Improved *R*-space resolution of EXAFS spectra using combined regularization methods and nonlinear least-squares fitting

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A number of methods have proven to be useful for extended x-ray-absorption fine-structure data analysis of disordered systems. Regularization methods, which describe the radial distribution function nonparametrically, have the advantages of eliminating bias caused by modeling the distribution with a specific functional form, properly including spherical wave effects, and allowing the imposition of physical constraints in a systematic way. In this work we find empirically that the regularization method reliably resolves subshells that are unresolved by Fourier transforms and provide unbiased starting models for nonlinear least-squares fitting. The method is demonstrated with experimental and simulated data. [S0163-1829(96)00526-7]

I. INTRODUCTION

Over the past two decades the extended x-ray-absorption fine-structure (EXAFS) technique of Sayers, Stern, and Lytle[1] has proven to be invaluable for characterizing the short-range order in a wide variety of materials. Among its recent applications are complex materials such as metalloproteins,[2] high-T_c superconductors[3–5] and catalysts.[6–11] In general, for simple systems, Fourier methods,[1] ratio-cumulant methods,[12] and nonlinear least-squares fitting[13] have provided satisfactory results when done correctly.

The basic techniques require experience and sophistication to use reliably in difficult cases, as when two or more subshells are poorly resolved or when any decomposition into shells is ambiguous. Fourier methods have the problem that the Fourier transforms are quite dependent on transform range, weighting, and other parameters. A nonparametric analysis of the radial distribution function by the cumulant-ratio method[14] and splice method is often useful in such cases, but suffers from limited convergence properties in the cumulant approach, and uncertainties owing to extrapolation and nonpositive definite distributions in the splice method. The cumulant expansion can be incorporated into extensions of ordinary nonlinear least-squares fitting, but still suffers from limited convergence in cases of large disorder. More flexible parametric models have been proposed[15] but still suffer from the potential for biased estimates. The maximum-entropy method,[16] as originally applied, was equivalent to a linear prediction,[17] which essentially approximated the EXAFS oscillations as a sum of exponentially damped sinusoids of minimal information content, in effect, a parametric model. More sophisticated maximum-entropy approaches have yet to be developed for EXAFS analysis.

The regularization approach of Erchov *et al.*[18] was introduced more than a decade ago, but has scarcely been used since, despite its theoretical benefits, in principle, it has the advantage of being nonparametric and relatively unbiased, while permitting inclusion of spherical-wave effects and physical constraints in a systematic way. It does not account for multiple types of atoms in the distribution.

The hybrid regularization method described here is modified from the original in that we isolate the first shell contribution from the higher shells by Fourier filtering, because the possibility of multiple scattering effects in higher shells would invalidate the method. Fourier filtering distortions were neglected because they are localized near the end of the filtering range and these regions were excluded from the analysis. In cases where this approximation is insufficient the experimental data and theoretical data can be filtered in the same manner, which effectively eliminates the problem.

In this work we demonstrate a synthesis of the regularization method[18–23] with conventional methods of data analysis. The combined method provides effectively better r-space resolution than than Fourier transform analysis and provides a robust starting point for least-squares fitting.

II. REGULARIZATION OF THE EXAFS INVERSION PROBLEM

The EXAFS equation proposed by Stern and co-workers is

$$\chi(k)=\frac{NS_0^2(k)F(k,r)}{k}\int_0^\infty \frac{g(r)}{r^2}\,e^{-2r/\lambda(k)} \times \sin[2kr+\varphi(k,r)]dr, \tag{1}$$

where $S_0^2(k)$ is the many-electron overlap factor, $F(k,r)$ is the effective backscattering amplitude, N is the coordination number, R is the interatomic distance, $\lambda(k)$ is the energy-dependent mean free path of the photoelectron, σ is the Debye-Waller parameter, $\varphi(k)$ is the phase shift due to the atomic potentials, and k is the photoelectron wave vector. Replacing the infinite upper limit of integration in Eq. (1) by a finite limit, we have

$$\mathbf{A}g=\int_0^\infty NK(k,r)g(r)dr, \tag{2}$$

where $\mathbf{A}$ is $m\times n$ matrix, g is a column vector, and

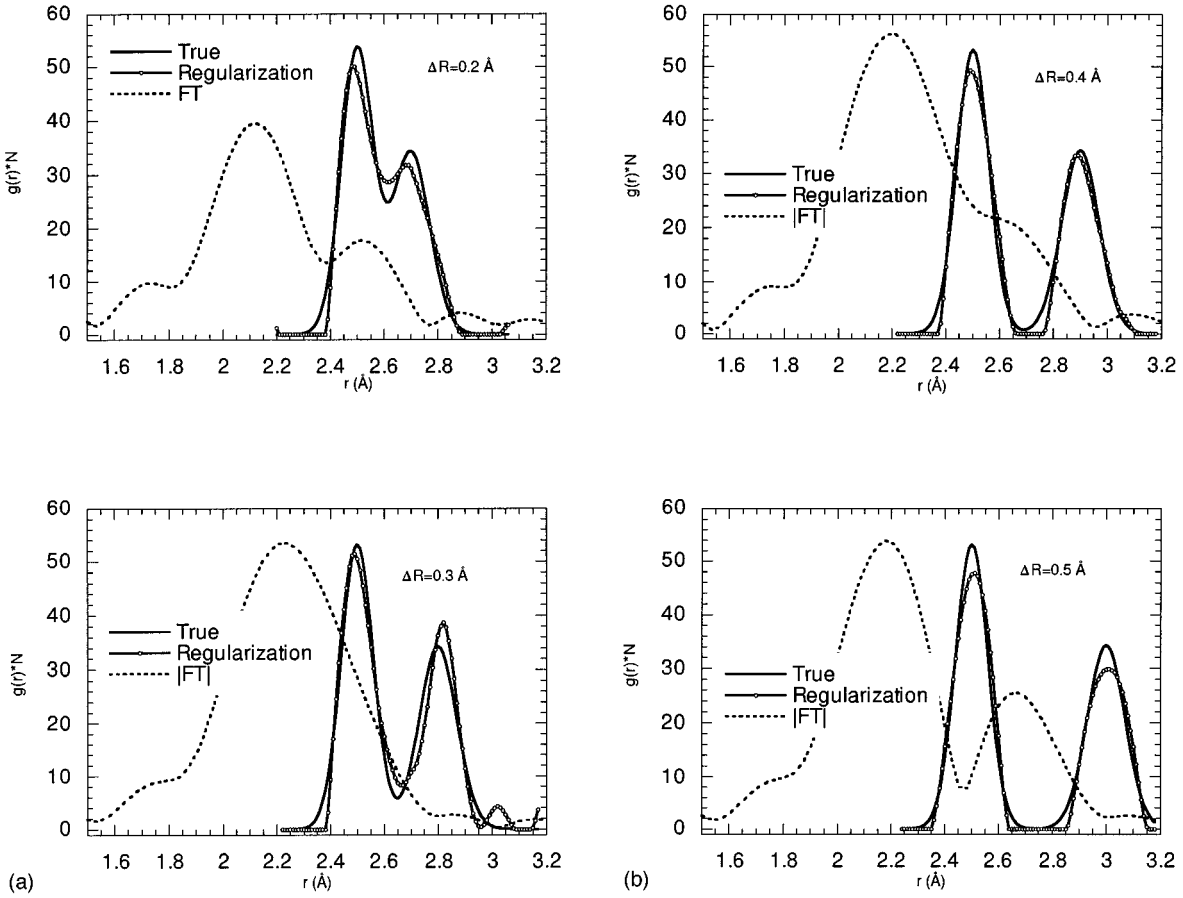

FIG. 1. Pair distributions reconstructed by the regularization method from the simulated spectra for iron with parameters $N_1=8$, $R_1=2.5$, $\sigma_1=0.06$, $N_2=6$, $\sigma_2=0.07$, and $R_2=2.7$, 2.8, 2.9, 3.0 and the Fourier transform of spectra weighted by k^3.

$$K(k,r)=\frac{S_0^2(k)F(k,r)}{k}\frac{g(r)}{r^2}\,e^{-2r/\lambda(k)}\,\sin[2kr+\varphi(k,r)]. \tag{3}$$

This ''ill-posed'' problem is solved by the regularization method introduced by Tikhonov.[19,20] The solution of g^n is obtained from the functional minimum condition[18]

$$\Psi(g,\alpha,\beta)=\|\chi-\mathbf{A}g\|^2+\alpha\int_0^\infty|g(r)|^2dr+\beta\int_0^\infty\left|\frac{d}{dr}\,g(r)\right|^2dr+\gamma\|g-|g|\,\|^2, \tag{4}$$

where α is a regularization parameter, β is a smoothness parameter, and γ is a positivity constant.

Without the penalty terms, inversion of the linear system $\chi=\mathbf{A}g$ is highly unstable. There exists a subspace of functions that could be added to $g(r)$ without appreciably altering the corresponding $\chi(k)$. For example, if an extremely broad Gaussian function were added to $g(r)$, its contribution to the data would only appear at very low k, below the start of usable data range, and therefore it would not alter the quality of the fit. The regularization term with parameter α suppresses spurious of ''gratuitous'' contributions through use of a penalty function: if a contribution to $g(r)$ is irrelevant in the sense that it does not improve the fit, it is suppressed, analogously to maximum entropy methods, which minimize the information content of the reconstructed $g(r)$. In effect, the term applies Occam's razor: the simplest model consistent with the best data. This term also renders the inversion procedure less sensitive to small variations in the input data.

In addition, a penalty term is included that tends to render $g(r)$ as smooth as possible, consistent with fitting the data well. It is important to realize this is *not* an aesthetic consideration. The smoothness constraint tends to suppress high spatial frequency κ modulations in the reconstructed $g(r)$, in proportion to κ^2. This reduces the information content consistent with adequately fitting the data, a feature at the heart of maximum-entropy methods. Finally, the physical requirement of a positive definite $g(r)$ is imposed through the parameter γ.

From the minimum condition of Eq. (4), we obtain algebraic equations[18]

$$\left(\sum_m A_{mn}^*A_{mn}+\tau(\alpha+2\gamma S^n)I+\beta\sum_m B^{mn}\right)g^n=\sum_m A_{mn}^*\chi^m, \tag{5}$$

$$S^n=\begin{cases}0 & \text{if } g^n\geqslant 0\\ 2 & \text{otherwise,}\end{cases} \tag{6}$$

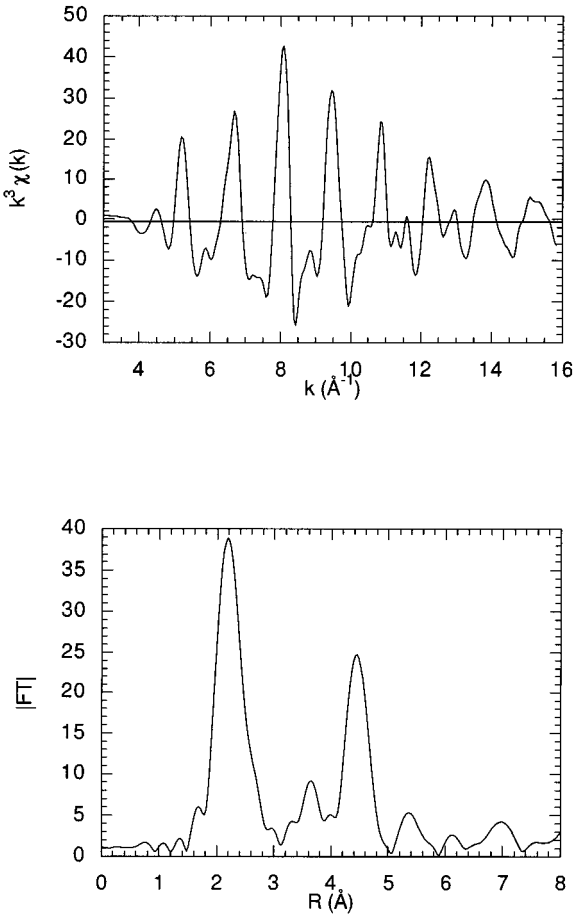

FIG. 2. Experimental XAFS spectrum and Fourier transform of pure iron thin film at 80 K.

where the matrix element a_{mn} is determined from Eq. (3) using the backscattering amplitude, phase differences, and $S_0^3(k)$ calculated from the theoretical standard FEFF4,[24] and the matrix **B** is

$$\mathbf{B}=\begin{pmatrix} 2h & -h & 0 & \cdots & 0 \\ -h & 2h & -h & \cdots & 0 \\ 0 & -h & 2h & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 2h \end{pmatrix},$$

with $\tau=\Delta r/\Delta k$ and $h=1/(\Delta r \Delta k)$. The optimal values of the regularization parameters α and β are obtained by minimizing $\|\chi-\mathbf{A}g\|^2$. The positivity parameter γ is determined by the program to be just large enough to make $g(r)$ be positive definite. It is important to realize that the optimum parameter values are determined automatically by the algorithm, minimizing the operator bias.

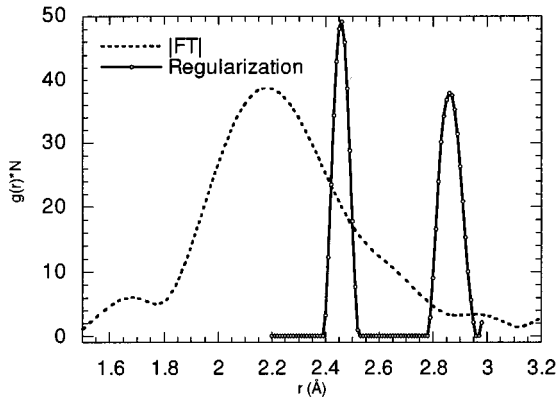

FIG. 3. Pair distribution determined by the regularization method from the spectrum filtered in the r range (1.8–2.9 Å) in Fourier transform.

III. COMPARISON OF THE RESOLUTION OF THE FOURIER TRANSFORM AND REGULARIZATION

To compare the resolution of the Fourier transform technique and regularization method, several EXAFS spectra containing two coordination shells of pure iron were simulated using the FEFF4 (Ref. 24) program on iron consisting two close shells with parameters $N_1=8.0$, $R_1=2.5$ Å, $\sigma_1=0.06$ Å, $N_2=6.0$, $\sigma_2=0.07$ Å, and $R_2=2.7$, 2.8, 2.9, and 3.0 Å separately, where σ is the Debye-Waller parameter. As shown in Fig. 1, two close-shells whose $\Delta R \geqslant 0.5$ Å were not resolved in the Fourier transform. However, the regularization method can resolve each shell definitely for $\Delta R \geqslant 0.2$ Å. The magnitude and width of the distribution in the first shell by the regularization method were not affected by the second shell (the regularization procedure is nearly linear) so that the first shell information is not distorted by the second shell for all simulations shown Fig. 1, whereas close shells in Fourier transform modules interfere and the first shell peaks are severely distorted. The average distance and the coordination number of each shell can be estimated from the distribution. A practical approach for this type of problem will be presented in the next section.

IV. EXAMPLES WITH EXPERIMENTAL SPECTRA

An experimental EXAFS spectrum of pure iron was used to test the resolution of two shells with small separation. The sample preparation and experimental procedure have been described elsewhere.[25] According to the analysis of crystal structure,[26] bcc iron has the eight nearest neighbors at $R_1=2.59$ Å and six second-nearest neighbor at $R_2=2.87$ Å. However, the two shells were not resolved in the Fourier transform of the EXAFS spectrum measured at 77 K shown

TABLE I. Fit parameters of the iron XAFS specturm using the combined method.

	First shell			Second shell			
	N	R (Å)	σ (Å)	N	R (Å)	σ (Å)	ε^2
true	8.0	2.48		6.0	2.87		
fit	7.7±1.4	2.48±0.01	0.06±0.01	4.3±3.0	2.86±0.02	0.06±0.03	1.04*e*+2

in Fig. 2. However, these two shells are well resolved by the regularization procedure, as shown in Fig. 3. With the initial guesses of the EXAFS parameters estimated from the pair distribution obtained by the regularization method, the final values were obtained by a nonlinear square fitting of the filtered spectra using two shell fittings. As shown in Table I, the local structural information of pure iron can be obtained very precisely by the regularization method. Tests with other compounds have shown that integrated peak areas are not always reliable, presumably because, while increasing the peak height and increasing the width of the distribution tend to have opposite effects in k space (changing the scale of the amplitude), they both increase the area (coordination number) of the peaks of $g(r)$.

V. DISCUSSION AND SUMMARY

In the cases examined, the pair distribution obtained by the regularization method yields an apparent improvement in spatial resolution over the Fourier transform method. This study has shown the regularization method combined with Fourier filtering and nonlinear least-squares fitting. The point of filtering is to eliminate higher shell contributions that may contain multiple-scattering contributions, which would render the method inapplicable. As shown in an experimental example of bcc iron, the combined method provided very precise results on the first shell without any further information or *ad hoc* assumptions by the user. Error estimates are obtained by conventional means in the least-squares fitting process.

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