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Estimation of the experimental standard deviations in EXAFS measurements

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We have studied the multiple recording method to estimate if it possible to obtain by this way reliable EXAFS data standard deviations. The examination of more than 10 different samples, each of them recorded at least 8 times, gave us the possibility to show that the partial standard deviations follow the expected probability laws. Even when the number of samples is small, it is possible to give a reasonable upper limit of ε wich could be used as the statistical contribution of the experimental error bars. In some cases we have found that a uniform weighting by $1/\varepsilon^2$ may fail to give a good fit, especially in the high part of k space. We present a simple method of weighting which lead to more satisfying fits without loosing the correct normalisation of the fitted $\Delta\chi^2$ necessary to obtain correct fitted parameters error bars.

Keywords : statisitcs; standard deviation; exafs error bars

1. Introduction

In order to provide standard methods for fitting and extractiong quantitative structural parameters from EXAFS data and modelling, the Standard and Criteria In XAS Comitee (Lytle, S&C report, 1988 and present XAFS conference, 1998) has proposed to use the statistics laws already applied in other structural methods, as crystallography. This short paper will not discuss these laws, but will focuss on the key parameter that should be evaluated if one want to use them : the standard deviation of the data, noted ε, wich appears in the statistical function to minimize in the fitting procedure as :

$$\Delta\chi^2 = (N_{ind}/N_{pts}) \sum_i (\chi_{ith}-\chi_{iexp})^2/\varepsilon_i^2$$

It has been underligned that ε should be the quadratic sum of several terms, including non statistical, or systematic errors. This work deals only with the statistical error term. In the published EXAFS codes many different methods for evaluating this standard deviation are proposed. We will discuss one of them : statistics on multiple recordings, named also the sampling method. Altough excitation spectra (fluorescence, electrons emission) should be studied in the same manner, we have restrained the present study only on transmission data.

2. The principles

We study a multiple recorded data set k_i, $\chi_j(k_i)$ with i=1,Npt (Npt = number of data points) and j=1,n (n= number of samples).

The degree of freedom of this sampled spectrum is ν = n-1.

For each data point we calculate the mean signal $<\chi(k_i)>_n$ and its standard deviation σ_{in}

$$<\chi(k_i)>_n = [\Sigma_j \chi_j(k_i)]/n \quad (1)$$

$$\sigma_{in} = \text{sqrt}\,[\Sigma_j(\chi_j(k_i)-<\chi(k_i)>_n)^2/(n-1)] \quad (2)$$

For fitting purpose it may be more convenient to use averaged values than point by point ones. Since it is a sine wave, the average EXAFS signal should be evaluated as the quadratic mean $S_n=\text{sqrt}[\Sigma_i(<\chi(k_i)>_n)^2/Npt]$ (3).

The average standard deviation can be calculated in three manners :

simple mean $\varepsilon_{sn} = \Sigma_i \sigma_{in}$ /Npt (4),

quadratic mean $\varepsilon_{qn} = \text{sqrt}[\Sigma_i \sigma_{in}^2$ /Npt] (5)

or, as recommanded by Bevington (Bevington, 1992), inverse quadratic mean $\varepsilon_{qin} = 1/\text{sqrt}[\Sigma_i (1/\sigma_{in})^2$ /Npt] (6).

The signal/noise ratio is defined as $S/B = S_n/\varepsilon_n$.

In our previous work we have systematically used ε_{qin} (equation 6), but after having remarked that this formula often underestimates the error bars, we prefere to calculate the three ε_n and choose the greatest one. One may remark that ε_n still depend on the number of samples n and is certainly not equal to the standard deviation of the parent distribution ε. In principle $\varepsilon = \lim(\varepsilon_n)$ (n->). If n is small the use of ε_n as a value of ε may be questionable. Of course, for economical reasons, it is impossible record infinity sets of data. Fortunately the statistics laws allows us to evaluate a confidence interval in which ε should lie with a given probability. In other words, it is possible to calculate an upper limit $\varepsilon_U = \varepsilon_n * B_U$ under which the parent value ε, should lie with the probability P. We suggest that this upper limit should be used as the value of ε instead of ε_n.

The values of B_U (P,ν) and B_L(P,ν) (for the lower limit) are tabulated (Taylor, 1990). However, it is quite easy to calculate them. The main idea is that the quantity $\nu*[\varepsilon_n/\varepsilon]^2$ obeys to the χ^2 probability law $P(>\chi^2, \nu)$ for ν degree of freedom (Mandel, 1964). The confidence interval for a probability P should be set symetrically between the two limits $P_L = (1-P)/2$ (7) and $P_U = (1+P)/2$ (8).

Thus, $\alpha_L < \nu*[\varepsilon_n/\varepsilon]^2 < \alpha_U$ (9).

The numerical values of α_L and α_U are the solutions of the equations $P(\alpha_L, \nu) = P_L$ (10) and $P(\alpha_U, \nu) = P_U$ (11). Finally we obtain the limits of ε in the confidence interval :

$B_L*\varepsilon_n<\varepsilon<B_U*\varepsilon_n$, with $B_L=\text{sqrt}(\nu/\alpha_U)$ and $B_U=\text{sqrt}(\nu/\alpha_L)$ (12)

We have already written the corresponding Fortran code. A free access in given on the web of LURE :

http://www.lure.u-psud.fr

Some examples of the numbers obtained by this program are displayed in table 1

n	BL	BU
3	0.52	6.28
4	0.57	3.70
5	0.60	3.07
6	0.62	2.45
7	0.64	2.20
8	0.66	2.03

Table 1 Value of BL and BU for n sampled spectraand a confidence interval of probabily P = 95%

3. Results : the standard deviation statistics

We have applied the preceeding principles to a set of more than 10 spectra of different kind of samples, each recorded at least 8 times, in transmission mode. The complete study of these spectra

will be published elsewhere (Andreatta). In this short paper we will just summarize the results. The behavior of ε_n versus n, the number of sample for one of the cases is displayed in figure 1. In all the studied examples we have found a similar behaviour : σ_n is a monotonic increasing function of n which saturates for n 8. In all these examples we can assume that $\varepsilon_8/\varepsilon_n \approx \varepsilon/\varepsilon_n$. In figure 2 we have plotted $\varepsilon_8/\varepsilon_n$ versus n for all the studied examples. The corresponding values of B_L and B_U for P = 95% are displayed as plain lines. It is clear that, except for n=3 in one spectrum, all the partial standard deviations plotted in this figure are largely inside the confidence interval defined in §III.

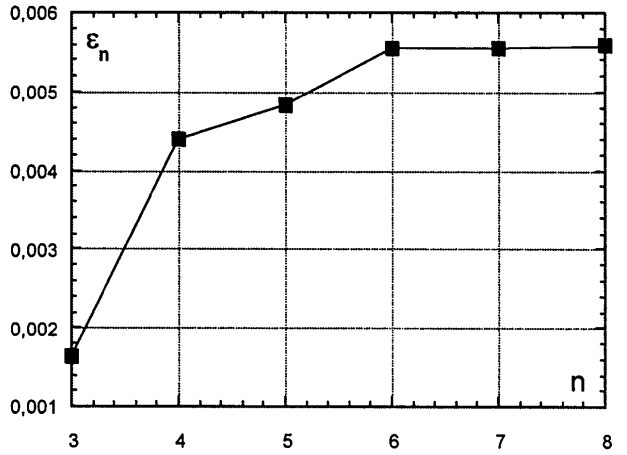

figure 1 typical plot of ε_n for one example

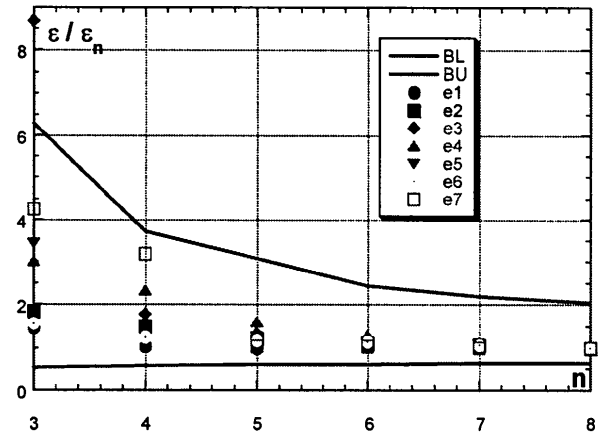

Figure 2 plot of e8/en for 7 selected spectra

In other words, this experimental study allows us to say that $\varepsilon < BU(P,n-1) * \varepsilon_n$ (13) with a probability at least equal to P. We think that this upper limit value of the standard deviation can be used as the maximum value that should be used in the estimation of the error bars in parameters fittings.

4. Standard deviation and fit weighting

In most cases fitting with a uniform weight $w=1/\varepsilon^2$ leads to correct fitting results and to a reasonable evaluation of the statistical contribution of the error bars. However, we have encourted some cases where uniform weight leads to significantly bad fits (by eyes) at the end of the spectrum (figure 3). Obviously, such a « bad » fit implies that the the errors bars are dominated by systematic errors. A way to improve such a fit is to apply a k^n weight.

Of course, if the standard deviation is modified accordingly (ε' = srqrt(k^n)*ε (14)) the new weight will cancel in the calculation of $\Delta\chi^2$ and will have only a cosmetic use in the displayed graphics. On the other hand, if we do not apply the k^n weighting to ε^2 the resulting normalisation will be incorrect and the estimation of the parameters error bars will be unrelevant. We have tried a very simple idea : the experimental weighting w = $1/\varepsilon^2$ is replaced by $w'(k)=k^n/A$.

Thus $\varepsilon'(k)$ = sqrt(1/w) = sqrt(A/k^n) (15). The value of A is estimated in order to get $<\varepsilon'>=<\varepsilon>$. This calculation is also provided in the cited Fortran code.

In the example displayed in figures 3 and 4 we have obtained A = 0.25 for ε = 0.015 and n = 3. The resulting k^n/A weighted two shell fit is shown on figure 4. The improvement of this fit at the end of the spectrum is clear. Fitting results are displayed in table 2. One may remark that these results are closer to the known crystal structure than the « bad » fit of figure 3, and that the corresponding normalization of $\Delta\chi^2$ lead to similar fitted parameters error bars.

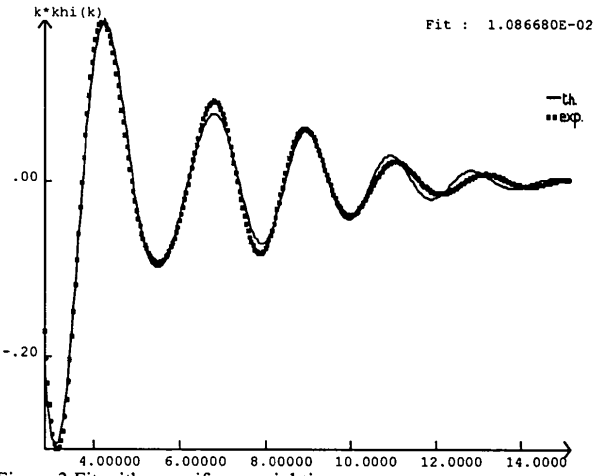

Figure 3 Fit with an uniform weighting

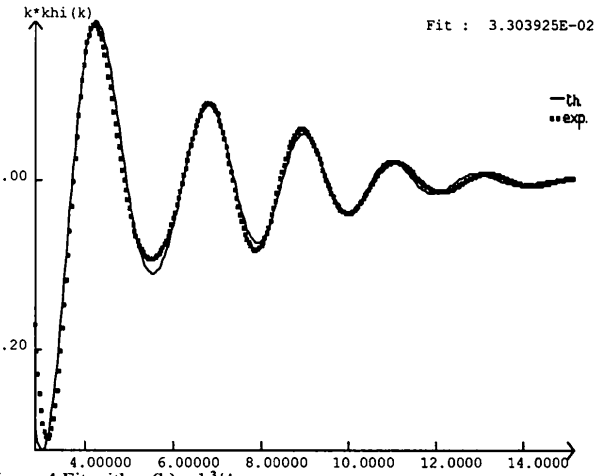

Figure 4 Fit with $w(k) = k^3/A$

	N	σ (Å)	R (Å)	ΔEo (eV)	$\Delta\chi^2_\nu$
$w(k) = 1/\varepsilon^2$	3.7(2) 2.3(2)	0.06(1) 0.06(1)	1.81(1) 2.08((2)	-0.3(1.0) -0.3(1.0)	1.6
$w(k) = k^3/A$	3.9(2) 2.1(2)	0.06(1) 0.06(1)	1.79(1) 2.07(2)	-2.9(1) -2.9(1)	0.98

Table 2

One may remark that, even normalized to the experimental standard deviation, k^n weighting violates the principles of statistical treatment. However, it is possible to justify this method, when standard statistical treatment fails to give satisfying fits. In figure 3 the fit is dominated by non statistical errors because the deviation between the experimental and then theoretical spectra is not randomly distributed from the beginning to the end of the spectrum. This fit is satisfying at low k and not at the end. This means that the assumed standard deviation is too small at low k, and too big after 10 $Å^{-1}$, In other words, the fitting weight is too big before 6 $Å^{-1}$ and too small after 10 $Å^{-1}$. Normalized k^n weighting preserves the average standard deviation and compensates the systematic errors observed at the end. During the last meeting of the Standard and Criteria comitee, it was stressed that if statistical treatment of EXAFS data was already well established, non statistical, systematic, errors were much difficult to handle. While the comitee works to try to overcome this difficulty, it was proposed to treat systematic errors the same way as statistical ones by adding a scaling factor to the standard deviation. The present normalized weighting procedure can be seen as an alternative method for the treatment of systematic errors. Its use should be limited to the cases where the systematic errors are small, increasing with k and cannot be treated by an improvement of the structural model.

5. Conclusion

In this work we have shown that experimental standard deviations obtained by multiple recording of EXAFS data are reliable even if the number of samples is small. Of course we cannot assume that we have found a general parent statistical distribution of the EXAFS data. However, we have shown that in all the studied cases, the experimental standard deviations are under the limits given by the statistical laws for a normal distribution of data. The upper limits can be used as a maximum practical value in fitting procedures and error bars estimations. Finally a way to use k^n weighting when uniform weight is less efficient is shown to be useful and applicable.

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