Calculating X-ray absorption spectra in ABINIT including spin-orbit effects

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Overview

- Theoretical Background
- Workflow
- Example Results

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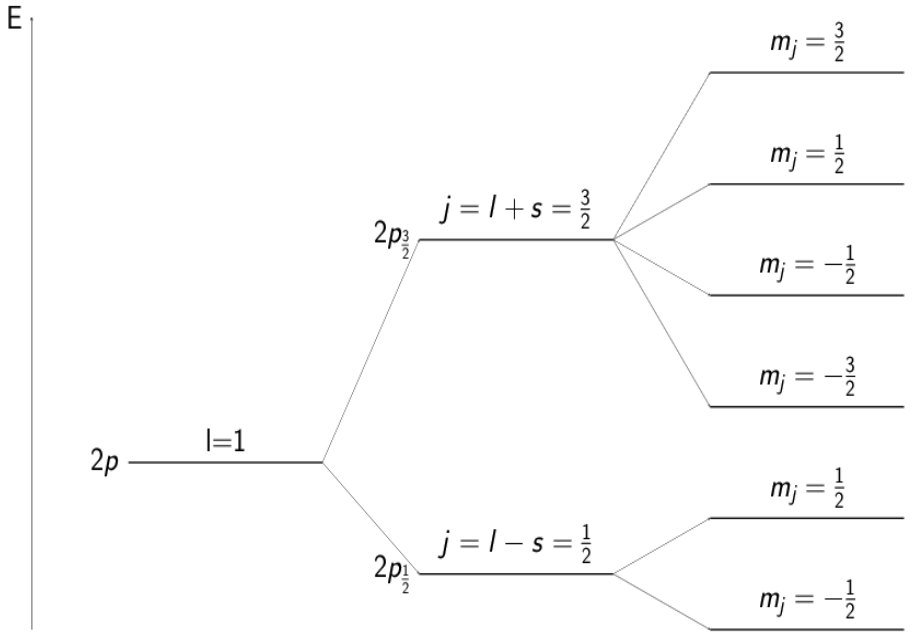
Spin-orbit coupling

- Spin-Orbit coupling (SOC) is a relativistic effect that can be extracted from the Dirac equation
- SOC leads to spin-orbit splitting, visible in X-ray spectra
- SOC adds the following term to the Hamiltonian:

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

- The operator $\vec{S}$ couples spin-up and spin-down states
- This results in 2-spinor wave functions



Spin-Orbit splitting

Dirac-relativistic core wave functions

- Solution of the radial-symmetric Dirac equation:

$$\Psi^{\pm}_{njm_j} = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = \begin{pmatrix} \frac{G_{nj}(r)}{r} \mathcal{Y}^{j,m_j}_{l=j\pm\frac{1}{2}} \\ -i\frac{F_{nj}(r)}{r} \mathcal{Y}^{j,m_j}_{l=j\mp\frac{1}{2}} \end{pmatrix}$$

- Radial equation

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa}{r}\right) F(r) = -\alpha\,(E - V(r))\,G(r)\ , \qquad \Psi^{+}_{njm_j} \rightarrow \kappa = j + \frac{1}{2}\ ,$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa}{r}\right) G(r) = \left(\frac{2}{\alpha} + \alpha\,(E - V(r))\right) F(r) \qquad \Psi^{-}_{njm_j} \rightarrow \kappa = -(j + \frac{1}{2})$$

- Relativistic spherical harmonics:

$$\mathcal{Y}^{j,m_j}_{l=j\mp\frac{1}{2}} = \sqrt{\frac{l \pm m_j + \frac{1}{2}}{2l+1}} Y_l^{m_j - \frac{1}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \pm \sqrt{\frac{l \mp m_j + \frac{1}{2}}{2l+1}} Y_l^{m_j + \frac{1}{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

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Workflow – Step 1: Generate core wave functions

- Start from atompaw input file provided at the end of every atompaw xml file (e.g. JTH) table
- Use keyword diracrelativistic instead of semirelativistic
- Define additional states due to removed degeneracy, e. g. instead of $2p^6$ we have $2p_{1/2}^2$ and $2p_{3/2}^4$
- Instead of n, l, occ, use n, l, kappa, occ, where kappa = -(l+1) for j=l+s and kappa = l for j=l-s
- Use keywords XMLOUT and PRTCOREWF to output a core wavefunction input file for abinit

Example: Adapt JTH input to produce core wave functions for ABINIT

```
<!--  Program:  atompaw - input data follows:
Al 13
XC_GGA_X_PBE+XC_GGA_C_PBE scalarrelativistic loggrid 2001
3 3 0 0 0 0
3 1 1
0 0 0
c
c
v
c
v
1
1.9 1.6 1.6 1.7
y
3.0
n
y
4.0
n
custom rrkj
2 0.0
1.9
1.9
1.9
1.9
XMLOUT
default
END
 Program:  atompaw - input end  -->
```

```
Al 13
XC_GGA_X_PBE+XC_GGA_C_PBE diracrelativistic loggrid 3001
3 3 0 0 0 0
3 1 1 1
3 1 -2 0
0 0 0 0
c
c
v
c
v
c
v
1
1.9 1.6 1.6 1.7
y
3.0
n
y
4.0
n
custom rrkj
2 0.0
1.9
1.9
1.9
1.9
1.9
XMLOUT
PRTCOREWF
END
```

Workflow – Step 2 Run ABINIT

- Use core wave function file (ending in .corewf.xml) and a normal PAW potential as usual
- Activate spinors and spin-orbit coupling with nspinor=2
- Use keywords prtnabla 3 and useria 29091988 (will be changed to prtnabla 5)
- If netcdf support is present, iomode 3 is strongly recommended
- Increase nband and later check convergence with respect to your spectrum
- Get *_OUT_OPT2(.nc) file with matrix element data

Workflow – Step 3: Run CONDUCTI

- Same as without SOC:
- Choose mode 5
- Input root name of the file (will autodetect whether .nc or not)
- Input parameters for the spectrum

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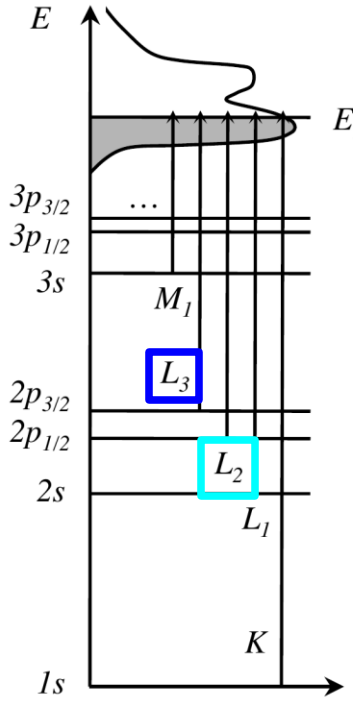
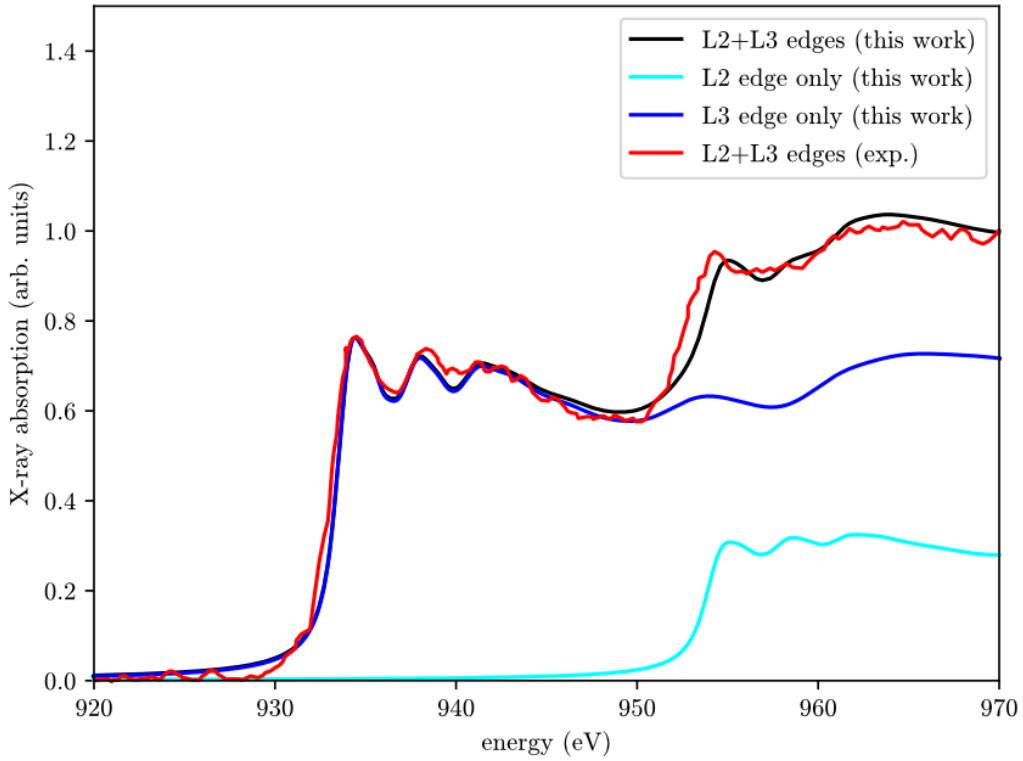
Copper XANES L2/L3 edge at 300K

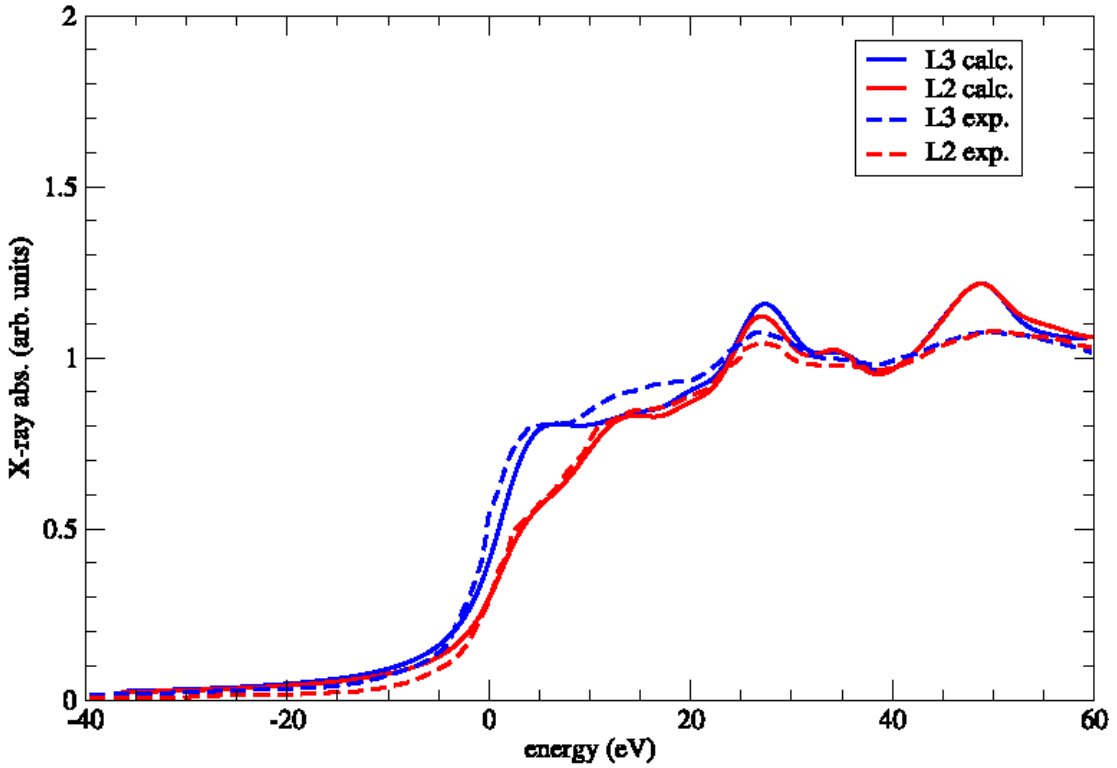
- Spin-orbit splitting not fitted, very close to experimental values
- Branching ratio results naturally with spin-multiplicity of spinor wave functions
- Smearing fitted to experiment with empirical formula based and Lorentzian line shapes
- Different shape of L2/L3-edge (partially due to different smearing)





- Simulation Cu XANES L2/L3 edge at 300K lattice temperature. Exp. Data from N. Jourdain et al., PRB 2015

XANES in Gold



- XANES of gold at room temperature. L2/L3-edge superimposed.
- Exp. data taken from Nishimura et al. (J. phys. Chem C 116 (2012) 4511.)

- XANES of Gold L2/L3-edge at room temperature.
- Same smearing for both edges.
- Clear difference in edge shape, like in the experiment.
- Can be scaled up to WDM conditions (slightly more challenging than copper).

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Thank you for your attention!