

Computer Programs

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X-FINE - a refinement program for FEFF input parameters

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X-FINE is an interactive and user-friendly tool to optimize input parameters (S_0^2 , σ^2 , ΔE) of the FEFF program, a package for EXAFS analysis.

Keywords: X-ray absorption; EXAFS refinement; polynomial fitting; downhill simplex; FEFF code.

1. Introduction

EXAFS (extended X-ray absorption fine structure) is a powerful spectroscopic method to determine the local order around an atom selected by its X-ray absorption edge (Lytle, Sayers & Stern, 1982). Several programs are available for analyzing spectra, such as EXCURVE (Binsted, Campbell, Gurman & Stephenson, 1991), Round Midnight (Michalowicz, 1989) and FEFF (Rehr, Mustre de Leon, Zabinsky & Albers, 1991). We describe a short program which can be used as a tool for the optimization of the FEFF input parameters.

2. General program organization

The program is organized in three modules dealing with the minimization of the amplitude reduction, S_0^2 , the global contribution of thermal agitation, σ^2 , and the individual values, σ_i^2 . For each theoretical spectrum generated by FEFF, the real part of ΔE will

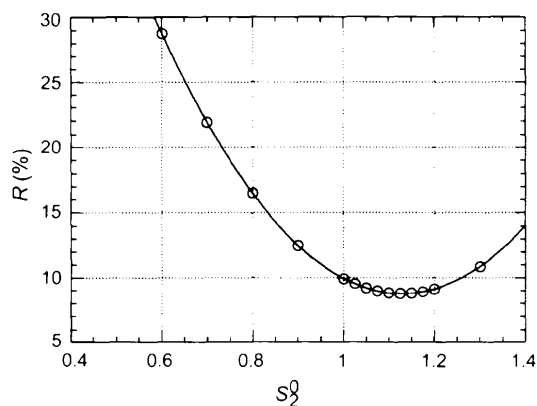


Figure 1 Polynomial regression of R on S_0^2 . The open circles are experimental points, the line is the theoretical curve (fitted by a fourth-degree polynomial), reliability factor 0.9.

be adjusted and the agreement factor, R , will be calculated by one of several methods offered to the user.

2.1. S_0^2 optimization

During the course of our study on a series of copper complexes (Alilou, Amadéi, Giorgi, Pierrot & Réglie, 1993), we have observed that S_0^2 is, at least at the beginning of the procedure, the most important parameter whose value must be approximated first. Moreover, we have observed that the variation of R is a regular and continuous function of S_0^2 , as indicated in Fig. 1. We have found an analytical relation between R and S_0^2 and the best result over our series of compounds has been obtained with a fourth-degree polynomial. A set of N calculated points in the (R , S_0^2) plane can be adjusted on a curve using the usual statistical equation system for this regression type:

$$\begin{aligned} \sum_{n=1}^N y &= dN + c \sum_{n=1}^N x + b \sum_{n=1}^N x^2 + a \sum_{n=1}^N x^3, \\ \sum_{n=1}^N yx &= d \sum_{n=1}^N x + c \sum_{n=1}^N x^2 + b \sum_{n=1}^N x^3 + a \sum_{n=1}^N x^4, \\ \sum_{n=1}^N yx^2 &= d \sum_{n=1}^N x^2 + c \sum_{n=1}^N x^3 + b \sum_{n=1}^N x^4 + a \sum_{n=1}^N x^5, \\ \sum_{n=1}^N yx^3 &= d \sum_{n=1}^N x^3 + c \sum_{n=1}^N x^4 + b \sum_{n=1}^N x^5 + a \sum_{n=1}^N x^6, \end{aligned}$$

where $S_0^2 = d + cR + bR^2 + aR^3$, and $N > 4$. a , b , c , d are the parameters of the fourth-degree polynomial.

It is worthwhile noting that in the region including the minimum value of the function it is necessary for the correlation factor between the N points and the polynomial to be as high as possible (better than 0.8). S_0^2 can adopt values greater than 1: this is a compensation effect of overevaluation attenuation of used potentials; this effect disappears when Dirac–Harras potentials are used (Rehr, private communication).

2.2. Global σ^2

Experience has shown that a fourth-degree polynomial can be used to adjust the global value of σ^2 and therefore the method described for S_0^2 can also be used for σ^2 .

2.3. Downhill simplex

Optimization of the individual values of σ_i^2 associated with each backscattering path is made using a downhill simplex (Press, Teukolsky, Vetterling & Flannery, 1992). If the value of S_0^2 generated by the first step is far from the expected value (for instance, given by another experimental method, *i.e.* X-ray diffraction, EPR *etc.*), a more reliable value can be obtained during this step. In order to give more flexibility and efficiency to the program, we have been led to define the σ_i parameters which will be optimized according to two ways:

(i) In the first case, σ_i is chosen according to the number, $nleg$, of legs (segment between two atoms) in a considered path. For instance, $nleg = 2$ corresponds to single scattering. The σ_i values which are not included in the $nleg$ window can have a global σ value or each $nleg$ value out of the $nleg$ window can have a global σ value.

(ii) In the second case, σ_i to be minimized is associated with paths which are included in a layer, the layer being limited by the minimum and maximum distances to the absorber. In that case, σ_i corresponding to paths outside of the layer can be minimized as a global parameter.

The first minimization method allows the minimum to be approached quickly. However, the second method allows the finest approach of the minimum and can be used to improve on the first method. If it is necessary to optimize S_0^2 , then the second method should be chosen.

3. Value of ΔE and definition of the reliability factors

After initialization of the parameters, ΔE will be adjusted using the following relation (Koenigsberger & Prins, 1988):

$$k = (2m\Delta E/\hbar^2)^{1/2} \Rightarrow \Delta E = (k_{\text{exp}}^2 - k_{\text{th}}^2)/0.262513,$$

where m is the photoelectron mass.

The adjustment of ΔE is made for each run of the *FEFF* program. Three reliability factors can be calculated by the program:

(i) The robust factor (*R1*), the statistical factor (*R2*), or the reliability factor (*R3*) related to the usual crystallographic *R* factor:

$$R1\% = \sum | \alpha k^n \chi(k)_{\text{th}} - k^n \chi(k)_{\text{exp}} | / \sum | k^n \chi(k)_{\text{exp}} | \times 100,$$

$$R2\% = \sum [\alpha k^n \chi(k)_{\text{th}} - k^n \chi(k)_{\text{exp}}]^2 / \sum [k^n \chi(k)_{\text{exp}}]^2 \times 100,$$

$$R3\% = \sum | \alpha k^n \chi(k)_{\text{th}} | - | k^n \chi(k)_{\text{exp}} | / \sum | k^n \chi(k)_{\text{exp}} | \times 100.$$

(ii) n allows the reliability factor for different powers of k (k , k^2 , k^3) to be calculated and thus it increases the relative weight of the large values of k where the EXAFS theory is more realistic.

(iii) α acts as a correction factor of S_0^2 and is introduced in the last step of the analysis.

4. Example

This program has been developed initially to investigate structures of copper complexes. The compound shown in Fig. 2 has been used to prove the efficiency of the program. The results of the various steps of the refinement are given in Table 1 (all refinement values are calculated with the *R2* formula and with k^3).

The theoretical and experimental $k\chi(k)$ are presented in Fig. 3.

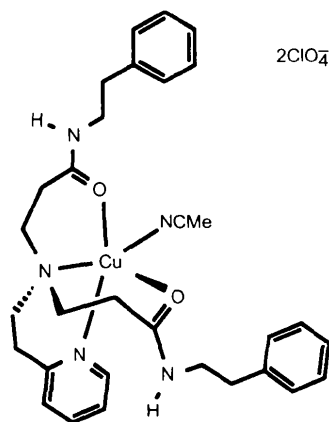


Figure 2

Acetonitrile {*N,N*-bis[(*N'*-phenylethylcarbamoyl)ethyl]-2-pyridylethylamine}copper(II) perchlorate (Amadéi *et al.*, 1992).

Table 1

Results of refinement for the compound shown in Fig. 2.

	S_0^2	σ^2	ΔE	α	<i>R</i> %
Starting values	1	0.005	0	1	63.45
S_0^2 step	1.2	0.005	6.7288	1	26.83
σ^2 step	1.2	0.0042	6.7288	1	26.80
Simplex step*	1.2	†	6.7288	0.9814	10.29

* After four runs with different values of tolerance and initial shift matrix. † The range of observed values is $0.0042 \leq \sigma_i^2 \leq 0.0104$.

5. Program availability and future development

The program was first written in FORTRAN77 on a DEC MicroVAX2000 computer and finally optimized and completed in FORTRAN77 on an SGI computer under UNIX. In order to allow a wide portability of *X-FINE*, the system primitives have been grouped in a subroutine that can be handled and modified at the user's requirement according to its system characteristics. *X-FINE* and its manual are provided by the authors on simple request. Two improvements are planned for the next version: (i) generation of a correlation matrix in order to obtain the *R* values with statistical meaning, and (ii) optimization of the distances of backscatters.

The program *FEFF* 6.00 used with *X-FINE* was developed at the University of Washington and the users are required to have a license from the *FEFF* Project, Department of Physics, University of Washington, Seattle, WA 98195, USA.

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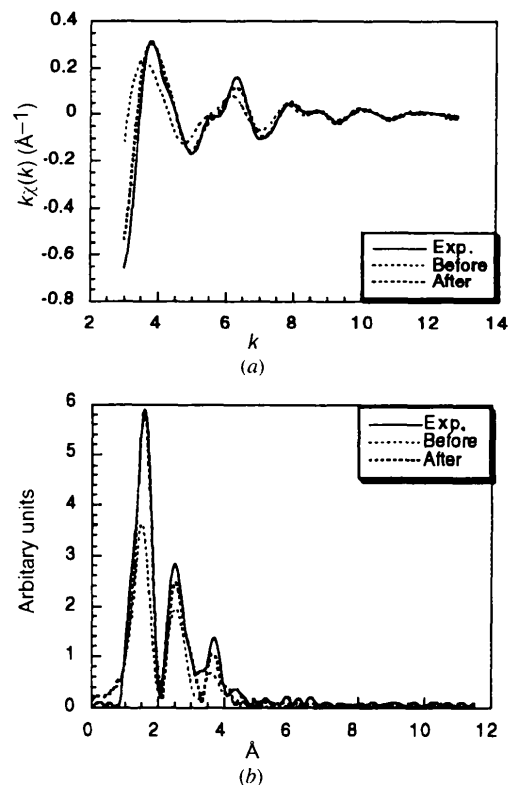


Figure 3

Experimental and calculated curves for the complex of Fig. 2 before and after refinement. (a) $k\chi(k)$. (b) Radial distribution function obtained by fast Fourier transform and Kaiser window. The cut-off of $k\chi(k)$ has been set from 3 to 13 \AA^{-1} .

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