Full-potential polarized XANES calculation by combining pseudopotential and multiple-scattering methods

A poor-man's solution

O. Šipr

Institute of Physics ASCR, Prague   http://www.fzu.cz/~sipr

XAS and DOS equations

XAS:

$$\mu(\hbar\omega) = -\frac{2\pi^2 m^2}{\hbar^5 k^2} \Im \sum_{LL'} M_L^* \, \tau_{LL'}^{00} \, M_{L'}$$

$$\tau_{LL'}^{00} = t_L^0 \delta_{LL'} + \sum_p \sum_{L''} t_L^0 \, G_{LL''}^{0p} \, \tau_{L''L'}^{p0}$$

DOS:

$$n^{(0)}(E) = -\frac{1}{V} \oint_{V^{(0)}} \mathrm{d}\mathbf{r} \, \frac{2}{\pi} \Im \, G(\mathbf{r}, \mathbf{r}; E) = -\frac{1}{k} \sum_L F_\ell^{(0)} \Im \, \tau_{LL}^{00}$$

$$F_\ell^{(j)} = \frac{1}{V^{(j)}} \int_0^{R_{WS}} \mathrm{d}r \, r^2 \, [\mathcal{R}_\ell(r)]^2$$

Non-muffin-tin XANES: basic strategy

(Polarised) XANES spectra can be taken as proportional to the (appropriate angular-momentum component) of the projected DOS.

- ► Smooth "proportionality function" corresponds to the square of the atomic transition matrix element M_L.
- ► Strictly true only if scattering path operator $\tau_{LL'}^{00}$ is diagonal.
- ► Core hole is neglected (but who cares).

XAS *can* be calculated via plane-waves code such as ABINIT or QUANTUM ESPRESSO directly if PAW scheme is involved.

Even earlier a pseudopotential code was used for XAS XAS calculations employing core wave function reconstruction [Šipr *et al.* PRB **56**, 13151 (1997); Vackář *et al.*PRB **58**, 12712 (1998)].

Non-muffin-tin XANES: Howto

- Projected DOS obtained via ABINIT.

- Polarisation sensitivity achieved by taking the ($\ell=1$,$m=0$) DOS component to get the XANES with the $\varepsilon \| z$ polarisation and the ($\ell=1$,$m=\pm1$) DOS component to get the XANES with the $\varepsilon \perp z$ polarisation.

- DOS multiplied by a smooth sinusoidal-like function which increases monotonously from 1.0 at the absorption edge to 1.6 at the end of the energy region.

ABINIT technicalities

- ▶ Self-consistent calculation done using 16 **k**-points in the irreducible Brillouin zone.

- ▶ Angular-momentum-projected DOS within a 1.24 Å-radius sphere around Cu calculated using 38 **k**-points.

- ▶ The results presented here obtained using a Hartwigsen-Goedeker-Hutter type pseudopotentials but very similar results obtained also for pseudopotentials of the Troullier-Martins type.

Creatinium tetrachlorocuprate (creat)$_2$CuCl$_4$

Legend:
- Cu
- Cl
- H
- O
- C
- N
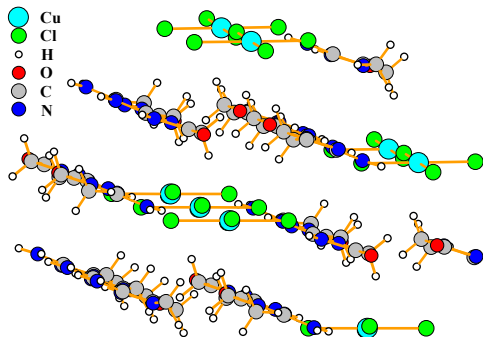
- Basically it is a CuCl$_4$ complex.
- Cu *K*-edge XAS attracted a lot of attention because of many-body effects close to the edge.
- Here the focus is on polarization dependence of the energy region $E > 20$ eV.
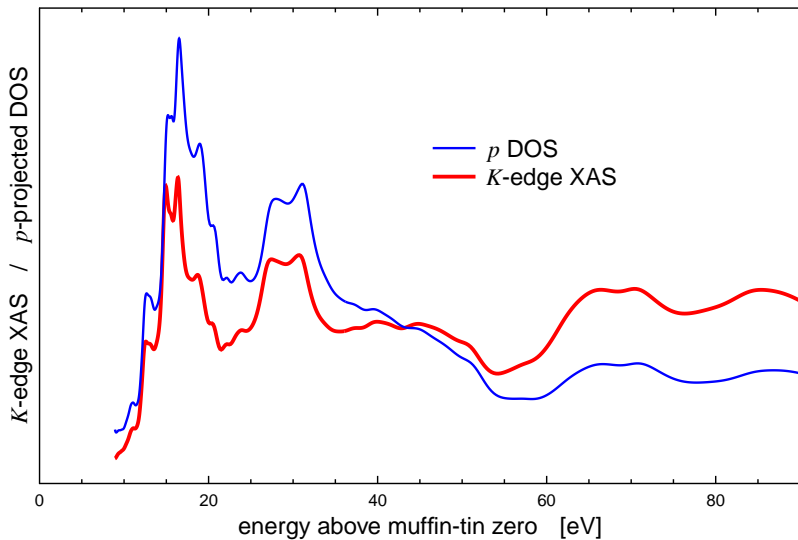 - Real reason for research are the vibrations but let us forget about this for now...

XAS, DOS and alike

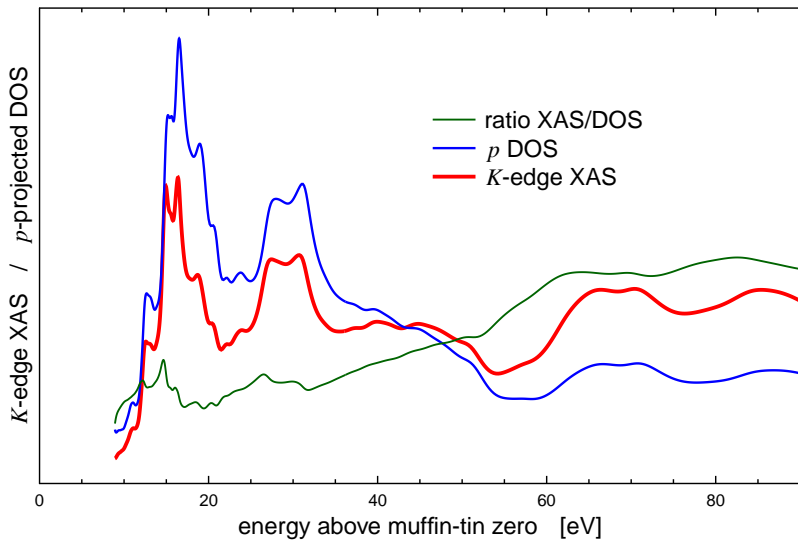Real-space multuiple-scattering calculations using an in-house RSMS code.
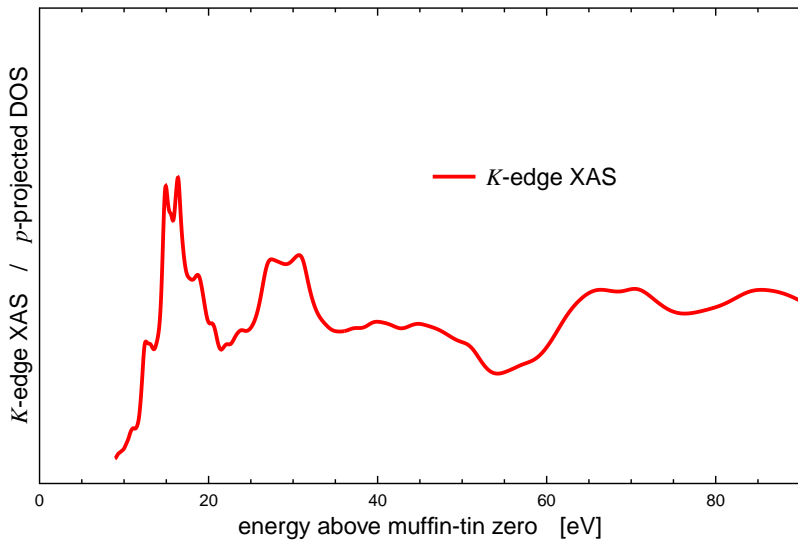
XAS, DOS and alike

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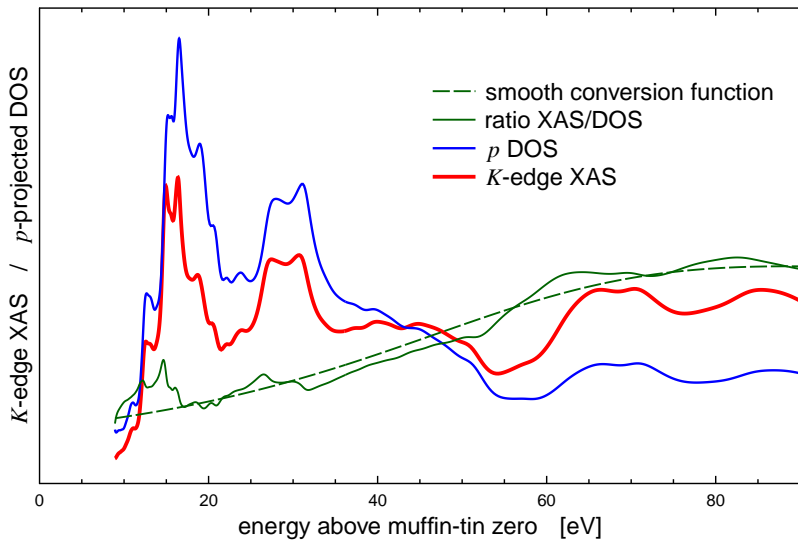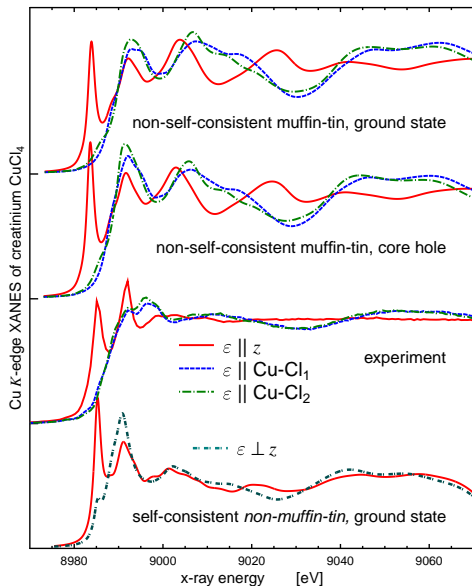
Polarized Cu K edge XANES (creat)$_2$CuCl$_4$

- Broad $\varepsilon \| z$ peak around 20–30 eV cannot be described accurately unless a self-consistent non-muffin-tin potential is used (note the three-sub-peaks structure).

- Do not look close to the edge, that is another discussion on another topic.

Few notes in the end

This is a quick and dirty method.
However, it is quite well-founded after all.

Proportionality between DOS and XAS is polarization-independent
in the first approximation $\rightarrow$ this approach is especially suited for
investigating polarization effects (a.k.a. linear dichroism), where
non-muffin-tin effects may be significant.