GNXAS DOCUMENTATION

Program deconv: deconvolution of lifetime broadening

by A. Filipponi, Aug 2000

1) Introduction

Modern facilities for x-ray absorption spectroscopy experiments allow scientist to collect high quality spectra characterized by low noise and high resolution. These spectra are ideally suited for the application of deconvolution procedures aimed at highlighting spectral features. A specific code `deconv` has been developed, for this purpose, within the GNXAS project. The code algorithm has been fully described elsewhere [1]. An extended discussion of the scientific issues and potential applications on atomic and molecular spectra, together with extensive references to alternative approaches developed by other authors, can also be found in Ref. [1].

Deconvolution procedures are particularly attractive for the possibility to deconvolve the Lorentzian core-hole lifetime width. In particular, the algorithm implemented in the `deconv` program, applied to high quality spectra with typical noise levels of the order of 10^{-4}, is able to deconvolve the entire core-hole lifetime broadening using a Gaussian filter with a standard deviation $\sigma \approx \Gamma/3$ (where Γ is the Lorentzian half width at half maximum). In these conditions any Lorentzian resonance is converted into a much narrower Gaussian peak and, similarly, an arc-tangent step is converted into an "erf" step function. Both reduced width and improved functional shapes, in which the long-range tails are eliminated, contribute to the sharpening of the spectral features.

The users of the program should be aware that the suggested deconvolution procedure is based on the assumption that the effect of the finite lifetime of the excited state is to introduce a Lorentzian broadening. While this is quite reasonable, especially for high energy edges, it is know that in several cases this is a over-simplified assumption. For instance, non-Lorentzian profiles occur in the case of autoionizing Fano resonances. Consequently the deconvolved spectra have to be always interpreted with caution.

The exact values of the core-hole widths may not be known with a sufficient accuracy. Useful tabulations of the known core-hole widths for most of the inner-shell excitations have been published by Krause and Oliver [2].

2) Program usage

The program usage is quite simple and requires only the input data file (ASCII format, with energy and absorption in the first 2 columns, comment lines beginning with "#" are ignored), and the following input lines.

```
data_file_name
out_string
0
E_tail, W_tail, E_match
D_Gamma,D_sigma
filter_parameters
```

These parameter input lines are described in details below:

`data_file_name` is the name of the input data file to be deconvolved.

`out_string` Is a string of a maximum length of 10 characters used to generate output file names.

`0` This input is left for future running options the integer number 0 should be supplied at present.

`E_tail, W_tail, E_match` These are the energy parameters in (keV) used for the automatic determination of a smoothed step function to eliminate the discontinuity at the high energy side of the spectrum to be deconvolved numerically. The functional form is that of eq. (5) in Ref. [1] or a simpler arctangent function. `E_tail` is the position of the step and it should be normally chosen well above the energy region of interest (It should not be the edge energy!!). `W_tail` is the Lorentzian width of this step contribution, it should be taken larger than the core-hole width to be deconvolved!! Finally `E_match` is the energy at which the matching in amplitude and slope between the step function and actual spectrum is made. This number should be greater that `E_tail` by at least a few `W_tail` widths.

`D_Gamma,D_sigma` are the Lorentzian (half width at half maximum) and Gaussian widths to be deconvolved. In order to deconvolve only a Lorentzian width, which is the normal program usage, the second parameter should be set to 0.

`filter_parameters` A filter is necessary to avoid noise blow up after deconvolution [1]. The Fourier transform of the filter should beat that of the deconvolved shape for high values of the conjugate variable value. The normal (and suggested) usage is to adopt a Gaussian filter for a Lorentzian deconvolution. A few other filters are available. The filter type is selected by the first character between quotes, the relevant parameters are entered on the same record in free format. Examples:

a) Gaussian filter, standard deviation 0.67 eV. Any positive number can be input, however, below a minimum value the high-frequency noise will not be suppressed. Reasonable values are in the range $\Gamma/3 < \sigma < \Gamma/2$.

`'G',0.67`

b) Filter, $w(q) = \exp[-(q-q_0)^2\sigma^2/2 - ((q-q_0)/q_3)^3 - ((q-q_0)/q_4)^4]$, ($w(q) = 1$ for $|q| < q_0$). The corresponding parameters are entered as:

`'S'`, q_0, σ, q_3, q_4

If $q_0 = 0$ and $1/q_{3,4} \simeq 0$ the Gaussian filter is retrieved, a small q_0 or a finite q_3 term will introduce side ripples. Notice that q_3 and q_4 should be very large numbers to be ineffective.

3) Output files

The program `deconv` normally generates three ASCII output files whose names are composed of the supplied `out_string` string followed by three different default extensions.

`.bkg` This file is intended for checking the effect of the tail background decomposition; the five columns contain:

1) Energy (keV),

2) Raw absorption data minus preliminary linear pre edge extrapolation,

3) Raw absorption data minus final linear pre-edge background,

4) Tail step function,

5) Absorption minus tail function (input for the numerical deconvolution).

`.ftr` This file contains the Fourier Transforms relevant to the deconvolution procedure.

1) q (eV-1): conjugated variable to the energy scale in eV,

2+3) Real and Imaginary part of Fourier transformed signal,

4+5) Real and Imaginary part of signal after deconvolution,

6) Fourier Transform of the filter (real).

`.dec` This file contains the final deconvolved spectrum in energy space.

1) Energy (keV),

2) Original spectrum on the same baseline of the deconvolved one,

3) Part of the spectrum numerically deconvolved, to be compared with col. 5 of `.bkg`,

4) Complete deconvolved spectrum (to be compared with column 2),

5) Filter in real space, (centered at the edge energy).

4) Recommendations

The deconvolved spectrum is calculated for nearly the whole energy interval of the original data, however, the energy region around the tail `E_tail` inflection point may contain small numerical artifacts and it is recommended that only the region $E <$`E_tail` is used for the subsequent physical interpretation.

Most high quality spectra should be suitable for the application of this algorithm, however we recommend:

a) to improve as much a possible the energy resolution, using a suitable monochromator crystal and slits, possibly down to 1/10 of the core-hole width.

b) to collect a suitably long pre-edge up to 100 times the core-hole width (a coarse spacing is anyway sufficient).

c) to adopt a fine energy sampling in the edge region possibly down to 1/20 of the core-hole width.

d) to achieve a noise to signal level of the order of 10^{-4} or better.

e) to make sure that the monochromator energy is calculated with a sufficient accuracy for the finite motor steps [1,3]. Notice that a 0.1 eV error on an absorption edge rising by 1 within 2 eV corresponds to an equivalent noise of 0.05. Noise in the 10^{-4} range requires energy accuracy of 0.001 eV or better!

Similar performances and procedures are normally achieved at the BM29 beamline of the ESRF [3].

4) References

[1] A. Filipponi, *"Deconvolution of the lifetime broadening from x-ray absorption spectra of atomic and molecular species."*, J. Phys. B **33**, 2835 (2000).

[2] M. O. Krause and J. H. Oliver, J. Phys. Chem. Ref. Data **8**, 329 (1979).

[3] A. Filipponi, M. Borowski, D. T. Bowron, S. Ansell, S. De Panfilis, A. Di Cicco, and J.-P. Itiè, *"An experimental station for advanced research on condensed matter under extreme conditions at the ESRF - BM29 beamline."*, Rev. Sci. Instr. **71**, 2422 (2000).