XAFS spectroscopy. II. Statistical evaluations in the fitting problems

K. V. Klementev
Moscow State Engineering Physics Institute, 115409 Kashirske sh. 31, Moscow, Russia
e-mail: klmn@htsc.mephi.ru

(January 24, 2022)

The problem of error analysis is addressed in stages beginning with the case of uncorrelated parameters and proceeding to the Bayesian problem that takes into account all possible correlations when a great deal of prior information about the accessible parameter space is available. The formulas for the standard deviations and deviations with arbitrary confidence levels are derived. Underestimation of the errors of XAFS-function extraction is shown to be a source of unjustified optimistic errors of fitting parameters. The applications of statistical $\chi^2$- and $F$-tests to the fitting problems are also discussed.

61.10.Ht

I. INTRODUCTION

In the Open Letter to the XAFS Community [1] Young and Dent, the leaders of the UK XAFS User Group, expressed their concern over the persistence of lingering common opinion that XAFS is a "sporting technique" and it is possible to obtain the "answer you want". Some way out they see in a special attention to the publishing XAFS data (first of all, to XAFS spectra) and have formulated several recommendations for editors and referees. Undoubtedly, in the matter of extraction of the real, not invented, information from XAFS experiments the quality of spectra is of great importance. We see here another problem as well. Not having some necessary elements of XAFS analysis (some values and the procedures for their determination), one has a quite natural desire to turn those values to advantage. Principally we mean the inability of the standard methods to find the errors of the atomic-like background $\mu_0$. Traditionally, the noise is assigned to these errors. However, as was shown in Ref. [2], the noise is essentially lower than the errors of the $\mu_0$ construction. Below, we will show that the underestimation of the errors of XAFS-function extraction is a source of the unreasonable optimistic errors of fitting parameters.

Practically all known programs for XAFS modeling [3] in some way calculate confidence limits of fitting parameters. However, since there is no standardized technique for that and since most published XAFS works do not contain any mention of methods for estimation of the errors of fitting parameters, the accuracy of the XAFS results remains to be field for trickery.

In the present article we derive the expressions for the errors of fitting parameters under different assumptions on the degree of their correlation. Besides, the prior information about parameters is possible to take into account in the framework of Bayesian approach. Moreover one can find the most probable weight of the prior information relative to the experimental information.

We also discuss the grounds and usage of the statistical tests. The special attention was focused on that where and how one can embellish the results and artificially facilitate the statistical tests to be passed.

All methods and tests described in the paper are realized in the program VIPER [6].

II. ERRORS IN DETERMINATION OF FITTING PARAMETERS

Let for the experimental curve $d$ defined on the mesh $x_1, \ldots , x_M$ there exists a model $m$ that depends on $N$ parameters $p$. In XAFS fitting problems as $d$ may serve both $\chi^2(k)$ (not weighted by $k^w$) and $\chi^2(r)$. The problem is to find the parameter vector $\hat{p}$ that gives the best coincidence of the experimental and model curves. Introduce the figure of merit, the $\chi^2$-statistics (do not confuse with the symbol of XAFS function):

$$\chi^2 = \sum_{i=1}^{M} \frac{(d_i - m_i)^2}{\varepsilon_i^2},$$

where $\varepsilon_i$ is the error of $d_i$. The variate $\chi^2$ obeys the $\chi^2$-distribution law with $M - N$ degrees of freedom. Of course, for the given spectrum $d$ and the given model $m$ the value of $\chi^2$ is fully determined; we call it "variate" bearing in mind its possible dispersion under different possible realizations of the noise and the experimental errors of $d_i$ extraction.
Often a preliminary processing (before fitting) is needed: smoothing, filtration etc. Naturally, during the pre-processing some part of the experimental information is lost, and on the variates \( \xi_i = (d_i - m_i)/\varepsilon_i \) additional dependencies are imposed (before, they were bound solely by the model \( m \)). It is necessary to determine the number of independent experimental points \( N_{\text{ind}} \). For the commonly used in XAFS spectroscopy Fourier filtering technique the number of independent points is given by [4]:

\[
N_{\text{ind}} = 2\Delta k \Delta r/\pi + 2, \tag{2}
\]

where \( \Delta k = k_{\text{max}} - k_{\text{min}} \) and \( \Delta r = r_{\text{max}} - r_{\text{min}} \) are the ranges in \( k- \) \( r \)-spaces used for the analysis, and \( r_{\text{min}} > 0 \). If \( r_{\text{min}} = 0 \) then

\[
N_{\text{ind}} = 2\Delta k \Delta r/\pi + 1. \tag{3}
\]

Instead of keeping in the sum (1) only \( N_{\text{ind}} \) items which are equidistantly spaced on the grid \( x_1, \ldots, x_M \), it is more convenient to introduce the scale factor \( N_{\text{ind}}/M \):

\[
\chi^2 = \frac{N_{\text{ind}}}{M} \sum_{i=1}^{M} \frac{(d_i - m_i)^2}{\varepsilon_i^2}. \tag{4}
\]

Now the variate \( \chi^2 \) follows the \( \chi^2 \)-distribution with \( N_{\text{ind}} - N \) degrees of freedom. It can be easily verified that with the use of all available data (\( r_{\text{min}} = 0 \) and \( r_{\text{max}} = \pi/2dk \)) the definition (4) turns into (1).

Let us now derive the expression for the posterior distribution for an arbitrary fitting parameter \( p_j \):

\[
P(p_j|d) = \int \cdots dp_{i\neq j} \cdots P(p|d), \tag{5}
\]

where \( P(p|d) \) is the joint probability density function for all values \( p \), and the integration is done over all \( p_{i\neq j} \). According to Bayes theorem,

\[
P(p|d) = \frac{P(d|p)P(p)}{P(d)}, \tag{6}
\]

\( P(p) \) being the joint prior probability for all \( p_i \), \( P(d) \) is a normalization constant. Assuming that \( N_{\text{ind}} \) values in \( d \) are independent and normally distributed with zero expected values and the standard deviations \( \varepsilon_i \), the probability \( P(d|\theta) \), so-called likelihood function, is given by

\[
P(d|\theta) \propto \exp \left( -\frac{\chi^2}{2} \right), \tag{7}
\]

where \( \chi^2 \) was defined above by (4). Its expansion in terms of \( p \) near the minimum (\( \nabla_p \chi^2 = 0 \)) which is reached at \( \hat{p} = \hat{p} \) yields:

\[
P(d|\theta) \propto \exp \left( -\frac{1}{4} (p - \hat{p})^T \cdot \hat{H} \cdot (p - \hat{p}) \right) = \left( -\frac{1}{4} \sum_{k,l=1}^{N} \frac{\partial^2 \chi^2}{\partial p_k \partial p_l} \Delta p_k \Delta p_l \right), \tag{8}
\]

where \( \Delta p_k = p_k - \hat{p}_k \), and the Hessian \( \hat{H} \) components (the second derivatives) are calculated in the fitting program at the minimum of \( \chi^2 \). The sufficient conditions for the minimum are \( \hat{H}_{kk} > 0 \) and \( \hat{H}_{kk} \hat{H}_{ll} - \hat{H}_{kl}^2 > 0 \), for any \( k, l \). Hence, the surfaces of constant level of \( P(d|\theta) \) are ellipsoids.

**A. Simplest cases**

If one ignores the prior then the posterior probability density function \( P(p|d) \) coincides with the likelihood \( P(d|p) \). Let us consider here two widely used approaches.

(a) **Parameters are perfectly uncorrelated.** In this case the Hessian is diagonal and

\[
P(p_j|d) \propto \exp \left( -\frac{1}{4} \hat{H}_{jj} \Delta p_j^2 \right). \tag{9}
\]

The standard deviation of \( p_j \) is just
\[ \delta^{(a)} p_j = (2/\hat{\mathbf{H}}_{jj})^{1/2}. \]  

(b) Parameter \( p_j \) essentially correlates solely with \( p_i \). In this case

\[
P(p_j|d) \propto \int dp_i P(p_i,p_j|d) \propto \int dp_i \exp \left( -\frac{1}{4} \hat{\mathbf{H}}_{jj} (\Delta p_j)^2 - \frac{1}{2} \hat{\mathbf{H}}_{ii} \Delta p_i \Delta p_j - \frac{1}{4} \hat{\mathbf{H}}_{ii} (\Delta p_i)^2 \right) \]

\[ \propto \exp \left( -\frac{1}{4} \left[ \hat{\mathbf{H}}_{jj} - \frac{\hat{\mathbf{H}}_{ij}^2}{\hat{\mathbf{H}}_{ii}} \right] (\Delta p_j)^2 \right), \]

from where one finds \( \bar{p}_j = \hat{p}_j \) and the mean-square deviation

\[
\delta^{(b)} p_j = \left( \frac{2\hat{\mathbf{H}}_{ii}}{\hat{\mathbf{H}}_{jj} - \hat{\mathbf{H}}_{ij}^2} \right)^{1/2}.
\]

In practice, to find the strongly correlated pairs of parameters, one finds the pair-correlation coefficients:

\[
r_{ij} = \frac{\langle \Delta p_i \Delta p_j \rangle - \langle \Delta p_i \rangle \langle \Delta p_j \rangle}{\delta(\Delta p_i) \delta(\Delta p_j)}.
\]

taking on the values from -1 to 1. Two parameters are uncorrelated if their correlation coefficient is close to zero. It is easy to calculate the average values over the distribution (11):

\[
\langle \Delta p_i^2 \rangle = 2\hat{\mathbf{H}}_{jj}/\text{Det}, \quad \langle \Delta p_j^2 \rangle = 2\hat{\mathbf{H}}_{ii}/\text{Det}, \quad \langle \Delta p_i \Delta p_j \rangle = -2\hat{\mathbf{H}}_{ij}/\text{Det},
\]

where \( \text{Det} = \hat{\mathbf{H}}_{jj} \hat{\mathbf{H}}_{ii} - \hat{\mathbf{H}}_{ij}^2 \). Notice, by the way, that these are the elements of the inverse matrix of \( \hat{\mathbf{H}}/2 \).

Now the pair-correlation coefficients are given by:

\[
r_{ij} = -\frac{\hat{\mathbf{H}}_{ij}}{\sqrt{\hat{\mathbf{H}}_{ii} \hat{\mathbf{H}}_{jj}}}.
\]

Via the correlation coefficient the mean-square deviations, found for the cases (a) and (b), are simply related:

\[
\delta^{(a)} p_j = \delta^{(b)} p_j \sqrt{1 - r_{ij}^2}.
\]

Consider an example of the error analysis. For \( L_3 \) Pb absorption spectrum\(^1\) for BaPbO\(_3\) compound the average error of the XAFS extraction from the measured absorption was \( \varepsilon_i = 0.007 \). For the filtered over the range 1.0 < \( r < 2.1 \) Å (the signal from the octahedral oxygen environment of lead atom) XAFS (see Fig. 1), the model function was calculated as follows. For one-dimensional the Hamiltonian of the lead-oxygen atomic pair with potential \( U \) (XAFS function) was used that calculates the Hessian of \( U \):

\[
\chi(k) = \frac{1}{k} F(k) \int_{r_{\min}}^{r_{\max}} g(r) \sin[2kr + \phi(k)]/r^2 dr.
\]

The phase shift \( \phi(k) \) and the scattering amplitude \( F(k) \) were calculated using feff6 program [5]. By variation of the parameters \( r_0, a, N \) (where \( N \) includes the factor \( S_0^2 \) and \( E_0 \), the shift of the origin for the wave number \( k \), one search for the best accordance between the model and experimental curves. Here for the fitting, the Viper program was used which, in particular, calculates the Hessian of \( \chi^2 \) (defind by (4) with \( N_{\text{ind}} = 11.8 \)) at the minimum. The correlation coefficients are listed in the Table I.

---

\(^1\)The spectrum was recorded at 50 K in transmission mode at D-21 line (XAS-13) of DCI (LURE,Orsay, France) at positron beam energy 1.85 GeV and the average current \( \sim 250 \) mA. Energy step — 2 eV, counting time — 1 s. Energy resolution of the double-crystal Si [311] monochromator (detuned to reject 50% of the incident signal in order to minimize harmonic contamination) with a 0.4 mm slit was about 2–3 eV at 13 keV.
FIG. 1. Experimental and model filtered XAFS $\chi(k) \cdot k^2$ (first coordination sphere) for BaPbO$_3$ (a) and the model potential with corresponding PRDF and energy levels (b).

TABLE I. Pair-correlation coefficients $r_{ij}$ for the example fitting.

| $N$ | $a$ | $r_0$ | $E_0$ |
|-----|-----|-------|-------|
| 1   | -0.286 | 0.092 | 0.041 |

TABLE II. Mean values and mean-square deviations of the fitting parameters. $\delta p$ are the mean-square deviations calculated: for perfectly uncorrelated parameters (a), through the maximum pair correlations (b), from the bayesian technique without prior information (maximum likelihood) (c), from the posterior probability that considers the most probable contribution of the prior information. $S_p$ are the sizes of the parameter space accessible for variation (± around the mean value).

| $p$ | $\hat{p}$ | $\delta^{(a)}p$ | $\delta^{(b)}p$ | $\delta^{(c)}p$ | $S_p$ | $\delta^{(d)}p$ |
|-----|--------|----------------|----------------|----------------|-------|----------------|
| $N$ | 4.05   | 0.090          | 0.094          | 0.096          | $N$   | 0.070          |
| $a$, K/Å$^2$ | 2.28·10$^5$ | 4.7·10$^4$     | 4.9·10$^4$     | 4.9·10$^4$     | $\hat{a}$ | 6.2·10$^3$     |
| $r_0$, Å | 2.1456 | 2.7·10$^{-3}$  | 3.9·10$^{-3}$  | 4.0·10$^{-3}$  | $\hat{r}_0$ | 3.6·10$^{-3}$  |
| $E_0$, eV | 4.42   | 0.23           | 0.34           | 0.35           | 10    | 0.21           |

We now turn our attention to the errors of fitting parameters. In ignoring the correlations, the errors $\delta^{(a)}p$ are rather small (see Table II). However, we know that the parameters $r_0$ and $E_0$ are highly correlated, and their real errors must be larger. In the traditional XAFS-analysis two-dimensional contour maps have long been used [7] for estimates of the correlation score and the error bars. Notice, that to do this requires, first, the definition and determination of the correct statistical function $\chi^2$ (but not a proportionate to it), and, second, a criterion to choose the critical value of $\chi^2$ (depending on the chosen confidence level).

For the most correlated pair, $r_0$ and $E_0$, find the joint probability density function $P(r_0E_0|d)$ using the Hessian elements found at the minimum of the $\chi^2$:

$$P(r_0E_0|d) \propto \exp \left( -\frac{1}{4} \hat{H}_{r_0r_0} (\Delta r_0)^2 - \frac{1}{2} \hat{H}_{r_0E_0} \Delta r_0 \Delta E_0 - \frac{1}{4} \hat{H}_{E_0E_0} (\Delta E_0)^2 \right)$$

(18)
FIG. 2. The joint probability density function $P(r_0E_0|d)$ calculated via the expansion (8) (solid lines) and using the exact $\chi^2$ function (on the right, dashed lines). Also shown the graphical interpretation of the mean-square deviations $\delta^{(a)}r_0$ and $\delta^{(b)}r_0$ given by (10) and (12). The ellipse of the standard deviation is drawn by the thick line.

which is depicted in Fig. 2 as a surface graph and as a contour map. The ellipses of the equal probability are described by:

$$
\widehat{H}_{r_0r_0}(\Delta r_0)^2 + 2\widehat{H}_{r_0E_0}\Delta r_0\Delta E_0 + \widehat{H}_{E_0E_0}(\Delta E_0)^2 = 4\lambda.
$$

In Fig. 2 they limit such areas that the probability for the random vector $(r_0,E_0)$ to find itself in them is equal to $\ell = 1 - e^{-\lambda} = 0.2, 0.6, 0.8, 0.9$ and 0.95. By the thick line is drawn the ellipse corresponding to the standard deviation: $\lambda = 1/2$ and $\ell = 1 - e^{-1/2} \approx 0.3935$. For this ellipse the point of intersection with the line $\Delta E_0 = 0$ and the point of maximum distance from the line $\Delta r_0 = 0$ give the standard mean-square deviations $\delta^{(a)}r_0$ and $\delta^{(b)}r_0$ that coincide with the expressions (10) and (12). To find the mean-square deviation $\delta^{(b)}$ for an arbitrary confidence level $\ell$, one should multiply the standard deviation by $\sqrt{-2\ln(1-\ell)}$.

In Table II the errors in the column $\delta^{(b)}_p$ were found as the largest errors among all those calculated from the pair correlations. For the parameters $N$ and $a$ all pair correlations are weak, so their $\delta^{(a)}$ and $\delta^{(b)}$ are hardly differ. For the parameters $r_0$ and $E_0$ these mean-square deviations differ remarkable.

Finally, we put the question, how much is rightful the expansion (8) for the likelihood function? In Fig. 2, on the right, the dashed ellipses of equal probability are found for the exact $\chi^2$ that was calculated by the VIPER program as well. Mainly, just-noticeable difference is caused by the realization of the fitting algorithm or to be more precise, by the values of the variations of the fitting parameters which determine the accuracy of the minimum itself and the accuracy of the derivatives at the minimum. Of course, this difference can be neglected.

**B. General case**

Often, a particular fitting parameter significantly correlates not with a one, but with several other parameters (in our example this is not so, but, for instance, the problem of approximation of the atomic-like background by interpolation spline drawn through the varied knots [8,2] is that very case). Now, the consideration of the two-dimensional probability density functions is not correct no more, one should search for the total joint posterior probability $P(p|d)$.

For that, first of all, one is to find the prior probability $P(p)$. Let we approximately know in advance the size $S_k$ of the variation range of the parameter $p_k$. Then the prior probability can be expressed as:

$$
P(p|\alpha) \propto \alpha^{N/2} \exp\left(-\frac{\alpha}{2} \sum_{k=1}^{N} \frac{\Delta p_k^2}{S_k^2}\right),
$$

(20)
where the regularizer $\alpha$ specifies the relative weight of the prior probability; at $\alpha = 0$ there is no prior information, at $\alpha \to \infty$ the fitting procedure gives nothing and the posterior distribution coincides with the prior one. In the expression (20) $\alpha$ appears as a known value. Later, we apply the rules of probability theory to remove it from the problem.

So, for the sought probability density functions we have:

$$
P(p_j|d, \alpha) \propto \int \cdots dp_{i\neq j} \cdots \alpha^{N/2} \exp\left(-\frac{1}{2} \sum_{k,l=1}^{N} g_{kl} \Delta p_k \Delta p_l \right), \tag{21}
$$

where

$$
g_{kl} = \frac{\alpha}{S_k^2} \delta_{kl} + \frac{\hat{H}_{kl}}{2}. \tag{22}
$$

Since there is no integral over $p_j$, separate it from the other integration variables:

$$
P(p_j|d, \alpha) \propto \alpha^{N/2} \exp\left(-\frac{1}{2} g_{jj} \Delta p_j^2 \right) \int \cdots dp_{i\neq j} \cdots \exp\left(-\frac{1}{2} \sum_{k,l=1}^{N} g_{kl} \Delta p_k \Delta p_l - \Delta p_j \sum_{k=1}^{N} g_{kj} \Delta p_k \right), \tag{23}
$$

Here, the symbol $j$ near the summation signs denotes the absence of $j$-th item. Further, find the eigenvalues $\lambda_i$ and corresponding eigenvectors $e_i$ of the matrix $g_{kl}$ in which the $j$-th row and column are deleted, and change the variables:

$$
b_i = \sqrt{\lambda_i} \sum_{k=1}^{j} \Delta p_k e_{ik}, \quad \Delta p_k = \sum_{k=1}^{N} \frac{b_i e_{ik}}{\sqrt{\lambda_i}} \quad (i, k \neq j). \tag{24}
$$

Using the properties of eigenvectors:

$$
\sum_{k=1}^{j} g_{ik} e_{ik} = \lambda_i e_{il}, \quad \sum_{k=1}^{j} e_{ik} e_{ik} = \delta_{ii} \quad (l, i \neq j), \tag{25}
$$

one obtains:

$$
P(p_j|d, \alpha) \propto \alpha^{N/2} \exp\left(-\frac{1}{2} [g_{jj} - u^2] \Delta p_j^2 \right) \int \cdots db_{i\neq j} \cdots \exp\left(-\frac{1}{2} \sum_{i=1}^{N} [b_i + u_i \Delta p_j]^2 \right)
\propto \alpha^{N/2} \exp\left(-\frac{1}{2} [g_{jj} - u^2] \Delta p_j^2 \right), \tag{26}
$$

where new quantities were introduced:

$$
u_i = \frac{1}{\sqrt{\lambda_i}} \sum_{k=1}^{j} g_{kj} e_{ik}, \quad u^2 = \sum_{i=1}^{N} u_i^2. \tag{27}
$$

Thus, we have found the explicit expression for the posterior distribution of an arbitrary fitting parameter. This is a Gaussian distribution with the mean $\bar{p}_j = \bar{p}_j$ and the standard deviation

$$
\delta^{(c)} p_j = (g_{jj} - u^2)^{-1/2}. \tag{28}
$$

The formulas (26)–(28) require to find the eigenvalues and eigenvectors for the matrix of rank $N - 1$ for each parameter. Those formulas have merely a methodological value: the explicit expressions for posterior probabilities enables one to find the average of arbitrary function of $p_j$. However, the standard deviations could be calculated significantly easier, having found the eigenvalues and eigenvectors for the matrix of rank $N$ one time.

$$
(\delta^{(c)} p_j)^2 = \frac{\int \Delta p_j^2 P(p_j|d, \alpha)dp_j}{\int P(p_j|d, \alpha)dp_j} = \frac{\int \Delta p_j^2 \exp\left(-\frac{1}{2} \sum_{k,l=1}^{N} g_{kl} \Delta p_k \Delta p_l \right)dp}{\int \exp\left(-\frac{1}{2} \sum_{k,l=1}^{N} g_{kl} \Delta p_k \Delta p_l \right)dp}. \tag{29}
$$
Analogously to what was done above, performing the diagonalization of $g_{kl}$, one obtains:

$$
(\delta^{(c)} p_j)^2 = \frac{\int d\mathbf{b} \left( \sum_{i=1}^{N} b_i e_{ij} / \sqrt{\lambda_i} \right)^2 \exp\left(-\frac{1}{2} \sum_{i=1}^{N} b_i^2 \right)}{\int d\mathbf{b} \exp\left(-\frac{1}{2} \sum_{i=1}^{N} b_i^2 \right)} = \sum_{i=1}^{N} \frac{e_{ij}^2}{\lambda_i},
$$

where the eigenvalues ($\lambda_i$) and eigenvectors ($e_i$) correspond to the full matrix $g_{kl}$.

One can give another interpretation of the $\delta^{(c)} p$-finding process. It is easy to verify that $\hat{\mathbf{H}}/2$ and the covariance matrix $C$ of the vector $\mathbf{p}$ are mutually inverse. Therefore

$$
(\delta^{(c)} p_j)^2 = C_{jj} = 2(\hat{\mathbf{H}}^{-1})_{jj},
$$

and the variate $(\mathbf{p} - \hat{\mathbf{p}})^T \cdot C^{-1} \cdot (\mathbf{p} - \hat{\mathbf{p}}) = \frac{1}{2}(\mathbf{p} - \hat{\mathbf{p}})^T \cdot \hat{\mathbf{H}} \cdot (\mathbf{p} - \hat{\mathbf{p}})$ is $\chi^2$-distributed with $N$ degrees of freedom if $\mathbf{p}$ is the $N$-dimensional normally distributed vector (by Eq. (26) this condition is met). The ellipsoid that determines the standard deviation is:

$$
(\mathbf{p} - \hat{\mathbf{p}})^T \cdot \hat{\mathbf{H}} \cdot (\mathbf{p} - \hat{\mathbf{p}}) = N.
$$

For an arbitrary confidence level $\ell$, on the r.h.s. would be $(\chi^2_N)_{\ell}$, the critical value of the $\chi^2$-distribution with $N$ degrees of freedom. The error $\delta^{(c)} p_k$ is equal to the half the ellipsoid size along the $k$-th axis.

In our example fitting, the errors found in the absence of any prior information ($\alpha = 0$) from the formula (30) are listed in Table II in the column $\delta^{(c)} p$. Due to every one parameter correlates at the most with one other parameter, all $\delta^{(c)} p$ are practically coincide with $\delta^{(b)} p$. Generally, this may be not so.

Finally, let us find the most probable value of $\alpha$. Its posterior distribution is given by:

$$
P(\alpha|\mathbf{d}) = \int d\mathbf{p} P(\alpha, \mathbf{p}|\mathbf{d}) = \int d\mathbf{p} P(\alpha) P(\mathbf{p}|\alpha, \mathbf{d}).
$$

Using a Jeffreys prior $P(\alpha) = 1/\alpha$ [9], one obtains for the posterior distribution:

$$
P(\alpha|\mathbf{d}) \propto \int d\alpha \alpha^{N/2-1} \exp\left(-\frac{1}{2} \sum_{k,l=1}^{N} g_{kl} \Delta p_k \Delta p_l \right) \propto \left(\lambda_1 \cdots \lambda_N\right)^{-1/2} \alpha^{N/2-1}.
$$

In our example we have set the variation range of the parameter $p_k$ to be equal to $S_k = \pm \hat{p}_k$ (this means that $p_k \in [0,2\hat{p}_k]$) for all parameters except for $E_0$; since it varies near zero, we have chosen $S_{E_0} = \pm 10$ eV. For the mentioned variation ranges, the distribution $P(\alpha|\mathbf{d})$ has its mode at $\alpha = 2.64 \cdot 10^3$ (see Fig. 3). The bayesian errors found for this regularizer are listed in the column $\delta^{(d)} p$ of Table II. As a result, we have got the mean-square errors that for some parameters are significantly lower than even $\delta^{(a)} p$. There is nothing surprising in that: any additional information narrows the posterior distribution. If we would choose $S_k$ to be less, $\delta^{(d)} p_k$ would be yet lower. For instance, XAFS is quite accurate in distance determination, and for many cases one can assume distances to be known within $\pm 0.2$ Å. In our case this leads to $\delta^{(d)} r_0 = 3.4 \cdot 10^{-3}$ Å.

![FIG. 3. The posterior distribution for the regularizer $\alpha$ found from Eq. (34).](image-url)
C. Important note

Having obtained the expressions (10), (12) and (30) for the errors of fitting parameters, we are able now to draw an important conclusion. If in the definition (4) one substitutes for \( \varepsilon_i \) the values that are smaller by a factor of \( \beta \) than the real ones, the \( \chi^2 \) and its Hessian’s elements are exaggerated by a factor of \( \beta^2 \), and from (10), (12) and (30) follows that the errors of fitting parameters are understated by a factor of \( \beta! \)

In the preceding paper [2] it was shown that the errors of the atomic-like absorption construction are essentially larger than the experimental noise, and therefore it is the former that should determine the degrees of freedom, correspondingly. From the linear regression problem (near the minimum of \( N_2 \)) was chosen (not calculated!) as low as possible to scarcely (with \( \ell \)) single coordination sphere is split into two.

between the diffraction data and the XAFS-result that was found within 0.002 \( \text{Å} \) impressive errors of the structural parameters were obtained. In such approach no wander that the difference of 0.01 \( \text{Å} \) presence of a small systematic error” [10].

larger than the experimental noise, and therefore it is the former that should determine the tail of this distribution. Strictly speaking, the following condition must be met:

\[
\chi^2 < (\chi^2)_\ell,
\]

where the critical value \((\chi^2)_\ell\) for the specified significance level \( \ell \) may be calculated exactly (for even \( \nu \)) or approximately (for odd \( \nu \)) using the known formulas [11].

Notice, that the choice of the true \( \varepsilon_i \) here also plays a cardinal role. However, it is important here that one would not use the overestimated \( \varepsilon_i \) values which facilitate to meet the requirement (35). As we have shown in [2], one could obtain the overestimated \( \varepsilon_i \), having assumed the Poisson distribution law for the detectors counts when the actual association between the probability of a single count event and the radiation intensity is unknown.

Thus, the exaggerated values \( \varepsilon_i \) tell about a quality fitting, but give the large errors of fitting parameters. The understated \( \varepsilon_i \) lead to the would-be small errors, but make difficult to pass the \( \chi^2 \)-test (i. e. to meet the condition (35)). We are aware of many works the authors of which do not describe explicitly the evaluation process for the errors of XAFS-function extraction and do not report their explicit values. However, by implication it is seen that \( \varepsilon_i \) were chosen (not calculated!) as low as possible to scarcely (with \( \ell = 0.9 - 0.95 \)) pass the \( \chi^2 \)-test; as a result, very impressive errors of the structural parameters were obtained. In such approach no wander that the difference of 0.01 \( \text{Å} \) between the diffraction data and the XAFS-result that was found within 0.002 \( \text{Å} \) was attributed to the “suggested presence of a small systematic error” [10].

III. STATISTICAL TESTS IN FITTING PROBLEMS

A. \( \chi^2 \)-test

Introducing the statistical function \( \chi^2 \), we assumed that it follows the \( \chi^2 \) distribution with \( \nu = M - N \) degrees of freedom. However for this would be really so, one should achieve a sufficient fitting quality. This “sufficient quality” could be defined as such that the variate (4) obeys the \( \chi^2 \) distribution law, that is this variate does not fall within the tail of this distribution. Strictly speaking, the following condition must be met:

\[
\chi^2 < (\chi^2)_\ell,
\]

B. \( F \)-test

Let there is a possibility to choose between two physical models depending on different numbers of parameters \( N_1 \) and \( N_2 \) (\( N_2 > N_1 \)). Which one of them is more statistically important? For instance one wish to decide whether a single coordination sphere is split into two.

Let for the two models the functions \( \chi_1^2 \) and \( \chi_2^2 \) obey the \( \chi^2 \)-distribution law with \( \nu_1 = N_{\text{ind}} - N_1 \) and \( \nu_2 = N_{\text{ind}} - N_2 \) degrees of freedom, correspondingly. From the linear regression problem (near the minimum of \( \chi^2 \), the likelihood function is expressed by (8) and is identical in form to that of the linear regression problem) it is known that the value

\[
f = \frac{(\chi_1^2 - \chi_2^2)/(\nu_1 - \nu_2)}{\chi_2^2/\nu_2}
\]

obeys the Fisher’s \( F \)-distribution law with \((\nu_1 - \nu_2, \nu_2)\) degrees of freedom if exactly \( r = \nu_1 - \nu_2 \) parameters in the second model are linearly dependent, that is if exist the \( r \times N_2 \) matrix \( C \) of rank \( r \) and the vector \( c \) of the dimension \( r \) such that \( C \mathbf{p} = \mathbf{c} \). In order for the linear restrictions on the second model parameters to be absent, the value \( f \) should not follow the \( F \)-distribution, that is it should be greater than the critical value \((F_{\nu_1 - \nu_2, \nu_2})_\ell \) for the specified significance level \( \ell \):
\( f > (F_{\nu_1-\nu_2,\nu_2})_{\ell} \) \hspace{1cm} (37)

or

\[ \chi^2_2 < \chi^2_1 \left( (F_{\nu_1-\nu_2,\nu_2})_{\ell} \frac{\nu_1-\nu_2}{\nu_2} + 1 \right)^{-1}. \] \hspace{1cm} (38)

Notice, that the expression (38) means the absence of exactly \( r \) linear restrictions on the second model parameters. Even if (38) is realized, the less number of linear dependencies are possible. If, for instance, the splitting of a single coordination sphere into two does not contradict to the \( F \)-test (38), some of the parameters of these two spheres may be dependent, but not all. This justifies the introduction of a new sphere into the model XAFS function.

Thus, having specified the significance level \( \ell \), one can answer the question “what decrease of \( \chi^2 \) must be achieved to increase the number of parameters from \( N_1 \) to \( N_2 \)?” or, inside out, “what is the probability that the model 2 is better than the model 1 at specified \( (N_1, \chi^2_1) \) and \( (N_2, \chi^2_2) \)?”

Notice, that since in the definition for \( f \) the ratio \( \chi^2_1/\chi^2_2 \) appears, the actual values of \( \varepsilon_i \) become not important for the \( F \)-test (only if they all are taken equal to a single value).

Consider an example of the statistical tests in the fitting problem. In Fig. 4 are shown the experimental curve with \( N_{\text{ind}} = 11.8 \) and two model curves with \( N_1 = 4 \) and \( N_2 = 7 \). The underlying physical models were described in Ref. [12]; here only the number of parameters is of importance. Let us apply the statistical tests. Through the fitting procedure for the model 1 we have: \( \nu_1 = 11 - 4 = 7 \), \( \chi^2_1 = 16.8 > 14.1 = (\chi^2)_{0.95} \), for the model 2: \( \nu_2 = 11 - 7 = 4 \), \( \chi^2_1 = 5.3 < 9.5 = (\chi^2)_{0.95} \). That is the first model does not pass the \( \chi^2 \)-test. Further, \( f = 2.89 = (F_{3,4})_{0.84} \), from where with the probability of 84% we can assert that the model 2 is better than the model 1.

In the XAFS analysis the \( F \)-test has long been in use [7]. However, the words substantiating the test are often wrong. The authors of Refs. [10,13], for example, even claimed that the value \( f \) (36) must follow the \( F \)-distribution, although then in Ref. [13] there appears a really correct inequality (38).

IV. CONCLUSION

The solution of the main task of the XAFS spectroscopy, determination of the structural parameters, becomes worthless if the confidence in this solution is unknown. Here we mean not only the confidence in the obtained fitting parameters that is their mean-square deviations, but also the credence to the very methods of the error analysis. It is excessive optimistic errors evaluations lead to the suspicious attitude to the XAFS results.

To improve the situation could the development of the reliable and well-grounded techniques that do not allow one to treat the data in an arbitrary way. First of all, this is a technique for determination of the real errors of the atomic-like absorption construction. Second, we regard as necessary to standardize the method for the correct taking into account of all pair correlation between fitting parameters. And third, (we have not raised this question here) programs for scattering phase and amplitude calculations should report on the confidence limits for the calculated values, that is report how sensitive the calculated values are to the choice of the parameters of scattering potentials.
[1] N. A. Young, A. J. Dent, Open Letter to the XAFS Community. Maintaining and improving the quality of published XAFS data: a view from the UK XAFS user group. J. Synchrotron Rad. 6, 799 (1999), (Proc. of Int. Conf. XAFS X).
[2] K. V. Klementev, XAFS analysis. I. Extracting the fine structure from the absorption spectra. The preceding article , (2000).
[3] Catalog of XAFS Analysis Programs, http://ixs.carri.iit.edu/catalog/XAFS_Programs .
[4] E. A. Stern, Number of relevant independent points in x-ray-absorption fine-structure spectra. Phys. Rev. B 48(13), 9825–9827 (1993).
[5] J. J. Rehr, J. Mustre de Leon, S. I. Zabinsky, R. C. Albers, Theoretical X-ray Absorption Fine Structure Standards. J. Am. Chem. Soc. 113, 5135–5140 (1991).
[6] K. V. Klementev, VIPER for Windows (Visual Processing in EXAFS Researches), freeware, http://www.crosswinds.net/~klmn/viper.html.
[7] R. W. Joyner, K. J. Martin, P. Meehan, Some applications of statistical tests in analysis of EXAFS and SEXAFS data. J. Phys. C: Solid State Phys. 20, 4005–4012 (1987).
[8] M. Newville, P. Liviš, Y. Yacoby, J. J. Rehr, E. A. Stern, Near-edge x-ray-absorption fine structure of Pb: A comparison of theory and experiment. Phys. Rev. B 47(21), 14126–14131 (1993).
[9] H. Jeffreys, Theory of Probability (Oxford University Press, London, 1939), later editions: 1948, 1961, 1983.
[10] A. Filipponi, A. Di Chicco, X-ray-absorption spectroscopy and n-body distribution functions in condensed matter. II. Data analysis and applications. Phys. Rev. B 52, 15135–15149 (1995).
[11] Handbook of mathematical functions with formulas, graphs and mathematical tables, edited by M. Abramowitz, I. Stegun (Applied mathematical series, 55, National bureau of standards, 1964).
[12] A. P. Menushenkov, K. V. Klementev, EXAFS indication of double-well potential for oxygen vibration in Ba$_{1-x}$K$_x$BiO$_3$. J. Phys.: Condens. Matter 12, (2000), (accepted).
[13] A. Michalowicz, K. Provost, S. Laruelle, A. Mimouni, F-test in EXAFS fitting of structural models. J. Synchrotron Rad. 6, 233–235 (1999), (Proc. of Int. Conf. XAFS X).