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Practical regularization methods for analysis of EXAFS spectra

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The method of Tikhonovs regularization was introduced to EXAFS analysis nearly two decades ago, but it has not gained widespread use despite its appeal from a formal point of view. We find that our implementation of the method, which automatically selects regularization parameters, shows promise for analysis of broad, complex distributions with closely spaced shells in presence of experimental noise.

1. Introduction

The extended x-ray absorption fine structure (EXAFS) technique is a very important tool for structure determination in a wide range of materials (Sayers, Stern and Lytle, (1971). In general, for simple systems, Fourier methods, ratio-cumulant methods, and nonlinear least-square fitting have proven to be reliable. In the case of disordered systems with a dense distribution of scattering centers, the above mentioned methods may not resolve the structure correctly.

The regularization method of numerical solution of Fredholm integral equation of first kind has been shown to be an attractive method of solving a variety of so-called "ill-posed problems" (Tikhonov and Arsenin, 1977). Nearly two decades ago it was suggested that it might be useful to apply this method to EXAFS analysis (Babanov, Vasin, Ageev and Ershov, 1981). This technique has seldom been applied to real data for reasons that remain obscure, with several exceptions (Yang and Bunker, 1996, Babanov et al 1995). The theory and implementation details of the regularization method will appear in a future publication (Khelashvili and Bunker, to be published). The aim of our use of regularization methods is to extend the practical utility and assess the limitations of this technique.

2. Results

The calculations described below used the "Mathematica 3.0" programming environment.

1. Run FEFF7 program (Mustre de Leon, J.J. Rehr and S.I. Zabinsky, 1991) to calculate EXAFS effective scattering amplitude $Amp(k,r)$ and phase $Phase(k,r)$ for Silver as a central absorbing atom and six Oxygen atoms octahedrally around it for single scattering and for different r distances $[1.5, 3.5]\AA$ from the central absorbing atom. This simple method is adequate for testing purposes but more sophisticated potentials should be used for data analysis.

2. Construct the kernel of EXAFS integral equation using effective scattering amplitude and phase calculated by FEFF7.

$$K(k,r) = Amp(k,r)\sin Phase(k,r) \qquad (1)$$

3. Input test radial distribution function and apply the kernel to this distribution function to construct $\chi(k)$ EXAFS data.

4. Treat the synthetic $\chi(k)$ as an experimental data, add synthetic noice using random number generator and reconstruct RDF by regularization method. The latter is a mathematical problem of solving the following "ill-posed" integral equation:

$$\chi(k) = \int_a^b K(k,r)g(r)dr \qquad (2)$$

where $g(r)$ is the RDF.

The following constraints must be sutisfied:

1) $g(r)$ is a smooth function.

2) $g(r) = 0$ if $0 \le r \le a$, and $g(r) = g_M$ for $r > b$. $g_M = 0$ for amorphous materials and $g_M = 1$ for crystal materials.

3) $g(r) \ge 0$ for $0 \le r \le \infty$

The iterational procedure implemented in the program as follows (Babanov at al 1995):

$$g_n^{k+1} = P^+(A^*_{mn}A_{mp} + \alpha\tau\delta_{np} + \beta hB_{np})^{-1} (A_{mp}\chi_m + \alpha\tau g_p^k + \beta hB_{pq}g_q^k) \qquad (3)$$

Here $k = 0, 1, \ldots$. P^+ is the projection operator to the initial information set, A_{mn} is the discretized approximation of the kernel (1), α and β are regularization parameters, δ_{np} is the identity matrix, B_{pq} is the derivative approximation matrix.

The program we have developed selects regularization parameters and number of iterations automatically, by comparing each iterational step with the previous one. The only external parameter input to the algorithm is the experimental error in measuring EXAFS $\chi(k)$, which can be estimated from experiment by comparing repeated scans.

If the regularization method and program are functioning correctly, the reconstructed RDF should closely resemble the initial test distribution function. These calculations were performed on a restricted region of k space - $[3, 12]\AA^{-1}$, with the sum of several Gaussian functions with very close spacing of peaks as a test distribution function. Usually, in this kind of situation the Fourier transformation method does not resolve closely spaced peaks and because of parameter correlation nonlinear least squares fitting becomes problematic. For comparison, we have performed phase corrected k^3 weighted Fourier transformation of $\chi(k)$ data over the same data range.

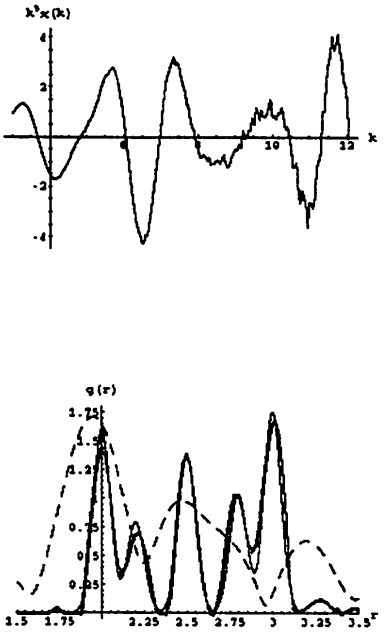

Figure 1
$k^3\chi(k)$ and RDF. Solid line - Test RDF, Thick line - Regularization RDF, Dashed line - Fourier Transform

As we see from Fig.1 , the regularization method is in very good agreement with the test RDF. On the other hand the Fourier transform was unable to resolve any of the peaks.

We have also considered the cases of two and three different types of atoms around the central silver atom absorber and achieved good agreement with test RDFs. In the next example we considered two different types of atoms around central absorber Silver atom. We used FEFF7 again for this purpose and incorporated Sulfur atoms along with Oxygen atoms in the same coordination shells. Then we constructed the new kernel and the new $\chi(k)$ (Fig. 2) for this case analogously to the case with one type backscattering atom. After performing the regularization we arrive at the results shown on the figures 3 and 4. As we see, the regularization method gives an almost identical match with the test RDF.

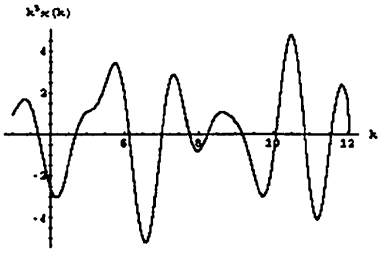

Figure 2
EXAFS $\chi(k)$ for two different types of backscattering atoms, weighted by k^3

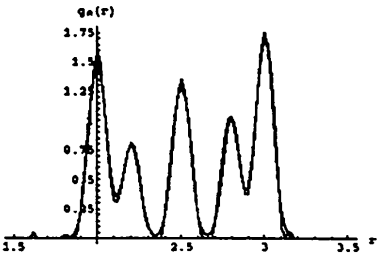

Figure 3
Test and Reconstructed RDFs for atom type A

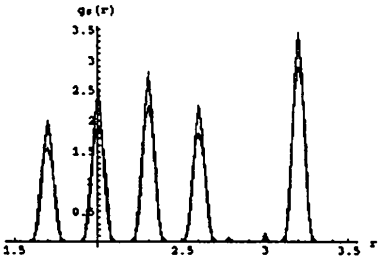

Figure 4
Test and Reconstructed RDFs for atom type B

In contrast with previous work, in the numerical experiments we have performed the scattering centers were located very close to each other. This scenario has not been considered before. In early publications (Babanov at all, 1981,1995) the structures under consideration could be analyzed successfully by conventional methods as well, the reason being that the distance between scattering centers were of the order of $1.5 - 2\mathring{A}$. The cases considered here have five distinct peaks distributed within an interval of $2\mathring{A}$. We find the resolution of the peak improves considerably by increasing the regularization parameters and the number of iterations. Correspondingly, the regularization parameters α and β turned out to be (in the range of $10^{-3} - 10^{-4}$) larger than reported in previous ($10^{-8} - 10^{-10}$) attempts to use the regularization method (Babanov at all, 1981,1995).

3. Conclusion

Using the rather "old" idea of applying regularization methods to EXAFS we evaluated its performance on difficult systems and with noise. From our point of view, this work is the first attempt to apply the regularization method to the situations where it is really needed and for which conventional methods are of limited utility.It was shown that the method

outperforms traditional methods of EXAFS data analysis in situations where multiple scattering can be neglected. We developed a program that authomatically selects regularization parameters and the number of iterations. The work to generalize this method for the case of multiple scattering and Fourier filtering to resolve "windowing effects" during separation of different shells is in progress.

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