X-ray Spectroscopy

- Lecture 1: Introduction & experimental aspects
- Lecture 2: Atomic Multiplet Theory
  - Crystal Field Theory
  - CTM4XAS program
- Lecture 3: Charge Transfer Multiplet Theory
  - Resonant Inelastic X-ray Scattering
  - X-ray Spectroscopy on nanomaterials

Röntgen's experiment in 1895

Interaction of x-rays with matter

Gas Discharge Tube

<table>
<thead>
<tr>
<th>In points of the cathode, moved the rays.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel to the cathode.</td>
</tr>
</tbody>
</table>

Wavelength: $10^{-10}$ m

Frequency: $C/\lambda = 3 \cdot 10^{18}$ Hz

x-rays
1.1 The Characteristics of Electromagnetic Radiation

- Interaction of x-rays with matter:
  - XAFS studies photoelectric absorption
  - Thompson scattering (Diffraction)
  - Compton scattering

**Interaction of x-rays with matter 1**

The photon moves towards the atom

<table>
<thead>
<tr>
<th>Interaction of x-rays with matter 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>The photon meets an electron and is annihilated</td>
</tr>
</tbody>
</table>

**Interaction of x-rays with matter 1**

The electron gains the energy of the photon and is turned into a blue electron.

**Interaction of x-rays with matter 1**

The blue electron (feeling lonely) leaves the atom and scatters of neighbors or escapes from the sample.
**Interaction of x-rays with matter**

The probability of photon annihilation determines the intensity of the transmitted photon beam.

\[ I_0 \rightarrow E_k \rightarrow I \]

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**XPS machine**

- Photo-Emitted Electrons (less than 2 eV) escape only from the very top surfaces: FE-SEM (Field Emission Scanning Electron Microscope)
- Ejection of photoelectrons typically requires a very high vacuum (>10⁻⁸ torr)

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**X-ray photoemission**

- Vacuum level
- Core level
- Fermi level

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**X-ray photoemission: workfunction**

- Vacuum level
- Work function
- Ionization energy

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**Figure 6.11**
**XPS and the photo-electric effect**

Photo-electric effect

\[ \hbar \nu = E_k + \Phi \]

XPS

\[ \hbar \nu = E_L + E_k + \Phi \]

**Binding Energy:**

defined versus highest occupied state

\[ E_{\text{vac}} \]

\[ E_F \]

\[ E_{\text{L}} \]

\[ E_{\text{K}} \]

\[ E_{\text{G}} \]

**X-ray photoemission**

XPS: Sample: Pd

**Atomic binding energies**

THE HIGH FREQUENCY SPECTRA OF THE ELEMENTS (1913)

Moseley (1887-1915)

**Atomic binding energies**

...simple laws have been found which [...] make it possible to predict with confidence the position of the principal lines in the spectrum of any element from aluminum to gold.

\[ \nu = 2.5 \times 10^{15} (Z-\alpha)^2 \text{ Hz} \]
Screening of charge: $\text{hC}^*(Z_{\alpha})^2 = 528 \text{ eV}, \text{ with } Z_{\alpha} = 7.2$

$\text{hC}^* (Z-\alpha)^2, \text{ with } \alpha = 0.8$

Transition from 1s to 2p in hydrogen:

$$h\nu = hR \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \approx 13.6 \times (1/1-1/4) \approx 10 \text{ eV}$$

Transition from 1s to 2p in oxygen:

$$h\nu = hR \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) Z^2$$

$$= 10 \times 8^2 = 10 \times 64 = 640 \text{ eV}$$

Paladium Electron binding energies

<table>
<thead>
<tr>
<th>K</th>
<th>3d</th>
<th>671.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>3p</td>
<td>599.9</td>
</tr>
<tr>
<td>L</td>
<td>3p3d</td>
<td>532.3</td>
</tr>
<tr>
<td>M</td>
<td>4s</td>
<td>340.5</td>
</tr>
<tr>
<td>M</td>
<td>3p</td>
<td>335.2</td>
</tr>
<tr>
<td>N</td>
<td>4s</td>
<td>87.1</td>
</tr>
<tr>
<td>N</td>
<td>3p3d</td>
<td>55.7</td>
</tr>
<tr>
<td>N</td>
<td>3p</td>
<td>50.9</td>
</tr>
</tbody>
</table>

http://www.webelements.com/
Interaction of x-rays with matter

\[ I_0 \rightarrow \bullet \rightarrow I \rightarrow \varepsilon \]

X-ray absorption experiments

\[ \text{DOS} \]

\[ \text{Energy (eV)} \]

X-ray absorption and X-ray photoemission

Jump at binding energy

Peak at binding energy

X-ray absorption and X-ray photoemission

X-ray absorption experiments
X-ray absorption and X-ray photoemission

\[ W_{ij} = \frac{e^2}{\hbar c \lambda} \sum_{\alpha} \langle \Phi_i | \Phi_j | \Phi_\alpha \rangle \delta(E_\alpha - E_j - E_i) \]

Electronic Structure; TiO₂

Electronic Structure: TiO₂

X-ray Absorption Spectroscopy

Electronic Structure; TiO₂
Excitation of core electrons to empty states.

Spectrum given by the Fermi Golden Rule

\[ I_{XAS} \sim \sum_f \left| \left< \Phi_f \right| \hat{\epsilon} \cdot r \left| \Phi_i \right> \right|^2 \delta_{E_f - E_i - \hbar \omega} \]

Fermi Golden Rule:

\[ I_{XAS} = \left| <\Phi_f|dipole|\Phi_i>\right|^2 \delta_{[\Delta E=0]} \]

\[ = \epsilon \left| \left< \Phi_f \right| \hat{\epsilon} \cdot r \left| \Phi_i \right> \right|^2 \]

Single electron (excitation) approximation:

\[ I_{XAS} = \left| <\Phi_{empty}|dipole|\Phi_{core}>\right|^2 \rho \]

X-ray absorption: core hole effect


\[ \text{Ground State} \]

\[
\begin{array}{c|c}
\text{Mn 4p} & - \\
\text{Mn 3d} & 0 \\
\text{O 2p} & 5 \\
\text{O 2s} & 20 \\
\text{Mn 3p} & 45 \\
\text{Mn 3s} & 80 \\
\text{O 1s} & 530 \\
\text{Mn 2p} & 650 \\
\text{Mn 2s} & 770 \\
\text{Mn 1s} & 6540 \\
\end{array}
\]

\[ \text{MnO 3d}^5 \]

\[ \text{Oxygen 1s XAS} \]

\[
\begin{array}{c|c}
\text{Mn 4p} & - \\
\text{Mn 3d} & 0 \\
\text{O 2p} & 5 \\
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\end{array}
\]

\[ \text{MnO 3d}^5 \]
The life of a Core Hole

Heisenberg uncertainty relation
\[ \tau \equiv \hbar (~ 10^{-16} \text{ eV s}). \]

Broadening of XAS: ~0.1 eV

Lifetime = 1 femtosecond

Oxygen 1s2p2p Auger

Auger spectroscopy

X-ray emission
Mn $1s^3p$ XES

Resonant X-ray emission spectroscopy

Energy [eV]

Fermi Golden Rule:

\[ I_{\text{XAS}} = |<\Phi_f|\text{dipole} |\Phi_i>|^2 \delta(\Delta E=0) \]

\[ = |\langle \Phi_f | \hat{\epsilon} \cdot r | \Phi_i \rangle |^2 \]

Single electron (excitation) approximation:

\[ I_{\text{XAS}} = |<\Phi_{\text{empty}}|\text{dipole} |\Phi_{\text{core}}>|^2 \rho \]

Multiplet Effects in XAS
Multiplet Effects in XAS

Overlap of core and valence wave functions

→ Single Particle model breaks down

<2p3d|1/r|2p3d>

PRB 42, 5459 (1990)

XAS

Single Particle:
1s edges
(DFT codes)

Multiplets:
2p, 3s, 3p edges
(CTM4XAS)

No Unified Interpretation!

Bethe-Salpeter calculations (Eric Shirley):

Excited state = linear superposition of all states produced by a single electron excitation.

In each such electron-hole pair state,

- electron in band $n'$ with crystal momentum $k+q$
- hole in [band or core-level] $n$ with crystal momentum $k$

Single Particle:
1s edges
(DFT + core hole (+U))

2-particle:
(TDDFT, BSE)
+ L edges of 3d$^0$

Many-particle:
2p, 3s, 3p edges
(CTM4XAS)
XAS: multiplet effects

- Single Particle:
  - 1s edges
  - (DFT + core hole (+U))

- 2-particle:
  - (TDDFT, BSE)
  - + L edges of 3d

- Many-particle:
  - 2p, 3s, 3p edges
  - (CTM4XAS)

No Unified Interpretation!

X-ray absorption and X-ray photoemission

X-rays from synchrotrons

Linear Accelerator

Storage Ring
**Magnets in the storage ring**

- Dipol
- Quadrupol
- Sextupol
- Bending magnet
- Accelerating cavity
- Wiggler & undulators

**Magnetic Force**

\[ F = q \cdot v \cdot B \]

- Perpendicular to Field and propagation direction

**X-rays from synchrotrons**

- **Bending Magnets**
- **Insertion Devices:**
  - Wiggler
  - Undulator

**Continuous Spectrum for Wiggler, Bending Magnet and Wave-length Shifter**

\[ I(1/\lambda) \]

- \( \lambda \) is the wavelength

\[ I(1/\lambda) \text{ undulator line spectrum} \]

1.\( \frac{1}{\lambda} \)
2.\( \frac{3}{\lambda} \)
3.\( \frac{5}{\lambda} \)
X-rays from synchrotrons

X-ray absorption beamline (transmission)

I  Entrance slits  II  Monochromator
III  Exit slits  IV  Ionisation chamber
V  Sample  VI  Ionisation chamber
VII  Reference material  VIII  Ionisation chamber

Beamline 18ID at the APS

http://www-als.lbl.gov/als/
**Why a synchrotron?**

- **Energy**: tunable source
- **Intensity**: $10^6$-$10^{12}$ higher than x-ray tube
- **Space**: spot-size 1x1 mm (unfocussed)
  - down to 20x20 nm (focussed)
- **Time**: pulse 50 ps, sliced down to 50 fs.
- **Polarization**: Angular dependence & Circular dichroism:
  - **NOT coherent** (no laser)

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**XAS: multiplet effects**

- **Single Particle**:
  - 1s edges
  - (DFT + core hole (+U))

- **2-particle**:
  - (TDDFT, BSE)
  - + L edges of 3d

- **Many-particle**:
  - 2p, 3s, 3p edges
  - (CTM4XAS)

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**Charge Transfer Multiplet program**

*Used for the analysis of XAS, EELS, Photoemission, Auger, XES,*

**ATOMIC PHYSICS**

⇓

**GROUP THEORY**

⇓

**MODEL HAMILTONIANS**

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**The CTM4XAS program**

*Charge Transfer Multiplet Calculations for X-ray Absorption Spectroscopy*

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