Improving Optical and X-Ray Spectroscopy in ABINIT

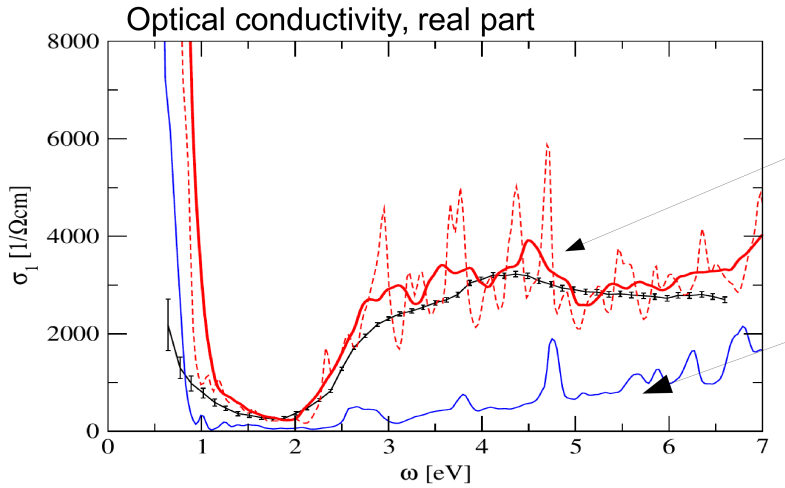
N. Brouwer, V. Recoules, M. Torrent

CEA, DAM, DIF, F91297 Arpajon, France

21.05.2019

Overview

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



Not the correct shape

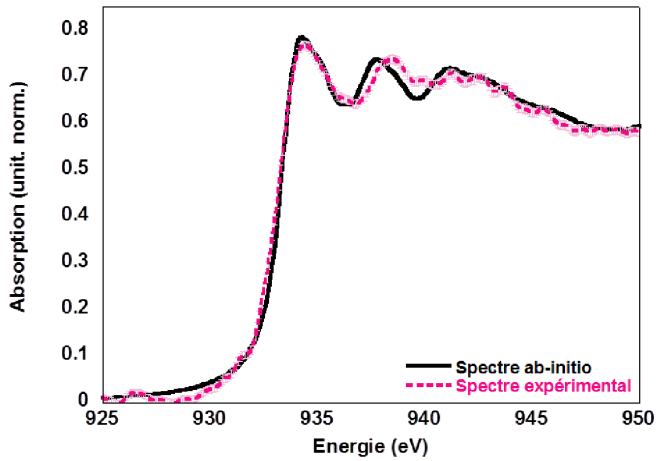
Computation with SO were wrong even if calculation were running.

1

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



[2]

XANES

- 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.

[2] Thesis N. Jourdain

Optical Conductivity

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

$$\sigma_1(\boldsymbol{k},\omega) = \frac{2\pi}{3\omega\Omega}\sum_{j=1}^{n_b}\sum_{i=1}^{n_b}\left(f(\epsilon_{i,\boldsymbol{k}}) - f(\epsilon_{j,\boldsymbol{k}})\right)|M|^2\,\delta(\epsilon_{j,\boldsymbol{k}} - \epsilon_{i,\boldsymbol{k}} - \omega)$$

Matrix Element

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

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

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:

$$H_{\mathrm{SO}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}V(r)}{\mathrm{d}r}\boldsymbol{L}\cdot\boldsymbol{S}$$

Kubo-Greewood Formula

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

$$M = \langle\psi_{j,\boldsymbol{k}}|\boldsymbol{v}|\psi_{i,\boldsymbol{k}}\rangle = \langle\psi_{j,\boldsymbol{k}}| - i\hbar\nabla + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\frac{\boldsymbol{r}}{r}\frac{\mathrm{d}V(r)}{\mathrm{d}r}|\psi_{i,\boldsymbol{k}}\rangle$$

Solution Provided by New Version of Atompaw

$$\Psi^{l}_{njm_j} = \begin{pmatrix} g_{nj}(r)\varphi^{l}_{jm_j} \\ if_{nj}(r)\frac{\hat{\sigma}\cdot\mathbf{r}}{r}\varphi^{l}_{jm_j} \end{pmatrix}$$

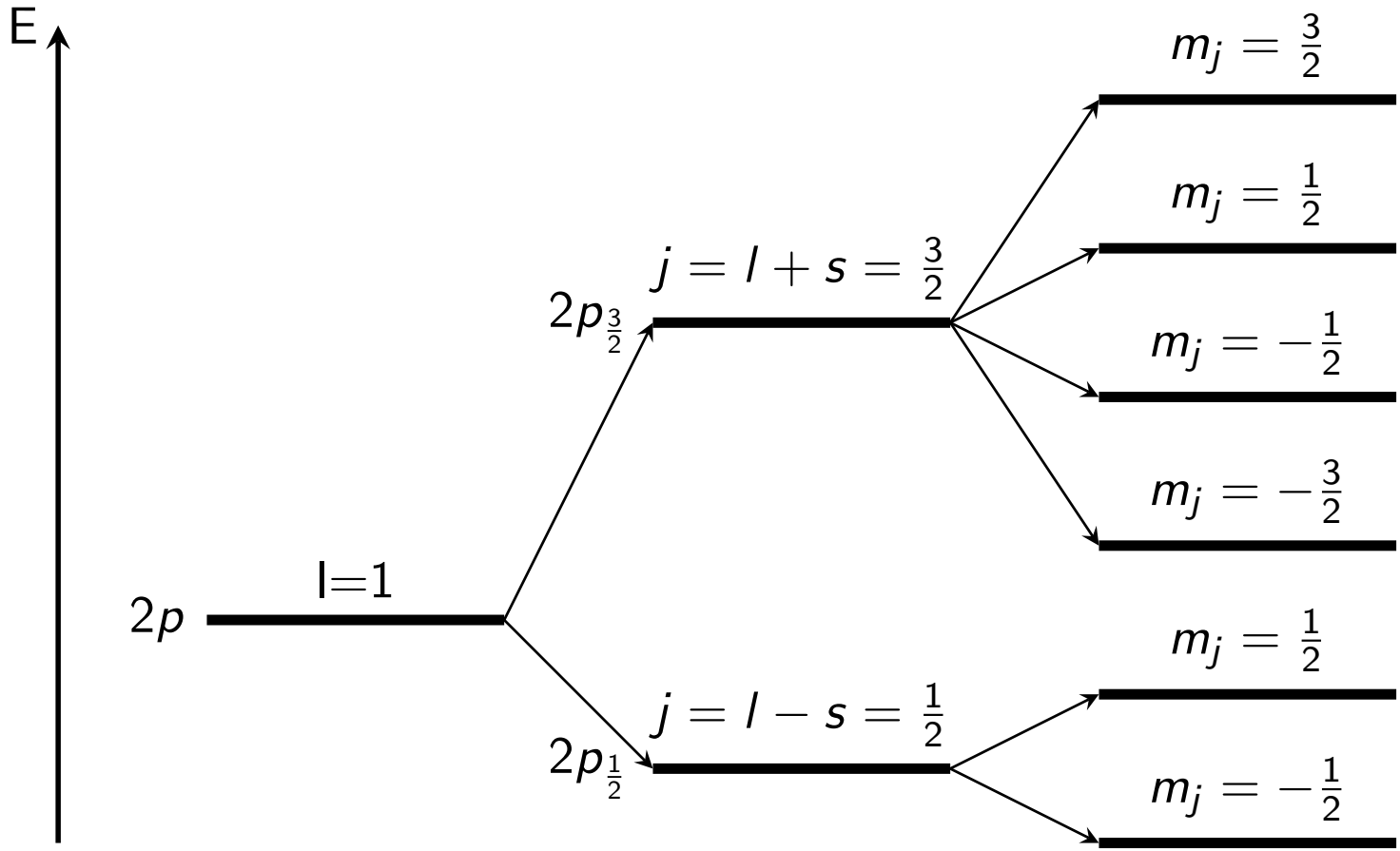
Angular Part

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

$$\varphi^{l}_{jm_j} = \sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}}\, Y_l^{m_j-\frac{1}{2}}\chi_{\frac{1}{2}} + \sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\, Y_l^{m_j+\frac{1}{2}}\chi_{-\frac{1}{2}}$$

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

$$\varphi^{l}_{jm_j} = \sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\, Y_l^{m_j-\frac{1}{2}}\chi_{\frac{1}{2}} - \sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}}\, Y_l^{m_j+\frac{1}{2}}\chi_{-\frac{1}{2}}$$



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:

```
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

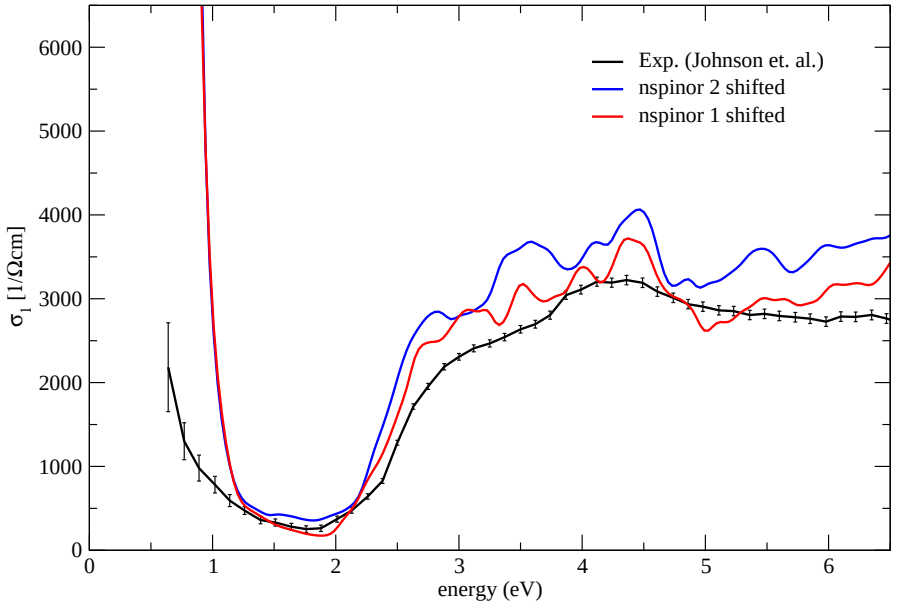
- Added output for both radial wave functions generated by the dirac-relativistic generator.
- Output as .abinit or .xml possible.
- Files indicate their generator type as well as the variable κ.
- Abinit can read both file types, support for dirac-relativistic core wave functions needs to be activated (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 of advantage of that, the indlmn_core data structure was modified to represent the structure of the angular solution.
- After that, the implementation was rather straight forward.
- Output with NetCDF is now also possible with prtnabla 3 + iomode 3

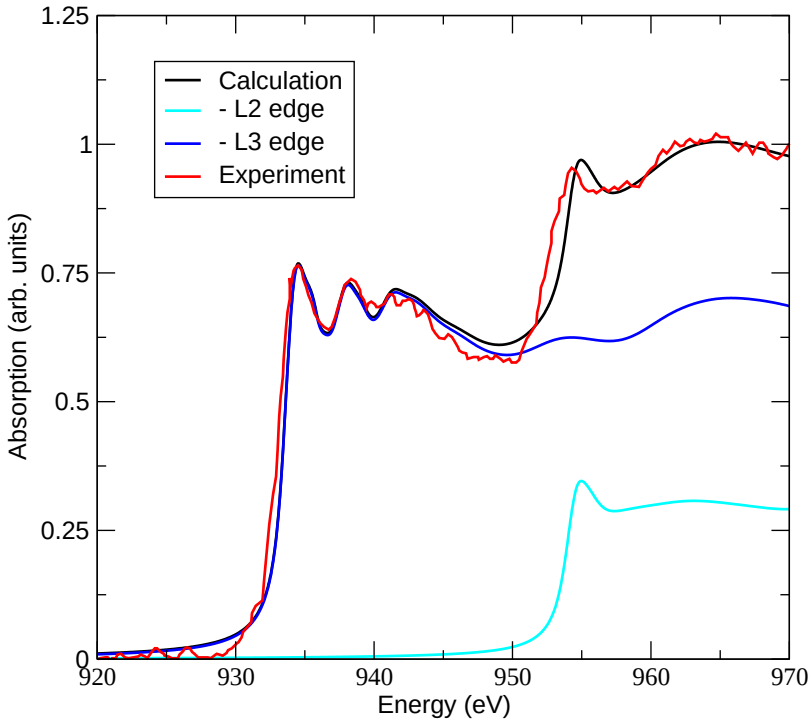
Conducti

- 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!