EXAFS

Extended X-Ray Absorption Fine Structure

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EXAFS

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1. Interaction of X-rays with matter
2. Basics aspects about XAFS
3. Understanding the EXAFS equation
Interaction of X-rays with matter

- Pair production: $h\nu > 1\text{MeV}$
- Photoelectric absorption
- Transmission
- Scattering: $h\nu' < h\nu$
  - Compton
  - Thomson
- Decay processes:
  - Fluorescence: $h\nu_f$
  - Auger electrons

Primary competing processes and some radiative and non-radiative decay processes
Interaction of X-rays with matter

Photoelectric effect is the dominating process at the x-ray energy range (200-100 keV)

X-rays are absorbed predominantly from the photo-electric effect in the range of energies ranging from 200 eV to 100 keV;

- X-ray absorption by an atom by photoelectric effect: absorption edge;
- An excited state with a hole ("core hole") is created;
- The excess energy of X-rays is transferred to the ejected photoelectron.
• What is XAFS?

– XAFS studies the details of the x-ray absorption coefficient around an absorption edge.

– It reveals a wealth of information regarding the geometric and electronic structure of materials.
Basics aspects about XAFS

Main characteristics of XAS technique

- Most atoms of the periodic table can be studied;
- Selectivity at the atomic level;
- Sensitive to oxidation state, coordination number and interatomic distance kind of atom;
- Structure of amorphous and crystalline materials and highly diluted systems;
- Solids, liquids and gases can have their specific local structure.
- Different environments (pressure, temperature, magnetic field, gas ...)
- **Limitations ....**
- We can not distinguish neighboring atoms in the periodic table;
- Only the local order can be precisely determined;
- A source of X-ray wavelength variable is required.
XAFS: Study the details of the variation on the absorption coefficient (fine structure) after the edge.
Basics aspects about XAFS

X-ray attenuation
Absorption coefficient:

\[ \frac{dI}{dt} = -\mu I dt \]

\[ I_1 = I_0 \exp(-\mu t) \]

\( \mu \) : linear absorption coefficient
\( t \) : thickness
\( \mu t \) : absorbance

Mass absorption coefficient:

\[ \frac{\mu}{\rho} = \sum_j g_j \left( \frac{\mu}{\rho} \right)_j \]

Mass fraction of el. \( j \)

Units (cm\(^2\)/g)

Atomic absorption coefficient:

\[ \mu_j^a = \left( \frac{\mu}{\rho} \right)_j \left[ \frac{A_j}{N} \right] \]

Units: \(10^{-24}\)cm\(^2\) (1 barn)

Includes contributions from all scattering and absorption processes.
Basics aspects about XAFS

Basic XAFS experiment – sequential mode

\[ \mu t = \log \left( \frac{I_0}{I_1} \right) \]
Basics aspects about EXAFS

- **EXAFS spectrum**
- Incident X-rays
- Transmitted X-rays
- Visible light (XEOL)
- Fluorescence X-rays
- TEY

\[ h \nu \]
\[ e^- \]
Basics aspects about XAFS

Which method for which application?

The most important criterion:
The best signal to noise ratio for the element of interest

Always transmission, if possible
Most accurate method, best overall S/N counting statistics of about $10^{-4}$ from beamlines with more than $10^8$ photons/s)

Fluorescence for very diluted samples
A specific signal reduces the large background (but maximum tolerable detector count-rate can result in very long measuring times).

Total electron yield (TEY)
for surface sensitivity and surface XAFS (adsorbates on surfaces)
TEY for thick samples that cannot be made uniform.

XEOL X-ray excited optical luminescence
VIS/UV detection from luminescent samples
**Basics aspects about XAFS**

XAFS = XANES + EXAFS

**InAs - As K-Edge**

*Extended X-ray Absorption Fine Structure*

*High Z elements*

**XANES**

*Low Z elements*

**NEXAFS**

XANES is the region ~50 eV around the edge
Basics aspects about XAFS

**XANES**: transitions to unoccupied states (localized and continuum)

\[
\text{low energy photoelectron} \rightarrow \text{multiple scattering (MS)}
\]

Information content

- Fermi energy
- Projected density of unoccupied states
- Oxidation states
- Coordination symmetry

**EXAFS**: high energy photoelectron \(\rightarrow\) single scattering + some important MS

Information content

- Interatomic distances
- Disorder
- Coordination numbers
- Bond-angle distributions
- Partial pair distribution
- Vibrational properties.
Basics aspects about XAFS

Fermi Energy

Binding Energy

Continuum

XANES

Unoccupied states

Occupied states

1s

2s, 2p

3s, 3p, 3d

4s, 4p, 4d, 4f

K

L

M

N

Photon
XANES: pre edge structure

Fermi Golden rule

\[
\begin{align*}
E & \quad \mu \\
\hbar \omega_0 & \quad |f > \\
\hbar \omega & \quad |i > \\
\end{align*}
\]

\[
\begin{align*}
E & \quad \mu \\
\hbar \omega_a & \quad |f > \\
\hbar \omega_b & \quad |i > \\
\end{align*}
\]

\[
\begin{align*}
E & \quad \mu \\
\hbar \omega_0 & \quad |i > \\
\end{align*}
\]
Basics aspects about XAFS

EXAFS

Fermi Energy

- 4s, 4p, 4d, 4f
- 3s, 3p, 3d
- fóton
- 2s, 2p
- 1s

0

Binding Energy

Continuum

Unoccupied states

Information obtained:
- Coordination number
- Interactomic distances
- Disorder

Occupied states
Basics aspects about XAFS
Basics aspects about XAFS

XAFS = XANES + EXAFS

Extended X-ray Absorption Fine Structure

InAs - As K-Edge

EXAFS

Fine Structure

EXAFS is the region from 50 – 1200 eV after the edge
Understanding the XAFS equation

• Photon energy \((E_\gamma) > \) Binding Energy \((E_b)\): Photoelectric effect.

• Kinetic energy of the photoelectron \((E_c)\) = \(E_\gamma - E_L\)

• Wave-Particle duality: The photoelectron travel as a esferic wave: \(E_c = h\nu\)

• Wavevector of the photoelectron: \(K\)

\[
k = \sqrt{\frac{2m_e (E_\gamma - E_L)}{\hbar^2}}
\]

• Quantical state of the photoelectron: superposition of the propagating wave with the retrodispersed waves on the neightbourgs

• Phase difference of the incoming and outgoing waves: \(\Delta\phi\)

\[
\Delta\phi \approx 2kR
\]

• Interference in between propagating waves and retrodispersed ones. This moduls the absorption coefficient.

• Oscillation frequence: 2R

• Oscillation amplitudes: number of neightbourgs and disorder
Here we add (superpose) oscillations of different frequencies (radial distances), one for each coordination shell.

- **Coordination shell**: Refers to the aggregation's of atoms at the same distance to the absorber atom.
- **Coordination Number**: Amount of atoms in a coordination shell.
Understanding the XAFS equation

**Principal hypothesis:**
- Final states are plane waves
- Gaussian disorder
- Dipolares transitions
- One active electron
- Photoelectron dispersion is single

\[ \mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | \hat{e} \cdot \hat{r} | i \rangle \right|^2 \delta(E_f) \]

\[ \chi(k) = \sum_{i} N_i \frac{S_0^2 F_i(k)}{k R_i^2} e^{-2k^2 \sigma_i^2} e^{\left[ \frac{-2R_i}{\lambda} \right]} \sin[2kR_i - \phi_i(k)] \]

**Estructural parameters**

- \( R_i \)
- \( N_i \)
- \( \sigma_i^2 \)

**Atomic parameters:**

- \( \lambda \)
- \( F(k) \)
- \( S_0^2 \)
- \( \phi(k) \)

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Sayers et al., PRL 27, 1204 (1971)

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**Ab initio**
Understanding the XAFS equation

\[ TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k)e^{i2Rk} dk \]

\[ \sin(2*R*k) \]
Understanding the XAFS equation

\[ TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k)e^{i2Rk} \, dk \]

\[ \sin(2*R*k) \]
Understanding the XAFS equation

$$TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} \chi(k) e^{i2Rk} dk$$

$$\sin(2*R*k)$$

$R=1$
$R=2$
$R=2.5$
$R=3$

$k(\text{Å}^{-1})$

$\chi(k)$

Módulo da TF

$R(\text{Å})$

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0

0 4 8 12 16 20 24 28 32 36
Understanding the XAFS equation

$$TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k) e^{i2Rk} \, dk$$

$$\sum \alpha_i \sin(2R_i k)$$

$$\chi(k) = \sum_i \frac{N_i}{kR_i^2} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{-\frac{-2R_i}{\lambda}} \sin[2kR_i - \phi_i(k)]$$
Understanding the XAFS equation

\[ \chi(k) = \sum_i \frac{N_i}{kR_i^2} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{-\frac{-2R_i}{\lambda}} \sin[2kR_i - \phi_i(k)] \]

FT: is not a Radial Distribution function but have some resemblance

1\textsuperscript{a} shell: \( R = 2.45 \text{ Å} \)
\( N = 4 \)

2\textsuperscript{a} shell: \( R = 4.00 \text{ Å} \)
\( N = 12 \)

3\textsuperscript{a} shell: \( R = 4.69 \text{ Å} \)
\( N = 12 \)

4\textsuperscript{a} shell: \( R = 5.66 \text{ Å} \)
\( N = 4 \)

Signal at Ge-K edge

Fourier Transform (FT)
Understanding the XAFS equation

Changes on the EXAFS signal with variations on the Coordination number

$\chi \times k^2$

$k(\text{Å}^{-1})$

$R(\text{Å})$

$N=4$
$N=3$
$N=2$
$N=1$

$Módulo da TF$

Understanding the XAFS equation

Changes on the EXAFS signal with variations on the Coordination number
Understanding the XAFS equation

Changes on the EXAFS signal with a variation on the

\[ \Delta R = 0.1 \text{Å} \]
Changes on the EXAFS with a variation on the structural disorder

Gaussian Disorder: $\sigma = 0.03 \text{ Å}$
Understanding the XAFS equation

1 – background extraction

Data treatment

\[ \chi = \frac{\mu - \mu_0}{\Delta \mu} \]

Energia (eV)

CdSe - Borda K do Se

[Graph showing absorbância and Energia (eV) with data points and lines]

[Graph showing \( \chi(E) \) with data points and lines]
Understanding the XAFS equation

Conversion $E \rightarrow k$

$$k = \sqrt{\frac{2m_e (E_\gamma - E_L)}{\hbar^2}}$$
Understanding the XAFS equation

Structural parameters: Minimal Square fitting

Phases and amplitudes of the retrodispersion
Understanding the XAFS equation

**Principal hypothesis:**
- Final states are plane waves
- Gaussian disorder
- Dipolares transitions
- One active electron
- Photoelectron dispersion is single

\[
\mu(E) \propto \sum_{f} \left| \langle f | \hat{e} \cdot \vec{r} | i \rangle \right|^2 \delta(E_f)
\]

\[
\chi(k) = \sum_{i} \frac{N_i}{kR_i^2} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{\left[\frac{-2R_i}{\lambda}\right]} \sin[2kR_i - \phi_i(k)]
\]

**Estructural parameters**
- \( R_i \)
- \( N_i \)
- \( \sigma_i^2 \)

**Atomic parameters:**
- Absorption and dispersion of the Photoelectron
- \( \lambda \)
- \( F(k) \)
- \( S_0^2 \)
- \( \phi(k) \)

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Sayers et al., PRL 27, 1204 (1971)
Studying a system with one technique is equivalent to studying it with zero techniques

- Bruce Ravel citing anonymous source
Obrigado pela sua atenção!

Questions, please email me: santiago.figueroa@lnls.br

More info about XAFS:
https://speakerdeck.com/bruceravel?page=2
http://cars.uchicago.edu/ifeffit/Mailing_List
http://xafs.org/Tutorials
http://www.ixasportal.net/ixas/
http://cars.uchicago.edu/ifeffit/Documentation

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