Nuclear Instruments and Methods in Physics Research B 285 (2012) 153–157

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

ESTRA-FitEXA: A software package for EXAFS data analysis

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ARTICLE INFO

Article history:
Received 1 March 2012
Received in revised form 12 April 2012
Available online 17 May 2012

Keywords:
EXAFS
Data analysis
Programs

ABSTRACT

ESTRA and FitEXA are two programs for processing X-ray absorption spectroscopy data, extraction of extended X-ray absorption fine structure (EXAFS) signal, and EXAFS data analysis via least square refinement procedure (shell fitting). ESTRA and FitEXA propose useful options such as the analysis of the noise on the raw $\chi(k)$ data and a high flexibility in the choice of the model distribution function: harmonic, anharmonic (cumulants) and hard sphere models. The minimization routines underneath the FitEXA code allow ample choice/control of the non-linear minimization procedure and check of the correlation among the parameters.

1. Introduction

The high energy region above an inner X-ray absorption edge (generally K or L) of an atomic species embedded in a condensed environment presents characteristics oscillations that are named extended X-ray absorption fine structure (EXAFS) [1–3] and contain valuable information on the average local structure around the absorbing species. The ample success of the EXAFS technique derives from its broad applicability in condensed matter studies, providing valuable chemical and structural information, and the relative simplicity of the experimental set-up and data analysis procedures. The EXAFS data analysis mainly consists in two steps: namely the extraction of the EXAFS (structural) signal, χ^{exp}, from the raw experimental data, and the data analysis by fitting the χ^{exp} to an opportune model function [2,3], χ^{mod}. The ESTRA program extracts the χ^{exp} signal, while FitEXA program is used for data analysis. ESTRA reads the raw experimental data, calculates the χ^{exp} and performs direct and inverse Fourier transforms of the χ^{exp} EXAFS signal. FitEXA fits the data to a model function via non linear least square refinement procedure. The data refinement algorithm is based on the MINUIT subroutines package [4], a well established and versatile multiparameter minimization code developed at the CERN. The MINUIT subroutines provide different minimization algorithms and allow an accurate treatment of statistical errors including the possibility to inspect the covariance matrices and cross correlation among the refined parameters.

ESTRA and FitEXA are designed to be light and portable: they are written in standard Fortran 77 language and do not require installation (i.e. they can be directly run from the executables). Both ESTRA and FitEXA run via command line interface or reading scripts from text ASCII files. All the input and output files are in ASCII format. The programs also generate scripts that can be loaded by Gnuplot [5], a light and free multi-platform plotting tool, to produce consumptive plots of the extraction and data analysis procedures.

ESTRA and FitEXA programs are freeware, the executables and manuals are available at the URL: http://preview.tinyurl.com/d5cv5vp.

The main features of ESTRA and FitEXA are described in the following paragraphs.

2. ESTRA

The ESTRA program contains different modules that allow to read, convert, and pre-treat (e.g. removal of bad data points or glitches) the experimental data, to calculate the structural EXAFS signal χ^{exp}, and to perform direct and inverse Fourier on the χ^{exp}. A script file is automatically generated by ESTRA at each run and can be loaded by the Gnuplot plotting tool [5], allowing to visualize the results of extraction procedures in a graphic window.

2.1. Data conversion

The first step in EXAFS data analysis usually consists in reading the raw experimental data, collected as a function of the energy across a specific atomic absorption edge and calculating the total absorption signal $\alpha(E)$, which, in transmission geometry is defined

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http://dx.doi.org/10.1016/j.nimb.2012.05.027

as $\alpha(E) = \ln I_o/I_t$, I_o and I_t being the X-ray intensity incident on the sample and the transmitted one, respectively. In fluorescence or Total Electron Yield (TEY) geometries $\alpha(E) \sim I_f/I_o$, I_f being the fluorescence or TEY intensity. Multi-element detectors are commonly used to improve the statistics of the data in fluorescence detection, and/or several spectra are collected and averaged. ESTRA reads data files in multi-column ASCII format collected in transmission or fluorescence/TEY geometry (single or multidetector) and calculate $\alpha(E)$. It is also possible to average several data files, interpolating the energy of each data file to the energy mesh of the first one, in case of not equal energy meshes.

2.2. EXAFS structural signal

The extraction of χ^{exp} signal represents the core task of ESTRA. The extraction is performed through the following steps, common to many EXAFS data analysis programs:

(i) The pre-edge background $\alpha_{pre}(E)$, representing the cumulative absorption of the sample, excluding the considered absorption edge, is modeled as straight line, $\alpha_{pre}(E) = aE + b$, calculated from the linear regression of $\alpha(E)$ in the energy region far before the edge. The α_{pre} is extrapolated to the high energy region and subtracted from $\alpha(E)$ to obtain:

$$\alpha'(E) = \alpha(E) - \alpha_{pre}(E)$$

(ii) The origin of the photoelectron energy scale E_o, is defined at the maximum of the first derivative of the absorption spectrum, $\alpha'(E)$, or can be set by the user. The photoelectron wavenumber is defined as: $k = \hbar^{-1}\sqrt{2m_e(E - E_o)}$. The k_i points are calculated on the experimental energy points, E_i, without interpolation.

(iii) The bare atomic-like background in the post edge region, α_o, is calculated using a N-knots polynomial spline trough the data, first derivative continue. The knot positions and the polynomial degrees are defined by the user. The knot positions of the α_o spline can be set in the energy (E) or wavevector (k) space. In addition, the spline can be weighted by x^w ($x = E,k$) and constrained to cross a fixed value at E_o (edge discontinuity). The edge step height, J, being used to normalize the data, is calculated averaging α_o in a user selected interval.

(iv) The EXAFS structural signal is calculated as:

$$\chi^{exp}(k) = \frac{\alpha'(k) - \alpha_o(k)}{\alpha_o(k)} J$$

(v) The ESTRA code also estimates the uncertainty on the experimental data providing some statistical information. The uncertainty on the i-th experimental point is defined as: $\epsilon_i = \chi_i^{exp} - \bar{\chi}_i$, with $\chi_i^{exp} = \chi^{exp}(k_i)$, and $\bar{\chi}_i$ represents the expected value of the EXAFS signal at k_i. ESTRA can calculate $\bar{\chi}_i$ in two ways: by default $\bar{\chi}_i$ is obtained by linear interpolating the values of the closest experimental data points: χ_{i-1}^{exp} and χ_{i+1}^{exp}, at k_i. Alternatively, $\bar{\chi}_i$ can be calculated by Fourier filtering the χ^{exp} up to a user defined cut-off distance R_{cut}. R_{cut} should be chosen to be large enough to include all the structural contributions, cutting off the high frequency noise. The interpolation method is preferable to check for discontinuities and glitches on the data but it is prone to follow the derivative $d\chi^{exp}/dk$ in the low k region (Fig. 1) where high frequency signals (long interatomic distances and multiple scattering terms) contribute to the total EXAFS signal. The average "noise" on χ^{exp} is estimated as:

$$\sigma_\chi = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\epsilon_i^2}$$

and the average signal to noise ratio is:

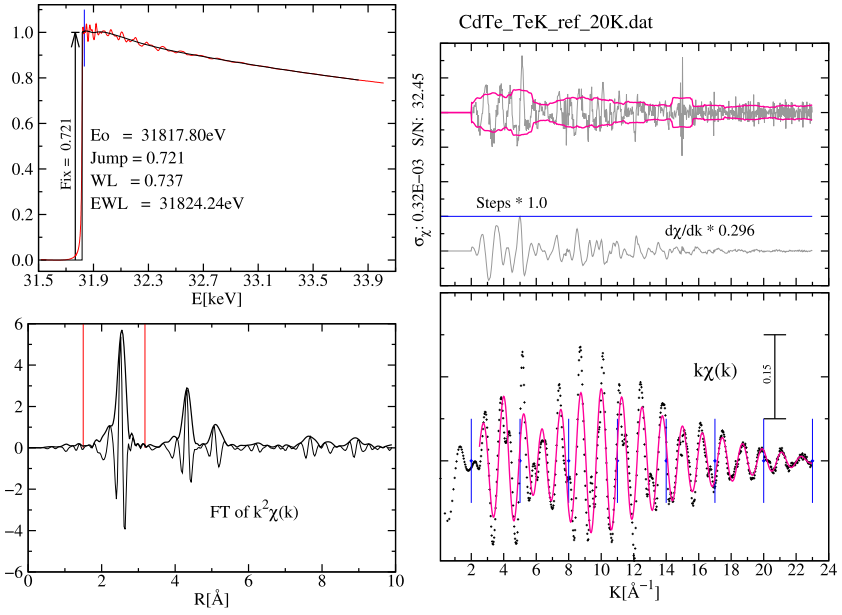

Fig. 1. Consumptive plots presenting the different steps of extraction procedure. Top left panel: raw data with pre-edge background subtracted and normalized to the edge step height α'/J. The post-edge atomic background α_o is also shown. The vertical line points out the first point for α_o spline calculation. The arrow signals the fixed edge discontinuity at E_o. The edge energy (E_o), edge step (Jump), the intensity of the first maximum above the edge (white line, WL) and its energy position (EWL) are also reported in this panel. Left bottom panel: the k^w weighted FT modulus and the limits for the inverse Fourier transform (vertical lines, red). Right bottom panel: $k^w\chi^{exp}$ data (points) and the Fourier filtered signal (full line, red). The vertical ticks (blue) mark the positions of the spline knots. Top right panel: the lower curve is the χ^{exp} derivative $\left(\frac{d\chi^{exp}}{dk}\right)$, the middle curve shows additional discontinuities, if any, and the top curve shows the estimated data uncertainty ϵ_i (linear interpolation method) and the $\bar{\sigma}_i$ (dark curve, magenta online) (see text). The comparison of ϵ_i and $\bar{\sigma}_i$ allows to individuate possible glitches and discontinuities in the spectrum. The values of the average noise (σ_χ) and the signal to noise ratio (S/N) are shown (see text). The name of the working file is reported above the top right panel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)