Core level spectroscopy: XPS, XAS, EELS, XES (XSPEC, TELNES)

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Ionization potential of core-e\(^-\), IP = \(E_{\text{tot}}(N) - E_{\text{tot}}(N-1)\)

- *gives information on charge state of the atom*

Core-eigenvalues \(\varepsilon_i\) are NOT a good approximation: \(\varepsilon_i = \frac{dE}{dn}\)

Slater’s “transition state”:
- Core-eigenvalues \(\varepsilon_i\) for half occupancy

\(\Delta\)-SCF-calculation with and without core-hole: \(E_{\text{tot}}(N) - E_{\text{tot}}(N-1)\)
- *supercells to reduce hole-hole interaction*

<table>
<thead>
<tr>
<th>C,N 1s</th>
<th>exp.(eV)</th>
<th>(\varepsilon_i)</th>
<th>(\Delta)-SCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>281.5</td>
<td>264.7</td>
<td>281.9</td>
</tr>
<tr>
<td>Ti(_4)C(_4)</td>
<td>281.5</td>
<td>263.3</td>
<td>281.1</td>
</tr>
<tr>
<td>TiN</td>
<td>397.0</td>
<td>377.5</td>
<td>397.1</td>
</tr>
</tbody>
</table>
XAS (XANES), EELS (ELNES), XES:

- core electrons are excited into a conduction band
- Each core shell introduces an absorption edge, (they are indexed by the principal number of a core level)
  - K-1s, L_1-2s, L_2-2p_{1/2}, L_3-p_{3/2}

XES:

- knock out a core electron, **valence electron** fills core hole and **hv** is emitted
X-ray absorption spectroscopy - XAS
Electron energy loss spectroscopy - EELS

EELS spectrum of various TM oxides

X-ray Absorption
Near-Edge Structure
Extended X-ray Absorption Fine Structure
Difference between EELS and XAS

XAS: synchrotron

EELS: microscope
XAS vs. EELS: theory

- Transition described by Fermi's "golden rule" between initial (core) and final (conduction-band) state and the electron or photon.

- Double differential cross section:

\[
\frac{\partial^2 \sigma}{\partial E \partial Q}(E, Q) = \zeta \sum \frac{k_F}{k_I} \left| \langle I | k_I | V | k_F F \rangle \right|^2 \delta(E_I - E_F)
\]

- Single differential cross section:

\[
\frac{\partial \sigma}{\partial E} \propto \sum \left| \langle I | e^{i\vec{q} \cdot \vec{R}} | F \rangle \right|^2
\]

- Momentum transfer \( \vec{q} \)

- Polarization vector \( \vec{e} \)

E - conservation
dipole approximation

\[ \vec{q} \vec{R} \ll 1 \rightarrow e^{i \vec{q} \vec{R}} = 1 + i \vec{q} \vec{R} + \frac{(\vec{q} \vec{R})^2}{2!} + \ldots \]

EELS

\[ \frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{q} \vec{R} | F \rangle \right|^2 \]

XAS

\[ \frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{e} \vec{R} | F \rangle \right|^2 \]

The polarization vector in XAS plays the same role as momentum transfer in (nonrelativistic) ELNES within the dipole approximation.

(TELNES3 can also handle non-dipole transitions + relativistic corrections)

core-valence spectroscopies give information on the local DOS (because of \( \langle \Psi_{\text{core}} | r | \Psi_{\text{val}} \rangle \)) of angular momentum character \( \ell \pm 1 \)
“Final state rule”:

“Final state” determines the spectrum:

- **Emission spectroscopy:**
  Final state has filled core, but valence hole.
  This is usually well screened, thus one “sees” the groundstate.

- **Absorption spectroscopy:**
  Final state has a “hole” in core state, but additional $e^-$ in conduction band.
  Core-hole has large effect on the spectrum
  - **electron – hole interaction, “excitonic effects”**

![Graph showing energy levels and states](image)
Treating the core hole within WIEN2k

- No core hole (= ground state, sudden approximation)
  - usually not a good approximation (maybe in metals ?)
- Z+1 approximation (eg., replace C by N)
  - also not very good
- Core-hole (supercell) calculations:
  - Remove 1 core electron on ONE atom in the supercell, add 1 electron to conduction band
  - Remove 1 core electron, add 1 electron as uniform background charge
    - considers statically screened e⁻ - h coulomb correlation
    - Fractional core hole (consider different screening)
- Explicit treatment of electron-hole interaction (excitonic effects) using Bethe-Salpeter equation (BSE)
“Final state rule” + core hole:

- 2x2x2 supercell calculation, with core hole in one of the Mg atoms. This allows the conduction state to relax (adjust to the larger effective nuclear charge), but also to have static screening from the environment.

core hole, no supercell:

Z+1 (AlO)

groundstate
XAS / TELNES in WIEN2k

- define your structure (structgen)
- initialize calculation (init_lapw)
- run scf-cycle (run_lapw)
- geometry optimization of your structure (min_lapw)
- generate supercell (x supercell)
- initialize supercell structure, define core hole/add valence e^{-}
- run scf-cycle
- remove extra valence e^{-}
- run XSPEC / TELNES3 task
XSPEC-task

Session: magnetite
/area51/pbla/la/pw/correlated/magnetite

XSPEC

[ Spin UP ] [ Spin DOWN ]

Spin UP selected.

If you want to include states with higher energy

- edit magnetite.in1 Edit in1
- x lapw1 -up Calculate eigenvalues ✔ interactively
- x lapw1 -dn Calculate eigenvalues ✔ interactively
- x lapw2 -qtl -up Calculate partial charges ✔ interactively
- edit magnetite.inxs Edit input-file for XSPEC
- x xspec -up Calculate X-ray spectra ✔ interactively
- plot Plot XSPEC

Title: Atom 1 L3 absorption spectrum
1 (atom)
2 (n core)
1 (l core)

0, 0.5, 0.5 (split, Int1, Int2)
-2, 0.02, 15 (EMIN, DE, EMAX)
ABS (type of spectrum)
1.00 (S)
2.0 (gamma0)
1.50 (W only for BMIS)
AUTO (AUTO or MANually select Energy
-6.93
-10.16
-13.9
B-K XANES in h-BN/Ni(111)

- B-K edge in BN and BN/Ni(111)
- Preobrajenski et al., PRB70, 165404 (2004): “The experiments contradict recent DFT calculations by Grad et al.”
Angle dependency of B-K edge in h-BN/Ni(111)

$\pi^*$-bands (they interact with Ni!)
Partial core hole screening in the Cu L₃ edge


Unexpected effect of core-hole!
L_{2,3} spectra: failure of the single particle approach

- In particular early 3d TM-compounds show a
  - non-standard $L_2/L_3$ branching ratio (1:2)
  - sometimes a completely different lineshape (TiO$_2$)
  - "wrong" SOC or CF splittings

![Diagram of L$_2$ and L$_3$ spectra for TiO$_2$ and CaF$_2$]
Beyond IPA

- **ab-initio** configuration interaction (solid is approximated by finite cluster)
  

- Linear response in time dependent DFT (TDDFT)
  

- Bethe-Salpeter equation (BSE)
  
**Bethe-Salpeter-equation: \( L(12;1'2') \)**

- solving a 2-particle (e⁻ - h) equation of large dimension (\( N_v N_c N_k \sim 100000 \))

\[
\sum_{v'c'k'} \left( H_{v'c'k',vck}^{eh} \right) A_{v'c'k'}^\lambda A_{vck}^\lambda = E^\lambda A_{vck}^\lambda
\]

\[
H^{eh} = H^{diag} + H^{dir} + 2H^x
\]

\[
H^{diag}_{vck'v'c'k'} = (E^e_{v,k} - E^c_{c,k}) \delta_{cc'} \delta_{vv'} \delta_{kk'}
\]

eigenvalue difference between hole (v) and electron(c) state

\[
H^{dir}_{vck'v'c'k'} = -\int d^3r d^3r' \Psi_{vk}(r) \Psi^{*}_{ck}(r') W(r,r') \Psi^{*}_{v'k'}(r) \Psi_{c'k'}(r')
\]

attractive screened static Coulomb interaction \( W; W \sim e^{-1} \)

\[
H^x_{vck'v'c'k'} = \int d^3r d^3r' \Psi_{vk}(r) \Psi^{*}_{ck}(r) \bar{v}(r,r') \Psi^{*}_{v'k'}(r') \Psi_{c'k'}(r') v^{es}
\]

e-h exchange with bare Coulomb potential \( v \)

**Excitons in LiF**
Ca-L$_{23}$ edge in CaF$_2$

- “ground-state” DOS
- Experiment
- BSE for $L_2$ and $L_3$ separately
- BSE with $p_{1/2}$ and $p_{3/2}$ together
- BSE without direct term $H_{\text{dir}}$
- BSE without exchange term $H_{\text{ex}}$
L$_{2,3}$ edge for Ca in CaF$_2$

Decomposition of $\varepsilon_2$ into the excitation from $p_{1/2}$ and $p_{3/2}$ states cross terms suppress the L$_3$ branch and enhance L$_2$
The experimental Ti L$_{2,3}$ edges are rather well reproduced.

- intensity ratio L$_3$/L$_2$ (not 2:1)
- ~t$_{2g}$/e$_g$~ ratio (not 3:2)
- left/right shoulder in L$_3$-~e$_g$~ peak of rutile/anatase
Ti L$_{2,3}$ in SrTiO$_3$, decomposition of $\varepsilon_2$

Decomposition into excitations from $p_{1/2}$ and $p_{3/2}$

cross term suppresses the L$_3$ branch and enhances the L$_2$

Decomposition into excitation into the e$_g$ and t$_{2g}$ bands

the first peak of L$_2$ or L$_3$ is related to excitations into t$_{2g}$, the second peak is associated with e$_g$
the cross term strongly modifies the ratio between these peaks
3d metal L_{2,3} branching ratio

The size of spin orbit splitting is a main factor determining the branching ratio (deviating from 0.5)

Ti L_{2,3} branching ratio in rutile-TiO_2 (SOC splitting is set to values from 5eV to 25eV)
fcc Ca, $L_{2,3}$ edge
“Practical aspects of running the WIEN2k code for electron spectroscopy”,
C. Hebert, Micron 38 (2007) 12–28

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Thank you for your attention!