EXAFS Phase Retrieval Solution Tracking for Complex Multi-Component System: Synthesized Topological Inverse Computation

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Abstract. Using the FEFF kernel \( A(k,r) \), we describe the inverse computation from \( \chi(k) \)-data to \( g(r) \)-solution in terms of a singularity regularization method based on complete Bayesian statistics process. In this work, we topologically decompose the system-matched invariant projection operators into two distinct types, \( (A^\dagger AA^\dagger A) \) and \( (AA^\dagger AA^\dagger) \), and achieved Synthesized Topological Inversion Computation (STIC), by employing a 12-operator-closed-loop emulator of the symplectic transformation. This leads to a numerically self-consistent solution as the optimal near-singular regularization parameters are sought, dramatically suppressing instability problems connected with finite precision arithmetic in ill-posed systems. By statistically correlating a pair of measured data, it was feasible to compute an optimal EXAFS phase retrieval solution expressed in terms of the complex-valued \( \chi(k) \), and this approach was successfully used to determine the optimal \( g(r) \) for a complex multi-component system.

1. Introduction

The numerical inverse computation method, which is fundamentally similar to a feedback stabilization of complex systems, has been investigated with substantial effort in a wide range of applications but there has been limited progress relative to its potential. Common numerical difficulties associated with the ill-posed nature of the problem stem from the statistical treatment of noise, the system configuration complexity in its topological aspects. Recent studies have shown the common applicability of concepts from topological mathematics, leading to computational feasibility of the phase retrieval solution [1]. Among these inverse-problem solving recipes, the singularity regularization method [2,3,4] has been received with significant interest as a unique way to seek the most reasonable solution under the so-called Bayesian statistics process [5,6], preserving maximum entropy under the time-sequential probability.

In EXAFS the essential goal is to construct the radial distribution function \( g(r) \) from \( \chi(k) \) data in the presence of noise. Although this is a linear transformation, it is unstable under inversion, and therefore stabilization procedures (regularization) and regularization parameters are typically used. [2,4] There is an inherent tradeoff between smoothness of the solution and its accuracy. Commonly, the goal is to determine the optimal tradeoff, but yet insufficient to reveal a topology-invariant trajectory through the regularization parameter space. Emphasized, nature exists in a complex dynamic system, and therefore Bayesian
treatment – based on causality of prior and posterior – should substitute Fourier filtering (originator of signal deformation), upon which EXAFS analysis was historically based [3,7]. Despite widespread interest by EXAFS investigators, optimal inverse computation code has not yet been developed in the framework of a linear matrix system. This paper describes an effort to address that need.

2. Numerical Procedures

Due to availability of complex-number kernel FEFF [8], the general EXAFS equation can be expressed as a linear matrix relationship: \( \chi_{\text{complex}}(k) = [A_{\text{complex}}(k,r)] g(r) \) or \( \chi_{\text{imag}}(k) = [A_{\text{imag}}(k,r)] g(r) \). [9] We defined the complex-number representation, \([A_{\text{imag}}; A_{\text{real}}]\)-arrangement, as shown in figure(1). In topological aspect, the complementary pair \([\chi_{\text{complex}}(k), g(r)]\) describes the dynamic phase space participating in self-consistent solution domain, but real EXAFS measurement can see only the imaginary part, \(\chi_{\text{imag}}(k)\). In a topological analogy with the dynamical phase spaces, \((x\text{-position}, p\text{-momentum})\), we take the conjugate observables, \((g(r), \chi(k))\). Simply, we can express \(A|g> = A[(A+A)…(A +A)]|g>\) where \(A\) represents the Hermitian conjugate matrix, i.e. the transposed complex conjugate. Consequently, \(A|g> = Q^2..A..P^2|g>\) illustrates two distinct projection blocks, \((P=A^TAA^T A)\) and \((Q^2=AA^TAA^T)\). The symplectic topological essence built into these phase-space projection filters is the system-matched (chemical-specific) character, ensuring the full performance of both “denoising” and “feature preservation”.

Figure (1)
Color-map matrix \([Q,A; A^{-1},P]\) for complete Hilbert four-space set with \(A\) (forward transformation), \(A^{-1}\) (inverse transformation), \(Q=AA^{-1}\) (k-space projection) and \(P=A^T\) (r-space projection). Red/blue colors indicate positively/negatively valued. From the Zn K-edge FEFF \(A(k,r)\) matrix, for two different backscattering species of Zn-O and Zn-S. \(A\)-matrix consists of eight Hanning-windowed segments in \(k[3, 12]\)-range and \(r[1.5, 4]\)-range, respectively, with intervals 0.05 and 0.02. This is corresponding to \(k^3\)-weighted EXAFS equation, \([\chi_{\text{imag}}(-k); \chi_{\text{real}}(k)] = [A_{\text{imag}}; A_{\text{real}}]\) \([g_2(r);g_1(-r);g_1(r);g_2(-r)]\).

Figure (2)
Illustration of STIC(synthesized topological inversion computation) methodology. The symplectic transformation linkage is applied to eliminate the numerical discontinuity arising at near field zone. The equivalent inverse matrix \((A^{-1})\) is related to:
\[
J_1 = A_1A_1^{-1} = Q_{1f}Q_{1b}(Q_{3b}Q_{3a}Q_{3a})Q_{1f} \\
J_3 = A_3A_3^{-1} = Q_{3f}Q_{3b}(Q_{1b}Q_{1f}Q_{1a})Q_{3f}
\]

Figure (3)
(a) The simulated RDF-\(g(r)\) including two different backscattering atoms. (b) The phase retrieved \(\chi(k)\) from imaginary space (blue-colored, simulated data with noise) to complex-number space (red-colored). Denoising efficiency is observed significantly.
To start our numerical procedure, let us introduce a novel singularity regularization method using dual parameters, fulfilling the complete feedback cycle requirement, as the following equations:

$$\text{Reg}(K, \alpha, \beta) = (K^T K + \alpha I)^{-1} K^T \left[ I + \alpha (1+\beta) \left( KK^T + \beta I \right)^{-1} \right]$$

$$W(A, \alpha) = \text{Reg}(A, \alpha, \alpha) \quad \text{when} \quad ||A^T A|| = 1$$

$$Z(W, \alpha) = \left( \text{Reg} \left( \begin{array}{c} W^T W \end{array} \right), \alpha, \alpha \right)$$

where $W$ and $Z$ pertain to, respectively, $A^+$ and $A$ matrices during progressive computation process. The parameters, $\alpha$ and $\beta$, are chosen for the projection domain, respectively, in r-space and k-space. As close as regularization parameters are approaching to zero, the optimal tracking status - between smoothing and distortion - gives rise to serious numerical instability relevant to ill-posed problem. (Refer to Tikhonov’s regularization [10]) Nevertheless, our numerical approach is attainable to force an isotropic selection (i.e. $\alpha=\beta$) into the near-singularity regime with extraordinary stability under the topological feature momentum preservation. To do this, we chose $W_1=ZWQ$ (where $Q=ZW$ initially) with $\lambda$-parameter, the optimal Lagrangian path under the constraint of $W_1Q_1A$ feature preservation. It is a way that a primitive set $(A, A^*)$ is consistent with $(AA^*, A^*AA^*)$. Straightforwardly, by successive selection of regularization parameters, $[\alpha_3, \beta_3, \alpha_s]$ for far-field and $[\alpha_t, \alpha_0]$ for near-field distant $(\alpha_s>\alpha_t>\alpha_0)$ from the inherent numerical singularity, we can enter a numerical gateway to the inverse solution. Subsequently, we need to suppress a numerical discontinuity at the vicinity of singularity. As shown in figure(2), we employed a 12-operator-closed-loop emulator of the symplectic transformation, $S, (A_2=SA_4$ with $S^2=I$) [11] This STIC (Synthesized Topological Inverse Computation) architecture is the singularity inhibitor algorithm. In quantum physics, the symplectic transformation implies that $\psi_{\text{complex}}$ and $\psi'_{\text{complex}}$ are indistinguishable. Equivalently, in our numerical recipe, a conjugated pair of $(\chi_{\text{imaginary}}; \chi_{\text{real}})$ and $(\chi_{\text{real}}; \chi_{\text{imaginary}})$ was taken to simplify complex-number matrix manipulation. At every cycle of STIC-loop, the polarity of $\chi_{\text{complex}}(k)$ is just reversed. As a consequence, the ill-posed instability was dramatically suppressed under this STIC architecture.

Dissimilar to simple mathematical solution formula, a real world requires formulating the $A^+$ equivalent operator, in terms of successive matrix multiplications. By satisfying a numerical self-consistency in conjugate observables, we can assert that a hypothesis solution of the priori-probability $g(r)$ can be computed from the posteriori-probability $\chi(k)$. This statistical approach satisfies the Bayesian requirement. According to the STIC methodology in figure(2), become a genuine inverse kernel. To increase the precision of inverse computation, primarily required is the numerical presetting of $A_r$-matrix refinement $(A_r=A_1+\lambda[J_1A_1-J_3A_3])$ in advance to other consecutive computations. In our experience, the numerical truncation error (a type of piled-up residuals producing r-domain glitches) can be removed with a better numerical presetting of $A_r$-matrix refinement. Therefore, instead of raw FEFF kernel generating such numerical glitches, we prefer to upgrade FEFF kernel (normally, norm($A_r-A_1$)/norm($A_1$) ~ 0.2%) by own iterative algorithm in progress. [13]

**Figure (4)**
Examples of STIC fine-tip probe for EXAFS applications. The best MEM pinning –red arrow - for $g(r)$ solution is slightly deviated from the parabolic apex. Even at excessive noise statistics, the solution tracking is independently stable and accurate. The simulated $\Delta R$-variation track was chosen in [-0.005, 0.005] ranges for two counterpart configurations; $[R_1, R_2, R_3]=$
[2.33+ΔR, 2.69, 3.13-ΔR] and [2.45+ΔR, 2.76, 3.19-ΔR], respectively, for g1(r) and g2(r), as shown in figure 3(a).

Throughout our study, we established the following procedures: (i). The g(r)-model vector, [g2(r);g1(-r);g1(r);g2(-r)] as shown in figure(3-a), was chosen with six shells from two different chemical species, i.e. multi-component complex system. (ii). A pair of measurement data, χimag(k), was plugged into one input set for individual simulation. (iii). In figure(3-b), [χimag(-k); χreal(k)] was computed by an iteration method, multi-component filtering and Kramers-Kronig transformation. [12] (ix). A paired set of χcomplex(k) and trial g(r) were plugged into the cross-correlation analysis, evaluating the numerical fidelity of inverse solution in terms of MEM (Maximum Entropy Method) estimator, minimizing χ²−λS where χ²—fitting and S-entropy.

The patterned g(r)-function representation can be probed within a selected region of variation. The quality of S-entropy can be traced by evaluating the covariance matrix between symplectic observables (using the MATLAB function corrcoef(x1, x2)).

A principal result is that this inverse computation approach dramatically enhances the numerical accuracy. Our numerical computation results indicate good performance even at relatively high noise level (e.g. 5%, noise-to-signal ratio). In a case of arbitrary track shown in figure(4), the tracking curve edge is highly sharpened at the pinning position for g(r)-solution. (This ΔR-variation track is different from conventional L-curve [4].) Also, our simulation results indicate that the optimal λ-parameter in (χ²—fitting, S-entropy) domain is empirically proportional to the noise level. Surprisingly, even at excessive noise level, our simulation results showed numerical feasibility of system-matched “de-noising” filtering and the ultra-fine probing despite the complexity of the multi-component system. Without our STIC method, such precise tracking is not achieved due to the hindrance of noise problem. When a trial g(r) is approaching closely to the true solution, it is possible to keep tracking while preserving solution stability. In case of huge complexity, it is still promising to track the derivative trends approaching the ultimate solution. Advanced procedures will be described later in another publication.[13]

Beyond this specific application to EXAFS data analysis, this work demonstrates that the completeness of numerical inverse computation was possible using topological methods. Mathematics is universal and this method can be applied elsewhere. It is hoped that this method will open a numerical gateway to understanding a broad class of numerically ill-posed problems in inverse computation.

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