Broadening calculated XANES by introducing complex energy: understanding the risks

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Before being compared to the experiment, the raw calculated XANES has to be modified to account for the finite core hole lifetime. This can be done by convoluting the calculated spectrum with a Lorentzian. The drawback is that to account for sharp resonances especially in the pre-edge region, the calculations have to be carried out on sometimes much finer energy mesh than needed in the end.

For multiple-scattering methods, there is another possibility: to add a small imaginary part to the energy. This results in spectra which are smoother from the beginning. If the cut-off of the spectra below the Fermi level E_F is neglected, calculating XAS on the energy grid with an imaginary component Im(E) is fully equivalent to convoluting the spectrum with a Lorentzian whose FWHM is $\Gamma = 2\,\mathrm{Im}(E)$. If the methods are combined, the total effective broadening is just a sum of both contributions.

The influence of the cut-off on the broadening via the imaginary energy component is negligible high above the edge. However, the situation may be different at the very edge, where neglecting the cut-off below E_F might be a too crude approximation. Our aim is to explore whether employing the imaginary energy component to calculate broadened XAS could introduce significant artefacts in comparison with convoluting the raw spectra on the real axis.

As a case study, we focus on the *K* edge and $L_{2,3}$ edge XAS and x-ray magnetic circular dichroism (XMCD) of Fe. We perform the broadening either by a Lorentzian convolution or by adding to the energy an imaginary component of equivalent size. We also check combinations of both methods, with different weights.

We find that for energies high above the edge there is practically no difference in the final spectra, no matter which broadening procedure has been applied. At the very edge, however, there are differences. They stem from the fact that if too much weight is put on broadening by the imaginary energy component, there is a sharp cut-off of the spectra at E_F, resulting in too sharp features at the edge.

The situation is especially instructive for the L_3 XMCD peak. Here a well-distinguished but in fact spurious fine structure appears on its low-energy side unless most of the broadening is done by means of Lorentzian convolution (arXiv:1709.07214 [cond-mat.mtrl-sci]).

Simulating the finite core hole lifetime by means of an imaginary energy component and by means of convoluting the raw spectra with a Lorentzian is thus equivalent only for energies higher than few core level FWHM's above the absorption edge. If too much weight is put on broadening via the imaginary energy component, spurious spectral features may appear close to the edge, especially for the XMCD spectra.