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Error analysis of EXAFS measurements

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A method to analyze EXAFS data is proposed which follows the error propagation from the measured input data to the output of the physical parameters taking into account experimental and systematic errors. The Bayesian approach is used to describe the modification of the *a priori* expectation for the model parameters due to the measurement. A description is discussed to determine the relative weight of the *a priori* information compared to the experimental information in their impact on the results for the *a posteriori* expectation values and their variances. Computer generated data above the Ta L_3-edge are used to demonstrate the robustness of the method.

Keywords: error analysis; Bayesian approach; FEFF code.

1. Introduction

Like most of the data analysis procedures in physics the EXAFS analysis requires the inference of model parameters from measured data. Generally a large parameter space is needed in order to make the model sufficiently flexible, which usually is in conflict with the limited information contained in a finite set of data. The ill-posed nature of this problem is treated by introducing *a priori* information. To avoid an *a priori* restriction of the number of model parameters, an algorithm is needed a) to construct a subspace of the whole model parameter space where the data determine the fit, and b) to define rules to associate *a priori* values with the remaining parameters.

We assign statistical errors and an estimate of systematic errors to the input data and introduce an uncertainty estimate for the model employed. The output of the fit then consists of probability distributions for the model parameters depending on the experimental uncertainties, the reliability estimate of the model, and the width of the *a priori* probability.

2. Formulation of the Model

The discussion will be based on the standard formula for X-ray absorption in a polycrystalline or amorphous sample

$$\chi(k)=\frac{S_0^2}{k}\sum_{i=1}^{p}N_i\frac{\left|f_{\mathrm{eff},i}(k,R_i)\right|}{R_i^2}e^{-2k^2\sigma_i^2-2R_i/\lambda(k)}\sin\left(2kR_i+\phi_i(k)\right)$$

with parameters as defined in Rehr et al. (1991) and with $E_0=h\nu-\hbar^2k^2/2m$ and the mean free path λ being the same in each term of the sum.

The parameter set of the EXAFS formula is separated into two vectors, the vector $\mathbf{x}$ with components to be defined by the fit to the experimental data, and the vector $\mathbf{y}$ with components given by the model. Thus, the EXAFS formula is written as $\chi(k)=g(k;\mathbf{x},\mathbf{y})$ with

$$\mathbf{x}=\left(S_0^2,E_0,R_1,..,R_p,\sigma_1,..,\sigma_p,N_1,...,N_p\right)\ ;$$
$$\mathbf{y}=\left(\lambda(k),\left|f_{\mathrm{eff},i}(k,R_1)\right|,..,\left|f_{\mathrm{eff},i}(k,R_p)\right|,\phi_1(k),..,\phi_p(k)\right).$$

In a typical case some estimate of $\mathbf{x}$ is known *a priori* ($\mathbf{x}^{(0)}$), though with large uncertainty perhaps. To get dimensionless fit variables, we redefine the components of $\mathbf{x}$ as

$$x_n:=\left(x_n-x_n^{(0)}\right)/\Delta x_n\quad ,$$

with Δx_n being in the order of magnitude of the range of (x_n-$x_n^{(0)}$). The uncertainty of $\mathbf{x}$ is modeled by a Gaussian probability distribution

$$P_{\mathrm{prior}}\propto e^{-\frac{1}{2}\chi^2_{\mathrm{prior}}(\mathbf{x})}\quad\text{with}\quad\chi^2_{\mathrm{prior}}=\sum_{n,n'=1}^{N}A_{nn'}x_nx_{n'}\,.$$

For the matrix $A_{nn'}$ we make the simplest ansatz setting it proportional to the unit matrix: $A_{nn'}=\alpha\delta_{nn'}$.

After the measurement of L values d_ℓ of the EXAFS signal at wave numbers k_ℓ with experimental errors Δd_ℓ the conditional probability distribution for a specific model parameter set ($\mathbf{x}$, $\mathbf{y}$) is given by

$$P(\mathbf{d}|\mathbf{x},\mathbf{y})=\prod_{\ell=1}^{L}\left(2\pi\Delta d_\ell^2\right)^{-1/2}e^{-\frac{1}{2}\chi^2_{\exp}}\quad\text{with}$$
$$\chi^2_{\exp}=\sum_{\ell=1}^{L}\left[\frac{d_\ell-g(k_\ell;\mathbf{x},\mathbf{y})}{\Delta d_\ell}\right]^2.$$

Integration over the parameter vector $\mathbf{y}$ weighted with the corresponding systematic errors $P_{\mathrm{syst}}(\mathbf{y})$, also assumed to be Gaussian, yields the conditional probability distribution $P_{\mathrm{cond}}(\mathbf{d}|\mathbf{x})$. According to Bayes' theorem the *a posteriori* probability to find $\mathbf{x}$ is defined as

$$P_{\mathrm{post}}=\frac{P_{\mathrm{prior}}(\mathbf{x})\,P_{\mathrm{cond}}(\mathbf{d}|\mathbf{x})}{\int P_{\mathrm{prior}}(\mathbf{x})P_{\mathrm{cond}}(\mathbf{d}|\mathbf{x})\,d^N\mathbf{x}}$$

which expresses the modification of the *a priori* expectation of the model parameters $\mathbf{x}$ as the result of the experiment.

A linear expansion of $g(k;\mathbf{x},\mathbf{y})$ in $\mathbf{x}$ and $\mathbf{y}-\mathbf{y}^{(0)}$ yields Gaussian probability distributions for

$P_{cond} \propto e^{-\frac{1}{2}\chi'^2_{exp}}$ and $P_{post} \propto e^{-\frac{1}{2}\chi^2_{post}}$ with $\chi^2_{post} = \chi^2_{prior} + \chi'^2_{exp}$.

The *a posteriori* expectation value of the model parameters $\bar{\mathbf{x}} := \langle \mathbf{x} \rangle_{post} = \int \mathbf{x}\, P_{post}(\mathbf{x})\, d^N\mathbf{x}$ follows from the normal equations

$$\frac{\partial \chi^2_{post}}{\partial x_n} = 0 \quad \text{for } n=1...N,$$

or, in terms of the information matrix **Q**, the *a priori* information matrix $\mathbf{A} = \alpha \mathbf{I}$, and the inhomogenity **b** one obtains $(\mathbf{Q} + \alpha \mathbf{I})\bar{\mathbf{x}} = \mathbf{b}$. The error correlations between x_n and $x_{n'}$ as well as the *a posteriori* errors of **x** are defined by the variance matrix $(\mathbf{Q} + \alpha \mathbf{I})^{-1}$.

The strength factor α determines the weight of the *a priori* information for the solution of the *a posteriori* probability and the expectation value. Following Turchin's suggestion (Turchin et al. (1971)) we choose α^* satisfying the condition

$$\chi'^2_{exp}(\bar{\mathbf{x}}) = L_{eff} = L - \sum_{n=1}^{N} \frac{q_n}{q_n + \alpha^*}.$$

Where q_n are the eigenvalues of the symmetric matrix Q. The sum on the r.h.s. generalizes the concept of the 'number of free parameters' to the present case of an ill-posed problem. In general the *a priori* guess of **x** and **y** is not close enough to the final solution to justify the linear expansion of the model function g(k;**x**,**y**) used above. One therefore has to use a regularized Newton iteration scheme first to come sufficiently close to the final solution $\mathbf{x}^{(*)}$.

3. Application

The model is tested for a computer generated EXAFS function above the Ta L_3-edge using the codes ATOM and FEFF and the known bcc structure with a=3.3 Å. The curved wave amplitude filter of FEFF was set to 4% and the variances σ_i^2 for the resulting 47 paths were set to 0.003 Å^2. The iteration started with an *a priori* data set (N=96 parameters) using values with a distinct offset relative to the true values ($S^2_{0,prior} = S^2_0 - 0.1$, $E_{0,prior} = E_0 - 2$ eV, $R_{i,prior} = R_i - 0.05$ Å, $\sigma^2_{i,prior} = \sigma^2_i - 0.001$ Å^2). The coordination numbers were left unchanged. We chose such a large model space and rather unrealistic *a priori* values for the model parameters to show the robustness of the method. We further assume unrealistically small values for the experimental and systematic errors $\Delta\chi_{exp} = 10^{-4}$, $\Delta\phi_i = 10^{-2}$ rad, $\Delta|f_{eff,i}|/|f_{eff,i}| = 0.1\%$, $\Delta\lambda/\lambda = 0.1\%$) in order to obtain a reasonably large dimension for the subspace P of the total model-parameter space, in which the data, rather than the *a priori* assumptions determine the fit. The deviations of the *a posteriori* expectation values from the true values come out to be 0.002 and 0.03 eV for S_0^2 and E_0, respectively. The first three single scattering path lengths deviate by less than 10^{-4} Å, and the deviation of all path lengths is less than 1 %. The corresponding values for the variances σ_i^2 are $3{*}10^{-5}$ Å^2 and less then 63 %. The regularization parameter $\alpha=\alpha^{(*)}$ defining the dimension of subspace P yields $N_P=48$, which is less then the usual definition of $N_{eff} \approx 2 \cdot \Delta k \cdot \Delta R / \pi = 66$.

4. Summary

A new method for an EXAFS analysis was presented which takes into account the error propagation from the measured input data to the output of the physical parameters. The method uses Bayes' theorem to introduce *a priori* knowledge on the parameters. A procedure first given by Turchin was applied to ensure that the information contained in the data is not distorted by *a priori* input into the fitting procedure. Its functioning was demonstrated for a computer-generated data set for Ta above the L_3-edge.

References

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