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Statistical errors in x-ray absorption fine-structure data analysis

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Abstract. General criteria for performing a rigorous statistical error determination in x-ray absorption fine-structure data analysis are formulated. The equivalence of the residual function increment approach ($\lambda: R(\{\lambda\}) < R_{min} + \chi_{p,0.95}^2$) with more rigorous Monte Carlo procedures is demonstrated in the case of the analysis of the Br₂ spectrum. The possible existence of nonlinear effects in parameter space is discussed and a specific example referring to the S–C=O molecule case is illustrated. Practical suggestions are given to improve data collection procedures and to select appropriate fitting parameters in the analysis.

1. Introduction

X-ray absorption spectroscopy (XAS) has become a widely used technique in condensed-matter physics, chemistry, earth sciences, and biology, to probe the local structural environment around photoabsorbing atoms [1]. XAS provides an insight that is sometimes complementary to that of other well established techniques while unique information is often obtained. Several advanced software packages suitable for performing a reliable analysis based on theoretical calculations have been developed [2, 3, 4, 5] and efforts have been recently devoted to establishing standard criteria of analysis [6].

In spite of the existence of many data analysis methodologies, very little attention has been paid to the establishment of correct procedures for error evaluation in the derived structural parameters. As a matter of fact quoted errors are often only estimated in a qualitative way—sometimes, even using questionable approaches. So far, very few papers have been devoted to a comprehensive discussion of this fundamental aspect of the extended x-ray absorption fine structure (EXAFS) data analysis.

It is generally assumed that the EXAFS accuracy is mainly limited by the presence of systematic errors due to the intrinsic approximations in the theoretical formulations. Recent comparisons of data analysis results in the case of model compounds with known structure [4, 5] indicate, however, that present theoretical approaches are quite reliable. Data analysis results are also found to be largely insensitive to variations of the free theoretical parameters, for instance the muffin-tin radii used in the construction of the phase-shifts. These findings suggest that the magnitude of systematic errors is low and that reliable structural results can nowadays be obtained from EXAFS analysis based on theoretical calculations. Under these circumstances a statistical error treatment becomes an essential step of the data analysis procedure. Statistical errors represent a bound for the accuracy of the information that

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can be extracted from experimental data and indicate the level to which structural results on model systems must be compared with the known values. Moreover they provide a reliable estimate for the actual error in the fitting parameters at least in those cases for which systematic errors in the analysis of model compounds are found to be negligible.

The statistical evaluation of the EXAFS fitting results was first addressed in a paper by Joyner *et al* [7], where large emphasis was given to pointing out the existence of strong correlations between some EXAFS parameters (such as E_0 and R) and on the necessity of accounting for this correlation in quoting the errors. The paper also dealt with applications of the F test to establishing the significance of the addition of a further coordination shell in the fit. Criteria for error evaluation were given in terms of the intersection of the fit index (FI) function with reference levels (the value $FI = FI_{min}/0.96$ was suggested as a rule-of-thumb criterion).

No further paper appeared on this subject until it was pointed out [8] that the information content in the oscillating EXAFS signals is limited by the extension in k and R space of the signal and that the number of independent points was actually only $N_{ind} = 2 \Delta k \Delta R / \pi + 2$, usually much smaller than the number of experimental points N . According to Stern [8] N_{ind} is also an upper limit for the number of parameters p that can be fitted to the corresponding EXAFS spectrum.

A method for error determination in the parameters was described in [9] where a χ^2 -like function scaled by a value of N_{ind} was incremented by the value of unity to define the confidence interval in parameter space. These latter prescriptions appear at variance with well established results in the field of nonlinear minimization procedures [10] that are currently adopted in different scientific contexts [11, 12].

As a result of the present considerations we feel it is important to raise the issue of a rigorous formulation of the error evaluation procedures in EXAFS data analysis, based on well founded statistical grounds. This paper is intended to provide an insight into this problem combining theoretical formulation with explicit examples.

2. Theory

2.1. General formulation

The XAS theory provides a framework in which to calculate model x-ray absorption spectra $\alpha_{mod}(E; \lambda_1, \lambda_2, \dots, \lambda_p)$ as a function of p structural parameters λ_j , $j = 1, \dots, p$, indicated as $\{\lambda\}$. The theory is assumed to be able to model the actual absorption coefficient $\alpha(E)$ for certain values $\{\tilde{\lambda}\}$ of the parameters. It is also assumed that the experimental signal is only affected by random Gaussian noise with standard deviation σ_i possibly depending on the energy point E_i , that is

$$\alpha_{exp}(E_i) = \alpha_{mod}(E_i, \{\tilde{\lambda}\}) + \xi_i \quad (1)$$

where ξ_i is such that $E\{\xi_i\} = 0$ and $E\{\xi_i \xi_j\} = \delta_{ij} \sigma_i^2$. In other words the probability density for a certain experimental spectrum outcome $\alpha_{exp}(E_i)$ is given by

$$f(\alpha_{exp}(E_i)) = \prod_{i=1}^N \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp \left[-\frac{1}{2} \left(\frac{\alpha_{exp}(E_i) - \alpha(E_i)}{\sigma_i} \right)^2 \right]. \quad (2)$$

In the spirit of the likelihood function estimators theory, the optimal estimate of $\{\bar{\lambda}\}$ for a certain experimental spectrum will be the set $\{\bar{\lambda}\}$ maximizing the likelihood function

$$P(\{\lambda\}) \sim \prod_{i=1}^N \exp \left[-\frac{1}{2} \left(\frac{\alpha_{exp}(E_i) - \alpha_{mod}(E_i, \{\lambda\})}{\sigma_i} \right)^2 \right]. \quad (3)$$

As is always the case for Gaussian noise, this is equivalent to a least-square prescription on the residuals between model and experiment.

Under these conditions it is natural to define a residual function as:

$$R(\{\lambda\}) = \sum_{i=1}^N \frac{[\alpha_{exp}(E_i) - \alpha_{mod}(E_i; \lambda_1, \lambda_2, \dots, \lambda_p)]^2}{\sigma_i^2} \quad (4)$$

and to write $P(\{\lambda\})$, that actually represents the probability density in the parameter space $\{\lambda\}$ for the given experiment, as

$$P(\{\lambda\}) \sim \exp \left(-\frac{1}{2} R(\{\lambda\}) \right). \quad (5)$$

The optimal values for the structural parameters will be the set $\{\lambda\} = \{\bar{\lambda}\}$ minimizing the residual function $R(\{\lambda\})$ in equation (4). The multi-dimensional minimization procedure can be handled with standard procedures and algorithms [10, 12]. We will not enter into a discussion of the well known problem of the global versus local minimization achievement here. The $\{\bar{\lambda}\}$ values will be, in general, sufficiently close to the true values $\{\lambda\}$.

Following very standard procedures for nonlinear fitting problems it is possible to apply several statistical tests that are useful in the evaluation of the results.

(i) The $R(\{\bar{\lambda}\})$ function on the space of the possible realization of the experimental noise is described by a χ_{N-p}^2 random variable. The statistical χ^2 test can be performed to check whether the actual value of $R(\{\bar{\lambda}\})$ is only due to residual noise or whether it still contains unexplained physical information.

(ii) The comparison between two different models M_1 and M_2 for the structure, depending on p_1 and p_2 parameters respectively, can be performed using the F test. Typical cases can for instance occur in considering the addition of a further signal contribution, from M_1 to M_2 , or the splitting of a shell into two, or they might be completely different structures from which one has to choose. Let us suppose that the two minima of the residual are R_1 and R_2 respectively. Then if both models were appropriate to explaining all of the signal one would expect the function

$$f = \frac{N - p_2}{p_2 - p_1} \left(\frac{R_1}{R_2} - 1 \right) \quad (6)$$

to follow an $F_{p_2-p_1, N-p_2}$ distribution. The F test applied to f shows in this case whether or not the reduction of the residual R obtained in the best model is actually large enough and not simply due to the increase of model parameters or to random fluctuations. The F test has been previously applied in EXAFS data analysis [7] especially by the users of the Daresbury EXCURVE package.

2.2. Statistical errors

The statistical error determination is a central topic of this paper and deserves a thorough discussion. Three approaches are described in the present section.

Statistical errors in the structural parameters are ideally given by the spread of the fitting parameters associated with an ensemble of equivalent experimental data, that is by the spread in the $\{\bar{\lambda}\}$ values generated by the different possible realizations of the experimental noise ξ

in equation (1). Unfortunately, only a single measurement is usually available. The effect of the random noise can be evaluated, however, even in this case, with the aid of a simulation. Once the noise level has been correctly determined, it is possible to generate random spectra adding different noise realizations to the reference experimental spectrum. The optimized structural parameters for this simulated ensemble of spectra will be centred around $\{\bar{\lambda}\}$ instead of $\{\lambda\}$ as in the case of an ideal ensemble of experimental spectra. However, their spread will mimic the spread occurring in the idealized case and is representative of the statistical uncertainty. In practice the observed spectrum parameters $\{\bar{\lambda}\}$ differ from $\{\lambda\}$ by a random component whose magnitude is visualized by the spread of points around the central values. This spread reproduces the probability distribution of the location of the actual values around the only available determination $\{\bar{\lambda}\}$, that is the error of the latter. An example of this random generation procedure for determining statistical errors will be presented in section 3.2. This procedure is reliable but not adoptable for routine analysis due to the large computing efforts required.

A second approach for determining statistical errors is based on the use of the Metropolis Monte Carlo algorithm [13] to sample the parameter probability distribution given by equation (5). A procedure of this kind is based on the same principle of the reverse Monte Carlo method [14] also proposed for the EXAFS data analysis [15]. As usual, a Markov chain in parameter space is generated by random moves $\{\lambda\} \rightarrow \{\lambda'\}$. At each step the tentative new position $\{\lambda'\}$ is accepted if $R(\{\lambda'\}) \leq R(\{\lambda\})$, and it is accepted with probability $\exp[-\frac{1}{2}(R(\{\lambda'\}) - R(\{\lambda\}))]$ if $R(\{\lambda'\}) > R(\{\lambda\})$. In the case of non-acceptance the step is performed maintaining the original position $\{\lambda\}$. The application of such a random process to experimental data will provide, after a sufficiently long equilibration period, a sequence of independent sets of parameter values, all producing equivalent best fits of the experimental spectrum within random noise. The sequence of $\{\lambda\}$ values will sample the parameter probability distribution $P(\{\lambda\})$ given by equation (5). The average values among these parameters represent an average best fit, while the spread in the sample represents the statistical uncertainty as in the previous case.

A third strategy for estimating statistical errors, that leads to a simple formulation suitable for routine analysis, is suggested by an analytical treatment. On expanding the function $R(\{\lambda\})$ to second order in λ and ξ about the minimum, it is found that the actual $\{\bar{\lambda}\}$ values are displaced from the real values $\{\lambda\}$ by a linear function of the noise ξ . The ensemble of ξ values corresponds to an ensemble of $\{\bar{\lambda}(\xi)\}$ values that, inserted into the $R(\{\lambda\})$ function, generate a random variable

$$R(\{\bar{\lambda}(\xi)\}) = R(\{\bar{\lambda}\}) + \chi_p^2 \quad (7)$$

that is a χ_p^2 random variable (with p degrees of freedom) shifted by the value of R in the minimum $R(\{\bar{\lambda}\}) = R_{min}$. Knowledge of the integral properties of the χ^2 distribution allows one to establish confidence intervals for the parameters. The region in the parameter space enclosing the fraction γ of the possible outcomes (usually $\gamma = 95\%$) will be defined by λ such that $R(\{\lambda\}) < R_{min} + C$, with C being a critical value of the $\chi_{p,0.95}^2$ distribution (p degrees of freedom and the 95% confidence level). Notice the dependence of C on p . An explicit example will be discussed in the next section.

3. Applications and examples

While the criteria discussed in the previous section are well established in the statistical field, the practical aspects involved in their application to EXAFS problems deserve a detailed treatment. In this section these aspects will be discussed and reference will be given to an

explicit example: the spectrum of the Br₂ molecule in gas phase. The measurement has been already published and has been the subject of detailed analysis [16, 17].

The fitting of the Br₂ spectrum is performed with $p = 4$ parameters, namely R , σ^2 , E_0 , and S_0^2 . The first two are structural parameters referring to the mean and variance (not to be confused with the noise variance at point i , σ_i^2) of the bond distance distribution. The other two are empirical parameters defining the matching of the experimental and theoretical energy scales (E_0) and an overall amplitude reduction factor (S_0^2) accounting for normalization uncertainties due also to the one electron approximation. The optimal values are found to be in excellent agreement with the known structure indicating the absence of systematic errors. As an example, the fitted optimal value of $R = 2.2884$ Å coincides to within 0.0001 Å with the expected value of this quantity calculated from spectroscopic parameters [18]. This comparison clearly indicates the absence of major systematic errors in this specific case.

3.1. Random noise

Equation (4) assumes that the experimental noise is Gaussian. This requirement is largely satisfied when the photon counting statistic is large enough and after the energy points corresponding to glitches of the monochromator are eliminated. Equation (4) also assumes that the noise variance is a known function of the energy.

Several approaches can be used to estimate the noise level in the spectra. Theoretical estimates of the noise level can be performed by a careful analysis of the data collection procedures and by considering the effects of the counting statistics and/or amplifier noise. Direct methods consist of performing several repeated measurements of the absorption coefficient on a representative set of energy points E_j along the spectrum. By assuming a smooth behaviour the noise level, $\sigma^2(E)$, directly calculated at E_j , can be interpolated on the whole spectrum.

More practical methods are based on the noise evaluation on the same spectrum subject to the EXAFS analysis. In previous papers, ways to isolate the noise component in EXAFS spectra by means of polynomial fitting or Fourier filtering have been proposed [19] and applied [20]. An accurate determination of the noise level requires a certain oversampling of the EXAFS oscillations. Ideal spectra contain at least 800–1000 energy points for a typical EXAFS acquisition. Two methods are found by us to be particularly efficient.

(i) By assuming a smooth behaviour of the actual absorption coefficient, it is possible to model energy regions containing M data points with polynomial functions of degree $q < M$. With a suitable choice of M , q , and energy intervals, the noise variance is estimated from the residual square difference (data minus polynomial fit) divided by $M - q$. This can be performed on successive subsets of M points suitable to be interpolated by a smooth $\sigma^2(E)$ function.

(ii) Another possible strategy is to assume the residual ($\alpha_{exp}(E_i) - \alpha_{mod}(E_i, \lambda)$) in the minimum as due entirely to statistical noise. The squared residual can then be evaluated as a function of the energy and a smooth function interpolated through the available data.

Equivalence of the noise level estimated with methods (1) and (2) occurs when the noise evaluation is reliable and the model signal has explained all of the structural EXAFS contribution. From the theoretical point of view the noise estimated from the residual variance as in (2) follows statistical fluctuations according to the χ_2 distribution and consequently may be also underestimated. In this case, in which the noise is estimated from R_{min} and an appropriate k weight is adopted, the condition $R = R_{min} + C$ for the error

confidence intervals reads $R = R_{min}(1 + C(N - P)/\chi_{N-p}^2)$. The term $C(N - p)/\chi_{N-p}^2$ is an F random variable, and, as a result, the constant defining the confidence interval results increased according to the F distribution critical values. These considerations have a mainly conceptual importance rather than any practical consequence. In general the fitting residual will contain other sources of discrepancy and for this reason the noise (and errors in the parameters) are usually overestimated in this way. This procedure appears therefore safe and conservative.

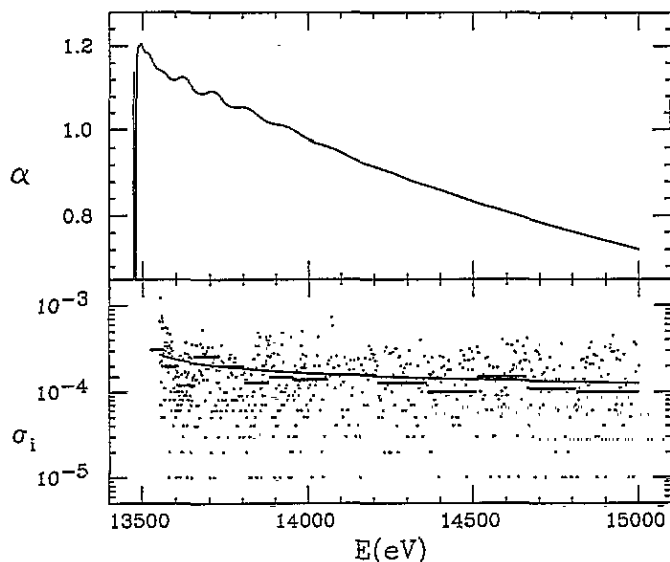


Figure 1. Upper panel: the K-edge x-ray absorption spectrum of Br_2 in gas phase at room temperature. Lower panel: the root mean square noise evaluated using different methods: root mean square deviations from fitting polynomials averaged over 50 points (thick horizontal segments), interpolating smooth function corresponding to k^1 weighting (solid line), absolute deviation from best fit (dots).

A practical example of the previous discussion is reported in figure 1. The top curve is a magnification of the raw absorption spectrum of Br_2 recorded adopting three energy regions in the range 13 400–13 650–14 000–15 000 eV with points equally spaced by 0.8, 1.5, and 3.0 eV, respectively. The lower part of figure 1 reports on a logarithmic scale the root mean square (rms) noise level estimated by different methods. The horizontal thick segments represent the average deviations from fitting seven-degree polynomials in successive regions including 50 energy points each. The scattered points represent the modulus of the residual function after fitting with the structural contribution. In this case the structural contribution has been completely accounted for and the residual contains only random noise. In fact the magnitude of the average noise is comparable. In this case both methods are suitable for evaluating the experimental noise and suggest the correct weight function to be used in the fit. The solid line refers to a smoothed version of the experimental noise function $\sigma(E)$ corresponding to a k^1 weight of the fitting. The energy dependence of the rms noise that decreases on increasing energy is in this case due mainly to the increasing transmission of the thin glass windows, used to confine the Br_2 gas in the experimental cell [16].

3.2. Error confidence intervals

Insight into the theoretical treatment given in section 2.2, regarding the statistical prescriptions used to determine the confidence intervals for the fitting parameters, is given by the discussion of explicit examples. All three different procedures are applied to the analysis of the Br₂ spectrum and proof of substantial equivalence will be provided.

An ensemble of 500 equivalent simulated spectra has been generated by adding to the available experimental spectrum random noise realization, with $\sigma(E)$ given by the continuous curve in figure 1 (lower panel). Each spectrum has been fitted by the same procedure and a sample of 500 corresponding sets of fitting parameter values has been obtained. The spread in these values mimics the spread occurring among the fitting parameters of an ideal ensemble of equivalent experimental spectra. The sample is in this case centred around the parameters $\{\bar{\lambda}\}$ corresponding to the experimental spectra that are displaced from the unknown 'exact' values $\{\hat{\lambda}\}$. The results of this procedure are presented in figure 2; panel (a) for the E_0, R subspace and panel (b) for the R, σ^2 subspace. The scattered points filling roughly ellipsoidal space regions correspond to two-dimensional projections onto the two subspaces of the fitting parameters for the ensemble of 500 simulated spectra. The cross at the centre refers to the fit of the reference spectrum. The existence of correlation between R and E_0 is quite evident in figure 2 (a); positive E_0 deviations are combined with positive R deviations (positive correlation).

The Metropolis Monte Carlo algorithm has been also applied to the Br₂ case. After a sufficient number of equilibration steps, during which the region of the optimal residual minimum was reached, the simulation in parameter space was extended for another 50 000 steps. The values of the parameters were sampled every 100 steps to insure an uncorrelated sampling. The random moves on each parameter were selected from uniform distributions centred around zero. The distribution widths were chosen to be 0.001 Å for R , 0.0001 Å² for σ^2 , 0.3 eV for E_0 , and 0.01 for S_0^2 , in order to optimize the acceptance rates and maximize the diffusion in parameter space. Since, after equilibration, any set $\{\lambda\}$ is an equivalently good fitting of the experimental data the resulting sample spread (in our case the sample dimension was 500 again) represents the uncertainty in parameter values. The set of parameter values is actually a sample of the parameter probability distribution. The weight 1/2 in the exponential of equation (5) and the correct noise level evaluation are essential to provide the correct error estimate. The results of this random process are presented in figure 3: panel (a) for the E_0, R subspace (as in figure 2) and panel (b) for the σ^2, S_0^2 subspace, that presents the projection on another pair of highly correlated variables. The plots are conceptually similar to those of figure 2.

The scatter of the points in the p -parameter space (in this case $p = 4$) indicates the shape and extension of the error confidence intervals. Standard criteria recommend the selection of a confidence level such that the confidence interval encloses 95% probability (i.e. 95% of scatter points). Due to the multi-dimensional nature of the space there is a large freedom in the choice of the enclosure shape. The natural choice for Gaussian distributions is given by ellipsoidal regions.

The random spectra generation approach for error determination is reliable but not adoptable for routine analysis due to the large computing efforts required in each case. The second approach based on the Metropolis Monte Carlo sampling of the maximum likelihood parameter probability distribution is extremely powerful. We hope that data analysis methods based on these ideas like the RMC approach [14] will find, in the future, wider application in the EXAFS community. For routine analysis the criteria given in section 2.2 in terms of the magnitude of the residual function are more practical. This latter approach, however,

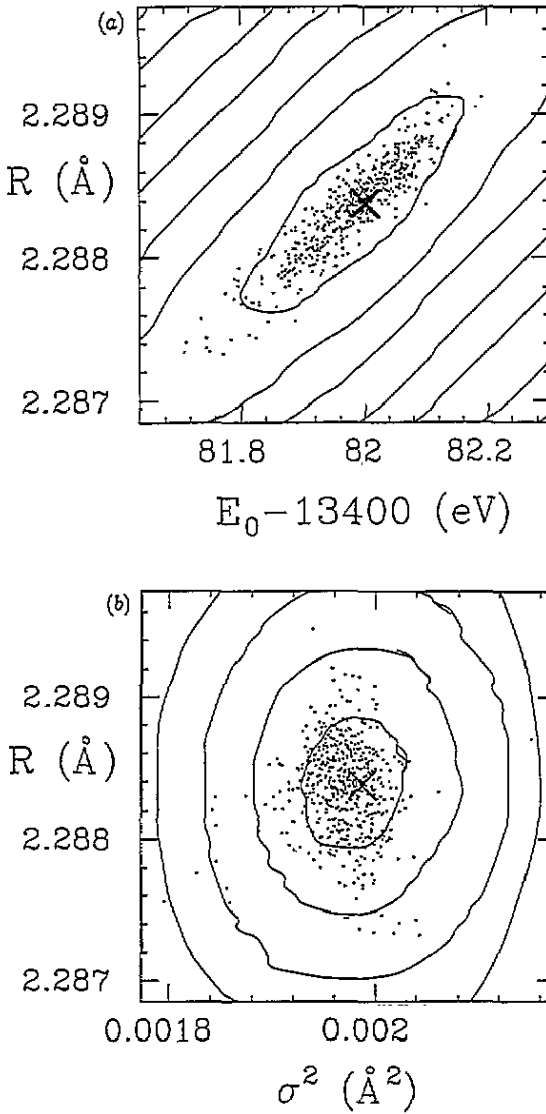


Figure 2. Two-dimensional sections of the parameter space referring to R and E_0 (a) and R and σ^2 (b). The dots are the projections of 500 fits performed on simulated spectra with added random noise. The elliptical contours are the intersections of the four-dimensional ellipsoidal regions defined by $R(\{\lambda\}) = R_{min} + n^2C$, with $n = 1, 2, \dots$. The $n = 1$ inner curve corresponds to the 95% confidence interval.

provides reliable confidence intervals only when the second-order expansion of the residual function in terms of the parameters λ and noise ξ is accurate. The establishment of the equivalence among the criteria for error determination is an important step to be verified when a new problem is treated.

The confidence intervals determined by $R(\{\lambda\}) < R_{min} + C$ are indicated by continuous lines in figure 2 and figure 3. The inner curves actually represent the intersection of the four-dimensional ellipsoid with the corresponding two-parameter planes, and refers to an increment $C = 9.49$, $p = 4$ with a 95% confidence level. The second and successive

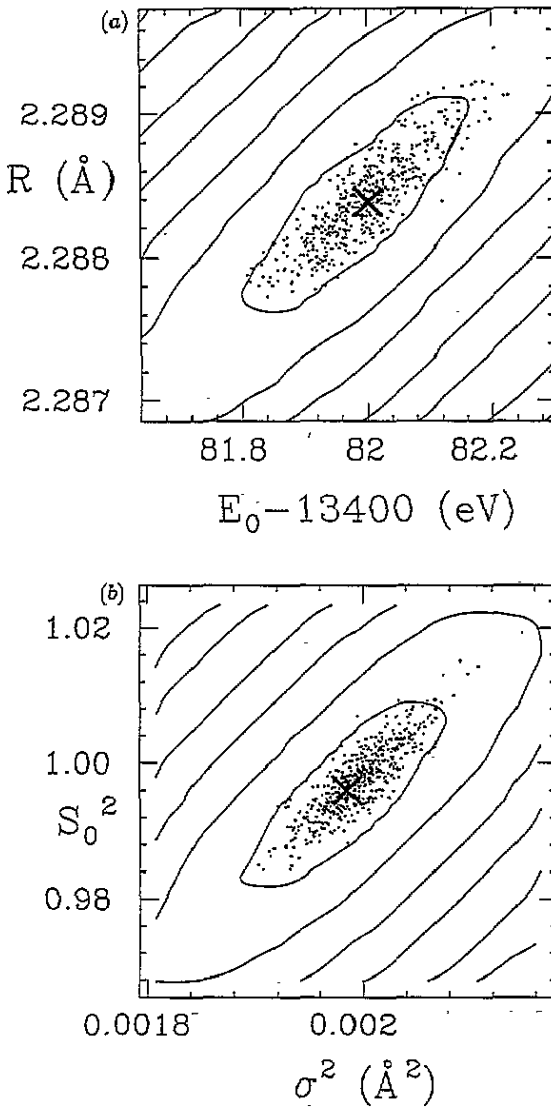


Figure 3. Two-dimensional sections of the parameter space referring to R and E_0 (a) and to S_0^2 and σ^2 (b). The dots are the projections of 500 parameter sets sampling the probability distribution in parameter space, obtained with the Metropolis Monte Carlo algorithm. The elliptical contours are the intersections of the four-dimensional ellipsoidal regions defined by $R\langle\{\lambda\}\rangle = R_{min} + n^2C$, with $n = 1, 2, \dots$. The $n = 1$ inner curve corresponds to the 95% confidence interval.

curves are drawn by putting an increment of n^2C instead of C , with $n = 2, 3, \dots$ so that they appear equally spaced in the case of a parabolic minimum. The inner ellipsoidal curves and the regions occupied by the scatter points nicely match in all cases; however, the comparison should be made with caution. The former include only the effect of correlation in the two-parameter subspace, whereas the latter is a two-dimensional projection of the four-dimensional scatter plot and includes the effect of correlations among all parameters. In the present case the largest correlations occur between R and E_0 , as is evident from

figure 2(a), and between σ^2 and S_0^2 as is evident from figure 3(b). The subspace R and E_0 already includes the major correlation involving either R or E_0 and about 95% of the points are actually enclosed by the inner contour. In contrast, in the R, σ^2 plot (figure 2(b)), a large percentage $> 5\%$ of the points fall outside the inner contour. The reason is that while parameters are correlated with other parameters external to the subspace, the contour intersection clearly does not show this effect, that is instead manifested by the projection of the simulation results.

Clearly the constant-residual-function approach is the most straightforward method for establishing confidence intervals and can be automatically adopted at the end of the fitting routine on the experimental data. This example indicates that extreme caution should be adopted in the estimation of the confidence intervals or parameter errors from contour maps, and that it is always advisable to view the two-dimensional contours between the most correlated couples of parameters. The random approach of simulating spectra with additional random noise is accurate but extremely time consuming. The substantial equivalence of the error estimate between this and the constant-residual-function approach, evident from figure 2, gives confidence of the validity of the second-order expansion of $R(\{\lambda\})$ in $\{\lambda\}$ and ξ and on the applicability of the present methodology to the EXAFS case.

A general remark should be made on the actual magnitude of the statistical error shown by present analysis. The statistical error in R is about 0.001 Å, as shown by figure 2(a). Such low statistical errors are obtained only in the case of first-shell analysis of EXAFS spectra characterized by low noise ($\sim 10^{-4}$) and wide k extension ($k_{max} \sim 20 \text{ \AA}^{-1}$). More usually errors in the 0.005 Å range are found. These numbers clearly refer to the statistical component and it should be kept in mind that systematic errors in the model calculation may lie in the 0.01 Å range. In the present case, however, as noted at the beginning of this section, the fitting values are indistinguishable from those calculated from spectroscopic parameters for the Br_2 molecule; as a consequence systematic errors are found to be negligible and the present treatment provides reliable estimates for the errors.

We will conclude this section with a few considerations on the modification of the confidence intervals as a function of p , and on the effect of external parameters like those defining the atomic background in EXAFS. The shape and extension of the confidence interval depends on the number of parameters that are simultaneously considered. If the analysis is restricted to a reduced number p among P parameters it is assumed that any value for the other $P - p$ parameters is acceptable, so the confidence intervals have an infinite extension in these directions. When p is increased the extension of the confidence interval is reduced along the new directions. In order to balance the loss and maintain the enclosed probability to 95% the enclosure bounds in the original p directions have to be extended. This is accomplished by the increasing dependence of C on p in the constant-residual-function condition $R(\{\lambda\}) = R_{min} + C$ to define confidence intervals. C is usually much larger than unity and errors are underestimated if $C = 1$ is adopted. In real EXAFS analysis the atomic absorption background is modelled with empirical functions or polynomial splines, depending on a certain number of parameters. These should be in principle treated as fitting parameters and included in the error analysis. It is usually found, however, that physical and background parameters are largely uncorrelated. As a consequence the statistical analysis can be restricted only to the p physical parameters. Empirical parameters like E_0 and S_0^2 , instead, must be included due to their large correlation with distances or coordination numbers and bond-length variances.

4. Nonlinear cases

There are cases in which the contour shape among selected couples of parameters departs from that of a parabolic minimum. This often happens when parameters affect the signal in a largely nonlinear way. One example of this behaviour is shown by the parameters associated with triatomic structures of nearly aligned atoms when the photoabsorber is on one side of the chain. Without loss of generality we parametrize the geometry using two distance coordinates R_1 , between atom A (photoabsorber) and atom B and R_2 between atom B and atom C, and one angular coordinate θ close to 180° describing the angle between A, B, and C. The three coordinates will vibrate around average values \bar{R}_1 , \bar{R}_2 , and 180° . The analysis of the experimental signal is usually performed assuming a model probability distribution for the geometrical coordinates $f(R_1, R_2, \theta)$ depending on a set of average and vibration parameters. Due to the curvilinear coordinates adopted $f(R_1, R_2, \theta)$ vanishes for $\theta = 180^\circ$. A simple but realistic model distribution is given by

$$f(R_1, R_2, \theta) = \frac{1}{2\pi(\text{Det } \mathbf{m})^{1/2}} \exp\left[-\frac{1}{2}(\mathbf{r}, \mathbf{m}^{-1}\mathbf{r})\right] \frac{(180^\circ - \theta)}{\delta_\theta^2} \exp\left[-\frac{(180^\circ - \theta)^2}{2\delta_\theta^2}\right] \quad (8)$$

where \mathbf{r} is a two-dimensional column vector of components $R_i - \bar{R}_i$, and $(\mathbf{r}, \mathbf{m}^{-1}\mathbf{r})$ is of quadratic form. The matrix

$$\mathbf{m} = \begin{pmatrix} \sigma_{R_1}^2 & \sigma_{R_1, R_2}^2 \\ \sigma_{R_1, R_2}^2 & \sigma_{R_2}^2 \end{pmatrix} \quad (9)$$

describes the covariance between the vibrations of the two bond lengths. The off-diagonal term can be written as $\sigma_{R_1, R_2}^2 = \rho_{R_1, R_2} \sqrt{\sigma_{R_1}^2 \sigma_{R_2}^2}$ with the bond-bond correlation satisfying $-1 \leq \rho_{R_1, R_2} \leq 1$. In this model the bond-length distribution is a two-dimensional Gaussian and is factorized with respect to the angular distribution. The latter, valid for $0^\circ \leq \theta \leq 180^\circ$, includes a Gaussian factor and a weight $(180^\circ - \theta)$ to accomplish the spherical volume element decrease. The normalization is strictly correct only in the limit $\delta_\theta \ll 180^\circ$. The most probable value for the angle is $180^\circ - \delta_\theta$, the average angle is $\bar{\theta} = 180^\circ - \sqrt{\pi/2}\delta_\theta$, and the angle variance is $\sigma_\theta^2 = (2 - \pi/2)\delta_\theta^2$. We point out that a vibrating collinear configuration can be easily mistaken for a configuration vibrating around a slightly bent angle. The justification of the factorization between the two distributions stems from the extremal angle position that makes, in the Gaussian limit, any correlation between angle and bond vibrations vanish. The model distribution depends on a total of six parameters \bar{R}_1 , \bar{R}_2 , $\sigma_{R_1}^2$, $\sigma_{R_2}^2$, ρ_{R_1, R_2} , and δ_θ .

In several cases it occurs that the middle atom B has a small weight with respect to atom C and that the major part of the signal comes from single-scattering and collinear-multiple-scattering components involving atom C. As a consequence the total signal of the configuration will have a leading frequency of the A-C distance, roughly $\bar{R}_1 + \bar{R}_2$, and a damping due mainly to the A-C bond distance variance, roughly

$$\sigma_{AC}^2 = \sigma_{R_1}^2 + \sigma_{R_2}^2 + 2\rho_{R_1, R_2}\sigma_{R_1}\sigma_{R_2}. \quad (10)$$

In this case it is clear that parameters \bar{R}_1 and \bar{R}_2 will be negatively correlated and that the resulting errors in each of the two will be much larger than the error in their sum. This suggests the use of the quantities $\bar{R}_1 + \bar{R}_2$ and $\bar{R}_1 - \bar{R}_2$ as independent parameters that are, instead, weakly correlated. The example of nonlinearity comes from the vibrational parameters. In general even a weak signal coming from the A-B couple will be sufficient to constrain the $\sigma_{R_1}^2$ parameter. On the other hand, the large sensitivity on σ_{AC}^2 introduces nonlinear effects among the other parameters.

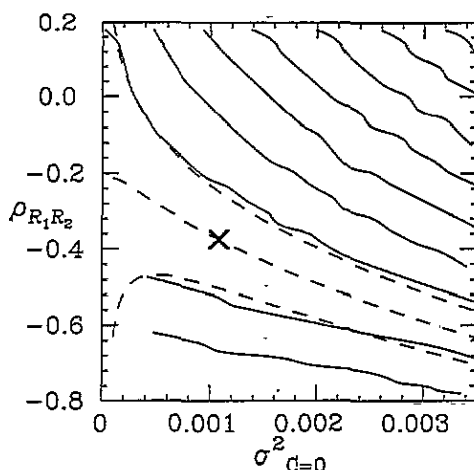


Figure 4. A two-dimensional $\sigma_{C=O}^2 - \rho_{R_1, R_2}$ section of the parameter space for the fitting of the S-C=O molecule. The solid contours are the intersections with the $(p-1)$ -dimensional surfaces defined by $R(\{\lambda\}) = R_{min} + n^2 C$, with $n = 1, 2, \dots$. The non-parabolic nature of the minimum is evident; the contours are aligned with a family of curves (dashed lines) corresponding to constant σ_{S-O} values. This suggests the adoption of a different set of independent parameters in the fitting.

A specific example of this occurrence is given by the spectrum of the S-C=O molecule studied at the S K edge [21]. The signal is largely dominated by the collinear contribution from the O atom. In figure 4 the intersection of the $R(\{\lambda\}) = R_{min} + n^2 C$ surfaces with the $\sigma_{C=O}^2 - \rho_{R_1, R_2}$ subspace are reported. Clearly, the contours greatly depart from those of a parabolic minimum and seem to follow hyperbolic patterns. This occurrence can be understood in terms of equation (10); that, in fact, for fixed $\sigma_{R_1}^2$ and variable σ_{AC}^2 describes a family of hyperbolae on the plane $\sigma_{R_2} - \rho_{R_1, R_2}$. The dashed lines in figure 4 are calculated using equation (10) by putting constant $\sigma_{R_1} = 0.048 \text{ \AA}$ and variable σ_{SO}^2 equal to 0.0018, 0.0022, and 0.0026 \AA^2 for the three dashed curves from bottom to top, respectively. The lower and upper curve match nicely with the $n = 1$ contour. It is clear that in this case $\sigma_{C=O}^2$ cannot be measured accurately by EXAFS, although the experiment is perfectly compatible with a typical zero-point vibration level. On the other hand the S-O vibrational variance can be determined accurately; it is found to be $\sigma_{SO}^2 = 0.0022(4) \text{ \AA}^2$.

This occurrence is not general for collinear cases and is due to the specific intensity and parameter dependence of the signals. In the present case the parameter choice is not ideal, and the hyperbolic pattern shown by figure 4 suggests the use of σ_{AC}^2 as an independent parameter rather than, for instance, $\sigma_{C=O}^2$. This latter choice yields parabolic-like minima and allows one to make a better estimate of the statistical errors.

This example has shown a typical case in which the flexibility in parameter selection can be fruitfully used to choose a set with an improved parabolic behaviour around the minimum of the residual function.

5. Conclusion

The present paper provides a general framework for the statistical error evaluation in the context of the EXAFS data analysis. The presented material is intended to enrich the current

discussion in the field and to clarify several aspects of the analysis.

A general formalism for the evaluation of the results is introduced and practical criteria for routine analysis are formulated. Particular emphasis is given to the error determination problem and to the establishment of confidence intervals in the parameter space. It is shown, with a specific example, that the surface specified by the $R(\{\lambda\}) = R_{min} + \chi_{p,0.95}^2$ criterion encloses multi-dimensional confidence intervals compatible with the scatter of results in parameter space given by more rigorous Monte Carlo approaches.

The explicit treatment of real examples has led to the discussion of two practical aspects: the need to evaluate the noise level on the EXAFS spectra and the caution required in the choice of fitting parameters. The first requirement certainly has consequences in the data acquisition phase and the suggestion is made that oversampled spectra, with at least 800–1000 energy points along a typical EXAFS scan, are always collected. The second requirement is essential for the validity and accuracy of the $R(\{\lambda\}) = R_{min} + \chi_{p,0.95}^2$ criterion for error determination and the suggestion of checking the parabolic nature of the minimum of the residual function $R(\{\lambda\})$ is made. Extended visualization of the error confidence interval along several two-dimensional projections is recommended.

It is hoped that this paper will draw general attention to well established statistical results and will contribute to improving the average level of current EXAFS analysis.

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