of accuracy independently of the aggregation state
XANES
XANES is the region of the absorption spectrum within ~ 60 eV of the absorption edge.

XANES includes also the “pre-edge features” if any.
K-edge XANES

Mn: [Ar] 3d⁵ 4s²

Ground state

Excited state

Mn³⁺

ε⁺
4p
3d
1s

ε⁺
4p
3d
1s

ε⁺
4p
3d
1s

ε⁺
4p
3d
1s

Ground state

Excited state

Mn³⁺

ε⁺
4p
3d
1s

ε⁺
4p
3d
1s

ε⁺
4p
3d
1s

ε⁺
4p
3d
1s

Energy (keV)

µt(ε) (arb. units.)

pre-edge

main edge

continuum

6510 6540 6570

0.0

0.4

0.8

1.2

XAS – smr3202
Chemical shift

Mn: [Ar] 3d$^5$ 4s$^2$

Ground state

Excited state

Mn$^{3+}$

Mn$^{4+}$

$\epsilon_p$
4p
3d
1s

$\epsilon_p$
4p
3d
1s

$\epsilon_p$
4p
3d
1s

$\epsilon_p$
4p
3d
1s

Energy (keV)

$\mu f(E)$ (arb. units.)
The edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
The heights and positions of pre-edge peaks can also be reliably used to determine Fe$^{3+}$/Fe$^{2+}$ ratios (and similar ratios for many cations)
XANES can be used simply as a fingerprint of phases and oxidation state.

XANES analysis can be as simple as making linear combinations of “known” spectra to get compositional fraction of these components.
Dipole selection rules apply:

\[ \Delta \ell = \pm 1 \]
\[ \Delta s = 0 \]
\[ \Delta j = \pm 1, 0 \]
\[ \Delta m = 0 \]

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The final state is usually not atomic-like and may have mixing (hybridization) with other orbitals.

This is often the interesting part of the XANES
Transition metals pre-edge peaks

Transition from 1s to 4p states

Pure octahedron
• Centro-symmetry: no p-d mixing allowed
• Only (weak) quadrupolar transitions
• No, or very low intensity prepeak

Distorted octahedron
• Centro-symmetry broken: p-d mixing allowed
• Dipole transition in the edge
• Moderate intensity prepeak

Tetrahedron
• No centro-symmetry: p-d mixing allowed
• Dipole transition in the edge
• High intensity prepeak
Prepeak: local coordination environment

Ti K-edge XANES shows dramatic dependence on the local coordination chemistry
The XANES of $\text{Cr}^{3+}$ and $\text{Cr}^{6+}$ shows a dramatic dependence on oxidation state and coordination chemistry.
White line intensity of L$_3$-edge of XANES of 4d metals

Transition from 2p$_{3/2}$ to 4d states

Linear correlation between white line area and number of 4d-holes for Mo to Ag

Increasing d states occupancy
Re $L_3$-edge: transition from $2p_{3/2}$ to $5d$ states

Re metal ($\text{Re}^0$) – $5d^5$

ReO$_2$ ($\text{Re}^{4+}$) – $5d^1$

$\text{NH}_4\text{ReO}_4$ ($\text{Re}^{7+}$) 5$d^0$
XANES: interpretation

The EXAFS equation breaks down at low-k, and the mean-free-path goes up.

This complicates XANES interpretation:

A simple equation for XANES does not exist

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of:

- **Coordination chemistry**: regular, distorted octahedral, tetrahedral, . . .
- **Molecular orbitals**: p-d orbital hybridization, crystal-field theory, . . .
- **Band-structure**: the density of available electronic states
- **Multiple-scattering**: multiple bounces of the photoelectron
XANES: conclusions

**XANES is a much larger signal than EXAFS**
- XANES can be done at lower concentrations, and less-than-perfect sample conditions

**XANES is easier to crudely interpret than EXAFS**
- For many systems, the XANES analysis based on linear combination of known spectra form “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.
Summary XANES

Local geometry

Orbital occupancy

redox

Normalized Absorption

Energy (eV)

Normalized Absorption

Energy (eV)

Normalized Absorption

Energy (eV)
EXAFS data analysis
Data treatment: 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 1 absorption event
4. remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS $\chi$.
5. identify the threshold energy $E_0$, and convert from E to k space: $k = \frac{\sqrt{2m(E-E_0)}}{\eta^2}$
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.
Converting raw data to $\mu(E)$

For transmission XAFS:

$I = I_0 \exp[-\mu(E) t]$

$\mu(E) t = \ln \left( \frac{I_0}{I} \right)$
Absorption measurements in real life

Transmission

The absorption is measured directly by measuring what is transmitted through the sample

\[ I = I_0 e^{-\mu(E)t} \]
\[ \mu(E)t = \alpha = \ln \frac{I_0}{I_1} \]

Fluorescence

The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured

\[ \alpha \propto \frac{I_F}{I_0} \]
Pre-edge subtraction and normalization

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$_1$ edge).

Normalization
We estimate the *edge step*, $\mu_0(E_0)$, by extrapolating a simple fit to the above $\mu(E)$ to the edge.
Determination of $E_0$

We can select $E_0$ roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we will keep in mind that we may need to refine this value later on.
Post-edge background subtraction

Post-edge background

• We do not 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.
• A flexible enough spline should not match the $\mu(E)$ and remove all the EXAFS. We want a spline that will match the low frequency components of $\mu_0(E)$. 
The raw EXAFS $\chi(k)$ usually decays quickly with $k$, and difficult to assess or interpret by itself. It is customary to weight the higher $k$ portion of the spectra by multiplying by $k^2$ or $k^3$.

$k$-weighted $\chi(k)$: $k^2\chi(k)$

$\chi(k)$ is composed of sine waves, so we’ll Fourier Transform from $k$ to $R$-space. To avoid “ringing”, we’ll multiply by a window function.
Fourier Transform: $\chi(R)$

$\chi(R)$
The Fourier Transform of $k^2(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe-Fe. The Fe-O distance in FeO is 2.14Å, but the first peak is at 1.66Å. This shift in the first peak is due to the phase-shift, $\delta(k)$: $\sin[2kR + \delta(k)]$.

A shift of -0.5 Å is typical.

$\chi(R)$ is complex:
The FT makes $\chi(R)$ complex. Usually only the amplitude is shown, but there are really oscillations in $\chi(R)$. Both real and imaginary components are used in modeling.
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 \( \Delta k \) and \( \Delta R \) are the k- and R-ranges of the usable data.

• For the typical ranges like \( k = [3.0, 12.0] \, \text{Å}^{-1} \) and \( R = [1.0, 3.0] \, \text{Å} \), there are \( \sim 11 \) 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 is often important to constrain parameters \( R, N, \sigma^2 \) 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!
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 $R = 2.14 \, \text{Å}$ (a regular octahedral coordination).

We will use these functions to refine the values $R$, $N$, $\sigma^2$, and $E_0$ so our model EXAFS function matches our data.

**Fit results**

$N = 5.8 \pm 1.8$

$R = 2.10 \pm 0.02 \, \text{Å}$

$E_0 = -3.1 \pm 2.5 \, \text{eV}$

$\sigma^2 = 0.015 \pm 0.005 \, \text{Å}^2$. 

$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).
Modeling the first shell of FeO - 2

$1^{st}$ shell fit in k space

The $1^{st}$ shell fit to FeO in k space. There is clearly another component in the XAFS

$1^{st}$ shell fit in R space

$|\chi(R)|$ and Re[$\chi(R)$] for FeO (blue), and a $1^{st}$ shell fit (red).
Modeling the second shell of FeO - 1

To add the second shell Fe to the model, we use calculation for \( f(k) \) and \( \delta(k) \) based on a guess of the Fe-Fe distance, and refine the values \( R, N, \sigma^2 \). Such a fit gives a result like this:

\[ |\chi(R)| \] data for FeO (blue), and fit of 1\textsuperscript{st} and 2\textsuperscript{nd} shells (red).

The results are fairly consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

<table>
<thead>
<tr>
<th>Shell</th>
<th>( N )</th>
<th>( R ) (Å)</th>
<th>( \sigma^2 ) (Å(^2))</th>
<th>( \Delta E_0 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O</td>
<td>6.0(1.0)</td>
<td>2.10(0.02)</td>
<td>0.015(0.003)</td>
<td>-2.1(0.8)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>11.7(1.3)</td>
<td>3.05(0.02)</td>
<td>0.014(0.002)</td>
<td>-2.1(0.8)</td>
</tr>
</tbody>
</table>
Modeling the second shell of FeO - 2

Other views of the data and two-shell fit:

The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS. Even in this simple system, there is some overlap of shells in R-space. The agreement in Re[χ(R)] look especially good – this is how the fits are done. The modeling can get more complicated than this.
Summary data analysis

1. Data collection
2. Preliminary data treatment
3. Extraction of XAFS structural signal: $\chi(k)$
4. Structural refinement
5. Check the results
6. END

Revision points:
- Preliminary data treatment
- Extraction of XAFS structural signal: $\chi(k)$
- Structural refinement
- Check the results