Broadening calculated spectra by introducing complex energy:
possible artefacts close to the edge

Ondřej Šipr

Institute of Physics, Czech Academy of Sciences, Praha
http://www.fzu.cz/~sipr

Ján Minár, Jiří Vackář, Hubert Ebert

Lisboa 19. February 2018

Outline

- Two ways to account for finite core hole lifetime
  - Disadvatages of both of them

- Assessing the risks: Case study of metallic Fe
  - When things (mostly) work: Fe K edge XAS and XMCD
  - When problems await us: Fe $L_{2,3}$ edge XMCD

- Lessons to be learned.

Broadening XAS spectra by a Lorentzian (1)

- Experimental x-ray absorption spectra (XAS) display broader features than theoretical spectra.

  - Core hole will be eventually filled — its lifetime is finite.
    Finite lifetime of the core is neglected in effectively one-electron calculations.
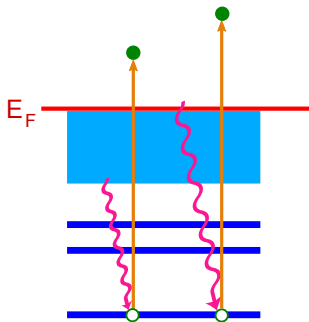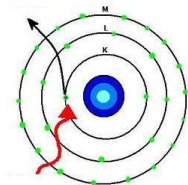
Broadening XAS spectra by a Lorentzian (2)

Spectra calculated within an effectively one-electron approach have to be broadened.

- ▶ A convenient way to introduce the broadening: Convolute the raw spectrum with a Lorentzian.

  - ▶ It can be honestly shown by perturbation theory that the core hole decay is exponential and that the line shape is Lorentzian [Messiah: Quantum Mechanics, vol. 2, chap. XXI].

  - ▶ Drawback: One has to perform the calculations on sometimes much finer energy mesh than actually needed.

Influence of the energy grid on XANES (1)

When density of the energy grid matters in a bit quirky way

Case study: B K-edge of calciborite CaB_2O_4
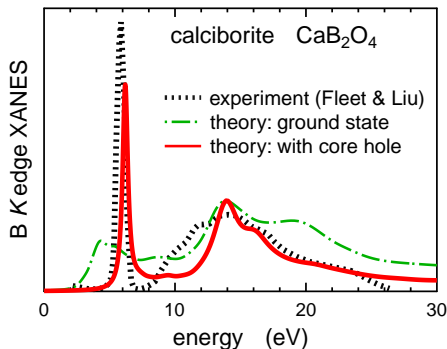
Sharp pre-peak is related to the core hole. (It is a marker of BO_3 structural units.)

To calculate the pre-peak correctly, an energy mesh with a step of 0.001 eV around the peak has to be used.

Šipr *et al.* J. Synchrotron Rad. **17**, 367 (2010)

For another demonstration, see Taranukhina *et al.* in *Multiple Scattering Theory for Spectroscopies*, edited by D. Sébilleau *et al.*, Chap. 13, p. 309.
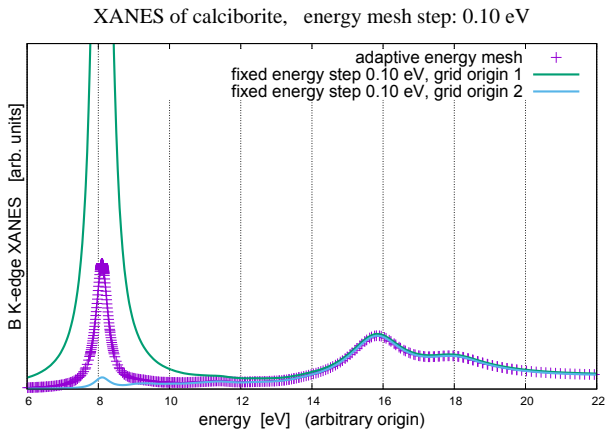
Influence of the energy grid on XANES (2)

Pre-edge resonance: very intensive and very narrow.

XANES of calciborite: convoluted and raw 'as calculated'
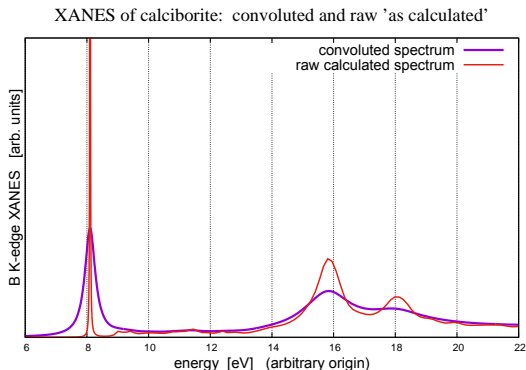
Technical details of how the energy mesh points are distributed around the resonance strongly influence the final convoluted spectrum.

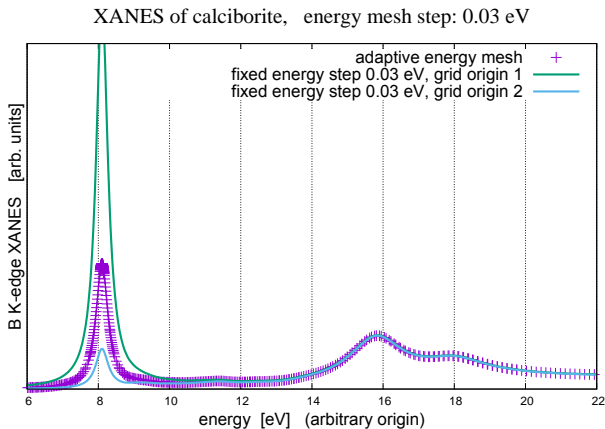# Influence of the energy grid on XANES (3)

Energy mesh with a fixed step, two (arbitrary) choices of the origin.

XANES of calciborite, energy mesh step: 0.10 eV

Influence of the energy grid on XANES (3)

Energy mesh with a fixed step, two (arbitrary) choices of the origin.

XANES of calciborite,   energy mesh step: 0.03 eV

Influence of the energy grid on XANES (3)

Energy mesh with a fixed step, two (arbitrary) choices of the origin.

XANES of calciborite,   energy mesh step: 0.01 eV
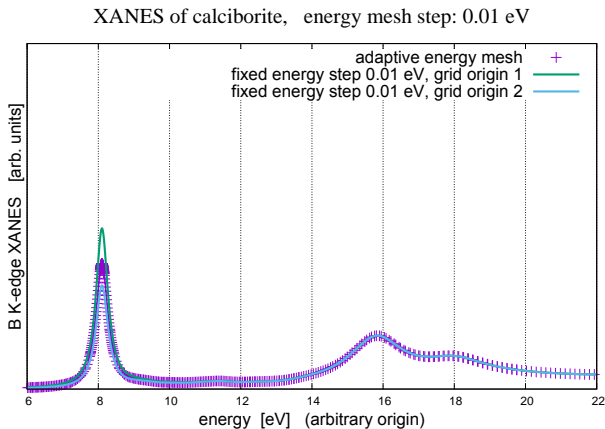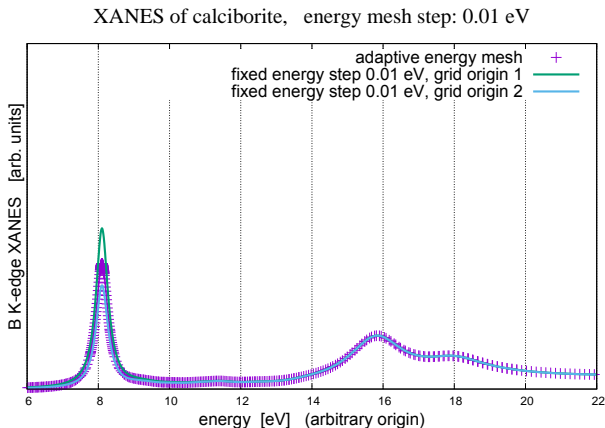
Influence of the energy grid on XANES (3)

Energy mesh with a fixed step, two (arbitrary) choices of the origin.

XANES of calciborite, energy mesh step: 0.01 eV

🙁 Even for a fine grid with a step of 0.01 eV, the intensity of the pre-peak depends on an arbitrary technical parameter (origin of the energy grid).

Alternative: add a small imaginary part to the energy

- ▶ For Green's function based or multiple-scattering methods: add a small imaginary part to the energy ("self-energy").

  - ▶ Results in smoother spectra "as calculated" ⇒ one can use a coarse energy mesh.
    Resonances are broadened from the beginning and hence easily captured.

  - ▶ When working in a reciprocal space, employing complex energies reduces the number of **k**-points needed for Brillouin zone integration.

- ▶ The two approaches can be combined: first calculate the spectrum using an imaginary energy component, then convolute it with a Lorentzian (possibly varying the parameters of the convoluting Lorentzian to achieve the best possible agreement with experiment.)

Problem with the Fermi energy cut-off

- Calculating x-ray absorption spectra for energies with an added imaginary component is strictly equivalent to a convolution with a Lorentzian only if there is no cut-off of the spectra below the Fermi level E_F, i.e., in the limit $E_F \to -\infty$ [Vedrinskii *et al.* pssb **111**, 433 (1982); Brouder *et al.* PRB **54**, 7334 (1996)].

- Brouder *et al.* (1996) derived a formally exact equation which accounts for the influence of E_F-related cut-off but one prefers to stay with established routines...

- Objective: Assess whether employment of an imaginary energy component to calculate broadened spectrum can introduce significant artefacts in comparison with broadening by a Lorentzian convolution of raw spectra on the real axis.

Equivalence of two methods to broaden the spectrum

Lorentzian with FWHM of Γ: $\quad L(E) = \frac{1}{\pi} \frac{\Gamma/2}{E^2 + (\Gamma/2)^2} \quad .$

XAS cross-section with the influence of the finite core hole lifetime included:

$$\sigma_{\text{broaden}}(E) = \int_{E_F}^{\infty} \mathrm{d}E' \, \sigma_{\text{raw}}(E') \, L(E - E') \qquad (1)$$

If the cut-off below E_F is ignored, convolution with a Lorentzian is equivalent to evaluating the spectrum for energies with added imaginary component $\Gamma/2$,

$$\int_{-\infty}^{\infty} \mathrm{d}E' \, \sigma_{\text{raw}}(E') \, L(E - E') = \sigma_{\text{raw}}(E + \mathrm{i}\Gamma/2) \quad .$$

XAS with the influence of finite core lifetime included:

$$\sigma_{\text{broaden}}(E) \approx \sigma_{\text{raw}}(E + \mathrm{i}\Gamma/2) \quad . \qquad (2)$$

Shifting the emphasis between ImE and Γ

Convoluting the spectrum by a Lorentzian with FWHM of Γ is equivalent[(*)] to adding imaginary part Im$E = \Gamma/2$ to the photoelectron energy.

Convolution of two Lorentzians is again a Lorentzian, with FWHM

$$\Gamma = \Gamma_1 + \Gamma_2 \ .$$

$\Rightarrow$ One can shift the weight of the broadening between
1. adding an imaginary part ImE to the energy and
2. convoluting the raw spectrum with a Lorentzian of width Γ,

while keeping total effective broadening constant:

$$2\,\mathrm{Im}E \ + \ \Gamma \ = \ \Gamma_{\mathrm{total}} \ .$$

(*) Apart from the E_F cut-off.

Fe K-edge XANES and XMCD (1)

Tabulated value of Γ_{core} of Fe K-edge is 1.19 eV [Campbell & Papp At. Data Nucl. Data Tables **7**, 1 (2001)].

Shift the weight of the broadening between $\mathrm{Im}\,E$ and Γ, making sure that the total effective broadening remains always the same by satisfying

$$2\,\mathrm{Im}\,E + \Gamma = \Gamma_{core} \ .$$

$\mathrm{Im}\,E$	Γ	$2\mathrm{Im}\,E + \Gamma$
0.014	1.163	1.190
0.408	0.374	1.190
0.594	0.002	1.190

Parameters (in eV) used for broadening by adding the imaginary part $\mathrm{Im}\,E$ to the energy and subsequent convolution of the spectra with a Lorentzian of the width Γ.

Fe *K*-edge XANES and XMCD (2)
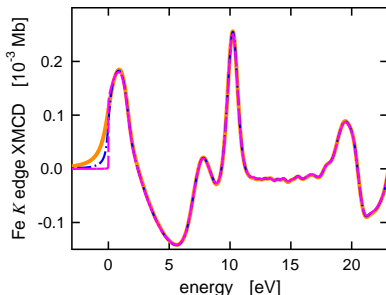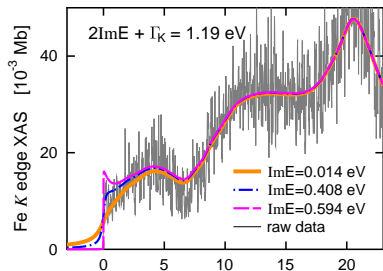
Šipr *et al.* PRB **72**, 134406 (2005); J. Synch. Rad. **25**, 523 (2018)

The edge region is (slightly) distorted if most of the broadening is done by adding an imaginary part to the energy.

When moving away from E_F, both procedures provide identical results.

Note: The *total* broadening is identical for all curves: $2\mathrm{Im}E + \Gamma = \mathrm{const.}$!
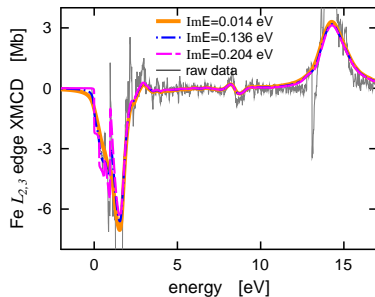
Fe $L_{2,3}$-edge XANES and XMCD (1)

$$2\,\mathrm{Im}E + \Gamma = \Gamma_{\text{core}}$$

Two edges (L_2 and L_3), the imaginary component of the energy $\mathrm{Im}E$ is the same for both of them, whereas the width of the convoluting Lorentzian Γ differs.

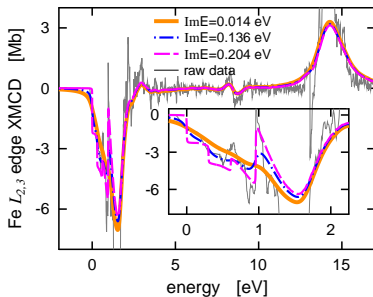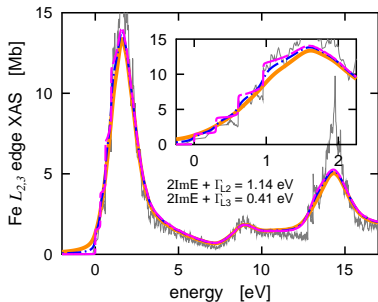| $\mathrm{Im}E$	Γ_{L_2}	Γ_{L_3}	$2\mathrm{Im}E + \Gamma_{L_2}$	$2\mathrm{Im}E + \Gamma_{L_3}$
0.014	1.113	0.383	1.140	0.410
0.136	0.868	0.138	1.140	0.410
0.204	0.732	0.002	1.140	0.410

Values chosen so that the total broadening corresponds to $\Gamma_{\text{core}} = 1.14$ eV for the L_2 edge and to $\Gamma_{\text{core}} = 0.41$ eV for the L_3 edge
[Campbell & Papp At. Data Nucl. Data Tables **7**, 1 (2001)].

Fe $L_{2,3}$-edge XANES and XMCD (2)
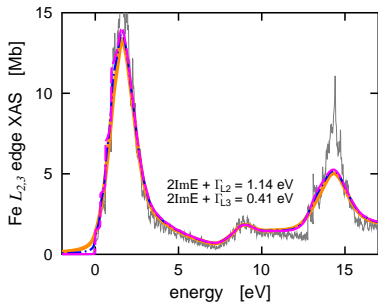
Šipr *et al.* PRB **72**, 134406 (2005); J. Synch. Rad. **25**, 523 (2018)

Fe $L_{2,3}$-edge XANES and XMCD (2)

Šipr *et al.* PRB **72**, 134406 (2005); J. Synch. Rad. **25**, 523 (2018)

If substantial portion of the broadening is included by means of adding an imaginary part to the energy, a spurious dublet appears at the L_3 edge XMCD peak.
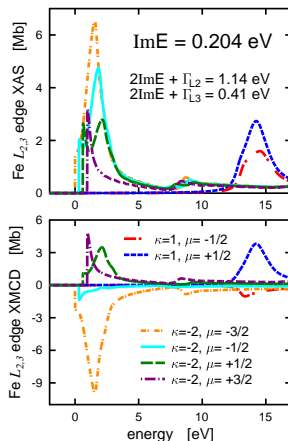
The $L_{2,3}$ XMCD appears to be hypersensitive to the way the broadening is split between ImE and Γ.

Note: The *total* broadening is identical for all curves: $2\text{Im}E + \Gamma = \text{const.}$!

Fe $L_{2,3}$-edge resolved according to the (κ,μ) components
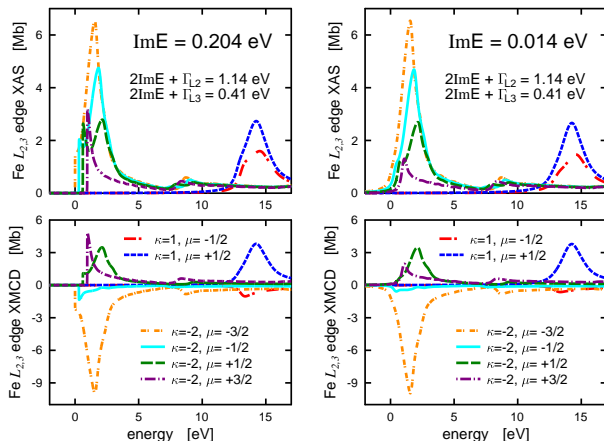
Relativistic
exchange splitting
of the core levels:

For the L_2 and
L_3 edges, core levels
are split by 0.3 eV.

Fe $L_{2,3}$-edge resolved according to the (κ,μ) components

Relativistic
exchange splitting
of the core levels:

For the L_2 and
L_3 edges, core levels
are split by 0.3 eV.

Šipr *et al.* J. Synch. Rad. **25**, 523 (2018)

Fe $L_{2,3}$-edge resolved according to the (κ, μ) components

Relativistic exchange splitting of the core levels:

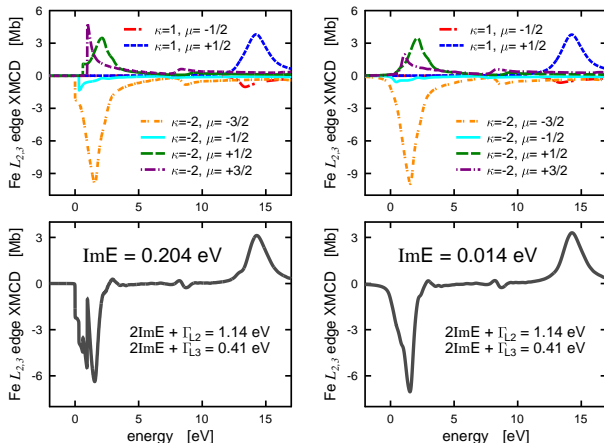For the L_2 and L_3 edges, core levels are split by 0.3 eV.

ImE = 0.204 eV

$2\text{ImE} + \Gamma_{L_2} = 1.14$ eV
$2\text{ImE} + \Gamma_{L_3} = 0.41$ eV

ImE = 0.014 eV

$2\text{ImE} + \Gamma_{L_2} = 1.14$ eV
$2\text{ImE} + \Gamma_{L_3} = 0.41$ eV

Šipr *et al.* J. Synch. Rad. **25**, 523 (2018)

If individual (κ, μ)-components are smoothed *before* the summation, the resulting spectrum is smooth, without the quasi-doublet at L_3 XMCD.

Conclusion

▶ Simulating the finite core hole lifetime by means of an imaginary energy component and by means of convoluting with a Lorentzian is equivalent only for energies well above the absorption edge.

▶ If too much weight is put on broadening via an imaginary energy component, spurious features may appear at the edge, especially for the dichroic spectra.

▶ Special care needed for XMCD spectra: $\text{Im}E$ should be about 0.01 eV or less.
(Typical values of the imaginary energy component used for XAS/XMCD calculations are $\text{Im}E \sim 0.1\text{–}0.2$ eV.)

Conclusion

▶ Simulating the finite core hole lifetime by means of an imaginary energy component and by means of convoluting with a Lorentzian is equivalent only for energies well above the absorption edge.

▶ If too much weight is put on broadening via an imaginary energy component, spurious features may appear at the edge, especially for the dichroic spectra.

▶ Special care needed for XMCD spectra: $\text{Im}E$ should be about 0.01 eV or less.
(Typical values of the imaginary energy component used for XAS/XMCD calculations are $\text{Im}E \sim 0.1\text{–}0.2$ eV.)