The First and Second Shell Correlation Analysis in Cu Metal by the Matched EXAFS PDF Projection Method

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Abstract. Through numerical simulation of inverse problem computation, our new method of EXAFS analysis was tested for a simple structure of copper metal. For a simulation test, we constructed a structural model with all possible paths of single and multiple scattering within 6 Å. Typically, the first-shell PDF (pair distribution function) is computed according to an algebraic equation describing the temperature dependence of specific anharmonic distribution. Through the MEPP (matched EXAFS PDF projection) method – combing iterative regularization and matched correction of Fourier filtering distortion, it is shown that the original function of anharmonic PDF is iteratively solved from the initial proximity model, even approximated in terms of non-realistic sub-shell mixture of anharmonic distribution feature. To remove the problem of extraneous pattern at intermediate PDF solution, we also tested a proper pattern fit on the anharmonic curve formula, resulting in significantly suitable convergence to the true PDF solution. Our simulation results indicate that the projection to true PDF solution is only reachable when the perfect background correction is selected. Our precision EXAFS analysis performance requires manipulating the apparent correlation between the first and second shells using a typical numerical process of first-shell matching Fourier filtering.

Keywords: EXAFS, PDF, Fourier filtering, anharmonic distribution, regularization
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INTRODUCTION

Extended X-ray absorption fine structure (EXAFS), from experiment to data analysis, is consistently a unique chemical specific analysis technique for probing the short-range (within 5 Å) structural geometry and atomic vibration features of new materials in chemical molecules and in solid state. The wide-spread use of computational analysis tools, such as Feffit [1] and Athena [2], is greatly helpful for many researchers to solve the structure, but less contributable for relatively complicated atomic configurations. For a multi-component complex system, conventional EXAFS data analysis is still far from providing high fidelity due to numerical difficulties associated with the so-called cross-correlation uncertainty of EXAFS fitting parameters, N (coordination number), R (inter-atomic distance) and σ^2 (Debye-Waller factor) at constituent shells. Although empirical effort is often made to acquire higher k-range chi-data at low temperature, the analysis result is insufficient to explore the specific fine structure at high accuracy. To better analyze the fine structure from even poor quality experimental data, one needs to upgrade the EXAFS analysis tool.

Known as the PDF reconstruction method, the so-called EXAFS regularization computation using Tikhonov's theorem [3] is one of several iterative solution projection methods under the "ill-posed" mathematical problem. With optimal regulation under unavoidable numerical truncation problems produced from computation of integration or matrix operations, it is possible to obtain the most reliable PDF solution in exactness and smoothness. In previous work [4,5], we described the numerical procedures towards a new analytical method, MEPP (Matched EXAFS PDF Projection); how the optimal regularization and perfect PDF projection is achievable with successful cooperation of FEFF computation and Fourier filtering computation. In this study, a simple example of copper metal was selected for the purpose of diagnosing the accuracy of MEPP computations.

A SIMPLE EXAMPLE: Cu

For an EXAFS analysis test, copper metal is good to choose as a model structure because of its simple crystallographic data. The space group for the face-centered cubic structure is Fm3m, and the lattice constant is 3.61 Å. From the FT EXAFS analysis

shown in Fig. 1, for the simulated chi-data at T=700 K, the individual shell contributions are displayed for illustration. The first shell (N_1=12 at R_1=2.55 Å) and the second shell (N_2=6 at R_2=3.61 Å) are ideally separated as SS (single scattering) paths. Apparent broad-range coverage between the first shell and the second shell is attributed to the specific DS (double scattering) paths along the triangular R_1-R_1-R_1 geometry (N_3=48 at R_3=3.83 Å, equivalently). After treatment of inverse Fourier transformation, the partial filtered chi-signal is displayed in Fig. 2. Compared to the second-shell contribution, this MS signal is more sensitive to background modification. In EXAFS analysis, when such cumbersome DS signal is treated as a negligible contribution, accurate EXAFS fitting is not reachable. Unlike the cross-correlation uncertainty of conventional EXAFS fitting parameters, our new analysis method (MEPP) is promising to provide a better feasibility to diagnose the first and second shell correlation in an analytic manner for copper metal (simple model).

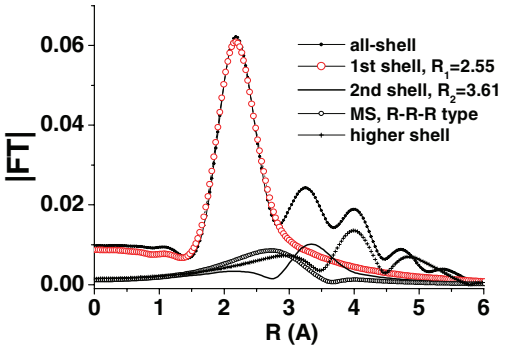

FIGURE 1. FT representation for a comparison of individual shell contributions. Cu K-edge chi-data are simulated for a simple model (Cu metal) at T=700 K. Apparent MS contribution is observed between the first shell and the second shell contents. Hanning window parameters for chi-data were chosen as: k_1=2.6, k_2=12, dk=1.0 and KW=0.

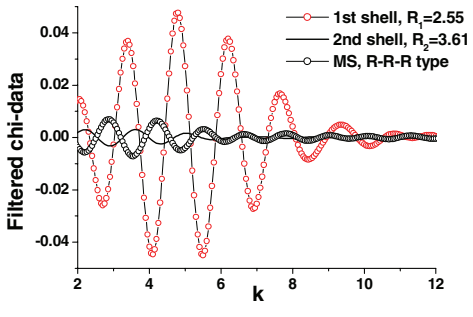

FIGURE 2. Filtered chi-data representation corresponding to individual shell contents in Fig. 1. Hanning window parameters for FT-data were chosen as: r_1=1.73, r_2=2.73 and dr=0.2.

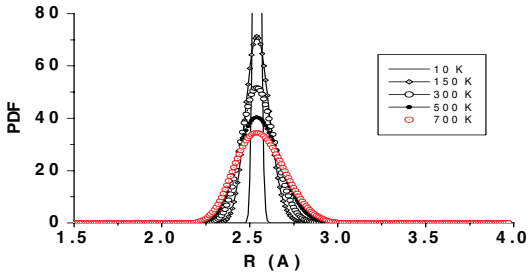

FIGURE 3. Anharmonic PDF feature computed according to Eq. (1). The datum at T=700 K is corresponds to the first shell content in Fig. 1.

For a realistic comparison with the experimental EXAFS data, we intended to choose a model of the anharmonic vibration at a relatively high measurement temperature (T=700 K). In Fig. 3, the anharmonic character of the first shell PDF obeying the Debye vibrational model is illustrated at various temperatures, T=10 K, 150 K, 300 K, 500 K and 700 K, according to the following formalism [6]:

$$g(x+r0) = g_N e^{\{-\frac{1}{kT}(\frac{1}{2}k_0x^2 - k_3x^3 + f_4x^4)\}} \qquad (1)$$

where materials constants are given as [7]: k_o=46 N/m (spring constant), k_3=2.5x10^{11} N/m^2 (anharmonic parameter) and f_4 (adjustable small value for renormalization) at the material's Debye temperature, 315 K.

SIMULATION RESULTS

As demonstrated in Fig. 2, after imposing the first-shell Fourier filtering using a Hanning window, the background content from MS contributions is still significant, and the second-shell contribution (R=3.61 Å) is hardly nullified. Fourier filtering is necessary to extract the first-shell information, but the filtered chi-signal is more distorted by narrowing a Hanning window. Such distortion in the lower k-range of chi-data hinders a precise analysis of the first and second shell correlation.

In progress, as a brief review of the MEPP (Matched EXAFS PDF Projection) method [5], the first step needs the first-shell matched correction of the Fourier signal distortion. Our trial for this first-step correction was basically acceptable along the iterative computation of the inverse solution from chi-data to PDF. MEPP involves an inverse problem solving computation which is well performed for solving PDF accurately from simulated data EXAFS based on FEFF. To restore the Fourier filtering signal distortion involved in the first sub-shell extracted information, it

is essential that the relevant distortion matching function is computed initially from the proximity model and iteratively from the prior-guess during consecutive regularization computation.

In our MEPP analysis, the Fourier transformation must be chosen with KW=0 (zero k-weighting factor) to exactly compensate the matched distortion. When none-zero k-weighting is imposed, the higher k-range will be seemingly better fitted, but the involved non-linearity makes the exact MCF (matched correction function) useless for MEPP computation. Importantly, MEPP requires lower k-range chi-data in perfect background correction. To avoid the unwanted signal distortion, the most probable background correction must be taken through the analytical correlation between the first and second shell information, as previously illustrated in Fig. 1 and Fig. 2. In our numerical test, when non-negligible second-shell contribution was taken into consideration for a background correction, the numerical convergence of the solution to the original PDF, given as typical anharmonic ensemble, is significantly better. More quantitative evaluation will be made in a later publication.

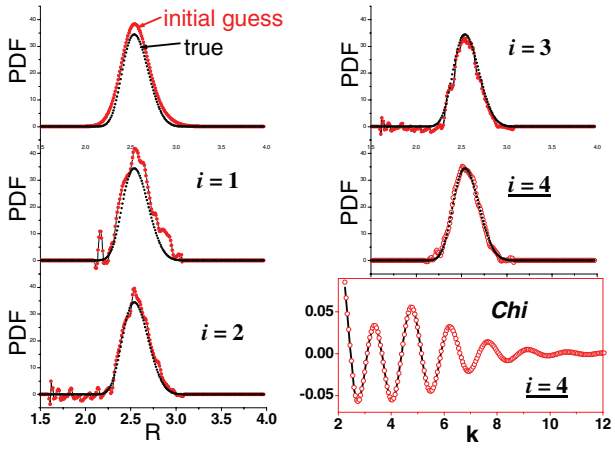

FIGURE 4. Numerical simulation results using MEPP computations [5]. Iterative PDF solution (large dots/red) is overlapped with respect to true solution (small dots/black) at initial guess (i=0), iterative trips (form i =1 to i =3) and the final trip (i =4) just after a proper pattern fit. The final chi-data solution is iteratively solved by the precise convergence to the true solution.

As our preliminary simulation results, displayed in Fig. 4, it is clearly demonstrated that the original function of specific anharmonic PDF is iteratively solved from the initial proximity guess (in case of i =0), tried with two-shell model approximating the anharmonic distribution feature with N_1=12, R_1=2.53, σ_1^2=0.02, N_2=3, R_2=2.7 and σ_2^2=0.03. But, at intermediate solution (from i =1 to i =3), unstable extraneous truncation pattern is propagating due to an actual difference between initial guess and origin function. At the iteration trip (in case of i =4), after taking a suitable pattern fit on the anharmonic curve formula in Eq. (1), significantly better PDF solution was obtained close to the true PDF solution. This exactness of the computation results indicates that the perfect background correction as ideally chosen for a simulation purpose. With some variation in the second shell feature, we tried the simulation for a comparison with experimental data EXAFS at higher temperature. These results will be reported later after further numerical precision analysis.

The inverse problem solving algorithm is applicable to the direct inverse computation from the simulated data EXAFS to the original function PDF. When theoretical FEFF data are compatible with the empirical data, the EXAFS PDF projection can be widely used. In our experience, our method is useful to analyze the experimental data only when the E_o-shift is precisely tuned. More generally, we expect that MEPP computations will provide a proper analytic criterion in determining the absolute position of the E_o-shift threshold energy and the perfect background correction function simultaneously.

In conclusion, we may point out that our MEPP computation is suitable for the practical use because our numerical simulation from chi-data to PDF is achievable and controllable without losing the benefit of Fourier filtering computation. Only required is that the empirically precise transfer function (actually, FEFF data) between EXAFS chi-signal and PDF must be specified.

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