Improving Optical and X-Ray Spectroscopy in ABINIT

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Overview

- Challenges
- Theory:
  - Kubo-Greenwood formula
  - Spin-Orbit Coupling
  - Relativistic core wave functions
- Implementation:
  - Optical spectroscopy
  - XANES
- Results
- Conclusions and Outlook
Introduction
Challenges

Optical Conductivity

- Optical spectra of simple metals, e.g. aluminium can reproduced well.
- Heavier elements, e.g. gold, still pose a challenge.
- Inclusion of spin-orbit coupling is important.
- But has been problematic in the past.

1 Abinit user meeting 2013
Near edge structures of single absorption edges can already be reproduced by ABINIT.

As usual in DFT, the total energy has to be corrected.

Spin orbit splitting of e.g. copper L2/3 edge could not be predicted in ABINIT.

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Thesis N. Jourdain
**Optical Conductivity**

The real part of the optical conductivity can be calculated using the Kubo-Greenwood formula:

\[
\sigma_1(k, \omega) = \frac{2\pi}{3\omega \Omega} \sum_{j=1}^{n_b} \sum_{i=1}^{n_b} (f(\epsilon_i, k) - f(\epsilon_j, k)) |M|^2 \delta(\epsilon_j, k - \epsilon_i, k - \omega)
\]

**Matrix Element**

Without spin orbit coupling, the matrix element has the following form:

\[
M = \langle \psi_{j,k} | v | \psi_{i,k} \rangle = \langle \psi_{j,k} | \frac{i}{\hbar} [H, r] | \psi_{i,k} \rangle = \langle \psi_{j,k} | - i\hbar \nabla | \psi_{i,k} \rangle
\]
Spin-Orbit Coupling

With increasing charge of the ion, relativistic effects have to be considered. One important effect is the so-called spin-orbit coupling.

Hamiltonian

Spin-orbit coupling is included in the Hamiltonian:

$$H_{SO} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{L} \cdot \mathbf{S}$$

Kubo-Greewood Formula

This also modifies the matrix element in the Kubo-Greewood formula for the optical conductivity:

$$M = \langle \psi_{j,k} | \mathbf{v} | \psi_{i,k} \rangle = \langle \psi_{j,k} | -i\hbar \nabla + \frac{\hbar}{4m^2c^2} \mathbf{\sigma} \times \frac{\mathbf{r}}{r} \frac{dV(r)}{dr} \rangle | \psi_{i,k} \rangle$$
**Theory**

**Dirac Relativistic Atomic Calculation**

### Solution Provided by New Version of Atompaw

\[
\psi_{njm}^l = \begin{pmatrix}
g_{nj}(r)\varphi_{jm}^l \\
if_{nj}(r)\hat{\sigma} \cdot \hat{r} \varphi_{jm}^l
\end{pmatrix}
\]

### Angular Part

\( \kappa < 0 \Leftrightarrow j = l + \frac{1}{2} : \)

\[
\varphi_{jm}^l = \sqrt{\frac{l + \frac{1}{2} + m_j}{2l + 1}} Y_l^{m_j - \frac{1}{2}} \chi_{\frac{1}{2}} + \sqrt{\frac{l + \frac{1}{2} - m_j}{2l + 1}} Y_l^{m_j + \frac{1}{2}} \chi_{-\frac{1}{2}}
\]

\( \kappa > 0 \Leftrightarrow j = l - \frac{1}{2} : \)

\[
\varphi_{jm}^l = \sqrt{\frac{l + \frac{1}{2} - m_j}{2l + 1}} Y_l^{m_j - \frac{1}{2}} \chi_{\frac{1}{2}} - \sqrt{\frac{l + \frac{1}{2} + m_j}{2l + 1}} Y_l^{m_j + \frac{1}{2}} \chi_{-\frac{1}{2}}
\]
Level scheme including spin-orbit coupling

Statistics are treated correctly by considering all valid $m_j$ of each level (actual $m_j$ energy split occurs only with external magnetic field or when considering hyper fine structure).
Fixing prtnabla 1 plus nspinor 2

- Corrected wrong ordering in 42_libpaw/pawcprj.F90:pawcprj_mpi_allgather in case of nspinor 2 and rank_ordered=false:

```fortran
do iproc=1,nproc
  do jj=1,n2dim/nsp
    do ispinor=1,nsp
      ibuf=ispinor+(iproc-1)*nsp+(jj-1)*nproc*nsp
      do iat=1,natom
        nn=nlmn(iat)
        cprj_gat(iat,ibuf)%cp(:,1:nn)=buffer_cpgr_all(:,1,ipck+1:ipck+nn)
        if(ncpgr/=0) cprj_gat(iat,ibuf)%dcp(:,1:ncpgr,1:nn)=&
        buffer_cpgr_all(:,2:1+ncpgr,ipck+1:ipck+nn)
        ipck=ipck+nn
      end do
    end do
  end do
end do
```

NetCDF Support

- prtnabla 1 will now produce a NetCDF file if iomode 3 is chosen.
SOC velocity matrix element

- Functions: 65_paw/m_paw_opitcs.F90:optics_paw_soc and optics_paw_soc_init
- Current keyword: useria 5121986 (will be changed to prtnabla 4 for release)
- Will calculate SOC term in the velocity operator.
- More memory intensive for high number of atoms, since the potential varies per atom and not only per atom type.
Implementation

Xanes

ATOMPAW data transfer

- Added output for both radial wave functions generated by the dirac-relativistic generator.
- Output as .abinit or .xml possible.
- Files indicate their generator type as well as the variable $\kappa$.
- Abinit can read both file types, support for dirac-relativistic core wave functions needs to be activated (currently useria 29091988, will be prtnabla 5).
Implementation of the angular solution

- ABINIT already calculates angular matrix element for the nabla operator using spherical harmonics.
- To take advantage of that, the indlmn_core data structure was modified to represent the structure of the angular solution.
- After that, the implementation was rather straightforward.
- Output with NetCDF is now also possible with prtnabla 3 + iomode 3

Conducti

- Can read the new NetCDF files.
- Can use MPI to parallelize on bands (just use mpirun -np n).
- XANES mode now supports variable width smearing.
- Small fixes to ensure nspinor 2 compatibility.
Optical Conductivity of Gold

- Calculation with nspinor 2 now give more reasonable results.
- However, d-band energies and experimental shape still can not be matched exactly.
- Recent works suggest, that other relativistic effects might be need to be considered.
**XANES of Copper**

- Branching ratio and spin-orbit splitting now confirm with experiment without fitting.
- Total energy and energy broadening still need to be fitted.
Conclusions

- prtnabla 1 plus nspinor 2 is no longer completely wrong.
- The optical spectra of gold need further improvement.
- Spin-orbit splitting in XANES spectra can now be predicted with good accuracy.
- Changes will merged to the main branch as soon as possible.

Outlook

- Include core relaxation (RCPAW) to improve change of core energy levels at higher temperatures/densities.
- Explore other options to improve optical spectra of gold.
Conclusions

Thank you...

...for your attention!