Materials Modelling as a Tool to Interpret EELS

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Electron Energy Loss

- Phantom Scattering
- Plasmon Scattering
- Single electron excitation
- Direct Radiation losses

Plasmons ~ 5-30 eV
Single excitations ~50-2000eV
Electronic Structure

Density of states

Core states

Semi-core states

Extended states

Energy

$E_F$
Electronic Structure

Fermi’s Golden rule

\[ T_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H | i \rangle|^2 \rho \]
The dielectric functions tell us about the response of a material to an electric field

\[ D(\omega, q) = \varepsilon(\omega, q) \cdot E(\omega, q) \]

\[ \varepsilon(\omega, q) = \varepsilon_1(\omega, q) + i\varepsilon_2(\omega, q) \]

Loss function:

\[ \text{Im} \left\{ \frac{-1}{\varepsilon(\omega, q)} \right\} \]

Kramers-Kronig:

\[ \varepsilon_1 \leftrightarrow \varepsilon_2 \]

When an electron moves through a medium it creates a displacement field D. The loss function gives the rate of energy absorption.
Core-loss

At high energies (ie transitions from core-states) the loss function is given by the imaginary part of the dielectric function.

\[
\text{Im} \left\{ \frac{-1}{\varepsilon(q, \omega)} \right\} = \varepsilon_2(q, \omega)
\]

\[
\varepsilon_2(q, E) = \frac{4\pi e^2}{\Omega q^2} \sum_{n,k} |\langle \psi^n_k | e^{i\mathbf{q} \cdot \mathbf{r}} | c \rangle|^2 \delta(E^c_k - E_{1s} - E)
\]
ELNES - Energy Loss Near Edge Structure
EXELFS - Extended Energy Loss Fine Structure

"bonding"
"nearest neigbour"
<table>
<thead>
<tr>
<th>Core electron</th>
<th>Edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s^{1/2}</td>
<td>K</td>
</tr>
<tr>
<td>2s^{1/2}</td>
<td>L_1</td>
</tr>
<tr>
<td>2p^{1/2}</td>
<td>L_2</td>
</tr>
<tr>
<td>2p^{3/2}</td>
<td>L_3</td>
</tr>
<tr>
<td>3s^{1/2}</td>
<td>M_1</td>
</tr>
<tr>
<td>3p^{1/2}</td>
<td>M_2</td>
</tr>
<tr>
<td>3p^{3/2}</td>
<td>M_3</td>
</tr>
<tr>
<td>3d^{3/2}</td>
<td>M_4</td>
</tr>
<tr>
<td>3d^{5/2}</td>
<td>M_5</td>
</tr>
</tbody>
</table>

Angular momentum state

2p^{1/2}

Principle quantum number

j quantum number (combination of spin and angular momentum)
Dipole Rule

\[ \langle f | e^{i \mathbf{q} \cdot \mathbf{r}} | i \rangle = \langle f | i \rangle + i \langle f | \mathbf{q} \cdot \mathbf{r} | i \rangle + \frac{1}{2} \langle f | (\mathbf{q} \cdot \mathbf{r})^2 | i \rangle - \frac{i}{6} \langle f | (\mathbf{q} \cdot \mathbf{r})^3 | i \rangle + \frac{1}{24} \langle f | (\mathbf{q} \cdot \mathbf{r})^4 | i \rangle + \cdots \]

Dipole term

\[ \langle f | x | 1s \rangle \approx \langle f | P_x \rangle \]

Core level spectra can be thought of as angular momentum projected density of states
EELS vs DOS

graphite
Numerically Accurate Spectral Properties

DOS BN nanoribbon

Adaptive Broadening
• Density of states (DOS)
• Projected DOS
• Joint-density of states (JDOS)
• Core-loss
  • Absorption and Emission
  • momentum (q) decomposition
  • Instrument and lifetime broadening
• Low loss
  • Metals & insulators

Adaptive Broadening
Practical Details

CASTEP

- computes core and valence wavefunctions
- forms matrix elements $\langle \psi_k^n | r | c \rangle$
- must use on-the-fly pseudo-potentials
- keywords
  - task : spectral
  - spectral_task : coreloss

OPTADOS www.optados.org

- Reads matrix elements
- Forms spectrum
- Can add instrument and lifetime broadening effects
- more details in this afternoon’s practical
Core-hole effects

Single-particle approximation

Beyond the “sudden” approximation
1) Core electron ejected
2) Lattice remains fixed
3) Final states relax
Initial core state from an atomic calculation
Final states from self consistent calculation with a single excited atom

Supercell approximation

• Core-hole atom breaks translational symmetry
• Create “supercell” of unit cell to reduce interaction between images
• Converge wrt supercell size
Excited Atom

Methods to include core-hole

• Z+1 approximation (*eg replace C with N*)
• Constrained calculation (*only possible with AE code*)
• Excited pseudopotentials

CASTEP’s *on-the-fly pseudopotential generator can create excited-state pseudopotentials* - see practical for details

Effect of core-hole depends on material
Momentum Decomposition
The low-loss dielectric function is a weighted joint-density of states

$$
e_2(E) = \frac{2\pi e^2}{\Omega \epsilon_0} \sum_{i,j,k} |\langle \psi_{ik}|\hat{u}.r|\psi_{jk}\rangle|^2 \delta(\epsilon_{ik} - \epsilon_{jk} - E)$$

$$jDOS(E) = \frac{1}{N_k} \sum_{i,j,k} \delta(\epsilon_{ik} - \epsilon_{jk} - E)$$
Practical Details

CASTEP

- computes valence wavefunctions
- forms optical matrix elements

Keywords

```
task : spectral
spectral_task : optics
```

OPTADOS www.optados.org

- Reads matrix elements
- Forms
- Uses Kramers-Kronig to obtain
- Computes loss function, conductivity, refractive index etc
- Can add broadening effects

more details in this afternoon’s practical
Low loss

\[ \varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega \varepsilon_0} \sum_{i,j,k} | \langle \psi_{ik} | \hat{u} | \psi_{jk} \rangle |^2 \delta(\varepsilon_{ik} - \varepsilon_{jk} - E) \]

\[ \mu \text{Kramers Kronig} \]

CASTEP

\[ \varepsilon_1(\omega) \]

OPTADOS

\[ \text{Im} \left\{ \frac{-1}{\varepsilon(\omega)} \right\} \]

OPTADOS

Graph showing the energy loss function with "epsilon 1", "epsilon 2", and "loss function" curves.
BN sheets

Experiment

Calculation

(b) Intensity (arb. scale) vs. Energy loss (eV)

- thick
- thin

(b) Intensity (arb. scale) vs. Energy loss (eV)

- bulk
- 1 layer
Going beyond the ground state

Many-body perturbation theory

Start with DFT
Use GW to get corrected excited states
Use BSE (Bethe-Salpeter Equation) to include electron-hole interaction (exciton)

Time-Dependent DFT

Exact solution of time-dependent QM
Need to devise exchange-correlation kernel - maybe useful for low-loss EELS

Multiplet Effects

For edges such as the L_{2,3} there can be strong overlap between the core and valence wavefunctions
BSE

Li-K edges of LiCl

T. Mizoguchi et al. / Micron 41 (2010) 695–709
Summary

Standard electronic structure tools can provide qualitative interpretation of core and low loss EELS.

Care must be taken in interpreting unoccupied DFT.

Many-body approaches provide a route to quantitative simulations, but at a very high computational cost.

Can TD-DFT provide a useful balance of speed and accuracy?

Also FEFF code - work of J.J. Rehr

More Info
www.optados.org