Introduction & Principles of X-Ray Absorption Spectroscopy

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1) On (radiation) Absorption and Spectroscopy

2) For what and for whom

3) (A not so) deep physics and math of XAS

4) XAS Setup and Features

5) XAS Data Analysis
**Spectroscopy**: study of the absorption and emission of radiation by matter, as related to the dependence of these processes on the wavelength of the radiation.
Spectroscopy: study of the absorption and emission of radiation by matter, as related to the dependence of these processes on the wavelength of the radiation.
Spectroscopy: study of the absorption and emission of radiation by matter, as related to the dependence of these processes on the wavelength of the radiation.

Exchange of Energy

- The measure of a system’s response as a function of the energy
- The energy can be that of the incident beam or that of the outgoing particles (photons in x-ray fluorescence, electrons in photoelectron spectroscopy)
- The incident radiation is light: upon its absorption the system ejects an electron (photoelectric effect)

**Photoelectric absorption**
An atom absorbs an x-ray photon. The photon energy is transferred to an electron which is expelled from the atom, leaving it ionized.
Inner shell spectroscopy: the x-ray interacts primarily with a deep-core electron rather than a valence electron.

XAS: how x-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom.
**Inner shell spectroscopy**: the x-ray interacts primarily with a deep-core electron rather than a valence electron.

**XAS**: how x-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom.

XAS spectra are especially sensitive to the **formal oxidation state**, **coordination chemistry**, and the **distances**, **coordination number** and **species** of the atoms immediately surrounding the **selected element**.
**Inner shell spectroscopy**: the x-ray interacts primarily with a deep-core electron rather than a valence electron.

**XAS**: how x-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom.

XAS spectra are especially sensitive to the **formal oxidation state**, **coordination chemistry**, and the **distances**, **coordination number** and **species of the atoms** immediately surrounding the **selected element**.

- If on your system one or more of these parameters are important to follow, the XAS is for you!!
(A not so) deep physics and math of XAS
The Absorption Coefficient ($\mu$)

- The attenuation of X-rays propagating in a medium is given by the linear absorption coefficient $m$.

- For an infinitesimal thickness $dz$, at depth $z$ (Beer-Lambert's Law):

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

$$\frac{dI}{I(z)} = -\mu dz \Rightarrow I(z) = I_0 e^{-\mu z}$$
The Absorption Coefficient ($\mu$)

- What happens, for a certain material, when we probe the $\mu$ as function of the energy?

$$I = I_0 e^{-\mu(E) \cdot L}$$

Absorption Coefficient (Energy dependent)

Sample thickness
(A not so) deep physics and math of XAS

The Absorption Coefficient ($\mu$)

- **What happens, for a certain material, when we probe the $\mu$ as function of the energy?**
The Absorption Coefficient ($\mu$)

$\mu$ strongly depends on:

- X-ray energy $E$
- Atomic number $Z$
- Density $\rho$
- Atomic mass $A$

$$I = I_0 e^{-\mu(E) \cdot L}$$

$$\mu(E) \approx \frac{\rho Z^4}{AE^3}$$
For photon energies between 1 - 30 keV the photoelectric absorption is the leading interaction with matter.
(A not so) deep physics and math of XAS
Radiation-Matter Interaction

- Incident photon: High-energy x-ray
- Core shell electron interaction
- Electronic Transition ⇔ Photoelectron emission

\[ E_{\text{foton}} \sim \lambda \]

\[ \text{Matter} \]

\[ n = 2 \]

\[ n = 1 \]

\[ \mu / \rho \text{ (barn/atom)} \]

\[ E \text{ (keV)} \]

\[ 10^7 \]

\[ 10^6 \]

\[ 10^5 \]

\[ 10^4 \]

\[ 10^3 \]

\[ 10^2 \]

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Radiation-Matter Interaction

- Incident photon: High-energy x-ray
- Core shell electron interaction
- Electronic Transition → Photoelectron emission

Each atom has its own electron distribution
→ Specific (unique) ionization energy
   (Elemental sensitivity)

\( E_{\text{foton}} \sim \lambda \)

\( n = 1 \)
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*. 
(A not so) deep physics and math of XAS

De-excitation process: the origin of elemental sensitivity

Absorption \rightarrow \text{Excited state} \rightarrow \text{Decay to the ground state}

**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.
(A not so) deep physics and math of XAS

Elemental sensitivity

### Absorption: periodic table of edge and line energies

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>7112</td>
</tr>
<tr>
<td>L3</td>
<td>706.8</td>
</tr>
<tr>
<td>L2</td>
<td>719.9</td>
</tr>
<tr>
<td>L1</td>
<td>844.6</td>
</tr>
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</table>

### Iron: Z=26

<table>
<thead>
<tr>
<th>Line</th>
<th>Transition</th>
<th>Energy (eV)</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kα1</td>
<td>K-L3</td>
<td>6405.2</td>
<td>0.580</td>
</tr>
<tr>
<td>Kα2</td>
<td>K-L2</td>
<td>6392.1</td>
<td>0.294</td>
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<tr>
<td>Kβ1</td>
<td>K-M3</td>
<td>7059.3</td>
<td>0.082</td>
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<tr>
<td>Kβ3</td>
<td>K-M2</td>
<td>7059.3</td>
<td>0.043</td>
</tr>
<tr>
<td>Kβ5</td>
<td>K-M4,5</td>
<td>7110.0</td>
<td>0.001</td>
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### Uranium: Z=92

<table>
<thead>
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<th>Line</th>
<th>Transition</th>
<th>Energy (eV)</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lα1</td>
<td>L3-M5</td>
<td>13614.0</td>
<td>0.686</td>
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<tr>
<td>Lα2</td>
<td>L3-M4</td>
<td>13438.0</td>
<td>0.077</td>
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<tr>
<td>Lβ2</td>
<td>L3-N4,5</td>
<td>16387.7</td>
<td>0.181</td>
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<tr>
<td>Lβ5</td>
<td>L3-O4,5</td>
<td>17063.2</td>
<td>0.038</td>
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<tr>
<td>Lβ6</td>
<td>L3-N1</td>
<td>15727.0</td>
<td>0.013</td>
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<tr>
<td>Lε</td>
<td>L3-M1</td>
<td>11618.0</td>
<td>0.005</td>
</tr>
</tbody>
</table>
X-Ray Absorption Spectroscopy (XAS)

- Incident photon: High-energy x-ray
- Core shell electron interaction
- Electronic Transition → Photoelectron emission
- Photoelectron ↔ Spherical wave
(A not so) deep physics and math of XAS

**X-ray absorption spectroscopy on isolated atoms**

- Incident photon: High-energy x-ray
- Core shell electron interaction
- Electronic Transition → Photoelectron emission
- Photoelectron → Spherical wave

When the incident x-ray energy is larger than the binding energy, there is a sharp increase in absorption.

For an isolated atom, μ(E) has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.
The ejected photo-electron can scatter from neighboring atoms. The distance between them has some relationship to $\lambda$ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.

This interference at the absorbing atom will vary with energy, causing...
X-ray absorption is a transition between two quantum states (from an initial state to a final state),

We can use the Fermi’s Golden Rule describe $\mu(E)$:

$$\mu(E) \propto |\langle i|H|f\rangle|^2$$

$|i\rangle$: 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

$H$ is the interaction term (time-dependent perturbation) between the E.M. field and the electrons
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 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
We must to use a series of approximations to deal with the equation

\[ \hat{H}_{\text{int}} = -\frac{e}{m} \sum_j A(r_j) \cdot p_j \]

\[ A(r_j) = \hat{\epsilon} A_0 e^{i k \cdot r} \]

1. Dipole Approximation: to describe \( \hat{H} \), in terms of a classical wave (photons) interacting with the momentum operator

2. One electron approximation:
   - only 1 electron out of N modifies its state
     - leaves its deep core level
   - all other N-1 “passive” electrons relax their orbitals to adapt to the new potential created by presence of core hole

3. Sudden approximation: If the photoelectron energy is high (E > 10 eV above the edge):
   - time to exit the atom << relaxation time of passive electrons
   - neglected interaction with the passive electrons

\[ \langle f | = \langle \Psi_f^{N-1} | \psi_f \rangle \]

\[ |i\rangle = |\Psi_i^{N-1} \psi_i\rangle \]

\[ \mu_{el}(\omega) \propto \left| \langle \psi_f | \hat{\epsilon} \cdot r | \psi_i \rangle \right|^2 S_0^2 \rho(\epsilon_f) \]

\[ S_0^2 = \left| \langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle \right|^2 \]

The atomic wavefunction can be factorized!
Dipole approximation: consequences

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

\[\begin{align*}
\Delta \ell &= \pm 1 \\
\Delta s &= 0 \\
\Delta j &= \pm 1, 0 \\
\Delta m &= 0
\end{align*}\]

<table>
<thead>
<tr>
<th>EDGE</th>
<th>INITIAL STATE</th>
<th>FINAL STATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>K, L_1</td>
<td>s (\ell=0)</td>
<td>p (\ell=1)</td>
</tr>
<tr>
<td>L_2, L_3</td>
<td>p (\ell=1)</td>
<td>s (\ell=0), d (\ell=2)</td>
</tr>
</tbody>
</table>
Finally, considering the final state as a perturbation of a “bare atom” part \( |f_0\rangle \) and one that is the effect of the neighboring atom \( |\Delta f\rangle \):

\[
|f\rangle = |f_0\rangle + |\Delta f\rangle,
\]

Which leads to

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

\( \mu_0 \) depend only on the absorbing atom

\( \chi(E) \) is the EXAFS, which is proportional to the amplitude of the scattered photo-electron at the absorbing atom (related to the interference of outgoing and backscattered waves)
EXAFS Equation:

\[ \chi (k) = \sum_i \chi_i(k) \]

\[ \chi_i(k) = \frac{(S_0^2 N_i f_i(k))}{k R_i^2} e^{-2\sigma_i^2 k^2} e^{-\frac{2R_i}{\lambda(k)}} \sin \left[ 2kR_i + \varphi_i(k) \right] \]

\[ R_i = R_0 + \Delta R \quad k^2 = 2m_e(E - E_0) \]

- Theoretically calculated values
  - \( f_i(k) \) effective scattering amplitude
  - \( \varphi_i(k) \) effective scattering phase shift
  - \( \lambda(k) \) mean free path

- Starting Values
  - \( R_0 \) initial path length

- Parameters from fit
  - \( N_i \) degeneracy of path
  - \( S_0^2 \) passive electron reduction factor
  - \( \sigma_i^2 \) mean squared displacement of half-path length
  - \( E_0 \) energy shift
  - \( \Delta R \) change in half-path length
Scattering amplitude and phase shift: $F(k)$ and $\delta(k)$

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

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.
EXAFS Equation:

\[ \chi(k) = \sum_i \chi_i(k) \]

\[ \chi_i(k) = \frac{(S_0^2 N_i) f_i(k)}{k R_i^2} e^{-2 \sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}} \sin [2kR_i + \varphi_i(k)] \]

\[ R_i = R_0 + \Delta R \quad k^2 = 2m_e(E - E_0) \]

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(A not so) deep physics and math of XAS

The Fine Structure
XAS Setup and Features

Short-range technique that probes local (atomic) structure
- No periodic structure needed: liquid, amorphous, glass
- Element specific
- Suitable for establish structure-properties relationship

Beer-Lambert’s Law:
\[ I = I_0 e^{-\mu(E) \cdot L} \]

Absorption Coefficient (Energy dependent)
Sample thickness
For a selected element (Mo), one measures 

$$\mu(E) \times E$$

XAS Setup and Features
For a selected element, one measures $\mu(E) \times E$.
For a selected element, one measures $\mu(E) \times E$.

**XANES** (X-ray Absorption Near Edge Structure)
- Oxidation State
- Symmetry
- “Fingerprint” for chemical species
- Quantitative information in developing XAS Setup and Features

**EXAFS** (Extended X-ray Absorption Fine Structure)

- Bond lengths
- Symmetry
- Ligands/charge
For a selected element, one measures \( \mu(E) \times E \). XANES (X-Ray Absorption Near Edge Structure) is used to determine the oxidation state, symmetry, and 'fingerprint' for chemical species. Quantitative information in developing EXAFS (Extended X-ray Absorption Fine Structure) studies is also possible.
For a selected element, one measures $\mu(E) \cdot E$. XANES (X-Ray Absorption Near Edge Structure) provides information about the oxidation state, symmetry, and "fingerprint" for chemical species. XAS Setup and Features include EXAFS (Extended X-ray Absorption Fine Structure) for quantitative information on bond lengths, symmetry, and ligands/charge. The diagram shows normalized absorbance spectra for different chemical species, including elemental, thiohemianthraquinone, sulfides, sulfoxide, sulfones, and sulfate, with corresponding molecular structures.
For a selected element, one measures $\mu(E) \times E$.

**XANES** (X-ray Absorption Near Edge Structure)
- Oxidation State
- Symmetry
- "Fingerprint" for chemical species
- Quantitative information in developing XANES

**XAS Setup and Features**
For a selected element, one measures $\mu(E) \times E$. XANES (X-Ray Absorption Near Edge Structure) provides information on:

- Oxidation State
- Symmetry
- "Fingerprint" for chemical species
- Quantitative information in developing XAS Setup and Features.
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
For a selected element, one measures $\mu(E) \times E$.

**EXAFS (Extended X-ray Absorption Fine Structure)**

Structural information:
- Bond distances
- Coordination number
- Type of neighbors
- Structural disorder

Quite similar but IT IS NOT A Radial Distribution Function!!!!
EXAFS: typical applications

- 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

Element selectivity
Local structure sensitivity
Knowing EXAFS spectra of a material, how to obtain its structure?
XAS Data Analysis: Workflow

Data collection

Preliminary data treatment

Extraction of EXAFS structure signal, $\chi(k)$

Modeling and Refinement of the Structure

Check of results (physically meaningful?)

Revise

Propose a Model

END
XAS Data Analysis

Glitches

Discontinuities

E₀ Definition

Preliminary data treatment
XAS Data Analysis

Extraction of EXAFS structure signal, $\chi(k)$

Normalization

Bkgd Removal
EXAFS and the Fourier Transform

EXAFS

\[ \chi(E) \sim \frac{\mu(E) - \mu_0(E)}{\Delta \mu(E_0)} \]

\[ k^2 = \frac{2m_e(E-E_0)}{\hbar} \]

Fourier transform:

\[ FT(r) = \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k) k^n \Omega(k) e^{-2ikr} \, dk \]
For a selected element, one measures \( \mu(E) \times E \) EXAFS \( \chi_E \) ~ \( \mu(E) - \mu_0(E) / \Delta \mu(E_0) \)

\[ k^2 = \frac{2m_e(E-E_0)}{\hbar} \]
Chose a Model
Define relevant structural contributions
Fitting and Refinement

XAS Data Analysis
MoS$_2$ Nanoparticle
MoS$_2$ Bulk

Support
XAS Data Analysis

Support

MoS\textsubscript{2} Nanoparticle

MoS\textsubscript{2} Bulk

Structural parameters:

- N (Number of Neighbors)
- R (Distance, bound length)
- Debye-Waller
- Energy of the transition
XAS Data Analysis

Support

MoS$_2$ Nanoparticle

MoS$_2$ Bulk

Chose a Model

Define relevant structural contributions

Fitting and Refinement
XAS Data Analysis: Interpretation

### Comparison of the Refined Parameters

<table>
<thead>
<tr>
<th>Bound Type</th>
<th>$\Delta E$ (eV)</th>
<th>N</th>
<th>R (Å)</th>
<th>$\Delta R$ (Å)</th>
<th>$\sigma^2$(Å$^2$)</th>
<th>$\Delta \sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-S</td>
<td>5.3</td>
<td>6</td>
<td>2.40</td>
<td>0.01</td>
<td>0.0032</td>
<td>0.0007</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>3.17</td>
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<td>0.01</td>
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<tr>
<td>Mo-S</td>
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<td>Mo-S</td>
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<td>Mo-Mo</td>
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</tbody>
</table>

XANES of nanometric structures may be far from bulk!